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Coordination of Ortho Chlorines in Nickel and Zinc 4-Substituted 2,6-Dichlorophenolates. Crystal and Molecular Structures of (*N,N,N′,N′*-Tetramethyl-1,2-ethanediamine)bis(2,4,6-trichlorophenolato-*O,Cl*)nickel(II) and Tris(pyridine)bis(2,4,6-trichlorophenolato-*O*)nickel(II)

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Nickel(II) and zinc(II) complexes of the 2,4,6-trichlorophenolate (tcp), 2,6-dichlorophenolate, and 4-bromo-2,6-dichlorophenolate ions were examined for organochlorine–metal secondary bonding by ^{35}Cl nuclear quadrupole resonance (NQR) spectroscopy and compared to analogous compounds with other transition metals. In chlorophenolate complexes of the type $M(OC_6H_2Cl_2X)_2(L)_2$, where L is an additional monodentate ligand, the strength of the M···Cl interaction is determined largely by the octahedral site stabilization energy and is greatest for the d^8 metal Ni^{2+}. Strong ligand fields that favor square coordination for d^7–d^9 metals and steric effects also play a role in M···Cl interactions, and the presence of additional ligands that form normal-strength bonds to the metal can prevent M···Cl interactions altogether. Ni(tcp-*O,Cl*)$_2$(TMED), where TMED is *N,N,N′,N′*-tetramethylethylenediamine, crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.191(2)$ Å, $b = 15.392(2)$ Å, $c = 18.436(3)$ Å, $\beta = 94.17(2)°$, and $Z = 4$. The structure was refined by least-squares techniques to $R = 0.039$ for 1418 reflections having $I > 3\sigma(I)$. Nickel is chelated to the two tcp ligands through the oxygen and the 2-chloro groups, with average distances 1.960 and 2.611 Å, respectively, as well as to the TMED ligand (average Ni–N = 2.097 Å). The chlorines are coordinated cis in the octahedron whereas the oxygens are trans. Ni(tcp)$_2$(py)$_3$ crystallizes in the monoclinic space group $C2/c$ with $a = 18.859(2)$ Å, $b = 11.670(2)$ Å, $c = 15.892(2)$ Å, $\beta = 121.83(1)°$, and $Z = 4$. The structure refined to $R = 0.047$ for the 1178 reflections having $I > 3\sigma(I)$. The square pyramidal molecules possess crystallographic 2-fold symmetry, and the closest Ni···Cl distance is 3.441(2) Å. The Ni–O, Ni–N, and Ni–N$_{ax}$ distances are 2.014(4), 2.074(4), and 2.052(7) Å, respectively. On the basis of NQR and crystallographic criteria, the Ni–Cl contact in Ni(tcp)$_2$(py)$_3$ is, at best, chemically insignificant, while the secondary bond in Ni(tcp-*O,Cl*)$_2$(TMED) is one of the strongest and shortest yet observed.

Introduction

Inorganic chemists have generally assumed that the unshared electron pairs found on halogen atoms in halocarbons cannot be donated to metal atoms, so that chlorocarbons can safely be used as inert solvents in inorganic and organometallic reactions. But in recent years a number of complexes of simple and chelating halocarbons were synthesized and characterized by X-ray crystallography; these have been reviewed by Kulawiec and Crabtree.[1] Observed secondary[2] metal–organohalogen distances range continuously from some which are almost as short as a single metal–inorganic halogen bond to others which may be about as long as the sum of the difficult-to-determine sum of the van der Waals raddi of the metal and halogen atoms. Hence it is desirable to supplement the X-ray crystallographic evidence for metal–organohalogen secondary bonding with data from other physical methods. Of these, only halogen NQR (nuclear quadrupole resonance) spectroscopy seems sufficiently sensitive to the small changes occurring at the coordinated chlorocarbon to give reliable results;[3] it can furthermore be used on samples with smaller, less perfect crystals that are unsuitable for X-ray studies.

