

Doctor of Arts Dissertation
Middle Tennessee State University
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Synthesis of the Salts of Weakly Coordination Stibate Ions

&

Students' Perceptions of
Two- and Three-Dimensional Animations
Depicting an Oxidation-Reduction Reaction

A dissertation presented to the
Graduate Faculty of Middle Tennessee State University
in partial fulfillment of the requirements
for the degree of

Chemistry
Doctor of Arts

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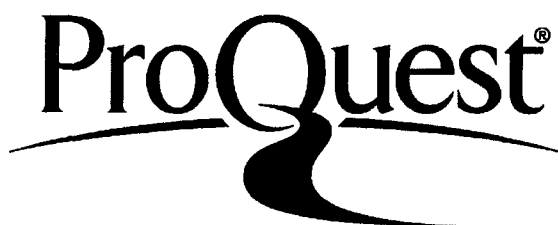
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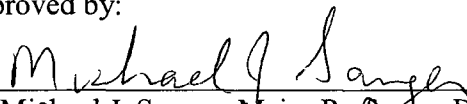
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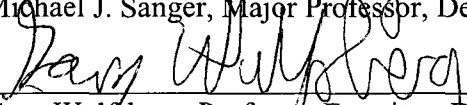
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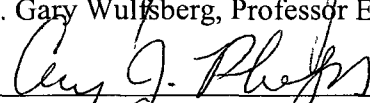
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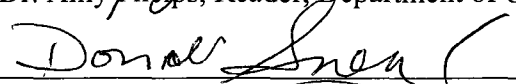
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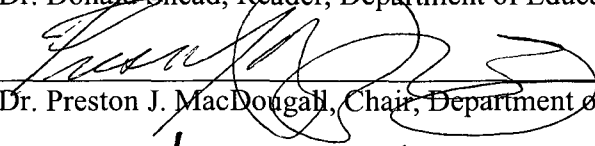
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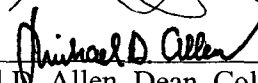
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This is dedicated to my grandparents whom always seem to be with me.

Anna Kreuzer and Peter Palmer

Beverly Shapero and Sidney Cohn

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ABSTRACT

SYNTHESIS OF SALTS OF WEAKLY COORDINATING STIBATE IONS

Weakly coordinating anions have many important applications including olefin polymerization co-catalysis. In an attempt to make tritibic acid, distibic acid and tetrastibic acid were made. Cesium, barium, nickel(II), and diethylammonium salts of tetrastibic acid were also synthesized. Tetrastibic acid and the ammonium salts were concluded to be stable. Elemental analyses showed that neither tritibic acid nor tritibic acid were stable under the reaction conditions employed.

STUDENTS' PERCEPTIONS OF

TWO- AND THREE-DIMENSIONAL ANIMATIONS

DEPICTING AN OXIDATION-REDUCTION REACTION

Electrochemistry is a difficult subject for many students to comprehend. In order to improve teaching in this area of chemistry, semi-structured clinical interviews on second-semester introductory chemistry students were conducted in which students' were asked to explain the particulate behavior of the chemicals in an oxidation-reduction reaction. The interviews included questions after students viewed the chemical demonstration and two computer animations depicting the particulate nature of the same chemical reaction. Misinterpretations of the two animations were identified and described in detail. The simpler 2-D animation was beneficial in helping students understand the oxidation-reduction reaction and write the balanced chemical equation. However, the 3-D animation did not appear to be detrimental to student understanding. Suggestions, taken from the students' comments in the interviews, for improving the animations and for teaching electrochemistry were discussed.

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CHAPTER I

SYNTHESIS OF SALTS OF WEAKLY COORDINATING STIBATE IONS

CHAPTER I

INTRODUCTION

Polymer History

As natural polymers such as wood, wool, and cotton became more expensive they tended to be replaced by synthetic polymers, and the manufacture of these is a multi-billion dollar industry. One of the first synthetic polymers was created in the mid-to-late 1800's. Cellulose was treated with an alcohol to produce a synthetic polymer. In 1848 Schonbein treated cellulose with nitric acid and sulfuric acid to form nitrate esters (Walton & Lorimer, 2000). The reaction conditions could be controlled to synthesize various products, which led to their mass production: 'Artificial skin' was used in medicine, 'Chardonnet silk' modernized the fashion industry, and celluloid revolutionized the photographic industry (Walton & Lorimer, 2000).

The next significant polymer reaction discovered was in 1865 by Shutzenberger (Walton & Lorimer, 2000). He formed cellulose triacetate by reacting cellulose with acetic acid and acetic anhydride. Because the triacetate produced was only soluble in expensive, halogenated solvents and the properties were not desirable, the process was never used in manufacturing. However, in the early 1900's cellulose diacetate, soluble in acetone, was formed by partial hydrolysis of the triacetate. The polymer was used to strengthen airplane wings in World War I and became a major thermoplastic molding material.

Another important early process was the polymerization of ethylene to produce polyethylene (Figure 1.1). Until the mid 1900's the polymerization of ethylene was

carried out at high pressure and moderate temperature to produce low-density polyethylene (LDPE) that had properties of limited utility. In 1953, Ziegler revolutionized polymer production by using a transition-metal catalyst at room temperature and atmospheric pressure to form high-density polyethylene (HDPE). In 1954, Natta polymerized propene using similar catalysts. The key to these olefin polymerization reactions is the reduction of a solid transition metal halide (such as TiCl_4) to a lower oxidation state (such as TiCl_3). This catalyst is supported on the surface of solid MgCl_2 ; the surface Ti atoms have vacant coordination sites which can coordinate alkenes such as propene. Ziegler-Natta catalysts are heterogeneous, so that active metal sites are only on the surface of crystals. Not all Ti coordination sites are identical, so the reaction gives a mixture of products with a broad molecular weight distribution. The exact mechanism of Ziegler-Natta catalysis is unknown, but a recent model has been suggested, which is based on the mechanism involving a novel octahedral complex that polymerizes propylene from propene (Corradini, P, Guerra, G, & Cavallo, L, 2004).

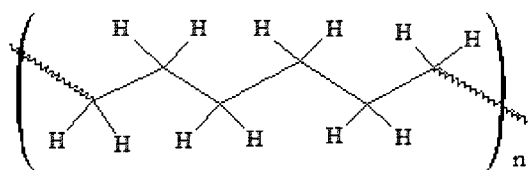


Figure 1. Polyethylene

Since the Ziegler-Natta reaction was discovered, research into olefin polymerization has progressed further, based on the use of novel organo-transition metal complexes known as *metallocenes*. Metallocene catalysts, discovered in the 1980's, are typically a transition metal sandwiched between two ring structures (Figure 1.2.). Steric

hindrance forms a well-defined single catalytic site. Although metallocene catalysts cost more per pound than Ziegler-Natta (Z-N) catalysts, the higher productivity of more desirable products makes them more cost efficient (Thayer, 1995).

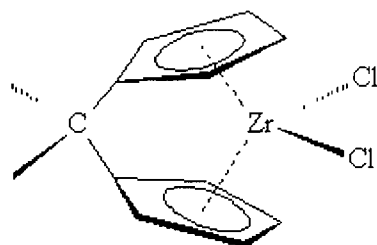


Figure 2. Example of a metallocene pre-catalyst. Reprinted from “Recent Advances In Metallocene Catalyzed Polymerization Of Olefins and Other Monomers,” by A. J. Reenen, 1999, presented at 2nd Annual UNESCO Trianing School and Poster Symposium, Johannesburg, South Africa. Reprinted with permission.

In contrast to the heterogeneous Z-N catalysts, metallocene catalysts coupled with co-catalysts act homogeneously in solution and can produce pure syndiotactic polypropylene with a narrow molecular weight distribution (MWD). Syndiotactic polypropylene consists of substituents that have alternating positions along the macromolecular backbone of the chain. This contrasts to isotactic polypropylene in which all substituents are located on the same side and to atactic polypropylent where substituents occur randomly along the chain (Figure 1.3.). Syndiotactic polypropylene is softer, clearer, and stronger, and which results in a higher economic profit than isotactic or atactic polypropylene (Thayer, 1995).

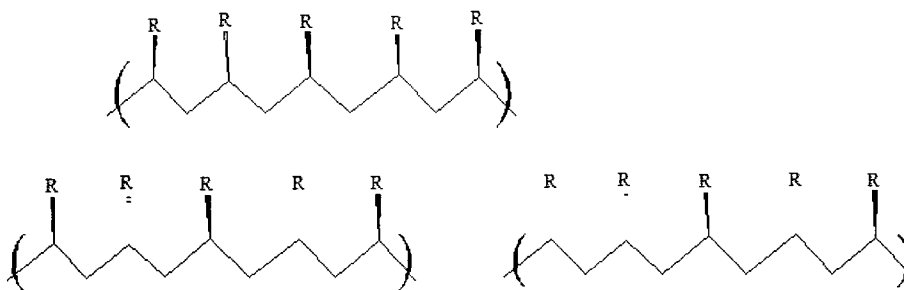
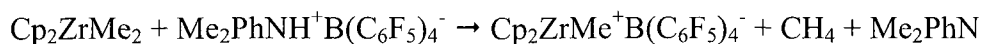


Figure 3. Syndiotactic (top), isotactic (bottom left), and atactic (bottom right) polymer representations.

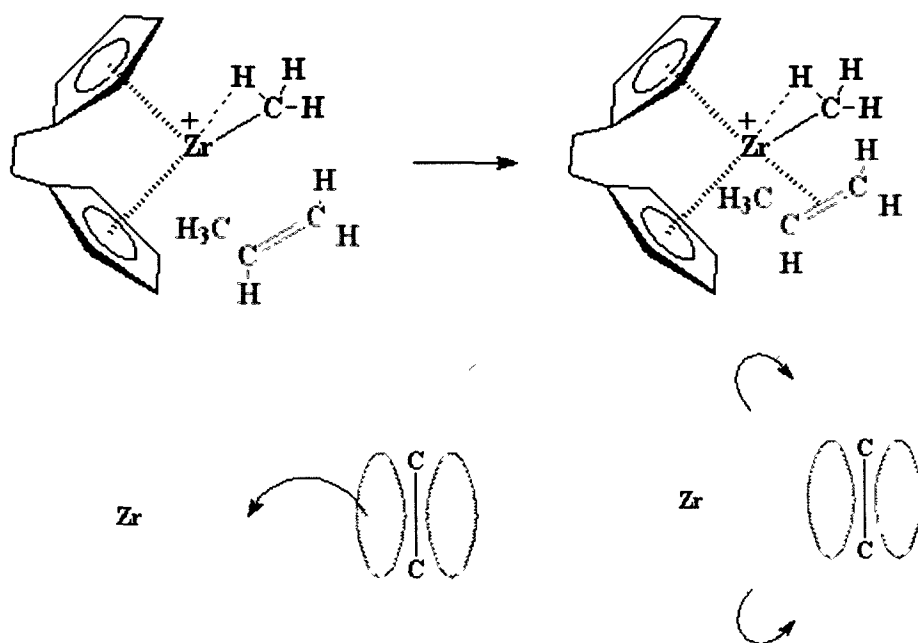
Metallocene Polymerization Overview

Metallocene catalysis is classified under chain polymerization. Chain polymerization has three common steps: initiation, propagation, and termination. The initiation step involves a pre-catalyst reacting with an initiator to generate the reactive catalytic species for the site of monomer addition. Chain polymerization progresses by propagation; individual monomers bond sequentially to the catalyst and are incorporated into the polymer chain. The length of the new polymer will be determined at termination, which ends the propagation process.

Before propagation of a polymer can occur, initiation of the catalyst is necessary. This is accomplished when a metallocene cation (with a positive charge on a transition metal) is formed as a result of a co-catalyst reacting with the metallocene precatalyst in one of five major activation processes (Chen & Marks, 2000). One example of an activation process is the following reaction (protonolysis of M-R bonds; Cp = cyclopentadienyl = C₅H₅; Me = CH₃; Ph – C₆H₅):



The co-catalyst removes methane from the metallocene catalyst resulting in a cation counterbalanced by the original anion. After initiation, the positively-charged catalyst can be involved in the second stage of polymerization (propagation). The cationic metallocene contains an empty d-orbital which can be filled by electrons from the π -bonding orbital of an alkene's double bond (Figure 1.4.) (Mathias, 2005).



The electrons from the alkene's π -bonding orbital fit nicely into the empty d -orbital of the zirconium.

Then electrons from one of the filled d -orbitals can slip into the alkene's p -antibonding orbital, making the zirconium alkene complex stronger.

Figure 4. Metallocene catalysis. Reprinted from "Polymer Science Learning Center Web Site," L. Mathias, 2005, University of Southern Mississippi. Reprinted with permission.

Although the metallocene complex is momentarily stabilized, electrons eventually shift. The double bond is broken when the propylene reacts with the methyl group on the zirconium to form a butyl group on the zirconium. The original monomer-metal bond

breaks and the zirconium is then ready to bind another propylene molecule for the chain can continue to lengthen (Figure 1.5.) (Mathias, 2005).

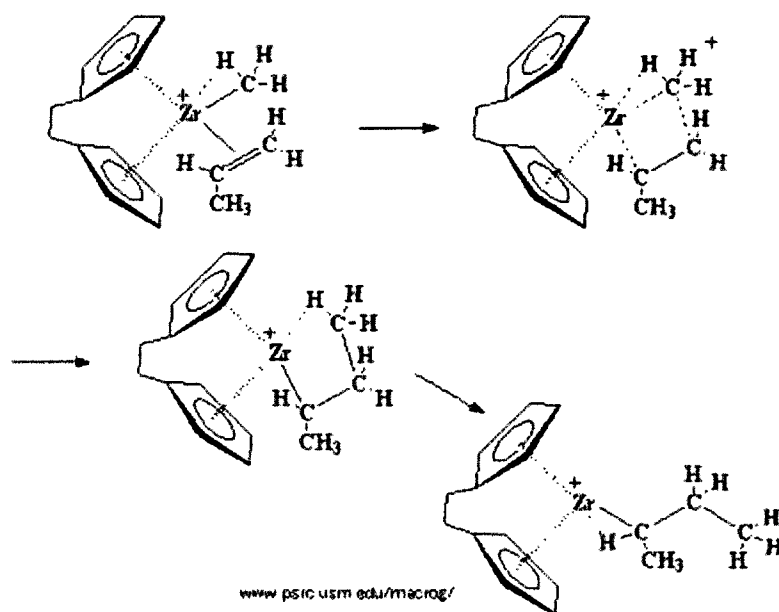
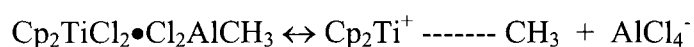


Figure 5. Propagation step of polymerization. Reprinted from “Polymer Science Learning Center Web Site,” L. Mathias, 2005, University of Southern Mississippi. Reprinted with permission.

Co-Catalysts

Polymer characteristics, and therefore structure, can be manipulated by variation in the concentration of reactants, solvent selection, monomer choice, reaction conditions, catalyst structure, and co-catalyst properties (Chien, Tsai, & Rausch, 1991; Coates & Wymouth, 1995; Ewen, 1984; Gauthier, Corrigan, Taylor, & Collins, 1995; Mallin, 1990; Spaleck et al., 1994; Stehling & et al., 1994). The majority of research has been conducted on varying temperature, pressure, catalyst structure, and concentrations to control polymer structure. As the understanding of polymerization mechanisms increases so does the interest in solvents and co-catalysts.

After years of successful olefin polymerization using metallocene catalysts, the exact nature of the active site was still not understood. Eisch, Piotrowski, Brownstein, Gabe, and Lee (1985) were the first to determine the structure of the initial insertion product. They concluded there must be an ion-pair for the activation of ethylene polymerization. (Eisch et al., 1985) The crucial step involves the ionization of the catalyst as shown in the following reaction:



Numerous research groups expanded on Eisch's concept of an ion-pair formation. For example, Yang, Stern, and Marks (1991) synthesized a cationic thorium alkyl, $\text{Cp}'_2\text{ThCH}_3^+\text{B}(\text{C}_6\text{F}_5)_4$, and confirmed that "the variation in adsorbate cation heterogeneous catalytic activity" is related to the counterion.

Eisch, Pombirk, and Zheng (1993) continued his research on polymerization mechanisms by investigating ion-pair equilibria. He began with the theory based on previous studies that during olefin polymerization there is a 1:1 Ti:Al ratio, a cationic titanium center is formed, and the active site involves a carbon-titanium bond. Specifically, he explored the existence of both a contact ion pair (CIP) and solvent separated ion pair (SSIP). Both the ^1H and ^{13}C NMR spectra at two different concentrations separated into two peaks as the temperature was decreased from 27°C to -30°C. This supported the idea of equilibrium between two types of ion pairs: CIP and SSIP. In addition, the ^{13}Al NMR revealed that two different tetra-coordinated aluminum components are present. At -30°C in the more polar solvent, the predominant peak was the high-field peak. So the high-field signal was assigned to the SSIP. The shorter Cp-Ti separation in cationic derivatives was suggested by Eisch et al. (1993) as another reason

to expect the SSIP NMR peak to be up field from the CIP peak due to additional shielding. At 25°C in the more polar solvent a downfield shift occurred for the ^1H NMR of SSIP, suggesting that a cation formed. Dilution caused the SSIP to predominate with a maximum peak height at around 0°. The polymerization number (PN) was investigated under varying conditions. The PN was found to increase with solvent dilution and increased solvent polarity. There was a maximum PN at around 0°C. Because these factors correspond to the SSIP, data Eisch et al. (1993) concluded that the SSIP is the more active site for ethylene polymerization.

Shiomura, Asanuma, and Inoue (1996) concluded that the stereoselectivity of polymerization depends on the co-catalyst. Data comparing the methylaluminoxane (MAO) to $\text{B}(\text{C}_6\text{F}_4)_4^-$ anion indicated that the formation of the SSIP allows chain migration and therefore the formation of syndiotactic polymers. The CIP lead to isotactic polymers due to stationary insertion (Shiomura et al., 1996).

Jia, Yang, Stern, and Marks (1997) studied olefin polymerization by varying the anion identity while using the same cation. The variation in activity led them to conclude that the tightness of ion pairing is significant in ethylene polymerization. Chen, Stern, and Marks (1997) results supported Jia's idea that olefin polymerization is sensitive to ion pairing. More specifically, stronger ion pairing increases syndioselectivity while weaker ion pairing enhances the rate of propylene polymerization.

These examples confirm the importance of the counter anion in olefin polymerization. The exact anion structure selected for polymerization depends on the polymer characteristics being sought. However, some characteristics are desirable in all counter anions.

Optimal Characteristics of Counter Anions

It is well established that polymerization productivity depends on not only the counter anion, but also the reaction medium. Bochmann and Jaggar (1992) studied solvent and anion effects of ethylene polymerization using $[(\text{Indenyl})_2\text{TiMe}]\text{BPh}_4$. They were aware that because the metal alkyl cation is highly electrophilic, the alkene monomer must compete with any available electrophile in solution. This includes, but is not limited to, the solvent and the counter anion. To allow alkene monomers accessibility to react with catalytic cations for olefin polymerization, anions with weak coordinating properties are the most desirable.

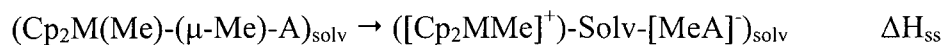
Although it is difficult to ignore solvent effects, the development of an anion with optimal characteristics is the focus of my research and will be the concentration of the remainder of the chapter. As stated by Dagani (1998), since not just one anion will be the best, or even effective, for every polymer application the synthesis of many counter anions to select from is desirable. Referred to as *weakly coordinating anions*, these counter anions should have a small delocalized charge, weakly interacting periphery groups, possess poor nucleophilic properties, and be as non-oxidizing and non-basic as possible. Properties that are more obvious include kinetic and thermodynamic stability, high purity, and low cost (Ewen, 1984; Strauss, 1992). A delocalized, low charge and poor basicity is best established by using anions consisting of a negative-one or negative-two charge.

Although there is probably no such thing as a non-coordinating anion, research continues to search for the least coordinating anion. In 1986, the carborane anion, $\text{B}_{10}\text{CH}_{12}^{1-}$, was believed to be the least coordinating anion (Lupenetti & Strauss, 1998;

Strauss, 1992). It has a large size, is thermodynamically stable, round and symmetrical in geometric shape, contains a low negative charge that is delocalized, and periphery atoms are not expected to form additional bonds.

It is also important that the peripheral groups on the surface of the anion be weakly coordinating. Therefore, fluorine atoms are often substituted for hydrogen atoms on the anion. Both form tight bonds and as a rule only bond with one other atom, but hydrogen often additionally has weak agostic interactions with metal sites, while C-F or other C-halogen bonds coordinate very weakly to metal ions (Deck, Beswick, & Marks, 1998). Thus, the anion $\text{CB}_{11}\text{H}_6\text{Br}_6^-$ not only has lower charge density than $\text{B}_{11}\text{CH}_{12}^{1-}$, but it also has electronegative weakly coordinating bromine atoms.

Vanka, Chan, Pye, & Ziegler (2000) explained Deck et al.'s direct relationship of polymerization activity to fluorine atoms on the cocatalyst by the increased negative enthalpy of the ion pair formation between the pre-catalyst (containing metal atom $\text{M} = \text{Ti, Zr, or Hf}$) and co-catalyst in order to form the most stable contact ion pair. The next step, formation of the cation and anion should have a low negative enthalpy and may actually be the formation of a solvent-separated ($\text{Solv} = \text{solvent}$) ion pair (Figure 1.6).



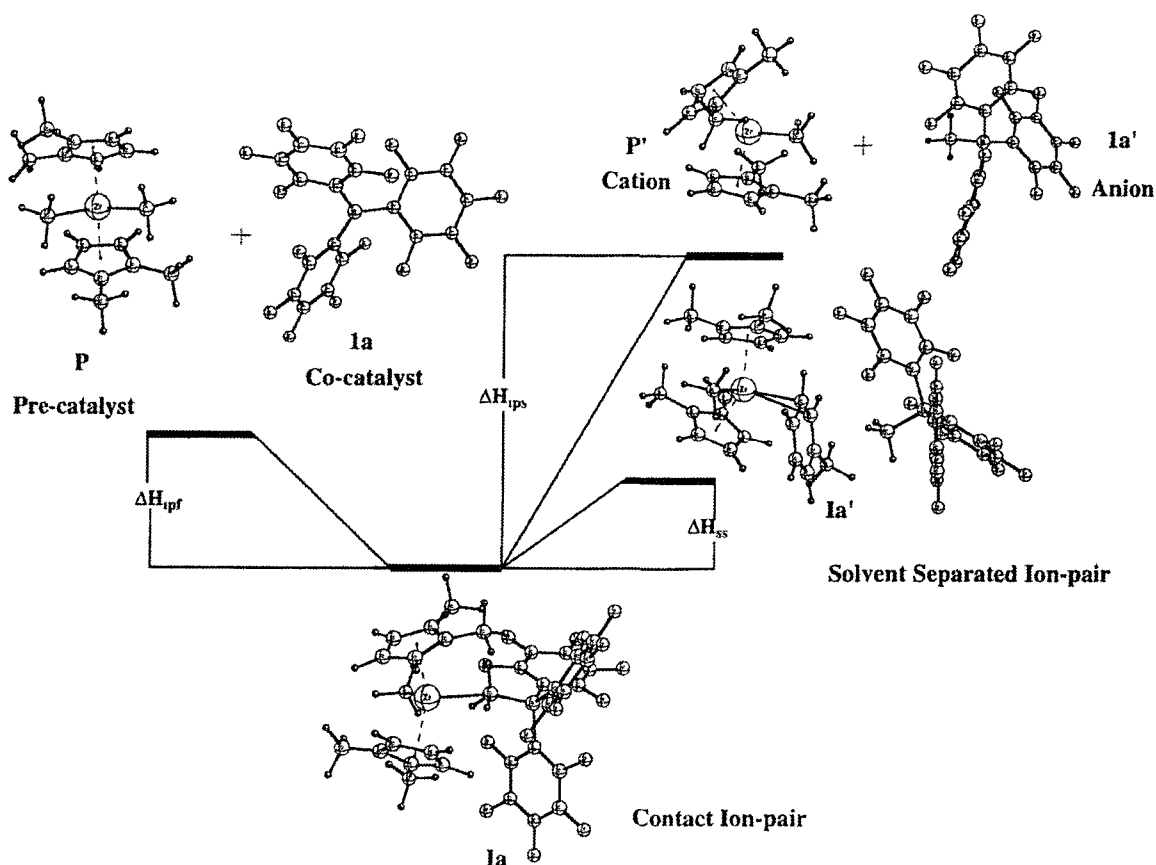


Figure 6. Relative ΔH for ion pairs of $[(1,2\text{Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]^-$. Reprinted from “A Density Functional Study of Ion-Pair Formation and Dissociation in the Reaction between boron- and Aluminum-Based Lewis Acids with $(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}_2$,” K. Vanka, 2000, *Organometallics*, 19, p. 1841-1849, Copyright 2000 by American Chemical Society. Reprinted with permission.

Trisphat Anion

Beginning in 1997, Lacour, Ginglinger, Grivet, and Bernardinelli (1997) and Favarger, Goujon-Ginglinger, Monchaud, and Lacour (2004) developed the synthesis and usage of “TRISPHAT”, the tris(tetrachlorobenzenediolato)phosphate(V) anion--a large, negative one anion containing a six-coordinate phosphorus with three chelating tetrachlorocatecholate ligands for uses such as the resolution of chiral cations, and

inducing chirality into syntheses. We hypothesized that this anion might also be weakly coordinating, since its only good donors atoms, oxygen, are buried within the anion. This anion contains a fairly uncommon, but by no means unique, coordination number of six for the phosphorus(V) central atom.

Before this, Hellwinkel (1965) investigated six-coordinate phosphorus compounds and synthesized the first tris bi-dentate phosphorus compound. Phosphorus pentachloride and 2,2-dilithium-biphenyl reacted to form a cation and anion. These were separated in a second step by reaction with sodium iodide (Figure 1.7.). Further studies confirmed the existence of two optical isomers of C_3 symmetry with three-fold rotation axes (Hellwinkel & Mason, 1970).

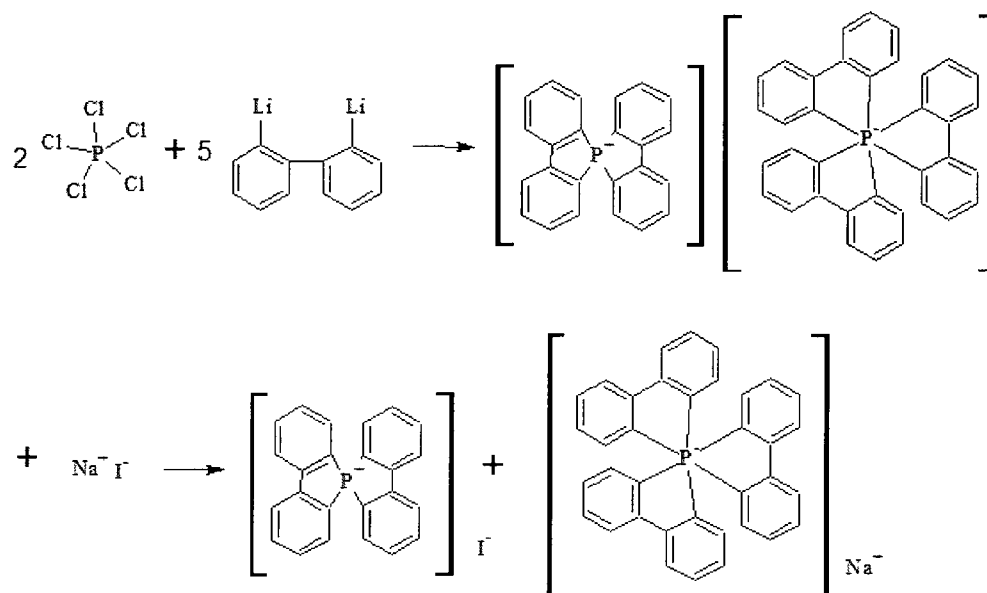


Figure 7. Steps for synthesis of a tris-bidentate chelated phosphorus anion. (Hellwinkel, 1965).

Allcock (1964) synthesized another tris-bidentate phosphorus anion in one step. Phosphonitrilic ester in tetrahydrofuran, or toluene, with six equivalents of catechol and

three equivalents of triethylamine resulted in either 2-(o-hydroxyphenoxy)-2,2'-spirobi[1,3,2-benzodioxaphosphole] triethylamine salt or the hexavalent phosphorus anion tautomer (Figure 1.8).

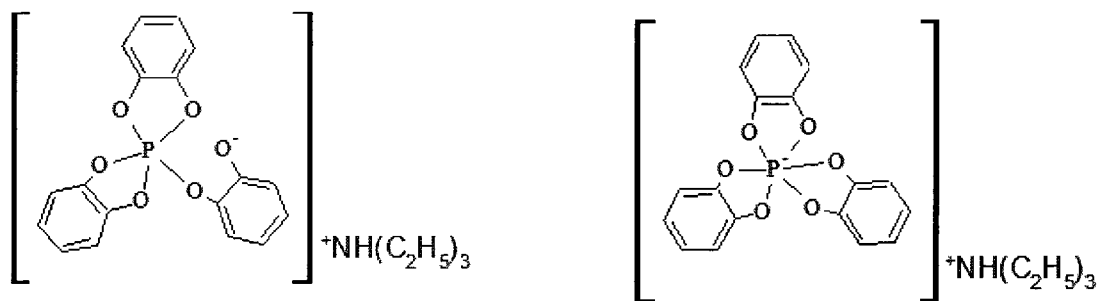


Figure 8. Suggested products of the 1964 synthesis. (Allcock, 1964).

Allcock continued his research (Allcock & Bissell, 1972) in order to determine if there was ring degradation as he had reported in 1964. X-ray crystallography confirmed the hexa-coordinated organophosphate structure.

Ramirez, Bigler, & Smith (1968) investigated various penta-coordinate phosphorus structures that had previously been reported in error. When reacting catechol with phosphorus pentachloride the mole equivalence affects the number of chlorides replaced by bidentate ligands (Figure 1.9).

