SYNTHESIS AND INVESTIGATION OF NICKEL(II)

4-SUBSTITUTED 2,6-DICHLOROPHENOLATES

David B. M^{C}Corkle, Jr.

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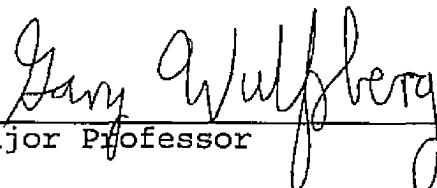May, 1995

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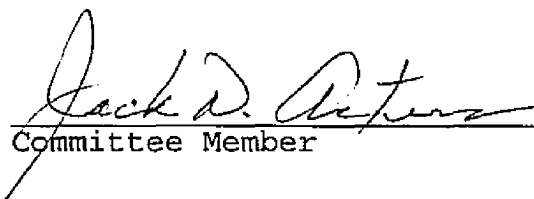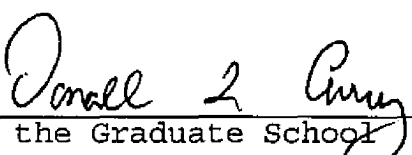
4-SUBSTITUTED 2,6-DICHLOROPHENOLATES

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Abstract

SYNTHESIS AND INVESTIGATION OF NICKEL(II)

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Monodentate or bidentate ligands (L) of nitrogen and phosphorus were used in the synthesis of nickel(II) complexes of the type $M(OC_6H_2Cl_2X)_2(L)_n$ (X= Cl, Br, H). Nuclear quadrupole resonance (NQR) spectroscopy was utilized to examine the secondary bonding of ortho-chlorines of 2,4,6-trichlorophenolate, 2,6-dichlorophenolate, and 4-bromo-2,6-dichlorophenolate ions to the nickel in the presence of various ligands. Trends in the strength of the M-Cl interaction as a function of M were explained by crystal field theory: they are largely determined by the octahedral site stabilization energy (OSSE) of the metal ion. Steric effects and strong ligand fields also play a role. Difficulties in forming complexes using both monodentate and bidentate phosphorus ligands may indicate only a small role for back bonding, while the presence of extra ligands capable of forming normal strength bonds to nickel(II) can prevent secondary bonding altogether. Secondary bonding in octahedral (N,N,N',N'-tetramethyl-1,2-ethanediamine)bis-(2,4,6-trichlorophenolato-O,Cl)nickel(II) and pentacoordinate tris(pyridine)bis(2,4,6-trichlorophenolato-O)nickel(II) is discussed.

David B. M^CCorkle, Jr., died suddenly on the night of October 20-21, 1994, when this dissertation was basically complete; his major professor, Dr. Gary Wulfsberg, added the final touches to the dissertation of this true scholar. Middle Tennessee State University is awarding the Doctor of Arts degree posthumously to David B. M^CCorkle, Jr. on May 13, 1995.

ACKNOWLEDGMENTS

I would like to thank Dr. Gary Wulfsberg for his Jobian patience, and persistent encouragement during the course of this project, its preceding classwork, and subsequent lingering conclusion. Also, I would like to thank the faculty and staff members of the Department of Chemistry and Physics at Middle Tennessee State University for their support of this project. The especially noteworthy include Dr. Howard for NMR help and computer assistance, Drs. Ilsley, Woods, and G. Clark for helpful courses, Dr. Hutchinson for financial support, and Ann Smith for minimizing the little things that can be so frustrating.

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CHAPTER I

INTRODUCTION

Inert solvents and gases have long been assumed by synthetic chemists to merit their names. These long known chemicals are now being seen in a new light. Neil Bartlett dispelled the notion of the inertness of the noble gases in 1962 with the production of several xenon fluorides (1). Among solvents, halocarbons have long been assumed to be inert to the extent that the outer electrons of a halogen bonded to carbon were not available for additional interactions. Evidence from spectroscopy, x-ray crystallography, and other sources has been accumulating since 1971 that these supposedly inert halogens are able to participate in limited interactions, termed "secondary bonding", with metals (2, 3).

The extremely weak nature of the secondary bonding can only be reliably characterized by two methods, X-ray crystallography and NQR spectroscopy. The extent of ligand interaction in any ligand-metal system is generally charac-terized by x-ray crystallography (4): the length of second-ary bonds range from only slightly greater than a single halogen-metal bond length to slightly less than the sum of the non-bonded Van der Waals radii of the atoms. In the solid state, secondary bonding may be either intermolecular or intramolecular. The 4-substituted chlorophenolate ions

1

2

2,4,6-trichlorophenolate (tcp), 2,6-dichlorophenolate (dcp), and 4-bromo-2,6-dichlorophenolate (Br-dcp) bond to many transition metals through the phenolic oxygen ion and through intramolecular secondary bonds involving one of the two ortho-chlorines (Figure 1).

Chlorophenolate anions bond to a transition metal through the phenolic oxygen atom before an ortho chlorine can be maneuvered and maintained in a position for secondary bonding to the metal. The secondary bond results primarily from the couloubic attraction of a pair of chlorine electrons in an unhybridized p orbital into the region of non-bonding d-orbitals of the metal (5). The C_2-Cl bond does not significantly bend or weaken to accommodate the secondary bond. The entire ligand can rotate around the C_1-O bond to minimize or maximize the length and strength of the M-Cl secondary bond. Rotation which removes Ni from the plane of the chlorophenolate ring increases the M-Cl secondary bond distance. When the metal and the ring are coplanar, alignment for secondary bonding primarily requires that the phenolic angle M-O-C_1, which is the most flexible, opportunistically places the ortho-chlorine near the metal. Enlarging the angles C_2-C_1-O or M-O-C_1 above 120^0 also increases the secondary bond distance.

The secondary bond itself, as before, ranges in length from the non-reactive sum of the Van der Waals radii to the average normal M-Cl bond for each metal: nickel(II), 2.441 Å; cobalt(II), 2.414 Å; copper(II), 2.354 Å; molybdenum(II),
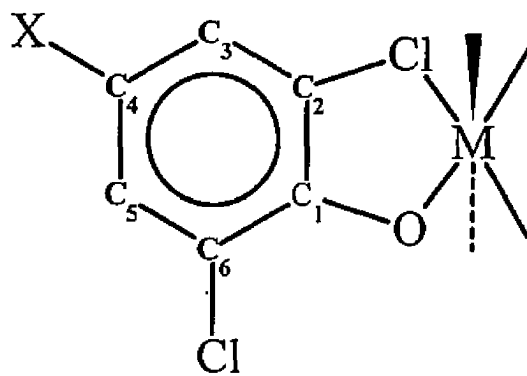
Figure 1.   Secondary Bonding by a Chlorophenolate Ortho
Chlorine

2.473 Å; and silver(I) 2.51 Å (14). The crystallographic-
ally-determined M-Cl distance minus the average normal bond
distance in an octahedral environment gives what shall be
called the excess M-Cl bond distance. The excess M-Cl
distance approaches zero as the secondary bond strengthens
and resembles a normal bond. An excess bond distance of 1.0
Å corresponds to the transfer of less than 0.01 electron
from the chlorine to the metal and is considered as the
lower limit of chemically significance secondary bonding.

Secondary bonding by halocarbons is also amenable to
study by nuclear quadrupole resonance (NQR) spectroscopy.
The use of NQR is limited to anhydrous, crystalline
materials. However, NQR is sensitive to very minor
interactions even in compounds which have small-sized
crystals or which are otherwise unsuitable for
crystallography. According to the approximate Townes-Dailey
treatment, the ^{35}Cl NQR frequency in megahertz (MHz) of a
coordinated chlorophenolate ortho-chlorine equals the higher
frequency of the other, non-coordinated ortho chlorine minus
27.4 times the number of electrons transferred (5, 6). This
large downward frequency shift makes NQR very useful in
detecting ortho-chlorine coordination. When present, the
NQR frequency of the noncoordinating para-chlorine, Cl-4,
cannot be distinguished from the noncoordinating ortho
chlorine, since frequency differences of these two
noncoordinating chlorines are smaller than 0.7 MHz. The
para-chlorine frequency can be identified by substituting

bromine in the para position. The ortho-chlorine frequencies, now alone, remain virtually unchanged.

Among chlorophenolates, the sodium salts of the 2,4-dichlorophenolate and 2,4,5-trichlorophenolate anions are important industrial intermediates in the production of herbicides and biocides such as 2,4-dichlorophenoxyacetic acid (2,4-D), hexachlorophene, 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), and 2(2,4,5-trichlorophenoxy)propionic acid (Silvex). These compounds have been of environmental concern because of dioxin contamination. Dioxins are a family of aromatic compounds which contain the pair of oxygen bridges found in 1,4-dioxane. Chlorinated dioxins derived from chlorophenols are environmentally persistent and toxic to certain animals. The chemical stability of aromatic chlorocarbons makes disposal of these materials a problem (7).

The cation in a chlorophenolate salt influences its properties including its decomposition. Sodium 2,4,5-trichlorophenolate decomposes above 230^0C by elimination of ortho-chlorines into products which include the teratogenic toxin 2,3,7,8-tetrachlorodibenzodioxin (dioxin) (8). Silver(I) and copper(I) trichlorophenolates do not decompose into dioxin: heating silver or copper trichlorophenolates eliminates para-chlorines and produces poly(2,6-dichlorophenylene oxides) (9). Cation-ortho-organochlorine interactions could conceivably direct the elimination of an ortho- rather than the para-chlorine in some chlorophenolate

salts. Complexation which weakens the chlorophenolate C-Cl bond without strengthening the metal-halogen bond to the point of oxidative addition can provide insight into possible mechanisms for catalytic degradation of aromatic chlorine compounds by nucleophilic aromatic substitution.

The transition metals known to from chlorophenolate complexes include iron(III), cobalt(II), nickel(II), copper(I), copper(II), silver(I), zinc, and mercury(II) (10). In the present study, borderline hard/soft base nitrogen-donor ligands were chosen to complement the interaction of the borderline acid nickel(II) and the coordinating organochlorine, which is probably a borderline base. These nitrogen-donor ligands included pyridine (py), 2,2'-dipyridyl (dpy), and 1,10-phenanthroline (phen). Additionally, ligands utilizing phosphorus donor atoms were used: 1,2-bis(diphenylphosphino)ethane (diphos), triphenylphosphine (Ph_3P), and methyldiphenylphosphine ($MePh_2P$). Phosphorus ligands depend upon back-bonding for their stability. All ligands used in this study are depicted in either Figure 2 or Figure 3. Abbreviations are located in the appendix.

Secondary bonding in nickel(II) coordination complexes of the formula $M(tcp)_2L_n$ which are the focal point of this study is expected to depend upon electrostatic effects of the ligand, steric hindrance by bulky ligands, and also upon the large octahedral site stabilization energy (OSSE) of the d^8 Ni^{+2} metal ion. Tolman (11) examined various R_3P ligands

Pyridine   2,2'-Bipyridyl

py   bipy   1,10-Phenanthroline

                                                          phen

N,N,N',N'-Tetramethyl-1,2-

ethanediamine

TMED   N,N,N',N",N"-Pentamethyl-

                                  1,4,7-triazaheptane
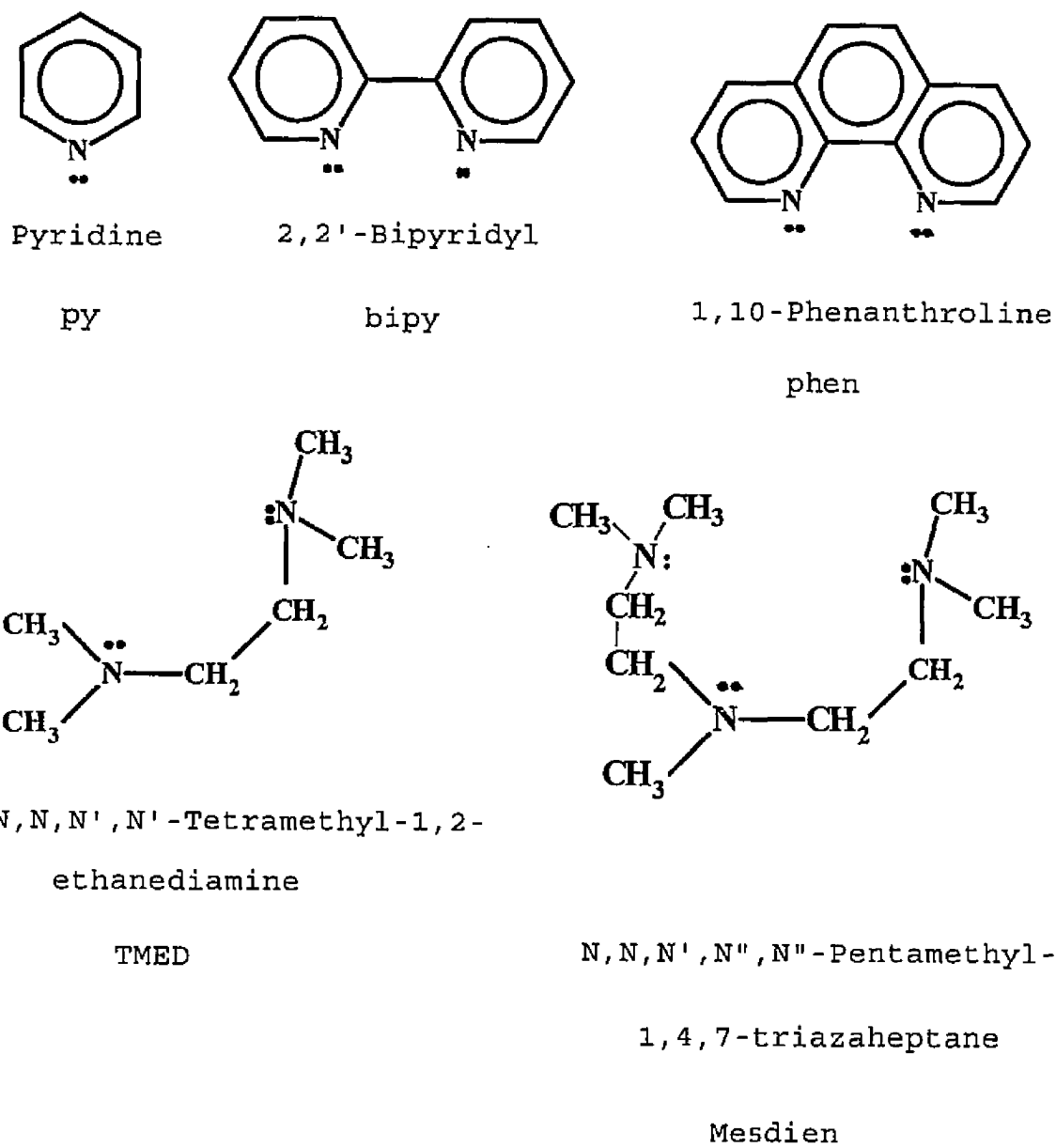
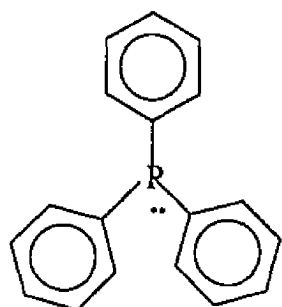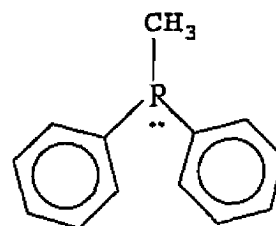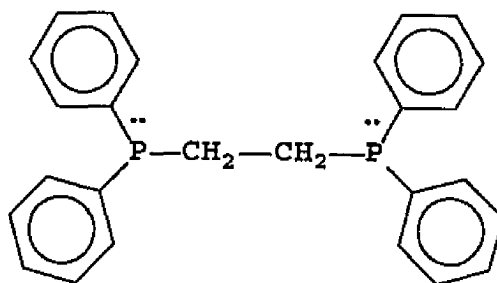   Mesdien

Figure 2.   Nitrogen-Donor Ligands in This Work

Triphenylphosphine   Methyldiphenylphosphine

Ph3P   MePh2P

1,2-Bis(diphenylphosphino)ethane

diphos

Figure 3. Phosphorus-Donor Ligands in This Work

and determined that the increasing bulk of a ligand adversely effects the stability of complexes. Habiyakare cited steric hindrance of large ligands for prohibiting the optimal tetrahedral arrangement of copper(I) compounds. Dimers and polymers resulted from the use of bulky 2-picoline as a ligand according to Habiyakare (12).