The 2,4,6-trichlorophenolate ion forms crystallographically-characterized complexes involving chelation through oxygen and chlorine donor atoms to iron(III),[4] cobalt(II),[5,6] nickel(II),[7] copper(II),[8–12] and silver(I)[13] ions; we have previously charac-

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terized copper(I),[13] silver(I),[13] mercury(II),[14] cobalt(II),[15] and copper(II)[16] 2,4,6-trichlorophenolates by ^{35}Cl NQR spectroscopy. Here we complete the data on the later fourth-period transition metal divalent cations by reporting the syntheses, characterizations, and ^{35}Cl NQR data for nickel(II) and zinc(II) complexes $M(OC_6H_2Cl_2X)_2L_n$ involving the ligands L = *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (TMED), pyridine (py), methanol and methoxide, triphenylphosphine, and 1,2-bis(diphenylphosphino)ethane (diphos), and the chlorophenolate ions 2,4,6-trichlorophenolate (tcp), 2,6-dichlorophenolate (dcp), and 4-bromo-2,6-dichlorophenolate (Br-dcp); in addition, NQR data are reported for one iron(III) compound, $[(C_6H_5)_4P][Fe(tcp)_4)]$.[4] We also report the crystal and molecular structures of two nickel(II) compounds, (*N,N,N′,N′*-tetramethyl-1,2-ethanediamine)bis(2,4,6-trichlorophenolato-*O,Cl*)nickel(II) ($Ni(tcp)_2(TMED)$) and tris(pyridine)bis(2,4,6-trichlorophenolato-*O*)nickel(II) ($Ni(tcp)_2(py)_3$). We shall find that the organochlorine–nickel bond in the former compound is nearly as short as the normal octahedral nickel(II)–chlorine single-bond distance, 2.44 Å,[17] and is substantially shorter than those found in nearly all 2,4,6-trichlorophenolates previously studied. And since the distances and NQR spectra seem to depend on the d^n electronic configuration of the metal ion and the geometry of the complex, we shall analyze the results in terms of the transition metal crystal field theory.

Such relatively short organohalogen–metal bonds have previously been found almost exclusively in complexes of soft halocarbon bases with soft-acid metal ions such as iridium(I) and silver.[1,3,18,19] Comparatively strong metal–organochlorine interactions involving economically more accessible metals such as nickel could have practical implications, since coordination of an organohalogen group to a metal ion is often postulated as the first step in providing metal assistance[20] to the notoriously-difficult process of nucleophilic aromatic substitution in aryl halides. The careful study of metal interactions with the 2,4,6-trichlorophenolato ligand allows us to extrapolate how bonding is altered in such a ligand as it begins the postulated first step in metal-assisted nucleophilic substitution. And such study could help us to select optimal metal ions to use in attempting to promote the dehalogenation of waste aromatic chlorocarbon pesticides, herbicides, and other such compounds.

Experimental Section

Table I lists the compounds prepared and the methods used; methods a–c are based on literature procedures summarized in the Discussion. $[(C_6H_5)_4P][Fe(tcp)_4]$ was provided by Stephen Koch.[4] 4-Bromo-2,6-dichlorophenol was obtained by the bromination of 2,6-dichlorophenol.

$Ni(tcp\text{-}O,Cl)_2(TMED)$ (Method d). Solutions of 41.5 g (0.21 mol) of 2,4,6-trichlorophenol in 150 mL of acetone, 11.22 g (0.20 mol) of KOH in 50 mL of water, and 15.1 mL (0.10 mol) of TMED were mixed; 29.08 g (0.10 mol) of $Ni(NO_3)_2{\cdot}6H_2O$ in 150 mL of acetone was added. After 2-h of stirring blue crystals deposited and were filtered off and dehydrated in an oven (100 °C, 2 h). The yellow anhydrous product was dissolved in hot toluene, and the solution was filtered from insoluble KNO_3. Cooling overnight gave crystals, which were washed with pentane and dried. Large crystals for X-ray crystallographic studies were grown from pentane solution (0.26 g/150 mL solubility) by slow evaporation in an insulated beaker.