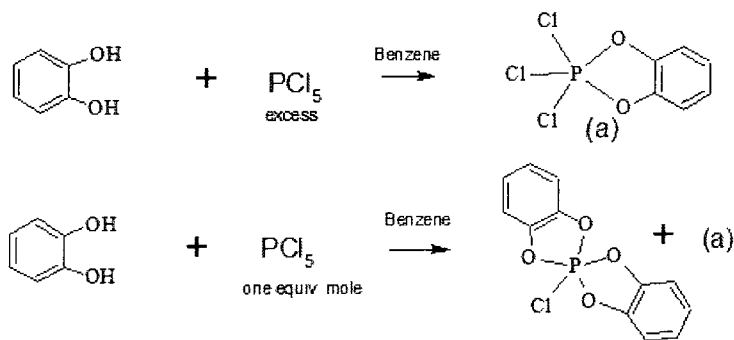


Figure 9. Products from catechol and phosphorus (V) chloride (Ramirez et al., 1968).

Ramirez also discovered that a tetra-chloro derivative could be formed by using 3,4,5,6-tetrachlorobenzoquinone in place of catechol. (Figure 1.10.)

Gloede and Gross (1976) expanded on Ramirez's work and proposed steps for the formation of the tris(catecholato)phosphate(V) or o-phenylene-orthophosphate anion from catechol and phosphorus pentachloride (Figure 1.11.).

Koenig, Kläbe, Munox, & Wolf (1979) confirmed the mechanism of forming a hexa-coordinated phosphate ion through a penta-coordinated intermediate by reacting phosphorus pentachloride with catechol. The addition of a base pushed the equilibrium toward the hexa-coordinated anion (Figure 1.12.).

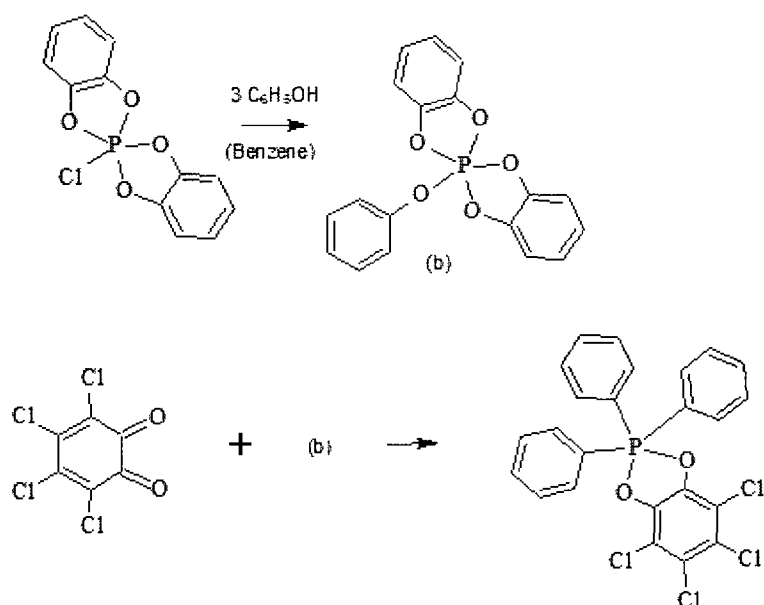


Figure 10. Formation of a tetrachlorocatechol derivative of penta-coordinated phosphorus (Ramirez et al., 1968).

Lacour et al. (1997) knew there were chemical applications of hexa-coordinated phosphorus anions. The studies by Koenig et al. (1979) suggested decreasing

the basicity of the oxygen atoms would stabilize the phosphate (V) ions. Lacour's proposal to accomplish this by adding electron-withdrawing groups to catechol was successful.

Tris(tetrachlorobenzenediolato)phosphate(V) anion (TRISPHAT) was prepared using phosphorus pentachloride, tetrachlorocatechol, and an amine in toluene (Figure 1.13). It was characterized crystallographically with P-O bond distances ranging from 170.0 pm to 172.6 pm, and ^{13}C NMR peaks at 114.7 pm (C-3/6), 123.6 pm (C-4/5), and 142.6 pm(C-1/2).

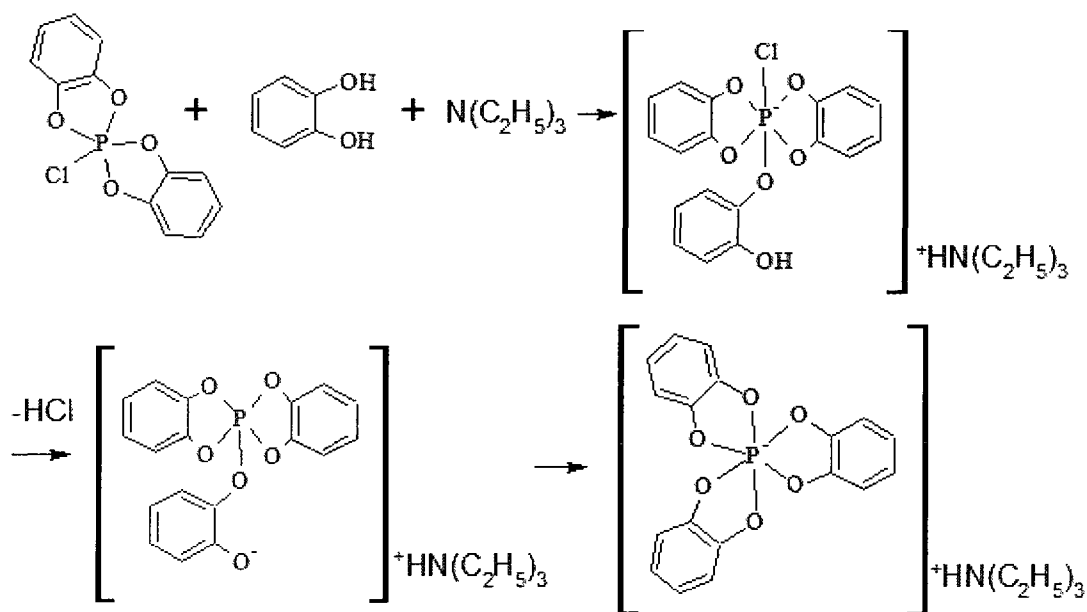


Figure 11. Steps for the synthesis of a hexa-coordinated tris(bidentate)phosphate anion (Gloede & Gross, 1976).

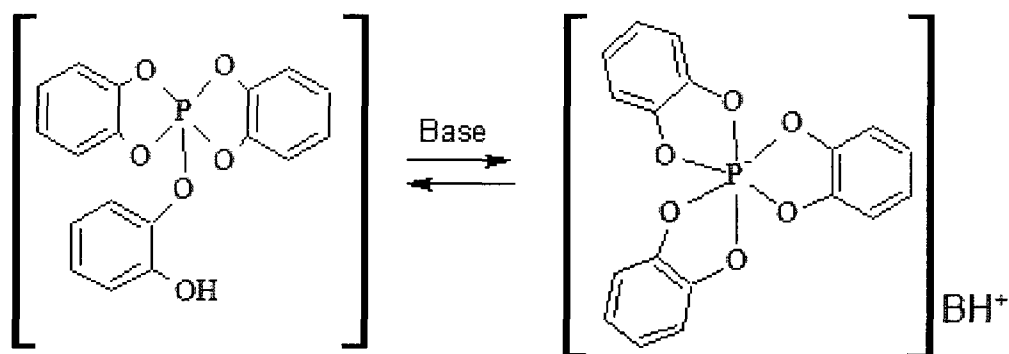


Figure 12. Base forcing equilibrium from a five to six-coordinated phosphorus central atom (Koenig et al., 1979).

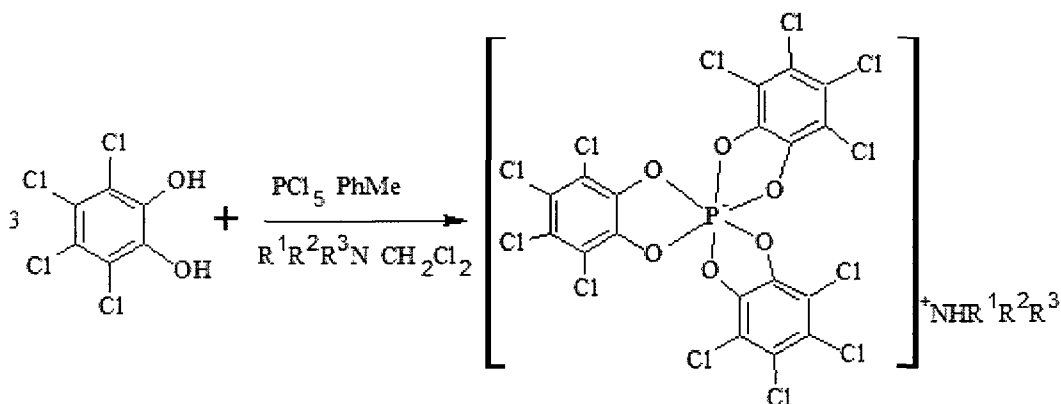


Figure 13. Synthesis of TRISPHAT anion (Lacour et al., 1997).

Successful application of racemic-tris(tetrachlorobenzenediolato)phosphate anion (TRISPHAT) to metallocene catalysis of olefin polymerization was accomplished by Lee (2006). Lee attempted to form single-handed polymers for many potential applications. He theorized that using a chiral anion would be possible and less expensive than using a chiral metallocene cation. Although the stereoregularity of the polymerization was not controlled, three polymerization procedures were successful in polymerizing tert-butyl vinyl ether in reasonable yield and with good molecular weights (MW) and MWD.

Tristibate Anion

Lacour's (1997) standard synthesis of the parent acid of the trisphat anion involves the reaction of PCl_5 and tetrachlorocatechol in dry toluene under argon in Schlenkware (Favarger et al., 2004). The intermediate acid form of TRISPHAT was found to be very unstable, decomposing within a week even if stored under vacuum or inert atmosphere. Wulfsberg hypothesized that using the larger antimony as the central atom (cationic radius of 74 pm versus 52 pm for phosphorus), the parent acid of the corresponding "tristibate" anion would be more stable given that the coordination number of six is more common for antimony than for phosphorus.

Lacour reacted his parent acid of TRISPHAT immediately after isolation with a solution of an amine (for example, tributylamine to give tributylammonium TRISPHAT). These salts are thought to be stabilized by hydrogen bonds between H atoms on the amine and an O atom from a catecholato ligand. Group 1A or metallocene cation salts of TRISPHAT would not be stabilizable by hydrogen bonds; they were first obtained by Lee (2006) using the drastic method of combining the very reactive compound sodium hydride with an amine salt of TRISPHAT.

In contrast, Shieh (2007) and Marella (2004) were able to make Group 1 salts of TRISPHAT in the presence of water by the neutralization of the unstable TRISPHAT acid with solid Group 1 metal oxides or even with concentrated aqueous metal hydroxides. Hall (2008) was also able to make these Group 1 salts of TRISPHAT by treatment of the amine salt of TRISPHAT with concentrated aqueous solutions of Group 1 metal hydroxides. These reactants are far less hazardous than the very flammable, water-sensitive sodium hydride. These researchers found the Group 1 salts of

TRISPHAT, which lacked hydrogen-bonding possibilities, were not very stable, but could be stored under vacuum for a few months. We hoped that the Group 1 salts of the larger tritribate anion would be more stable than those of the TRISPHAT anion.

A logical extension of research to find a more stable polymerization co-catalyst ion than TRISPHAT ion is to substitute phosphorus with a larger metal in the same group (column). Lamberth, Machell, Mingos, and Stolberg, (1991) synthesized an analogous anion using the even larger (83 pm) fourth-period Sn^{4+} ion. The reaction of SnCl_4 , three moles of tetrachlorocatechol (TCC), and tributylamine gave the STANNAT salt $\{\text{HN}(\text{C}_4\text{H}_9)_3\}_2[\text{Sn}(\text{O}_2\text{C}_6\text{Cl}_4)_3]$, in which the STANNAT anion has a -2 charge. However, we theorize that the -2 charge would make this anion more basic than TRISPHAT.

Keeping the central-atom with an oxidation state of +5 would result in a complex with the lowest charge possible (-1) but larger size, resulting in a greater dispersion of the negative charge. Antimony was chosen over arsenic to avoid toxic exposure, although we subsequently learned that antimony is also very toxic (Emsley, 2005). Hence we decided to attempt to synthesize and study the analogous tris(tetrachlorobenzenediolato)stibate(V) (or alternately named, -antimonate(V)) anion, which we designate as tristibate, following the synthesis of its parent acid. With its small charge and large size, it was hoped that it would be a more useful counteranion to zirconocene cations in metallocene catalysis.

A mixture of trivalent and pentavalent antimony compounds were patented in 1972 by E. I. du Pont de Nemours and Company (Chay, Cumbo, Randolph, & Yates, 1972). The invention formed an ester that was soluble in polar organic solvents in order to enhance flame resistance in polymers. The beginning reagent used was antimony (III)

oxide, Sb_2O_3 , and an aliphatic polyhydroxy compound containing two to six carbons and vicinal hydroxy groups. In order to be effectively soluble a minimum percentage of pentavalent antimony had to be obtained. The oxidation was accomplished using hydrogen peroxide and removing water. The resulting pentavalent product was known to be hexa-coordinated. However, the sixth coordination site could either involve the third bidentate ligand or an electron-donating atom. (Figure 1.14.).

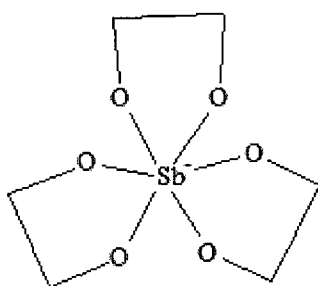


Figure 14. Possible structure of an antimonate(V) anion synthesized from antimony (III), a polyhydroxy alcohol, and hydrogen peroxide (Chay et al., 1972).

Mazieres and Lefebvre (1976) studied the kinetics of the coordination of the hexahydroxoantimonate (V) anion with pyrocatechol. The result was complexation by one bidentate ligand (Figure 1.15.).

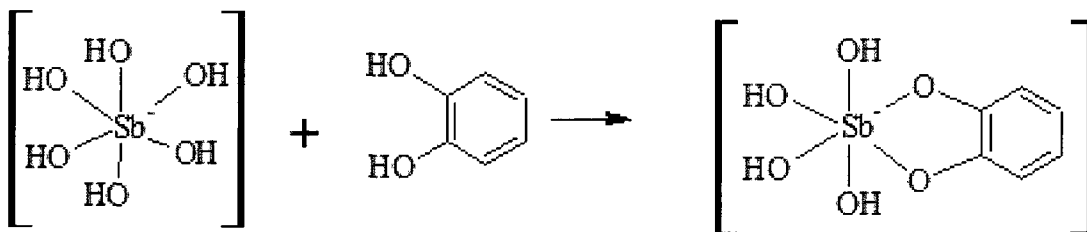


Figure 15. Synthesis of (catecholato)tetrahydroxyantimonate(V) anion (Holmes, Day, Chandrasekhar, & Holmes, 1987).

Another antimony(V) complex of one bidentate catecholato ligand was synthesized by Hall and Sowerby in 1979 (Hall & Sowerby, 1980) by the reaction of triphenylantimony dichloride and catechol in ammonia; the product was a hemihydrate, $2\text{Ph}_3\text{Sb}(\text{O}_2\text{C}_6\text{H}_4) \cdot \text{H}_2\text{O}$.

Holmes, Day, Chandrasekhar, and Holmes (1987) carried out several investigations of the formation of organoantimony(V) complexes with bidentate chelating diols. They synthesized the triethylammonium salt of a six-coordinated organoantimony(V) anion, $[\text{Ph}_3\text{Sb}(\text{Cl})(\text{O}_2\text{C}_{10}\text{H}_6)] [\text{Et}_3\text{NH}]$, with one chelating naphthalenediolato ligand, by reacting triphenylantimony dichloride with naphthalenediol and triethylamine (Figure 1.16).

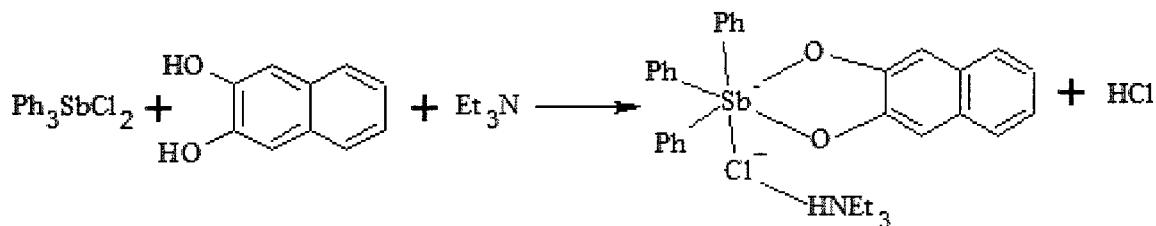


Figure 16. Synthesis of an organoantimony(V) complex anion with one chelating naphthalenediolato ligand (Holmes et al., 1987).

Hall and Sowerby (1980) found that reacting triphenylantimony dichloride and catechol gave a product that contained both five- and six-coordinated antimony atoms. (Figure 1.17).

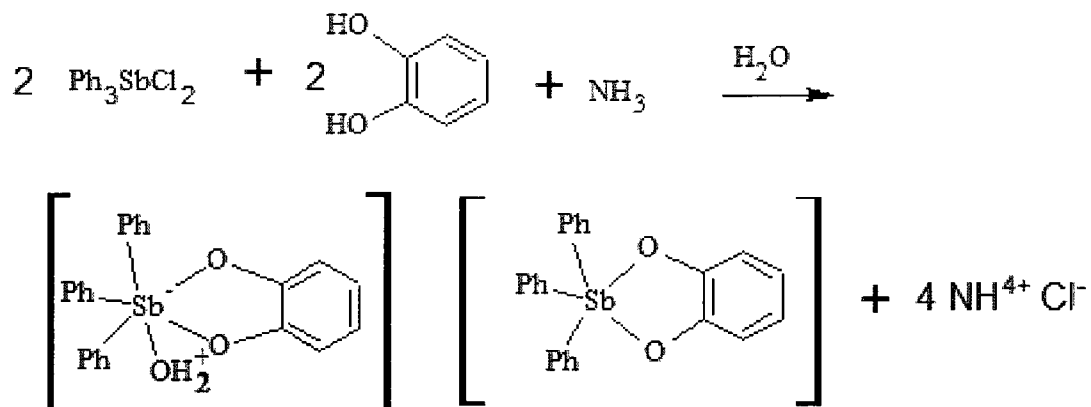


Figure 17. Synthesis of a product containing five- and six-coordinated antimony atoms using catechol as a reactant (Holmes and Sowerby, 1980).

Holmes et al. (1987) also investigated analogous reactions of 3,4,5,6-tetrachloro-1,2-benzoquinone. They synthesized a five-coordinate antimony(V) complex via an oxidation-reduction reaction of 3,4,5,6-tetrachloro-1,2-benzoquinone and triphenylantimony, obtaining $(\text{C}_6\text{H}_5)_3\text{Sb}(\text{o-O}_2\text{C}_6\text{Cl}_4)$, which was found by X-ray crystallography to have Sb-O distances of 201.9 pm and 210.7 pm.

They also synthesized a six-coordinate antimony(V) complex with one bidentate tetrachlorocatecholato ligand via an oxidation-reduction reaction between tetrachlorobenzoquinone and phenyl(2,2'-biphenylene)stibine to form $(\text{Cl}_4\text{C}_6\text{O}_2)(\text{C}_{12}\text{H}_8)\text{SbPh}$ (Figure 1.18), with Sb-O bond distances of 202.7 pm and 205.5 pm.

Gibbons, Begley, Blake, and Sowerby (1997) followed this reaction with a reaction of $\text{C}_6\text{H}_5\text{SbCl}_2$ and 3,4,5,6-tetrachloro-1,2-benzoquinone in ether to give another six-coordinate antimony(V) complex of TCC, $\text{PhSb}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{Cl}_2 \bullet (\text{C}_2\text{H}_5)_2\text{O}$, the structure of which was confirmed by X-ray crystallography (but for which complete ^{13}C

NMR spectra could not be obtained). In this compound Sb-O(TCC) distances were 199.1 and 202.6 pm.

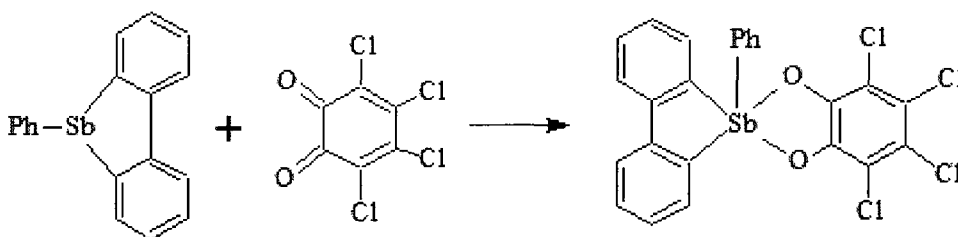


Figure 18. Synthesis of an organoantimony (V) complex with one chelating tetrachlorocatecholato ligand (Hall and Sowerby, 1980).

Tian and Tuck (1993) reported a reaction between antimony metal and 3,4,5,6-tetrachloro-1,2-benzoquinone to give a compound of stoichiometry $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$. They speculated that this compound, with ^{13}C NMR peaks at 116.9 ppm (C-3), 121.8 ppm (C-4), and 142.4 ppm (C-1), might contain the tristibate anion as a salt of the $[(\text{Sb}(\text{O}_2\text{C}_6\text{Cl}_4)_2(\text{ether})_2)]^+$ cation, but they were unable to obtain a crystal structure to establish this. (The occurrence of only three ^{13}C NMR peaks for six inequivalent carbon atoms could indicate rapid exchange of tetrachlorocatecholato anions between the cation and anion.)

Although chelation of antimony(V) by three bidentate tetrachlorocatecholate anions has not been published in the literature, examples of tris-chelation of tin(IV), rhenium(VI), molybdenum(VI), and tungsten(VI) are known (deLearie, Haltiwanger, & Pierpont, 1987; deLearie & Pierpont, 1988; Pierpoint & Downs, 1975; Holmes et al., 1988). The compound $[\text{Re}(\text{C}_6\text{Cl}_4\text{O}_2)_3]$ was formed by a redox reaction of $\text{C}_6\text{Cl}_4\text{O}_2$ (deLearie et al., 1987), with Re-O bond distances ranging from 192.5 pm to 194.3 pm.

Similar redox reactions were employed to prepare complexes of Mo(VI) and W(VI) (deLearie & Pierpont, 1988; Pierpont & Downs), which turned out to be dimeric $M_2(O_2C_6Cl_4)_6$ complexes with both chelating and bridging tetrachlorocatecholate ligands, (deLearie et al., 1987; deLearie & Pierpont, 1988; Holmes et. al., 1988; Pierpont & Downs, 1975) with chelating bond distances for Mo-O 193.8 pm and 195.5 pm and, for W-O of 192.6 pm and 195.1 pm. Different salts of the dianion $[Sn(C_6Cl_4O_2)_3]^{2-}$ with the cations Et_3NH^+ (Lamberth et al., 1991), $(CH_3)_2NCH_2CH_2N(CH_3)_2H^+$ (Annan, Chadha, Tuck, & Watson, 1987), and the chiral tris{4,4'-bis(dibutylaminostyryl)-2,2'-bipyridine}ruthenium(II) (Feuvrie, Ledoux, Zyss, Le Bozec, & Maury, 2005) cation have been reported, with Sn-O distances such as 205.1 to 207.9 pm (Holmes et al., 1988). Since the cationic radius of W(VI) is the same as that of Sb(V), 74 pm, and that of Sn(IV) is only somewhat larger, 83 pm, this suggested that a stable tristibate anion might be possible, with expected Sn-O distances near 200 pm (ca. 30 pm longer than the P-O distances in TRISPHAT).

Our initial thought was that this would make the tristibate anion larger than TRISPHAT and therefore less basic. Such a prediction would not hold if the cation were small enough to penetrate a threefold cleft of the TRISPHAT anion (Fig. 1.19) to coordinate closely to the oxygens. (The twofold clefts of TRISPHAT are even more open and less hindered, and might be a more likely site for coordination.) Because the oxygen donor atoms of tristibate are further from the central atom than are those of TRISPHAT, coordination of a small cation or Lewis acid might be easier for tristibate than TRISPHAT. However, zirconocene cations are not small, and we focus on using large +1-charged cations as models for these catalytically active cations.

Because of the larger size of the antimony atom and the small bite angle of the two oxygen atoms in the chelating catecholato ligand, we also considered the possibility that its coordination number might exceed six, for example, a tetrastibate ion. The coordination number eight appears to be quite unusual for antimony(V), but has been noted with at least one chelating ligand, the tropolonate anion $C_7H_5O_2^-$ (Muetterties & Wright, 1965), which gives stable eight-coordinate +1-charged cations with niobium(V) and tantalum(V) and a less stable cation with antimony(V). In contrast, coordination number seven is well-known for Sb(V) in the fluoro anion SbF_7^{2-} (Kukushkin, 1990).

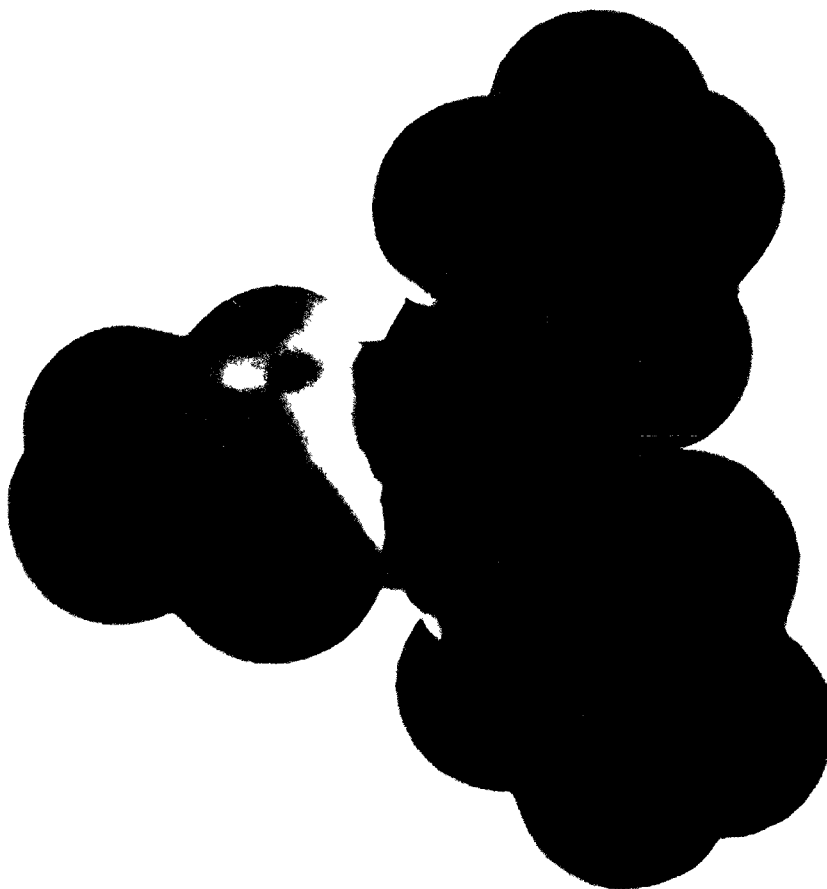


Figure 19. ELPOT diagram computed for the TRISPHAT anion, viewed along its threefold axis. William Ilsley, private communication. Used by permission.

Attempts to prepare tristibate anion were carried out by Shieh, (2007) using a reaction analogous to the reaction of Lacour to produce TRISPHAT, (Lacour, 1997) substituting antimony(V) chloride for phosphorus(V) chloride. Shieh characterized his products by ^{13}C NMR and IR spectroscopy, but generally not elemental analysis. The ^{13}C NMR spectra, however, were problematic. For the tristibate salts, he measured ^{13}C NMR peaks of about 117, 119, and 151 ppm, and for “tristibic acid” usually about 119, 123, and 142 ppm. However, the 151 ppm peak in particular does not resemble any found by Tien and Tuck for their antimony tetrachlorocatecholate, nor those found by Lacour for TRISPHAT. Toward the end of his work, some of Shieh’s products were characterized by inductively couple plasma (ICP) elemental analysis and scanning electron microscopic dispersive x-ray (SEM-EDXA). Some of these products turned out to contain no antimony, while others did contain antimony. The SEM-EXDA analysis was not able to give accurate percentages of antimony, however. The tristibic acid intermediates were also characterized by their equivalent weights as obtained by titration, but these tended to come out too low, with much uncertainty due to interfering color changes at the endpoint. Hence a major purpose of this research is to confirm or refute Cheng-Nien Shieh’s novel synthesis of the salts of the tris(tetrachlorobenzenediolato)antimonate(V) (tristibate) anion, and its parent acid.

EXPERIMENTAL

Methods and Material

Spectra for ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) were measured on a JEOL ECX 500 MHz NMR spectrometer. Infrared (IR) spectra were measured on a Varian 7000 FT-IR spectrometer. The cell was washed with 50:50 methanol:water. The resolution was set to 4 cm^{-1} and the number of scans was set to 32. Elemental analysis was done by Galbraith Analytical Laboratories in Knoxville, TN.

Tetrachlorocatechol (98%) was from Avocado Research chemicals Ltd. Antimony(V) chloride, 1.0 M (99%) solution in dichloromethane, liquid (99.99%) antimony(V) chloride, Nickel (II) carbonate hydroxide tetrahydrate, TMS (NMR grade, 99.9+%), cesium carbonate (99%), deuterium oxide (99.9% D), and diethylamine (99.5+%) were from Aldrich. Dry (sealed) toluene (99.8% anhydrous AcroSealTM), dichloromethane (99.9% AcroSealTM), and antimony(V) oxide (99.995%) were from Acros Company. Acetonitrile was Biotech grade (99.93+%) from Sigma-Aldrich. Barium carbonate (99.8%) and hexane were from Fisher Scientific. Fluka was the source for >98% 3, 4, 5, 6-tetrachloro-1,2-benzoquinone. CD_3CN , d^6 -DMSO, and CDCl_3 used for NMR spectra (99.6%) were in 0.75 mL ampoules from Acros Organics. Thionyl chloride had a density of 1.63 g/mL.