Barring steric hindrance and electronic effects, the factors affecting ligand coordination are described in terms of the octahedral site stabilization energy (OSSE). A rapid review of crystal field theory and nomenclature is appropriate.

An arbitrary 3-dimensional Cartesian coordinate system centered on the metal atom can be oriented so that six evenly distributed ligands approach the metal along the axes. The approach of the electron-rich ligands removes the degeneracy of the metal d-orbitals. The axial $d_{(x2-y2)}$ and the $d_{(z2)}$ orbitals are raised in energy. Less energy is required by d-electrons in the $d_{(xz)}$, $d_{(yz)}$, and $d_{(xy)}$ orbitals which are not along the axes and do not repel the ligands. When unopposed by the $d_{(x2-y2)}$ and the $d_{(z2)}$ orbitals the ligands are able to bond to the metal in a more stable, lower energy, bond. The increase in ligand bond strength compared to the bond strength formed when the ligand is opposed by equally distributed charges in a hypothetical spherical compound with equal opposing charge distribution is referred to as the crystal field stabilization energy (CFSE). The crystal field splitting,

10 Dq, the difference in energy between the two groups of degenerate d-orbitals, corresponds to the frequency of the lowest energy absorption transition in the near-infrared or visible spectrum (13).

Crystal field stabilization energies of different geometries can be compared to each other. The difference between the CFSE in the energetically preferred octahedral complex and the CFSE of another ligand orientation, often tetrahedral, is called the octahedral site stabilization energy (OSSE). The difference between the octahedral CFSE and the tetrahedral CFSE, appropriately converted, is highest (8.45 Dq) for d^8 ions like Ni^{+2}. This means that nickel(II) shows the highest preference for an octahedral environment. The completion of octahedral coordination in $Ni(tcp)_2L_2$ however, requires the formation of secondary bonds to ortho chlorines.

In summary, secondary bonds should be possible with M-Cl distances spanning the entire range between a normal metal-Cl bond and the combined Van der Waals radii of the two atoms (14). This work will continue the investigation of M-Cl bonding in nickel(II) 2,6-dichlorophenolates and 2,4,6-trichlorophenolates in an attempt to expand the known range of M-Cl bond distances, determine the effects on the corresponding NQR frequency, and compare the results with nickel to previous results involving other metals.

CHAPTER II

DISCUSSION

A recent search (10) of the Cambridge Crystallographic Database (1991 version) for chlorophenolate-metal bonding, discounting chlorinated catechols because O,O- chelation competitively eliminates O,Cl- chelation, found twelve transition metal complexes which fall within reasonable limits for excess M-Cl distance and can be considered to display secondary bonding to ortho-chlorine(s) (Table 1). These complexes exhibit considerable diversity and establish a necessary foundation to any search for new complexes with secondary bonding to chlorophenolate ions.

Complex methoxy bridged cubane structures, $[M(tcp)(OMe)(MeOH)]_4$, involving ortho-chlorine coordinating chlorophenolates have been synthesized with cobalt(II) (15) and nickel(II) (16, 17) (Figure 4). The two crystallographically independent M^{2+} ions in the cubane structures have distorted octahedral coordination formed by three μ_3-bridging methoxy groups. The remaining apical position is occupied by methanol. The methanolic hydrogen has been vaguely located and appears to H-bond to the adjacent axial phenolic oxygen. The ortho-chlorine of the chlorophenolate completes the octahedron around each metal(II) ion. The cobalt(II)-chlorine bond distance is about 2.63 Å. Similar coordination was obtained with Br-dcp. The ^{35}Cl NQR

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Table 1. Selected Structural Parameters for Describing
Metal-Organochlorine Interactions in o-Chlorophenolates.[a]

Compound	R(M-Cl), Å	$\angle$M-Cl-C, degrees	Reference
[Co(tcp)(OMe)(MeOH)]$_4$	2.624	92.6	(15)
	2.636	94.6	
[Ni(tcp)(OMe)(MeOH)]$_4$	2.483	93.7	(17)
	2.503	95.6	
	2.530	94.5	
	2.506	95.4	
[M(tcp)(OMe)(MeOH)]$_4$	(M = 5:1 Cu:Zn)		[b]
	2.821	90.7	
	2.755	90.3	
	2.742	91.8	
	2.821	89.9	
[Cu(tcp)(OMe)quin]$_2$	2.987	85.0	(19)
Ni(tcp)$_2$(TMED)	2.586	94.8	(10)
	2.637	93.9	
Co(tcp)$_2$(Meim)$_2$	3.100	86.5	(25)
	3.367	82.8	
Cu(tcp)$_2$(py)$_2$	2.916	87.9	(21)
	2.915	87.6	(23)
Cu(tcp)$_2$(im)$_2$·H$_2$O	2.847	92.2	(20)
Ag(2,4,5-tcp)	3.003	91.9	(27)
Ag(tcp)(Ph$_3$P)$_2$	3.160	90.2	(4)
Ph$_3$PAu(pcp)	3.153	89.0	[c]

Table 1 (continued)

PhHg(2-Cl-4-BrC$_6$H$_3$O)   3.023   89.4   d

a. Abbreviations: tcp = 2,4,6-trichlorophenolate; 2,4,5-
    tcp = 2,4,5-trichlorophenolate; pcp =
    pentachlorophenolate; quin = 8 hydroxyquinoline; im =
    imidazole; Meim = N-methylimidazole; TMED = 1,2-
    bis(dimethylamino)ethane; py = pyridine.

b. Yablokov, Yu. V.; Simonov, Yu. A.; Yampol'skaya, M. A.;
    Matuzenko, G. S.; Voronkova, V. K.; Mosina, L. V. *Russ.
    J. Inorg. Chem. (Engl. Transl.)* **1980**, *25*, 1364.

c. Kuz'mina, L. G.; Struchkov, Yu. T. *Koord. Khim.*, **1988**,
    14, 1262-1267.

d. Kuz'mina, L. G.; Bokii, N. G.; Struchkov, Yu. T.;
    Kravtsov, D. N.; Golovchenko, L. S. *J. Struct.
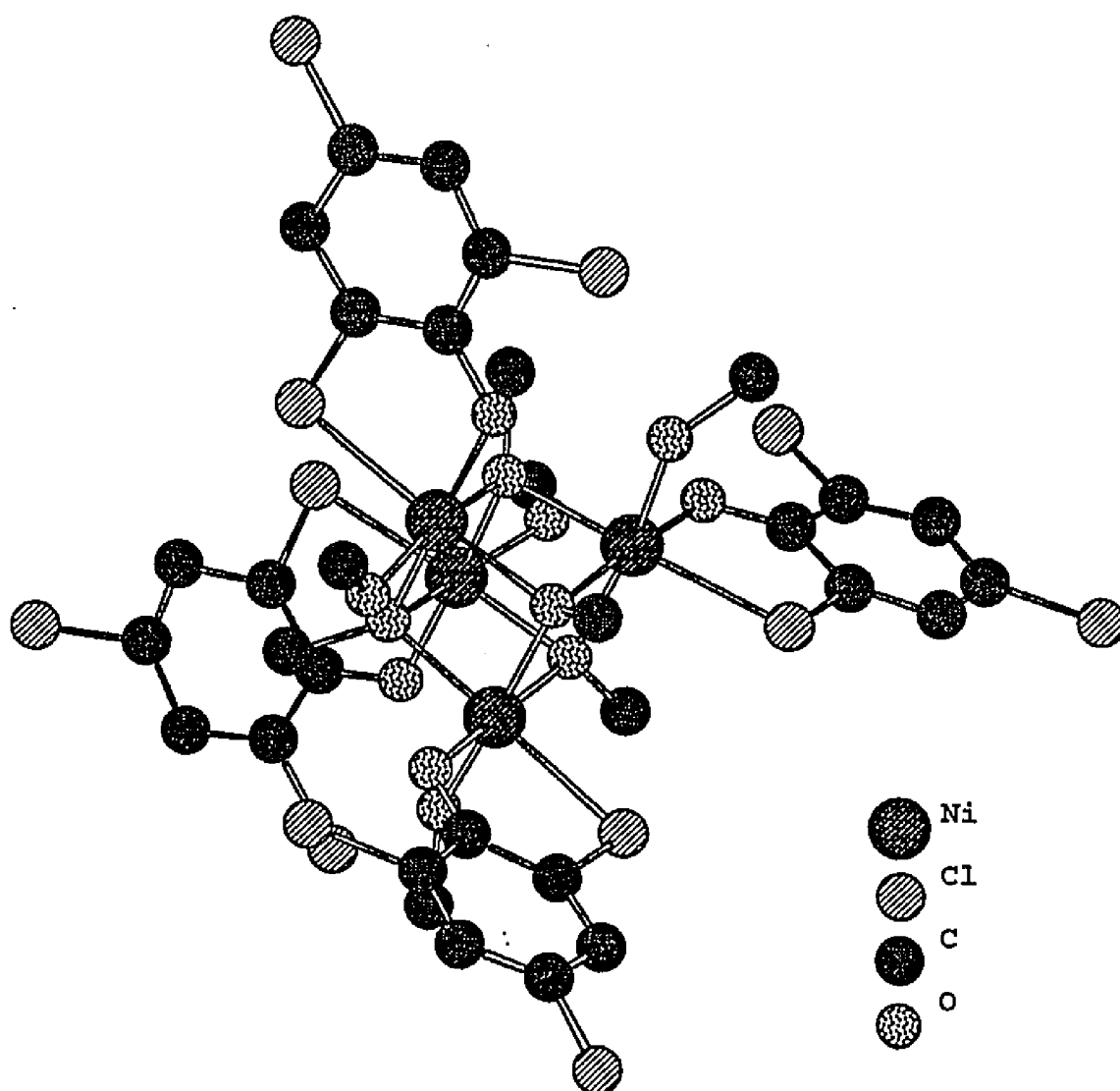   Chem. (Engl. Trans.)*, **1973**, *14*, 463-468.

●	Ni
◑	Cl
●	C
○	O

Figure 4. The Methoxy-Bridged Cubane Structure of

$[Ni(OCH_3)(CH_3OH)(tcp)_4]$

spectrum of [Co(tcp)(OMe)(MeOH)]$_4$ demonstrates a difference of up to 3 MHz between the frequency of the coordinating and noncoordinating ortho-chlorines on each chlorophenolate and corresponds to the secondary donation of about 0.1 electron to the metal (18). The corresponding nickel(II) cubane complex failed to give an NQR spectrum (10).

When the tetranuclear complex [Cu(tcp)(OMe)(MeOH)]$_4$, interacts with an equimolar amount of quinoline, the methanol molecules are replaced by quinoline and the product is the compound [Cu(tcp)(OMe)(quin)]$_2$. Two oxygen atoms of the methoxo group, the nitrogen atom of the quinoline molecule, and the phenolic oxygen atom are located in the base of the pyramid with the ortho-chlorine of the chlorophenolate at the apex of the pyramid. The Cu-Cl distance is 2.983(6) Å (19). Two bridging methoxo groups link the Cu^{+2} ions in the dimeric crystal.

Two secondary bonds per copper(II) atom complete the distorted octahedral complex Cu(tcp)$_2$(im)$_2$.H$_2$O (20). The two imidazole rings and phenolic oxygen atoms occupy the equatorial plane in a trans configuration with an ortho-chlorine from each chlorophenolate bonding from either above or below the metal. The tetrameric crystals of bis(2,4,6-trichlorophenolato)bis(imidazole)copper(II) monohydrate are held together by hydrogen bonds from one water molecule to two nitrogen and to two phenolic oxygen atoms on four separate metal complexes.

Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) forms monomeric crystals which are not connected by H-bonds. As above with Cu(im)$_2$(tcp)$_2$, the pyridine ligands occupy the equatorial plane in a trans configuration with the phenolic oxygens. Ortho-chlorines secondarily bond to the metal from above and below the equatorial plane (21).

Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) and bis(2,4,6-trichlorophenolato)bis(imidazole)copper(II) monohydrate demonstrate the importance of NQR in conjunction with x-ray crystallography and other techniques used to assign structures. The diffuse reflectance spectrum of Cu(tcp)$_2$(py)$_2$ was used to assign a tetrahedral conformation (22). The C-Cl bond distance in Cu(tcp)$_2$(im)$_2$.H$_2$O was considered too long for "semi-coordinated" bonding (23). In opposition to these conclusions, it was found that both complexes satisfy the NQR criteria for identifying secondary bonding (24).

Cobalt(II) forms a purple, monomeric crystal with 2,4,6-trichlorophenolate and methyl imidazole, Co(tcp)$_2$-(Meim)$_2$. The basal plane of the tetragonal pyramid contains linkages to both phenolic oxygens, but unlike the copper(II) complexes, the solitary ortho-chlorine coordination is in the basal plane. Methyl imidazole occupies the apex of the pyramid. The square pyramidal complex appears octahedral due to the ortho-chlorine from the remaining chlorophenolate which occupies a position 3.3 Å below the basal plane (25);

the NQR spectrum shows that any secondary bonding to this chlorine is very weak at best.

Van Landschoot, van Hest, and Reedijk synthesized Co(II), Ni(II), Cu(II), and Zn(II) 2,4,6-trichlorophenolates coordinated by imidazole, N-methylimidazole, and 1,2-dimethylimidazole (26). The hydrated complexes were prepared in water and acetone; anhydrous complexes were produced from the hydrated complexes by heating. No chlorine coordination was observed. The monomeric crystals of Ni(tcp)$_2$(Meim)$_2$.3H$_2$O and Ni(tcp)$_2$(Me$_2$im)$_2$.4H$_2$O become amorphous after losing water in a vacuum at 80^0 C. The hydrated complexes decomposed and the amorphous forms melted below 212^0 C. Relatively low melting points are an indication for the monomeric nature of the complex. Nickel and imidazole combined under these conditions produce the complex cation [Ni(im)$_6$]$^{2+}$.