Table I. Compounds Prepared, Methods of Preparation, Magnetic Susceptibilities (μ_B), Colors, Longest-Wavelength Absorptions (nm), and 10*Dq* (cm^{-1})

compd prepared	prep	μ_{eff}	color	ν_1	10*Dq*
$Ni(Br\text{-}dcp)_2(TMED)$	*a*	3.40	yellow	1395	7170
$Ni(tcp)_2(TMED)$	*a, d*		yellow	1385	7220
$Ni(tcp)_2(TMED)(H_2O)_4$	*c*	3.28[f]	blue	1087[f]	9200[f]
$Zn(tcp)_2(TMED)$	*a*		colorless		
$Ni(dcp)_2(TMED)$	*a*		yellow	1370	7580
$Zn(dcp)_2(TMED)$	*a*		colorless		
$Ni(Br\text{-}dcp)_2(py)_2$	*a, j*		yellow		
$Ni(tcp)_2(py)_2$	*d*	3.17[f]	yellow	1428[f]	7000
$Ni(tcp)_2(py)_2(H_2O)_4$	*c*	3.17[f]	blue	1041[f]	9600
$Zn(tcp)_2(py)_2$	*a*		colorless		
$Ni(dcp)_2(py)_2$	*a*		yellow		
$Zn(dcp)_2(py)_2$	*b*		colorless		
$Ni(Br\text{-}dcp)_2(py)_3$	*c*		green		
$Ni(tcp)_2(py)_3$	*c*		green		
$[Ni(OMe)(MeOH)(Br\text{-}dcp)]_4$	*e, g*		green		
$[Ni(OMe)(MeOH)(tcp)]_4$	*e*		green		
$[Ni(OMe)(MeOH)(dcp)]_4$	*e*		green		
$Ni(tcp)_2(Ph_3P)_{2?}$	*b, h*	2.09	green	920	
$Ni(tcp)_2(diphos)_{1?}$	*b, h*	dia[i]	red	600	
$Ni(dcp)_2(diphos)_{1?}$	*b, h*	dia[i]	red	550	

[a–e] For synthetic methods see discussion of syntheses in text. [f] Reported by Bullock and Hobson.[25] [g] Not submitted for elemental analysis due to its high sensitivity to atmospheric moisture. [h] Unstable in air as a solid or in solution; data obtained on impure samples. Although qualitatively identified by their IR spectra, the samples were unsuitable for elemental analysis, so the number of moles of ligands in the complex is shown with a question mark (?). [i] Diamagnetic. [j] Not analyzed since quantitative separation from $Ni(Br\text{-}dcp)_2(py)_2$ was impossible; identified by its IR spectrum and the extreme similarity of its NQR spectrum to that of $Ni(tcp)_2(py)_2$.

$[Ni(OMe)(MeOH)(dcp)]_4$, $[Ni(OMe)(MeOH)(Br\text{-}dcp)]_4$, and $[Ni(OMe)(MeOH)(tcp)]_4$ (Method e). $Ni(NO_3)_2{\cdot}6H_2O$ (3.63 g, 12.5 mmol) and triethyl orthoformate (15 mL, 90 mmol) were dissolved in 200 mL of methanol. After the mixture was allowed to stand overnight, 12.5 mmol of phenol $HOC_6H_2Cl_2X$ and 5.7 mL of 25% $NaOCH_3$ solution (Aldrich; 25 mmol) in 95 mL of methanol was added dropwise with stirring. A precipitate was filtered off; the clear yellow filtrate deposited large green crystals of the very moisture-sensitive product after 24 h. Although this synthesis differs slightly from that used to prepare the crystallographically-characterized sample of $[Ni(OMe)(MeOH)(tcp)]_4$,[7] the elemental analyses of $[Ni(OMe)(MeOH)(tcp)]_4$ and $[Ni(OMe)(MeOH)(dcp)]_4$ show that the products have the same stoichiometry.

Characterization. All products were initially characterized by their infrared spectra, obtained on Perkin-Elmer 567 and 727b spectrophotometers. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and by Midwest Microlabs, Indianapolis, IN; water was determined by titration with a Mettler DL-18 Karl Fischer titrator using Hydranal titrant. Satisfactory analytical results were obtained for all compounds except the very air-sensitive ones noted in Table I; these analyses are given in the supplementary material. Visible and near-infrared spectra of complexes were measured in dichloromethane or chloroform solution on a Hewlett Packard 8451A diode-array and a Cary 17D spectrophotometer, respectively. Magnetic susceptibilities were determined on solid samples at room temperature using a JME magnetic susceptibility balance. The longest-wavelength absorptions detected and the effective magnetic moments of the complexes are listed in Table I. ^{35}Cl NQR spectra were obtained on a Decca superregenerative NQR spectrometer using Zeeman modulation at 77, 195, and 273 K; the frequencies, S/N ratios, and temperature dependences are listed in Table II.