Tetrachlorocatechol Sublimation

A 13.04 g sample of impure (98% and partially hydrated) tetrachlorocatechol, TCC, was weighed and transferred to a vacuum sublimation apparatus. A test tube was used to compress the TCC so it would not contact the cold finger. The apparatus was submerged in a high-temperature silicone oil bath in a beaker. The apparatus was

connected to a vacuum pump protected by two liquid nitrogen traps. The pump was turned on and the vacuum line was checked for leaks by its sound, and by isolating sections, using a mercury pressure gauge. Cold water was turned on for condensation. The temperature of the oil was slowly brought to approximately 185°C by using the Variac power supply. The sublimation appeared to be finished within two hours. The process was allowed to continue for over two and a half hours to ensure complete sublimation. The apparatus was cooled down to room temperature and then disconnected under the hood to reduce exposure to the gas released. The cold finger was transferred to an argon-flushed glove bag. The TCC was scraped into a test tube. The TCC collected weighed 11.23 g (45.31 mmol, 86.0% yield, based on the assumption that the starting TCC was anhydrous) and was stored under argon. There was 0.23 g of black residue remaining. It was determined to be highly soluble in acetone. Liquid was noted in the liquid nitrogen traps.

The ^{13}C NMR spectra of TCC were measured in the following solvents: d^6 -DMSO, 119.9, 121.6, and 144.0 ppm (proton decoupling, no TMS reference); CD_3CN , 118.8, 122.2, and 141.7 ppm from TMS; CDCl_3 , 118.8, 123.8, and 139.9 ppm from TMS.

Tetrachlorocatechol Comparison. Tetrachlorocatechol from an opened and unopened bottle were analyzed. The IR spectra of the two bottled samples had the same peaks: 672, 752, 813, 951, 996, 1165, 1274, ~1288, 1310, 1396, and 1447 cm^{-1} . The IR spectrum from the sublimed tetrachlorocatechol had peaks at 672, 752, 813, 950, 996, 1166, 1275, ~1290, ~1397, and 1448 cm^{-1} .

Distibic Acid, First Attempted Synthesis

A three-neck 250-mL round-bottom flask and syringe were cleaned with acetone and dried overnight in the oven. A manifold for the house vacuum and argon gas was equipped with a mineral oil bubbler. A glove was flushed with argon gas at least six times. The round-bottom flask and a 5 g bottle of antimony(V) chloride were transferred to the glove bag. A 5.08 g (17.00 mmol) sample of antimony(V) chloride was transferred to the flask. The left and middle necks of the flask were sealed with glass stopper. The right neck was sealed with a rubber septum. The flask was submerged in a low temperature oil bath. With argon flowing through, the left opening was equipped with a thermometer, and the middle opening was equipped with a water condenser, instead of stoppers. As toluene was transferred through the septum, using a glass/metal syringe, the left glass stopper was violently forced out by the production of a white cloud. More toluene was added but no additional cloud was formed. Approximately 30 mL total of toluene were used. Using the manifold, the air was removed and replaced with argon gas five times. An 11.2 g (45.2 mmol) sample of TCC was transferred to a 50-mL Aldrich System 45™ powder addition funnel in an argon glove bag. The TCC was added slowly over 10 to 15 minutes. The funnel was rinsed with 10 mL of toluene. The apparatus was rearranged so the exit port of the bubbler had a very slow flow of argon flowing in the right opening and out the condenser. The pH of the gas coming out of the bubbler was checked with moist pH paper. The pH paper turned red, which indicated an acid was being released from the reaction. The heat for the oil bath was turned on and allowed to reach 95°C. The reaction was stirred for 48 hours until the pH paper failed to turn red. The flask was purged with argon, sealed, and stored in the freezer for four days,

whereupon a solid crystallized out. It was washed with 30 mL of cool toluene and then 20 mL of pentane using suction filtration and a medium porosity glass filter. The product (10.22 g) was transferred to a test tube and stored under house vacuum.

Seven days later the product was observed under a microscope. Long clear needles had appeared on the side of the test tube. The product and TCC were each dissolved in separate test tubes of acetone. A phenol test using FeCl_3 in acetone (1 g/100 mL) turned dark purple in both cases. The product appeared to form a precipitate with FeCl_3 . When FeCl_3 was added to the TCC solution no precipitate was formed.

The product would not dissolve and turned yellow when added to d^6 -DMSO. No ^{13}C NMR spectrum in d^6 -DMSO was observed. The ^{13}C NMR spectra of the product were measured in the following solvents: d^3 - CD_3CN , 120.2, 123.6, 126.3, 129.3, 130.0, and 143.1 ppm from TMS; d-CDCl_3 , 118.8, 123.8, 125.3, 128.2, 129.0, and 140.0 ppm from TMS. The IR spectrum had peaks at 673, 753, 790, 813, 951, 964, 996, 1167, 1276, 1289, 1310, 1397, and 1449 cm^{-1} .

First Cesium Distibate Synthesis

A 100-mL round-bottom flask was cleaned with acetonitrile. A 0.49 g (0.76 mmol) sample of distibic acid was weighed on paper and transferred to the flask. Approximately 6 mL of acetonitrile was transferred to the flask with a glass/metal syringe. The solution was swirled for a few minutes. Some solid remained in the bottom of the flask. An additional 4 mL of acetonitrile was added. The solution was swirled until the transparent solution had no visible solid on the bottom of the flask. A 0.12 g (0.37 mmol) sample of cesium carbonate was weighed in a 10 mL beaker. Approximately 2 mL of distilled water was added and the solution was stirred with the

metal spatula. The cesium carbonate dissolved immediately. A few drops of cesium carbonate solution were added to the distibic acid solution. A liquid separation could be seen. The flask was swirled until there was one phase. This was continued until the cesium carbonate solution was completely added. A few times a white precipitate would form but it quickly disappeared. The solution was rotary evaporated to dryness in less than 10 minutes. A fine, white, crystalline product remained on the sides of the flask. The pH of the product was checked with pH paper and found to be 6.

A 0.02 g sample of the product would not dissolve in d^3 -CD₃CN with TMS. Because the product did not dissolve well in d -CDCl₃ the NMR tube was centrifuged, the supernatant solution was transferred to another NMR tube, and peaks were found in the ¹³C spectrum at 118.9, 123.9, and 140.0 ppm (no TMS reference). No peaks were found with 0.01 g of product in d^6 -DMSO with TMS. Additional product was added to d^6 -DMSO; it dissolved but quickly clouded when exposed to decreased temperatures. A second ¹³C NMR spectrum in d^6 -DMSO (2 sec delay, coupled) had the following peaks: 115.8, 116.8, 151.0 ppm from TMS.

Second Cesium Distibate Synthesis

A 2.2 g (3.40 mmol) sample of distibic acid was added to a clean, dry round-bottom flask. Approximately 40 mL of acetonitrile was added and the mixture and swirled. A small amount of distibic acid would not dissolve so an additional 10 mL of acetonitrile was added. After 10 minutes of swirling the solid had completely dissolved. A 0.54 g (1.66 mmol) sample of cesium carbonate was added to 5 mL of distilled water. The cesium carbonate solution was slowly added in approximately 1 mL increments to the distibic acid solution and swirled. The solution turned to a rose color. The solution

was concentrated by rotary evaporation; it became cloudy. The ^{13}C spectra of the cesium distibate in $\text{d}^6\text{-DMSO}$ had peaks at 117.5, 118.8, and 143.5 ppm from TMS.

The product was again concentrated by rotary evaporation for an additional hour or more and stored under house vacuum for 11 days. The solvent evaporated to give 2.73 g dry product. No ^{13}C peaks were found in $\text{d}^6\text{-DMSO}$ with TMS. Needles could be seen using a microscope. As a test, a few drops of acetonitrile were added to a small mass of the product on a watch glass. The needles appeared to dissolve and leave a white solid. Therefore, the remainder of the product was washed with acetonitrile, filtered using a medium porosity filter, and dried under house vacuum to give 0.86 g (0.94 mmol, 28% yield) dry product.

Under the microscope this dry product appeared to contain no needles of TCC, so it was sealed in a glass ampoule and submitted for elemental analysis. Elemental analysis determined it to be 17.37% C, <0.5% H, 32.09% Cl (total halogens), 27.2% Cs. Calculated ions for dicesium distibate $\text{Cs}_2[\text{SbO}(\text{OH})(\text{O}_2\text{C}_6\text{Cl}_4)_2]$: C 15.99%, H 0.11%, Cl 31.47%, Cs 27.02%.

A $\text{d}^6\text{-DMSO}$ NMR (prepared a week earlier) had ^{13}C peaks at 115.9, 116.8, 119.4, 121.1, 143.6 and 151.2 ppm from TMS. Another $\text{d}^6\text{-DMSO}$ NMR (of a freshly made solution) had peaks at 115.7, 117.2, and 151.0 ppm from TMS. The IR spectra of TCC had peaks at 671, 753, 813, 950, 996, 1166, 1275, 1397, and 1448 cm^{-1} . The IR spectra of distibic acid had peaks at 673, 753, 790, 813, 951, 964, 996, 1167, 1276, 1289, 1310, 1397, and 1449 cm^{-1} . The IR spectrum of the precipitate had peaks at 787, 807, 971, 1245, 1382, and 1425 cm^{-1} . The IR spectrum of the dicesium distibate had peaks at 673, 751, 809, 949, 995, 1169, 1276, 1311, 1396, and 1446 cm^{-1} .

Microscopic Views of Crystals. Small samples of cesium distibate, distibic acid, sublimed tetrachlorocatechol, and Avocado tetrachlorocatechol were placed on watch glasses. A few drops of acetonitrile were added to each solid until it dissolved. The solution was allowed to evaporate for 3 days. The results of viewing under a microscope are as follows: cesium distibate gave small chunky white crystals; distibic acid gave smooth white crystals; sublimed tetrachlorocatechol gave long smooth white crystals; Avocado tetrachlorocatechol gave dark chunky jagged-edged crystals.

Barium Distibate Synthesis

Approximately 7 mL of acetonitrile was added to 0.54 g (0.83 mmol) of distibic acid in a round bottom flask. An additional 3 mL of acetonitrile was added. The flask was swirled until most of the solid dissolved. A 0.06 g (0.30 mmol) sample of barium carbonate was mixed with 5 mL of distilled water in a beaker. An additional 5 mL of distilled water was added. The mixture was stirred with a metal scupula then gently heated. The barium carbonate never dissolved completely. The barium carbonate mixture was slowly added, in ~2 mL increments, to the distibate solution and swirled between additions. The mixture became transparent. The solution was concentrated by rotary evaporation. A great volume of gas was released during evaporation. The white solid product was stored under house vacuum. The product turned an aqua color. Since chloroform seemed to dissolve needles from the product and leave purer white crystals, the product was washed with a small amount of chloroform, dried, and stored under house vacuum (0.31 g, 72% yield).

An IR spectrum of the solid product had peaks at 672, 753, 790, 813, 966, 996, 1166, 1246, 1289, ~1311, 1397, ~1420 and 1448 cm^{-1} . The solid product was washed

again with chloroform and dried; the green product weighed 0.02 g. The product ^{13}C NMR in $\text{d}^6\text{-DMSO}$ had peaks at 115.7, 116.7, and 151.1 ppm from TMS. The product IR had peaks at 790, 811, 963, 1241, 1380, and 1419 cm^{-1} .

The rinse chloroform from the filtrate was evaporated and long white crystals formed. The filtrate solid had an IR spectrum with peaks at 752, 813, ~ 935 , 964, 994, 1168, ~ 1248 , ~ 1312 , 1288, ~ 1312 , 1396, and 1447 cm^{-1} .

Control. A 0.11 g sample of TCC was dissolved in 3 mL of acetonitrile. A 0.10 g sample of barium carbonate was added to 5 mL of distilled water. The two solutions were mixed together. No change was detected to indicate a reaction had occurred.

Nickel (II) Distibate Synthesis

A 0.75 g (1.16 mmol) sample of distibic acid was added to a round-bottom flask and quickly dissolved in 10 mL of acetonitrile. A 0.19 g (0.32 mmol) sample of nickel (II) carbonate hydroxide tetrahydrate was suspended in 10 mL of distilled water. The nickel (II) carbonate suspension was added to the distibate solution in 2 mL increments and swirled for 30 seconds between additions. The mixture became very cold and gave a transparent light lime solution except for a dark green solid that settled to the bottom. The solvent was removed by rotary evaporation and a green solid remained. The solid was redissolved in 14 mL of acetonitrile and filtered with a glass filter. The transparent green solution was reduced to a small volume by rotary evaporation, whereupon a dark green sludge was formed. The product was partially dissolved in a small amount of chloroform; a white precipitate formed when filtering using a glass filter. The remaining solution was filtered with an analytical paper filter and allowed to dry.

IR spectra was measured for the following (all in cm^{-1}): Nickel (II) carbonate hydroxide tetrahydrate (reactant), 679, 831, and 1360; Nickel (II) distibate, 672, 691, 751, 793, 812, 970, 1178, 1246, 1288, 1311, 1379, 1402, 1422, and 1608; filtrate, 672, 753, 813, 951, 996, 1168, 1274, 1311, 1397, and 1448.

Dehydration of Distibic Acid/Tetrachlorocatechol using Thionyl Chloride

An IR of distibic acid (contaminated with needles of TCC?) had peaks at 752, 791, 813, 951, 965, 1167, 1275, 1290, 1312, 1396, and 1448, and 1570 cm^{-1} . The ^{13}C NMR in $\text{d}^3\text{-CD}_3\text{CN}$ had peaks at 118.8, 122.2, and 141.7 ppm from TMS.

A 4.72 g (7.3 mmol) sample of distibic acid and 19 mL of dry toluene were added to a three-neck round-bottom flask. The distibic acid did not dissolve in the toluene. The left neck was equipped with a condenser/bubbler, the middle neck with an addition funnel, and the right neck with a stopper, which was replaced by a thermometer after the addition of 2 mL (27.40 mmol) of thionyl chloride and 10 mL of dry toluene. The thionyl chloride solution was added slowly to the flask and nothing was observed. The flask was submerged in a hot oil bath and the heat turned on. A piece of pH paper held over the bubbler indicated an acidic gas was being released. The reaction remained for 24 hours at greater than 103°C . The plum colored solution was cooled to room temperature and then stored in the freezer. No changes were observed. The solution was concentrated by rotary evaporation around 70°C . A plum colored solid remained (4.05 g). A white cloud was evolved when the vacuum seal was broken. The product was filtered and washed with pentane. The filtrate was white and became sticky when the pentane evaporated.

An IR spectrum of the plum-colored solid had peaks at 648, 673, 714, 99, 821, 980, 1170, 1198, 1236, 1245, 1388, and 1415 cm^{-1} . A ^{13}C NMR in $\text{d}^3\text{-CD}_3\text{CN}$ had the following peaks: 13.0 (small), 21.7 (small), 116.0, 127.4, and 140.5 ppm from TMS. The solid from the pentane filtrate had IR had peaks at 673, 752, 981, 1170, 1254, 1396, and 1449 cm^{-1} .

Control Reaction: Tetrachlorocatechol and Thionyl Chloride

The same procedure used in reacting distibic acid with thionyl chloride was done using 5 g (20.2 mmol) of tetrachlorocatechol and 2 mL (27.4 mmol) thionyl chloride. The only procedural difference was the heat was turned up immediately instead of slowly over a few hours. The observational differences were the following: the color was more brown than plum, there was no bad odor noticed from the product, the filtrate was brown, and the product (4.52 g) was difficult to filter. The ^{13}C NMR of the product in $\text{d}^3\text{-CD}_3\text{CN}$ had the following peaks: 12.8, 21.5, 33.7 (small), 116.0, 127.5, and 140.6 ppm from TMS. The IR had peaks at 675, 689, 803, 982, 1235, 1252, 1385, and 1416 cm^{-1} .

First Alternate Distibic Acid Synthesis

A 3.30 g (13.30 mmol) sample of tetrachlorocatechol, 38 mL of toluene, and 0.67 g (2.07 mmol) of antimony(V) oxide were added to a three-neck round-bottom flask. The flask was equipped with a thermometer, Dean-Stark apparatus, and a rubber stopper. The heat was turned on and the solution heated for over an hour. It remained brown and never appeared to reflux as expected. The solution was allowed to cool to 34°C. Using a 10 mL beaker, 2 mL (27.4 mmol) of thionyl chloride was added. The solution was heated overnight, cooled for two hours at room temperature, and in the freezer for 24 hours. A small amount of purple solid was filtered off from a dark purple

solution. The precipitate was washed with pentane, leaving behind a white mushy precipitate. The solvent was removed from the filtrate by rotary evaporation, with evolution of much gas and a production of a dark solid. The white precipitate formed a cloudy rose mixture when acetonitrile was added to 0.02 g to prepare an NMR sample. The rotary evaporated product formed a transparent purple solution when mixed with acetonitrile.

The ^{13}C NMR spectrum was all noise. The IR spectra gave the following peaks (all in cm^{-1}): purple solid product, 694, 730, 800, 814, 911, 936, 971, 1004, 1027, 1386, 1416, and 1578; white precipitate, 706, 804, 817, 832, 966, 1180, 1238, 1311, 1349, 1388, 1415, and 1605; very dark solid from rotary evaporation, 673, 691, 749, 805, 813, 823, 901, 951, 983, 990, 1171, 1255, 1264, 1283, 1311, 1386, 1397, 1418, and 1448.

Second Alternate Distibic Acid Synthesis

The reaction was repeated using water traps in both the filtration and rotary evaporation steps to eliminate water contacting the product. The Dean-Stark apparatus was eliminated in attempt to achieve proper refluxing during the reaction.

A three-neck 500-mL round-bottom flask was fitted with a condenser and bubbler in one neck, stopper in another neck, and addition funnel in the last neck. A 3.22 g (12.99 mmol) sample of tetrachlorocatechol, 35 mL of toluene, and 1.31 g (4.05 mmol) of antimony(V) oxide were added to the flask. Using the addition funnel, 3 mL of thionyl chloride and 20 mL of toluene were quickly added to the flask. The temperature was increased to 140°C . The solution refluxed overnight, producing gas. The brown liquid was allowed to cool to room temperature. The liquid was transferred to a 100-mL flask submerged in a hot oil bath subjected to rotary evaporation. Violent bubbling began

again and lasted for a few seconds; most of the liquid evaporated. The liquid finally evaporated at 140°C and turned purple. At 150°-180°C the product turned green. The green product was left in the stoppered flask. Two days later the product (5.37 g) was a black-purple solid. The IR spectra had peaks at the following: 675, 748, 803, 817, 965, 983, 1182, 1235, 1255, 1286, 1357, 1386, 1414, and 1573 cm^{-1} .

Third Alternate Distibic Synthesis

The same synthesis was performed with lower maximum heat. A 3.17 g (12.79 mmol) sample of tetrachlorocatechol, 1.31 g (4.05 mmol) of antimony(V) oxide, and 55 mL of toluene were added to a 500-mL three-neck round-bottom flask. It was equipped with a condenser and bubbler in the first neck, stopper in the second neck, and addition funnel in the third neck. Using a 10-mL graduated cylinder, 4 mL (54.8 mmol) of thionyl chloride was added to the addition funnel. Using a glass/metal syringe, 5 mL of toluene was added to the addition funnel. The solution in the addition funnel was slowly added to the flask. The solution in the flask turned a transparent gold color. The temperature was increased to 140°C. The heat was decreased. The solution became a darker color. The solution was heated overnight at 120°C. In the morning, the product was a very dark purple color. It was cooled to room temperature. When the product was transferred to a smaller round-bottom flask a white cloud appeared. The flask was attached to the rotary evaporator and submerged in a hot oil bath. Bubbling began at 40°C. Most of the liquid evaporated at an oil temperature of 90°C. Rotary evaporation continued until the oil reached 100°C. After two days, the product was a purple solid with a few white dots.

The IR gave peaks a following (all in cm^{-1}): 644, 677, 686, 752, 803, 820, 982, 1051, 1171, 1252, 1281, 1338, 1384, and 1416 cm^{-1} . The ^{13}C NMR in $\text{d}^3\text{-CD}_3\text{CN}$ had peaks at 115.1 and 139.6 ppm from TMS and numerous peaks from 114 to 131 ppm with the larger ones at 126.6, 127.0, 127.7, 129.4, and 129.8 ppm from TMS. The ^{13}C NMR in $\text{d}^6\text{-DMSO}$ was not as clean as $\text{d}^3\text{-CD}_3\text{CN}$. The larger peaks were around 116, 117, 121, 122, 128, 129, 130, 131, 143, and 144 ppm.

Cesium Distibate Synthesis, Alternate-Route Product as Reactant

Approximately 10 mL of acetonitrile was added to 0.8 g of the purple product from the above reaction of TCC, SOCl_2 , and Sb_2O_5 . The entire solid did not dissolve. A 0.3 g (0.92 mmol) sample of cesium carbonate was added to acetonitrile. It did not dissolve. The two mixtures were combined in a flask and swirled. A light brown solution formed and a purple and white solid remained. Additional acetonitrile was added to bring the total to 30 mL. A white solid remained on the bottom of the flask. The white solid was filtered from a brown solution; the brown solution turned purple.

The ^{13}C NMR, in $\text{d}^3\text{-CD}_3\text{CN}$, was not clean. It had peaks at approximately 100, 123, 129, 130, 131, and 143 ppm. The IR spectra had peaks at the following (all in cm^{-1}): white solid product, 752, 791, 807, 952, 985, 1173, 1248, 1286, 1310, 1403, and 1454; solid from filtrate, 691, 780, 912, 1007, and 1027; cesium carbonate, 875, 1040, 1309, 1331, and 1422.

Tetrachlorocatechol and Thionyl Chloride Product Recrystallization

A 2.02 g sample of product from the tetrachlorocatechol and thionyl chloride reaction was added to 20 mL of acetonitrile in a 50-mL Erlenmeyer flask. The solution was warmed in a 70°C hot water bath. The brown-gold colored solution was vacuum

filtered with a medium porosity glass funnel. A small amount of white chunks and a purple crust were collected. Upon refrigeration of the filtrate, brown crystals in a burgundy solution formed. The product was filtered and the crystals were washed with cold acetonitrile.

The brown crystals did not dissolve easily in d^6 -DMSO. The spectrum peaks were as follows: ^1H , 2.1 ppm (s); ^{13}C 1.0, 16.2, 132.4, 138.5, 167.7 ppm from TMS; IR (strong), 675, 801, 981, 1250, 1389, and 1415 cm^{-1} ; IR (weak) 649, 713, 1171, 1287, 1337, and 1460 cm^{-1} .

For the purposes of comparison, the spectra for 3,4,5,6-tetrachloro-1,2-benzoquinone were as follows: ^1H in d^6 -DMSO, 1.05 ppm; ^{13}C in d^6 -DMSO, 133, 139, 168 ppm; IR 686(w), 776(s), 812(s), 902(w), 982(w), 1000(w), 1029(w), 1153(s), 1167(m), 1229(s), 1251(s), 1286(m), 1358(m), 1417(m), 1512(m), 1556(m), 1592(w), 1677(s), and 1701(w) cm^{-1} .

Tetrastibic Acid Synthesis

A 13.00 g sample of tetrachlorocatechol was sublimed using the same procedure as the first sublimation. The temperature remained at 180°C for three hours and cooled overnight. Most of the 10.54 g (45.52 mmol) crystals were a deep yellow color. There was a great deal of black solid on the bottom of the container and on the thumb.

In order to test the toluene for dryness, approximately 2 mL (2 mmol) of antimony(V) chloride in dichloromethane was added to 45 mL of toluene. No reaction occurred except a white cloud upon initial contact with air.

A three-neck round-bottom flask was equipped with a thermometer in the left neck, condenser in a middle neck, and a rubber septum in the right neck. The flask was

mounted in a silicone oil bath. The condenser was hooked to a bubbler, house vacuum, and argon. The flask was purged with argon and evacuated a few times. A bubbler was added to the condenser. Approximately 35 mL of toluene was added through the septum using a glass/metal syringe. A white cloud formed when 15 mL (15 mmol) of 1.0 M antimony(V) chloride in dichloromethane was added. The mixture turned dark brown when 10.54 g (45.52 mmol) of tetrachlorocatechol was added. At 60°C the mixture began to turn red. It was heated at 110°C for 24 hours. At the end of this time, a dark green product had formed, but a piece of pH paper turned pink when held over the bubbler. After flushing with argon the pH paper still turned pink. House vacuum was applied, then the mixture heated further until morning. The flask was disconnected from its accessories, stoppered, and stored in the freezer for two days. The dark green product was vacuum-filtered under an argon atmosphere, then rinsed three times with a total of 30 mL of toluene. The filtrate was very dark green. The filtered solid became lighter with each wash until it became light gray. The solid became even lighter in color when it was rinsed with 20 mL of pentane. The product (6.65 g, 5.8 mmol, 51% yield) appeared to be a shiny gray solid, which was free from needles when viewed under the microscope.

The product would not dissolve in chloroform. The ^{13}C NMR in CD_3CN had peaks at 118.8, 121.2, and 141.6 ppm from TMS. The ^1H NMR in CD_3CN had peaks at 1.9 and 7.5 ppm from TMS. The IR yielded peaks as follows (all in cm^{-1}): product, 748, 791, 813, 966, 1172, 1244, 1251, 1313, 1382, 1397, 1421, and 1451; filtrate, 672, 747, 813, 950, 967, 995, 1163, 1274, 1309, 1396, and 1447. Elemental analysis of samples sealed in glass ampoules established the product to contain 24.18% C, 0.95% H, 50.70% Cl (total halogens), and 10.7% Sb. Calculations for tetrastibic acid dihydrate

$(\text{H}_3\text{O})_2\text{H}[\text{Sb}(\text{O}_2\text{C}_6\text{Cl}_4)_4]$ are: C 25.19%, H 0.62%, Cl 49.57%, Sb 10.64%. Calculations for tetrastibic acid hydrate $(\text{H}_3\text{O})\text{H}_2[\text{Sb}(\text{O}_2\text{C}_6\text{Cl}_4)_4]$ are: C 25.59%, H 0.48%, Cl 50.36%, Sb 10.81%.

Third Cesium Distibate Synthesis

Approximately 10 mL of acetonitrile and 1 g (0.9 mmol) of tetrastibic acid (from the second synthesis) were added to a 100-mL round-bottom flask. The tetrastibic acid did not dissolve well. A 0.2 g (0.61 mmol) sample of cesium carbonate was added to the flask. At first it appeared cesium carbonate was not dissolving because there was a white solid on the bottom of the flask. After 10 minutes a khaki colored solid began to form. The solution also became a khaki color. The product, a light-gray very flaky solid (0.44 g, 0.58 mmol, 64.1% yield) was filtered off and washed with acetonitrile. The green filtrate was rotary evaporated, filtered, and rinsed with acetonitrile. The second filtrate was transparent gold.

The product would not dissolve in acetonitrile. It turned brown when mixed with d^6 -DMSO. The ^{13}C NMR spectrum in d^6 -DMSO had peaks at the following: 114.6, 115.6, and 150.0 ppm from TMS. The IR spectra were as follows (all in cm^{-1}): product, 688, 786, 807, 971, 984, 1245, 1382, and 1424; first filtrate, ~680, 751, 790, 811, 926, 951, 961, 986, 1179, 1248, 1281, 1310, 1371, 1402, 1421, and 1454.

Fourth Cesium Distibate Synthesis

A 50-mL round-bottom flask was cleaned with methanol, put in an oven to dry, and removed from the oven to cool. A 12 mL sample of acetonitrile was added to the flask. A 1.24 g (1.08 mmol) sample of tetrastibic acid was added to the acetonitrile. The solution immediately turned green and all the tetrastibic acid appeared to dissolve. A

0.22 g (0.67 mmol) sample of cesium carbonate was added to the solution. The mixture was filtered and rinsed with 4 mL of acetonitrile to yield a product of mass 0.6 g (0.79 mmol, 72.9% yield).

The ^{13}C NMR spectrum of the product in $\text{d}^6\text{-DMSO}$ had peaks at 115.7, 116.6, and 151.0 ppm from TMS. The IR had peaks at 688, 786, 806, 971, 1219, 1245, 1296, 1382, 1423, and 1451 cm^{-1} . Elemental analysis of samples sealed in glass ampoules established the product to contain 19.66% C, <0.5% H, 37.45% Cl (total Halogens), 18.1% Cs, and 20.1% Sb. The calculation for cesium distibate, $\text{Cs}[\text{SbO}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ is: C 18.90%, H 0.0%, Cl 37.20%, Cs 17.43%, Sb 15.97%.

First Diethylammonium Distibate Synthesis

A 1.01 g (0.88 mmol) sample of tetrastibic acid (from the second synthesis) and 10 mL of dichloromethane were added to a 50-mL round-bottom flask. A cloudy gray mixture was formed. Two distinct layers were formed when 10 mL of hexane was added to the mixture. The mixture was stirred with a magnetic stir bar and the two layers appeared to mix. In a beaker, 10 mL of dichloromethane and 1 mL (1.1 mmol) of diethylamine were mixed. The diethylamine solution was added to the tetrastibic acid solution. A white precipitate formed. The liquid portion of the product was a transparent tan color. After 40 hours, the solution was a transparent khaki color; no solid was present. The product was filtered with a medium porosity glass filter. A small amount (0.03 g, 2.73% yield) of white precipitate was collected. It was washed with hexanes.

When mixed with $\text{d}^6\text{-DMSO}$ and TMS the white solid became darker. Bubbles formed. The product dissolved. The ^{13}C NMR spectrum had peaks at 11.6, 41.9, 100.0,

115.5, 117.3, and 151.6 ppm from TMS. The ^1H spectrum had peaks at 1.1 (triplet), 2.5 (DMSO?), 2.9 (quartet), 3 (singlet) and 8.5 (singlet).