In conjunction with this work Richardson and Zaghonni determined the crystal structure of two nickel 2,4,6-trichlorophenolate complexes (27). Figures 5 and 6 show the structures of [Ni(TMED)(tcp-O,Cl)$_2$] and [Ni(py)$_3$(tcp)$_2$].

The tcp ligands are chelated to the nickel in [Ni(TMED)(tcp-O,Cl)$_2$], with the oxygens *trans* and the chlorines *cis* in the octahedron; this is in contrast to the (poorly-refined and incompletely-reported) structure of the copper(II) analogue, Cu(TMED)(tcp-O,Cl)$_2$, in which the oxygens are *cis* and chlorines *trans* (28). The Ni-Cl distances, 2.586(2) and 2.637(2) Å, are somewhat longer than
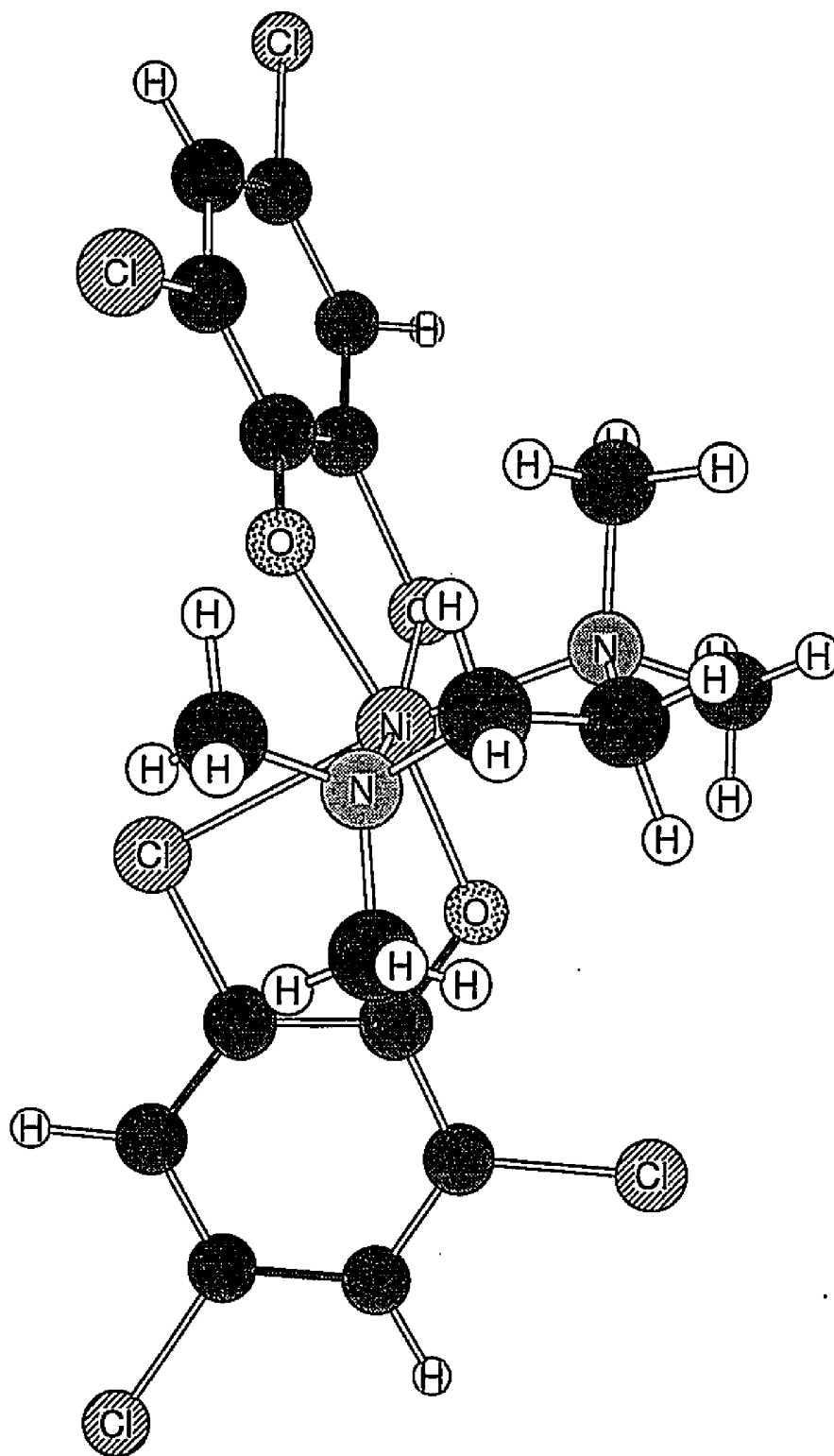
Figure 5. Molecular Structure of [Ni⁻(TMED)(tcp)₂]

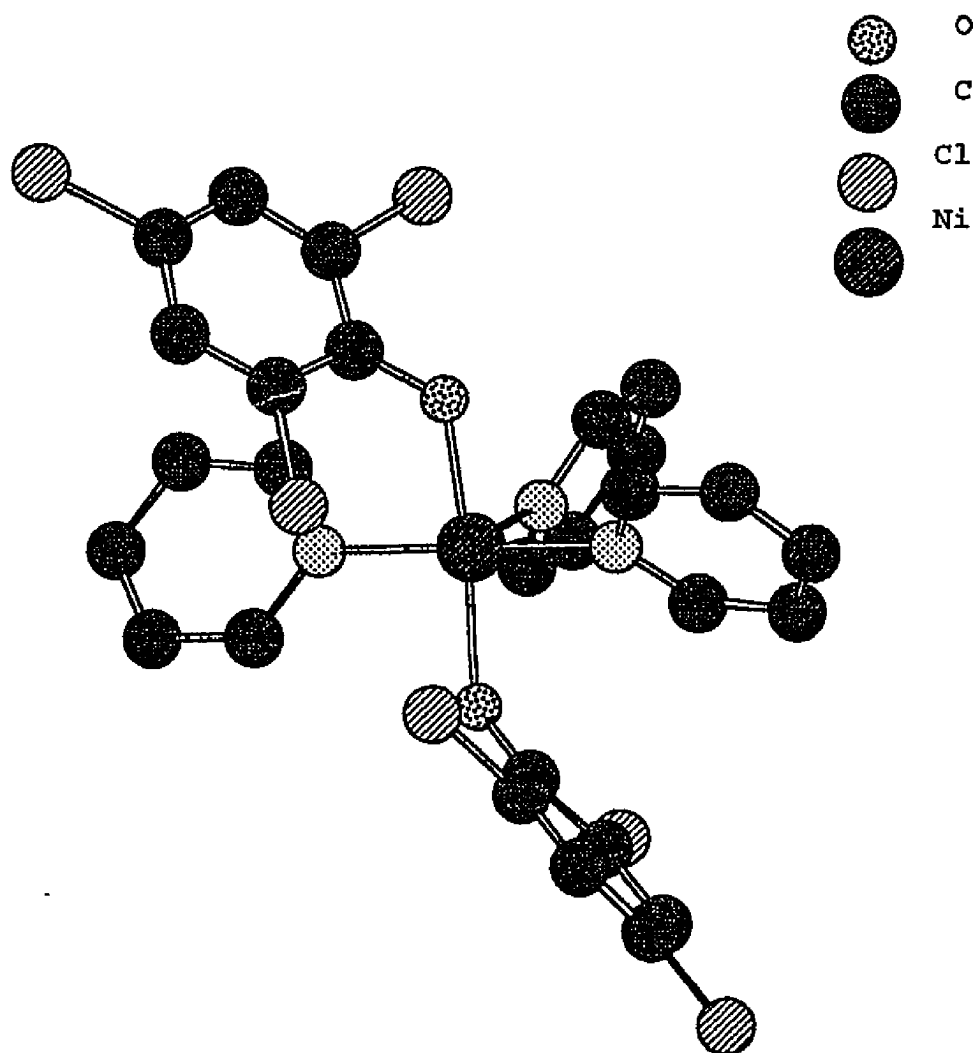Figure 6. Molecular Structure of [Ni(py)$_3$(tcp)$_2$]

Legend:
- O
- C
- Cl
- Ni

the usual octahedral Ni-terminal chloride distance, 2.441 Å (14), but much shorter than the estimated 3.3-3.5 Å van der Waals contact distance (29). The O(1)-Ni-O(2) angle is 161.2 (2)°. The average Ni-O and Ni-N distances are 1.960 and 2.097 Å, respectively, slightly shorter than the average values of 2.023 and 2.144 Å compiled for octahedral nickel complexes with comparable ligands (14). The C-Cl-Ni angles, 93.9(2) and 94.8(2)°, fall within the range of angles observed for intermolecular C-Cl...M contacts (4, 30).

The five-coordinate complex [Ni(py)$_3$(tcp)$_2$] lies on a crystallographic two-fold symmetry axis, and the geometry about the nickel is best described as a distorted square pyramid with one of the pyridine ligands occupying an axial position. The closest Ni...Cl contacts are to two symmetry related Cl(3) atoms below the base of the pyramid; the distance of 3.441(2) Å is at the van der Waals contact limit and can be regarded as nonbonding. The N(1)-Ni-N(1)' and O(1)-Ni-O(1)" angles are 177.0 and 164.1(2)°, respectively, so that the actual geometry lies along the coordinate linking square pyramidal and trigonal bipyramidal geometries (31). The trichlorophenolate and pyridine rings are twisted about the Ni-N(1), Ni-O(1), and O(1)-C(1) axes to create a propeller shape that maximizes aromatic ring interactions. The axial pyridine ligand is positioned so that its plane approximately bisects the O(1)-Ni-N(1) angle.

Ortho-chlorine coordination complexes are also found which involve the softer and singly charged transition

metals copper(I) and silver(I), as well as mercury(II).
Weak secondary bonding completes the trigonal bipyramidal
conformation around each silver in the polymer $Ag(2,4,5-tcp)_n$ (32) and weak secondary bonds complete the
tetrahedral conformation of $Ag(tcp)(Ph_3P)_2$ (4).

The compounds chosen for synthesis in this study were
selected so as to complement the nickel(II) complexes
prepared by previous students (33, 34, 35); additional
measurements were also made using newly-available techniques
(such as the magnetic susceptibility measurements) on
samples previously prepared by those students. In
particular, the nickel(II) 2,6-dichlorophenolates and 2,4,6-
trichlorophenolates with the monodentate nitrogen-donor
ligand pyridine and the chelating nitrogen-donor ligand TMED
had previously been obtained, and the crystal structures of
two of these compounds were being performed (27). However,
these crystallographic studies were of 2,4,6-
trichlorophenolates, which include a 4-chlorine which can
neither be involved in intramolecular secondary bonding to a
metal atom, nor can serve as a reference non-secondary-
bonding *ortho* chlorine; nonetheless this chlorine gives an
NQR signal in the region of interest, which must be
identified if possible. Hence this study included 4-bromo-
2,6-dichlorophenolate analogues of the compounds being
studied crystallographically; the 4-bromo substituent is
nearly identical electronically to a 4-chloro substituent

but is silent in chlorine NQR spectroscopy (while giving
bromine NQR spectra to confirm its presence).

Since the results of the NQR and crystallographic
studies of these compounds were so interesting, it was
deemed desirable to extend the range of compounds studied,
especially because of the interesting stereochemical and
magnetic diversity of nickel complexes, which range from
four-coordinate tetrahedral complexes with two unpaired
electrons with very weak-field ligands, through six-
coordinate octahedral complexes with two unpaired electrons
with moderate-field ligands such as most nitrogen-donor
ligands, to four-coordinate square planar complexes with no
unpaired electrons with strong-field ligands such as some
chelating nitrogen ligands such as (perhaps) 1,10-
phenanthroline and 2,2'-bipyridyl, and most phosphorus-donor
ligands, including certainly the chelating 1,2-
bis(diphenylphosphino)ethane and perhaps some of the
monodentate phosphines such as triphenylphosphine and
methyldiphenylphosphine. It was anticipated to be
particularly interesting to see what would happen to
secondary bonding at the crossover between six-coordinate
octahedral and four-coordinate square planar geometries,
since in the latter the *ortho* chlorines should not formally
be coordinated, yet would likely be situated above and below
the nickel in just the positions expected for coordination.

The diversity of known complexes with coordinating
ortho-chlorines would seem to necessitate a shotgun approach

to the search for new complexes. However, Harris and McKenzie (36) have synthesized several bis-chelate complexes of the formula $NiLX_2 \cdot nH_2O$ (X = halide), which seem to be rational starting materials for the synthesis of $NiL(chlorophenolate)_2$ if the chlorophenolate ion can be substituted for the halide; these chlorophenolates have the potential to show secondary bonding of ortho-chlorines in order to complete octahedral coordination about nickel.

CHAPTER III

EXPERIMENTAL

The majority of reactions were performed in Schlenkware maintained under an atmosphere of argon and subjected to continuous magnetic stirring. Chemicals were reagent grade. Solvents were dried over either 3 or 4 Å molecular sieves, potassium carbonate, or calcium chloride. Solutions were concentrated by distillation either using house vacuum lines or a Welch Duo-Seal vacuum pump; products were recrystallized by temperature depression and/or addition of a less polar solvent, then were collected by vacuum filtration.

Products were characterized by a variety of common techniques. A Mel-Temp apparatus was employed for melting/decomposition points. Infrared spectroscopy was performed utilizing either a Perkin-Elmer 567 Grating Infrared Spectrophotometer or a Perkin-Elmer Model 727b infrared spectrophotometer; samples were Nujol mulls between KBr plates. Visible wavelength spectra of samples in solution were obtained utilizing a Hewlett Packard 8451A Diode Array Spectrophotometer. Near infrared spectra were obtained with a Cary Model 17D NIR-visible-UV Spectrophotometer. Magnetic susceptibilities were determined on solid samples at room temperature using a JME magnetic susceptibility balance. NMR spectra

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were obtained with a Bruker AC 200 MHz nuclear magnetic
resonance spectrometer equipped with an Aspect 3000 data
processing system. Nuclear quadrupole resonance spectra
were obtained either with a Decca NQR spectrometer
operated at temperatures from 77 K to 273 K or at room
temperature with a Wilks NQR-1A spectrometer. Elemental
analysis were performed by Galbraith Laboratories, Inc.,
Knoxville, Tennessee.

Visible, near infrared, infrared, NMR, and NQR
spectra were compared with both published and previously
obtained spectra of known compounds and with spectra of
the starting materials.