Crystallography. Unit cell dimensions were determined from the angular setting of 25 reflections measured with graphite-monochromatized Mo Kα radiation. Intensities were measured by the ω–2θ technique at room temperature (293–298 K) with an Enraf-Nonius CAD4 single-crystal diffractometer and corrected for Lorentz and polarization effects but not for absorption. The intensity of the standard reflection for $Ni(tcp)_2(TMED)$ was constant with time (±2% maximum variation), but that of $Ni(tcp)_2(py)_3$ decreased to 75% of its original value by the end of the data collection for the second quadrant of data; reflections were

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

compd	Cl-4 freq[a]	Cl-6 freq	Cl-2 freq	$\Delta\nu$
$Zn(dcp)_2(TMED)$		34.754(5)[*b*]	33.813(8)[*b*]	0.941
		34.696(6)[*b*]	33.813(8)[*b*]	0.941
		34.602(6)[*b*]	33.433(3)[*b*]	1.321
		34.403(5)[*b*]	33.331(4)[*b*]	1.423
$Zn(dcp)_2(py)_2$		34.997(3)[0.62]	33.793(3)[0.57]	1.204
		34.579(3)[0.90]	33.401(3)[0.49]	1.596
$Ni(dcp)_2(TMED)$		34.721(9)[0.61]	32.196(17)[0.45]	2.525
		34.482(9)[0.72]	32.033(18)[0.43]	2.688
$Ni(dcp)_2(py)_2$		34.711(11)[0.53]	31.931(9)[0.33]	2.780
		34.568(7)[0.40]	31.537(7)[0.38]	3.174
$[Ni(OMe)(MeOH)(dcp)]_4$		34.937(6)	*c*	
		34.904(5)	*c*	
		34.802(7)	*c*	
		34.706(8)	*c*	
$[Ni(OMe)(MeOH)(Br\text{-}dcp)]_4$		35.565(4)	*c*	
		35.484(3)	*c*	
$Zn(tcp)_2(TMED)$	35.909(4)[0.73]	35.332(4)[0.71]	34.050(5)[0.43]	1.282
	35.761(4)[0.86]	35.145(4)[0.67]	34.050(5)[>0.5]	1.282
$Zn(tcp)_2(py)_2$	35.243(3)[0.60]	35.102(6)[0.48]	34.598(4)[0.70]	0.504
	35.189(4)[0.63]	35.053(6)[0.87]	34.484(3)[0.72]	0.618
$Ni(tcp)_2(TMED)$	35.735(8)[0.67]	35.381(11)[0.66]	32.592(15)[0.41]	2.789
	35.641(8)[0.67]	35.381(11)[0.71]	32.199(12)[0.36]	3.182
$Ni(Br\text{-}dcp)_2(TMED)$		36.036[d]	32.951[d]	3.085
		35.680[d]	32.912[d]	3.124
		35.413[d]	32.814[d]	3.222
		35.241[d]	32.745[d]	3.291
		34.935[d]	32.445[d]	3.591
$Ni(tcp)_2(py)_2$	35.385(3)[0.54]	35.100(3)[0.63]	33.123(7)[0.48]	1.977
	35.187(4)[0.51]	35.040(3)[0.62]	35.529(6)[0.42]	2.571
$Ni(Br\text{-}dcp)_2(py)_2$		35.215(3)[0.54]	33.098(7)[0.52]	2.117
		35.121(4)[0.80]	32.500(5)[0.37]	2.715
$Ni(tcp)_2(py)_3$	34.948(30)[0.52]	34.846(32)[0.49]	34.177(13)[0.58]	0.669
$Ni(Br\text{-}dcp)_2(py)_3$	222.6(100)[e]	34.871(22)[0.49]	34.067(12)[0.56]	0.804
$Ni(tcp)_2(diphos)_{1?}$	35.461(2)	35.039(2)	34.635(2)	0.404
	35.363(2)	34.879(2)	34.530(2)	0.509
$[Ph_4P][Fe(tcp)_4]$	36.290(2)	35.822(2)	35.499(2)	0.323
	36.026(3)	35.602(2)	35.434(2)	0.388
	35.926(3)	35.534(2)	35.192(2)	0.630
$Ni(tcp)_2(TMED)(H_2O)_4$	35.627(4)	35.270(4)	34.891(3)	0.379
	35.475(3)	35.037(5)	34.803(5)	0.467
$Ni(tcp)_2(py)_2(H_2O)_4$	35.400(2)	35.043(2)	34.820(3)	0.223
	35.093(2)	34.883(2)		