Diethylamine and Tetrachlorocatechol Control Reaction

A 0.3 g sample (0.12 mmol) of tetrachlorocatechol and 10 mL of dichloromethane were added to a 50-mL round-bottom flask. A transparent green solution was formed. The solution became green-brown upon the addition of 10 mL of hexanes. In beaker, 10 mL of dichloromethane and 1 mL (1.1 mmol) of diethylamine were mixed. The diethylamine solution was added to the tetrachlorocatechol solution. A transparent red-brown solution with no precipitate was formed. After 40 hours, the product was a dark brown-green with no precipitate. The product was filtered using a medium porosity filter. A small amount (0.34 g) of brown precipitate was collected and washed with hexanes.

There was no peak on the ^{13}C NMR in $\text{d}^6\text{-DMSO}$. The ^1H NMR did not resemble the amine distibate spectra.

Second Diethylammonium Distibate Synthesis

A 0.65 g (0.57 mmol) sample of tetrastibic acid, 10 mL of dichloromethane, and 10 mL of hexanes were added to a 50-mL round-bottom flask. In a beaker, 1 mL (1.1 mmol) of diethylamine and 10 mL of dichloromethane were mixed. The diethylamine solution was added to the trisibic acid solution and stirred for 30 minutes with a magnetic stir bar. A khaki solid was formed. The product was filtered and rinsed with hexanes.

The ^{13}C $\text{d}^6\text{-DMSO}$ spectrum had peaks at 8.5, 41.3, 48.6, 115.8, 117.0, and 151.5 ppm from TMS. The ^1H $\text{d}^6\text{-DMSO}$ spectrum had peaks at 1.2 (t), 2.5 (t), 3.0 (q), 3.3 (s), and 8.2 (s) ppm. The product (0.22 g, 31.2% yield) was dried under house vacuum for 5

days. The IR spectrum had peaks at 688(w), 791(s), 811(s), 968(s), 984(w), 996(w), 1213(w), 1244(s), 1382(s), 1427(2), 1446(w), and 1589(w) cm^{-1} . Samples were sealed in glass ampoules and sent for elemental analysis. The data found 27.31% C, 1.72% H, 1.99% N, and 40.31% Cl. Calculations for diethylammonium distibate $[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{SbO}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ are: C 27.31%, H 1.72%, N 1.99%, Cl 40.31%.

RESULTS AND DISCUSSION

Methods and Materials

Sublimation and Dehydration of Tetrachlorocatechol. Tetrachlorocatechol, TCC, from Avocado is considered to be partially hydrated and 99% pure. More critical than the impurity being involved in an unwanted reaction is a reaction with water. When antimony(V) chloride is exposed to water it readily reacts to form hydrochloric acid. In order to synthesize derivatives of TCC using antimony(V) chloride the TCC was sublimed using a vacuum sublimation apparatus submerged in a silicone oil bath and connected to a vacuum pump. The same procedure was utilized twice; once before each attempt to synthesize tristibic acid. In both cases sublimation was for a minimum of two and a half hours, the oil bath temperature was 180-185°C, and the product was allowed to cool before being collected in an argon-filled glove bag. Both sublimations began with around 13 g of hydrated TCC and produced over 10 g of sublimed TCC. Because black residue was separated from yellow crystals the TCC was considered to be purified at the same time it was dehydrated. The sublimed TCC was stored under house vacuum to reduce exposure to water.

The literature ^{13}C NMR spectrum of TCC in C_6D_6 is given in Table 3.1. The ^{13}C NMR spectral results measured in three solvents were similar except for the α -carbon attached to the hydroxide groups (C-1), which shifted upfield with progressively less polar solvents. (Table 1.1).

Table 1. ^{13}C Nuclear Magnetic Resonance Spectra of Tetrachlorocatechol

Solvent	^{13}C Chemical shifts from TMS (ppm)		
CDCl_3	118.8	123.8	139.9
CD_3CN	118.8	122.2	141.7
$\text{d}^6\text{-DMSO}$	119.9	121.6	144.0
$^*\text{C}_6\text{D}_6$	119.0 (C-3)	122.0 (C-4)	142.5 (C-1)

*Knuutinen (1980) assigned ring position for 3,4,5,6-tetrachlorobenzene-1,2-diol (TCC) in parentheses.

Since ^{13}C NMR is proposed to be used as an aid in identifying products of structure similar to TRISPHAT, other relevant literature ^{13}C NMR spectra are gathered in Table 1.2. It may immediately be noticed that the ^{13}C NMR spectrum of TRISPHAT is fairly similar to that of TCC; this caused Shieh (2007) a great deal of confusion. However, as heavier atoms (Ru, and Sn in “STANNAT”) are coordinated by the tetrachlorocatecholato ligand, the ^{13}C NMR shift of the carbon atoms closest to the oxygen and metal atom are shifted to higher ppm values. The compound $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$, however, appears to be an exception to this trend.

Tetrachlorocatechol Comparison. To ensure TCC was not changing composition once a bottle was opened and/or during sublimation a comparison study was performed. The IR spectra of a bottle opened within the hour, a bottle opened months prior, and sublimed TCC were the same as on another, including unrecorded peaks, and the same as the spectra from SciFinder[®] Scholar of 3,4,5,6-tetrachloro1,2-benzenediol. (Figure 1.20)

Table 2. Literature ^{13}C Nuclear Magnetic Resonance Spectra of Tetrachlorocatecholates

Compound	Solvent	^{13}C NMR shifts (ppm)
TCC	CD_3CN	118.8 (C-3), 122.2 (C-4), 141.7(C-1)
TRISPHAT ^a	CDCl_3	114.7 (C-3), 123.6 (C-4), 142.6 (C-1)
$\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}^b$	d^6 -DMSO	116.9, 121.8, 142.4
$[\text{Ru}]\text{STANNAT}^c$	CD_2Cl_2	116.1, 117.5, 149.3
$\text{Cl}_4\text{C}_6\text{O}_2\text{SnCl}_2 \cdot \text{phen}^d$	d^6 -DMSO	113.9, 115.0, 146.7
$\text{Cl}_4\text{C}_6\text{O}_2\text{SnCl}_2 \cdot \text{tmen} \cdot \text{EtOH}^d$	d^6 -DMSO	115.6, 117.0, 148.5
$[\text{tmenH}]_2\text{STANNAT}^d$	d^6 -DMSO	115.9, 117.2, 149.0

^a(Lacour et al., 1997); ^b(Tian & Tuck, 1993); ^c(Lamberth et al., 1991); ^d(Holmes et al., 1988)

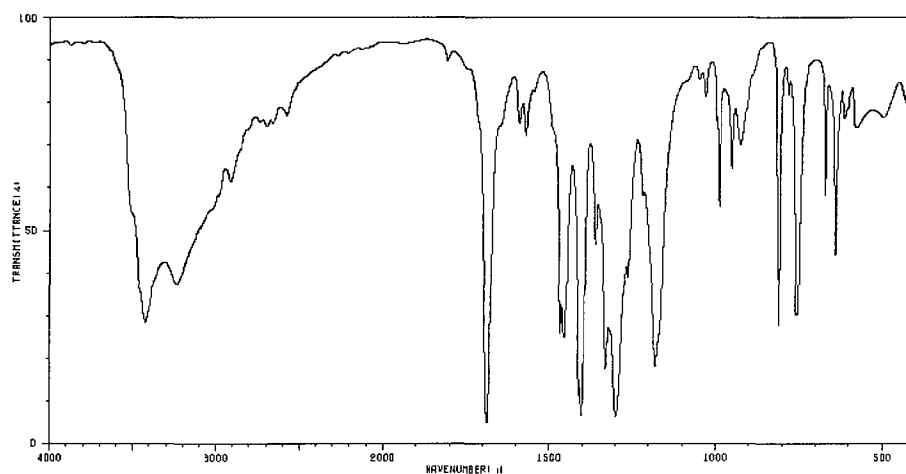


Figure 20. SciFinder[®] JASCO FT/IR-410 spectra of 3,4,5,6-tetrachloro-1,2-benzenediol, (CAS registry number 1198-55-6)

In Table 1.3 we reproduce the major IR spectral peaks reported for TCC, $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$, TRISPHAT, and for some of Shieh's products. Annan et al. (1987) report that the characteristic symmetric and antisymmetric carbon-oxygen stretching

frequencies are to be found at about 1430 cm^{-1} and 1240 cm^{-1} in the $o\text{-C}_6\text{Cl}_4\text{O}_2^{2-}$ (tetrachlorocatecholato) ligand, respectively.

The 1240 cm^{-1} frequency in particular is not to be found in TCC, in Marella's (2004) parent acids of TRISPHAT (Lacour, 1997), or in Shieh's (2007) "tristibic acids," but is found in TRISPHAT salts and Shieh's "tristibate" salts, as indicated by asterisks in Table 1.3. It may also be noted that TRISPHATs and "tristibates" have simpler IR spectra, which is consistent with higher symmetry for chelating TCC anions.

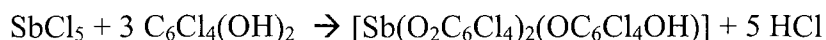
Table 3. Literature Infrared Spectra of Tetrachlorocatecholates

Product	wave numbers, cm^{-1}
Tetrachlorocatechol ^a	671, 755, 813, 951, 998, 1176, 1289, 1316, 1357, 1402, 1450, 1567
TRISPHAT ^b	673, 717, 826, 989, 1235*, 1387, 1447*
Parent acid of TRISPHAT ^c	Four types of spectra, depending on treatment
$\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}^a$	802, 816, 964, 1238*, 1389, 1412
Tristibic acid, trial 2 ^a	672, 755, 814, 953, 996, 1086, 1176, 1291, 1397, 1449, 1575
Tristibic acid, trial 3 ^a	696, 753, 790, 813, 965, 1189, 1244, 1292, 1314, 1382, 1417, 1560, 1711, 765
Cesium tristibate ^a	688, (751), 787, 807, 967, 1244*, 1423, 1452*

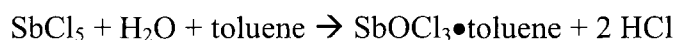
*C-O stretching vibrations peaks of $o\text{-C}_6\text{Cl}_4\text{O}_2^{2-}$ ligand ($1430, 1240\text{ cm}^{-1}$) (Feuvrie, 2005)
^a(Shieh, 2007); ^b(Lacour, 1997); ^c(Marella, 2004)

Di- and Tetrastibic Acid Syntheses

The synthesis of tristibic acid was attempted twice:



This reaction was modeled on Lacour's corresponding synthesis of the acid form of the TRISPHAT anion. With both attempts a dry 250-mL flask and "dry" toluene were used, and the tetrachlorocatechol was vacuum-sublimed and dehydrated. In the first attempt liquid SbCl_5 was preweighed in a glove bag into the dry 250-mL flask, and the "dry" toluene was added by syringe to the flask. This resulted in a violent explosion that blew a stopper out of the flask. Since this could have been due to the heat of adduct formation between the powerful Lewis acid SbCl_5 and the toluene, we stoppered the flask and continued the reaction. Only after further experimentation did we decide that the explosion was because the AcroSeal™ seal on the bottle of "dry" toluene was no longer intact, but had an opening in it, so that the toluene absorbed water from the air, leading to the following reaction:



In the second attempt a new bottle of dry toluene with an intact seal was used. To minimize the risk of exothermic adduct formation, a 1.0 M solution of SbCl_5 in dichloromethane was used instead of pure SbCl_5 , and it was added to the toluene, rather than toluene being added to SbCl_5 . This dissolution proceeded smoothly without undue pressure buildup.

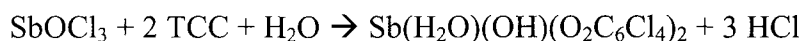
In both attempts three molar equivalents of resublimed tetrachlorocatechol were then slowly added from a powder addition funnel to the antimony solution, and the solution was heated for at least 24 hours at 95°C to 110° C until the gases exiting from the bubbler no longer tested strongly acidic due to the evolved HCl (g). The flask was then stoppered and stored in the freezer for at least two days; the product crystallized out

of the solution. This product was vacuum filtered and rinsed with cold dry toluene, then pentane, and was then aspirated dry under argon.

In the first attempt, examination of the product under the microscope showed the presence of long needles, which were suspected to be tetrachlorocatechol (TCC); this was confirmed when a purple color was produced with FeCl_3 in acetone. In the second attempt, examination of the product showed that no needles were present; the product appeared to be a homogeneous gray crystalline product.

NMR spectra of the two products confirmed that they were different and were different from the NMR spectra of tetrachlorocatecholato complexes (Table 1.2). The first product gave six ^{13}C NMR peaks in CDCl_3 , with three (120.2, 123.6, and 143.1 ppm) being assignable to TCC, and three peaks (126.3, 129.3, and 130.0 ppm) being new. The second product gave only three ^{13}C NMR peaks, with none being assignable to TCC, and the three observed peaks in CD_3CN (118.8, 121.2, and 141.6 ppm) being different from those found for the first product. Both products were soluble in CD_3CN . The two products differed in solubility in CDCl_3 ; only the first product dissolved.

Since it was not pure, the first product was not analyzed. As will be seen later, its cesium salt was purified and analyzed to be a (di)cesium distibate. So we hypothesize that the first product was a distibic acid such as $\text{Sb}(\text{H}_2\text{O})(\text{OH})(\text{O}_2\text{C}_6\text{Cl}_4)_2$ (Figure 1.21):



Since three molar equivalents of TCC were used in the reaction, this would account for the contamination of the product with the excess TCC.

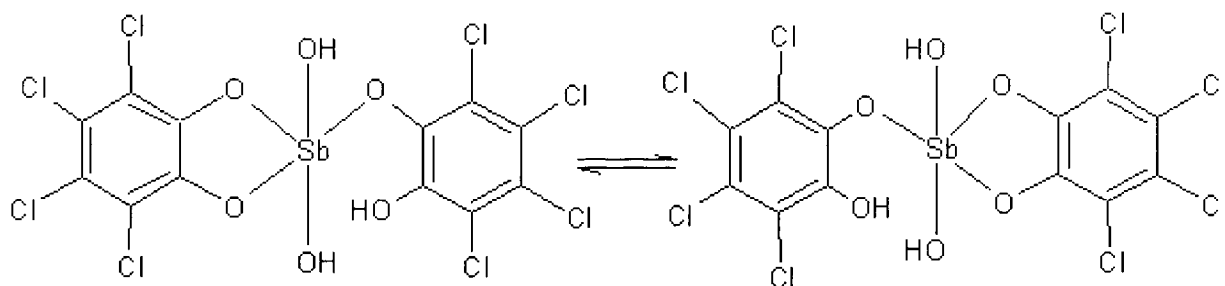


Figure 21. Possible Structures of Distibic Acid.

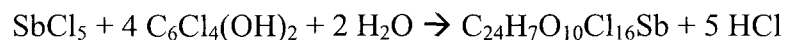
Table 4. Elemental Analyses

Product	Percent composition (^E experimental, ^c calculated)
Tetrastibic acid ^E	24.18% C, 0.95% H, 50.70% Cl*, 10.7% Sb.
(H ₃ O) ₂ H[Sb(O ₂ C ₆ Cl ₄) ₄] ^c	C 25.19%, H 0.62%, Cl 49.57%, Sb 10.64%.
(H ₃ O) ₂ H ₂ [Sb(O ₂ C ₆ Cl ₄) ₄] ^c	C 25.59%, H 0.48%, Cl 50.36%, Sb 10.81%.
Dicesium distibate ^E	17.37% C, <0.5% H, 32.09% Cl*, 27.2% Cs.
Cs ₂ [SbO(OH)(O ₂ C ₆ Cl ₄) ₂] ^c	C 15.99%, H 0.11%, Cl 31.47%, Cs 27.02%.
Cesium distibate ^E	19.66% C, <0.5% H, 37.45% Cl*, 18.1% Cs, 20.1% Sb
Cs[SbO(O ₂ C ₆ Cl ₄) ₂] ^c	C 18.90%, H 0.0%, Cl 37.20%, Cs 17.43%, Sb 15.97%
Diethylamonium distibate ^E	27.87% C, 1.84% H, 2.14% N, 38.49% Cl*.
[(C ₂ H ₅) ₂ NH ₂][SbO(O ₂ C ₆ Cl ₄) ₂] ^c	C 27.31%, H 1.72%, N 1.99%, Cl 40.31%.

*Total halogens analyzed and reported as %Cl.

Elemental analysis of the second product (Table 1.4) indicated that, if it was pure as it appeared under microscopy, it has a composition corresponding to either a monohydrate or a dihydrate of tetrastibic acid (Figure 1.22; Table 1.4). This suggests

that the 0.2% water in the toluene, or water in the argon used in the atmosphere, was involved:



This was not the case for Lacour's TRISPHAT synthesis.

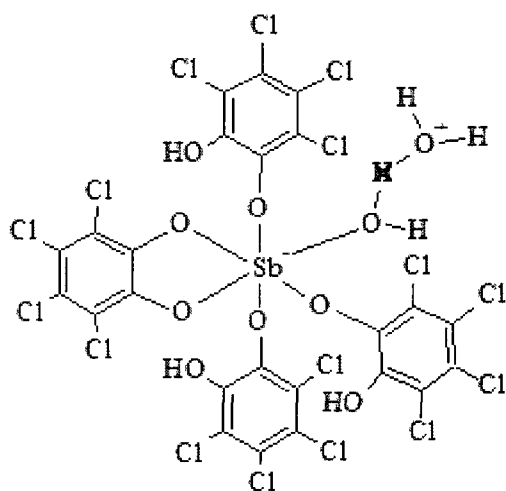
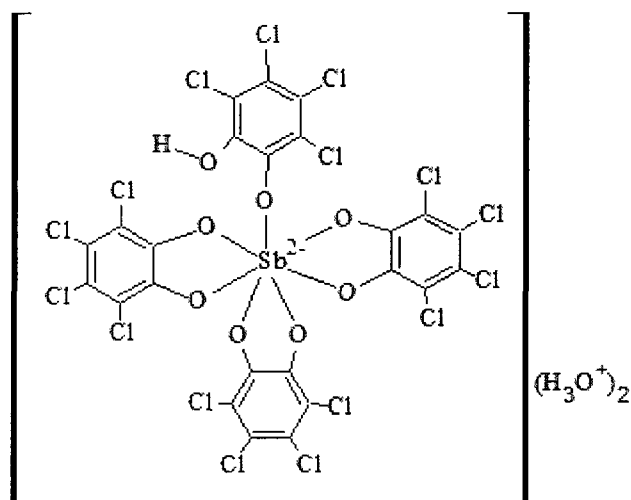


Figure 22. Two possible structures of tetrastibic acid, involving coordination numbers for Sb of seven and six, respectively.

The two stibic acids differ in stability. The ^{13}C NMR of a four-month-old sample of the first product (distibic acid) shows only three peaks, which are assignable to TCC.

In contrast, the NMR of a several-month-old sample of the second product (tetrastibic acid) was unchanged. We should note that the first sample was stored under “house vacuum,” which is only a partial vacuum, while the second sample was stored under argon after a vacuum-pump evacuation.

Thus the goal of increased stability of the acid as compared to Lacour’s unstable TRISPHAT acid was achieved, but the product is not similar to Lacour’s (1997).

Attempted Synthesis of Tristibic Acid by Alternate Routes

Evidence suggests that tristibic acid was not formed by the analogous procedure used by Lacour to synthesize the acid of TRISPHAT ion synthesis, reacting tetrachlorocatechol with antimony(V) chloride. Elemental analysis of the cesium salt implies the product from the first attempted tristibic acid synthesis was actually a distibic acid.

Therefore two alternate routes to tristibic acid were attempted. One is dehydrating the product, or decomposed product, to tristibic acid using thionyl chloride. The second alternate-route synthesis involved reacting tetrachlorocatechol with thionyl chloride and antimony(V) oxide. These routes were based on the known use of thionyl chloride as a dehydrating or chlorinating agent (Gamayurova et al., 1991), and the literature reaction of TCC with As_2O_5 to give a compound with the elemental analysis of a “DIARSATE”, $\text{O}[\text{As}(\text{O}_2\text{C}_6\text{Cl}_4)_2]_2$ (Gamayurova et al., 1991)

Attempted Dehydration of Distibic Acid and Tetrachlorocatechol Acid Using Thionyl Chloride. The product obtained by the first attempted synthesis of tristibic acid was never identified conclusively, but was hypothesized to include distibic acid,

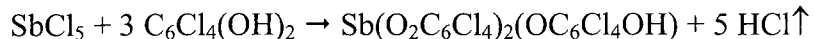
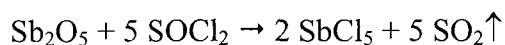
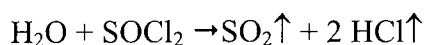
$\text{Sb}(\text{H}_2\text{O})(\text{OH})(\text{O}_2\text{C}_6\text{Cl}_4)_2$. The ^{13}C NMR spectrum allowed us to conclude that TCC was also present in this mixture.

Our working hypothesis was that our mixture of distibic acid and tetrachlorocatechol could be converted to tristibic acid by dehydration with thionyl chloride, SOCl_2 :

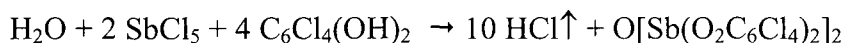


Utilizing an addition funnel, a thionyl chloride/toluene solution was added to a distibic acid/tetrachlorocatechol mixture in toluene in a three-neck, round-bottom flask submerged in a hot oil bath. As expected, the evolution of an acidic gas was detected with pH paper. The mixture was heated for 24 hours, cooled, stored in the freezer, rotary evaporated, filtered, and washed with pentane. The plum-colored solid gave a new ^{13}C NMR spectrum (Table 1.2).

Attempted Synthesis from Tetrachlorocatechol, Thionyl Chloride and Antimony(V) Oxide. Because neither the first method, based on Lacour's TRISPHAT, nor the dehydration method to synthesize tristibic acid was successful, a third method was devised based on a hoped-for reaction of tetrachlorocatechol, antimony(V) oxide, and thionyl chloride in toluene. The mechanism hypothesized was the reaction of the thionyl chloride with residual water in toluene, and with the antimony(V) oxide to convert it to antimony(V) chloride, which would react with tetrachlorocatechol as before, this time under rigorously anhydrous conditions:



Alternately, in view of the literature (Gamayurova et al., 1991), the final step of this reaction could have been:



The first attempt, which involved a Dean-Stark apparatus, failed to reach a reflux temperature. Upon rotary evaporation, the system backed up with water, and the product reacted with the backed-up tap water to produce a white sludge-like solid. This attempt was therefore disregarded.

The second attempt eliminated the Dean-Stark apparatus and appeared to reflux properly. Both the rotary evaporation system and the filtration system were equipped with water traps to eliminate contact with tap water. Unfortunately, during rotary evaporation the oil bath was allowed to obtain a temperature of 180°C, causing the product to turn purple to green, suggesting oxidation to give a purple solid, probably a paramagnetic semiquinone.

The third synthesis involved adding tetrachlorocatechol, antimony(V) oxide, and toluene to a three-neck, round-bottom flask submerged in a hot oil bath and equipped with a condenser, but no Dean-Stark apparatus. Thionyl chloride was added with an addition funnel. The gold solution was allowed to reflux overnight and turned a dark purple. The product was rotary evaporated with a water trap, cooled, and filtered using a water trap to give a purple solid, which gave numerous ^{13}C NMR peaks in CD_3CN (Table 1.5).

The IR spectra were obtained for the products of the second and third syntheses (Table 1.6); there was not much difference in these two spectra. Based on the results for

the thionyl chloride/tetrachlorocatechol reaction, the products produced in these three attempts, most importantly the third attempt, are not believed to be tristibic acid.

Table 5. ^{13}C NMR Spectra for Thionyl Chloride Reaction Products

Reactants	solvent	^{13}C NMR shifts in ppm
TCC	CD_3CN	118.8, 122.2, 141.7
TCC + SOCl_2	CD_3CN	12.8, 21.5, *33.7, 116.0, 127.5, 140.6
Distibic acid/TCC + SOCl_2	CD_3CN	*13.0, *21.7, 116.0, 127.4, 140.5
TCC + SOCl_2 + Sb_2O_5	CD_3CN	115.1, 126.6, 127.0, 127.7, 129.4, 129.8, 139.6 (additional peaks 114-131)

*Weak peak

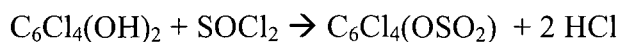
Thionyl Chloride and Tetrachlorocatechol. Unexplained products were obtained upon reacting distibic acid (containing TCC) with thionyl chloride (SOCl_2). As a control, a reaction of TCC itself with thionyl chloride was carried out using the same procedure in the absence of any antimony source. The ^{13}C NMR of the TCC + SOCl_2 product in CD_3CN was the same as the NMR of distibic acid/TCC + SOCl_2 . However, it was not the same pure TCC, nor was it the same as the very complex spectrum of the product of TCC + SOCl_2 + Sb_2O_5 (Table 1.5). In comparing the IR spectra of the same three products, we find fairly close agreement among them (Table 1.6), but none of the three IR spectra matches that of TCC itself. There remains an unexplained discrepancy between the IR results and the NMR results for TCC + SOCl_2 + Sb_2O_5 . Although the NMR points to a complex mixture of new products, the IR spectrum points to the same product as in the other two reactions. Overall it is provisionally concluded that the

Table 6. FT Infrared Spectra for Thionyl Chloride Reaction Products

Reactants	Wave numbers, cm ⁻¹
TCC	672, 753, 813, 950, 996, *1031, 1166, 1275, ~1280, ~1310, 1397, 1448
3,4,5,6-tetrachlorobenzoquinone	*686, *738, 776, 812, *902, *982, *1000, *1029, 1153, 1187, 1229/1251, *1286, *1358, 1417/1444, 1512, 1556, *1592, 1677, *1701
TCC + SOCl ₂	645, 675/689, *736, 803/820, 982, *1030, *1173, 1235/1252, *1283, 1338, 1385/1416
Recrystallized TCC + SOCl ₂	*649, 675/690, *713, 801/817, 981, *1171, *1200, 1250, *1287, *1337, 1389/1415
distibic acid/TCC + SOCl ₂	*621, *648, 673, *714, 799/821, 980, *1171, *1198, 1236/1245, *1286, *1336, 1388/1415
TCC + SOCl ₂ + Sb ₂ O ₅ tr. 2	675, *748, 803/817, 965/983, *1182, 1235/1255, *1286, *1357, 1386/1414, 1573
TCC + SOCl ₂ + Sb ₂ O ₅ tr. 3	644, 677/686, *752, 803/820, 983, *1052, *1087, 1172, 1252, *1282, 1338, 1384/1416
*Weak peak	

products of these three reactions do not contain antimony, but are not TCC either.

Perhaps a possible identity of the product is the cyclic sulfite ester of tetrachlorocatechol:

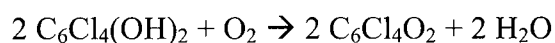


However, the formation of a sulfite ester seems unlikely based on earlier work by Bissinger and Kung (1948) using phenol and thionyl chloride, which showed that no sulfite is formed in the presence of HCl. In order to form the sulfite ester and prevent side reactions or rapid decomposition a refluxing solvent in which the reactants and

products, but not HCl, were soluble was used. A SciFinder Scholar search for such a sulfite did not find any evidence that it has been prepared or even exists.

Recrystallization of Reaction Product from Tetrachlorocatechol and Thionyl Chloride. Because the product of reacting TCC and SOCl₂ had clean NMR and IR spectra, the product was recrystallized for further investigation. Crystals were redissolved in acetonitrile and warmed in a hot water bath. The solution darkened to give brown crystals and burgundy crystals. It was filtered, refrigerated, refiltered, and washed with cold acetonitrile. The recrystallized TCC + SOCl₂ product had three ¹³C NMR peaks in d⁶-DMSO that were the same as the peaks of 3,4,5,6-tetrachloro-1,2-benzoquinone and the same as the original TCC + SOCl₂ product before recrystallization (Table 1.5).

The brown compound 3,4,5,6-tetrachloro-1,2-benzoquinone can arise from TCC by air oxidation:



The 3,4,5,6-tetrachloro-1,2-benzoquinone-like NMR spectrum was also found for the unrecrystallized TCC + SOCl₂ product in d⁶-DMSO (Table 1.7, line 2), but not in CD₃CN (Table 1.5, line 2). Tetrachlorocatechol alone does not give the 3,4,5,6-tetrachloro-1,2-benzoquinone-like NMR spectrum in either d⁶-DMSO or CD₃CN.

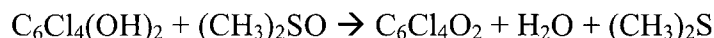
Examination of the ¹³C NMR spectrum in d⁶-DMSO would suggest the product of the TCC + SOCl₂ reaction is 3,4,5,6-tetrachlorobenzoquinone. However, the IR spectra, measured in the solid state with no exposure to d⁶-DMSO, are very different (Table 1.6).

Table 7. ^{13}C NMR Spectra of Thionyl Chloride Products after Recrystallization

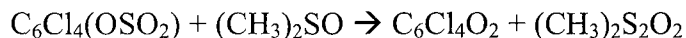
Reactants	solvent	^{13}C NMR shifts in ppm
TCC	$\text{d}^6\text{-DMSO}$	119.9, 121.6, 144.0
3,4,5,6-tetrachloro-1,2-benzoquinone	$\text{d}^6\text{-DMSO}$	133, 139, 168
TCC + SOCl_2	$\text{d}^6\text{-DMSO}$	132.6, 138.6, 167.9
TCC + SOCl_2 (Recrystallized)	$\text{d}^6\text{-DMSO}$	*1.0, *16.2, 132.4, 138.5, 167.7

*Very weak peak

Hence the DMSO may play an active role in producing 3,4,5,6-tetrachlorobenzoquinone. To explain the apparent dependence of the ^{13}C NMR spectrum on the choice of solvent (CD_3CN versus $\text{d}^6\text{-DMSO}$), we can write a reaction of TCC with $\text{d}^6\text{-DMSO}$ as an oxidizing agent to produce 3,4,5,6-tetrachlorobenzoquinone:



However, the byproduct, dimethyl sulfide, has an unbearable skunk-like odor, and this was not noted in the reaction. If, however, the product of the TCC with thionyl chloride is a cyclic ester, some other byproduct might have been produced:



In summary, we have been unable conclusively to identify the product of the control reaction of TCC with SOCl_2 .