A.   Syntheses of the Thallium Chlorophenolates

Thallium 2,4,6-trichlorophenolate

Htcp + KOH ---> K(tcp) + H_2O

K(tcp) + $TlNO_3$ ---> Tl(tcp) + KNO_3
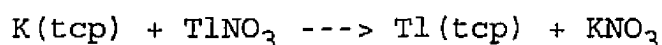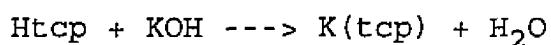
Potassium 2,4,6-trichlorophenolate was prepared by
the addition of 50 mL 4.0 M KOH to 7.9 g (40 mmol) of
2,4,6-trichlorophenol (Aldrich) dissolved in 20 mL of
methanol. The basic solution of chlorophenolate was
stirred in a boiling flask for 10 minutes. The thallium
salt of the chlorophenolate precipitated upon addition of
thallium nitrate (Alfa Chemicals, 10.65 g, 40 mmol)
dissolved in 50 mL of boiling water. Thallium 2,4,6-
trichlorophenolate was collected by vacuum filtration on

a glass frit. Completion of the reaction was confirmed by the addition of 4.0 M KOH to the filtrate without production of additional precipitate. The white precipitate was washed twice with 10 mL distilled water, washed twice with 10 mL methanol, and dried in a desiccator under reduced pressure. A typical yield was 14.52 g (36.29 mmol, 90.7%). Originally, the synthesis of thallium 2,4,6-trichlorophenolate was carried out under argon, but an inert atmosphere proved to be an unnecessary precaution.

Thallium 2,6-dichlorophenolate

$$Hdcp + KOH \longrightarrow K(dcp) + H_2O$$

$$K(dcp) + TlNO_3 \longrightarrow Tl(dcp) + KNO_3$$
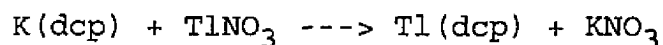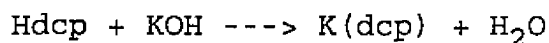
Addition of 50 mL 4.0 M KOH to 6.52 g (40 mmol) of 2,6-dichlorophenol (Aldrich) dissolved in 20 mL of methanol produced potassium 2,6-dichlorophenolate. The chlorophenolate solution was stirred in a round bottom flask for 10 minutes before adding thallium nitrate (10.65 g, 40 mmol) dissolved in 50 mL of boiling distilled water. Thallium 2,6-dichlorophenolate was collected by vacuum filtration, washed wit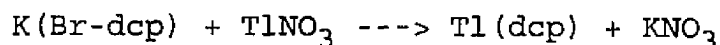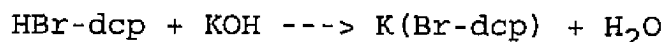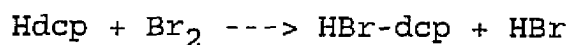h distilled water followed by methanol, and dried in a desiccator under reduced pressure. A typical yield was 10.05 g (24.4 mmol, 68.5%) when performed in excess KOH.

Thallium 4-bromo-2,6-dichlorophenolate

Hdcp + Br$_2$ ---> HBr-dcp + HBr

HBr-dcp + KOH ---> K(Br-dcp) + H$_2$O

K(Br-dcp) + TlNO$_3$ ---> Tl(dcp) + KNO$_3$

A large volume of methanol (110 mL) was used to dissolve 3.26 g (20 mmol) of 2,6-dichlorophenol. To this solution were added 50 mL of saturated bromine water, 5 mL of 48% hydrobromic acid, and 0.25 mL of liquid bromine. Aqueous bromine was then added until the clear solution remained yellow or the phenol separated as an oily bottom layer; the added volume varied from 30 to 100 mL. When the solution had remained yellow for 1 hour, it was left stirring overnight to reduce the methanol concentration. A low yield (2.7 g, 65%) of the bromophenol was produced by precipitation at -4°C. Higher yields (>73%) were obtained by addition of 100 mL of distilled water followed by immediate filtration upon a large Büchner funnel.

Recrystallization was difficult unless the solid was held under reduced pressure overnight to remove the water and methanol. The solid was dissolved in 50 mL of boiling hexane and stored at -4°C overnight to form long crystals of the 4-bromo-2,6-dichlorophenol. The crystals, when examined by IR spectroscopy, exhibited four peaks between 1350 and 1150 cm^{-1}, characteristic of triply substituted phenols, and lacked the dichlorophenol peaks at 1050 and 1100 cm^{-1}. A typical yield after again drying under reduced pressure was 14.3 millimoles (73%).

The brominated chlorophenol melted at 80-82°C and gave a characteristic NQR spectrum.

The procedure for the synthesis of thallium 4-bromo-2,6-dichlorophenolate from 4-bromo-2,6-dichlorophenol was directly analogous to the synthesis of the thallium trichlorophenolate.

B. Syntheses of Nickel Chlorophenolate Complexes with Monodentate Nitrogen-Donor Ligands

Bis(4-bromo-2,6-dichlorophenolato)bis(pyridine)nickel(II)

$$NiBr_2 \cdot 3H_2O + 2\ py + 2\ Tl(Br\text{-}dcp) \longrightarrow$$
$$Ni(Br\text{-}dcp)_2(py)_2 + 2\ TlBr$$
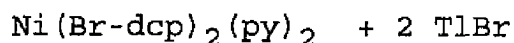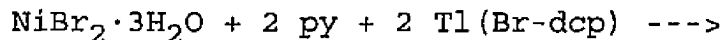
Nickel bromide trihydrate (1.50 g, 5.5 mmol) was dissolved in 50 mL of acetone in Schlenkware under argon. Water was removed by addition of 5 mL 2,2'-dimethoxypropane to the solution. The addition of pyridine (0.89 mL, 11 mmol) was immediately followed by the addition of 4.90 g (11 mmol) of thallium 4-bromo-2,6-dichlorophenolate. The green solution and white precipitate were stirred for 2 hours. After settling for a minute, the solution was decanted onto a glass frit under argon and vacuum filtered. The bottom residue with the thallium bromide was gravity filtered on a Whatman #1 filter paper in a funnel and washed with approximately 5 mL of acetone. Both solutions remained green and were recombined before distillation under vacuum to a volume

of 25 milliliters. Carbon tetrachloride, 50 mL, was added without causing precipitation. The solution was further vacuum distilled to a final volume of 25 mL before storage (-4°C overnight) under argon. Pentane (25 mL) precipitated a yellow powder upon addition to the filtrate. The powder was collected on a glass frit by vacuum filtration and dried under reduced pressure.

A suspension of 1.74 g of the yellow powder in 8.00 mL heptane was redissolved by the addition of 8.00 mL methylene chloride. The methylene chloride was added in 0.5 mL increments over the course of 45 minutes as the mixture was vigorously stirred in a water bath at 38-42°C. Two drops of pyridine were added after the yellow solution turned green. Storage for eight days under argon at -4°C precipitated a green powder. The powder was collected by vacuum filtration. Addition of 22 mL pentane to the filtrate precipitated a fluffy solid. The filtrate was concentrated by reduced pressure. Removal of the pentane resulted in the precipitation of a mixture of large clear yellow crystals and transparent emerald green crystals.

Infrared spectroscopy of Nujol mulls of both the title compound and liquid pyridine exhibited a shift to lower energy for the coordinated pyridine. The yellow powder was not amenable to NQR. Decomposition occurs above 112°C before the powder begins to melt.

C.   Syntheses of Nickel Chlorophenolate Complexes with
     Chelating Nitrogen-Donor Ligands

Bis(2,4,6-trichlorophenolato)(1,10-phenanthroline)-
nickel(II)

$$NiI_2 \ + \ phen \ \text{---}\text{>} \ (phen)NiI_2$$

$$Ni(phen)I_2 + 2\ Tl(tcp) \ \text{---}\text{>} \ Ni(tcp)_2(phen) + 2\ TlI$$
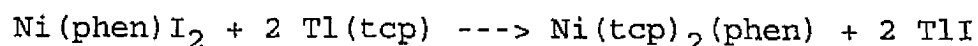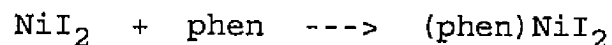
Nickel iodide (1.56 g, 5 mmol) was dissolved in 35
mL methylene chloride in a Schlenkware flask under argon.
1,10-phenanthroline (0.99 g, 5 mmol) in 10 mL methylene
chloride, then 1.5 mL 2,2'-dimethoxypropane followed by
30 mL of additional methylene chloride were added to the
metal iodide solution. The purple mixture was stirred
under argon for 21 hours (4 hours later proved adequate)
and gave a yellow solution having a red particulate
suspension. Solid thallium 2,4,6-trichlorophenolate (4.0
g, 10 mmol) added to the solution precipitated yellow
thallium iodide. The yellow solution turned green while
the combined red and yellow solids turned brown as the
mixture stirred under argon for another 2.5 hours.

The mixture was vacuum filtered in air through a
medium porosity glass frit and washed twice with 8 mL
portions of methylene chloride. The emerald green
filtrate was concentrated with a vacuum pump. The damp
crystals were transferred to a filter paper and dried
under reduced pressure. The yield of bis(2,4,6-
trichlorophenolato)(1,10-phenanthroline)nickel(II) was

2.36 g (73%). Infrared spectroscopy confirmed the presence of only 1,10-phenanthroline and 2,4,6-trichlorophenolate in the crystals. The product did not visibly decompose until above $130^{\circ}C$. No NQR signal was detected in the unrecrystallized crystals.

Bis(2,6-dichlorophenolato)(1,10-phenanthroline)nickel(II)

$$NiI_2 + phen \longrightarrow Ni(phen)I_2$$

$$Ni(phen)I_2 + 2\ Tl(dcp) \longrightarrow Ni(dcp)_2(phen) + 2\ TlI$$
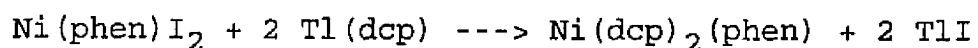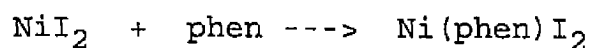
Solid nickel iodide (1.56 g, 5 mmol) and solid 1,10-phenanthroline (0.99 g, 5.0 mmol) were dissolved in methylene chloride (100 mL) with 2,2'-dimethoxypropane (1.5 mL, drying agent). A rubber septum, pierced by a needle attached to an argon line, sealed the vent of the boiling flask. The sealed flask was magnetically stirred for 4 hours, giving a yellow solution with a red precipitate. The precipitate turned green upon addition of 3.66 g (10 mmol) thallium 2,6-dichlorophenolate. The mixture was magnetically stirred for 19 hours, then gravity filtered twice through a glass frit to remove very fine particles. A large quantity (250 mL) of methylene chloride was required to leach the fine green precipitate from the yellow thallium iodide during the filtration. The emerald green solution was transferred to a 500 mL reaction flask and vacuum concentrated to 100 mL with a vacuum pump equipped with an additional solvent trap. Concentration was continued to a volume of 20 mL

after transfer into a 100 mL Schlenkware flask. Green crystals, precipitated upon addition of an equal volume of heptane to the concentrate, were collected by gravity filtration through a medium porosity glass frit and dried under reduced pressure in a desiccator.

IR spectroscopy indicated the presence of both of the ligands. Magnetic susceptibility suggested the anticipated coordination compound. However, no NQR spectrum was detected. The product began to visibly decompose above 82°C.

Diiodo(2,2'-dipyridyl)nickel(II)

$$NiI_2 + dpy \longrightarrow (dpy)NiI_2$$
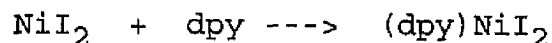
Benzene (10 mL) was used to dissolve 1.5618 g of 2,2'-dipyridine (Frederick Smith). The ligand solution was then added to nickel iodide (3.1249 g, 10.0 mmol) dissolved in 60 mL acetone containing 1.5 mL of the drying agent 2,2'-dimethoxypropane. After stirring overnight, the dark green mixture turned red and deposited an orange solid. The flask was kept at -4°C for four hours, and the contents vacuum filtered with a Büchner funnel. The precipitate contained blue, green, and grey particles as well as the orange-red monochelated nickel iodide. The extraneous particles proved to be more soluble in acetone than the desired product, so the solid was extracted with 250 mL acetone, stirred for four hours, and allowed to settle overnight. The red solution

was decanted from the solid, which was dried for seven days under reduced pressure and gave a granular red-brown powder. The identity of the product was partially confirmed by IR, magnetic susceptibility, and visible/near IR spectroscopy.

Bis(2,4,6-trichlorophenolato)(2,2'-dipyridyl)nickel(II)

$$Ni(dpy)I_2 + 2\ Tl(tcp) \longrightarrow Ni(tcp)_2(dpy) + 2\ TlI$$
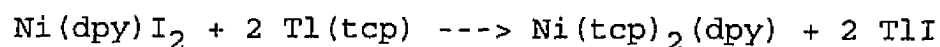
Diiodo(2,2'-dipyridyl)nickel(II) (2.43 g, 5.18 mmol, an excess) and thallium 2,4,6-trichlorophenolate (4.0 g, 10 mmol) were combined as solids and added to 200 mL of methylene chloride. The yellow mixture, with 2.0 mL 2,2'-dimethoxypropane, was stirred overnight and turned green. The precipitated thallium iodide could not be collected on a medium porosity glass frit by either vacuum or gravity filtration. A series of decantations and residue washes were employed to remove the fine particles. The green solution was reduced in volume under vacuum. Addition of 25 mL carbon tetrachloride to the final 25 mL of the solution produced a very fine precipitate which could not be collected on a medium porosity glass frit, so was left to settle for 3 days. A large crop of yellow powder was collected by decantation and dried under reduced pressure. The color, IR, and magnetic susceptibility indicated the anticipated product. No NQR signal was detected.

Bis(2,6-dichlorophenolato)(2,2'-dipyridyl)nickel(II)

$$Ni(dpy)I_2 + 2 Tl(dcp) \longrightarrow Ni(dcp)_2(dpy) + 2 TlI$$
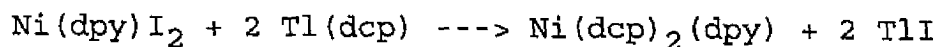
Diiodo(2,2'-dipyridyl)nickel(II) (1.36 g, 2.90 mmol) and thallium 2,6-dichlorophenolate (2.12 g, 5.81 mmol) were combined in 200 mL of dichloromethane under argon. Ten mL of 2,2'-dimethoxypropane was added to the yellow solution, which was stirred for nine hours. The solution, now a cloudy green, was filtered twice through a medium porosity glass frit and vacuum filtered twice through a less porous frit to remove a white precipitate from the solution. The transparent dark green solution was distilled under vacuum to a volume of 50 mL. Addition of 2 parts CCl_4 to 1 part solution produced a fine yellow precipitate. Addition of 100 mL of pentane to the remainder produced large green crystals which were collected by vacuum filtration on a medium porosity glass frit. The green crystals turned yellow upon drying. The yellow product produces a dark green solution in either acetone or dichloromethane. No NQR signal was detected for bis(2,6-dichlorophenolato)(2,2'-dipyridyl)nickel(II).