[a] Signal-to-noise ratios given in parentheses; temperature dependence of the frequencies (frequency at 77 K minus frequency at 273 K) 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. [b] Undergoes phase transition above 77 K. [c] Signal could not be detected. [d] Obtained as mixed phases; signal intensities vary from 2 to 4 depending on treatment of sample. [e] ^{81}Br NQR frequency at ambient temperature, recorded on a Wilks NQR-1A spectrometer.

corrected for the variation in the standard and averaged. The structures were solved by Patterson methods and refined by full-matrix least-squares procedures, with anisotropic displacement parameters for all atoms heavier than carbon. Scattering factors, including the real and imaginary parts of the anomalous scattering, were taken from ref 21. The form of the anisotropic displacement parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*\ldots)]$. The weighting scheme was $w = [\sigma^2(F) + pF^2]^{-1}$ with a value of p assigned to minimize the variance as a function of reflection intensity. Programs used included SHELX-76[22] and ORTEP.[23] The crystal data and experimental details are listed in Table III. The final parameters are given in Tables IV and V.

Table III. Crystallographic Data for $Ni(tcp\text{-}O,Cl)_2(TMED)$ and $Ni(tcp\text{-}O)_2(py)_3$

	$Ni(tcp\text{-}O,Cl)_2(TMED)$	$Ni(tcp\text{-}O)_2(py)_3$
formula	$C_{18}H_{20}Cl_6N_2NiO_2$	$C_{27}H_{19}Cl_6N_3NiO_2$
fw	567.78	688.87
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
α, Å	8.191(2)	18.859(2)
b, Å	15.392(2)	11.670(2)
c, Å	18.436(3)	15.892(2)
β, deg	94.17(2)	121.83(1)
V, Å^3	2318.1(7)	2971.6(6)
Z	4	4
D_{calcd}, g/cm^3	1.63	1.54
D_{measd}, g/cm^3	1.61	1.52
μ, cm^{-1} (Mo Kα)	15.6	12.2
T, °C	20–25	20–25
no. of refls [$I > 3\sigma(I)$]	1418	1178
residuals R, R_w[a]	0.039, 0.046	0.047, 0.052

[a] $R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Discussion

Syntheses. Three of the compounds in this study ($Ni(tcp)_2(TMED)(H_2O)_4$, $Ni(tcp)_2(py)_2(H_2O)_4$, and $Ni(tcp)_2(py)_2$) were first prepared by Bullock and Hobson;[24] $[Ni(OMe)(MeOH)(tcp)]_4$ has also previously been studied.[7,25] In most cases, one of three synthetic routes sufficed. (a) Anhydrous $ZnCl_2$ or anhydrous (yellow) $NiBr_2$[26] or NiI_2 and the appropriate amount of ligand in dry acetone were reacted with 2 mol of $TlOC_6H_2Cl_2X$ as previously reported for the cobalt analogues.[15] (b)

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Table IV. Fractional Coordinates and Displacement Parameters for Ni(tcp-*O*,*Cl*)$_2$(TMED)