Synthesis of Distibate Salts

Dicesium Distibate Syntheses. Utilizing the same procedure used by Shieh (2007), two attempts were made to synthesize the corresponding cesium stibate salt from the starting stibic acid. Cesium carbonate in water was added in small increments to a sample of the first (distibic) acid in acetonitrile and swirled between additions. The

solution was rotary evaporated to dryness. The product would not dissolve in acetonitrile, and had NMR peaks similar to TCC in CDCl_3 , in which it barely dissolved (Table 1.8). The ^{13}C NMR peaks in dimethylsulfoxide were experimentally the same as Shieh obtained in his synthesis (Table 1.9), and featured the distinctive peak at 151 ppm from TMS.

Table 8. ^{13}C Nuclear Magnetic Resonance Spectra of Distibates

Reactants	solvent	^{13}C NMR shifts in ppm
Distibic acid	CD_3CN	120.2, 123.6, 126.3, 129.3, 130.0, 143.1
	CDCl_3	118.8, 123.8, 125.3, 128.2, 129.0, 140.0
Dicesium distibate, trial 1	CDCl_3	118.9, 123.9, 140.0
	$\text{d}^6\text{-DMSO}$	115.8, 116.8, 151.0
dicesium distibate, trial 2	$\text{d}^6\text{-DMSO}$	117.5, 118.8, 143.5
	* $\text{d}^6\text{-DMSO}$	115.9, 116.8, 119.4, 121.1, 143.6, 151.2
	* $^{\Psi}\text{d}^6\text{-DMSO}$	115.7, 117.2, 151.0
tetrastibic acid	CD_3CN	118.8, 121.2, 141.6
cesium distibate, trial 1	$\text{d}^6\text{-DMSO}$	114.6, 115.6, 150.0
cesium distibate, trial 2	$\text{d}^6\text{-DMSO}$	115.7, 116.6, 151.0
barium distibate	$\text{d}^6\text{-DMSO}$	115.7, 116.7, 151.1

*Rotary Evaporated second time and washed with acetonitrile $^{\Psi}$ NMR spectra collected immediately upon addition of solvent to product.

A similar, second, larger-scale synthesis was carried out. After filtering off some initial unidentified precipitate (^{13}C NMR peaks in $\text{d}^6\text{-DMSO}$ at 117.5, 118.8, 143.5 ppm), the filtrate was concentrated by rotary evaporation and cooled for eleven days.

Examination of the product under a microscope showed the presence of needles, which are characteristic of TCC. Therefore, the product was washed with acetonitrile and

Table 9. Shieh's ^{13}C Nuclear Magnetic Resonance Spectra of "Tristibates"

reactants	solvent/other	^{13}C NMR shifts in ppm
tristibic acid, trial 1	CDCl_3	118.9, 123.9, 140.0
recrystallized	d^6 -acetone	118, 122, 150.8
tristibic acid, trial 2	CD_3CN	119.5, 123.0, 142.5
recrystallized	d^6 -acetone	*118, *122, 150.8
tristibic acid, trial 3	CD_3CN	119, 122, 142, 150
	d^6 -acetone	119.3, 122.2, *128, *127, 142.8, *150
cesium "tristibate"	d^6 -DMSO	115.7, 116.7, 151.0

*minor peak

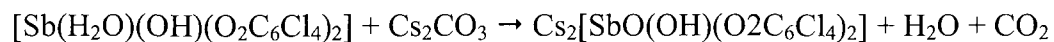
allowed to dry to give a needle-free product. A ^{13}C NMR spectrum in d^6 -DMSO had only three peaks with the same chemical shifts as found after the first synthesis, and the same as those found by Shieh (2007) in his syntheses.

The IR spectrum of the solid obtained from the acetonitrile showed it to be tetrachlorocatechol (Table 1.10). The IR spectrum of the cesium salt was very clean, with fewer peaks than the parent acid; this would be expected for a high-symmetry anion such as tristibate. However, the major peaks did not match that of TCC, the "tristibic" acid, or the cesium salt that Shieh had obtained (the spectrum of which was also very clean (Table 1.3)).

Table 10. FT Infrared Spectra of Distibates

product	wave numbers, cm ⁻¹
sublimed TCC	672, 752, 813, 950, 996, 1166, 1275, ~1290, ~1397, 1448
distibic acid	673, 753, 790, 813, 951, 964, 996, 1167, 1276, 1289, 1310, 1397, 1449
dicesium distibate, trial 2	787, 807, 971, 1245*, 1382, 1425*
filtrate	673, 751, 809, 949, 995, 1169, 1276, 1311, 1396, 1446
tetrastibic acid	748, 791, 813, 966, 1172, 1244, 1251, 1313, 1382, 1397, 1421, 1451
filtrate	672, 747, 813, 950, 967, 995, 163, 1274, 1309, 1396, 1447
cesium distibate, trial 1	688, 786, 807, 971, 984, 1245*, 1382, 1424*, 1454
filtrate	680, 751, 790, 811, 926, 951, 961, 986, 1179, 1248, 1281, 1310
cesium distibate, trial 2	688, 786, 806, 971, 1219, 1245*, 1296, 1382, 1423*, 1451
*weak peak	

This cesium salt was sent for elemental analysis. The results (Table 1.4) were somewhat high in carbon, but fit well for hydrogen, chlorine, and cesium to those calculated for dicesium oxo(hydroxo) distibate, Cs₂[SbO(OH)(O₂C₆Cl₄)₂] (Figure 1.22). Therefore, we hypothesize that it was in fact a mixture of tetrachlorocatechol and distibic acid, [Sb(H₂O)(OH)(O₂C₆Cl₄)₂] The following reaction is proposed for the formation of the cesium salt:



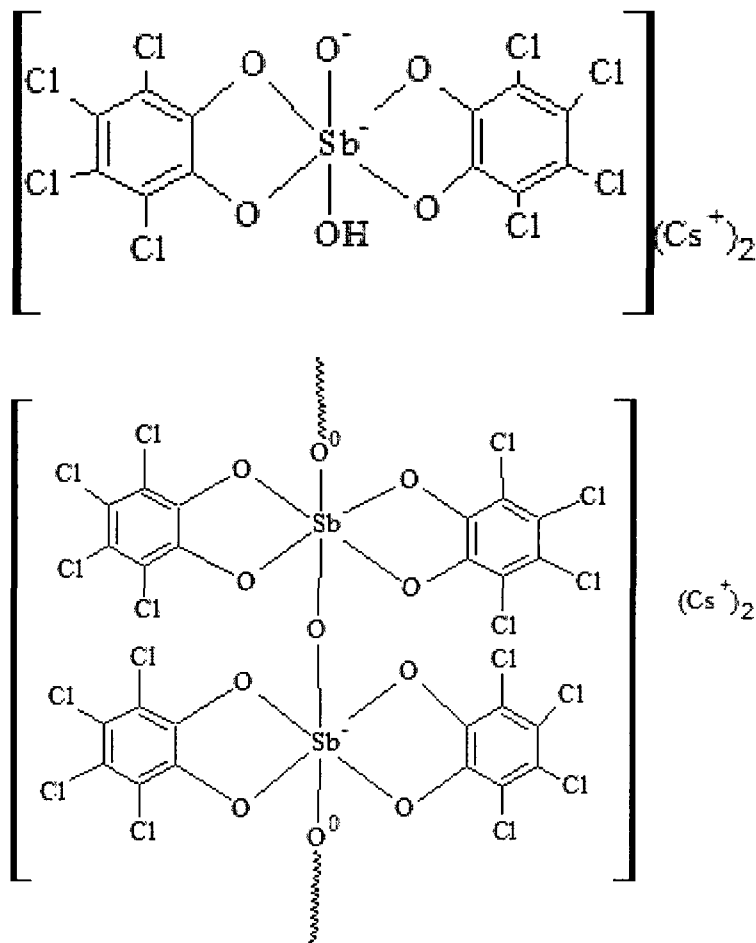
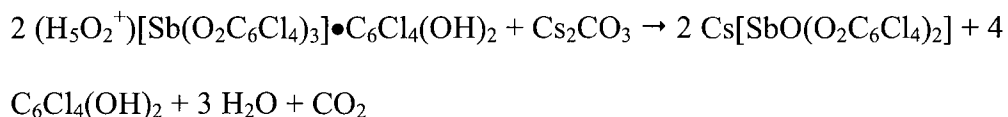


Figure 23. Possible structures of dicesium distibate (top) and cesium distibate (bottom).

Our tentative conclusion is that cesium tristibate was not formed and the first attempt to synthesize tristibic acid resulted in the formation of a distibic acid.

Cesium distibate syntheses. The synthesis of cesium tristibate was attempted two more times using the newer (second) batch of tetrastibic acid, with the same procedure as the first two trials. Tetrastibic acid dissolved in acetonitrile was treated with solid cesium carbonate. Khaki-colored precipitates formed and were filtered off, washed with acetonitrile, and dried; the yields of the precipitate were 64% and 73%. These products were not soluble in acetonitrile. The ¹³C NMR spectra in d⁶-DMSO of the two products

matched one another (Table 3.8) and Shieh's (2007) data (Table 1.9). The Infrared spectra were also similar to one another (Table 1.10), and matched Shieh's (2007) spectrum (Table 1.3). The fourth product was submitted for elemental analysis of carbon, hydrogen, chlorine, cesium, and antimony. A reasonably good fit was obtained with calculated percentages based on its formulation as cesium oxodistibate, $\text{Cs}[\text{SbO}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$, although the percent cesium was higher than calculated (perhaps some dicesium distibate is incorporated). The balanced reaction for this synthesis therefore would be:



Therefore, we conclude that the tetrastibic acid loses two moles of tetrachlorocatechol upon neutralization, and gives another distibate, rather than either a tetrastibate or a tristibate. This result contrasts with results for cesium trisphat, which can be made by straightforward neutralization of Lacour's (1997) trisphat acid.

Comparisons were done for the relatively simple IR spectrum of our cesium distibates with the simple IR spectra of Lacour's trisphat salts. An obvious difference expected is the replacement of the contribution of the P-O stretching frequency near 1200 cm^{-1} with the much lower Sb-O stretching frequency. In the literature (Robertson & McNaughton, 2003), the computed IR element-oxygen stretching frequencies of the four-coordinate species OSbCl_3 and OPCl_3 were compared. With MP-2, the Sb-O frequency was computed at 1004 cm^{-1} , well below the P-O frequency of 1343 cm^{-1} . Using the B3LYP method, these are 892 and 1321 cm^{-1} , respectively, for these four-coordinate and therefore possible partially element-oxygen double-bonded species. The infrared

spectrum of potassium hexahydroxoantimonate (with six-coordinate antimony) contained a major peak between 700 and 800 cm^{-1} . The peak at 790 cm^{-1} is found in the IR spectra of most distibic acid, tetrastibic acid, and the cesium salts, and may therefore correspond to the antimony-oxygen bond. This peak was not in tetrachlorocatechol or most of the filtrates. The peak at 790 cm^{-1} is also not found in Lacour's trisphate (Table 1.3). However, this peak would be expected to be coupled with other vibrations in the same region of the IR spectrum, and in fact there are a number of shifts between the IR spectra of stibates and trisphate.

Barium Distibate Synthesis. Distibic acid was dissolved in acetonitrile in a round-bottom flask. Barium carbonate was swirled in water in a beaker. This barium carbonate suspension was slowly added to the distibic acid solution and swirled between additions. A transparent solution quickly formed. Gas was released when it was rotary evaporated. The white solid was stored under house vacuum. The aqua-colored product was washed with chloroform, which appeared to remove needles and leave a pure, white powder. The ^{13}C NMR spectrum of the white powder in d^6 -DMSO had three peaks (115.7, 116.7, and 151.1 ppm from TMS) as expected for a stibate. The IR spectrum (Table 1.3) appeared to contain TCC so the product was washed again with chloroform whereupon it turned back to green. The twice-washed product had a much cleaner IR spectrum with most of the TCC peaks being removed (Table 1.11). The chloroform filtrate was rotary evaporated to leave a white solid. The IR spectrum was very similar to that of tetrachlorocatechol (Table 1.11).

A control reaction, using the same procedure, was performed using tetrachlorocatechol and barium carbonate. No change was observed upon attempting to mix the tetrachlorocatechol/acetonitrile solution with the barium carbonate/water mixture. It was concluded that tetrachlorocatechol does not react with barium carbonate.

Table 11. FT Infrared Spectra of Additional Distibate Salts

Salt	Wave numbers, cm ⁻¹
barium distibate	673, 753, 790, 812, 966, 996, 1166, 1246, 1276/1289/1311, 1397, 1420/1448
^o barium distibate	790, 811, 963, 1241, 1380, 1419
^o filtrate	752, 790, 813, 935/964, 995, 1168, 1248/1275/1289, 1312, 1396, 1447
nickel (II) distibate	672, 691, 752, 793, 812, 970, 1178, 1246, 1288/1311, ~1379, 1402, 1423, 1608
filtrate	672, 752, 813, 951, 996, 118, 1274/~1280/1311, 1397, 1448
nickel (II) carbonate hydroxide tetrahydrate	679, 831, 1360
diethylammonium distibate	688, 791, 811, 968, *984, *996, *1213, 1244, 1382, 1427, *1446, *1589

*weak picks ^owashed twice

Nickel (II) Distibate Synthesis. Nickel (II) carbonate hydroxide tetrahydrate was added with swirling to a solution of distibic acid in acetonitrile in a round-bottom flask. The reaction produced a transparent, lime-green, cold solution, and a dark green solid settled on the bottom. The filtrate was rotary evaporated. The green solid was redissolved in acetonitrile, producing a transparent green solution, which was rotary

evaporated. The dark green sludge was partially dissolved in chloroform then filtered in a glass funnel, whereupon a white precipitate formed.

The IR spectrum of the precipitate was similar to the (one chloroform-washed) barium distibate spectrum; the filtrate IR spectrum was almost identical to that of tetrachlorocatechol (Table 1.11). It was concluded that a nickel (II) stibate was formed. Based on the elemental analysis of cesium distibate, it was assumed that the nickel (II) stibate produced would also be a distibate.

Diethylammonium Distibate Synthesis. This reaction was carried out with procedures analogous to Lacour's synthesis of tributylammonium TRISPHAT (Lacour, 1997). A cloudy, gray mixture was formed when tetrastibic acid and dichloromethane were mixed together in a round-bottom flask. A white precipitate in a transparent, tan solution was formed when a solution of diethylamine in dichloromethane was added to the tetrastibic acid/dichloromethane mixture. After forty hours the solution was transparent with a khaki color; no solid was present. The product was filtered and washed with hexanes; a white solid was collected for analysis. In addition to a gas being released, the solid became darker when it was added to d^6 -DMSO. The ^1H NMR spectrum had a triplet at 1.1 ppm, a triplet at 2.5 ppm (assigned to solvent), a quartet at 2.9 ppm, a singlet at 3.3 ppm, and a singlet at 8.5 ppm, as expected for the diethylammonium ion. The ^{13}C NMR spectrum had the three peaks expected for a stibic acid (115.5, 117.3, and 151.6 ppm from TMS) and three additional peaks (11.6 ppm, 41.9 ppm, and 100.0 ppm from TMS) assigned of which two are expected to be assigned to the diethylamine; the last is unexplained.

The synthesis was repeated a second time. All the qualitative observations were identical. The product was dried under house vacuum for five days. The ^1H NMR spectrum of the product was almost identical to that obtained from the first synthesis (1.2, 2.5, 3.0, 3.3, and 8.2 ppm). The ^{13}C NMR spectrum of the product was identical for the peaks assigned to the TCC ring (115.8 ppm, 117.0 ppm, and 151.5 ppm from TMS) but the peaks for the alkane chain were slightly different (8.5 ppm, 41.3 ppm, and 48.6 ppm from TMS). Except for an additional of a peak at 996 cm^{-1} , the IR spectrum (Table 3.11) was almost identical to the trial #2 cesium distibate spectrum. When disregarding the weak peaks of the diethylammonium distibate, it has the same peaks as the very clean trial #2 dicesium distibate (Table 1.10). Except for the percent chlorine, the elemental analysis of the product (Table 1.4) confirms a formula of $[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{SbO}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$. The IR spectra would suggest this synthesis has a major and minor product, with the major product being similar in structure to dicesium distibate.

To confirm that tetrachlorocatechol, TCC, was not reacting just with the diethylamine, a control reaction was carried out. A solution of diethylamine in dichloromethane was added to a solution of TCC and dichloromethane. A transparent green solution turned to a green-brown color when hexanes were added. After 40 hours the solution turned dark brown-green; no solid was present. The solution was rotary evaporated; the ^{13}C NMR spectrum of the product in d^6 -DMSO had no peaks. The ^1H NMR spectrum did not resemble that of diethylammonium distibate at all. From the difference in qualitative and quantitative observations, it was concluded that the product from the control reaction of TCC and diethylamine was not the same as the product from the diethylammonium distibate synthesis.

CONCLUSIONS

Applying Lacour's (1997) reaction of tetrachlorocatechol with PCl_5 in dry toluene to the corresponding reaction of SbCl_5 was not straightforward. Our first attempt inadvertently involved toluene that had been exposed to atmospheric moisture, and a mild explosion ensued. The reaction was continued anyway, and seemed to have produced a distibic acid rather than the expected tristibic acid. The second attempt involved 99.8% dry toluene (synged from a bottle with an AcroSeal™). No explosion ensued, and a stable parent acid resulted, which gave an elemental analysis corresponding to a tetrastibic acid. Neither of these acids gave IR or NMR spectra characteristic of products with only chelating tetrachlorocatecholate ligands.

SbCl_5 seems to be acting as a stronger Lewis acid than PCl_5 . Its stronger reaction with water makes it imperative that the toluene be as dry as possible. The SbCl_5 should be loaded into Schlenkware in a glove box (which we did not have) rather than a glove bag. The toluene should be further dried by distillation from a drying agent such as sodium metal. In contrast, glove bags and 99.8% dry toluene were satisfactory for producing TRISPHAT acid.

Although elemental analyses suggested that a tetrastibic acid was produced when drier toluene was used, it could not be neutralized (even by a dry amine) to give either a tetrastibate or a tristibate, but rather distibates of Cs^+ , Ba^{2+} , Et_2NH_2^+ , etc. In contrast, Shieh (2007) and Marella (2004) were able to make Group 1 salts of TRISPHAT in the presence of water by the neutralization of the unstable TRISPHAT acid with solid Group 1 metal oxide or even with concentrated aqueous metal hydroxide. Hall (1980) was also

able to make these Group 1 salts of TRISPHAT by treatment of the amine salt of TRISPHAT with concentrated aqueous solutions of Group 1 metal hydroxides.

Since the Sb-O bond length in tritribates is expected to be at least 30 pm longer than the P-O bond length in TRISPHATs, we hypothesized that the tritribate anion would be larger and thus less basic than the TRISPHAT anion. However, the molecular model (Fig. 1.19) suggests that a longer Sb-O bond length, which would push each of the chelating ligands further outward from the central atom, would also push the partially-negative oxygen atoms further out into the “clefts” of the ligand, thus exposing them MORE to attack by water molecules. This might explain why tritribates would more readily be attacked by water than TRISPHATES. We have no reason to believe that, in the absence of water, tritribates would be unstable: tris(TCC) derivatives of similarly large +4 to +6-charged cations (Sn, Re, W, and Mo) have been characterized crystallographically.

We were handicapped somewhat by the fact that ^{13}C NMR data is less abundant in the literature than crystallographic data (which is not available to us). A number of relevant products give the ^{13}C NMR peak furthest from TMS (highest δ value) at about 143 ppm: TCC itself, TRISPHAT, Tian and Tuck’s (1993) $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$, our distibic and tetrastibic acids. However, other relevant products give a ^{13}C NMR peak with significantly higher δ value around 150 ppm: Feuvrie et al.’s (2005) $[\text{Ru}]\text{STANNAT}$, Annan et al.’s (1987) $\text{Cl}_4\text{C}_6\text{O}_2\text{SnCl}_2 \cdot \text{phen}$, $\text{Cl}_4\text{C}_6\text{O}_2\text{SnCl}_2 \cdot \text{tmen} \cdot \text{EtOH}$, and $[\text{tmenH}]_2\text{STANNAT}$, and our “distibate” salts. Our tentative interpretation of these ^{13}C NMR peaks is that they seem to be due to *chelating* $\text{C}_6\text{Cl}_4\text{O}_2$ groups bonded to *heavy* atoms such as Sn or Sb, but it does *not* indicate the presence of a tritribate anion. Note

that if this is true, the structure proposed for Tian and Tuck (1993) for $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$ probably needs to be revisited. We need to consider the possibility of *rapid exchange* (fluxional behavior) in $\text{Sb}_2(\text{C}_6\text{Cl}_4\text{O}_2)_5 \cdot 3\text{Et}_2\text{O}$, distibic acid, and tetrastibic acid, which would average the 150 ppm chemical shift with lower shifts in *monodentate* TCC rings.

It is probably true that we could have shipped crystals elsewhere for X-ray structure determination if we had been able to recrystallize our products and grow single crystals. Given our moisture-sensitivity issues, slow recrystallization probably would have had to be carried out in a glove box, which we did not have.

The solid-state IR spectra of TRISPHAT anion, and our distibate salts, are characterized by greater simplicity than the spectra of the acid forms of TRISPHAT or distibate or tetrastibate; greater simplicity suggests higher symmetry (i.e., chelating TCC rings rather than monodentate). We note that, in solid-state IR spectra, rapid exchange (fluxional behavior) is extremely unlikely.

Our di- or tetra-stibic acids do indeed seem to have much more stability than Lacour's parent acid of the TRISPHAT anion, which decomposes within a week even when stored under inert atmosphere or a vacuum. However, the converse is true of the salts. Lacour's tributylammonium tristibate is indefinitely stable in (even humid) air, and the Cs^+ , Rb^+ , and K^+ salts prepared by Shieh (2007) are stable for a few months, at least in desiccators. However, our diethylammonium and Cs^+ salts appeared to decompose in air in a substantially shorter time.

We used synthesis methods very similar to those carried out by Shieh (2007), but we also obtained elemental analyses in addition to IR and NMR spectra. The IR and NMR spectra of our stibate salts matched those of Shieh. However, our elemental analyses indicate that the stibate salts are not tristibates, but rather are distibates. Therefore, we have failed to support Shieh's conclusions, and we are unable to conclude that we have produced the desired TRISTIBATE anion.

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CHAPTER II

STUDENTS' PERCEPTIONS

OF TWO- AND THREE-DIMENSIONAL ANIMATIONS

DEPICTING AN OXIDATION-REDUCTION REACTION

CHAPTER II

INTRODUCTION

Educational Research

Educational Research, particularly in the area of science, technology, engineering, and mathematics (STEM) continues to expand, and is slowly gaining acceptance as a field in which research can provide qualitative and statistical evidence for best practices. As an example, Middle Tennessee State University in Murfreesboro, TN, just approved a Ph.D. program which requires candidates to publish sound research that will ultimately improve the teaching methods used in the area of science and mathematics education. The expectation is that teaching that is research based will be more effective for student learning. Learning represents changes in behavior that are caused by experience (Lefrancois, 1972) so once these research methods have been applied to the classroom, it will encourage future teachers to educate differently than their predecessors.

The interest in improving learning is not a novel idea. In 1964, Donald Graffam published an article on a new educational methodology he was using (Graffam, 1964). His intent was to supply teachers with a method for improving learning in the changing society. He advocated that emphasis in the classroom should be on learners and learning, and not teachers and teaching. Although his methods were not research based, he emphasized it was easy, inexpensive, and in agreement with the latest theories in psychology and sociology that were applicable to education.

Graffam's article was one of forty-eight articles included in a publication by Bernard and Huckins (1967). The editors argued that education had neglected human needs and that teachers needed to be less authoritarian and instead learn to work with

students. Since the authors wanted teachers to be continually searching for answers, they included “a preponderance of the most recent articles in the field” (Bernard & Huckins, 1967). The articles were based on the leaders in educational psychology at the time, and included (but were not limited to) Bruner, Coladarci, Pressey, Rogers, Skinner, and Torrance.

Another article in Bernard and Huckins’ book (Berg, 1965) was a response to the changes affecting society due to the impact of automation. His comments about automation apply more generally to all forms of instructional technology, and it is easy to imagine that if every statement regarding automation’s impact was changed to another technological technique the article could be published in a contemporary journal without objection. Berg states there will be “. . . trained persons who have . . . skills to offer but skills society no longer needs” leading to “. . . decreased annual earnings and declining job opportunities.” Although his suggestion for solving these problems was in the behavioral sciences; looking to science and mathematics education to solve these societal and economic issues. Consistent with Berg’s recommendation, today’s society is calling on educational psychology to help improve the interest and comprehension of STEM topics in order to generate a competitive workforce in a global market.

Bernard and Huckin’s publication included articles on creativity, motivation, teacher personality, individual differences, cultural influences, emotional aspects, self-esteem, poverty, and language development. Six of the articles (12.5%) included statistical data to support their findings. Some of the remaining articles referenced supporting material that may have contained statistical data, but many of these articles were purely sound advice for educators based on anecdotal evidence. For example, styles

of learning were discussed and it was recommended for teachers to recognize that children have a wide range of learning styles, which should influence their classroom lesson plans (Reissman, 1966). Class and socio-economic status differences were addressed and it was suggested that professionals try to understand students in terms of individual cultural and economic needs (Haas, 1963). Despite the lack of statistical research to support many of these articles, the same messages are still conveyed to pre-service teachers today.

Modern accepted psychological education theories were also described in this book. It included a paper presented by Skinner in 1954 in which he clearly states that education needs drastic changes (Skinner, 1954). Immediate positive reinforcement is needed for every child if they are expected to learn. Because teachers cannot possibly provide this he concluded teachers must be replaced by mechanical and electrical means that are capable of such 'precise contingencies'. In the subsequent article, Weir (1965) dismisses Skinner's proposal to exploit rat behavior as a basis for redesigning education. Weir objects to "... technological and curricular gadgetry as the nostrum for the ailments of education" and instead believes teachers need to relate to students in order to be able to help them discover, test, analyze, and think reflectively. His underlying philosophy is that students must have the opportunity to find meaning in a situation if they are to respond and learn.

Both Skinner and Weir's theories were an answer to modern educational concerns and contributed to the continuing development of teaching and learning. Although these theories may seem limited or have questionable claims, they still carry validity that is imbedded in educational psychology and practice. Bernard and Huckin's (1967) support

for Skinner was expressed by their concurrence that immediate responses “. . . can more consistently and quickly give impetus to effective learning”. There may have been a time when educators did not recognize positive reinforcement is more productive than physical or emotional punishment. Contrary to the past, current educational curriculum assumes teachers know and utilize results of Skinner’s reinforcement research on student learning and legal policies. The essence of his theory is still intertwined in education.

Learning Theories

Educational theories are typically discussed in chronological order of development. The two broadest categories of learning theories are Behaviorism and Cognitivism. Behaviorists include, but are not limited to, Ivan Pavlov, Edward Thorndike, John Watson, B. F. Skinner, and Clark Hull. Thorndike divided learning theories into pre-behavioral, behavioral, and contemporary. Subcategories of behavioral theories include connectionism, associationism, structuralism, and functionalism (Maples & Webster, 1980). Behavioral theorists measure behavioral outcomes of learning, called responses, which result from environmental stimuli (Jarvis, Holford, & Griffin, 1998). Some authors identify neobehaviorism as a third division of behaviorism (Lefrancois, 1972). Neobehaviorists contend there is a biological or mental process that intervenes between stimuli and response (Kendler, 1995).

Cognitive theorists, on the other hand, concentrate on human development that influences information processing through awareness. Cognitivists include Jean Piaget, Lawrence Kohlberg, James Fowler, Lev Vygotsky, and Jack Mezirow (Jarvis et al., 1998). Developmental neuropsychobiology, or developmental neuropsychology, is a more recent branch of experimental psychology in the area of neurosciences (Amsel,

1989). Neurological techniques are employed to study neuropsychology. This science is referred to as cognitive neuroscience when the information gained from biology, neurology, and psychologies are applied to the process of learning (Goswami, 2004).

Many cognitive theorists resist or reject behavioral theories. Abram Amsel attributes this resistance to cognitive theorists failing to recognize scientific knowledge is a collective quality. He claims that because cognitivists do not acknowledge the distinction between behaviorists and neobehaviorists, they fail to see the accumulating knowledge from facts, paradigms, models, and theories (Amsel, 1989). He uses a three-dimensional spiral that widens as a metaphor for the accumulation of knowledge that rises with scientific progress, and continually circles back among four principles: Radical behaviorism, neobehaviorism, cognitivism, and cognitive neobehaviorism.

Marcus's book *Kluge* complements Amsel's metaphor of Learning Theories (Marcus, 2008). Marcus' foundation of claims that the human brain which has three main sections-hindbrain, midbrain, and forebrain-was designed sequentially on top of one another. This development, which is similar to other human organs, was a progression of technology already in place. Organs are amazing machines which all contain limitations. For example, the human eye has a blind spot, the spine is terrible for up-right support, the vas deferens is too long, and molar teeth are useless. Since 98.5% of the human genome is equivalent to that of chimpanzees, it's not surprising that the divisions of the human brain respond similarly to other animals' nervous systems. This may not represent the highest level of cognitive thinking, but even at that status, our 'animal' brain is still functioning simultaneously with cognitive processes. Marcus states that although we are more comfortable focusing on the highest level of human intelligence, we can't develop a

true picture by ignoring other brain functions (Marcus, 2008). Amsel stated in 1972 that the human mind can have various levels that are simultaneously and independently processing learning and memory. This was later supported by neuropsychological investigations (Amsel, 1989). Educational practices would benefit by considering all learning theories when making decisions regarding effective teaching. Although this research focuses on cognitive theories, the precursors are briefly described below to reveal the evolution towards, and contrast of, cognitive theories.