Bis(4-bromo-2,6-dichlorophenolato)(N,N,N',N'-tetramethyl-1,2-ethanediamine)nickel(II)

$$NiBr_2 \cdot 3H_2O + TMED \longrightarrow Ni(TMED)Br_2 + 3 H_2O$$

$$Ni(TMED)Br_2 + 2 Tl(Br\text{-}dcp) \longrightarrow Ni(Br\text{-}dcp)_2(TMED)$$
$$+ 2 TlBr$$
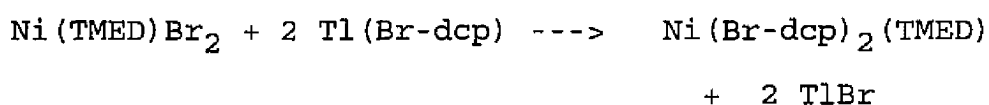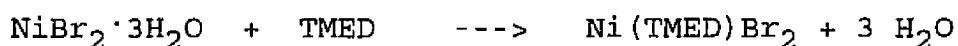
Nickel bromide trihydrate (1.65 g, 6.0 mmol), 90 mL dry acetone, and 6 mL 2,2'-dimethoxypropane were thoroughly mixed and held under argon. N,N,N',N'-tetramethyl-1,2-ethanediamine (0.54 mL, 6.0 mmol) was then injected into the solution, which turned intensely purple; this was followed by the addition of 5.34 g (12.0 mmol) thallium 4-bromo-2,6-dichlorophenolate and 6 mL of acetone. The resulting yellow mixture was stirred for two hours. Thallium bromide was removed by vacuum filtration through a medium porosity glass frit under argon. The filtrate was distilled under vacuum until a solid precipitated, then was stored in a freezer under argon overnight. The green solution was decanted from the yellow crystals, which were dried under house vacuum.

Dibromo(N,N,N',N",N"-pentamethyl-1,4,7-triazaheptane)-nickel(II)

$$(CH_3)_2NCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)_2 + NiBr_2 \cdot 3H_2O \longrightarrow$$
$$[Ni(CH_3)_2NCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)_2Br_2]$$
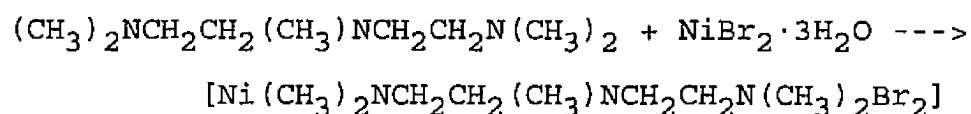
Nickel bromide trihydrate (2.861 g, 10.5 mmol) was placed in 100 mL acetone and 5 mL 2,2'-dimethoxypropane in a Schlenk flask, which was purged with argon, and was stirred continuously until the nickel salt dissolved. N,N,N',N",N"-pentamethyl-1,4,7-triazaheptane (1.51 mL = 1.82 g = 10.5 mmol) was then injected; this produced a brown-black solution. This was stirred for 0.5 hr, then the solvent was removed under vacuum. Further workup

gave a variety of different-colored solids, so the attempt to isolate this intermediate was abandoned.

(N,N,N',N",N"-pentamethyl-1,4,7-triazaheptane)bis(2,4,6-trichlorophenolato)nickel(II)

$(CH_3)_2NCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)_2 + NiBr_2 \cdot 3H_2O$

$+ 2\ Tl(tcp)\ ---> \ 2\ TlBr + 3\ H_2O +$

$[Ni(CH_3)_2NCH_2CH_2(CH_3)NCH_2CH_2N(CH_3)_2(tcp)_2]$
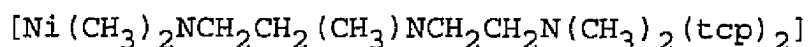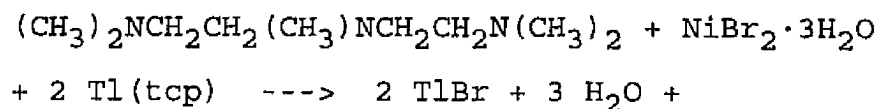
Acetone (100 mL), 2,2'-dimethoxypropane (5 mL), and $NiBr_2 \cdot 3H_2O$ (1.43 g, 5.25 mmol) were stirred together in a Schlenk flask under argon until the nickel salt dissolved; this required about 1 hr. Then N,N,N',N",N"-pentamethyl-1,4,7-triazaheptane (0.75 mL, 5.25 mmol) was injected; the solution turned brown. Immediately thallium 2,4,6-trichlorophenolate (4.2 g, 10.5 mmol) was added with stirring; the solution turned slightly red-brown. After stirring for 1.5 hr under argon, the solution turned purple. The white precipitate of TlBr was removed by filtration under argon; the purple solution was distilled down under vacuum to a volume of about 25 mL. The solution then was treated with 25 mL pentane and 50 mL hexane, and distilled down in volume under vacuum; this yielded a purple gelatinous (noncrystalline) solid which could not be crystallized.

D.   Syntheses of Nickel Chlorophenolate Complexes with

    Monodentate Phosphorus-Donor Ligands

Dibromobis(triphenylphosphine)nickel(II)

$$NiBr_2 \cdot 3H_2O + 2\ Ph_3P \longrightarrow Ni(Ph_3P)_2Br_2 + 3\ H_2O$$
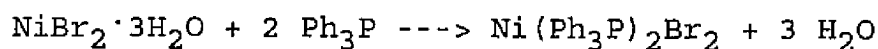
Solutions of 7.88 g (30 mmol) triphenylphosphine
(Aldrich) in 75.0 mL boiling 1-butanol and 4.08 g (14.97
mmol) nickel(II)bromide trihydrate in 75.0 mL boiling 1-
butanol were combined in a 250 mL boiling flask equipped
with a magnetic stirring bar. Dark green iridescent
crystals precipitated upon cooling. The mixture was
sealed under argon and placed in a freezer at -4°C for
four hours. The precipitate was collected by vacuum
filtration through multiple (2-3) Whatman #1 filter
papers, washed twice with five mL portions of cold carbon
tetrachloride, and dried in a desiccator under reduced
pressure. The yield of dibromobis(triphenylphosphine)-
nickel(II) was 7.32 g (9.8 mmol, 65%); it was stored in a
desiccator under reduced pressure.

Bis(2,4,6-trichlorophenolato)bis(triphenylphosphine)-
nickel(II)

$$NiBr_2(Ph_3P)_2 + 2\ Tl(tcp) \longrightarrow Ni(Ph_3P)_2(tcp)_2$$
$$+ 2\ TlBr$$
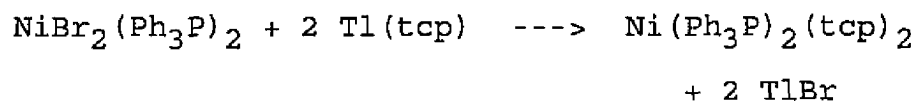
Due to its reactivity with the environment,
bis(2,4,6-trichlorophenolato)bis(triphenylphosphine)-
nickel(II) was produced in Schlenkware under argon. The

reactants, 2.97 g (4.0 mmol) dibromobis(triphenyl-phosphine)nickel(II) dissolved in 50.0 mL dry acetone and 3.2 g (8.0 mmol) thallium 2,4,6-trichlorophenolate suspended by rapid stirring in 50.0 mL dry acetone, were combined to produce the substitution product. After stirring for two hours, the white thallium bromide was removed by vacuum filtration through a glass frit. The emerald green solution was collected directly into 75.0 mL heptane. The closed system was necessarily exposed to air while connecting the Schlenkware for filtration and again for distillation. The product was distilled under vacuum to a final volume of 75 mL and further concentrated to 2.0 mL by utilizing a vacuum pump. The damp product was dried on a glass frit in a glove bag under Ar and patted dry between two filter papers. Alternatively, the product was distilled under vacuum to a final volume of 50 mL, precipitated under argon overnight at -4°C, and vacuum filtered and dried. Magnetic susceptibility measurements on the crystals indicated the presence of the two free electrons of the d^8 nickel(II) ion, and an IR spectrum demonstrated the presence of both the phosphine and the chlorophenolate ingredients. However, no NQR spectra was detected. The product decomposed at 60°C.

Bis(2,6-dichlorophenolato)bis(triphenylphosphine)-nickel(II)

$$NiBr_2(Ph_3P)_2 + 2\ Tl(dcp) \quad ---> \quad Ni(Ph_3P)_2(dcp)_2$$
$$+ 2\ TlBr$$
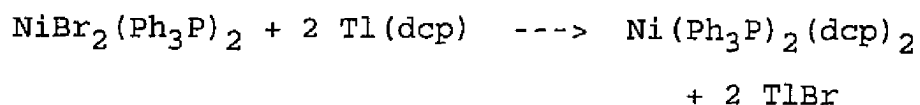
Dibromobis(triphenylphosphine)nickel(II) (3.02 g, 4.06 mmol) and thallium 2,6-dichlorophenolate (2.97 g, 8.12 mmol) in 100 mL CH_2Cl_2 were stirred together in a Schlenk flask under argon for 2 hr, producing a red solution with a white precipitate. After settling, the fine precipitate was gravity filtered in air; four filtrations were required to remove it completely. The filtrate was then reduced in volume under vacuum to 30 mL, and 30 mL heptane were added. The volume was again reduced to 30 mL under vacuum, which produced brown crystals, but upon vacuum drying these became colorless to very slightly green. Magnetic susceptibility measurements showed that these crystals were diamagnetic.

In a second run, the experiment was repeated essentially as above (but using chloroform as solvent), except that the filtrations were conducted under argon, and the solution was never observed to be red. The crystals gave no NQR spectrum.

Dibromobis(methyldiphenylphosphine)nickel(II)

$$NiBr_2 \cdot 3H_2O + 2\ MePh_2P \quad ---> \quad (MePh_2P)_2NiBr_2 + 3\ H_2O$$
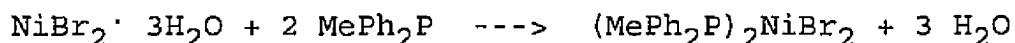
Nickel bromide trihydrate (1.64 g, 6.0 mmol) was dissolved in 30.0 mL boiling 1-butanol in a Schlenk flask, which was then purged with argon. Then, using a syringe, 2.4 mL (12.0 mmol) of liquid methyldiphenyl-

phosphine (Strem Chemicals) was injected into the solution through a septum. The Schlenk flask was then remove from its heating mantle and evacuated. A black precipitate formed in about an hour; this was suction filtered in air on a medium frit and washed twice with 10 mL CCl_4. The brownish-purple crystals were dried with a vacuum pump. The yield was 3.46 g (5.59 mmol), which is a 93% yield.

Bis(methyldiphenylphosphine)bis(2,4,6-trichlorophenolato)nickel(II)

$$(MePh_2P)_2NiBr_2 + 2\ Tl(tcp) \longrightarrow (MePh_2P)_2Ni(tcp)_2$$
$$+ 2\ TlBr$$
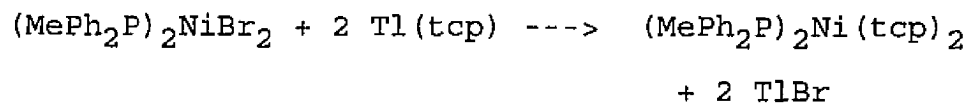
Dibromobis(methyldiphenylphosphine)nickel(II) (3.09 g, 5.0 mmol), thallium 2,4,6-trichlorophenolate (4.0 g, 10.0 mmol), and 2 mL 2,2'-dimethoxypropane were combined in 100 mL CH_2Cl_2 in a Schlenk flask which was repeatedly purged with argon. The solution was stirred for 16 hours, and gave a blue-black solution with a white precipitate of TlBr, which was filtered under argon. Heptane (15 mL) was added, and the solution was put under house vacuum for two days. However, the solvent came off too slowly, and the product was not collected successfully: when the materials were redissolved in acetone and dried in air, a pale green solid ($Ni(OH)_2$) and a blue crystal were obtained.

E.   Syntheses of Nickel Chlorophenolate Complexes with
      Chelating Phosphorus-Donor Ligands

(1,2-Bis(diphenylphosphino)ethane)bis(trichloro-
phenolato)nickel(II)

Ni(diphos)Cl$_2$ + 2 Tl(tcp) --> Ni(diphos)(tcp)$_2$

+ 2 TlCl
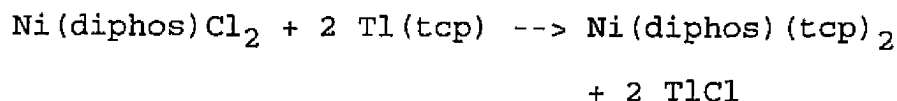
To a suspension of 4.00 g (10.0 mmol) thallium
2,4,6-trichlorophenolate in 50 mL chloroform in a Schlenk
flask was added a solution of 2.88 g (5.0 mmol)
dichloro(bis(1,2-diphenylphosphino)ethane)nickel(II)
(Strem Chemicals) in 50 mL chloroform; the mixture was
stirred under argon for 21 hours. The solution was
vacuum filtered in air on a medium frit filtering funnel;
the white precipitate was washed with 25 mL chloroform.
To the red solution 25 mL heptane was added, and the
volume was reduced under vacuum to 25 mL, and then to
dryness. Long dark red crystals were produced (1.70 g),
which ultimately decomposed in air, giving long white
crystals.

(1,2-Bis(diphenylphosphino)ethane)bis(dichloro-
phenolato)nickel(II)

Ni(diphos)Cl$_2$ + 2 Tl(dcp) --> Ni(diphos)(dcp)$_2$

+ 2 TlCl
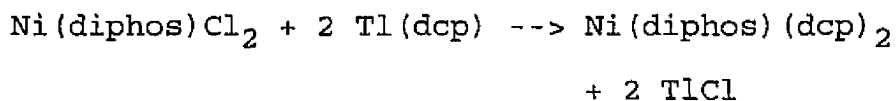
A suspension of 3.66 g (10.0 mmol) thallium
trichlorophenolate in 50 mL was combined with a solution

of 2.88 g (5.0 mmol) of dichloro(bis(1,2-diphenyl-phosphino)ethane)nickel(II) in 50 mL chloroform; 1.0 mL 2,2'-dimethoxypropane was also added. The mixture was stirred under argon for 21 hours. The solution was vacuum filtered under argon on a medium frit filtering funnel; the white precipitate was washed with 25 mL chloroform. To the red solution 25 mL heptane was added, and the volume was reduced under vacuum to 25 mL, and then to dryness. Long dark red crystals were produced, which acquired a purple surface tinge in the air. The yield was 3.40 g (68% yield).

CHAPTER IV

RESULTS AND CONCLUSIONS

A. Syntheses of Precursors

The 4-bromo-2,6-dichlorophenol ligand used in this study was prepared by standard bromination of 2,6-dichlorophenol; its identity was confirmed by its ir spectrum, melting point, and NQR spectrum. The thallium chlorophenolates were prepared by precipitation as previously described (18).

