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WEAKLY-COORDINATING HALOGENATED LIGANDS

By Katherine Duncan Parks

A dissertation presented to the
Graduate Faculty of Middle Tennessee State University
in partial fulfillment of the requirements
for the degree, Doctor of Arts
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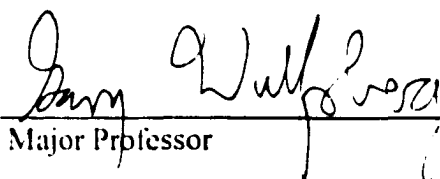
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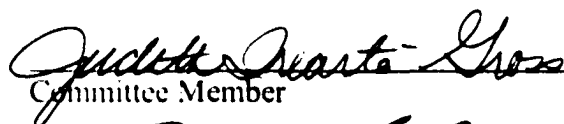
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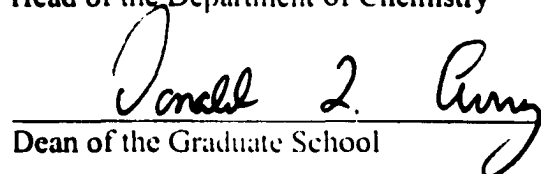
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WEAKLY-COORDINATING HALOGENATED LIGANDS

Potassium, sodium, silver, and thallium(I) halomethanesulfonates and crown adducts of the type MXCH_2SO_3 and $\text{M}(18\text{-crown-}6)\text{XCH}_2\text{SO}_3$ ($\text{M} = \text{K}, \text{Na}, \text{Ag}, \text{Tl}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) were synthesized. Halomethanesulfonates, postulated to be useful as weakly coordinating anions for homogeneous zirconocene catalysts, are commonly produced from dihalomethanes by nucleophilic substitution reactions, but the reaction is slow and often requires vigorous conditions. The use of the soft metal ions Ag^+ and Tl^+ was found to facilitate the syntheses. Although the addition of a crown transfer catalyst was also found to decrease the reaction time, the catalyst proved difficult to remove from the final product. In the absence of crown ether, the reactions gave a better yield of products of higher purity. A procedure was found for recycling waste thallium halides into more useable soluble salts, Tl_2SO_4 and Tl_2SO_3 , which were used in the synthesis of thallium halomethanesulfonates. We were able to prepare crowned cation halomethanesulfonates, $[\text{K}(18\text{-crown-}6)]^+(\text{ICH}_2\text{SO}_3)^-$, $[\text{Tl}(18\text{-crown-}6)]^+(\text{BrCH}_2\text{SO}_3)^-$, and $[\text{Tl}(18\text{-crown-}6)]^+(\text{ClCH}_2\text{SO}_3)^-$, as models for the zirconocene complex, $[(\text{C}_5\text{H}_5)_2(\text{CH}_3)\text{Zr}][\text{XCH}_2\text{SO}_3]$. The attempted synthesis of an Ag^+ analogue resulted in the production of a suspected triple-crown complex, which probably would not be a good model for the zirconocene. The synthesis of $\text{NaICH}_2\text{SO}_3$ was improved. Proton NMR, IR, TGA, and elemental analyses were used to characterize the products. Nuclear quadrupole resonance (NQR) spectra were used to show the presence of coordination between the metal and halogen atom of the halomethanesulfonates of Ag^+ , and its absence in those of Tl^+ .

ACKNOWLEDGEMENTS

Frankly, none of this research would have been possible without the assistance, patience, and continuous support of my advisor, Dr. Gary Wulfsberg. What an inspiration he has been to me throughout this research and professional transition in my career! Via his careful instruction and watchful eye, the depth of my knowledge of chemistry has increased exponentially. I must also thank Dr. James Hutchison and Dr. Ed Woods (both now retired), who not only encouraged me to pursue this degree, but also made the educational endeavor financially obtainable. Due to the receipt of the MTSU Chemistry Fellowship and other support provided by the department, a leave of absence from my teaching job became possible so that I could pursue this degree unhindered. Other members of the Chemistry department who should be acknowledged for their invaluable support during this research are Dr. Gayle Clark and Dr. James Howard. These gentlemen provided much assistance in the use of sophisticated instrumentation to which I had not previously been exposed. A special thank you goes to Dr. Judith-Iriarte Gross, Dr. William Hsley, Dr. Bob Womack, Dr. John Divincenzo, Dr. N.S. Chong, Mr. Lewis Tigg, and Graduate Dean Dr. Donald Curry, whose extraordinarily supportive comments, kindness, and guidance helped make this goal, once envisioned only in my dreams, a reality. Last, but not least, a heart-felt thank you goes to the new Chemistry Chairman Dr. Earl Pearson, D.A. Coordinator Dr. Paul Kline, and Secretaries Mrs. Ann Smith, Mrs. Ann Nored, and Mrs. Clara Todd for lending an ear when the itinerary seemed unfeasible! Each one mentioned here will be affectionately remembered as I make my way down a road that is new to me, but has become so familiar to you.

DEDICATION

This manuscript is dedicated to my loving parents, Mr. Cecil Moore Duncan & Mrs. Sara Collins Rieves Duncan, whose true wisdom extends far past the pages of any textbook, and to my amazing daughter, Ms. Angie Parks, all who endured many hours of my *divided* attention, in order that I could successfully complete this degree. Knowing that I cannot make up the time lost, I can only tell the three of you how very much I appreciate your never-ending understanding, compassion, and confidence in me, and say "thank you" for allowing me this opportunity to grow.

The Road to the Future

This sojourn sends me, now, a different way.
Thus far, I've seen something new each day!
No doubt, I chose a road 'less traveled by'
And, albeit at times have met danger,
I continue on, not knowing what will come to be
Nor, where this road will lead me;
But, for the taking I can truly say
That, hitherto, along the way
Both challenges and rewards have been high,
And disappointment has been a stranger!

Katherine Duncan Parks (6/2K)

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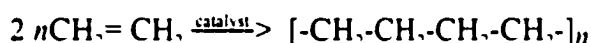
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CHAPTER I

INTRODUCTION

A rapidly evolving field of industrial significance is single-site or metallocene catalysis of the polymerization of alkenes to give polymers such as polyethylene, polypropylene, and styrene:



This polymerization once required the use of heterogeneous Ziegler-Natta catalysts, which produced polymers with relatively poor physical properties. More versatile homogeneous metallocene catalysts had their debut in the 1980's. Since their introduction, chemists have worked to develop unique metallocene cations equipped with a well-defined coordination environment that can be used to control stereoregularity in olefin polymerization processes (Brintzinger et al., 1995; Deutsch, 1997; Dagani, 1998). These single-site catalysts are impressive because they give producers the power to design precision polymers with improved physical and chemical characteristics. Materials produced from these catalysts have enhanced performance properties, which include augmented toughness, strength, clarity, gloss, and ease of handling. The phrase single-site catalysis is derived from the fact that polymerization occurs at a single location on a metallocene moiety (Morse, 1998).

Single-site catalysts differ from conventional polyolefin catalysts in that the metal atom is usually in a constrained environment. The limiting environment allows single access by monomers to the catalytically active site. The resulting polymers grow by a single mechanism, in contrast to the multiple routes that occur in traditional Ziegler-Natta

systems. Heterogeneous Ziegler-Natta catalysts contain highly active metal centers (titanium, chromium), or low activity vanadium centers, and generally produce polymers having a broad range of molecular weights. The materials produced from the new single-site catalysts (having high to medium activity) boast more uniform and reproducible polymeric structures than materials produced using Ziegler-Natta systems (Morse, 1998).

With several production units in operation today, the products of single-site catalysts are quickly becoming commercial realities. Elastomers made by Dow Chemical's Insite Group have been used to make shoe soles and some specialized tubing products. Univation Technologies recently celebrated its third anniversary as a joint venture between polyolefin producers, Exxon Chemical and Union Carbide. Others who have researched the development of these new catalysts are Phillips, Mobile, Fina, BP Chemical, BASF/Elenac, Borealis, Tagor, Mitsui Chemicals, Japan Polyolefin, Sumitomo, Ube, Asahi, Hoechst, and Du Pont. Exxon and Dow Chemical Divisions have been the most successful designers of metallocene single-site catalysts, but both continue to actively form alliances with other companies for the benefit of all involved in the production of polyethylene and polypropylene. Primarily due to a metallocene patent stranglehold held by Exxon and Dow, there is more innovative research being done toward the development of *non*metallocene catalysts, not only for expanding the versatility of current polyolefins, but also for the development of new, performance-oriented materials (Morse, 1998). In the past, metallocenes have been employed as UV absorbers, reducing agents, free radical scavengers, anti-knock agents (Lewis, 1993), and fire retardants (Long, 1998a).

The general formula of metallocenes or dicyclopentadienyl-metal compounds is $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}$, while that of the halides is $(\eta^5\text{-C}_5\text{H}_5)_2\text{MX}_{1-3}$. Today, these compounds are often referred to as 'sandwich molecules', due to the location of the two cyclopentadienyl (Cp) rings in planes above and below the metal atom. Historically, the term metallocene was exclusively associated with the *pi*-bound cyclopentadienyl ring structures discovered in the early 1950's, such as ferrocene (Cp_2Fe), nickelocene (Cp_2Ni), and the 'bent-sandwich' molecule, zirconocene dichloride (Cp_2ZrCl_2), properly known as dichlorobis-(cyclopentadienyl)zirconium [Figure 1]. The most active of the new single-site catalysts used today are derivatives of zirconocene dichloride. The most important industrial method of production of metallocenes is the reaction of sodium cyclopentadienide with a transition metal-halide in an aprotic organic solvent (Long, 1998b).

The explanation of the bonding scheme of the first metallocene, ferrocene, is credited both to England's Geoffrey Wilkinson (who characterized it using chemical, physical, and spectroscopic methods while at Harvard) and Germany's Ernst Fischer (who used X-ray crystallography). Both agreed that the metal cation was bonded to the Cp ring by π -electrons moving in *p* orbitals (extending above and below the plane of the ring) that overlapped with the *d* orbitals of the metal. They attributed the compound's extraordinary stability to the π bonding. Additionally, Gouy magnetic susceptibility measurements, made by Harvard's R.B. Woodward and co-workers, showed that ferrocene had no unpaired electrons, giving the structure an effectively zero dipole moment (Long, 1998c).

Many physical and chemical properties of metallocene complexes are similar.

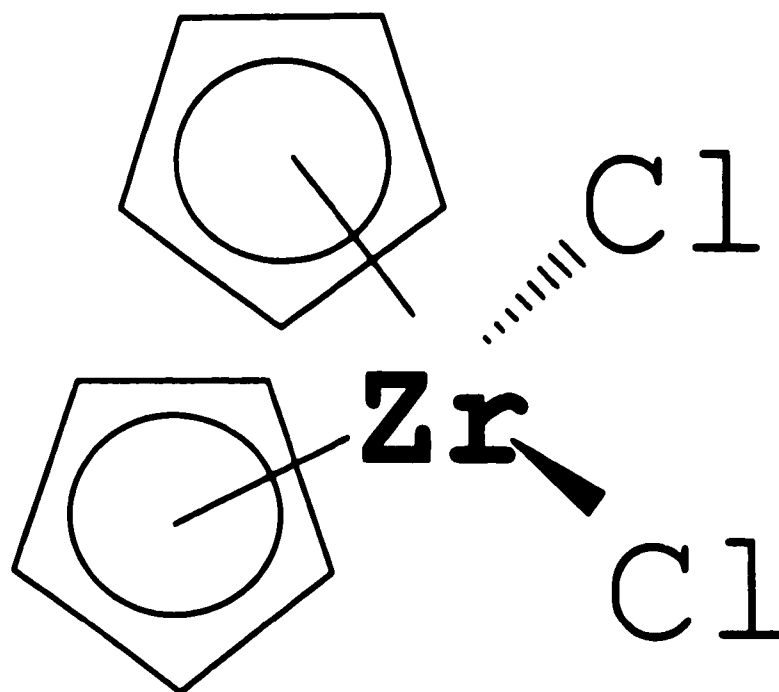


Figure 1. Zirconocene dichloride, Cp_2ZrCl_2 .

Most are crystalline in nature. Those that incorporate an element from the first transition series of the periodic table (vanadium to nickel) all melt at 173 °C. These catalysts are soluble in many organic solvents. However, those that also contain halides are primarily soluble in polar solvents. When the metal center is in a stable oxidation state, a metallocene exhibits extraordinary stability. Decomposition of the complex is negligible at high temperatures, in water or air, and/or when in contact with strong acids or bases. Ferrocene, and several other metallocenes, can undergo a variety of aromatic ring substitution reactions (Friedel-Craft, acylation, arylation, and sulfonation), but a few others (e.g., nickelocene and cobaltocene) are too unstable to be directly substituted (Lewis, 1993).

One of the latest commercial single-site catalysts is a 'half-sandwich' monocyclopentadienyl metal compound containing only a single Cp ring, but the ring includes a bridging heteroatom moiety that is also bonded to the metal. The catalyst has the general formula, $C_5H_5ML_{1,3}$, where L = CO, NO, a variable number of halide or alkyl groups, or even heteropolyatomics (Long, 1998d). This species, often referred to as a 2-, 3-, or 4-legged 'piano stool' (Long, 1998e), is sometimes called a *non*metallocene. One such catalyst was used to produce the novel elastomers, having improved light and solvent resistance, made by Dow's Insite Catalyst Group (Morse, 1998; Möhring et al., 1994).

The functional nature of all types of single-site catalysts is similar. The active forms are cations. In order for the most active metallocene cations (i.e., zirconocene cation, Cp_2ZrR^+ [Figure 2], and other derivatives of zirconocene dichloride)

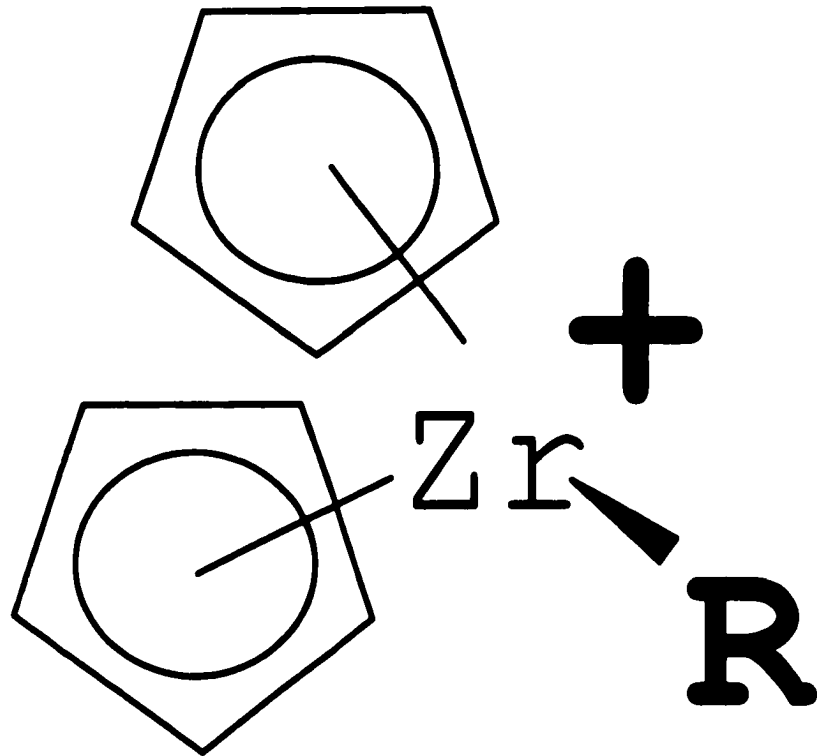


Figure 2. Typical Activated Zirconocene, Cp_2ZrR^+

to be effective, it is necessary that the anion be as weakly coordinating to the zirconium atom as possible. Weak coordination is characterized by bond distances less than the sum of the van der Waals radii for unbonded atoms, but greater than the sum of the covalent radii for single-bonded atoms (Strauss, 1993). A poorly coordinating anion is necessary for pairing with a cationic metallocene moiety so that the more reactive olefin can easily replace the temporary, place-holding anion. Other uses for these "superweak" anions (Lupinetti et al., 1998) include catalytic formation of C-C bonds and/or the activation of C-H bonds during various chemical syntheses, and the manufacture of high-current density lithium batteries. The search for 'superacids' has been associated with the discovery of these anions, as has the synthesis of a strongly oxidizing fullerene cation in a salt with a 'superweak' anion (Reed, 1998). In recent years, much research has revolved around the search for suitable bulky, nonbasic halogenated anions that can be weakly coordinated to the new single-site catalysts (Wulfsberg et al., manuscript in preparation).