Connectionism. Thorndike's connectionism is often absent from the discussion of learning theories. In his 1913 publication of *Law of Exercise* Thorndike asserts that there are connections between stimuli and responses that are made by neural bonds (Thorndike, 1913). If the connection results in satisfaction, it will increase and if the results are annoying, it will result in a decreased connection (Maples & Webster, 1980). These bonds can be strengthened by increasing the frequency of connections and decreasing response time. An organism's responses depend on his or her attitude, and could be the result of trial and error. Not all elements elicit responses, and responses can be shifted to other situations or stimuli (Lefrancois, 1972).

Contiguity. Guthrie differs from Thorndike in the sense that his theory is based on the belief that relationships between stimuli and responses are formed by the co-occurrence of the events. A habit that is learned will never be forgotten, just replaced rather than recalled (Lefrancois, 1972). Extinction, according to Guthrie, is characterized by a new action replacing an incompatible response due to internal motivation (Carlson, 1980).

Classical Conditioning. Pavlov was aware his dogs were born with unconditioned responses to unconditioned stimuli. His experiments showed that these unconditioned responses and stimuli could be converted to conditioned responses by manipulating conditioned stimuli through timing, intensity, and extinction (Perkins, 1980).

Operant Conditioning. The major difference between Skinner's operant conditioning and Pavlov's classical conditioning is in the response. While Pavlov dealt with known responses, Skinner's reasoned responses could be behaviors that occurred by chance, such as a mouse accidentally hitting a lever. These behaviors can include mental processing, vary by species, and depend on past consequences (Catania, 1980).

Drive Theory. Hull studied humans and provided data to show the mental development in children. He claimed the underlying principles were the same for the differences in preferential order of responses that varied among species and individuals. Between a stimulus and overt response are intervening covert mental processes (Kendler, 1995). His system to predict an individual's behavior included input variables, intervening variables, and output variables. The intervening variables contained the strength of the habit, internal drive, reward incentive, the potential for a reaction, and the amount of physical exertion necessary (Lefrancois, 1972).

Theory of Mind. Hebb's theories were based on the activities in the central nervous system that develop through experiences. This build-up of cell assemblies allowed for the formation of images, in the absence of external stimuli, in the mind (McGuigan, 1978) which is the basis for higher mental processes.

Osgood Model. Osgood's model parallels Hebb's theory in explaining higher mental processes based on activities of the central nervous system. His model consists of an organism decoding the environment through projection, integration, and representation. Projection is very simple in complexity and is nothing more than the transmission of neural impulses, while integration is due to repeated activity that causes the connection of two central neural correlates. Decoding is followed by encoding through representation, integration, and projection. Decoding is the interpretation of stimuli and encoding is the reaction. The major distinction between Hebb and Osgood is in the representation stage. Representation is where decoding ends and encoding begins. It is meaning based on experience (LeFrancois, 1972).

Gestalt. Kohler studied apes for four years and came to the conclusion that both they and humans could solve problems through perception of relationships, not by trial and error. Wertheimer and Koffka extended this to the laws of the perception of wholes. Humans naturally like to complete patterns (principle of closure), perceive phenomena as continuous (principle of continuity), view similar objects as related (principle of similarity), and group items according to their proximity (principle of proximity). There are also laws of memory to explain why what we remember changes what we perceive. People tend to make things symmetrical (leveling), emphasize distinctness (sharpening), and make modifications (normalizing). Lewin's contribution is in the area of life space. Life space includes a person, and their psychological and physical environment. It is what a person perceives, not necessarily reality (Lafrancois, 1972).

Stages of Cognitive Development. Piaget's contributions to psychology continue to have significant influence on educational practices at all age levels (Herron 1975,

1978). The stages include sensori-motor, pre-operational, intuitive, concrete operational, and formal operational (Jarvis et al., 1998). The formal operational stage is reached when an individual becomes an abstract verbal learner. And there is no longer a need for concrete examples to reach for comprehension. Students raised in a cultivating environment are typically expected to enter the formal operational age by high school. The timing will vary by child, culture, environment, and academic subject. It will depend on the success of prior concept formation. Concepts are represented by a symbol, word, picture, or sign. They are developed from direct experience in which the child abstracts similar attributes through discovery learning (Ausubel, 1978).

Constructivism. People develop mental models to represent knowledge of the world. These models represent exclusive properties which can be correct or incorrect, and are usually incomplete. Environmental stimulus insists on constant simulation of models with new information. If there is no conflict with a mental simulation, models will be reinforced. If there is an inconsistency, the individual can ignore the new information or refine their model, which is considered learning (Bodner, 1986). The changes that can be made to a mental model are adding, deleting, replacing, generalizing, or differentiating (Stevens & Collins, 1980). A person who has formed concepts in a particular subject is capable of developing new concepts through concept assimilation. Although direct experience is always useful, it is no longer necessary. It is not merely the formation of prior concepts, but also the organization of these concepts that has a direct influence on the success of concept assimilation.

The Principle of Readiness. Prior knowledge and its organization are the most influential factors in determining the ability of an individual to comprehend and retain

new information. A 'transfer' can only occur when accessible concepts are influenced by newly presented material. If there are no relevant ideas to anchor new meaning, the alternative is rote learning. A child exposed to instructional material before they have reached sufficient cognitive development may fail to form concepts, form misconceptions, or develop a dislike for the material. The most effective way to create advance organizers is to present material in order from a lesser to a greater level of differentiation, which is consistent with the way humans naturally categorize concepts. Unfortunately, textbooks and teachers more commonly present material in the opposite order (Ausubel, 1960).

Learning Styles. The most common list of learning styles include visual, auditory, and kinesthetic mode. However, there is an endless assortment of learning style categories that can include from four to seven different styles. The theory and usefulness of learning styles has been hotly debated. Proponents often agree varying teaching methods can be helpful, especially when using subject-specific material. But just because a student has a preference of learning styles does not mean that this is the only (or best) way for this student to learn. Numerous studies have been conducted to invalidate the theory of learning styles (Hall, 2005; Pashler, McDaniel, Rohrer, & Bjork, 2009; Scott, 2010), but they have not succeeded in convincing teachers or other researchers to abandon the popular theory of learning styles.

Neurophysiology. Cognitive processes can only be measured by overt actions. Therefore, one can only theorize, but never really prove what is occurring within the brain. Recent advances in brain research can measure impulses within the brain and utilize the data to understand the brain, and are not just the results of its control on human

interactions with the environment. Of the three ways to study neural activity, only event related potential (ERP) is considered safe and practical for children. It maps the latency, amplitude, and distribution of electrical signals in the brain. The information gained does not determine how to teach, but it can support or refute theories pertaining to learning.

One myth, the existence of 'left brain' and 'right brain', has been disproven.

Neurological studies have shown that both sides of the brain's hemisphere work together on every cognitive task. An argument can be made for acknowledging primitive learning when teaching. The emotional system is in the limbic system, and it has strong connections with the frontal cortex, the site of reasoning and problem solving. As a result, if a student is stressed or fearful, learning will not occur because of synaptic obstruction (Goswami, 2004).

Cognitive Load Theory. Humans have an unlimited long-term memory and a limited working load (short-term) memory. Information 'packaged' and 'stored' in long-term memory is called schema, which consist of elements of information that are related to one another. Constructivism assumes that a simple schema is incorporated with additional schema to form a larger schema. Short-term working memory can only handle around seven items at one time. These items can be as simple as the symbol of Fe for iron, or as complex as quantum mechanics. It is the number of items, not the complexity of the items, which is the limiting factor for the conscious mind. The way intelligence is increased is by schema being converted from low-level to high-level so more information can be manipulated in the short-term working memory at any one time (Sweller & Chandler, 1994; Sweller, van Merriënboer, & Paas, 1998).

The seven-digit telephone number is based on this theory. A person can remember 8, 6, 7, 5, 3, 0, and 9 with little difficulty. But, to remember 3, 1, 3, 8, 6, 7, 5, 3, 0, and 9 is more difficult unless it can be schematically revised into area code, town prefix, and 5, 3, 0, and 9. Instead of having ten schemes to remember there are just six.

Misconceptions in Chemistry

Social constructivism recognizes that what is scientifically correct is defined as 'what is accepted by the scientific community' (i.e., that knowledge is negotiated and not absolute). Any contradictory or inconsistent model is referred to as a misconception, alternate conception, or alternate framework. The educational community has become aware that students can answer questions correctly without understanding the concept it was intended to check (Nurrenbern & Pickering, 1987). Students can guess, memorize, or achieve the correct answer through incorrect reasoning. A correct answer from an incorrect conceptual base is more likely to occur in multiple choice tests. The use of open-ended questions increases the likelihood of identifying students' existing misconceptions. However, even open-ended questions may not allow for complete analysis of someone's entire conceptual base. An expert in any field must develop both predictive and explanatory abilities (Rogers, Rutherford, & Bibby, 1992). Predictive and explanatory knowledge do not necessarily develop simultaneously. Predictions can be made by compromising principles or by using knowledge from experience. Explanations must use intuitive knowledge in the form of theories or models.

Young children often develop misconceptions before they ever enter a classroom. Even after formal science exposure, children are often very 'different' than a scientist. For example, their language has different meanings, their experiences for building mental

models are limited and self-centered, and they are not as concerned with explanations being coherent (Osborne, Bell, & Gilbert, 1982). These characteristics, coupled with formal education, result in a scaffold of misconceptions that lead to more misconceptions, which are frequently retained through post-college years.

A common area for children's misconceptions in chemistry is the nature of matter. The first definition young children develop for material is 'fabric'. Later, they may associate the word with 'building material' or 'drawing material'. This usually leads to a misconception when encountering the concept of breaking material down to the atomic level. Most students retain the continuous model of material, which leads them to conclude that an atom has the same properties as the solid it composes (Driver, 1994). Children also learn that the terms 'nothing' and 'empty' are the same. So, when they encounter the term 'vacuum' in school, it is often a difficult concept to visualize. A questionnaire given to high school students asked them what was between the gas molecules of butane in a closed container upon expanding the volume. Only fifty percent of the students chose 'nothing' or 'empty' (Barke, Hazari, & Yitbarek, 2009).

Mulford was interested in the report by the American Chemical Society that the average score on the Conceptual General Chemistry Examination is only 55%. He developed a twenty-two question, open-ended response test for common chemistry misconceptions. The topics covered in this test included the particulate nature of matter, properties of atoms, bonding, gases, liquids, solutions, conservation of mass and atoms, symbols, equations, stoichiometry, chemical reactions, heat, temperature, phase changes, and macroscopic versus molecular properties. Students were given the test preceding and following their general chemistry course. The pre-test scores averaged 46%, and the

post-test scores averaged 51%. As a result of these data, he concluded that most misconceptions students possess before their general chemistry course are retained through out the entire course (Mulford & Robinson, 2002).

Pinarbasi conducted a study to identify misconceptions of prospective secondary-science teachers. The results were alarming. Nine open-ended questions concerning boiling points and freezing points were administered. The percentage of incorrect answers ranged from 17 - 65% (Pinarbasi, Sozbilir, & Canpolat, 2009). These students had completed all of the science courses required to become a teacher and should have understood all of these concepts.

Student misconceptions are not just the result of pre-school children's environment and limited mental development. Many misconceptions are the result of faulty or careless teaching practices. Teachers are often unaware of the misconceptions held by their students and that their instruction could lead to misconceptions. The imprecise use of language can lead to misconceptions because terminology can be interpreted literally by students. For example, the statement that water contains hydrogen and oxygen can lead to misconceptions. Also, teachers use atomic models without explaining the significance (or arbitrary nature) of the color-coding. Therefore, students can interpret the model to indicate the atoms are actually colored (Barke et al, 2009). Inconsistencies between subject matters can also be extremely detrimental. For example, the fields of physics and chemistry still have different and often contradictory descriptions of electricity and this can lead to student misconceptions (Garnett & Treagust, 1992).

Another huge realization in chemical education is that students may be able to perform algorithmic problems without having adequate conceptual understanding. Numerous studies have been conducted regarding the conceptual understanding behind algorithmic problem solving (Bunce, Nurrenbern & Pickering, 1987; Gabel, & Samuel, 1991; Lythcott, 1990; Nakhleh, 1993; Nakhleh and Mitchell, 1993; Pickering, 1990; Sanger & Greenbowe, 1997a; Yaroch, 1985; Zoller & Lubezky, 1995). All the authors came to the same conclusion; proficiency in chemical algorithmic problem solving (calculations) does not constitute, nor guarantee, conceptual understanding. In other words, students can hold misconceptions in chemistry but still solve algorithmic problems, including balancing chemical equations correctly. Zoller and Lubezky concluded that traditional methods of teaching chemistry do not typically result in conceptual learning. Nakhleh and coworkers designed a chemistry course to address the issue. It incorporated a 50-minute 'special session' each week devoted exclusively to conceptual learning, which was assessed by the addition of conceptual questions to the exams. The results demonstrated there can be a narrowing of the difference in algorithmic problem solving versus conceptual understanding with the proper use of instructional methods (Nakhleh, Lowrey, & Mitchell, 1996).

Sawrey (1990) elaborated on the work of Nurrenbern and Pickering (1987) by determining if successful students in the chemistry classes were better at answering conceptual questions than less successful students. The top 27% of students in these class performed better in the class than the lower 27% of the class, but their success on the conceptual questions was still exceedingly low. The success rate on the traditional algorithmic questions for the top 27% of all students was 96% and 91% for gas law and

stoichiometry algorithmic problems, respectively. However, it was only 44% and 21% for conceptual problems on the same topics.

Nakhleh (1993) proposed a second reason to be concerned with a student's lack of conceptual progress in chemistry. She stated that the brightest students in chemistry are more interested in the 'why' of chemistry as opposed to solving rote algorithmic problems. However, due to the design of introductory college chemistry courses, these students are usually second-tier grade performers. Their grades and the traditional teaching style are a source of discouragement, resulting in these students becoming dispassionate for chemistry. She asserted that designing instruction for these second-tier students will encourage them to remain a science field.

Learning Science

In general, children do not contemplate their beliefs in relation to reality. The limitation of human senses is a complex notion reserved for formal operational cognition. For children, learning is the result of experience, not intentional formal cognitive analysis, as they look for order and regularity in their environment to construct meaning (von Glasersfeld, 1984). Stated scientifically, a schematic shift occurs in the form of a mental model modification due to the sensory processing of a conflict with their prior interpretation of reality (Bodner, 1986).

Rote memorization is not equivalent to understanding. Items can be memorized without having any prior knowledge of the subject. To understand new information it must be related to existing mental schema (Carey, 1986). Ausubel and coworkers state that the most important factor in learning is what the learner already knows (Ausubel, Novak, & Hanesiona, 1978). Learning begins with sensory input of data that can result in

ignoring or assimilating. No changes will be made to previous mental models or theories if the input is ignored; only acknowledged data is assimilated. Assimilation is the application of new data to existing schemes, and assimilation can result in equilibrium or disequilibrium. Equilibrium will occur if the learner has determined the new information coincides with existing mental models and theories. Disequilibrium results when there is a cognitive conflict. If the previous knowledge is modified, accommodation (the final step of learning) will occur (Bodner, 1986). Learning does not necessitate that assimilation or accommodation result in 'correct' schema formation. On the contrary, accommodation can lead to incorrect models transforming into additional erroneous theories.

Chinn and Brewer (1998) state, that at the cognitive level of disequilibrium, inconsistent data can be processed in one of seven manners. The list includes ignoring, rejection, exclusion, abeyance, reinterpretation, peripheral theory change, and theory change. The first two are indicative of the data not being accepted as true. The difference is that upon rejection, an explanation is given for why the data are determined as not valid. Exclusion of data is based on the notion the data are irrelevant, regardless of the validity. The last four are the possibilities for data that are accepted as correct and relevant. Abeyance is when the observer can't explain the data in terms of their theory but believes someone else will in the future. Reinterpretation involves trying to explain the data within the confines of an unyielding theory. The last two choices differ in the extent of theory modification. They are similar in the complete acceptance of the data accompanied by the realization an existing theory must change.

There are those who believe that students do not really have consistent theories, just intuitions. Even if this argument were true, it still supports the notion that they do not possess correct scaffolding models for learning. In order to learn new information, the learner must be able to relate it to prior knowledge. Of course, it helps if the learner is interested or concerned with the information (Carey, 1986). Taber's longitudinal study on college student's understanding of chemical bonding may shed light on why some think that students are operating on intuition only. He conducted 23 interviews over the course of two years. His conclusion is that the progression of mental theories in chemistry can incorporate a series of explanations. At any one time, a student may hold multiple ideas and switch between which one is utilized in overt justification (Taber, 2001).

Bransford and Johnson conducted a simple, but spectacular experiment. Only half of their subjects were shown a picture of a man deciding how to serenade a female (Appendix A). After reading a passage related to the graphic representation, most of the group that did not see the picture claimed the passage was incomprehensible and could not recall the ideas of the passage (Bransford & Johnson, 1973).

If the balloons popped the sound wouldn't be able to carry since everything would be too far away from the correct floor. A closed window would also prevent the sound from carrying, since most buildings tend to be well insulated. Since the whole operation depends on a steady flow of electricity, a break in the middle of the wire would also cause problems. Of course, the fellow could shout, but the human voice is not loud enough to carry that instrument. Then there could be no accompaniment to the message. It is clear that the best situation would involve less distance. Then there would be fewer potential problems. With face to face contact, the least number of things could go wrong. (Bransford & Johnson, 1973, pp. 392-393)

This brings up an important question. How can science be learned when the learner has no prior knowledge or the ability for it to be experienced? In particular, how can students understand theories based on the nature of particulate matter? The answer may lie in Skinner's suggestion to utilize technological gadgetry to save education.

Teaching Chemistry

There are objections to the constructivism. Matthews (2002), who claims he has many supporters, ascertains any contribution constructivism has had to science is not novel and can be found in a list of diverse thinkers. His main argument is that constructivism is intolerant of knowledge being imparted to the learner. He asks how anyone is able to learn science if teachers cannot initially convey information which is impossible to experience. Furthermore, he quotes Driver, a renowned supporter of constructivism, and asserts that if constructivists would face their own statements, they would realize knowledge must be able to be imparted. It is not just a product of an individual's own cognitive achievements.

However, Matthews may be wrong in his claim that constructivists do not believe knowledge can be imparted. Teachers will always supply students with basic facts and students are unlikely to question them. This is not necessarily because students must store knowledge in order to continue with complex concepts as much as the fact that teachers feel pressure to do so because of time constraints or standardized test requirements. In the future, constructivism may be replaced by a subsequent theory of learning, but, even as Matthews himself admits, it is an answer to many present-day concerns. The theory of constructivism is a response to the problems of misconceptions in science. As more theories develop, the evolution of learning, and therefore teaching,

will be built on a historical scaffold. The contribution of constructivism to education will also be in the treatment of student misconceptions. Teaching will always involve imparting basic knowledge. But, as constructivists know, it also includes considering knowledge that was not imparted in the classroom.

Two radical, though logical, solutions are proposed for decreasing student misconceptions in chemistry. The underlying objectives are to change the method used to teach students about the particulate nature of matter. One suggestion is to postpone its inclusion in the curriculum until high school senior year. Harrison and Treagust (2002) argue that introducing the particulate nature of matter too early is harmful to student's enjoyment and curiosity in science. Students should be taught scientific literacy and macroscopic chemical concepts at younger ages. They believe high school seniors are cognitively developed and mature enough to be ready for discussions of the particulate nature of matter.

The second suggestion is to completely revamp the concept of molecules. Taber (2003) claims the entire molecular model is based on historical views. These models are not scientifically sound and are the same models that impeded early scientists. Successful chemists are able to disregard the model when needed even while using the out-of-date terminology. The idea is that the concept of the atom should be eliminated and replaced by subatomic particles. There is no need to distinguish between elements and compounds. For example, water should not be referred to as being made of hydrogen and oxygen. It should be discussed exclusively in terms of the number of protons, electrons, and neutrons.

K-12 education is state- and federally-driven. Standardized testing has become the currently accepted means of assessing student learning. Parents, educators, and politicians focus on the assessment of knowledge in the earliest grades possible with the belief it will guarantee success for these students as adults. Even if longitudinal studies prove that particulate concepts are being taught too soon, the public will never agree to postpone its introduction. Likewise, subatomic particles are not going to be the major building blocks for the particulate conceptualization in K-12 or subsequent education because it would require scientists to abandon a model that they used when first learning science. Accepting that these two suggestions will never be put in motion requires college chemistry instructors to learn how to effectively teach with their students' prior experiences in mind.

Particulate Models

Matter can be represented on three different levels: symbolic, macroscopic, and particulate representations. Symbolic representations include chemical symbols, chemical formulas, balanced equations, mathematical formulas, tabulated data, and graphs. The macroscopic level involves data and observations of matter made using the five senses. The particulate, or microscopic, level must be represented by physical or visual models. Because students cannot see the particulate level, they often need help designing mental models. Numerous studies have shown that students who can mentally visualize the particulate nature of matter are much more successful at answering conceptual questions at the particulate level and solving algorithmic problems (Gabel, 1993; Gabel, Samuel, & Hunn, 1987; Kelly, Phelps, & Sanger, 2004; Russell et al., 1997; Sanger, Phelps, & Fienhold, 2000; Sanger, 2005; Smith & Metz, 1996;

Williamson, & Abraham, 1995). Since students are unlikely to develop scientifically-accurate conceptions of the particulate nature of matter on their own, teachers need to introduce students to physical models of the particulate world. In doing so, it should always be made explicit that particulate representations are not scaled-down models of the macroscopic world. They are tools based on known properties that help chemists make chemical predictions at the particulate level (Taber, 2010).

When introducing particulate models to students, teachers need to be aware that students are not always able to make connections among the three levels of matter. So, instructors should take the time to explicitly make the connections for students. Learners also may not be able to differentiate between the properties of the macroscopic world and those of the particulate world. Few students are able to come to the conclusion on their own that atoms do not have the same colors (or other properties) as the object they form and therefore, must be told. An even more complex, but equally important, notion that is often overlooked is the limitations of models. Analyzing various models for their similarities, differences, limitations, and advantages can help students realize that scientists have a rationale for switching among the three representations.

The use of particulate models should not be confused with catering to visual learners. Particulate models are intended for all students to help them develop a particulate understanding of chemistry. As stated earlier, most learners resort to concrete operational cognition upon initial exposure to a new concept. Although the continual use of particulate graphics may improve student interest or attitude toward chemistry, many students may only need them at the first exposure to these concepts.

The age of technology has allowed the drawings of atoms and molecules to extend to computer animations. The ability to show particles in motion has been shown to be more beneficial than static drawings (Sanger, Campbell, Felker, & Spencer, 2007; Sanger, Phelps, & Fienhold, 2000). This could be related to the fact that computer animations allow the visualization of time-dependent motion which may be crucial for explaining the macroscopic properties of these chemical reactions.

Computer Animations

Numerous studies have been conducted on multimedia to determine the qualities which are most conducive to learning, especially in the field of chemistry (Kelly et al., 2004; Russell et al., 1997; Sanger & Greenbowe, 1997b; Sanger et al., 2000; Williamson & Abraham, 1995). The explanations for the results are usually based on the cognitive load theory.

Coherence Effect. Educators know if a student is interested in a subject they are more likely to learn the material. Teachers often interpret this as meaning that entertainment and fun are a necessity for learning. Although a positive classroom atmosphere is usually the most productive, this does not mean seductive details should be incorporated. Seductive details are defined as snippets of related, but cognitively irrelevant, information intended to spark interest or rouse prior knowledge. Research on including seductive details in texts, lectures, and multimedia suggest inclusion of seductive details can often illicit extraneous prior knowledge and therefore can be more harmful than beneficial in focusing cognitive development (Harp, 2005; Mayer, 2001).

Dual-Modality. Visual and auditory processing do not use the same cognitive channels in the human brain. Therefore, more cognitive information can be addressed if

both channels are utilized simultaneously. This is consistent with the results of educational research showing that learning improves when narration is included with visual graphics and animations (Mayer & Anderson, 1991; Mayer & Moreno, 1998; Mousavi, Low, & Sweller, 1995).

Redundancy Effect. Since the short-term working memory has a limited capacity, when a lesson involving graphics is narrated both visually (with text on the screen) and orally, it is less effective than when the narration is only presented orally. One explanation is that the working memory must be devoted to decipher which material is redundant so it can be disregarded (Kalyuga, Chandler, & Sweller, 1999, 2000; Moreno, 2002a, 2002b).

Contiguity. If a short written explanation placed next to appropriate graphics, it can be advantageous (Mayer & Johnson, 2008). In this manner, the information is contiguous both spatially and temporally. Students do not have to split their attention, which would require more use of their short-term working memory (Mayer & Johnson, 2008). Research by Ginns (2006) supported this assertion and extended that it would be more applicable for novice learners and complex material.

Purpose

The focus of this research was to determine how students use a 2-D and 3-D animation to build an efficient mental model of the particulate nature of a simple oxidation-reduction reaction. The advent of technology has increased its use in the classroom as supplemental teaching material and as the major source for on-line learning. Intuition and anecdotal evidence regarding the optimal teaching design of animations

must be replaced by research to ensure our students are receiving the best teaching experiences that can be delivered.

The specific topic, electrochemistry (which includes oxidation-reduction reactions), was selected because it has been documented as cognitively challenging for introductory chemistry students (Sanger & Greenbowe, 1997a, 1997b, 1999; Schmidt, Marohn, & Harrison, 2007). Writing balanced oxidation-reduction reactions is another topic of electrochemistry where students have difficulties (Garnett & Treagust, 1992). The focus of this research on this subcategory of electrochemistry was chosen because there were existing 2-D and 3-D animations representing the macroscopic, symbolic, and particulate levels of an oxidation-reduction reaction. There is evidence that when the associations between these three levels of representations are optimized, student comprehension will improve (Kelly et al., 2004).

The overall goal was to determine what specific attributes of these two animations facilitate or hamper student connections between symbols, particulate representations, and macroscopic observations. This was measured by analyzing students' responses to specific questions and their ability to write balanced oxidation-reduction equations. Five major objectives were established as part of this research project to achieve this goal. What are the comprehension differences when viewing a 2-D animation versus a 3-D animation? What narration is the most appropriate for inclusion in these animations? What visual improvements should be made to these animations? What is the effect of the 2-D and 3-D animations on students' abilities to write balanced chemical equations? What is the effect of reversing the order of presenting these animations?

These underlying goals were addressed by interviewing students to reveal their comprehension (including their ability to write a balanced oxidation-reduction equation) after viewing a macroscopic demonstration and after viewing two animations depicting the same chemical reaction. The intention was to use the data to determine misunderstandings of the visual animations that appeared during the dynamic interaction.

Animations are more constructive with narration, whether it is done electronically or in person (Jeung, Chandler, & Sweller, 1997). However, unsolicited narration can be more detrimental than helpful. Narration needs to include information that is temporally contiguous and not redundant (Mayer & Anderson, 1991). Text can be added to graphics if it is relevant, simple, and spatially contiguous. Since narration can positively or negatively affect student comprehension, it was decided to show these animations without narration to eliminate any possible narration effects.

METHODOLOGY

Research Design

Thirty-four semi-structured clinical interviews were conducted with college students enrolled in the second semester of Introductory Chemistry at a Southern state university during the fall of 2007 and the spring of 2008. The interviews were conducted within a few days following the course lectures and laboratory instruction pertaining to electrochemistry. Most interviews included two student interviewees and one or two interviewers. There was a wide range of social backgrounds, genders, anticipated chemistry grades, and academic majors represented in the subject profiles. However, data regarding differences between these groups were not collected as part of this study. Clinical interviews can be a means of scientific data acquisition if one designs the interviews as a natural pattern of interaction (diSessa, 2007). In order to increase the validity of conclusions made from the data, the interviews were designed to address three major criticisms of clinical interviews. The interviews were recorded in the chemistry building so interviewees would be familiar with their surroundings. To encourage a genuine interest in committing an hour of time, students were told the experience would be a beneficial review for their final exam. After each interview, the interviewers (who were experts in chemistry instruction) provided a debriefing that included a discussion of any incorrect responses given by the students. The questions asked in the interviews were the same as those expected from a college professor teaching an introductory chemistry course. Anonymity, permission for recording, and voluntary relinquishment of participation or use of data was explained at the beginning of each interview.

Interview Protocol

Each interview began with a demonstration of an oxidation-reduction reaction. This consisted of adding solid silver nitrate to water, stirring it until the solid dissolved in water, and then submerging a copper wire into the solution. After viewing the reaction, students were asked to answer a series of questions (Table 1). After the demonstration and a question-answer portion, interviewees watched two different computer animations depicting this chemical reaction at the particulate level. The same series of questions was asked after each animation. For half of the interviews, students viewed the 2-D animation first and 3-D animation second. The order of the animations was reversed for the other interview sessions on an alternating basis. The interviews were recorded using a digital audio recorder.

Data Analysis

Each interview protocol was transcribed verbatim. Examples where students misinterpreted the computer animations were identified for each interview. The accuracy of the student-generated chemical equations was analyzed for improvement after viewing each animation. The researcher and the major advisor analyzed each interview transcript for examples of student misinterpretations and tabulated each incorrect idea, including how many and which students demonstrated these ideas. Misinterpretations made by fewer than eight of the 32 interviewees were discarded; the remaining recurring misinterpretations are discussed in this dissertation. The balanced chemical equations were categorized as correct if all of the chemical formulas, states of matter designations, and coefficients were correct. The correct equation is: $\text{Cu (s)} + 2 \text{AgNO}_3 \text{ (aq)} \rightarrow$

$\text{Cu}(\text{NO}_3)_2 (\text{aq}) + 2 \text{Ag} (\text{s})$. The equation was determined to be correct if the order of reactants or products in the balanced equation was reversed.