The preformed complexes of nickel(II) bromide with triphenylphosphine, $Ni(Ph_3)_2Br_2$, and the corresponding complex with methyldiphenylphosphine were prepared by reaction of the halide with the ligand in refluxing 1-butanol under argon, as described by Venanzi for the triphenylphosphine complex (37).

The monochelated dihalo(1,10-phenanthroline)-nickel(II) proved to be difficult to isolate. Elevated temperatures, long reaction time, and simple concentration of the ligand and halide in solution apparently promoted formation of the more stable dichelated complex $Ni(phen)_2X_2$. The red phenanthroline nickel halide turned brown after a week in air. An inert atmosphere and Schlenkware did not assist the reaction. Similar difficulties were experienced in the attempts to

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preform the complex of nickel halides with just one mole
of the bidentate nitrogen-donor ligand bpy; it appears
that disproportionation to give (presumably) complexes
such as $Ni(bpy)_2X_2$ occurred to at least some degree,
since multicolored products were obtained after reacting
nickel(II) iodide or bromide and one mole of the ligand
in dichloromethane.

B.   Syntheses of Complexes

The success or failure of the syntheses were
assessed first of all by isolating crystalline products
that appeared homogeneous under a microscope, and that
gave satisfactory ir spectra indicating the presence of
the halophenolate and the other ligand, but no other
components. Next NQR spectra were measured; if these
could be detected the samples were submitted for
elemental analyses (Table 2); if NQR spectra could not be
detected (which was essential for the project) they were
not submitted for elemental analysis (which costs about
$50 per sample). Then other spectroscopic measurements
were made; these will be discussed after the details of
synthesis.

The 4-bromo-2,6-dichlorophenolates of nickel with
the nitrogen-donor ligands pyridine and TMED,
$[Ni(TMED)(Br-dcp)_2]$, $[Ni(py)_2(Br-dcp)_2]$, and $[Ni(py)_3(Br-dcp)_2]$, were successfully synthesized by reacting nickel
bromide trihydrate in acetone with the dehydrating agent

Table 2. Elemental Analyses of Nickel Chlorophenolates.

Complex[a]	%C	%H	%N	%Cl,H_2O
$Ni(TMED)(OC_6H_2Cl_2Br)_2$	32.92	3.07	4.27	
	32.78	3.14	4.24	
$Ni(TMED)(OC_6H_2Cl_3)_2$	38.07	3.55	4.93	0.00
	37.77	3.67	5.10	0.81
$Ni(TMED)(OC_6H_2Cl_3)_2(H_2O)_4$				12.69
				10.82
$Ni(TMED)(OC_6H_3Cl_2)_2$	43.34	4.45		
	43.39	4.53		
$Ni(py)_2(OC_6H_2Cl_2Br)_2$	b			
$Ni(py)_2(OC_6H_2Cl_3)_2$	43.33	2.31	4.59	0.00
	43.01	2.31	4.46	0.67
$Ni(py)_2(OC_6H_2Cl_3)_2(H_2O)_4$				11.82
				12.17
$Ni(py)_2(OC_6H_3Cl_2)_2$	48.85	2.98	5.18	
	48.57	3.18	5.22	
$Ni(py)_3(OC_6H_2Cl_2Br)_2$	41.69	2.46	5.40	
	41.61	2.49	5.53	
$Ni(py)_3(OC_6H_2Cl_3)_2$	47.08	2.78	6.10	0.00
	46.08	2.80	5.89	1.45
$Ni(Ph_3P)_2(OC_6H_2Cl_3)_2$	c			
$Ni(diphos)(OC_6H_2Cl_3)_2$	d			
$Ni(diphos)(OC_6H_3Cl_2)_2$	c			

Table 2 continued

a. First line gives theoretical percentage; second gives
   percentage found.

b. Not analyzed because adducts were inseparable.

c. Not analyzed because compound gave no NQR spectrum.

d. Not analyzed because there was rapid decomposition of
   the compound in air.

2,2-dimethoxypropane, followed by the addition of the
nitrogen-donor ligand, followed by the addition of
thallium 4-bromo-2,6-dichlorophenolate. After removing
thallium bromide by filtration, the green solutions were
reduced in volume, treated with pentane, and cooled to
give yellow crystals or powders of the TMED and bis-
(pyridine) adducts, respectively; the TMED adduct gave a
satisfactory elemental analysis. Recrystallization of
the bis(pyridine) adduct from dichloromethane containing
a small excess of pyridine gave a mixture of yellow and
green crystals, which could not be quantitatively
separated for elemental analysis; recrystallization with
a larger amount of pyridine gave green crystals which
analyzed satisfactorily as the tris(pyridine) adduct.
From the previous experiments with bis(pyridine) and
tris(pyridine) adducts involving the trichlorophenolate
ligand, however, it was deduced that the yellow adduct
was likely the bis(pyridine) adduct; this was supported
by the similarity of the NQR spectra of the physically
separated yellow component [Ni(py)$_2$(Br-dcp)$_2$] to that of
the known yellow [Ni(py)$_2$(tcp)$_2$].

Because the nickel halide adducts of bpy and phen
could not be prepared pure, the syntheses of the
chlorophenolates of these two ligands were carried out
using stoichiometric quantities of the nickel iodide, the
ligand, and the thallium chlorophenolate in
dichloromethane. After filtration of the precipitated

thallium halides, the solutions were concentrated under vacuum and then generally treated with an equal volume of a poor solvent (heptane or carbon tetrachloride) to precipitate the product. [Ni(phen)(tcp)$_2$] and [Ni(phen)(dcp)$_2$] were apparently obtained as green crystals uncontaminated with products of other colors; [Ni(dpy)(tcp)$_2$] and [Ni(dpy)(dcp)$_2$] were also obtained as green crystals which turned yellow upon drying under vacuum (hence they may originally have been hydrates). The ir spectra of these four compounds were consistent with the presence of only the nitrogen-base and chlorophenolate ligands, but of course the stoichiometry could not so be determined. None of the four compounds gave an NQR spectrum, so they were not submitted for elemental analysis.

Difficulties were experienced with the syntheses of the products containing phosphine ligands. Only [Ni(diphos)(tcp)$_2$] could be isolated in a seemingly pure state and gave an apparent NQR spectrum, but it reacted extremely rapidly in solution and as a solid with air to give a colorless product tentatively identified (on the basis of its infrared spectrum) as an oxide of the phosphine ligand. The diphos ligand in the related complex [Ni(diphos)Cl$_2$] is known to undergo oxidation in methanol over several hours or days (38, 39); the rate of this reaction is evidently dramatically enhanced in chlorophenolate complexes. [Ni(diphos)(dcp)$_2$] did not

even appear pure when isolated; [Ni(Ph$_3$P)$_2$(tcp)$_2$] was even more obviously impure when isolated and gave no NQR spectrum, while Ni(Ph$_3$P)$_2$(tcp)$_2$ could not be synthesized at all; only a colorless diamagnetic product (presumably Ph$_3$P or Ph$_3$PO) was isolated from a very pale green solution; it also gave no NQR spectrum.

C. Visible and Near-IR Spectra

As discussed in Chapter 1, there are three main geometries of nickel(II) complexes; a major factor in determining the geometry of complex formed by a given ligand is the position of the ligand in the spectrochemical series of ligands. In turn, a major factor in determining the position of a ligand in this series is the identity of the donor atom: roughly speaking, Group 17/VII donor atoms (such as chlorine) give the weakest crystal field splitting, followed by Group 16/VI donor atoms in ligands such as water and phenolates, followed by nitrogen donor atoms, then phosphorus donor atoms from Group 15/V; (13) it is also found that chelating ligands tend to give slightly stronger crystal fields than do monodentate ligands. The weakest donor ligands tend to give tetrahedral complexes with nickel(II), but this tendency is severely restricted by the strong Octahedral Site Stabilization Energy experienced by the d^8 Ni^{2+} ion, which means that many more complexes are octahedral in geometry.

For octahedral complexes, the magnitude of the crystal field splitting, *10Dq,* produced by the ligands can most simply be measured by noting the lowest-energy electronic transition due to electrons being excited from the t_{2g} set of orbitals $(d_{(xy)},\ d_{(xz)},\ d_{(yz)})$ to the e_g set of orbitals $(d_{(z^2)},\ d_{(x^2-y^2)})$. This absorption is normally found in the near-infrared spectrum of these complexes, a region of the spectrum not accessible on most spectrophotometers but which is accessible on our Cary 17D instrument. Hence the spectra of many chlorophenolate complexes, including a number synthesized by previous students, were recorded and are listed in Table 3.

Several conclusions can be drawn from the near-ir absorption frequencies in this table. First, we may notice from the first three spectra that the spectra of the corresponding tcp, dcp, and Br-dcp complexes are very similar (identical within the experimental uncertainty); this is to be expected, since only the *para*-substituent is being changed in this series, and the *para* substituent is very remote from the nickel.

Second, we may note that the hydrated forms of the tcp complexes are quite different spectroscopically from the corresponding anhydrous forms, both in terms of the longest-wavelength absorptions and in terms of their visible spectra (the hydrated forms are blue to the eye, while the anhydrous are yellow). Bullock and Hobson

Table 3. Colors, Longest-Wavelength Absorptions (v_1, nm), Crystal Field Splittings (10Dq, in cm^{-1}), and Magnetic Susceptibilities (B.M.) of Nickel Complexes.

Complex	Color	v_1, nm	10Dq	μeff
Ni(TMED)(OC$_6$H$_2$Cl$_2$Br)$_2$	Yellow	1395	7170	3.40
Ni(TMED)(OC$_6$H$_2$Cl$_3$)$_2$	Yellow	1385	7220	3.40
Ni(TMED)(OC$_6$H$_3$Cl$_2$)$_2$	Yellow	1370	7580	3.40
Ni(TMED)(OC$_6$H$_2$Cl$_3$)$_2$(H$_2$O)$_4$	Blue	1087	9200	3.28
Ni(py)$_2$(OC$_6$H$_2$Cl$_2$Br)$_2$	Yellow			
Ni(py)$_2$(OC$_6$H$_2$Cl$_3$)$_2$	Yellow	1428	7000	3.17
Ni(py)$_2$(OC$_6$H$_3$Cl$_2$)$_2$	Yellow			
Ni(py)$_2$(OC$_6$H$_2$Cl$_3$)$_2$(H$_2$O)$_4$	Blue	1041	9600	3.17
Ni(py)$_3$(OC$_6$H$_2$Cl$_2$Br)$_2$	Green			
Ni(py)$_3$(OC$_6$H$_2$Cl$_3$)$_2$	Green			
Ni(Ph$_3$P)$_2$(OC$_6$H$_2$Cl$_3$)$_2$	Green	920		2.09
Ni(diphos)(OC$_6$H$_2$Cl$_3$)$_2$	Red	600		0
Ni(diphos)(OC$_6$H$_3$Cl$_2$)$_2$	Red	550		0

measured the magnetic susceptibilities and visible
spectra of the hydrated and anhydrous nitrogen-ligand
nickel(II) 2,4,6-trichlorophenolates (22), and proposed
that the lower crystal field splitting in the yellow
anhydrous compounds was due to the presence of bridging
μ_2-2,4,6-trichlorophenolato-O ligands. However, the
crystal structure of [Ni(TMED)(tcp)$_2$] shows that there
are no bridging μ_2-2,4,6-trichlorophenolato-O ligands
present. Evidently the reason for the lower crystal
field splitting in the yellow anhydrous complexes is due
to coordination of two very weak-field organochlorine
donor atoms rather than two stronger-field water
molecules (in the blue hydrated complexes).

Third, we had hoped to record separately the spectra
of the corresponding green tris(pyridine) and yellow
bis(pyridine) complexes. However, these spectra turned
out to be identical in solution, which suggests that the
third pyridine dissociates almost completely in solution.

Finally, we note that the longest-wavelength
absorptions of the phosphorus-donor complexes (the last
three in Table 3) occur at much shorter wavelengths than
the other complexes. This suggests that the phosphorus
complexes contain much stronger-field ligands, as we
expected from the spectrochemical series of ligands. The
difference between triphenylphosphine and diphos is quite
striking, however.

D. Magnetic Susceptibility Measurements

Since a Johnson-Matthey magnetic susceptibility apparatus for making measurements at room temperature had recently become available, the magnetic susceptibilities (in Bohr magnetons) of the new and previously-synthesized complexes were also measured; the results are also included in Table 3. The theoretical spin-only magnetic susceptibility of a Ni^{2+} ion with two unpaired electrons is 2.83 B.M.; the normally observed range of values is from 2.8 to 4.0 B.M. (40). It may be seen that all measurements except the last three fall within this range. Thus these complexes have two unpaired electrons, which suggests that they are *not* square planar complexes. (This is consistent with the absorption spectra of these complexes, which suggests octahedral geometries.) Square planar nickel(II) complexes are expected to be diamagnetic, hence to show zero (or slightly negative) magnetic susceptibilities. This was in fact observed for the two diphos complexes, which are therefore concluded to be square planar (it should be noted that square planar nickel(II) complexes often are red). The data for the triphenylphosphine complex is intermediate between that expected for an octahedral and a square planar complex; it is tempting to suggest the presence of a spin-crossover phenomenon, but it must be remembered that this complex was very air-sensitive and probably not pure; furthermore, the magnetic susceptibility

measurements were made in capillary tubes open to the air. But in view of its fairly large crystal field splitting, it does seem unlikely that this complex is purely tetrahedral, which might have been a possibility given the large cone angle of the triphenylphosphine ligand.

E. Nuclear Quadrupole Resonance (NQR) Spectra (41)

The ^{35}Cl NQR spectra of the compounds in this study are reported in Table 4. Frequencies measured at 77K are given in MHz, followed by the signal-to-noise ratio for each line (in parentheses), followed by the decrease of that frequency when measured at 273K (in brackets). Spectra were also generally measured at 195 K and sometimes at other temperatures to detect crossings of frequencies. Frequency assignments in the tcp derivatives [Ni(TMED)(tcp)$_2$], [Ni(py)$_2$(tcp)$_2$], and [Ni(py)$_3$(tcp)$_2$] were confirmed by preparing the extremely similar derivatives [Ni(TMED)(Br-dcp)$_2$], [Ni(py)$_2$(Br-dcp)$_2$], and [Ni(py)$_3$(Br-dcp)$_2$], in which the frequencies assigned to the para-chlorines disappeared while those assigned to the ortho-chlorines were but slightly altered.

As mentioned in Chapter 1, the ^{35}Cl NQR frequency, ν, of a coordinated chlorophenolate ortho-chlorine (Cl-2) is expected to be lower than that of the non-coordinated ortho-chlorine (Cl-6):

Table 4. ^{35}Cl NQR Frequencies (MHz at 77K) of Chlorophenolates.