Some desirable properties for a weakly coordinating anion are (a) low charge, preferably -1 or -2 ; (b) delocalization of charge, such that the charge is evenly distributed across the anion's surface; (c) the presence of only weakly basic sites on the periphery; and (d) kinetic stability, with respect to oxidation and the ability to evade chemical dissociation (Strauss, 1993). Since metal cations such as the zirconocene moiety are rather strong Lewis acids, for the anion to be weakly coordinating it must also be a weak nucleophile and a weak base. Two major factors that make an anion a weak base are large size and low overall charge (Strauss, 1993; Wulfsberg, 2000a). Several representative bulky (-1) -charged Lewis bases, like methanesulfonate (CH_3SO_3^-),

tetraphenylborate [$B(C_6H_5)_4$], and 1-carba-*closo*-dodecaborate ions ($CB_{11}H_{12}$) are very weakly basic. These anions have been considered for use as weakly coordinating ligands with the new single-site catalysts (Reed, 1998).

Further reduction of coordinating capability can be rendered by the substitution of halogen atoms onto the bulky surface of these counteranions (Lawrance, 1986; Van Seggen et al., 1992; Lambert et al., 1993; Xie et al., 1994a, 1994b), since increasing electron-withdrawing power (nucleophilicity) of substituents also decreases the basicity of anions (for example, trifluoroacetate is a much weaker nucleophile and less basic anion than acetate). It was thought that a halomethanesulfonate ligand would be good candidate for use as the weakly coordinating anion of a metallocene single-site catalyst due to its large size and low overall charge that can be dispersed over the bulk of the counterion. ($XCH_2SO_3^-$ X = Cl, Br, or I (Wulfsberg et al., manuscript in preparation). Halogenated ligands such as these have been recognized as good "non-coordinating" anions (Notice to Authors, 2000). Zirconocene precursors containing perfluorinated sulfonate anions, $(C_5H_5)_2Zr(CF_3SO_3)_2$, are available from Aldrich but are extremely expensive (\$48 per g).

The use of highly fluorinated anions such as $CF_3SO_3^-$ or $B(C_6F_5)_4^-$ have, in fact, not resulted in the most active zirconocene catalysts (Strauss, 1993; Seppelt, 1993). The most active catalysts known today incorporate the chlorinated, brominated, or iodinated anions ($CB_{11}H_6X_6^-$) [X=Cl, Br, I] and were developed by Christopher Reed and co-workers (Xie et al., 1994a, 1994b; 1996; 1997; Reed, 1998). This seems paradoxical, because these less-electronegative halogen atoms are less electron withdrawing than fluorine.

To understand this apparent paradox we may apply the theory of hard and soft acids and bases (HSAB principle) (Wulfsberg, 2000b), which states that hard Lewis bases (those containing fluorine and oxygen donor atoms) prefer to bond to hard Lewis acids (those metal ions with electronegativity 1.16 or below, including Zr), while soft Lewis bases (for example, those containing chlorine, bromine, and iodine atoms) do not prefer to bond to the hard Lewis acids but instead prefer to bond to soft Lewis acids [those metal ions of high electronegativity near that of gold (Pauling electronegativity= 2.54), such as Ag^+ (Pauling electronegativity=1.93) and Tl^+ (Pauling electronegativity = 1.60)].

A bulky base, made softer by the substitution of chlorine onto its surface, would be most likely to coordinate weakly to a softly acidic cation, such as Ag^+ (Wulfsberg, 2000c). Although stronger Ag^+ coordination would be expected to an iodine atom when substituted on a bulky base (e.g., iodomethanesulfonate, $\text{ICH}_2\text{SO}_3^-$), the anion should still perform satisfactorily as a weakly coordinating anion with a hard Lewis acid, such as the zirconocene cation, $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$. By the same token, we would expect the least coordination of the hard zirconocene cation to an iodine atom in an anion such as iodomethanesulfonate.

The detection of coordination of fluorinated weak anions is feasible using ^{19}F NMR (nuclear magnetic resonance) spectroscopy. However, NMR is impractical for the heavier halogen atoms because their nuclear spin exceeds $\frac{1}{2}$. Some uncertainties can also be encountered during x-ray crystallographic interpretation, since values for Bondi's and Pauling's van der Waals radii of halides are known to vary as much as 0.15 Å (Strauss, 1994). Instead, ^{35}Cl , $^{79,81}\text{Br}$, and ^{127}I nuclear quadrupole resonance (NQR) spectroscopy

are more appropriate for this task, and have often been used in the past to show that the supposedly "non-coordinating" halocarbons, such as CH_2Cl_2 and CH_2I_2 , do in fact coordinate to silver ion (Newbound et al., 1989; Colman et al., 1990). The general principle employed in NQR spectroscopy is that coordinated halogen atoms have lower frequencies than otherwise identical non-coordinating halogen atoms. Since NQR frequencies are very sensitive to small changes in electron populations, differences between coordinated and non-coordinated donor atoms and the degree of M-X coordination can be shown clearly (Newbound et al., 1989; Colman et al., 1990). This measurement can make the distinction between weak secondary bonding interaction and incidental nonbonding contacts within the crystal lattice, and would be preferred for determining whether the anion was or was not coordinated to a model metallocene cation.

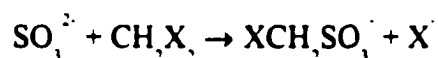
This study has not considered the properties of zirconocene halomethane-sulfonates, since (a) zirconocene itself is quite expensive, and (b) its cation is very likely to react with the moisture of the air. Instead, we began with this study with the less reactive, less expensive hard-acid metal ion, K^+ , and the soft acid metal ions, Ag^+ and Tl^+ .

One potential problem with metal ions such as K^+ , Tl^+ , and Ag^+ is that they are far from being single-site. In fact, they have multiple coordination sites which could easily coordinate all of the donor atoms of a halogenated weakly-coordinating anion, making it impossible to see the contrast of the NQR frequencies of coordinated and non-coordinated halogen atoms. This study also began the investigation of the possibility that single-site zirconocene cations could perhaps be modeled reasonably well by the less reactive, more readily available double-site complexes of metal ions, such as K^+ , Ag^+ , and

Tl⁺ with the “crown ether” ligand (CH₂CH₂O)₆, commonly known as 18-crown-6 [Figure 3].

Crown ethers tend to form stable complexes with alkali metal ions that have a size that matches their internal cavity size, but have been found to bind less strongly to transition metal ions. The general principle behind this electrostatic relationship is that the ring of crown ether serves to provide a replacement for the solvent shell that would otherwise surround the free metal atom (Lindoy, 1989). An attempt was made to synthesize crown adducts of K⁺, Ag⁺, and Tl⁺ in this research. These, and other adducts containing cations of similarly charge and size, should make reasonable models for a zirconocenium cation. They would have a restricted number of ‘virtual’ coordination sites, so that the cation in these complexes should not coordinate all donor atoms in the weakly coordinating anion, but instead would coordinate only two. With other weakly coordinating anions having no exposed oxygen donor atoms and multiple halogen donor atoms, the situation would then require weak coordination of only some of the halogen donor atoms.

Halomethanesulfonates are generally expensive or difficult to make. Syntheses involve either using the expensive ClCH₂SO₂Cl (Senning, 1976) or long, difficult reactions between aqueous solutions of M₂SO₃ with immiscible CH₂X₂ (for X=Cl, this is done in an autoclave) via the general reaction (Smith et al., 1953):



Thus far, in applicable prior research at MTSU:

(a) D. Jones (1989) used a variety of routes to prepare the silver chloro- and

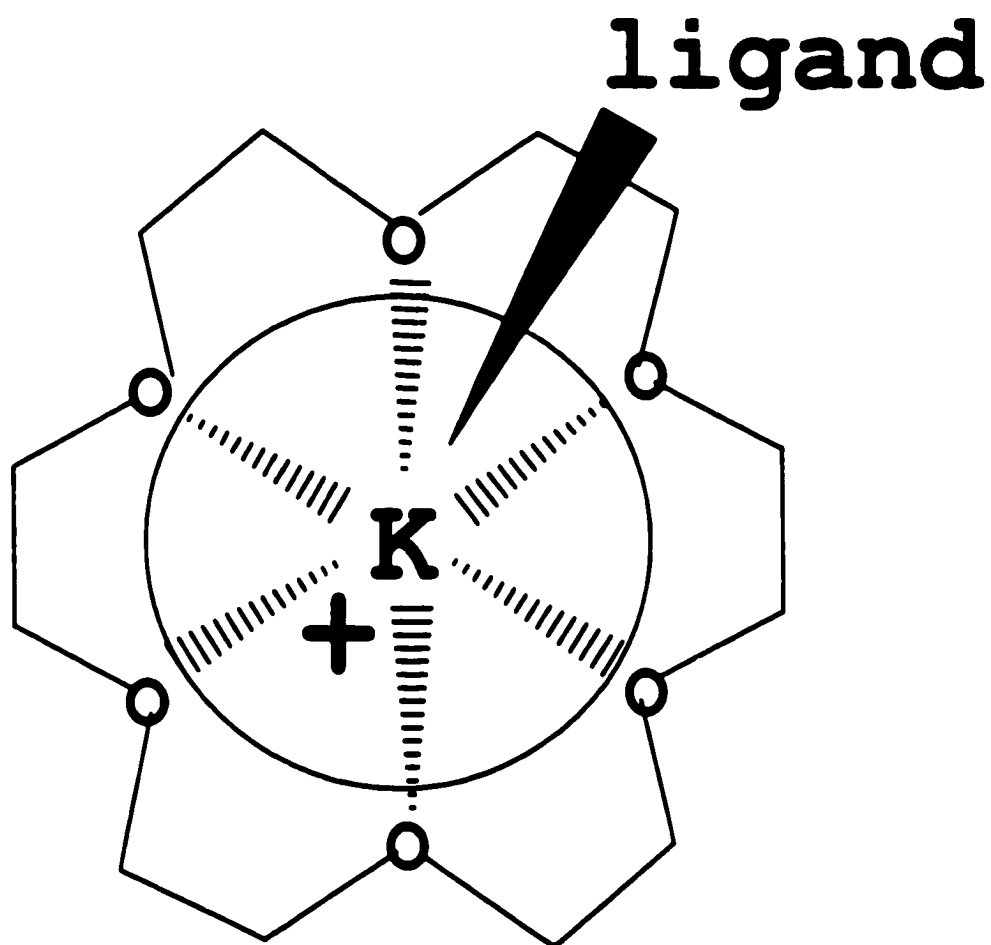


Figure 3. Structure of $[K(CH_2CH_2O)_6]^+$

bromo- organosulfonates. The results from this research suggested that coordination of silver to chlorine probably did not exist in trichloromethanesulfonates, but that there was evidence of silver coordination to bromine in the bromomethanesulfonate counterion.

(b) F. Jones (1994) predicted that the soft iodo-organosulfonate counterions would coordinate more strongly to soft acids than any other halo-organosulfonate. It was suggested that there was no coordination between the borderline acid, Tl^+ , and halomethanesulfonate ions.

(c) R. Rutherford (1996) found a double displacement reaction that gave a high yield of silver iodomethanesulfonate, and test results suggested that there was indeed coordination of silver to iodine. Steven Strauss of Colorado State University performed X-ray crystallography on silver chloromethanesulfonate and silver iodomethanesulfonate. Due to a "twinning" problem within the crystal, the structure of the latter could not be determined, but the crystal structure of the chloromethanesulfonate was determined (Wulfsberg et al., manuscript in preparation)[Figure 4]. Strauss found the structure to be extraordinarily similar to that of $Ag^+(BrCH_2SO_3)^-$ previously determined by Charbonnier et al. (1978).

In the $Ag^+(ClCH_2SO_3)^-$ lattice, each Ag atom is bonded to four oxygen atoms from the neighboring sulfonate groups, and to 2 chlorine atoms from neighboring chloromethyl groups. Interestingly, the structure shows apical (3-coordinate) Cl atoms (i.e., each Cl atom coordinated to 2 silver atoms while covalently bonded to a C atom). Dichloromethane generally coordinates to Ag^+ in bidentate fashion, but previous studies had shown that its Cl atom can bridge two Ag atoms (Colsman et al., 1990). Studies by

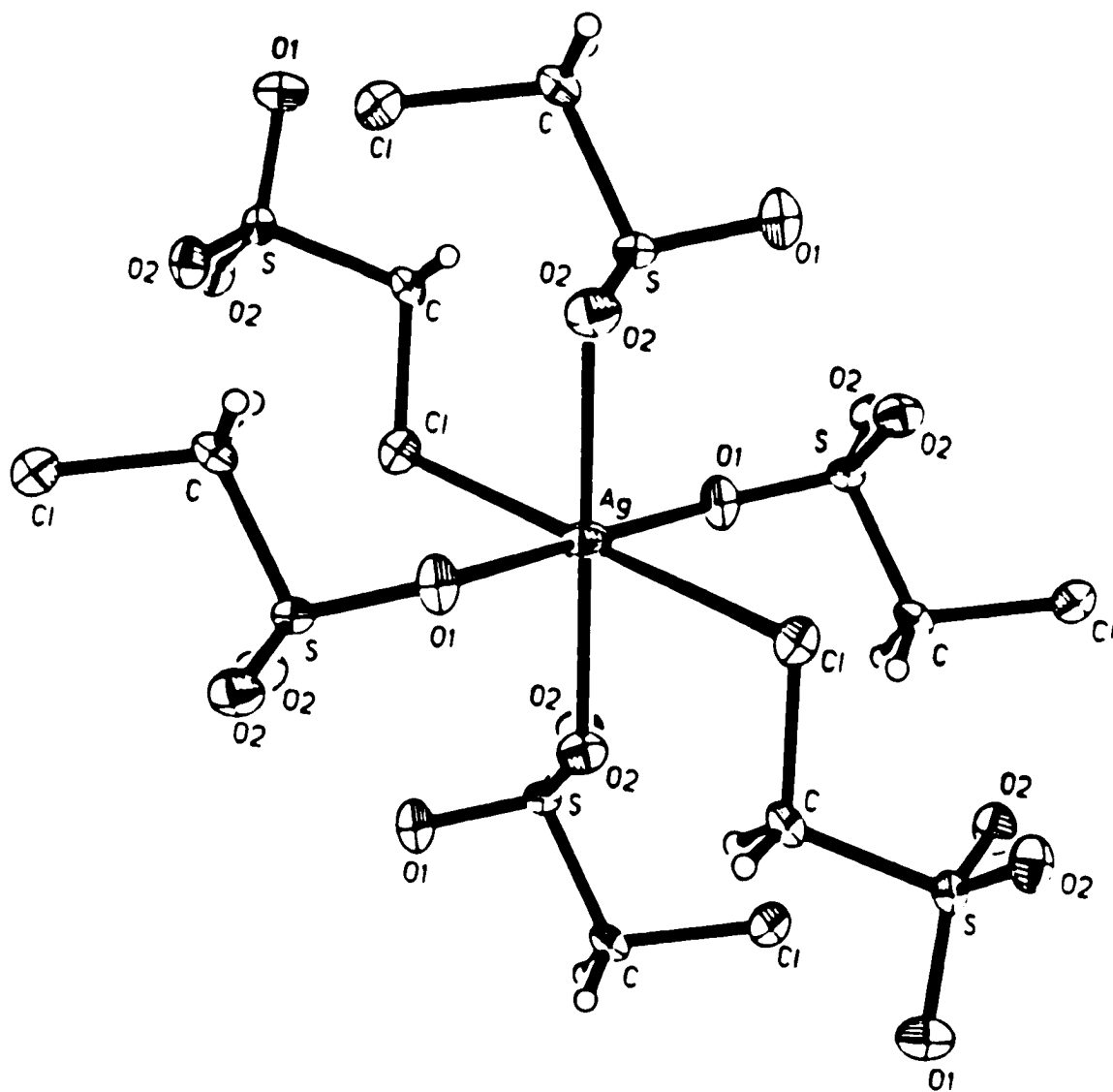
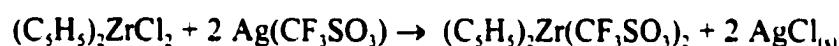


Figure 4. Crystal Structure of $\text{Ag}^+(\text{ClCH}_2\text{SO}_3^-)$

Powell and co-workers (Powell et al., 1993a, 1996b; 1997; 1998) of silver complexes of more than 50 iodocarbon ligands showed only two structures with such apical halogen atoms. Strauss has reported the only known case in which Tl^I coordinates organohalogenatoms (Hurlburt et al., 1992). A portion of this investigation addressed the question of whether Tl^I might coordinate halomethane-sulfonate ions in Tl^I (XCH₂SO₃) complexes.