Computer Animations

One of the computer animations, created by Michael J. Sanger, appeared two-dimensional (2-D) in nature (Figure 1). It had several stationary yellow circles in the center of the screen to represent copper atoms. The silver ions were depicted as gray circles with a '+' symbol in the middle. The nitrate ions (NO_3^-) were depicted as three red circles surrounding a blue circle with a '-' symbol on it. This animation showed an equal number of silver ions and nitrate ions moving around the screen. Every time two of the gray circles would hit the conglomeration of yellow circles, two tiny pink 'e-'s would move from a single yellow circle to one of each of the gray circles. The two gray circles would enlarge and attach to the cluster of yellow atoms. At the same time, one yellow circle would become smaller, gain a '+2' symbol and begin moving in the open space near the nitrate ions. As the animation progressed, the blue background became darker every time one of these collisions occurred.

The other animation, created by Roy Tasker, was designed to appear three-dimensional (3-D) in nature (Figure 2). The viewing angle of the camera was constantly changing in this animation. Copper was represented by several yellow spheres that were slightly vibrating and separated by an off-white coating referred to as 'fuzzy' or 'fuzziness' in the interviews. Most of the remaining screen was packed with representations of water molecules (one red and two white spheres connected together) that were constantly rotating and moving laterally across the screen. Gray spheres among

Table 1. Interview Questions

-
1. Describe what you see and what it represents.
 2. What are the reactants and products?
 3. What is the ratio of the reactants to the products?
 4. Where does the reaction occur?
 5. What is causing the color changes of the metal surface and aqueous solution?
 6. Describe any changes you see in terms of states of matter, size, or charge.
 7. What is the purpose of each reactant?
 8. What is the driving force for the reaction?
 9. Write a balanced chemical equation for the reaction that includes phases.
 10. Did this animation help you to understand the chemical reaction?
 11. What is your opinion of the animations and the order in which they were presented?*
-

*asked only asked at the end of the interview

the water molecules were used to depict the silver ions. When a gray sphere would come in contact with the yellow mass of spheres, the ‘fuzz’ appeared to be transferred from the yellow sphere to the gray sphere. The silver spheres with the ‘fuzziness’ would remain in the location of contact and the yellow spheres without the ‘fuzziness’ would appear to be surrounded by the water molecules and its distance from its original location would increase until it was eventually no longer in view. A nitrate ion (consisting three red spheres around a smaller blue spheres) would occasionally pass across the screen.

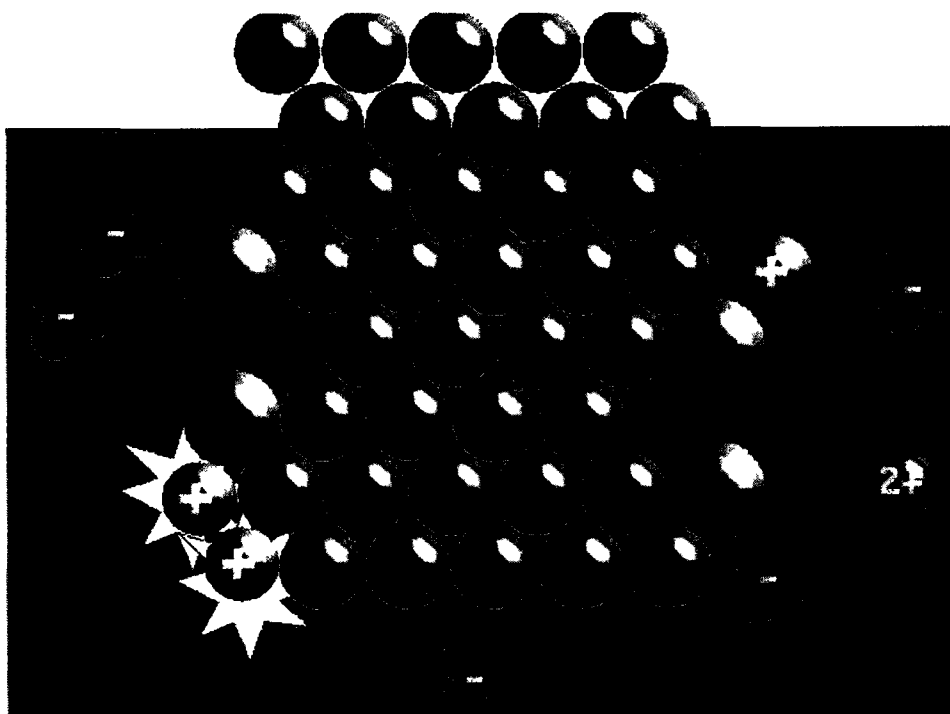


Figure 1. 2-D animation. (Sanger, M. J.) Reprinted with permission.



Figure 2. 3-D animation. (Tasker, R.) Reprinted with permission.

RESULTS AND DISCUSSION

The interviews revealed several student misinterpretations of the 2-D and 3-D oxidation-reduction animations. The most frequently encountered incorrect interpretations of the animations are listed in Table 2 and are underlined in the discussion below.

Table 2. Incorrect Interpretations of Animations

-
1. Water molecules are nitrate ions.
 - 2a. Water's only purpose is as the solvent.
 - 2b. Water is causing the reaction to occur.
 3. There is not a 1:1 ratio of silver and nitrate ions.
 4. Ionic salts do not dissociate into separate ions ion solution.
 5. There is not a 2:1 ratio of silver ions to copper atoms in this reaction.
 6. The valence electrons between atoms in a metal represent 'bonding'.
 7. Gaining or losing electrons has not effect on the size of an atom or ion.
 8. It is not possible to determine how many electrons were exchanged during the reaction.
 9. The blue atom in the nitrate ion causes the aqueous solution to turn blue.
-

Student Misinterpretations of the Animations

Identification of Water Molecules and Nitrate Ions. The 3-D animation depicted water molecules with two small white spheres attached to a larger red sphere. I had anticipated most students would be familiar with the water molecules being drawn as "Mickey Mouse" and that oxygen is larger than hydrogen. It was assumed that students

would know that red is the scientifically-accepted color used to indicate oxygen. A few students were able to come to the correct conclusion that water was being represented as the red and white molecules in the 3-D animation.

“There are water molecules instead of nitrate because they don’t have a third.” (3D)

“I knew it was water because that is what water looks like.” (3D)

“Hydrogen is not bigger than oxygen. Red is bigger so we have water molecules.” (3D)

“Water looks like Mickey Mouse ears; big hydrogen and two little oxygen [sic]. A whole bunch are floating around and bouncing off each other. They are moving around more than the solid.” (3D)

Many students who were confident in their decision that red and white represented water were often critical of its inclusion in the 3-D animation.

“The water seems to be getting in the way in the animation. It takes your focus away from what is going on in the reaction.” (3D)

Some students had difficulty coming to a final conclusion regarding the identity of the red and white molecule. The waters were in such close proximity and constantly rotating that it was difficult for students to count how many white spheres were attached to a red sphere.

“I am trying to pick apart the red and white. Red is nitrogen and white oxygen but there are two white like halves attached that I can see, unless there is a third one so those are throwing me off.” (3D)

In about half of the interviews, students misinterpreted the water (H_2O) molecules in the 3-D animation as being nitrate (NO_3^-) ions. This is understandable because many particulate representations of aqueous chemical reactions leave out water molecules, including the 2-D animation used in this study.

“I guess that is silver and nitrates all floating around it.” (3D)

“The red is the nitrate and the silver ball is the silver.” (3D)

In a few cases, students initially identified the water molecules correctly but as the interview progressed they decided the “red and white things” were nitrate ions. Their attempts to explain the reaction of solid copper with aqueous silver nitrate seemed to require having nitrate ions as visible as the copper and silver ions. In some cases, they invented their own color scheme to support their explanations.

“The big red one with three white pieces on it is nitrate. The red is nitrogen and the three white are oxygen.” (3D)

“I’m starting to think the red are nitrogen.” (3D)

Difficulty in this interpretation often led to discussions between students in the interviews. For example, one student held tightly to his or her belief even when the other interviewee said the red and white were water molecules. Several students realized the red and white molecules were water when they were faced with interpreting the few nitrate ions containing a blue center with three red outer spheres that passed through the screen or when they could see only two white spheres attached to the inner red sphere.

“Blue is nitrogen and red is oxygen and the combination is nitrate.” (3D)

However, many students were unable to change their schema even after viewing the blue nitrogen.

“I am thinking they [red/white] might be the nitrates. Maybe, but I don’t know. Some of them looked like they only had two oxygen. That is why I am confused.” (3D)

“I don’t know why it is blue all of the sudden; maybe to tell us that it changed. I think it would be a good idea to keep it the same color.” (3D)

The 2-D animation did not include water molecules so there was no issue concerning student interpretation of red and white molecules.

The Role of Water Molecules and Nitrate Ions. Water molecules and nitrate ions are necessary spectators in this chemical reaction, but were not part of the oxidation-reduction half reactions.

“We have to have water. Its function is to break apart the ions” (3D)

“Water is the substance that allows it to happen; the system.” (3D)

“I think the water allows it to happen but I would not say it causes it to happen.” (3D)

Why are nitrates in there?

“You needed silver ions. (2D)

“[The nitrate] are just floating around. They are not really involved in the reaction.” (3D)

“Nitrate enables silver to be part of the reaction, but it is not part of the reaction.” (2D)

Almost all of the students (94%) understood water was implied but not shown at the particulate level in the 2-D animation. The absence of water molecules did not seem to cause misconceptions concerning water, but may have led to a lack of understanding of water's role.

What about the water? What is it doing

“Absolutely nothing. It is just the space that everything is in.” (2D)

When students saw the visual particulate representation in the 3-D animation, they seemed to form a better understanding of the hydration of aqueous ions by water molecules.

“I could see the molecules wrapping around them. The copper was attracted to the water.” (3D)

Although their idea of water's behavior was often anthropomorphic in nature, it also gave them a visual representation of the water that was sometimes detrimental to their understanding of water's role in this reaction. Many of the students viewing the 3-D animation assumed that water molecules were causing the reaction to occur.

“It looks like water molecules are delivering the silver and carrying the copper away.” (3D)

Misidentifying the water molecules as nitrate ions led to a number of other misinterpretations in the animation. Many students were quoted as suggesting the nitrate was assisting in the reaction.

“They [nitrates] are assisting the silver to make contact with copper.” (3D)

“It looks like the nitrates are pulling copper ions away . . . causing the reaction.” (3D)

“You can see that nitrate has a part in the reaction.” (3D)

“They [nitrates] are directing the silver over to the copper for it to react and then once the reaction releases the copper they are directed away from the rest of it.” (3D)

Ratio of Silver to Nitrate. The 2-D animation showed the same number of silver ions as nitrate ions on the screen at all times. All of the students viewing the 2-D animation noted this ratio, and several explained this in terms of ion charges.

“Silver and nitrate are the same ratio because silver ions are plus one and nitrate is minus one.” (2D)

“For every one silver, there is one nitrate.”

Is that right?

“Yah. We had A G N O 3. It has to be neutral.” (2D)

Since the 3-D animation is very visually dense and oriented to focus on the metal surface (the site of the oxidation-reaction), it showed very few nitrate ions compared to the

number of silver ions in solution. Only one student expressed that they could interpret the animator's intentions correctly.

How many nitrates should be in this?

"Equal to silver atoms."

Is that what you see?

"No"

What does that mean

"Either I am wrong or the nitrates are in a different part of the environment because this animation is really focused on the surface of the copper which is what I said earlier. This is where the reaction is taking place." (3D)

Other students knew that the silver to nitrate ratio should be the same (1:1), did not see this in the 3-D animation.

"Honestly, I expect to see more nitrates." (3D)

"I see mostly silver, not much nitrate." (3D)

Confusing the water molecules for nitrate ions caused many students to either become more confused, estimate the wrong ratio of silver to nitrate, or in an extreme case, to invent or keep a previous incorrect formula for silver nitrate.

"... there seems to be a surplus of nitrate which is not realistic in regards to the equation itself, so it skews my perception." (3D)

"If I were to write down what I see, there would be a significantly greater amount of nitrogen or nitrate than there is silver." (3D)

"... the animation has like four or five of them [nitrates] escorting silver towards the surface and then extracting the copper ... " (3D)

"A G 2 N O 3 because so many more. I think one for every two. Two silvers for every nitrate." (3D)

Dissociation of Ionic Salts in Aqueous Solution. The demonstration purposely began with students observing solid silver nitrate being added to water to make an aqueous solution. The intention was to determine their understanding of the dissociation

of ions when soluble ionic compounds are placed in water. Only a few students viewing the 3-D animation were able to recognize the hydration of ions in water. None of the students viewing the 2-D animation mentioned this hydration process; probably because this process was not shown in this animation.

“It dissociates because the ions can stick to the water and the water is surrounding copper ions . . . “ (3D)

What made you think the silver nitrate is aqueous?
 “. . . broken apart, not attached, floating separate.” (2D)

As seen before, the misidentification of water molecules as nitrate ions in the 3-D animation contributed to additional misconceptions. The misconception that aqueous ions remain together as ion pairs has been documented in previous research (Noah, 2011). One reason why students may have confused water molecules and nitrate ions in the 3-D animation is that they had expected silver ions and nitrate ions to be connected, so they interpreted the water molecule attached to the silver ions as nitrate ions.

“I think the red larger atoms with the white ones are the nitrate and the silver with the red and the white are the silver nitrate.” (3D)

I would guess this whole molecule is a silver nitrate . . . but I know it is probably not.” (3D)

Two students were able to abandon their previous belief that aqueous ions are connected in favor of the idea that they are disassociated in water.

“That is what I thought originally. The copper would make a compound with nitrate.” (3D)

“I think the nitrates will stay together and silver and nitrate will break up. I am pretty sure nitrate is not connected. I am confused about the silver and nitrate. Maybe it stayed as one and did not separate. It seems like water is surrounding the silver nitrate and dropping something on there and pulling the piece of copper off.” (3D)

Ratio of Copper to Silver. The 2-D animation very clearly showed the two-to-one ratio of silver to copper by having all three objects react with each other at the same instant in the animation. Every student (100%) was able to determine this ratio based on viewing this animation.

“I am not connecting this very well, but I did notice that in the replacement that two silvers were attaching for every one copper that was coming off.” (2D)

The 3-D animation, however, stresses the fact that the reaction and exchange of electrons can occur all over the metal surface, and not necessarily between atoms or ions reacting at the exact same region or at the exact same time. Although this may be a more realistic depiction of the reaction, few of the students were able to determine the reacting ratio of silver and copper from the 3-D animation.

“Just from the animation I see a lot more silvers being added and less copper taken away . . . They are showing one silver come in contact with the copper at a time and one copper being taken away but in the previous one [2-D animation] for every two silvers that came in contact with copper one copper would go away and the two would stay there.”

“It looks like two silver to one copper at least. It’s not real obvious. They show a cluster of silver and every once in a while a copper comes out.” (3D)

“It looks like a one-to-one ratio in this because you can’t tell it drops in and randomly comes over and grabs a copper.” (3D)

How many silvers are reacting and how many coppers are reacting?

“It is like there are more silver so like a five-to-one ratio.” (3D)

“... you can barely see the copper leave and I wouldn’t have even caught that if I hadn’t seen the first animation that explained it.” (3D)

Representation of Valence Electrons. The 3-D animation had a ‘fuzzy’ appearance surrounding the atoms in the solid metals, which represents the delocalized electrons in a solid metal as explained below by students.

“The electrons were represented by fuzzy stuff and when the copper ions were in solid and then when one got pulled away it was no longer covered with fuzzy stuff.” (3D)

“An electron cloudy almost but it is so cloudy it is hard to tell.” (3D)

“It bounces a little bit and then it sticks. It turns a weird color. It looks like a fuzzy thing surrounds it?”

What is it?

“Maybe electrons” (3D)

However, an equal number of students incorrectly identified the valence electrons as a bond or force.

“Maybe that is supposed to represent the forces that make it a solid.” (3D)

What is the swirling (fuzziness)?

“... the bonding” (3D)

In a few cases, students thought the fuzzy appearance was water even when they knew the copper was a solid. Not realizing the outer electrons were being represented separate from the inner part of the atom disturbed some students' vision of how atoms in a sample of a solid metal should be represented.

“... copper too far apart. They should be close together.” (3D)

Valence Electrons Effect on Atomic Size. The 3-D animation depicted the atomic nucleus and core electrons as a colored sphere that is surrounded by a fuzzy appearance in solid metal, but missing this fuzziness for metal ions. The 2-D animation depicted the atom, its core electrons, and its valence electrons as a colored circle that gets larger when electrons are gained and gets smaller when electrons are lost. As a result, 100% of the students were able to determine from the 2-D animation there was a change in the atomic sizes of the copper atoms and silver ions during the reaction.

“The silver is becoming bigger.”

What about the coppers?

“... a little bit smaller.” (2D)

“The silver gets bigger and copper gets smaller . . . The copper is losing electrons from its valence shell and the silver is gaining electrons in its outer shell.” (2D)

Only 38% were able to see this from the 3-D animation. The successful students were able to realize the swirling around the copper and silver were valence electrons that contributed to the atomic size.

Does silver get bigger?

“You have to watch for the white halo to develop.”

Are you counting the halo in the size?

“You have to. The electrons are part of the size.” (3D)

“Well the spheres themselves don’t look like they are changing in size, but when it develops the fuzzy cloud around; it increases the overall radius of the image. I guess so, if you count the cloud, it gets bigger as it gains electrons and smaller as it loses electrons, but if you don’t know that that is a cloud then that is just a ball.” (3D)

“Maybe if you count the almost transparent casing, but it is not real clear, but it could have gotten bigger.” (3D)

If students could not make a connection between the cloudy area, valence electrons, and the definition of atomic size, then they were unable to see the change in atomic size.

“Losing electrons should be smaller but it looks the same.” (3D)

“I think it keeps relatively the same size it just has that electron cloud over it.” (3D)

So the haze is what?

“The electron shells.”

What happens to the size of silver as it reacts?

“Good question.”

What about the copper when it leaves

“I think the copper stays the same too.” (3D)

By having the silver on the surface and getting swirling does it change size?

“No” 3D)

Number of Electrons Gained or Lost. The 2-D animation depicted the valence electrons as pink 'e-' symbols. When the silver ions reacted at the copper surface, a copper atom (which had two 'e-' symbols) gave one 'e-' to each silver ion. When the copper atom gave up the two electrons, its size decreased and a '2+' symbol appeared on the sphere. Similarly, when each silver ion gained an electron, its size increased and it lost its '+' symbol. Since the number of electrons transferred in each reaction was quantified, few of the students had difficulty determining how many electrons were transferred in the 2-D animation.

“You see that two silver atoms react with the copper, and one copper is released that has a plus two charge. So, that must mean that two electrons were donated from the copper, one to each silver.” (2D)

The 3-D animation shows the electron transfer as the fuzzy appearance leaving the copper atom as it became hydrated and joined the aqueous solution. The fuzzy appearance engulfs the silver ions as they attached to the copper surface. However, the animation does not quantify the number of electrons transferred. So, students were not able to determine the number of electrons exchanged between copper and student by viewing the 3-D animation.

So, the cloudiness is telling you the electron change, but how many?
“... non-specific and confusing.” (3D)

“The halos pulsating around the atoms don't explain much.” (3D)

“They have mass. Not much, but they do contribute something. So, I guess this video does show electron exchange, I just did not notice it.” (3D)

Cause of the Water Solution Turning Blue. In the 2-D animation the light blue background representing the water solution was animated to become a slightly darker

blue color each time two silver ions reacted with a copper atom. Students seemed to effortlessly perceive that the water darkening occurred when copper ions became detached from the solid and became aqueous.

“As the copper is breaking off, it [solution] turns blue so that obviously is because of copper.” (2D)

A few students were able to expand beyond what was considered an adequate answer to explain the cause of the color change.

“The blue attached to the water. It is the copper aqueous solution. It is the bond between the copper and water that makes it blue.” (3D)

“At first, silver nitrate was aqueous with water and now copper is aqueous with water so I guess the outside of the copper is making the color change.” (2D)

An unexpected, but recurring, theme in the many of the 3-D the interviews was when students saw the blue sphere of nitrogen within the nitrate ion, they often decided that was related to the water turning blue. Their explanations were not only erroneous, but often caused them to abandon their belief that the blue color in water was associated with copper.

“Well the nitrate had some blue stuff.” (3D)

“No, the only thing I can think is maybe the red molecules that had the blue in them were copper mixed with the nitrate that would cause the blue.” (3D)

“So the nitrogen in the water is turning it blue. I thought the copper was turning it blue.” (3D)

“The blue thing is water. Now the red is confusing. I think the copper becomes an ion and attaches with the nitrate.” (3D)

“Is the water the blue thing? I thought that was copper because it is making copper nitrate.” (3D)

Conflating Macromolecular and Particulate Properties. The most interesting misinterpretation of the animations was not correlated to any specific concept. It involved conflating the properties of models used to represent particle behavior (particulate representation) with descriptions of student observations (macroscopic representation). As an example, when students saw the blue atom in the nitrate ion as it passed through the screen, they would assume it represented the water turning blue. In this case, students confused the scientifically-accepted (but arbitrary) convention of depicting nitrogen atoms as blue with the macroscopic observation that the solution turned blue, which was caused by copper dissolving in water.

“It [nitrogen atom] looks like the same blue that the water turned.” (3D)

“ . . . the water molecule . . . that is blue . . . ” (3D)

“When it shows the one that has the blue in the middle, the red. I don’t know why I say this because the copper is yellow, but somehow the copper with the nitrates is blue . . . is what makes the solution blue.” (3D)

A statement made by one student that may provide greater insight into this student’s cognitive processing. He or she recognized on the macroscopic level that dissolved copper ions were the source of the blue color in the water and on the particulate level that the animation used yellow to represent the copper ions formed. Even being able to recall the proper color-coding scheme in particulate pictures was not enough to deter students from confusing the macroscopic and particulate colors.

“I would assume the blue molecule in the animation is the blue in the water. But blue is nitrate [nitrogen]. I would assume blue is just nitrate. There is a color code. Oxygen is red.” (3D)

Another example of students confusing the macroscopic and particulate representations is revealed in the following quotes in which the student believed the water molecules should be blue because the water solution was blue.

What are the red and white things?

“Water”

Is that what you think water would look like?

“No”

What should water look like?

“Blue” (3D)

In the 3-D animation, several students mentioned that the white hydrogen atoms and the gray silver ions appeared to be the same color. This may have led one student to believe that the reaction with copper was with the water molecules and not the silver ions. They decided the gray fuzzy solid forming on the copper in the demonstration was analogous to the white balls from water turning into gray balls in the animation when they attached to the copper.

“I think there it is showing a copper taking an electron from water. It turns gray down there. It looks like it is chemical reaction that gets fuzzy and forms crystals.” (3D)

Chemical Equations

Only three of the 32 interviewees wrote the correct balanced chemical equation, including states of matter, after observing the demonstration but before observing either animation. One goal of the study was to determine if viewing the animations will help students write a correct chemical equation. Since three students were able to write a correct equation before viewing either animation, the results from three interviews were omitted in subsequent comparisons. The remaining student-generated chemical equations were analyzed for improvement after each animation, with particular attention paid to

student having correct reactants, products, charges, chemical formulas, coefficients, and states of matter.

After the 2-D animation, 53% (8/15) of the students wrote the chemical equation correctly but after the 3-D animation 0% (0/14) had the chemical equation correct. A chi-square test ($\chi^2 = 10.31$; $p = 0.0013$) confirms the 2-D animation was significantly more useful for teaching students to write balanced chemical equations than the 3-D animation. However, the 2-D animation did not appear to help in 30% (6/29) of the interviews. A one-property z -test suggest, with 95% confidence, the 2-D animation will help 41-77% of students in the general introductory chemistry population write the correct chemical equation. The percentage of student improvements after the 2-D animation were 85% (17/29) for balancing, 72% (21/29) for charges, 14% (4/29) for correct states of matter, and 3% (1/29) for correct the correct nitrate formula.

The 3-D animation, on the other hand, did not appear to cause many changes in students' chemical equations. Most (9/16 or 56%) of these students either rewrote the identical chemical equation or stated that there would be no change in their equation based on the 3-D animation. Of the seven that change their chemical equation after the 3-D animation, only one included correct changes.

It should be noted that some of the student-generated equations were already demonstrating correct answers for some of these properties (especially states of matter and nitrate formula), so modest gains should not be alarming.

Order of Animations

None of the students viewing the 3-D animation after the 2-D animation changed their chemical equation. However, 64% (9/14) of the students viewing the 2-D animation

after the 3-D animation wrote correct chemical equations after viewing the 2-D animation.

At the end of the interviews, 53% (8/15) in the 2-D/3-D group and 64% (9/14) of the 3-D/2-D group had the chemical equation correct. It appears that the 2-D has a strong positive influence on the students' ability to write the correct chemical equation. The 3-D animation, on the other hand, did not appear to affect the student's ability to write the chemical equations. There was no statistical advantage for either order of presenting the animations.

Among the students who saw the 3-D animation first, only 31% (5/16) confused the red and white spheres, which represent water molecules, with nitrate ions. When viewing the 3-D animation after first seeing the 2-D animation 50% (8/16) identified the red and white molecules as nitrate ions. The difference may suggest the 2-D animation set the mental tone that water does not need to be depicted in animations. However, the chi-square test ($\chi^2 = 1.17$; $p = 0.28$) showed that this difference was not significant enough to conclude that showing the 2-D animation first influenced the misinterpretation of water molecules in the 3-D animation.

Student Opinions

Most of the students claimed to be visual learners and were thrilled to see a representation to facilitate their understanding of reactions at the particulate level. Both animations were helpful in guiding students to understand the concepts of oxidation-reduction reactions and electrochemistry; each with different qualities that depicted specific topics. When asked for their opinions, many students felt both animations should be used in the classroom.

“I would show both. They each have something that the other one doesn’t have. Each has pros and cons. They are both good for supplemental material.”

“If we could study all reactions in chemistry with animations, we would all be making A’s.”

“The image changes this from words you have to relate in your head to an image you can label.”

“It helped give an idea of what is going on at the atomic level. It is hard to imagine what is going on even though she told us. If she had shown this, it would be easier to remember. I think that is why I have such a hard time even with simple things like writing equations. I can imagine a periodic table all day long, but I can’t imagine what is going on.”

The 2-D animation was preferred by all of the students for writing the chemical equation. The areas they felt it was the most valuable were in showing charges, the exchange of electrons, size changes, charge changes, and the ratio of silver to copper.

“It did help write the balanced equation. It is visual, not some abstract numbers and letters. It is the theory you need to remember to put the whole problem together. It helps you to see how they fit together and the state they are in.” (2D)

“I liked where you can see the electrons moving. In the demonstration, you do not see the molecules moving out so it kind of helps you understand what is going on.” (2D)

“There is obviously two silver atoms which will only react with one atom of copper because when two silvers touch only one copper is released.” (2D)

“I am still not completely sure of the charges but it helps to have them labeled and know before they react and after they react.” (2D)

Many students felt overwhelmed by the complicated screen and viewing angles of the 3-D animation. They could not focus on individual items because the camera motion was distracting:

“I think I can’t see anything because the balls are just almost as big as the screen itself. Maybe if you zoomed out you could see a little more. I feel like all I can see is the water.” (3D)

“I do not think this one is clear. There is so much going on that I can’t process it. I can’t pick apart all that is moving and that is in 3-D.” (3D)

“There are so many elements involved and it is so close up that it is hard to determine stuff from each other.” (3D)

The fact that the gray silver and the white hydrogen atoms were so similar in color may have contributed to the confusion of water and nitrates.

“Because of the shade of the oxygen [the white in the red/white molecule misinterpreted as a nitrate ion] bound to the nitrogen it just looks like the other one. You can’t really tell. There needs to be more clarity in the color differentiation.” (3D)

There were several specific areas students felt the 3-D animation helped them understand concepts or solidified what they already knew.

“This one is good for general use in water.” (3D)

“It confirmed to me what we learned in class; how electrons can just float everywhere because each copper atom does not have its own cloud.” (3D)

“I think it is showing how unimportant the nitrate is.” (3D)

Some of the students felt the 3-D animation was very entertaining and would be great to grab the attention of students. Others felt the 3-D animation was excellent for challenging students.

“As a student it challenges you to think through. The whole process teaches you as a student to explore and not be scared to be wrong. So, from that aspect I think it helps you to grow, and just from that perspective I think it is good to have the show that one.” (3D)

Even students who preferred the 2-D animation believed there was something to be gained from viewing the 3-D animation, especially for more advanced topics.

“It is a good animation for really advanced students that already understand concepts but if it is the first time you encounter the reaction and have not talked about it it’s really confusing.” (3D)

“The 2-D is simpler to see what each atom is doing. But, the 3-D is fascinating to look at; not as useful to see but more realistic.” (3D)

“ . . . it [3-D] is obviously more involved and accurate because it shows the Brownian motion of the copper and all the atoms moving . . .” (3D)

“The 3-D might help to understand the physical chemistry behind it.” (3D)

Students felt very comfortable making suggestions to improve the animations or how they could be most effectively utilized in the classroom.

“If you took some details from the first one [2D] and put it in the second one [3D].”

“I might be able to eventually interpret it [3D] with some extra help, but probably not just sitting at my desk at home and trying to do my homework.”

“The 3-D might be more helpful with commentary or someone narrating and explaining.”

CONCLUSIONS

No man-made model representing the particulate level of chemistry can accurately describe every aspect of the particulate nature of matter. One model cannot be exclusively better than another model. However, one model can be more successful for reaching specific goal. Based on the results of this research, it appears that the 2-D model was more beneficial for facilitating a novice learner's development of the complex concepts associated with oxidation-reduction reactions. Although the 3-D animation was created to be a more realistic depiction of the oxidation-reduction reaction, students benefitted more from the more simplistic 2-D animation.

The two animations were shown to college-freshmen chemistry students without narration. The results indicated that even though students can correctly interpret many aspects of these two animations, aspects of a particulate model were misinterpreted. The most common difficulties experienced by the students involved identifying atoms, molecules, and ions properly, and not being able to distinguish between particulate and macroscopic properties. These issues also resulted in confusion with respect to the ratios of chemical species, the purpose of the reactants, the properties and charge of ions in solutions, and the process of electron transfer. Although misconceptions were identified for students after viewing both animations, it appears that the complex nature of the 3-D animation results in a higher frequency of student errors compared to the 2-D animation.