Compound;			
ν(Cl-4)[a]	ν(Cl-6)	ν(Cl-2)	$\Delta\nu$

A. 2,6-Dichlorophenolates

Ni(TMED)(dcp)$_2$	34.721(9)[.61]	32.196(17)[.45]	2.525
	34.482(9)[.72]	32.033(18)[.43]	2.688
Ni(py)$_2$(dcp)$_2$	34.711(11)[.53]	31.931(9)[.33]	2.780
	34.568(7)[.40]	31.537(7)[.38]	3.174
[Ni(OMe)(MeOH)(dcp)$_2$]$_4$			
	34.937(6)	b	
	34.904(5)	b	
	34.802(7)	b	
	34.706(8)	b	

B. 4-Bromo-2,6-Dichlorophenolates

[Ni(TMED)(Br-dcp)$_2$][c]			
	36.036	32.951	3.085
	35.680	32.912	3.124
	35.413	32.814	3.222
	35.241	32.745	3.291
	34.935	32.445	3.591
[Ni(py)$_2$(Br-dcp)$_2$]			
	35.215(3)[.54]	33.098(7)[.52]	2.117
	35.121(4)[.80]	32.500(5)[.37]	2.715

Table 4 continued

[Ni(OMe)(MeOH)(Br-dcp)₂]₄

35.565(4)	b		
35.484(3)	b		

[Ni(py)₃(Br-dcp)₂]

| 222.6(100)[d] | 34.871(22)[.49] | 34.067(12)[.56] | 0.804 |

C. 2,4,6-Trichlorophenolates

[Ni(TMED)(tcp)₂]

| 35.735(8)[.67] | 35.381(11)[.66] | 32.592(15)[.41] | 2.789 |
| 35.641(8)[.67] | 35.381(11)[.71] | 32.199(12)[.36] | 3.182 |

[Ni(py)₂(tcp)₂]

| 35.385(3)[.54] | 35.100(3)[.63] | 33.123(7)[.48] | 1.977 |
| 35.187(4)[.51] | 35.040(3)[.62] | 32.529(6)[.42] | 2.571 |

[Ni(py)₃(tcp)₂]

| 34.948(30)[.52] | 34.846(32)[.49] | 34.177(13)[.58] | 0.669 |

[Ni(diphos)(tcp)₂]

| 35.461(2) | 35.039(2) | 34.635(2) | 0.404 |
| 35.363(2) | 34.879(2) | 34.530(2) | 0.509 |

[Ni(TMED)(tcp)₂(H₂O)₄]

| 35.627(4) | 35.270(4) | 34.891(3) | 0.379 |
| 35.475(3) | 35.037(5) | 34.803(5) | 0.467 |

[Ni(py)₂(tcp)₂(H₂O)₄]

| 35.400(2) | 35.043(2) | 34.820(3) | 0.223 |
| 35.093(2) | 34.883(2) | | |

Table 4 continued

a. Signal-to-noise ratios given in parentheses; temperature dependence of the frequencies ν (frequency at 77K minus frequency at 273K) given in brackets. In the case of closely-spaced Cl-4 and Cl-6 frequencies, the higher frequencies are assigned to Cl-4. $\Delta\nu$ = the frequency difference of Cl-6 and Cl-2 at 77K.

b. Signal could not be detected.

c. Obtained as mixed phases; signal intensities vary from 2 to 4 depending on treatment of sample.

d. ^{81}Br NQR frequency at ambient temperature, recorded on a Wilks NQR-1A spectrometer.

$$\nu(Cl-2) = \nu(Cl-6) - (27.4 \times No. \text{ electrons transferred})$$

This equation is better used for qualitative comparisons (as of the effects of the four metals Co, Ni, Cu, Zn) than of quantitative calculations of numbers of electrons transferred from an ortho-chlorine to a metal ion. Part of the frequency difference $\Delta\nu$ observed (probably not more than 0.7 MHz (42)) may be due not to chemical but rather to crystallographic inequivalence of ortho-chlorines in the solid state. Part may also be due to Sternheimer polarization of the core electrons of the ortho-chlorine by the partially-ionic M^{2+} group. (43)

We have previously observed (4, 18, 24) among the silver(I), cobalt(II), and copper(II) derivatives of known structure that, the shorter the metal-chlorine distance, the greater the $\Delta\nu$ between the two types of ortho-chlorine, Cl-2 and Cl-6. Figure 7 shows the average $\Delta\nu$ for the corresponding complexes $ML_n(\text{chlorophenolate})_2$ with the same ligands but different divalent metals: by far the greatest $\Delta\nu$ is found for M = Ni. If the above equation is taken literally, then at least one-tenth of an electron is being transferred from chlorine to nickel in $[\text{Ni(TMED)(tcp)}_2]$, which is a small but not negligible bonding interaction. Using the previously-established correlation (18) between $\Delta\nu$ and M-Cl secondary bond distance, we predicted that the Ni-Cl bond distance in $[\text{Ni(TMED)(tcp)}_2]$ would be about 2.6 Å, which the crystallographic study subsequently confirmed.

The fact that the apparent bonding is greatest for nickel can be rationalized using the crystal field theory. We may suppose that the nitrogen-ligand metal 2,4,6-trichlorophenolates would be tetrahedrally coordinated in the absence of organochlorine coordination, since the ligands are not likely to be sufficiently strong-field to promote square-planar promotion. In the presence of organochlorine coordination, octahedral coordination is found. Thus the energetics of organochlorine coordination would involve the octahedral site stabilization energy (OSSE) for the high-spin metal ion. In units appropriate for octahedral complexes, Dq_{oct}, this stabilization is 2.67 Dq_{oct} for d^7, 8.45 Dq_{oct} for d^8, 4.22 Dq_{oct} for d^9, and zero for d^{10}, i.e. is greatest for the d^8 metal ion, e.g. Ni^{2+}. As suggested by Figure 7, the Δv and a measure of the OSSE correlate well, with both showing strong maxima at the d^8 metal ion, Ni^{2+}.

We may similarly rationalize the fact that, among the nitrogen-ligand metal 2,4,6-trichlorophenolates, only the nickel ones tend to form hydrates: a greater OSSE results (in absolute terms) if a stronger-field ligand, water, is used to complete the octahedral coordination than if the very weak-field organochlorine ligand, is used. Presumably the fact that these complexes can be dehydrated is connected with the steric advantages of organochlorine coordination in forming a chelate ring,
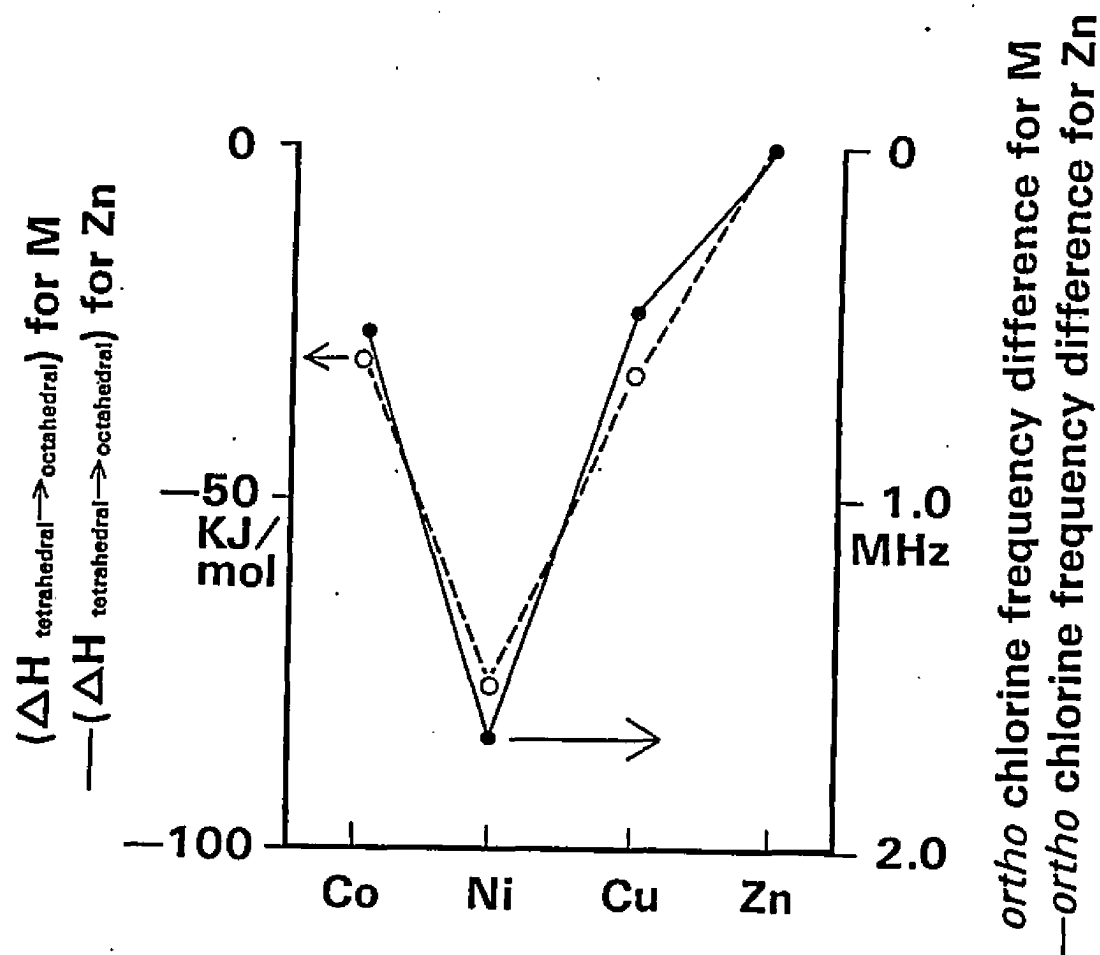
Figure 7. Average ^{35}Cl NQR frequency difference of coordinated o-Cl (Cl-2) and non-coordinated o-Cl (Cl-6) as a function of the metal ion, compared to Zn as a reference (solid line, right scale). OSSE's (octahedral site stabilization energies) for conversion of tetrahedral to octahedral metal complexes are compared to that of the Zn complex as a reference (broken line, left scale). The quantitative measure of the OSSE used is ΔH for the reaction $MCl_4^{2-} + 6\ H_2O \dashrightarrow M(H_2O)_6^{2+} + 4\ Cl^-$.

and the entropy advantages in liberating water. In Table 4 we also show the NQR spectra of two hydrates, [Ni(TMED)(tcp)$_2$(H$_2$O)$_4$] and [Ni(py)$_2$(tcp)$_2$(H$_2$O)$_4$]: these show no low NQR frequencies characteristic of coordinated organochlorines.

The compounds [Ni(diphos)(tcp)$_2$] and [Ni(diphos)(dcp)$_2$] were of interest since the parent halides Ni(diphos)X$_2$ are diamagnetic and square planar, a geometry which has a strong crystal field stabilization energy and in which we would not anticipate there to be a strong driving force for organochlorine coordination. [Ni(diphos)(tcp)$_2$] and [Ni(diphos)(dcp)$_2$] are diamagnetic and red, which indicates square-planar coordination: if organochlorine coordination is present, it must be very weak indeed, since two unpaired electrons are characteristic of octahedral coordination of Ni^{2+}. A weak NQR spectrum was obtained for [Ni(diphos)(tcp)$_2$]; *if* this spectrum is complete, then there is no organochlorine complexation; however, in such a weak spectrum, other signals due to coordinated chlorines could easily have been missed.

In Figure 8 we update the correlation of NQR frequency distance with excess M-Cl distance in metal complexes of chloroaromatic ligands (in almost all cases, chlorophenolates). The excess M-Cl distance we define as the observed secondary M-Cl bond distance minus the normal M-Cl primary bond distance found in octahedral

complexes of the metal in question. (14) The NQR and

structural data for the compound [Ni(TMED)(tcp)$_2$]

provides one of the points at the upper left (strong M-Cl

interactions), while the data for the compound

[Ni(py)$_3$(tcp)$_2$] provides a point at the lower right (very

weak or nonexistent M-Cl interactions). The addition of

the last point allows us to see that the correlation is

distinctly nonlinear (the correlation coefficient for the

best linear fit is 0.933; that for the curve of Figure 8

is 0.963). A curve of this type is expected and normally

found when bonding properties are plotted as a function

of bond distance; bonding does not suddenly cease at a

certain distance but rather fades away.

The two enveloping lines (_._._.) around the data in

Figure 8 represent the normal spread found in NQR

frequencies of chloroaromatics due to solid-state

effects, 99.6% of which fall within a range of 0.70 MHz

of each other. (42) However, it is possible that solid

state effects are inherently larger in coordination

compounds than in organic compounds; we note that data

point 11 falls substantially outside the envelope. As a

second example, we note that the five chlorine NQR

signals assigned (Table 4) to the non-coordinated

chlorines (Cl-6) in [Ni(TMED)(Br-dcp)$_2$] show a frequency

spread of 1.101 MHz, well in excess of 0.7 MHz. However,

the number of coordination compounds that show frequency
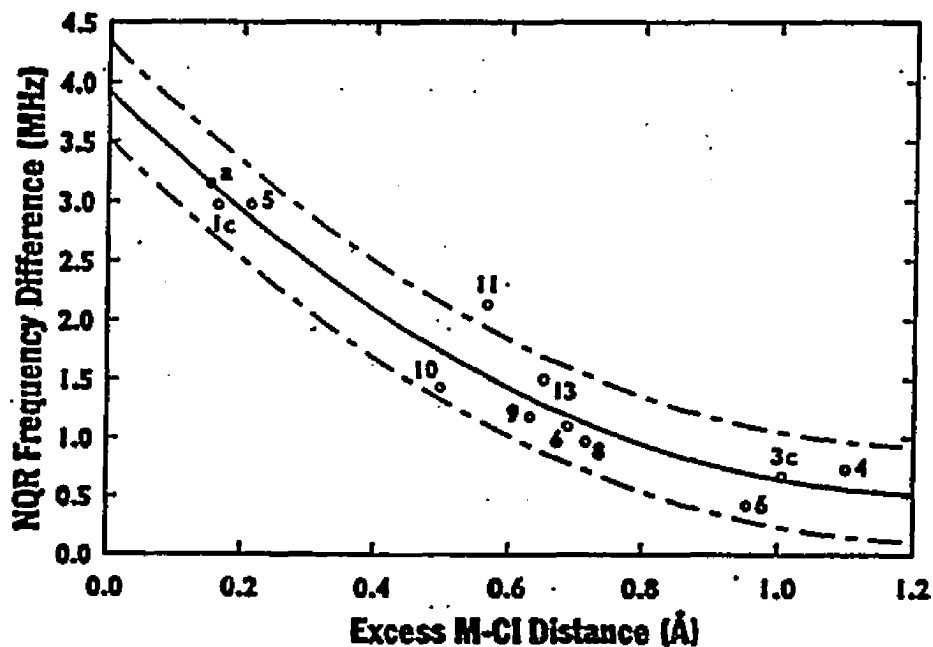
Figure 8. Average [35]Cl NQR frequency difference of coordinated o-Cl (Cl-2) and non-coordinated o-Cl (Cl-6) as a function of the excess M-Cl distance (defined as the observed M-Cl distance minus the normal M-Cl single bond distance in octahedral complexes, from ref. 17). Solid line = best-fit curve; broken line (._._._) encloses the expected scatter (±0.35 MHz) in the frequency differences due to solid-state effects. Numbers on points give literature references (as cited in reference (10)) to the corresponding crystal structures.

differences of less than 0.70 MHz is much larger; these exceptions may be statistical flukes. The envelope of frequencies should converge with the bottom of Figure 8 at a distance at which all bonding interactions cease. With the best linear fit this happens at an excess M-Cl distance of just over 1.0 Å, while the envelope to our curved fit does not converge even at an excess bond distance of 1.2 Å; but it would if the envelope were significantly wider than 0.35 MHz. In view of these uncertainties, a 1.0-Å excess-distance cutoff for secondary bonding seems reasonable; although there may in fact be some metal-organochlorine interaction at this distance, it likely is chemically insignificant for most purposes (application of eq 1 suggests an apparent electron transfer of less than 0.01 electron at this distance).