Crown ethers (performing the role of phase transfer catalyst) should aid the synthesis because they should help make water-soluble sulfites, e.g., Na₂SO₃ and/or K₂SO₃, soluble in the organic phase. The thallium(I) and silver sulfites should provide superior metal cations for the proposed syntheses because they can assist the nucleophilic displacement of halide by sulfite ion, and more effectively precipitate the byproduct halides (as AgX or TlX) (Strauss, 1993). Since Tl₂SO₃ is slightly water-soluble and Ag₂SO₃ is not, the choice reaction for the synthesis of halomethanesulfonates may well involve the reflux of Tl₂SO₃ with CH₂X₂ in the presence of crown ether.

Weakly coordinating anions, such as the halogenated sulfonate ions, are usually introduced into organometallic compounds by precipitation reactions using silver salts, as the following suggests:



From a metathesis perspective, silver(I) and thallium(I) salts (of weakly coordinating anions) have been recognized as useful reagents for halide abstraction reactions resulting in the precipitation of the corresponding metal halide (Reed, 1998). In our research, the formation of the desired product was often indicated by the appearance of a precipitate of

TlCl and/or AgCl formed from the metal ion-assisted nucleophilic displacement of a single halide ion from dihalomethane, while the halomethylene fragment attaches onto the anionic moiety (sulfite in our case). However, sometimes these reactions fail when, for example, the soft acid Ag^+ coordinates to the Cl bonded to Zr rather than precipitating it (Reed, 1998). In such cases, substitution of the thallium salt may prove advantageous: Tl^+ is soft enough to precipitate Cl^- , Br^- , and I^- , but it seldom forms complexes with them.

Thallium(I) ions are known to replace potassium (K^+) ions in muscle tissue and can disrupt the action of K^+ activated enzymes, an ability contributed to the identical charges and similar sizes of these monovalent cations. Thallium(I) salts are generally water-soluble salts and resemble potassium salts (e.g., thallium forms a strongly basic hydroxide much like that of potassium). Although Tl^+ salts are somewhat less soluble than corresponding K^+ salts, the ionic radii of these two cations are very close (Tl^+ , 1.49 Å; K^+ , 1.33 Å) (Reese, 1991). If given the opportunity, Tl^+ competes with potassium ions in the body and accumulates in tissue having the highest concentrations of K^+ . As a result, Tl^+ can disrupt some cellular transport and energy production mechanisms and can block the body's ability to metabolize oxygen, features which contribute to the ion's toxicity (Farago, 1976; Reese, 1990).

Because of their noxious nature, thallium wastes are extremely expensive to properly dispose. The initial objective of this research was to attempt to convert a hazardous thallium halide laboratory waste, which also contained some organic material, into the valuable and reusable compounds, thallium(I) sulfate (Tl_2SO_4) and thallium(I) sulfite (Tl_2SO_3). Thallium salts are notoriously expensive. The current cost of Tl_2SO_4 is

about \$1 per g, which is about the same as the price as silver sulfate! Thallium(I) sulfite was needed as a starting material for some of our reactions, but is not commercially available. Since thallium halides are insoluble, they are not very practical starting materials for further reactions. By converting the laboratory waste into useful products, we can avoid both the costs of disposal and the cost of purchasing Tl_2SO_4 . It has been said that wastes are simply misplaced resources. Recycled Tl_2SO_3 obtained from the research could be used to attempt the synthesis of desired weakly coordinating counterions, such as the halomethanesulfonate ions.

A literature search revealed no information on prior recycling of thallium-containing waste. In earlier remediation efforts in the United Kingdom, attempts to immobilize unwanted thallium-containing waste were made by incorporation of the waste into cement-like sludge. The sludge was then incinerated in kilns in order to try to reduce its total mass. Environmentalists had expressed concern for a number of years before it was discovered that the plumes from the kilns contained dangerous levels of thallium. Researchers now suspect that thallium reintroduced into the environment in this manner may have been partially responsible for some illnesses developed within communities and wildlife areas located near these waste management facilities (Pearce, 1996). There was mention of the use of a new synthetic mineral immobilization technology (SMITE) for stabilization of toxic metal concentrates, including thallium chromate sludge, which involves the formation of minerals from waste without the production of a secondary waste stream. SMITE allows the resulting minerals to be stored above ground for future recycling of valuable resources (White et al., 1996).

CHAPTER II

EXPERIMENTAL

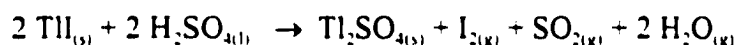
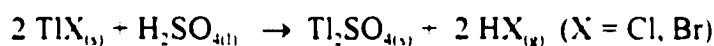
Most of the chemical reactions described were conducted in the dark or under red light and in an argon atmosphere. Schlenkware reaction vessels were used whenever necessary. All chemicals that were used in the experiments were of reagent grade quality. Reaction vessels, vacuum desiccators, and storage containers were covered with foil to help prevent decomposition of light sensitive products. Final products were generally collected using vacuum filtration, dried under house vacuum, and stored in the laboratory freezer in containers that had been wrapped in foil.

Proton nuclear magnetic resonance (^1H) data were obtained using a Bruker AC 200 MHz spectrometer equipped with a FT Aspect 3000 signal processing system. Nearly all spectra were recorded in D_2O solution. The sodium salt of 3-trimethylsilylpropionic- 2,2,3,3- d_4 acid, $(\text{CH}_3)_3\text{SiCD}_2\text{CD}_2\text{CO}_2^- \text{Na}^+$ or TMSP, was added to sample solutions whenever possible to reference zero. The ^{35}Cl NQR spectra were measured at 77K on a Decca NQR spectrometer. Most ^{79}Br , ^{81}Br , and ^{127}I NQR spectra were measured on a Wilks NQR-IA instrument at ambient temperature. The Wilks instrument is usually satisfactory for detecting ^{81}Br NQR spectra, but usually fails to detect ^{127}I NQR spectra of halogenated organics. Since ^{127}I NQR spectra are much more readily detected at 77 K on pulse instruments not available in North America, some samples were sent to Russia for measurement on these instruments. Individuals who made the measurements were E.A. Kravchenko and V.G. Morgunov at the Russian Academy of Sciences, Moscow; T.A. Babushkina at the Ministry of Health, Moscow; and

S.I. Gushchin at Perm State University in Perm. Infrared (IR) analyses were performed on a Perkin-Elmer Model 1700 FTIR. Nujol mulls were prepared and placed on a single KBr plate for qualitative analysis. A Perkin-Elmer 7 Series Thermal Analysis system was used for thermal gravimetric determination of hydrates. Melting and decomposition points were checked using a Mel-Temp apparatus. All elemental analyses (% halide, %C, and %H) on products were performed by Galbraith Laboratories, Inc. Results were compared to the spectra of previously published and/or standard compounds when available.

A. Thallium Recycling Project

1. Conversion of Toxic Laboratory Thallium Halide Waste to Tl_2SO_4



A dry, powdery, bright yellow, thallium-containing laboratory waste (mostly the poisonous halides $TlCl$, $TlBr$, and TlI), was first pulverized with a mortar and pestle in order to homogenize the contents of the starting material. In an attempt to remove some of the suspected organic acid contaminants, a 50-g sample of the waste was stirred in a 250-mL beaker with a mixture of 50 mL of research grade ethanol and 5 mL of concentrated HCl. The mixture was covered with a watch glass and brought to a gentle boil for 15 minutes. The resulting hot slurry was vacuum-filtered through a glass frit to separate any dissolved organic acids from the insoluble thallium halide portion of the

waste. The ethanol fraction was allowed to evaporate and stored as hazardous material. This process alone reduced the amount of waste by about 2 percent of the original mass.

Next, the ethanol-washed, thallium halide waste was placed in another 250-mL beaker and mixed with 25 mL of concentrated H_2SO_4 . The mixture was slowly brought to a boil, using medium heat, with constant stirring via a magnetic stirring bar. As the mixture was heated, it appeared to char, and a purple gas, presumably iodine (I_2), was evolved. The mixture was heated and stirred until the evolution of gas was no longer observed, a process that took approximately one hour. The mixture was removed from the heat and allowed to cool slightly before 75 mL of deionized water was added. The mixture was again brought to a boil while stirring continuously, then quickly vacuum-filtered through a glass frit in order to remove the char from the digestate. A white, crystalline precipitate formed immediately in the vacuum filter flask below a light yellow-green colored filtrate. The filtrate with white crystalline material was refrigerated overnight.

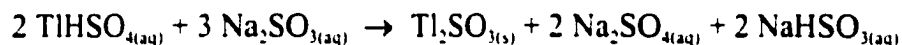
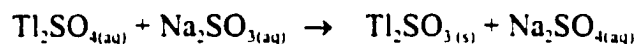
After refrigeration, the filtrate containing the precipitated crystalline material was vacuum filtered through a glass frit. The crystals were washed with 25 mL of ethanol. Test results at pH 8 of a portion of the crystals placed in de-ionized water indicated that this crystalline material was probably Tl_2SO_4 , of unknown purity. Another white, powdery precipitate formed in the filter flask as the initial crystals were washed with ethanol. An additional 100 mL of ethanol was mixed with the filtrate so as to force any further precipitation of solid material. The volume of the filtrate was then better than 50% ethanol. The filtrate was again vacuum filtered to collect the second generation of

powdery crystals. Test results at pH 6 indicated that this additional crystalline material probably contained some TiHSO_4 . A total of 34.1 g of $(\text{Ti}_2\text{SO}_4 + \text{TiHSO}_4)$ crystals was recovered from the initial 50-g mass of thallium halide lab waste. In addition, an unmeasured volume of gases, composed of iodine, hydrogen bromide, and hydrogen chloride, was produced. This method provided a 68.2% conversion of the mixed waste to a reusable material.

In order to recover any remaining thallium that might yet be present, 2 mL of concentrated HCl were added to the final filtrate. This amount of HCl was sufficient to precipitate the remainder of thallium as 1.24 g TiCl_3 , which was simply recovered by gravity filtration and added back to the original batch of mixed waste for recycling.

The entire procedure for the recovery of thallium and subsequent conversion to the more useful thallium sulfates was repeated with another 50-g portion of the mixed thallium halide laboratory waste. Although similar observations were recorded during the recovery procedures, the amount of mixed sulfates obtained from a second attempt was only 24.3 g, a 48.6% conversion of the waste to reusable material. Clearly, the difference was due to the varied nature of the wastes, even though special care was taken to homogenize the waste thoroughly before beginning the experiment. The second attempt to recycle the waste ultimately resulted in the return of 13.4 g TiCl_3 and 5.11 g of organic material to the recycling bin that could also be recycled at a later date.

2. Conversion of Ti_2SO_4 to Ti_2SO_3



An approximately 1.0 M Na_2SO_3 solution was prepared by dissolving 12.54 g (0.0995 moles) in 100 mL of deionized water in a 250-mL beaker. In another beaker, a 15.1 g sample of $\text{Ti}_2\text{SO}_4/\text{TiHSO}_4$ (about 0.3M) was dissolved in 100 mL deionized water by heating the solution to 100 °C. The boiling solution was immediately poured into the 250-mL beaker containing the 1.0 M Na_2SO_3 solution. The sudden appearance of a light yellow precipitate was observed as the two solutions were mixed. The products were refrigerated overnight. The resulting yellow crystals were separated from the remaining solution by vacuum filtration and collected on a quantitative, Whatman No.1 filter paper. The crystals were washed with about 100 mL of cold de-ionized water. As the yellow crystals were washed, additional fine, white precipitate was formed in the filter flask. The addition of concentrated HCl to the contents of the filter flask did not cause further precipitation, so it was assumed that this precipitate and filtrate were relatively halide-free. The presumed chemistry of the white precipitate was that of an insoluble sodium salt. The yellow crystals were dried using house vacuum filtration and desiccation. Approximately 9.54 g of the desired product, a bright yellow powder, Ti_2SO_3 , were recovered. Using this method, there was a 63.2% conversion of the $\text{Ti}_2\text{SO}_4/\text{TiHSO}_4$ to Ti_2SO_3 .

This procedure was repeated with another batch of $\text{Ti}_2\text{SO}_4/\text{TiHSO}_4$ recovered from the method described in Procedure 1. In the second attempt, 24.3 g of

$\text{Ti}_2\text{SO}_4/\text{TiHSO}_4$ were converted to 9.87 g of the reusable Ti_2SO_3 (a 40.6% conversion). Interestingly enough, very close to the same amount of Ti_2SO_3 was recovered from the two attempts to recycle the mixed thallium-waste material. The average amount of Ti_2SO_3 recovered from both trials was 9.71 g, which provided a 19.4% conversion of the original mixed waste to the desired reagent, Ti_2SO_3 .

3. Testing the Purity of the Na_2SO_3 Reactant and the Ti_2SO_3 Product

The Standard Methods procedure 429 for Sulfite (1975) was followed for testing the purity of the yellow crystalline product obtained from Procedure 2. Reagents were freshly prepared before the analysis. These included a 18 N H_2SO_4 (1:1) solution, a soluble starch indicator (5 g L, preserved by adding 1.30 g salicylic acid and 4.00 g ZnCl_2), and a standard 0.0125 N potassium iodide-iodate (KI-KIO_3) titrant, prepared by dissolving 0.446 g anhydrous potassium iodate (which had been dried for several hours), 4.35 g KI, and 0.310 g NaHCO_3 in distilled water and diluting to 1 liter.

An approximately 1 mM solution of the Ti_2SO_3 product was made by dissolving 0.0245 g in 50 mL (490 mg/L) of deionized water. The sample was acidified with 1 mL of 13 N H_2SO_4 , treated with 1 mL of starch indicator, then titrated using the 0.0125 N KI-KIO_3 solution. Samples of similarly treated 1 mM solutions of Na_2SO_3 (from two separate MTSU stockroom supply bottles), and another sample of white crystals, suspected to be composed mostly of Ti_2SO_3 , were titrated alongside the 1mM solution of yellow product to add validity to the test results. The deionized water in the laboratory was likewise treated and tested as the reference blank.

Calculations, based on the Standard Methods procedure 429 for Sulfite and using the following equation,

$$\% \text{SO}_3^{2-} = \frac{(\text{mL titrant}) (0.0125 \text{ N titrant}) (40,000)}{(\text{mL sample})}$$

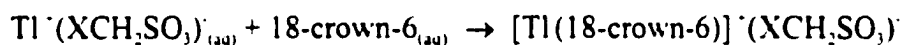
showed that the concentration of SO_3^{2-} in the 1 mM solution of the yellow crystalline product from Procedure 2 was about 75 milligrams/liter (mg/L), which indicated that the crystals themselves were about 15.4% SO_3^{2-} . A pure sample of Ti_2SO_3 is 16.4% SO_3^{2-} . Therefore, the test results indicated that the light yellow product was relatively pure.

Both old and "new" supplies of the Na_2SO_3 reagent were also tested for % purity. Samples from each bottle, each weighing 6.4 mg, were used to prepare solutions for analysis by placing the reagent in a 50 mL volumetric flask and bringing to the calibrated volume with deionized water. A 6.3-mg portion of pure Na_2SO_3 dissolved in a 50-mL volume would have resulted in the preparation of a 1mMol solution. Since pure Na_2SO_3 is 63.5% (by weight) SO_3^{2-} , a 1 mMol standard solution would have a concentration of 80 mg/L SO_3^{2-} . Results obtained from the test showed the old bottle of reagent grade Na_2SO_3 composition to be just 19% SO_3^{2-} , and that the "newer" reagent grade Na_2SO_3 contained only 46% SO_3^{2-} . As a result of these finding, a bottle of fresh reagent grade Na_2SO_3 was ordered from the manufacturer for future use. It is well known that Na_2SO_3 converts to Na_2SO_4 upon exposure to the atmosphere.

It should be noted that these tests were performed to check for relative (rather than exact) purity of the yellow product before the next experimentation was conducted. The KI-KIO₃ titrant was not normalized. Therefore, all of the % SO_3^{2-} test results are

approximate.

B. Syntheses of Thallium Halomethanesulfonates and Crown Adducts using Recycled Thallium



1. Synthesis of $\text{Tl}^+(\text{ICH}_2\text{SO}_3)^-$



a. Synthesis Using 18-crown-6 Catalyst

A 4.89 g (10.0 mmol) sample of the recycled Tl_2SO_3 was mixed with 20 mL deionized water. A 1.21 mL (15.0 mmol, or 4.02 g) portion of CH_2I_2 , along with 0.130 g (0.492 mmol) 18-crown-6, was added to the Tl_2SO_3 solution. The mixture was stirred in the absence of light and in an argon atmosphere for 2 days. However, no reaction was observed until the solution was heated to about 85 °C in a hot water bath for about 1 hour.