For the task of writing a balanced chemical reaction, the simpler 2-D animation was more helpful. In addition to the simpler design, the 2-D animation also labeled the charges of metal atoms and the ions, depicted electrons in a contiguous, quantifiable manner, and showed the ratio of reaction in a single animated event. The number of

atoms moving on the screen was smaller compared to the 3-D animation, so the exact ratio between reactants and products and the process of electron transfer could easily be determined. The color differentiation between atom types was easily detectable, the 2-D animation did not depict water molecules which were unnecessary for writing the chemical equation, and the camera viewing angle did not change. Because none of the cognitive exercises in this study depended on the ability to visualize the more realistic 3-D model, the more simplistic 2-D scheme was sufficient for concept development in this study.

Several students stated the 3-D animation was very difficult to comprehend. There was a great deal of movement regarding the camera viewing angle, some of the colors were indistinguishable, and addition of the Brownian motion of the metal atoms was extraneous. The valence electrons were depicted much more abstractly than the rest of the molecules that it was harder for students to interpret. The 3-D animation only helped one of the 32 interviewees write the balanced chemical equation. This apparent lack of an effect can be explained by the cognitive load theory (Sweller & Chandler, 1994; Sweller et al., 1998). Because the students were trying so hard to interpret the more realistic 3-D model, they could not concentrate on the relevant issues necessary for writing a balanced chemical equation. These results are consistent with the coherence effect (Harp & Maslich, 2005; Mayer, Heiser, & Lonn, 2001). Even though the 3-D animation did not help students with the chemical equations, its inclusion did not appear to be a detriment when viewed before or after the 2-D animation.

Students provided several positive comments about both animations and felt they should be incorporated into chemistry classes. Even students who found the 3-D

animation very confusing stated they would not object it to being shown. They suggested it could spark interest, or that other students might find it helpful.

It should be noted that the conclusions made in this study were not relevant to the animations dimensions. Although the 3-D animation was more complicated, this research does not make claims that difficulties from the 3-D animation were because it was 3-dimensional, as opposed to 2-dimensional. This is in agreement with Wang's research on 2-D versus 3-D animations for influencing spatial visualization skills. Although Wang found there was a difference in how 2-D and 3-D multimedia affected student learning, it was non-conclusive whether one was better than the other for a task that needed the ability to visualize in 3-dimensions (Wang, Change, & Li, 2007).

Suggestions for Improving the Animations

The suggestions made for improving the animations, which came directly from student interview quotes, are specifically for use in understanding the oxidation-reduction reaction and writing the balanced chemical equation. The 3-D animation could be improved by having a stationary view.

“Yah, the viewing angle is weird. . . It looks like the camera is trying to get what is happening over the entire surface of the copper wire in as short of time as possible and if it would focus on one area you would see copper is leaving and silver is coming but it is trying to get too much in the viewing area.” (3D)

“But the problem is it shows it all at once and the camera never stops moving and it is hard to pick out the relevant information.” (3D)

“If this one was not moving so much, I think it would be better.” (3D)

It may also help if the camera zoomed out to have a wider view.

“I think I can't see anything 'cause the balls are just almost as big as the screen itself. Maybe if you zoomed out, you could see a little more.” (3D)

The 3-D may be less confusing if it had fewer water molecules or showed the water in the beginning and then removed them for simplicity sake.

“I feel all you can see is water.” (3D)

“Water is confusing because it does not do anything, but that is all you can see.” (3D)

“They could have done with less water. It is not confusing; it is distracting. It has a lot of water. I get that they are trying to get that across.” (3D)

The 3-D animation would also benefit by showing ion charges, and by adding small ‘e-s’ to the electron cloud.

“I think this one makes it harder for me to understand ‘cause there no charges depicted in this animation.” (3D)

“The only issue that remains is the charges. If I knew the charges of silver and copper I would know charges of nitrate and that would change my subscripts.” (3D)

“It showed the charges change, but not what it was. There was just a white cloud.” (3D)

The 2-D animation may be improved by having red and white water molecules present before the animation begins. When the animation begins they could be removed and a small text stating the water molecules were removed simply for simplicity sake could appear.

“Maybe put waters, but it would be too confusing. Just make sure to say the blue background is the water.” (2D)

Implications for the classroom

Models of particulate matter are not data designed for students to practice the scientific method. Nor are they art work for analyzing the artist’s allegories. Particulate models are tools to aid in the learning of science, explaining theories, and making

predictions. Teachers must present these models in a concise manner, including explanations so students can use their short-term working memory to understand science.

“I might be able to eventually interpret it with some extra help but just sitting at my desk at home and trying to do my homework probably not. I understand but it did not really teach me anything new where you taught me something new.” (3D)

Because the short-term working memory of humans is limited, when an instructor is choosing a model to explain a concept, they should concentrate on seeking one that includes the most relevant information. Emphasis should also be placed on using a model that includes non-redundant, contiguous aspects to decrease the chance of cognitive overload. Small symbols or words should be on top, or very close to the actual object it is representing. Narration should also be included at the appropriate time to explain the aspects most open to misinterpretation so students are not forced to decipher them on their own. Animations have been shown to be excellent tools for teaching chemistry concepts. Although some animations may require further explanation to be helpful to students, it is still possible for these ‘correct’ animations to be detrimental to learning for some students. Therefore, teachers should keep in mind the specific topic they are trying to teach when they choose an animation. For example, if learning to write the balanced chemical equation for an oxidation-reduction reaction is the goal, it would be beneficial to choose a simple animation with charges labeled, visible electrons being exchanged, and the atoms in the exact reacting ratio as the chemical equation. Helping students to focus on relevant specifics (such as exact reacting ratios) requires that they be presented with a simple visual tool that has only the necessary details and few other irrelevant features. On the other hand, if a teacher wants students to understand the

process of water molecules hydrating ions in water, then they should pick a model that includes water molecules.

No model can perfectly explain or exhibit every concept simultaneously, especially if it is to be useful in focusing students' attention to the relevant details of the model. Therefore, the advantages, disadvantages, and limitations of models must be imparted to students. The similarities and differences of particulate and macroscopic representations of chemical reactions must also be explained to students. For example, atoms are not only smaller than our ability to see, but also smaller than a wavelength of visible light and therefore cannot have color in the visible spectrum. Therefore, students must be told that when color is used to represent an atom, it is a color-coding scheme invented by humans and does not mean that is the actual color of the atom. However, when colors are used to represent macroscopic level observations, it may or may not represent actual observable colors.

Even if there appears to be a 'best' animation for any specific topic, using it alone may not be the 'best' way to teach the topic. Multiple instructional methods can also be used in conjunction in an endless array of variations depending on time constraints. For teaching how to balance the oxidation-reduction reaction between silver ions and copper metal, both animations could be used. For example, the 3-D could be shown first to spark interest and promote conversation. Then, the 2-D could be shown to assist in writing the balanced chemical equation. Switching back to the 3-D again and using narration would then help solidify concepts that may have been misunderstood and allow for discussion of similarities and differences in the models.

Future Studies

The *dual-modality effect* (Mayer & Anderson, 1991; Mayer and Anderson, 1998; Mousavi et al., 1995) warrants adding coherent, contiguous, non-redundant narration and/or text to both of the animations. The changes should be made in ways to address the identified misinterpretations of the models identified in this study. A subsequent study could be conducted in which the appropriate changes are made and the same interview protocol is used in order to determine whether in the frequency of student misinterpretations have decreased and if students' abilities to write the chemical equation have improved.

The 3-D animation contains a narrated audio track that was disabled during these interviews. The interviews could also be repeated with the narrative activated to see if the combined visual and audio information would improve students' comprehension of this oxidation-reduction reaction. Based on student suggestions, the usefulness of the 3-D animation may be enhanced if the camera angle was kept stationary, charges of ions were labeled, and the ratio of chemical species was made clear. If these changes were made to the 3-D animation, the interviews (without narration) could be repeated to see if the updated 3-D animation was more useful for improving students' comprehension of the reaction in this study.

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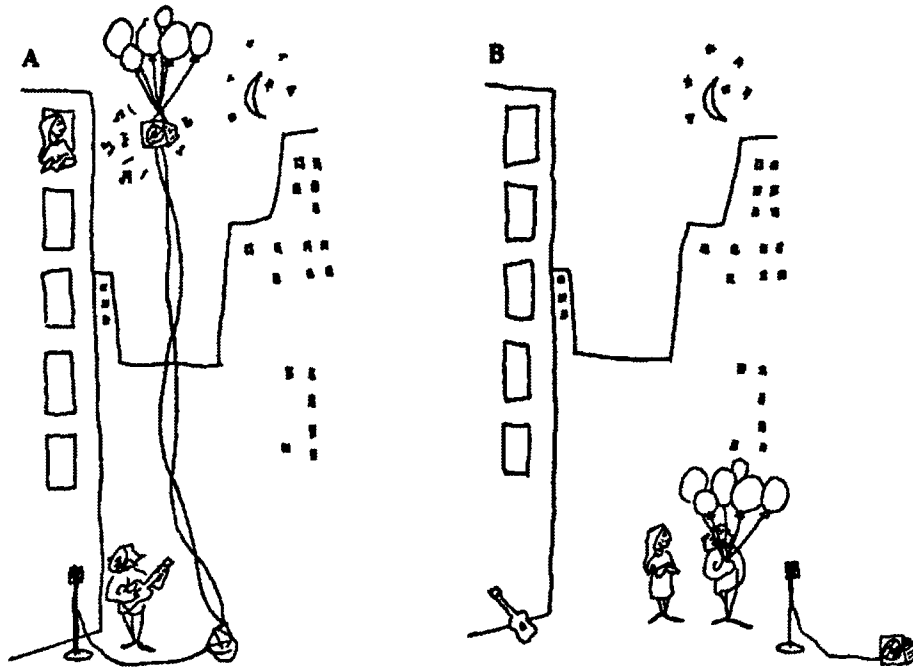
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APPENDICES

APPENDIX A Bransford's Serenade Picture



Reprinted from Consideration of Some Problems in Comprehension. By Bransford, J. D., & Johnson, M. K. in W.G. Chase (Ed.), *Visual Information Processing*, pp. 383-438. Copyright 1973 by Academic Press. Reprinted with permission.

APPENDIX B Permission to Reprint

RE: permission to reprint request

Thursday, March 17, 2011 9:49 AM

From:

"Ravey, Michelle (ELS-OXF)" <M.Ravey@elsevier.com>

[Add sender to Contacts](#)**To:**

"Debby" <deborahreneerosenthal@yahoo.com>

Dear Debby

As per your letter dated 14th of March 2011, Elsevier has no objection to granting its permission for you to use the aforementioned material subject to suitable acknowledgement to the source as follows:

Reprinted from Publication title, Vol number, Author(s), Title of article, Pages No., Copyright (Year).

However we haven't been able to locate the contract for this title in our archives so we are unable to confirm that we are the legal copyright holders of this material. Therefore it is important that you also obtain permission from the author(s) prior to use. If any part of the material to be used (for example, figures) has appeared in the original publication with credit or acknowledgement to another source, permission must also be sought from that source.

Best wishes,

Michelle

Michelle Ravey :: Rights Associate :: Global Rights :: ELSEVIER

T: +44 (0)1865 843517 :: F: +44 (0)1865 853333

E: m.ravey2@elsevier.com

From: Debby [mailto:deborahreneerosenthal@yahoo.com]

Sent: 14 March 2011 19:16

To: Rights and Permissions (ELS)

Cc: Debby

Subject: permission to reprint request

I am trying to gain permission to reproduce a picture for my doctoral thesis in Chemical Education for Middle Tennessee State University in Murfreesboro, TN, USA. Would you direct me to the proper contact? It is on page 394 of Bransford, J. D., and Johnson, M. K. (1973) "Consideration of Some Problems in Comprehension" In W. G. Chase (Ed.), Visual Information Processing, New York: Academic Press.

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Kidlington, Oxford, OX5 1GB, United Kingdom, Registration No. 1982084
(England and Wales.

Re: Permission to reprint

Saturday, April 16, 2011 1:37 PM

From:

"John Bransford" <bransj@u.washington.edu>

[Add sender to Contacts](#)

To:

"Debby" <deborahreneerosenthal@yahoo.com>

By all means feel free to add this to your thesis. I'm not sure who really "owns" the picture (some publisher?). But you definitely have my permission to use. All the best.

On Apr 16, 2011, at 10:29 AM, Debby wrote:

Dr. Bansford,

I am writing to ask your permission to reproduce a picture and paragraph for my doctoral thesis in Chemical Education for Middle Tennessee State University in Murfreesboro, TN.

It is from

Bransford, J. D., and Johnson, M. K. (1973) "Consideration of Some Problems in Comprehension" In W. G. Chase (Ed.), Visual Information Processing, New York: Academic Press.

My doctoral work is on optimizing computer animations to help students form mental pictures of the particulate nature of chemistry. Your picture and quote involving the ballon, etc. is an excellent example of how a picture can change a completely nonsensical passage to an easily understand concept.

Deborah Rosenthal

RE: permission to print picture

Sunday, June 6, 2010 10:41 PM

"Lon Mathias" <Lon.Mathias@usm.edu>

[Add sender to Contacts](#)**From:**

"Debby" <deborahreneerosenthal@yahoo.com>

To:

Yes, but please make reference to where you obtained them. Thanks.

LJM

From: Debby [mailto:deborahreneerosenthal@yahoo.com]
Sent: Sunday, June 06, 2010 6:25 PM**To:** Lon Mathias**Subject:** permission to print picture

I am writing my dissertation at MTSU.

The introduction discusses polymers.

May I use three pictures from pslc.ws?

Debby

From: R.Tasker@uws.edu.au

Subject: RE: Use of Animation Still in Book Chapter

Date: August 24, 2005 9:23:34 PM CDT

To: mjsanger@mtsu.edu

Cc: tgreenbo@iastate.edu, R.Dalton@uws.edu.au

G'Day Michael (and Tom),

Thanks for sending this passage from your chapter. Of course, you certainly have my permission to use the frame grab from the VisChem animation depicting AgCl precipitation. I also took the opportunity in the attached version to give you some

constructive feedback (which of course you are free to ignore completely!) on what you wrote, or intend to write. In short, I believe there are fundamental mistakes in the way educators are using animations. We developed the VisChem Learning Design, on the basis of our research with students, to describe what we regard as 'best practice' in using molecular-level animations. I described these thoughts in my chapter in the first volume of "The Chemist's Guide to Effective Teaching", and if you do not have that, please have a look at -

<http://www.learningdesigns.uow.edu.au/exemplars/info/LD9/index.html>

I believe it is essential that:

- 1 Using the recommended constructivist approach, students should communicate their mental models of the molecular world to explain macroscopic observations, BEFORE ever seeing ours! Then they should be encouraged to amend their version in the light of any new insight.
- 2 It is ESSENTIAL that students are familiar with the visual symbols used in an animation before they see the animation. Otherwise, as you correctly point out, the cognitive load can be overwhelming.
- 3 Cognitive load can be ameliorated by prior exposure to analogous animations and their symbolism, simultaneous narration, pausing the animation regularly to point out key features, and motivating students to look for key features based on their own models.

Anyway, best wishes for your writing, and I will look forward to reading your contribution.

Cheers

Roy

.....

Assoc Prof Roy Tasker MRACI

One of my latest projects is described on Web Page:

<http://www.learningdesigns.uow.edu.au/exemplars/info/LD9/index.html>

School of Science, Food & Horticulture

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Ph: +61 2 4570 1437

Fax: +61 2 4570 1621

Have a look at our web site for the VisChem Project:

Vischem.cadre.com.au

And for CADRE design, the interactive multimedia company I work with -

www.cadre.com.au

.....

"Van Reenen, Albert, Prof <ajvr@sun.ac.za>" <AJVR@sun.ac.za>

Add sender to Contacts

To:

"Debby" <deborahreneerosenthal@yahoo.com>

Go right ahead!

Prof AJ van Reenen
 Department of Chemistry and Polymer Science
 University of Stellenbosch
 Private Bag X1
 Matieland 7602
 South Africa
 Tel +27-21-8083168
 Fax +27-21-8084967
 E-Mail: ajvr@sun.ac.za

From: Debby [mailto:deborahreneerosenthal@yahoo.com]

Sent: 07 June 2010 00:43

To: Van Reenen, Albert, Prof <ajvr@sun.ac.za>

Cc: Debby

Subject: permission to use picture requested.

Dr. Reenen,

I am writing a dissertation at Middle Tennessee State University.

My introduction discusses polymer catalysts.

May I have permission to use your diagram in my introduction?

I found the diagram at:

[academic.sun.ac.za/UNESCO/conference1999/Lectures1999/VanReene99/VAN%20REENE
N.html](http://academic.sun.ac.za/UNESCO/conference1999/Lectures1999/VanReene99/VAN%20REENE%20N.html)

Debby

RE: permission requested

Monday, June 28, 2010 12:11 AM

"Kumar Vanka" <k.vanka@ncl.res.in>

[Add sender to Contacts](#)**From:**

"Debby" <deborahreneerosenthal@yahoo.com>, "Sourav Pal" <s.pal@ncl.res.in>

To:

Dear Ms. Rosenthal,

Please feel free to duplicate the structure.

-Regards,

Kumar

From: Debby [deborahreneerosenthal@yahoo.com]

Sent: Monday, June 28, 2010 2:57 AM

To: Kumar Vanka

Subject: permission requested

Dr. Vanka,

I am writing my dissertation for a Doctor of Arts in chemistry at Middle Tennessee State University. I would like permission to duplicate a structure in your paper (Organometallics 2000, 19, 1841-1849) for the purpose of explaining polymer synthesis in my introduction.

Sincerely,

D.R. Rosenthal

Middle Tennessee State University

Office of Compliance

Completion Certificate

This is to certify that Deborah Rosenthal has completed the **Why, What, and Who of Human Participants Protection Education** presentation and passed by 92.5% on the test following the presentation.

This course included the following:

- Key historical events and current issues that impact guidelines and legislation on human participant protection in research.
 - Ethical principles and guidelines that should assist in resolving the ethical issues inherent in the conduct of research with human participants.
 - The use of key ethical principles and federal regulations to protect human participants at various stages in the research process.
 - A description of guidelines for the protection of special populations in research.
 - A definition of informed consent and components necessary for a valid consent.
 - A description of the role of the IRB in the research process.
 - The roles, responsibilities, and interactions of federal agencies, institutions, and researchers in conducting research with human participants.
-

Tara M. Prairie
Compliance Officer
October 11, 2007

December 4, 2007

Deborah Rosenthal & Dr. Michael Sanger
Department of Chemistry
drc2e@mtsu.edu, mjsanger@mtsu.edu

Subject: "Minimizing Student's Chemistry Misconceptions Through Improved Use of..."
IRB # 08-138, **Expedited Research**

Dear Investigator(s):

I have reviewed the research proposal identified above and determined that the study poses minimal risk to participants and qualifies for an expedited review under 45 CFR 46.110 Category 7.

Approval is for one (1) year from the date of this letter for **100** participants. Your expiration date is **December 4, 2008**.

According to MTSU Policy, a researcher is defined as anyone who works with data or has contact with participants. Anyone meeting this definition needs to be listed on the protocol and needs to provide a certificate of training to the Office of Compliance. **If you add researchers to an approved project, please forward an updated list of researchers and their certificates of training to the Office of Compliance before they begin to work on the project. Any changes to the protocol must be submitted to the IRB before implementing this change.**

Any unanticipated harms to participants or adverse events must be reported to the Office of Compliance at (615) 494-8918 as soon as possible.

You will need to submit an end-of-project report to the Office of Compliance upon completion of your research. Complete research means that you have finished collecting and analyzing data. **Should you not finish your research within the one (1) year period, you must submit a Progress Report and request a continuation prior to the expiration date.** Please allow time for review and requested revisions.

Please note, **all research materials must be retained** by the PI or **faculty advisor (if the PI is a student)** for at least **three (3) years after study completion**. Should you have any questions or need additional information, please do not hesitate to contact me.

Sincerely,

Tara M. Prairie
Compliance Officer

PLEASE TYPE

PROTOCOL NUMBER:

SUBMISSION DATE:

162

**MIDDLE TENNESSEE STATE UNIVERSITY
INSTITUTIONAL REVIEW BOARD
HUMAN PARTICIPANTS RESEARCH REVIEW FORM**

Expedited Review Request

RESEARCHER INFORMATION

Attach documentation of IRB training for ALL Investigators and ALL Faculty Supervisors:

☐ Internet Training Certificate

Project Title: Minimizing student's chemistry misconceptions through improved use of electrochemical animations

Principle Investigator: Deborah Rosenthal

Principle Investigator e-mail: drc2e@mtsu.edu

Principal Investigator Address: 5415 Stanford Drive, Nashville TN, 37215

Principal Investigator Telephone: 615-665-1895

Co-Investigator(s): Michael J. Sanger

Faculty Advisor Name: Michael J. Sanger

Faculty Advisor e-mail: mjsanger@mtsu.edu

Faculty Advisor Address & Telephone: 615-904-8558
Chemistry Department
POB#68
MTSU
Murfreesboro, TN 37132

Department or University Unit: Chemistry

Investigator Status (For Each Investigator):

☐ Graduate

If the principal investigator is a student, complete the information for the faculty supervisor.
Please note that **THE FACULTY ADVISOR MUST INDICATE KNOWLEDGE AND APPROVAL OF THIS PROPOSAL BY SIGNING THIS FORM.**

PROJECT DESCRIPTION

Source of funding for project: none

Is this project expected to continue for more than one year?

☐ No

Anticipated completion date? December, 2008

Approval for project is valid for one year only. Investigators must request a continuation of the approval yearly if the activity lasts more than one year. Progress reports must be filed annually. Only two continuations will be granted for a given project. After three years, the project must be resubmitted.

The IRB committee is charged with assessing the scientific merit of research presented for review. It is incumbent upon applicants to provide sufficient information to the committee to assist in making this determination. Remember that the committee members may not be familiar with your research area. When completing the boxes below you should describe the research project and make the case that the proposed research has scientific merit.

In addition to answering the questions below, you should include a copy of all documents that will be presented to participants (including questionnaires, testing instruments, interview protocols, instructions, and cover letters). Anything included should be in the final form that will be presented to participants. Any documents provided to participants must be free of grammatical and spelling errors.

What is the research question being addressed in the study? Does the complexity of chemical animations affect student understanding of electrochemistry? Does changing the presentation order of two different animations change their effect on student understanding of electrochemistry? What are common student misconceptions in electrochemistry?

Describe relevant research that has been done previously (include citations; you may limit this section to a sample of the most relevant research).

Dr. Sanger has published numerous articles on student misconceptions in chemistry and the use of animations in chemistry. A quote from The Chemical Educator (2004, 9, 184-189) is "... computer animations that display chemical processes at the microscopic level can be effective instructional tools to improve students' conceptual understanding of chemical concepts." This research supports the idea that animations help students understand chemistry. We would like to extend this further and see if the complexity/simplicity of the animations makes a difference in students' conceptual understanding and also if the order a simple and a more complex animation are shown to the student will make a difference. We will also investigate the particular misconceptions that commonly arise in electrochemistry.

Describe the design of the study (e.g., qualitative, correlation, factorial, etc.).

This is qualitative research. Students will be shown a demonstration and asked questions orally. The students will then be shown an animation and asked similar questions (orally). A second animation will be shown and more questions asked orally.

What is your plan for analyzing the data?

Student answers will be analyzed for misconceptions that occur. We will determine if changes occur in student understanding as the animations are shown. Students' perception of animation

usefulness and order preference will be determined. We will be looking for repetition of misconceptions, animation usefulness, and effects of the order the animations are shown.

How will this design allow you to address the research question?

The question topics are misconceptions, animation complexity, and animation order. We will be asking students to explain concepts. If they are not correct we will know where the students' misconceptions. As the animations are shown we will ask many of the same questions to see if their answers change. If incorrect answers change to correct answers, we will know the animations helped student understanding. The order of the animations will be reversed on every other interview. This will help us determine if the order of the animations makes a difference.

If there are special qualifications required to conduct research in this area, how will the researcher(s) meet these qualifications?

Students must be in chemistry II (CHEM 1120) at the end of the semester because that is when electrochemistry is taught. Participants are volunteers. There are no other qualifications.

How will participants be debriefed (in addition to describing the debriefing procedure, attach a copy of all debriefing information)?

Students will be told that the purpose of the interviews is to have a better understanding of how to present material in chemistry courses, particularly in electrochemistry, to improve student learning. They will be told that their name will not be used in any manner, they are welcome to leave at any time, and they may request the data from their interview is not used in the research.

List the potential risks to participants. List the potential benefits to participants. List the potential benefits to science and society if the research is conducted. Evaluate the level of risk relative to the potential benefits.

There are not potential risks to the students.

The benefits to society are to have a better understanding of student misconceptions in electrochemistry so teachers/instructors can focus on those areas to avoid misconceptions. The research will also help understand what level of complexity of animations are the best to use during instruction and if the order material is presented affects students' conceptual understanding.

Note: If your study involves risk (including sensitive information), minors as participants, psychological intervention, deception, physiological intervention, or biomedical procedures, you should also complete the appropriate section at the end of the form.

Number of Participants: 80+

Participant population (check all that will be specifically targeted to participate in the research):

ADULT:

☐ Yes

MINOR:

☐ No

PRISONER:

☐ No

MENTALLY HANDICAPPED:

☐ No

MENTALLY DISABLED:

☐ No

PHYSICALLY ILL:

☐ No

DISABLED:

☐ No

OTHER:

☐ No

IF YES, PLEASE SPECIFY:

N/A

Participant selection:

Are participants to be drawn from the Psychology Research Pool?

☐ No

- If yes, include the title, a brief abstract, and detailed description below.
- If no, describe how participants will be selected for participation in this project.
- In all cases, describe any payment to be received by the participant.

NOTE: If the participants are to be drawn from an institution or organization (e.g., hospital, social service agency, prison, school, etc.) which has the responsibility for the participants, then documentation of permission from that institution must be submitted to the Board before final approval can be given.

Participant Inclusion/Exclusion Criteria:

Provide a list of inclusion/exclusion criteria for the proposed research and justify any demographics (e.g. sex, race, economic status, sexual orientation) that have been excluded. Students must be in chemistry II (CHEM 1120) at the end of the semester because that is when electrochemistry is taught. There are no other qualifications.

There are no demographic criteria.

CONFIDENTIALITY

Specify steps to be taken to guard the anonymity of participants and/or the confidentiality of their responses. Indicate what personal identifying indicators will be kept on participants. Specify procedures for storage and ultimate disposal of personal information. Federal guidelines require all study related documents (documentation of informed consent, surveys, study notes, data analysis, and all study-related correspondence) be kept for at least 3 years. For student research, all study related documents must be stored in the faculty supervisor's office when the research is completed.

Students will not be writing or stating their names for the research.

Students will be interviewed orally and the interviews will be taped. The tapes will not identify the students except by the sound of their voices. Tapes will not be available to anyone but the researchers.

CONSENT

Specify how participants will provide consent. Researchers should always collect written consent except:

- When the main risk to participants is identification and documented consent could expose them to risk of identification.
- When the research presents minimal risk to participants and the information on the consent form is included at the beginning of the test instrument.
- When the research is being conducted online.

Researchers should use the approved informed consent template. The template may be modified to remove information that is not relevant to the study. If a consent form is being used, attach a copy. If presented orally, a copy of the presentation must be submitted.

There is no risk to the participants so written consent will not be collected.

Oral consent will be audio taped.

ADDITIONAL PROCEDURAL INFORMATION

INDICATE BELOW WHETHER YOUR PROJECT INVOLVES ANY OF THE FOLLOWING. FOR EACH ITEM CHECKED, PROVIDE THE REQUESTED INFORMATION IN THE ADDITIONAL PROCEDURAL INFORMATION SECTION BEGINNING AFTER THE SIGNATURE SECTION OF THIS FORM.

☐ Risk (pg. 1)

☐ Minors as Participants (pg. 1)

**SEE THE PAGE
INDICATED FOR A MORE
DETAILED DESCRIPTION
OF THESE CATEGORIES**

- ☐ Psychological Intervention (pg. 2)
- ☐ Deception (pg. 3)
- ☐ Physiological Intervention (pg. 3)
- ☐ Biomedical Procedures (pg. 4)

APPLICATION CHECKLIST

Investigator(s): Please read and initial each item.

Checklist item	Initial
Is all information typed?	
Is documentation of IRB training attached for each investigator and for the faculty supervisor?	
Is the investigator email address and other contact information included?	
If student research, is the faculty supervisor email and other contact information included?	
Are surveys, questionnaires, tests, interview forms / scripts attached?	
Is the number of participants indicated?	
Is the method of participant selection indicated?	
If using the Psychology Department research pool, is signup information included?	NA
If a consent form is being used, is a copy of the consent form attached?	NA
For research involving minors, is an assent form attached?	NA
For research at outside institutions (e.g., schools), are permission letters on official letterhead attached?	NA

Incomplete applications will result in delay of research approval.

SIGNATURES

The **Principal Investigator** must sign this form.

I certify that 1) the information provided for this project is accurate, b) no other procedures will be used in this project, and c) any modifications in this project will be submitted for approval prior to use.

Signature of Investigator

Date

If the P.I. is a student, his/her **Faculty Advisor must also sign this form.**

I certify that this project is under my direct supervision and that I am responsible for insuring that all provisions of approval are complied with by the investigator.

Signature of Faculty Advisor

Date

Committee Use Only

NOTE: APPROVAL OF THIS PROJECT BY THE IRB ONLY SIGNIFIES THAT THE PROCEDURES ADEQUATELY PROTECT THE RIGHTS AND WELFARE OF THE PARTICIPANTS AND SHOULD NOT BE TAKEN TO INDICATE UNIVERSITY APPROVAL TO CONDUCT THE RESEARCH.

Expedited Review

Approved: _____
Committee Member

Date _____

Committee Review

Approved: _____
Committee Chair

Date _____