The fact that secondary bonding involves a continuous range of excess bond distances, including some just at the borderline corresponding to the sums of van der Waals distances, shows the advantages of techniques such as NQR to determine the extent of the bonding. The Ni...Cl distances in [Ni(TMED)(tcp)$_2$] are among the shortest known, both in an absolute sense and with respect to normal M^{n+}-Cl$^-$ distances.

Very short secondary bonds are also found among the related methoxo-bridged cobalt(II), nickel(II), and copper(II) 2,4,6-trichlorophenolato complexes; the

shortest metal-organochlorine distances (2.48-2.53 Å) are found in the nickel(II) complex $[Ni(OCH_3)(CH_3OH)(tcp)]_4$ (17). The cobalt(II) analogue (15) still has rather short Co-Cl distances of 2.62 and 2.64 Å; but the copper(II) compound has distances ranging from 2.74 to 2.98 Å (44).

A similar argument based on octahedral site stabilization energies can be made. The methoxo-bridged complexes would be five-coordinate (either square pyramidal or trigonal bipyramidal) without coordination of the organochlorine. For high-spin metal ions, the OSSE as compared to a square-pyramidal complex is: $d^7 = -2.86\ Dq_{oct} < d^8 = +2\ Dq_{oct} > d^9 = -2.86\ Dq_{oct}$, again favoring Ni^{2+}. The OSSE as compared to a trigonal-bipyramidal complex is: $d^7 = +2.56\ Dq_{oct} < d^8 = +5.75\ Dq_{oct} > d^9 = -1.07\ Dq_{oct}$, also favoring Ni^{2+}. Note that although the OSSE favors octahedral coordination for $[Ni(py)_3(tcp)_2]$, the steric crowding would increase. Thus the non-preferred five-coordinate geometry is preserved.

Unfortunately we failed to find the expected large *ortho*-chlorine NQR Dn's for nickel in the methoxo-bridged compounds, for which the very short Ni-Cl distances would lead one to anticipate a Δv of perhaps 4 MHz. The methoxo compound of known structure, $[Ni(OCH_3)(CH_3OH)(tcp)]$, failed to give an NQR spectrum at all; from its structure twelve signals were anticipated.

$[Ni(OCH_3)(CH_3OH)(Br-dcp)]_4$ gave only two high-frequency signals, while $[Ni(OCH_3)(CH_3OH)(dcp)]_4$ gave four. It is possible that half of the observed signals are due to Cl-2 and half to Cl-6, in which case either these analogues have no organochlorine coordination and are thus grossly not isostructural to the X = Cl compound, or that these represent two serious cases in which the frequency splittings predicted by the equation above fail to materialize.

But it is also known that the detection of NQR signals requires that they have relaxation times which are neither too long nor too short. Ni^{2+} has unpaired electrons, which can greatly shorten relaxation times. One of these unpaired electrons is located in the nickel $d_{(z2)}$ or $d_{(x2-y2)}$ orbital, which is directed straight at the coordinated organochlorine. So possibly our failure to observe NQR signals clearly attributable to the coordinated chlorines in $[Ni(OCH_3)(CH_3OH)(dcp)]_4$ or $[Ni(OCH_3)(CH_3OH)(Br-dcp)]_4$ (or in the cases of $[Ni(OCH_3)(CH_3OH)(tcp)]_4$ or $[Ni(Ph_3P)_2(tcp)_2]$, to any chlorines) is a result of excessively short chlorine relaxation times due to delocalization of unpaired nickel electrons into the chlorophenolate ligand. (Although this problem could in principle be overcome by recording the NQR spectrum at liquid helium temperature, we do not have the capability of doing this experiment.) We hypothesize that this problem does not occur in the other

nickel chlorophenolates or in any of the cobalt
chlorophenolates because these have longer M-Cl distances
and hence probably less extensive delocalization of the
unpaired electrons.

Some inconclusive support for this hypothesis
results by comparing the apparent signal-to-noise ratios
of the coordinated and the non-coordinated ortho-
chlorines in a given compound. In the copper(II),
zinc(II), and mercury(II) chlorophenolates these apparent
signal-to-noise ratios tend to be similar for all
chlorines, presumably due to the absence of great
dissimilarities in the relaxation times of the
coordinated and the non-coordinated chlorines. Fairly
frequently in the nickel and cobalt chlorophenolates,
however, there are great disparities in the apparent
signal-to-noise ratios. This could result if the
delocalization of the unpaired $d_{(z2)}$ or $d_{(x2-y2)}$ electron
changed the relaxation times of the two types of ortho-
chlorine so drastically that one or the other could much
more efficiently be detected by the NQR spectrometer
(45). But since our superregenerative Decca instrument
does not give true lineshapes, much less measurements of
the spin-spin relaxation time T_2, this speculation would
need verification with data from a pulse NQR
spectrometer.

We have previously found (24) that the NQR
frequencies of strongly coordinated ortho-chlorines show

reduced temperature dependencies (in brackets in Table II) as compared to other *ortho* chlorines; this trend is also shown by the nickel chlorophenolates with nitrogen-donor ligands. The reason for this behavior is purely speculative: perhaps in these compounds the metal-chlorine bond is now strong enough to impede appreciably the chlorophenolate torsional vibrations that are responsible for the normal negative temperature dependence of NQR frequencies (6).

APPENDIX

APPENDIX

TABLE OF ABBREVIATIONS

Abbrev.	Ligand Name	Ligand Formula

Phenolate Anions

tcp	2,4,6-trichlorophenolate	$Cl_3C_6H_2O^-$
dcp	2,6-dichlorophenolate	$Cl_2C_6H_3O^-$
Br-dcp	4-bromo-2,6-dichlorophenolate	$BrCl_2C_6H_2O^-$

Nitrogen-Donor Ligands (see also Figure 2)

py	pyridine	C_5H_5N
dpy	2,2-dipyridyl	$NC_5H_4-C_5H_4N$
phen	1,10-phenanthroline	$C_{10}H_8N_2$
TMED	N,N,N',N'-tetramethyl-1,2-ethanediamine	

$$(CH_3)_2NC_2H_4N(CH_3)_2$$

| Me_5dien | N,N,N',N",N"-pentamethyl-1,4,7-triazaheptane | |

$$(CH_3)_2NC_2H_4N(CH_3)C_2H_4N(CH_3)_2$$

| im | imidazole | $C_3N_2H_4$ |
| Meim | 1-Methylimidazole | $C_4H_6N_2$ |

Phosphorus-Donor Ligands (see also Figure 3)

Ph_3P	triphenylphosphine	$(C_6H_5)_3P$
$MePh_2P$	methyldiphenylphosphine	$(CH_3)(C_6H_5)_2P$
diphos	1,2-bis(diphenylphosphino)ethane	

$$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$$

LITERATURE CITED

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1. Bartlett, N. *Proc. Chem. Soc. (London)*, **1962**, 218.

2. Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.*, **1990**, *99*, 89-115.

3. Alcock, N. W. *Adv. Inorg. Chem. Radiochem.*, **1972**, *15*, 1-58.

4. Wulfsberg, G. P.; Jackson, D.; Ilsley, W.; Dou, S.; Weiss, A.; Gagliardi, J. *Z. Naturforsch.*, **1992**, *47a*, 75-84.

5. Wulfsberg, G. P.; Yanisch, J.; Meyer, R.; Bowers, J.; Essig, M. *Inorg. Chem.*, **1984**, *23*, 715-719.

6. Das, T. P.; Hahn, E. L. *Nuclear Quadrupole Resonance Spectroscopy*; Academic Press, New York, 1958.

7. *Disposal and Decontamination of Pesticides*; M. V. Kennedy, Ed.; ACS Symposium Series 73; American Chemical Society, Washington, D.C., 1978.

8. Langer, H. G.; Brady, T. P.; Dalton, L. A.; Shannon, T. W.; Priggs, P. R. In *Chlorodioxins--Origin and Fate*, Advances in Chemistry 120; American Chemical Society, Washington, D.C., 1973.

9. Harrod, J. F. *Can. J. Chem.*, **1969**, 47, 637-645.

10. Richardson, M. F.; Wulfsberg, G. P.; Marlow, R.; Zaghonni, S.; M^{C}Corkle, D.; Shadid, K.; Gagliardi, J.; Farris, B. *Inorg. Chem.*, **1993**, *32*, 1913-9 and Supplementary Material.

11. Tolman, C. A. *Chem. Rev.*, **1977**, 77, 313.

12. Habiyakare, A.; Lucken, E. A. C. *J. Mol. Struct.*, **1989**, *213*, 231-237.

13. Wulfsberg, G. *Inorganic Chemistry;* University Science Books: Mill Valley, in preparation; Chapter 8.

14. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc. Dalton Trans.*, **1989**, S1-S71.

15. Simonov, Yu. A.; Matuzenko, G. S.; Botoshanskii, M. M.; Yampol'skaya, M. A.; Gerbeleu, N. V.; Malinovskii. T. I.; *Russ. J. Inorg. Chem.*, (*Engl. Trans.*) **1982**, *27*, 231-234.

16. Matuzenko, G.S.; Ablov, A. V.; Yampol'skaya, M. A.; Turte, K. I. *Sov. J. Coord. Chem.* (*Engl. Trans.*) **1979**, *5*, 377-382; *Koord. Khim.*, **1979**, *5*, 495-500.

17. Simonov, Yu. A.; Dvorkin, A. A.; Matuzenko, G. S.; Yampol'skaya, M. A.; Gifeisman, T. *Koord. Khim.*, **1984**, *10*, 1247-1252.

18. Meyer, R.; Gagliardi, J.; Wulfsberg,G. *J. Mol. Struct.*, **1983**, *111*, 311-316.

19. Yampol'skaya, M. A.; Dvorkin, A. A.; Simonov, Yu. A.; Voronkova, V. K.; Mosina, L. V.; Yablokov, Yu. V.; Turte, K. I.; Ablov, A. V.; Malinovskii, T. J. *Zh. Neorg. Khim.*, **1980**, *25*, 174-179; *Russ. J. Inorganic Chem.*, (*Engl. Transl.*) **1980**, *25*, 94-97.

20. Wong, R. Y.; Palmer, K. J.; Tomimatsu, Y. *Acta. Cryst.*, **1976**, *B32*, 567-571.

21. Ladd, M. F. C.; Perrins, D. H. G. *Acta. Cryst.*, **1980**, *B36*, 2260-2266.

22. Bullock, J. I.; Hobson, R. J.; Povey, D. C. *J. Chem. Soc. (Dalton Trans.)*, **1974**, *14*, 2037-2043.

23. Marengo-Rullan, J. R.; Willett, R. D. *Acta. Cryst.*, **1986**, *C42*, 1487-1489.

24. Wulfsberg, G.; Janisch, J.; Bowers, J.; Essig, M. *Inorg. Chem.*, **1984**, 715-719.

25. Cingi, M. B.; Lanfredi, A. M.; Tiripicchio, A.; Reedijk, J.; Landschoot, R. V. *Inorg. Chim. Acta.*, **1980**, *39*, 181-186.

26. Van Landschoot, R. C.; van Hest, J. A. M.; Reedijk, J. *Inorg. Chim. Acta.*, **1980**, *46*, 41-44.

27. Zaghonni, S. B.S. Honors Thesis, Brock University, March 1990.

28. Vogt, L. H.; LaPlaca, S. J.; Bednowitz, A. H. American Chemical Society Meeting, Inorganic Division, San Francisco, March 1968, abstract #123, and as reported in: Bullock, J. I.; Hobson, R. J.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1974**, 2037.

29. Huheey, James E. *Inorganic Chemistry: Principles of Structure and Reactivity,*" 3rd ed., Harper and Row, New York, 1983; pp 73-6; 258-9.

30. Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308.

31. Holmes, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3745.

32. Smith, G.; O'Reilly, E. J.; Reynolds, B. J.; Kennard, C. H. L.; Mak, T. C. W. *J. Organometal. Chem.*, **1987**, *331*, 275-279.

33. Gagliardi, J. B.S. Thesis; St. John's University, MN, 1980.

34. Shadid, K. M.S. Thesis, Middle Tennessee State University, Aug. 1986.

35. Farris, B. M.S. Thesis, Middle Tennessee State University, Dec. 1987.

36. Harris, C. M.; McKenzie, E. D. *J. Inorg. Nucl. Chem.*, **1967**, *29*, 1047-1068.

37. Venanzi, L. M. *J. Chem. Soc.*, **1958**, 722; **1962**, 719.

38. Jarrett, P. S.; Sadler, P. J. *Inorganic Chem.*, **1991**, *30*, 2098-2104.

39. Sentemov, V. V.; Krasil'nikova, E. A.; Berdnik, I. V.; Morozov, V. I.; Il'yasov, A. V.; Shagvaleev, F. Sh.; Zykova, T. V. *J. Gen. Chem. USSR (Engl. Trans.)* **1989**, *59*, 1574.

40. Drago, R. S. *Physical Methods in Chemistry*, 1st ed.; Saunders: Philadelphia, 1977, p. 424.

41. David M^{C}Corkle, Jr. died before he could begin writing this section, which is taken in large parts verbatim from Mr. M^{C}Corkle's article published in *Inorganic Chemistry*, reference (10).

42. Weiss, A. *Fortschr. chem. Forschung*, **1972**, *30*, 1 (see Figure III.1, p. 34).

43. Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*, London, Academic Press, 1969, Chapter 5.

44. Yablokov, Yu. V.; Simonov, Yu. A.; Yampol'skaya, M. S.; Dvorkin, A. A.; Matuzenko, G. S.; Voronkova, V. K.; Mosina, L. V. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1980, *25*, 1364; *Zh. Neorg. Khim.* 1980, *25*, 2468.

45. The compound $[Ni(py)_3(tcp)_2]$, in which there is a 1.0 Å excess bond distance and a 0.66 MHz frequency difference between one Cl-2 and the other Cl-2 and Cl-6 chlorines, also shows a significant difference in S/N ratios between the "coordinated" and the other chlorines; this might be taken as extremely weak evidence that there is still some bonding interaction at this long distance.