Upon heating, an orange precipitate formed in the reaction flask. At this point, the sample was removed from the hot water bath and vacuum filtered in order to remove the orange precipitate (probably TlI). The precipitate was washed with 20 mL of hot deionized water in order to remove any $\text{Tl}^+(\text{ICH}_2\text{SO}_3)^-$ that might be trapped in the solid material. The filtrate, which appeared slightly cloudy, was allowed to evaporate in the laboratory hood over the weekend.

The filtrate evaporated to produce a cloudy-white, crystalline material with

a slightly yellow tint. The air-dried crystals were then rinsed with 10 mL ethanol. The rinse appeared to have a slightly yellowish tint. The rinse was poured into a separate evaporating dish and allowed to dry. About 0.22 g of organic material was extracted from the product, which may have included some 18-crown-6 residue.

Even after the ethanol washing, the crystals maintained a slightly yellow tint. Three small portions of the product were tested for solubility in methanol, ethanol, and acetone. Since the crystals seemed to be more soluble in methanol, the remainder was placed in a beaker with 50 mL methanol, covered with a watch glass, then heated to reflux temperature while stirring constantly with a magnetic stirrer, in hopes of removing any traces of TII. The filtrate was again allowed to evaporate under the laboratory hood. Approximately 2.90 g of the initial crystalline product was reduced to 2.00 g (4.70 mmol), providing only a 47.1% yield after the solvent washing.

The ^{127}I pulse NQR spectrum at 77K on the washed sample contained two absorptions at 300.28 MHz and 599.76 MHz. This does not match the earlier data obtained on an unanalyzed sample prepared by Ricky Rutherford. Rutherford's sample gave a CW-NQR spectrum at 77K that contained absorptions at 287.51 MHz, 286.57 MHz, and 284.81 MHz. The higher frequencies were not measured.

Two ^1H NMR peaks were found in the washed initial product in D_2O solution; a major one at δ 4.41 (methylene) and a minor one at δ 3.70 (crown ether). Elemental analysis [Table 1] also confirmed the presence of a trace

(1/12 mol) of 18-crown-6 in the purified compound.

b. Synthesis in the Absence of 18-crown-6 Catalyst

A 4.534 g (9.28 mmol) sample of freshly prepared Ti_2SO_3 was mixed with 50 mL deionized water. A 1.20 mL (14.9 mmol, or 4.00 g) portion of CH_2I_2 was added to the reaction flask, and the mixture was stirred under argon in a hot water bath maintained at approximately 85 °C. During the first hour, the gradual appearance of a bright yellow precipitate was noted. After 2 hours, 3.01 g (9.09 mmol, 97.9% yield) TiI was filtered off and washed with 30 mL of hot deionized water. The volume of the filtrate was reduced using vacuum desiccation. The first crop of 0.693 g mixed yellow and white crystals from the liquor, which could have contained some unreacted Ti_2SO_3 or Ti_2SO_4 , were removed by filtration, and the volume was reduced nearly to dryness to give 3.058 g (7.19 mmol, 77.5% yield) of white $\text{Ti}(\text{ICH}_2\text{SO}_3)$ which was washed with 1.5 mL of cold deionized water. The evaporated wash water yielded 0.988 g white crystals, suggesting that the cold water solubility of the $\text{Ti}(\text{ICH}_2\text{SO}_3)$ was about 0.660 g/mL. This product was characterized successfully by NMR, NQR, and elemental analysis. A single ^1H NMR peak was found at δ 4.41 (methylene), suggesting that the synthesis had succeeded without the crown catalyst.

2. Synthesis of $\text{Tl}^+(\text{BrCH}_2\text{SO}_3)^-$



a. Synthesis Using 18-crown-6 Catalyst

In a 100-mL reaction flask, 45 mL of deionized water were mixed with 4.50 g recycled Tl_2SO_3 (9.21 mmol). To this mixture, 3.00 mL of CH_2Br_2 (7.43 g, or 42.7 mmol) were added, along with 0.120 g (0.454 mmol) 18-crown-6 employed in the reaction as a phase transfer catalyst. The mixture was stirred electronically while refluxing for approximately 2 hours under a blanket of argon. After only about 30 minutes the reaction appeared to be complete, as evidenced by the appearance of a pale yellow precipitate around the sides of the reaction vessel, and the disappearance of the Tl_2SO_3 from the bottom of the flask. The resulting products were filtered to remove 2.74 g of insoluble precipitate, presumably TlBr (5% above the theoretical yield). The unreacted CH_2Br_2 was removed from the bottom of the filtrate using a Pasteur pipette. The water-soluble portion of the filtrate and rinse was placed in a beaker under house vacuum to allow crystallization of the product, $\text{Tl}^+(\text{BrCH}_2\text{SO}_3)^-$. The amount of $\text{Tl}^+(\text{BrCH}_2\text{SO}_3)^-$ recovered, after all solvent had evaporated, was 3.725 g (9.850 mmol, 7 % above the theoretical yield).

Microscopic examination of the crystalline product revealed the presence of two types of crystals. The ^{81}Br NQR spectrum recorded at ambient temperature on our Wilks NQR included two strong peaks at 228.7 MHz (within experimental error of the expected signal, 229.2 MHz) and 236.9 MHz. Only the peak at 229.2 MHz

was present in the earlier products of S. Jones. Hence, the presence of a second component was suggested. The ^1H NMR in D_2O showed two significant peaks at δ 4.44 (methylene, CH_2Br) and at δ 3.70 (crown ether), with an integration ratio of 1 to 0.84, indicating the presence of slightly less than 1/12 mole of crown ether. This suggested that the synthesis had been improved, but that the product was contaminated with the crown ether adduct. The entire sample was recrystallized from boiling deionized water. A first crop of 0.340 g NMR-inactive product may be Tl_2SO_4 . The second crop of 1.060 g of crystals gave a single NMR peak at δ 4.44 and gave a ^{209}Bi NQR peak at 228.7 MHz; this was submitted for elemental analysis. The third crop of 0.880 g of fluffier crystals gave two NMR peaks with integration 1: 0.67 (CH_2Br protons: crown protons) and a single ^{209}Bi NQR peak at 236.9 MHz.

b. Synthesis in the Absence of 18-crown-6 Catalyst

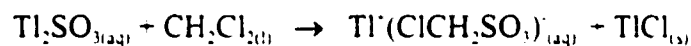
A 4.500 g (9.21 mmol) portion of freshly prepared Tl_2SO_4 was dissolved in 50 mL boiling deionized water with continuous stirring. The solution was placed under argon before adding 3.0 mL CH_2Br_2 . A light precipitate formed immediately upon addition of the CH_2Br_2 , but the mixture was allowed to reflux for 2 hours. The product was filtered while hot to remove the 2.817 g of initial precipitate (presumably TlBr , but 8% above the theoretical yield), and then placed in the refrigerator overnight. Another 0.057 g of a fine precipitate was filtered from the liquor, and the filtrate was placed in the vacuum desiccator. After 2 days, a crop of 0.808 g light yellow crystalline material (possibly unreacted

Tl₂SO₃) was removed by filtration. The remaining filtrate was placed back under house vacuum until dry, which produced a crop of 0.964 g of clear crystals. No surplus of CH₂Br₂ was recovered from the reaction as expected. Since CH₂Br₂ boils at 97 °C, it is possible that it was blown away by rapidly flowing argon gas.

Since the light yellow crop of crystals was not soluble in D₂O, no meaningful ¹H NMR spectrum was recorded. The clear crop of crystals produced a single proton signal at δ 4.44 (methylene, CH₂Br), but gave no Br NQR results.

3. Synthesis of Tl⁺(ClCH₂SO₃)⁻

a. Synthesis from Dichloromethane



A solution of Tl₂SO₃ was prepared by dissolving 4.455 g (9.114 mmol) in 45 mL boiling deionized water. Next, 0.100 g (0.378 mmol) 18-crown-6 was added to the hot aqueous solution of Tl₂SO₃. The reaction flask was allowed to cool slightly, then placed under a blanket of argon in a glove bag. While the solution was still warm, 25 mL CH₂Cl₂ were added to the reaction flask. After only a few minutes of stirring following the addition of the CH₂Cl₂, a fine white precipitate was observed clinging to the sides of the reaction vessel (presumably TlCl). The sealed mixture was stirred for 7 days before attempting to remove the white precipitate by vacuum filtration. The amount of precipitate observed did not appear to increase after 2 days of stirring, indicating that the reaction was complete.

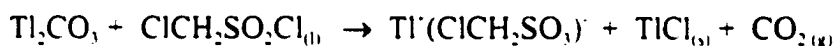
The amount of precipitate filtered from the reaction mixture after 7 days was 1.202 g (5.01 mmol, 55% of the amount of TiCl_4 expected). Washing the TiCl_4 -containing precipitate with hot deionized water and evaporating the water wash yielded 0.885 g (2.65 mmol) of $\text{Ti}^+(\text{ClCH}_2\text{SO}_3)^-$ crystals. Integration of the proton NMR spectrum of this crop gave a 1: 5.44 methylene: crown ratio, which suggests a mixture or a structure having a single crown sandwiched between two Ti^+ ions. The filtrate contained two phases, aqueous and dichloromethane. The phases were separated by using a Pasteur pipette, and placed under house vacuum. Crystals (0.108 g) obtained from the evaporation of the excess CH_2Cl_2 gave a ^1H NMR spectrum which showed a 1: 14.33 ratio, suggested the presence of a classical 1: 1 complex between Ti^+ and 18-crown-6.

Upon evaporation of most of the aqueous layer, 2.059 g (6.167 mmol) of crystals presumed to be $\text{Ti}^+(\text{ClCH}_2\text{SO}_3)^-$ were recovered. These crystals gave a weak NQR spectrum. The ^1H NMR spectrum of this crop showed two significant peaks δ 4.52 (methylene, CH_2Cl) and at δ 3.72 (crown ether) (ratio of 1: 0.67 methylene: crown ether). This crop was recrystallized using boiling deionized water. The process first gave two crops of long flat rectangular crystals; the first batch was produced directly from refrigeration overnight; the second after 2 days of partial evaporation of the filtrate. The elemental analysis of these crystals showed them to be inorganic and halogen-free. They gave no NQR spectrum. A ^1H NMR spectrum showed neither methylene nor crown protons in the first crop of crystals obtained from the purification (only a tiny crown peak was seen on the

second crop). We concluded that these crystals may have been Ti_2SO_4 .

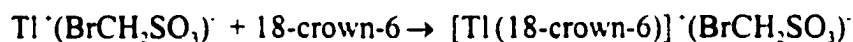
The last crop of crystals (obtained by taking the remaining solution to dryness) gave a 1:12.6 CH_2Cl : crown ratio by ^1H NMR spectroscopy! This crop also gave no NQR spectrum.

b. Synthesis from Chloromethanesulfonyl Chloride



A solution of $\text{ClCH}_2\text{SO}_2\text{Cl}$ was prepared by mixing 1.53 mL (2.552 g 17.12 mmol) with 20 mL methanol (under argon). As 8.028 g (17.12 mmol) Ti_2CO_3 were added slowly while stirring, a small amount of heat was generated and bubbles of CO_2 gas formed. The reaction flask was vented to the atmosphere and covered with foil while being stirred overnight without heat. A white precipitate was filtered off and washed with five 20 mL portions of boiling methanol, giving a final weight of 4.257 g (17.75 mmol if pure TiCl_3 , 3.7% above the theoretical yield). A small amount of fluffy white precipitate (0.298 g) was filtered off; the filtrate was allowed to evaporate in a vacuum desiccator over H_2SO_4 . A total of 5.296 g (15.86 mmol, 92.6% yield) of product was recovered. Although the crystallization appeared to produce three types of crystals (yellow 'fluff', dense fine white powder, and clear crystalline sheets), the ^1H NMR of all types of crystals showed a strong peak at δ 4.52. These data suggested that all of the crystalline types were $\text{Ti}(\text{ClCH}_2\text{SO}_3)_2$. A strong NQR signal was obtained from the crystalline sheets, which were also submitted for elemental analysis.

4. Synthesis of [Tl(18-crown-6)]⁺(BrCH₂SO₃)⁻

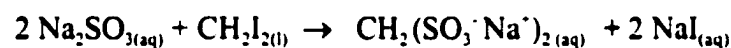


A 1.068 g portion of Tl⁺(BrCH₂SO₃)⁻ containing a trace of crown (less than 1/12 mole, from Procedure 2a) was dissolved in 20 mL deionized water, then mixed while under argon with 0.630 g (2.64 mmol) 18-crown-6 (an estimated stoichiometric amount) that had been dissolved in 10 mL deionized water. The solution was heated to boiling while stirring continuously, then placed under house vacuum for the evaporation of water. After washing the product with about 15 mL diethyl ether, 0.981 g (1.53 mmol, 58.0% yield) of very fluffy, white [Tl(18-crown-6)]⁺(BrCH₂SO₃)⁻ was recovered by vacuum filtration.

The product gave no ²⁰⁹Pb NQR spectrum. The ¹H NMR spectrum of the product in D₂O gave approximately a 1:11 integration ratio (1:12 is expected) between the peaks at δ 4.43 (CH₂Cl group protons) and at δ 3.70 (crown ether protons).

C. Synthesis of other Halomethanesulfonates and Crown Adducts

1. Improved Synthesis of Na⁺(ICH₂SO₃)⁻•H₂O



A 12.0 g- (0.064 mol) sample of the Na₂SO₃ from stock (having test results of 43% SO₃²⁻, compared to pure Na₂SO₃ with assay of 63.5% SO₃²⁻) was dissolved in 50 mL of ultrapure deionized water with vigorous stirring. A 4.06 mL (0.05 mol or 13.5 g) portion of CH₂I₂ and 25 mL ethanol were added to the reaction flask. The reactants were

allowed to stir overnight at 70 °C. The products were vacuum filtered to remove 4.40 g of a fine, white precipitate. The suspicion is that the precipitate, identified as Crop 1, was the byproduct, $\text{Na}_2[\text{CH}_2(\text{SO}_3)_2]$, formed by the second reaction shown above. However, this was not confirmed.

The mother liquor was poured into an evaporating dish and placed under vacuum desiccation for 12 days. A healthy second batch of crystals formed in the mother liquor. One single crystal of relatively pure $\text{Na}(\text{ICH}_2\text{SO}_3)\cdot\text{H}_2\text{O}$ weighed over 11 g! The huge crystal was rinsed with acetone to remove traces of NaI on its surface. After the third washing, the crystal showed a weight loss of only 0.040 g. The final weight of the huge crystal of $\text{Na}^+(\text{ICH}_2\text{SO}_3^-)$ was approximately 10.6 g (0.043 mol). The ^1H NMR peak at δ 4.41 in D_2O confirmed the presence of equivalent methylene protons in a CH_2I group.

The Thermal Gravimetric Analyzer (TGA) results showed that the product was actually a monohydrate (weight loss of 7.6 % between 25 °C and 235 °C, including 6.0% between 146 °C and 235 °C; theoretical, 7.26% H_2O). This confirmed the conclusion of the old patent literature, that this compound is actually a monohydrate (Ossenbeck et al., 1932; Allardt, 1932).

A third batch of much smaller crystals, initially having a more granular appearance, was manually separated from around the perimeter of the huge crystal. When dried, this crop of crystals weighed 3.40 g. This third crop must have contained a high concentration of NaI, as the crystals were mostly soluble in acetone, but the insoluble residue gave the same NMR spectrum as the huge crystal (signal at δ 4.41 in D_2O). The fourth crop of crystals was recovered from the mother liquor. Nearly three-

fourths of this crop was soluble in acetone.

2. Synthesis of $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$



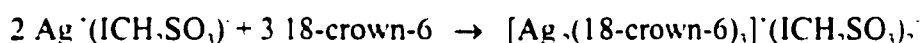
Exactly 2.22 g of $\text{Na}^+(\text{ICH}_2\text{SO}_3)^- \cdot \text{H}_2\text{O}$ (8.47 mmol, from the huge crystal) were dissolved in 85 mL of boiling ethanol while stirring. A separate 20-mL portion of ethanol was brought to a boil, and 1.40 g (8.24 mmol) AgNO_3 was added in the dark while stirring. When both reactants had completely dissolved in the boiling ethanol, and while still very hot, the AgNO_3 solution was poured into the boiling $\text{Na}^+(\text{ICH}_2\text{SO}_3)^- \cdot \text{H}_2\text{O}$ solution. The beaker containing the mixture was then covered with a watch glass and allowed to stir for an additional 10 minutes. The mixture was filtered while very hot to remove the NaNO_3 . The filtrate was placed in a beaker under house vacuum for 5 days (in the dark) until the solvent had evaporated. The dried $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$ weighed 1.81 g (5.50 mmol, 66.8% yield). The weight of the dried filter material was 1.55 g (18.2 mmol of NaNO_3 , 218% yield). With such a high apparent yield of NaNO_3 , we postulated that much of the product also crystallized from the hot solution along with the NaNO_3 .

This experiment was repeated using the exact same weight of reactants and volumes of ethanol. In the second trial, the amount of dried filter material (again, presumably NaNO_3) was 1.35 g (seemingly 16.0 mmol, again well over 100% yield). The weight of $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$ from the second trial was 1.96 g (5.96 mmol, 72.3% yield). Average yield of the product, $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$, from the two trials was about 70%.

Future syntheses should use larger volumes of boiling ethanol to prevent the product

from precipitating prematurely, or else should extract the initial precipitate with hot ethanol. A ^1H NMR peak observed at δ 4.41 in D_2O confirms the presence of methylene protons.

3. Synthesis of $[\text{Ag}_2(18\text{-crown-6})_3]^+(\text{ICH}_2\text{SO}_3)_2^-$



Equimolar quantities of $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$ and 18-crown-6 were reacted: 1.20 g (4.54 mmol) of the crown ether were dissolved in 20 mL of methanol; 1.50 g (4.56 mmol) $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$ were dissolved in 20 mL of deionized water. The two solutions were mixed together in the dark while stirring at room temperature. A small amount of heat was generated upon mixing, and the resulting solution was clear. The combined solutions were allowed to stir for 4 hours in the dark under argon, then placed under house vacuum until all liquid had evaporated and crystals had formed. This required ten days. Very light yellowish-tan, crystalline solids were deposited only at the bottom of the beaker, suggesting the crystallization had taken place at the very end of the evaporation process. The weight of the product, assumed to be the desired $[\text{Ag}(18\text{-crown-6})]^+(\text{ICH}_2\text{SO}_3)^-$, was 2.81 g, a 102% yield.

Although light sensitive, the product did not appear to be hygroscopic when exposed to air. The ^1H NMR spectrum in D_2O showed 2 peaks; integration gave a 1: 20.1 ratio for methylene group protons (δ 4.41) and crown (δ 3.69), instead of the expected 1 to 12 ratio. A TGA analysis suggested that the compound was not a hydrate. No ^{127}I NQR was detected on our Wilks instrument at room temperature.

The melting point of the product, now suspected to be $[\text{Ag}_2(18\text{-crown-6})_3]^+(\text{ICH}_2\text{SO}_3)_2^-$, was determined to be 105 °C. The substance appeared to boil at 120 °C, then thicken, and turn a canary yellow at 150 °C. The product showed no further signs of decomposition until approximately 160 °C, at which temperature it appeared to begin to char.

An attempt was made to purify the product by first dissolving it in boiling acetone, then adding an equal volume of n-heptane. Less than one half of the product was recovered by refrigerating overnight. A ^1H NMR spectrum of this product showed it to be crown ether free $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$. Water aspiration of the sample to remove most of the acetone provided no further precipitation of the product. The flask containing the remaining filtrate was heated over boiling water to further reduce the volume of the volatile solution, which provided only a few mg of second product. The ^1H NMR spectrum of this product showed it to be 18-crown-6. It is postulated that the product was decomposed by the attempted purification.

4. Synthesis of $[\text{K}(18\text{-crown-6})]^+(\text{ICH}_2\text{SO}_3)^-$

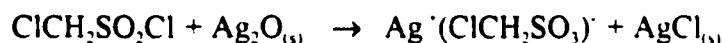


The $\text{K}^+(\text{ICH}_2\text{SO}_3)^-$ previously prepared by Rutherford (1996) was used, so its ^1H NMR spectrum was first run in D_2O to confirm its stability: only one peak was found at δ 4.41 in D_2O . Exactly 1.07 g (4.05 mmol) of 18-crown-6 were dissolved in 20 mL of methanol under a blanket of argon. Next, 1.07 g (4.11 mmol) of $\text{K}^+(\text{ICH}_2\text{SO}_3)^-$ were dissolved in 20 mL of deionized water, also under a blanket of argon. When the two

solutions were then mixed together in the dark while stirring at room temperature, a mildly exothermic reaction occurred. A clear solution resulted. The reaction mixture was allowed to stir for 2 hours under a blanket of argon. The resulting solution was placed into an evaporating dish. The reaction flask was rinsed with about 5 mL of a 1:1 solution of methanol and ultra-pure deionized water. The combined solution was placed under house vacuum until all liquid had evaporated, which required several days. After 10 days, a check on the product revealed what appeared to be a single substance, but a crust had formed above some of the liquor still trapped below. These crystals were swept aside to complete the drying process under house vacuum. A white, crystalline solid material resulted. The weight of the product, presumably the desired [K (18-crown-6)]⁺(CH₃SO₃)⁻, was 2.13 g (4.06 mmol, 99.1% yield). The product was recrystallized by initially dissolving in boiling acetone, and then adding an equal volume of n-heptane. Approximately 82% of the product was recovered by a combination of refrigerating overnight, then using water aspiration to remove most of the acetone. The sample gave a satisfactory elemental analysis [Table 1].

It should be noted that the melting point of this substance was not clearly defined. The substance appeared to melt at 152 °C, but the melting point was not sharp. No charring or other decomposition was observed. The ¹H NMR spectrum of the product in D₂O gave approximately a 13:1 integration ratio (12:1 is expected) between the peaks at δ 3.69 (crown ether protons) and at δ 4.41 (CH₃ protons). No other solvent was found for the product that would have been suitable for NMR spectroscopy. No ¹²⁷I NQR was detected by our Wilks instrument at room temperature.

5. Synthesis of $\text{Ag}^+(\text{ClCH}_2\text{SO}_3)^-$



A solution of chloromethanesulfonyl chloride (Alfa Chemical), previously opened years ago and showing contaminant peaks in its ^1H NMR spectrum, was made by dissolving 3.00 g (20.1 mmol) $\text{ClCH}_2\text{SO}_2\text{Cl}$ in 10 mL methanol in a 100-mL round bottom flask while under an atmosphere of argon. The solution was allowed to stir for 1 hour in order to remove any acetic anhydride contaminant, and the reaction vessel was placed under house vacuum while stirring to allow the evaporation of the methanol. Another 20 mL of methanol were added to the purified $\text{ClCH}_2\text{SO}_2\text{Cl}$ in the flask, and a drop of the resulting solution was found to have a pH of between 1 and 0. Another drop of the solution was removed and mixed with a drop of 1 M AgNO_3 , to give a positive test for the presence of chloride.

After a gradual addition of 4.63 g (20.0 mmol) Ag_2O to the reaction flask (in the dark, while mixing under an atmosphere of argon), the flask was covered with foil and allowed to continue stirring. After only two hours of mixing, the reaction flask was found to contain a much lighter tan-colored mixture than the originally black silver oxide-methanol mixture. The mixture was allowed to stir overnight. The precipitate that resulted from the reaction was filtered off by vacuum filtration and washed with another 25 mL of methanol. The combined filtrates were placed in a beaker under house vacuum to allow evaporation of the methanol from the desired product. The yield of the white crystals of $\text{Ag}^+(\text{ClCH}_2\text{SO}_3)^-$ from the reaction was 4.47 g (18.8 mmol, 94.1% yield.)

The product failed to give a ^{35}Cl -NQR spectrum. The product was recrystallized

using methanol, but again no NQR spectrum could be recorded. The IR spectrum was recorded and found to be quite similar to that of $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$, except that it showed a peak at 1650 cm^{-1} which might be due to a trace of contaminant. The ^1H NMR spectrum of the product in D_2O had only one significant peak, at δ 4.50.

The TGA of the recrystallized $\text{Ag}^+(\text{ClCH}_2\text{SO}_3)^-$ indicated that the product was not a hydrate, since only 0.30% weight loss was recorded as the substance was ramped from room temperature to $200\text{ }^\circ\text{C}$ at $20\text{ }^\circ\text{C}/\text{minute}$.

CHAPTER III

RESULTS and DISCUSSION

A. Elemental Analyses (Table 1)

Single elemental analyses for percent (by weight) carbon, hydrogen, and halogen were performed by Gailbraith Labs, Inc., Knoxville, TN, and are reported in Table 1.

B. NMR Spectra (Tables 2, 3)

Proton NMR spectra, recorded in D₂O using TMSP as an internal standard ($\delta = 0.000$), are listed in Table 2. Due to a precipitation problem, an external reference to zero had to be used for most products whose composition contained both silver and 18-crown-6. The NMR peak picking software enabled us to record reproducible trends in chemical shifts for the various halomethanesulfonate complexes [Table 3]. In D₂O solution, all metal halomethanesulfonates are likely to be ionized:



The NMR results support this prediction, as no additional shift was observed with a change of +1 cations within the products, nor upon the complexation of the cation by 18-crown-6. Coupling of methylene protons to halogen atoms was not observed in the spectra, due to the strong electrical quadrupole moments of the halogen nuclei (Silverstein et al., 1998a).

General trends were discovered in frequencies of $-CH_2X$ protons bonded to the metal atoms included in our research. As tabulated by Silverstein and Webster (1998b), the chemical shifts of halomethylene groups move upfield (to the right) as the halogen is

Table 1. Elemental Analysis of Products

Compound	% Carbon	% Hydrogen	% Halogen
Tl ⁺ (ICH ₂ SO ₃) ⁻ Exptl	5.23	1.42	30.34 (I)
Calcd Tl ⁺ (ICH ₂ SO ₃) ⁻ with 1/12(C ₁₂ H ₂₄ O ₆)	5.37	0.90	28.36 (I)
Calcd Tl ⁺ (ICH ₂ SO ₃) ⁻	2.82	0.47	29.83 (I)
Tl ⁺ (BrCH ₂ SO ₃) ⁻ Exptl	2.40	<0.5	20.91 (Br)
Calcd Tl ⁺ (BrCH ₂ SO ₃) ⁻	3.17	0.53	21.12 (Br)
Tl ⁺ (ClCH ₂ SO ₃) ⁻ Exptl	3.65	0.59	10.31 (Cl)
Calcd Tl ⁺ (ClCH ₂ SO ₃) ⁻	3.60	0.60	10.62 (Cl)
K [18-crown-6] ⁺ (ICH ₂ SO ₃) ⁻ Exptl	29.86	5.22	23.83 (I)
Calcd K [18-crown-6] ⁺ (ICH ₂ SO ₃) ⁻	29.77	5.00	24.20 (I)

(Elemental analyses were performed by Gailbraith Labs, Inc., Knoxville, TN).

Table 2. ¹H NMR Results for Halomethanesulfonates and Crown Adducts

Compound	Halomethylene, δ (ppm) in D₂O	18-Crown-6, δ (ppm) in D₂O	¹H Ratio -XCH₂: 18-Crown-6
NaICH ₂ SO ₃	4.41		
Ag ₂ [18-crown-6], (ICH ₂ SO ₃) ₂	4.41	3.69	1: 20.1
KICH ₂ SO ₃	4.39		
K[18-crown-6] (ICH ₂ SO ₃)	4.41	3.69	1: 12.8
TlICH ₂ SO ₃	4.41		
TlBrCH ₂ SO ₃	4.44		
Tl[18-crown-6] (BrCH ₂ SO ₃)	4.43	3.70	1: 11.2
TlClCH ₂ SO ₃	4.52		
Tl[18-crown-6] (ClCH ₂ SO ₃)	4.52	3.71	1: 12.6
AgClCH ₂ SO ₃	4.50		
18-crown-6		3.69	

Table 3. Trends in ^1H NMR Chemical Shifts in Halomethanesulfonates

Halomethanesulfonate Ligand	^1H Chemical Shifts, δ (Observed Range)	*Est. ^1H Chemical Shifts, δ (Silverstein et al., 1998f)
$-\text{ICH}_2\text{SO}_3$	4.41 – 4.39	3.13, for CH_2 -I group
$-\text{BrCH}_2\text{SO}_3$	4.44 – 4.43	3.40, for CH_2 -Br group
$-\text{ClCH}_2\text{SO}_3$	4.52 – 4.50	3.45, for CH_2 -Cl group

* In the absence of an (untabulated) additional shift due to the presence of the SO_3^- group.

changed from Cl to Br to I. We found this trend to hold in our compounds as well.

However, all peaks were shifted downfield from the positioning tabulated by Silverstein and Webster, due to the inclusion of a sulfonate group in each compound. These shifts were not appreciably affected by the presence of 18-crown-6 (δ 3.70 \pm 0.01).

C. IR Spectra

The IR spectra confirmed that the products likely are halomethanesulfonates. However, no major difference between ClCH₂, BrCH₂, and ICH₂ groups were observed in the spectra, since the X-C stretching frequency is not particularly strong in halomethanesulfonate complexes. Usually, a CH₂X (X=Cl, Br, I) absorption [“wagging”] band is observed between 1300 - 1150 cm⁻¹, along with aliphatic C-Cl absorption: 850 - 550 cm⁻¹; C-Br absorption: 690 - 515 cm⁻¹; and C-I absorption: 600-500 cm⁻¹ (Silverstein et al., 1998c). All spectra showed a broad absorption due to S-O stretching modes as expected in the ranges of 1200 – 1145 cm⁻¹ (Silverstein et al., 1998d). A weaker sulfonate absorption band between 1420 – 1330 cm⁻¹ is buried by absorptions of the Nujol (mineral oil) IR medium. Crown ether complexes have shown C-O stretching frequencies between 1140 and 1110 cm⁻¹ (Wulfsberg, 1977; Silverstein et al., 1998). Although sulfonate absorption bands appear to be a little higher than those for ether, there is some overlap of these functional group stretches in the spectra that can cause confusion in interpretation.

D. NQR Spectra (Table 4)

In the absence of metal-halogen coordination, the halogen NQR frequencies of potassium, silver, and thallium(I) halomethanesulfonates should all be about equal, since the three ions have the same charge and approximately same size radii. However, metal-halogen coordination should lower the NQR frequency (Newbound et al., 1989; Colman et al., 1990). The NQR frequencies of thallium(I) and potassium iodomethanesulfonates are similar, suggesting the same degree of coordination of the metal ion to each. Since the hard potassium ion (K^+) is not expected to be coordinated to the soft iodine atom, we think that thallium(I) ion (Tl^+) is also not coordinated. There is a close resemblance of these spectra to those of $Na(CH_2SO_3) \cdot H_2O$ and $Tl(CH_2SO_3) \cdot 1/12$ mol 18-crown-6, again suggesting the absence of coordination, but the ^{127}I NQR frequency of silver iodomethanesulfonate is much lower, suggesting the presence of coordination in the silver compounds.

The NQR frequencies of thallium(I) and potassium bromomethanesulfonates are similar, signifying the absence of coordination of the halogen to either metal ion. In contrast, the frequency of the silver salt is substantially lower, suggesting the presence of silver-bromine coordination that was indeed shown to be present by X-ray crystallography (Charbonnier et al., 1978).

The NQR frequencies of thallium(I) and potassium chloromethanesulfonates are also similar, but the spectra give different numbers of ^{35}Cl peaks. It follows that they must solidify in different crystal lattice types. In contrast, the frequency of the silver salt is substantially lower, suggesting the presence of silver-chlorine coordination that was

Table 4. Halogen NQR Frequencies of Halomethanesulfonates (MHz)

A. ^{127}I NQR Frequencies at 77K (Measured in Russia or Japan)			
$\text{Na}(\text{ICH}_2\text{SO}_3)\cdot\text{H}_2\text{O}$	300.32	301.81	
$\text{Tl}(\text{ICH}_2\text{SO}_3)\cdot 1/12(\text{C}_{12}\text{H}_{24}\text{O}_6)$	300.28		
$\text{Tl}(\text{ICH}_2\text{SO}_3)$	284.81	286.52	287.51
$\text{K}(\text{ICH}_2\text{SO}_3)$	286.95	288.19	288.90
$\text{Ag}(\text{ICH}_2\text{SO}_3)$	264.85		

B. ^{81}Br NQR Rrequencies at Room Temperature (Measured on Wilks NQR)	
$\text{K}(\text{BrCH}_2\text{SO}_3)$	230.36 (Russia)
$\text{Tl}(\text{BrCH}_2\text{SO}_3)$	229.2
$\text{Ag}(\text{BrCH}_2\text{SO}_3)$	218.3

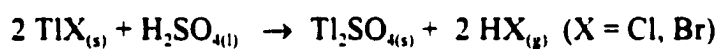
C. ^{35}Cl NQR Frequencies at 77K (Measured on Decca NQR)			
$\text{K}(\text{ClCH}_2\text{SO}_3)$	36.500	36.254	36.171
$\text{Tl}(\text{ClCH}_2\text{SO}_3)$	35.915		
$\text{Ag}(\text{ClCH}_2\text{SO}_3)$	34.545		

indeed shown to be present by x-ray crystallography, performed by Steven Strauss of Colorado State University.

E. Syntheses

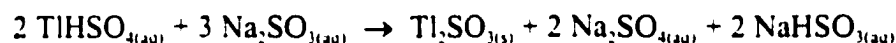
Thallium halides are toxic (Merck Index, 1976), insoluble products generated from reactions involving other expensive thallium salts. They are not very useful as starting materials for further reactions. A simple, reliable method was sought to convert a mixed thallium halide laboratory waste (contaminated with organic compounds) to more useable, high purity Tl_2SO_4 and subsequently, to useful Tl_2SO_3 , with a good yield. The procedure employed should digest organic material that might be present, as well as remove the halides (chloride, bromide, and iodide) from the waste material.

A mélange of solid, thallium-containing waste consisting of white and yellow crystals and powder was pulverized and well mixed. The resulting bright yellow powder was first boiled with ethanol and concentrated HCl to convert any soluble thallium compounds to insoluble $TlCl$, which along with insoluble $TlBr$ and TlI was filtered off; many organic contaminants should have remained in the ethanol. The mixed halides were heated with concentrated H_2SO_4 to produce soluble Tl_2SO_4 along with some $TlHSO_4$.

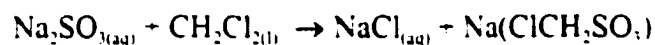


Precipitation of the yellow, high purity starting material, Tl_2SO_3 , was achieved

through use of an excess of 1.0 M Na₂SO₃ of medium purity through a simple exchange of the similarly charged SO₄²⁻ and SO₃²⁻ ions. This procedure closely resembles that used in the first reported syntheses of thallium(I) sulfite (Seubert et al., 1892; Reuter et al., 1952).



Halomethanesulfonates are usually made by prolonged, even high-pressure nucleophilic substitution reactions of aqueous sodium sulfite with water-insoluble, unreactive dihalomethane (Ossenbeck et al., 1932; Allardt, 1932)



The use of phase transfer catalysts such as 18-crown-6 was found by D. Jones (1989) to promote the speed of this reaction. The use of silver salts should also increase the speed of the reaction by metal-assisted nucleophilic substitution to give insoluble silver halide. However, silver(I) sulfite has very low solubility in water, and Rutherford (1996) got very poor yields in this type of reaction even in the presence of 18-crown-6 and with the most reactive dihalomethane, CH₂I₂. Since Tl₂SO₃ is moderately soluble in hot water, its use along with 18-crown-6 was tested.



Although Tl₂SO₃ and CH₂I₂ with catalytic amounts of 18-crown-6 did not react at room temperature, heating to 85 °C gave reaction within an hour. The products obtained were contaminated with a 18-crown-6 complex thought to be Tl(ICH₂SO₃)•1/12 C₁₂H₂₄O₆. Another reaction was conducted in the absence of crown, which appeared to be

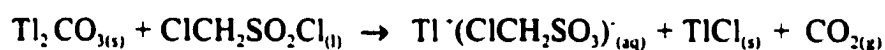
successful. Percent yield results were approximately 30% higher for the synthesis performed without the crown ether!



The corresponding reaction using CH_2Br_2 was run for two hours, but appeared to be complete within 0.5 hour. Again, the products were contaminated with a similar crown ether complex of appropriate stoichiometry $\text{Tl}(\text{BrCH}_2\text{SO}_3) \cdot 1/12 \text{C}_{12}\text{H}_{24}\text{O}_6$, which gave a distinctive NQR spectrum and which could partially be separated from the crown-free salt. Another reaction was conducted in which the thallium salt was provided with a stoichiometric quantity of 18-crown-6, producing $\text{TlBrCH}_2\text{SO}_3 \cdot \text{C}_{12}\text{H}_{24}\text{O}_6$; this complex, however, gave no NQR spectrum at room temperature.

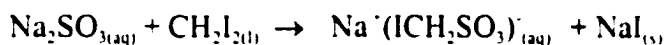


Although it was anticipated that the corresponding reaction using CH_2Cl_2 would require days (due to its unreactivity and very low boiling point, which precluded reaction temperatures above 40°C), and although the reaction in fact was run for several days, it appeared that the reaction was over in about two days. The diverse set of products obtained apparently included Tl_2SO_4 (from oxidation of unreacted Tl_2SO_3) and a crown ether complex $\text{Tl}(\text{ClCH}_2\text{SO}_3) \cdot 1/12 \text{C}_{12}\text{H}_{24}\text{O}_6$, but no clear evidence was obtained for the successful isolation of the simple salt, $\text{Tl}^+(\text{ClCH}_2\text{SO}_3)^-$. So, an independent crown-free synthesis was carried out:

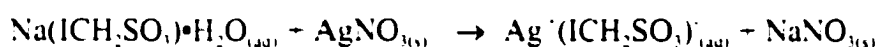


Stirring these reactants overnight led to complete reaction. The TlCl precipitate was extracted with hot methanol; evaporation of the methanol gave a good yield of Tl^+

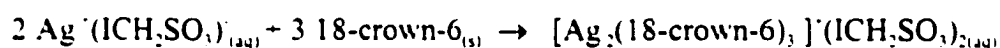
(ICH₂SO₃)⁻ with the expected single ¹H NMR peak at δ 4.52 and a strong NQR signal.



This experiment was a repeat of Rutherford's work (1996). Improvements were made in the crystallization and purification of the product, as repeated acetone washes removed the NaI byproduct. One single crystal of relatively pure product weighed over 11 g! The TGA results showed that the product was actually a monohydrate, Na(ICH₂SO₃)•H₂O. This confirmed what had been suggested in the conclusions of the old patent literature (Ossenbeck et al., 1932; Allardt, 1932).



This procedure was also a repeat of Rutherford's work (1996). Average yield of the product, Ag⁺(ICH₂SO₃)⁻, from two trials was about 70%. Our results indicate that future syntheses should probably use larger volumes of boiling ethanol to prevent the product from precipitating prematurely, or the initial precipitate of NaNO₃ should be extracted with hot ethanol to recover product that could be trapped in the precipitate.



An aqueous reaction with equimolar quantities of Ag⁺(ICH₂SO₃)⁻ and 18-crown-6, followed by complete evaporation of the water, produced good yield of a very water-soluble product with a sharp melting point. The ¹H NMR spectrum in D₂O showed 2 peaks; integration gave a 20 to 1 ratio for crown to methylene group protons, instead of the expected 12 to 1 ratio. The calculated proton ratio suggested that the product might be a triple-decker crown sandwich complex [Figure 5]. If this were true, the compound would not serve as a good metallocene model, since no bonding sites would be left

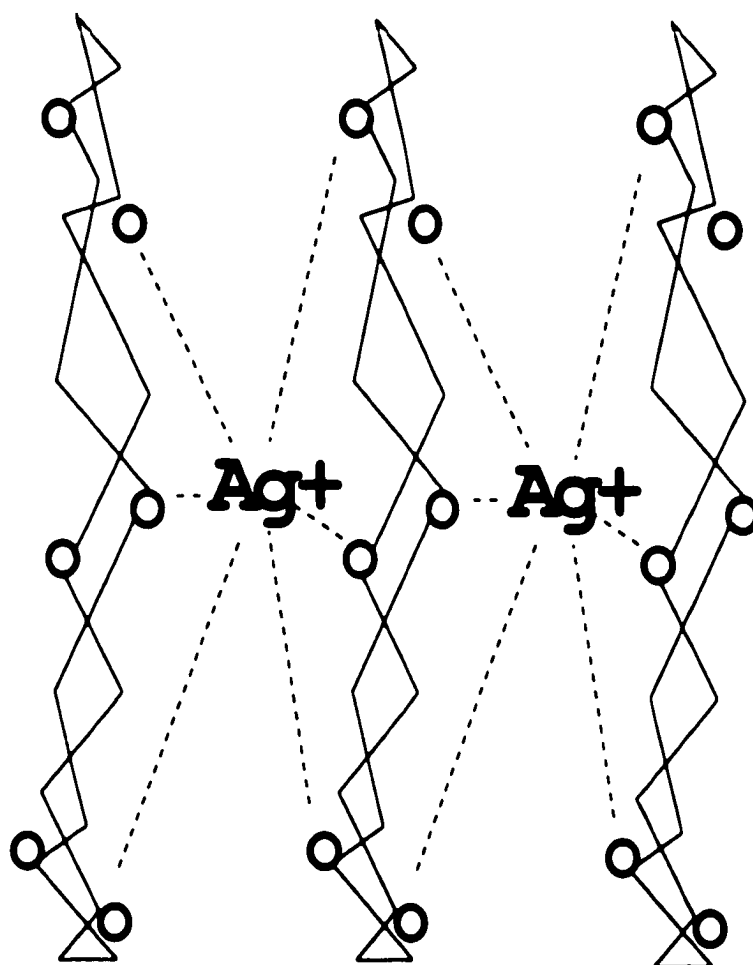
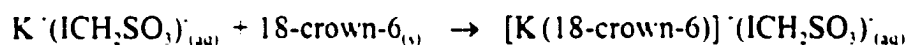
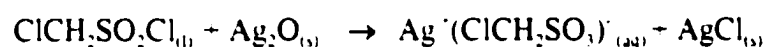


Figure 5. Triple Crown Sandwich, $Ag_2(18\text{-crown-}6)_3$ Cation

available for coordination with a polymer. Triple crown thallium complexes have previously been reported (Farago, 1976), but these are more commonly seen when the metal ion is too large to fit inside the crown cavity. The ionic radius of silver(I) cation is about 0.2 Å smaller than the cavity of 18-crown-6. Attempts to recrystallize the product from an acetone (soluble)/ heptane (insoluble) co-solvent system were less than satisfactory, since the complex broke down into $\text{Ag}^+(\text{ICH}_2\text{SO}_3)^-$ and 18-crown-6.



Nearly equimolar portions of $\text{K}^+(\text{ICH}_2\text{SO}_3)^-$ and 18-crown-6 ether were reacted under conditions similar to the method that had been used to prepare the $[\text{Ag}_2(18\text{-crown-6})]_3^+(\text{ICH}_2\text{SO}_3)_2^-$. The reaction provided a 99.1% yield of product. By ^1H NMR and elemental analyses, the stoichiometry of this adduct was 1:1 (crown ether):(potassium salt). However, no ^{127}I NQR was detected by our Wilks instrument at room temperature.



Even though the yield of the white crystals of $\text{Ag}^+(\text{ClICH}_2\text{SO}_3)^-$ from the reaction was 94.1%, the product failed to give a ^{35}Cl -NQR spectrum using our Decca instrument. Although Cl signals of chloromethanesulfonates are generally weak, results should be reproducible. Three hypotheses were formulated to explain the negative Cl NQR results:

1. Two bottles of $\text{ClICH}_2\text{SO}_2\text{Cl}$ had been stored in the lab for some time (6 years or more). One previously opened bottle was found to have decomposed as witnessed by the formation of two immiscible layers, one of them brown. Due to the very high cost of this substance (over \$10 per gram, when shipping costs are included) it was decided to attempt the reaction using what was

available in the second bottle, a slightly viscous, clear liquid that had been opened but did not appear to have decomposed substantially.

2. The $\text{Ag}^+(\text{ClCH}_2\text{SO}_3)^-$ re-crystallized from the methanol was a hydrate or a methanolate.
3. The synthesis might be faulty, in that the wrong chloride ion from the reagent, $\text{ClCH}_2\text{SO}_2\text{Cl}$, may have been replaced by ^-OH or CH_3O^- under the influence of Ag_2O , giving possible products $\text{Ag}^+(\text{HOCH}_2\text{SO}_3)^-$ or $\text{Ag}^+(\text{CH}_3\text{OCH}_2\text{SO}_3)^-$.

The following plan was devised and carried out in order to determine if a synthesis failure was responsible for the inability to obtain an NQR spectrum.

1. Test the pH of a drop of the new $\text{ClCH}_2\text{SO}_2\text{Cl}$ recently obtained. The pH on the old batch was highly acidic, having a reading between 0 and 1 using pH paper. The newly purchased material gave a pH of 4 in methanol solution. This difference suggested that the older reagent had reacted with the moisture from the atmosphere and could have caused difficulties with the synthesis using Ag_2O . The faulty hydrolysis of the starting material would also have altered the NMR spectra. In the ^1H NMR spectrum, the peak for CH_2Cl might be partially or completely replaced by a peak for CH_2OH . (Unfortunately, Silverstein predicts almost identical chemical shifts for these two functional groups, δ 3.57 and δ 3.56 respectively.) The ^1NMR data of the old $\text{ClCH}_2\text{SO}_2\text{Cl}$ revealed the complicated spectrum of a compound that was partially decomposed. The ^1NMR spectrum of the new $\text{ClCH}_2\text{SO}_2\text{Cl}$ showed

fewer extraneous peaks for protons, and did not appear to include acetic anhydride as a contaminant near δ 2.20 (Aldrich, 1983).

2. Perform a TGA analysis on the product to test for the loss of water upon heating. The TGA of the product from Reaction 14 refuted this hypothesis, since the weight loss was only 0.31% between room temperature and 194 °C.
3. Conduct IR and proton NMR analyses of the product, and compare to the spectra obtained for other chloromethanesulfonates. If the reaction using Ag_2O replaced the chlorine on carbon to give either $\text{Ag}(\text{HOCH}_2\text{SO}_3^-)$ or $\text{Ag}(\text{CH}_3\text{OCH}_2\text{SO}_3^-)$, the IR and the NMR spectra of the product should be clearly different from the spectra of other chloromethanesulfonates produced from sulfites and dihalomethane. The IR spectrum was recorded and found to be quite similar to that of $\text{Ag}^+(\text{ICH}_2\text{SO}_3^-)$, except that an additional weak peak was found at about 1650 cm^{-1} . The ^1H NMR spectrum showed a strong signal for the equivalent methylene protons at δ 4.50, which is the value expected for the $\text{ClCH}_2\text{SO}_3^-$ anion. However, there were also some very weak peaks for other types of protons both upfield and downfield of the D_2O solvent.

CHAPTER IV

CONCLUSIONS

1. A satisfactory procedure has been found to recycle waste insoluble thallium halides into the useful soluble salts, Tl_2SO_4 and Tl_2SO_3 .

2. Halomethanesulfonates are commonly produced from dihalomethanes by nucleophilic substitution reactions using SO_3^{2-} to displace X^- from CH_2X_2 .

The reaction is slow. We have found three ways to expedite the synthesis.

- (a) Since reactants are not soluble in a common solvent, the reaction requires phases to mix slowly over an extended period of time. The reaction is catalyzed by the addition of small amounts of 18-crown-6. However, if the cation is thallium, the products are seriously contaminated by crown ether adducts of the expected salt.
- (b) Reaction time can be further reduced by metal ion assistance using a soft Lewis acid, such as Tl^+ or Ag^+ .
- (c) Tl^+ is superior to Ag^+ , probably because Tl_2SO_3 is more water-soluble than Ag_2SO_3 .

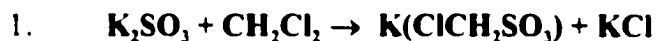
3. It is possible to prepare crowned cation iodomethanesulfonates, $[K(18\text{-crown-}6)]^+(ICH_2SO_3)^-$ and $[Tl(18\text{-crown-}6)]^+(BrCH_2SO_3)^-$, as models for a zirconocene iodomethanesulfonate, $[(C_5H_5)_2(CH_3)Zr][ICH_2SO_3]$, but not for silver, which seems to form a triple-crown adduct, $[Ag_3(18\text{-crown-}6)]_3$.

(ICH_2SO_3)₂. This complex would probably not make a good model since it has no easily accessible sites open for coordination. The product could not be successfully recrystallized.

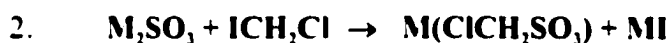
4. Silver ion is known to have the ability to complex halocarbon functional groups in the three silver halomethanesulfonates. This has been confirmed in two of these by crystal structure determinations. However, thallium(I) does not show this ability in its halomethanesulfonates.

CHAPTER V

SUGGESTIONS FOR FUTURE RESEARCH

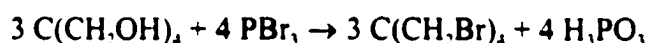


Try reacting potassium sulfite with dichloromethane using a crown-ether catalyst at 1 atm pressure. The reaction would not produce any precipitate, since KCl is soluble, so would be much harder to follow, but the product hopefully would not be contaminated with unusual crown ether adducts such as are found using thallium(I) sulfite.



Reactions similar to those previously conducted could be repeated using reagent grade ICH_2Cl , also available from Aldrich. Incorporation of iodine into the reagent would provide a better leaving group for the substitution reaction, and the byproduct NaI could be easily washed away using acetone.

3. **Synthesis of Ag^+ Complexes of Pentaerythriol Tetrahalides, $\text{C}(\text{CH}_2\text{X})_4$**



Other future work could investigate the unknown Ag^+ and Tl^+ complexes of even more symmetrical, strongly chelating and elimination resistant weakly

coordinating sulfonate anions, $(XCH_2)_3(CCH_2SO_3)^-$, derived by the reaction of (for example) thallium(I) sulfite with the pentaerythritol tetrahalides, $C(CH_2X)_4$.

The tetrachloride and tetrabromide are available from Aldrich, but the tetraiodide, $C(CH_2I)_4$, is not. A literature search was conducted and methods for making pentaerythritol tetrabromide and pentaerythritol tetraiodide were found (Backer et al., 1931; Schurink, 1937). Reaction of $C(CH_2X)_4$ with a deficiency of Ag_2SO_3 should produce a water-soluble product, $C(CH_2X)_3(CH_2SO_3)^- Ag^+$, that could be extracted from excess $C(CH_2X)_4$. An alternate way may be to monohalogenate pentaerythritol, react the product with M_2SO_3 to produce $C(CH_2OH)_3(CH_2SO_3)^- M^+$, then trihalogenate this product. Efforts to synthesize various Ag and K salts of this anion could be made to check for organo-halogen coordination.

Coordination of these ligands to silver should produce ordered structures that are NQR active.

APPENDICES

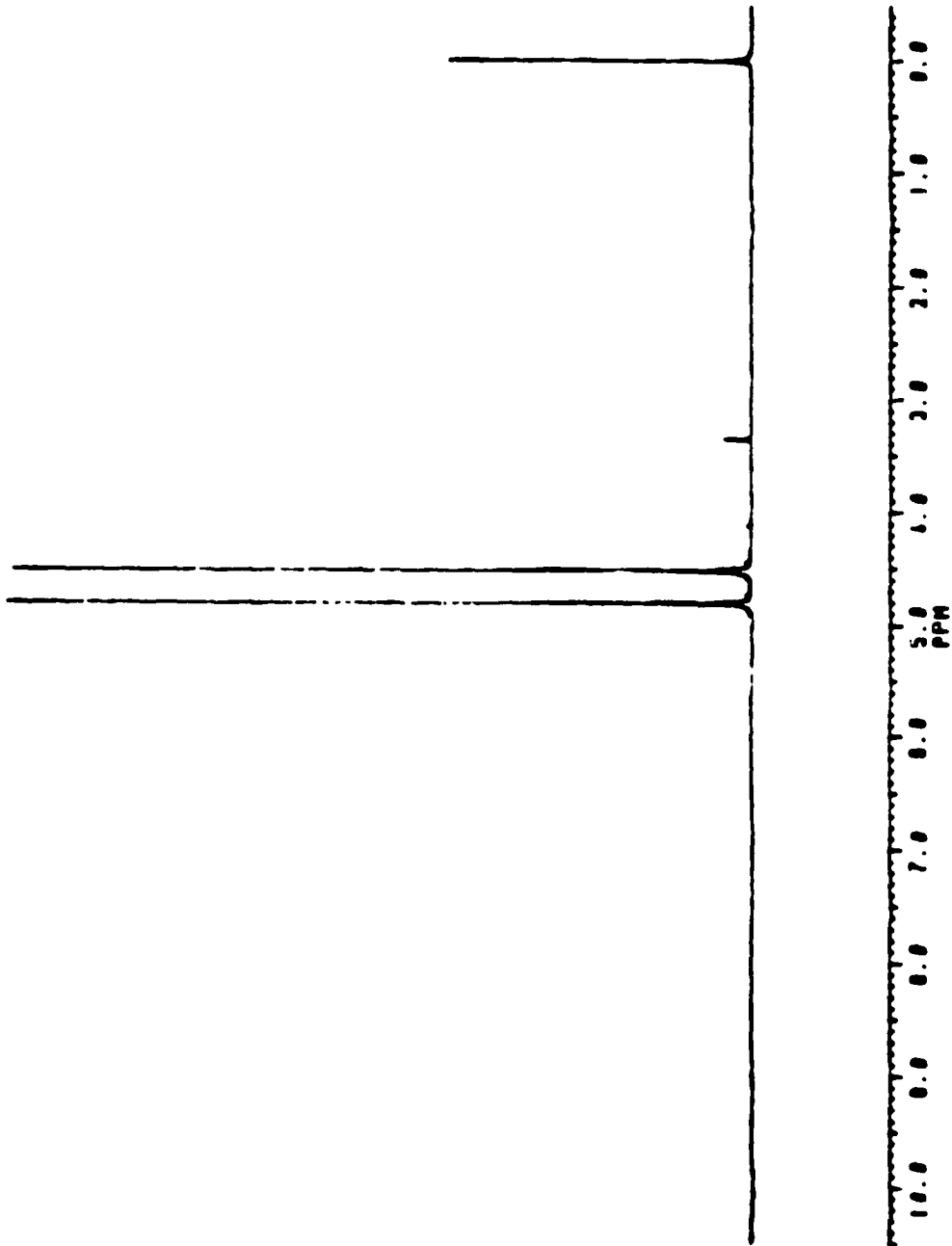
APPENDIX I**REPRESENTATIVE SPECTRA**

	Page
A. ¹H NMR SPECTRA	
1. TlClCH ₂ SO ₃	62
2. TlBrCH ₂ SO ₃	63
3. Tl(18-crown-6)BrCH ₂ SO ₃	64
4. K(18-crown-6)ICH ₂ SO ₃	65
5. Ag ₂ [18-crown-6] ₃ (ICH ₂ SO ₃) ₂	66
B. TGA RESULTS	
1. NaICH ₂ SO ₃ •H ₂ O.....	67


1LCLCH2903 FROM 1L2C03 WITH CLCH2902CL



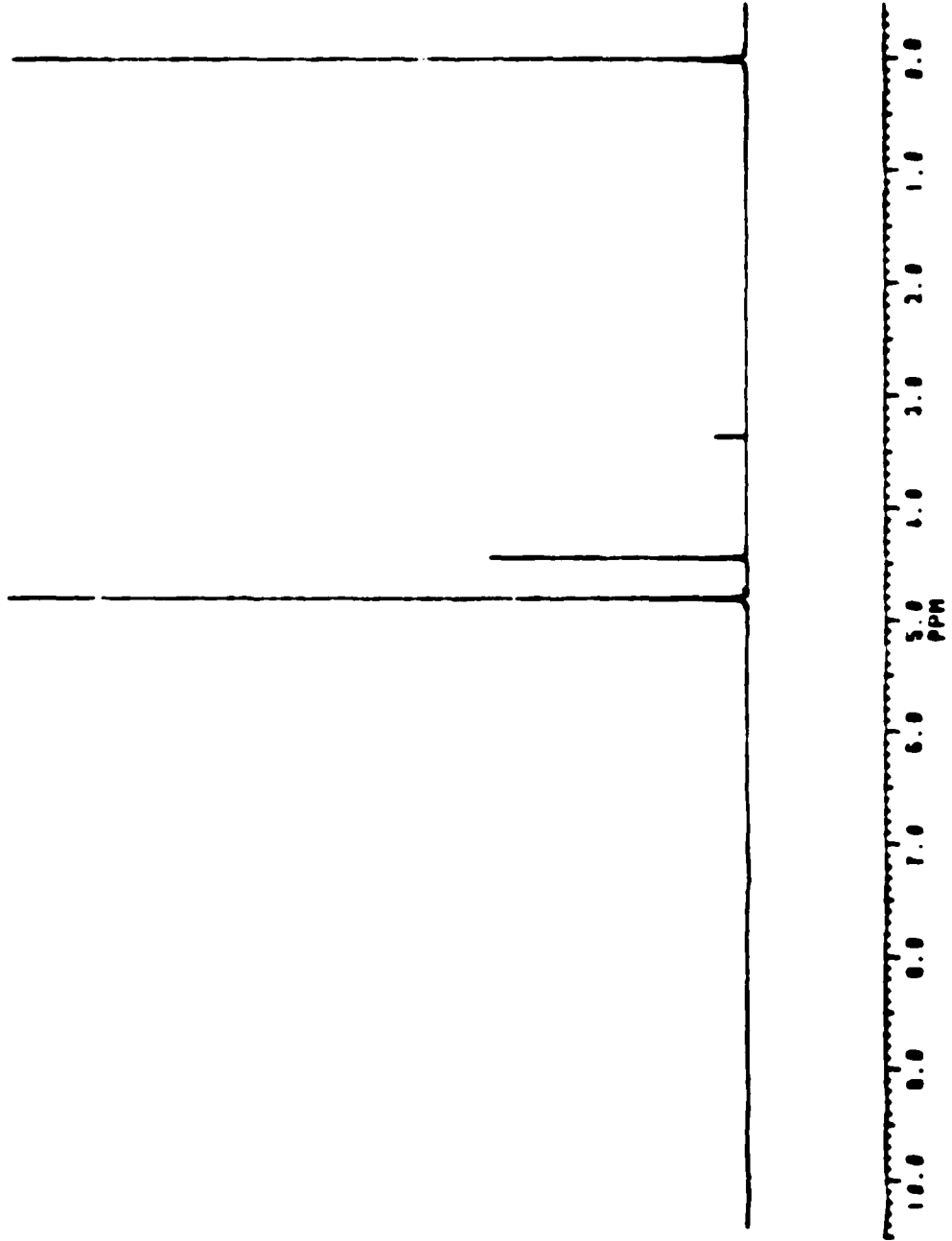
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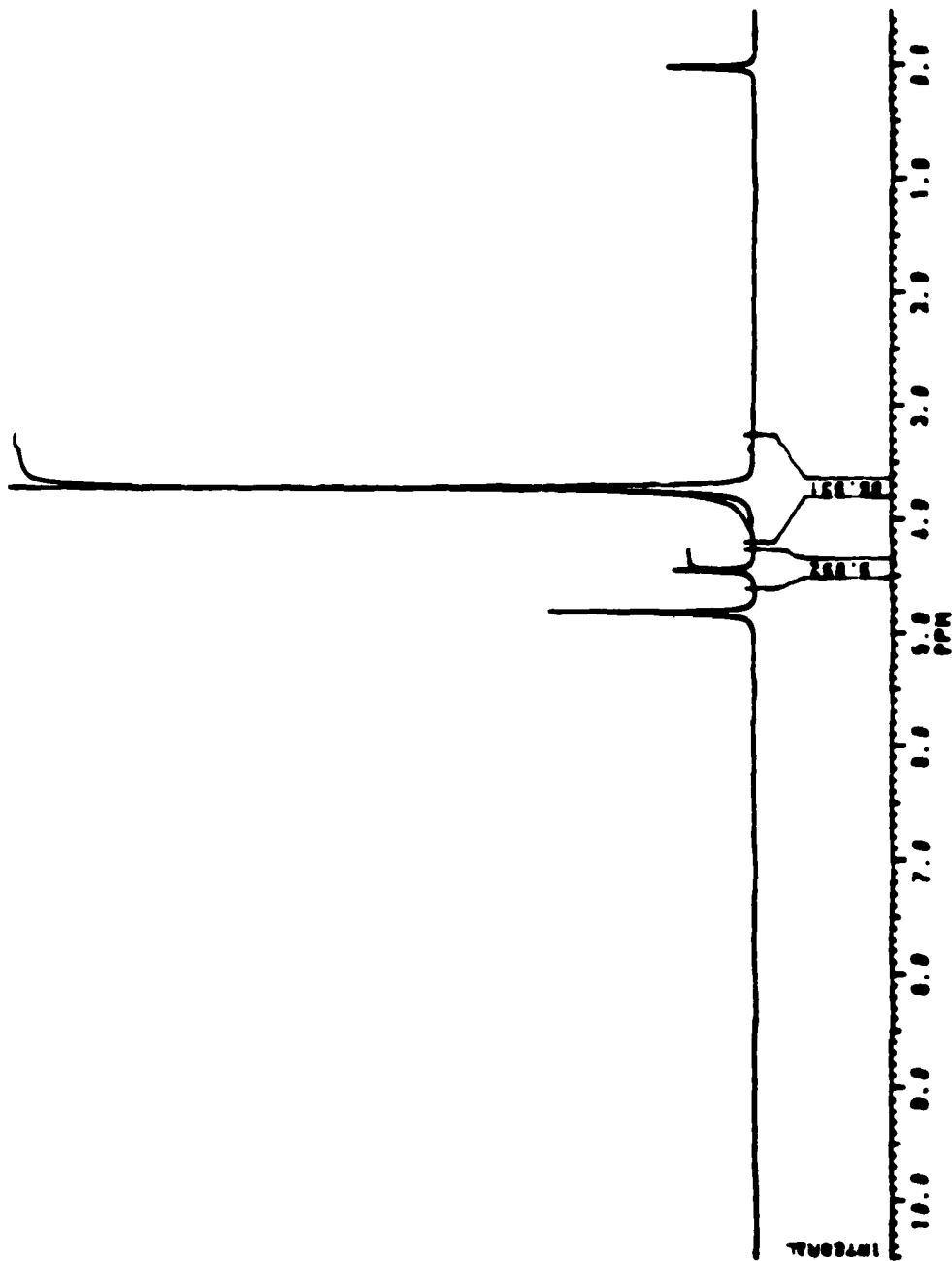
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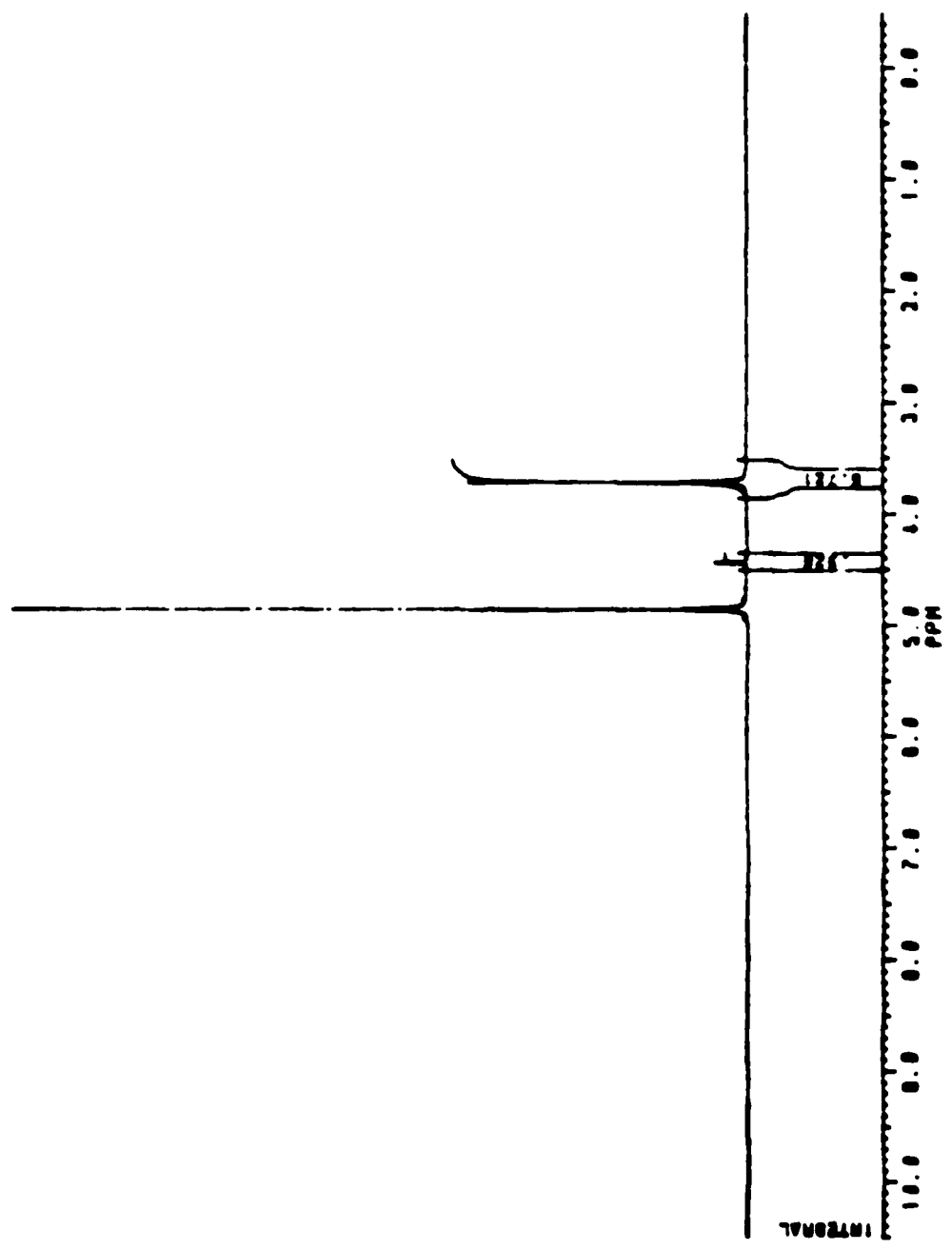
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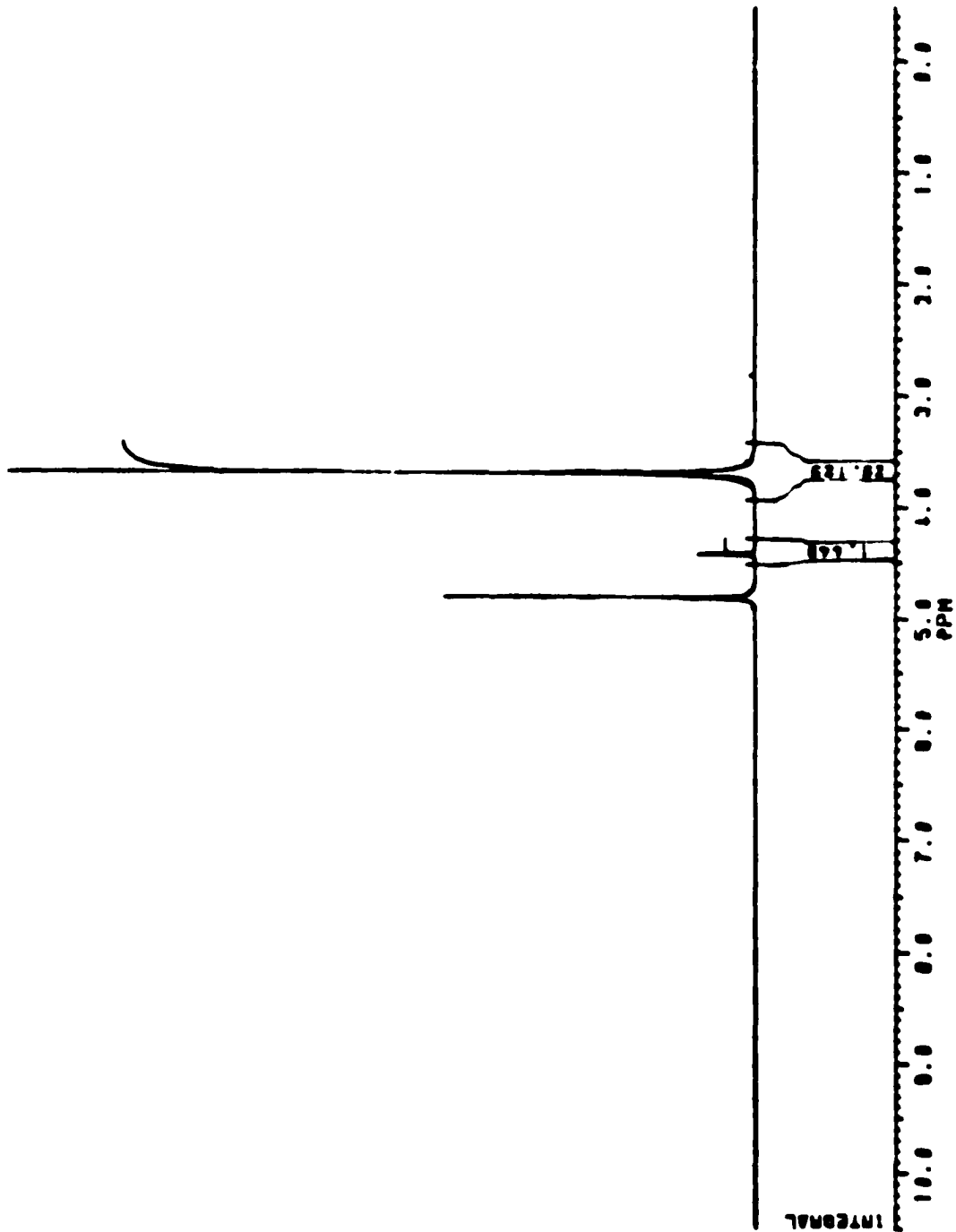
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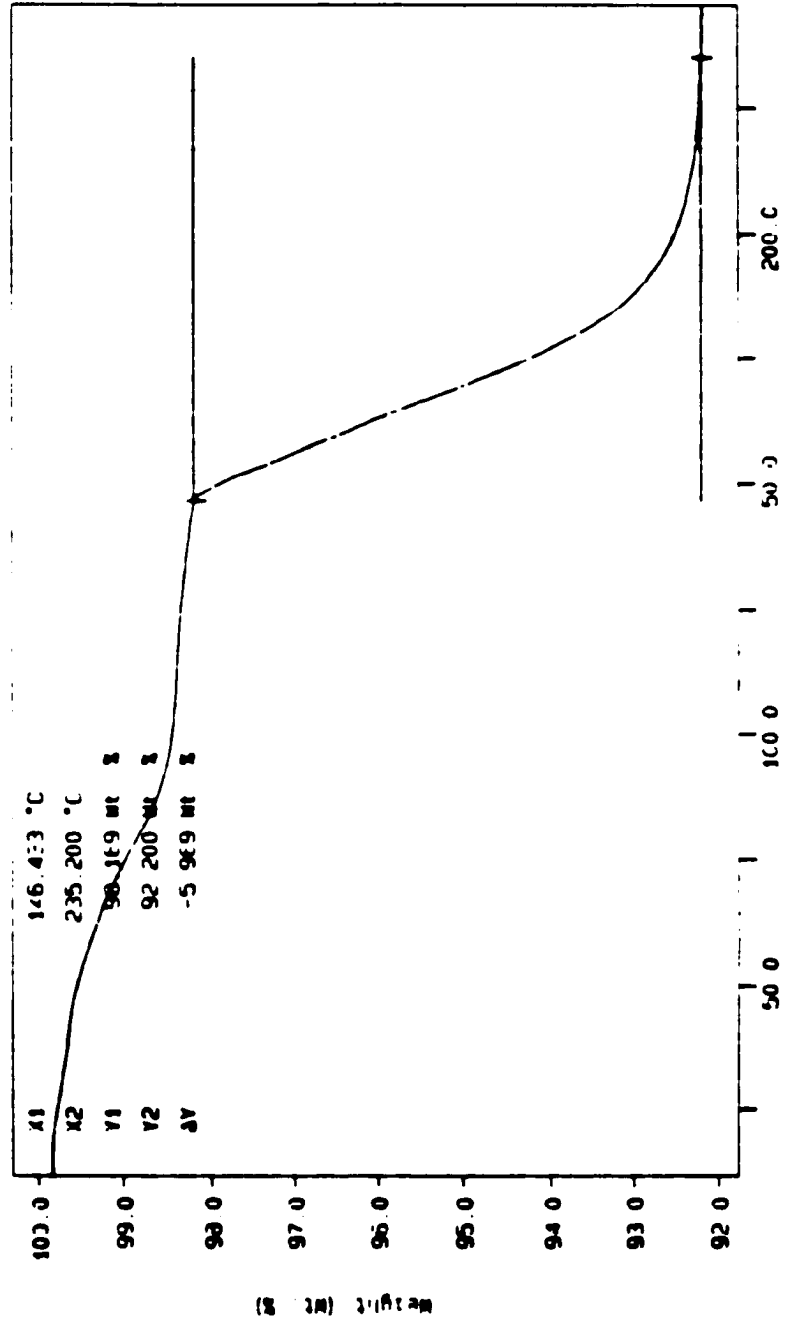
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APPENDIX II

ABBREVIATIONS and SYMBOLS

°C	degrees Celsius	K	Kelvin
atm	atmosphere		
g	gram (s)	mg	milligram (s)
mL	milliliter (s)	cm	centimeter (s)
mol	mole (s)	M	molarity
mmol	millimole (s)	N	normality
mM	millimolar		
Cp	cyclopentadienyl ring, C ₅ H ₅	M ⁺	metal cation
IR	infrared	TGA	thermal gravimetric analyzer
NMR	nuclear magnetic resonance	NQR	nuclear quadrupole resonance
MHz	megahertz	UV	ultraviolet
%	percent	calcd	calculated
π	pi-bound	exptl	experimental
η ^x	number of electrons contributed to pi cloud from p orbitals		
δ	chemical shift, in parts per million		

LITERATURE CITED

Aldrich Library of NMR Spectra, 2nd ed.; Pouchert, C. J., Aldrich Chemical Co:

Milwaukee, WI, 1983, *1*, p 601(A).

Allardt, H.G. Method of Producing Alkali Salts of Iodomethyl Sulphonic Acid, U.S.

Patent 1,867,793, Jul 19, 1932.

Armstrong, D.R.; Edwards, A.J.; Moncrieff, D. J. *Chem. Soc., Chem. Commun.*

1995, 927.

Backer, H.J.; Schurink, H.B.J. *Rec. Trav Chim.* **1931**, *50*, 921-30.

Charbonnier, R.F.; Loiseleur, H. *Acta Cryst.* **1978**, *B34*, 3598.

Colsman, M.R.; Noirot, M.D.; Miller, M.M.; Anderson, O.P.; Strauss, S.H. *J. Am*

Chem. Soc. **1988**, *110*, 6886-8.

Colsman, M.R.; Newbound, T.D.; Marshall, L.J.; Noirot, M.D.; Miller, M.M.; Wulfsberg,

G.P.; Frye, J.S.; Anderson, O.P.; Strauss, S.H. *J. Am. Chem. Soc.* **1990**, *112*,

2349-62.

Dagani, R. *Chem. Eng. News* **1998**, *76*, 49-54.

Deutsch, C.H.; *Finding Flexibility in Plastics: High Technology Could Add New Life to*

an Old Product, New York Times, Sept. 9, 1997, pp C1, C6.

Farago, M.E. *Inorg. Chim. Acta.* **1977**, *23*, 211-3.

Hurlburt, P.K.; Anderson, O.P.; Strauss, S.H. *Can. J. Chem.* **1992**, *70*, 726-31.

Jones, D.C. Synthesis and NQR Studies of Silver Chlorophenolates and

Haloorganosulfonates. Master's Thesis, Middle Tennessee State University,

Murfreesboro, TN, Dec 1989.

Jones, F.E. Comparison of Coordinating Abilities of Corresponding Chlorocarbon and Bromocarbon Anions for Borderline and Soft Metal Ions. Undergraduate Research, Middle Tennessee State University, Murfreesboro, TN, July 1994.

Kravchenko, E.A., Formal Report, Institute of General and Organic Chemistry, Russian Academy of Sciences, Moscow.

Lambert, J.B.; Shizhong Z.; Stern, C.L.; Huffman, J.C. *Science* **1993**, *260*, 1917-8.

Lawrance, G.A. *Chem. Rev.* **1986**, *86*, 17-33.

Lewis, Sr., R. J. *Hawley's Condensed Chemical Dictionary*; 12th ed.; Van Nostrand Reinhold: New York, 1993, p 748.

Long, R.N. *Metallocenes: An Introduction to Sandwich Compounds*; Blackwell Science Ltd: UK, 1998; (a) p 269; (b) p 20; (c) p 3-5; (d) p 10; (e) p 11.

Lupinetti, A.J.; Strauss, S.H. *Inorg. Chem.* **1998**, *11*, 565-95.

Merck Index, 9th ed.; Merck & Co., Inc., 1976, entry nos. 8972, 8974, 8977, & 8983, pp 1193-4.

Möhring, P.C.; Covill, N.J. *J. Organometall. Chem.* **1994**, *479*, 1-29.

Morse, P. M. *Chem. Eng. News* **1998**, *76*, 11-16.

Newbound, T.D.; Colman, M.R.; Miller, M.M.; Wulfsberg, G.P.; Anderson, O.P.; Strauss, S.H. *J. Am. Chem. Soc.* **1989**, *111*, 3762-4.

"Notice to Authors," *Inorg. Chem.* **2000**, *39*, 11A.

Ossenbeck, A.; Hecht, G. Iodomethane Sulphonic Acid and Homologues Thereof, U.S. Patent 1,842,626, Jan 26, 1932.

Pearce, F. *New Scientist* **1996**, *149*, p 14-5.

- (a) Powell, J.; Horvath, M.; Lough, A. *J. Organometall. Chem.* **1993**, 456, C27-C28.
- (b) Powell, J.; Horvath, M.; Lough, A. *J. Chem. Soc., Chem. Commun.* **1993**, 733-5.
- Powell, J.; Horvath, M.; Lough, A. *J. Chem. Soc., Dalton Trans.* **1996**, 1669-77.
- Powell, J.; Lough, A.; Saeed, T. *J. Chem. Soc., Dalton Trans.* **1997**, 4137-8.
- Powell, J.; Horvath, M.; Lough, A.; Phillips, A.; Brunet, J. *J. Chem. Soc., Dalton Trans.* **1998**, 637-45.
- Reed, C.A. *Acc. Chem. Res.* **1998**, 31, 133-9.
- Reese, K.M. *J. Chem. Educ.* **1990**, 67, 1019-21.
- Reese, K.M. *Chem. Eng. News* **1991**, 69, 90-1.
- Reuter, V.B.; Levi, H.W. *Z. Anorg. Allg. Chem.* **1952**, 270, 100-13.
- Rutherford, R.L. Synthesis and NQR Studies of Some Metal Iodomethanesulfonates and *p*-Halobenzenesulfonates. Master's Thesis, Middle Tennessee State University, Murfreesboro, TN, May 1996.
- Schurink, H.B. *Org. Syn.* **1937**, 17, 73-5.
- Senning, A.; Buchholt, H. C.; Bierling, R. *Arzneim.-Forsch. (Drug Res.)* **1976**, 26, 1800-9.
- Seppelt, K. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1025-7.
- Seubert, K.; Elten, M. *Z. Anorg. Allg. Chem.* **1892**, 2, 434-6.
- Silverstein, R.M.; Webster, F.X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley & Sons: New York, 1998; (a) p 168; (b) p 200; (c) p 108; (d) p 139; (e) p 137; (f) p 200.
- Smith, T. L.; Elliott, J. H. *J. Am. Chem. Soc.* **1953**, 75, 3566-70.

Standard Methods for the Examination of Water and Wastewater, 14th ed.; APHA-

AWWA-WPCF: Washington, D.C., 1975, pp 508-9.

Strauss, S.H. *Chem. Rev.* **1993**, *93*, 927-42.

Strauss, S.H. *Chemtracts-Inorg. Chem* **1994**, *6*, pp 1-13.

Van Seggen, D.M.; Hurlburt, P.K.; Anderson, O.P.; Strauss, S.H. *J. Am. Chem. Soc.*

1992, *114*, 10995-7.

White, T.; Toor, I. *JOM* **1996**, *48*, pp 54-8.

Wulfsberg, G. P.; Weiss, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1640-9.

Wulfsberg, G. P. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000;

(a) Ch. 2; (b) Chs. 2 & 5; (c) pp 204 –214.

Wulfsberg, G.P.; Parks, K.D.; Rutherford, R.; Jackson, D. J.; Jones, F.E.; Derrick, D.;

Ilisley, W.; Strauss, S. H.; Miller, S.; Anderson, O.P.; Babushkina, T.A.;

Gushshin, S.I.; Kravchenko, E.A. *Weakly Coordinating Anions: NQR Studies of*

Modes of Bonding of Surface Halogen Atoms to Silver Ion, manuscript in

preparation.

(a) Xie, Z.; Bau, R.; Reed, C.A. *Angew. Chem. Intl. De Ed.* **1994**, *33*, 2433-4.

(b) Xie, Z.; Jelinek, T.; Bau, R.; Reed, C.A. *J. Am. Chem. Soc.* **1994**, *116*, 1907-13.

Xie, Z.; Manning, J.; Reed, R.; Mathur, R.; Boyd, P.D.W.; Benesi, A.; Reed, C.A.

J. Am. Chem. Soc. **1996**, *118*, 2922-8.

Xie, Z.; Wu, B.M.; Mak, T.C.W.; Manning, J.; Reed, C.A. *J. Chem. Soc., Dalton Trans.*

1997, 1213-17.