atom	x/a	y/b	z/c	U or U_{eq},[a] Å^2
Ni	0.87782(9)	0.19542(5)	0.17724(5)	0.0454
Cl(1)	0.6048(2)	0.1199(1)	0.1357(1)	0.0676
Cl(2)	0.5487(3)	−0.2091(1)	0.0381(1)	0.0906
Cl(3)	1.1433(2)	−0.0656(1)	0.0896(1)	0.0707
Cl(4)	0.8850(2)	0.2621(1)	0.0458(1)	0.0668
Cl(5)	0.7196(3)	0.5915(1)	−0.0221(1)	0.0960
Cl(6)	0.5854(3)	0.4585(1)	0.2371(1)	0.0789
O(1)	0.9591(4)	0.0868(2)	0.1376(2)	0.0488
O(2)	0.7523(5)	0.3026(3)	0.1869(2)	0.0520
N(1)	1.1130(6)	0.2408(3)	0.2107(3)	0.0510
N(2)	0.8583(6)	0.1587(3)	0.2857(3)	0.0520
C(1)	0.8675(7)	0.0222(4)	0.1127(4)	0.042(2)
C(2)	0.6966(7)	0.0242(4)	0.1085(4)	0.045(2)
C(3)	0.5956(9)	−0.0447(4)	0.0847(4)	0.058(2)
C(4)	0.6699(7)	−0.1193(4)	0.0640(4)	0.053(2)
C(5)	0.8372(7)	−0.1248(4)	0.0641(4)	0.050(2)
C(6)	0.9316(7)	−0.0563(4)	0.0884(3)	0.044(2)
C(7)	0.7419(7)	0.3657(4)	0.1395(4)	0.042(2)
C(8)	0.8019(7)	0.3609(4)	0.0701(4)	0.046(2)
C(9)	0.7977(8)	0.4293(4)	0.0208(4)	0.062(2)
C(10)	0.7257(8)	0.5055(5)	0.0396(4)	0.058(2)
C(11)	0.6605(7)	0.5148(4)	0.1050(4)	0.052(2)
C(12)	0.6675(8)	0.4463(4)	0.1538(4)	0.050(2)
C(13)	1.1220(8)	0.3368(5)	0.2187(4)	0.064(2)
C(14)	1.2404(9)	0.2162(5)	0.1603(4)	0.068(2)
C(15)	0.8738(8)	0.0617(4)	0.2933(4)	0.062(2)
C(16)	0.7058(9)	0.1870(5)	0.3170(4)	0.072(2)
C(17)	1.1471(8)	0.1989(5)	0.2811(4)	0.066(2)
C(18)	0.9988(8)	0.2025(5)	0.3252(4)	0.066(2)

[a] $U_{eq} = {}^1/_3\sum\sum U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$.

Table V. Fractional Coordinates and Displacement Parameters for Ni(tcp-*O*)$_2$(py)$_3$

atom	x/a	y/b	z/c	U or U_{eq},[a] Å^2
Ni[b]	0.5000	0.20164(9)	0.2500	0.040
Cl(1)	0.2977(1)	0.0713(2)	0.2969(1)	0.078
Cl(2)	0.3191(1)	0.4199(2)	0.5291(2)	0.089
Cl(3)	0.4488(1)	0.4643(2)	0.3019(2)	0.099
O(1)	0.3902(2)	0.2255(4)	0.2405(3)	0.061
N(1)	0.4353(3)	0.2064(4)	0.0965(3)	0.042
N(2)[b]	0.5000	0.0258(6)	0.2500	0.049
C(1)	0.3739(4)	0.2704(5)	0.3041(5)	0.048(2)
C(2)	0.3309(4)	0.2094(5)	0.3400(4)	0.047(2)
C(3)	0.3134(4)	0.2528(5)	0.4071(4)	0.049(2)
C(4)	0.3392(4)	0.3621(6)	0.4422(5)	0.054(2)
C(5)	0.3817(4)	0.4277(6)	0.4104(5)	0.054(2)
C(6)	0.3968(4)	0.3806(5)	0.3425(5)	0.052(2)
C(7)	0.3660(4)	0.2698(5)	0.0442(5)	0.050(2)
C(8)	0.3237(5)	0.2777(6)	−0.0590(5)	0.062(2)
C(9)	0.3557(5)	0.2206(6)	−0.1076(6)	0.072(2)
C(10)	0.4283(4)	0.1555(6)	−0.0528(5)	0.065(2)
C(11)	0.4639(4)	0.1505(5)	0.0477(5)	0.049(2)
C(12)	0.5718(4)	−0.0331(6)	0.3010(5)	0.058(2)
C(13)	0.5741(5)	−0.1513(7)	0.3031(6)	0.075(2)
C(14)[b]	0.5000	−0.2095(10)	0.2500	0.085(4)

[a] $U_{eq} = {}^1/_3\sum\sum U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j$. [b] Occupancy factor 0.5.

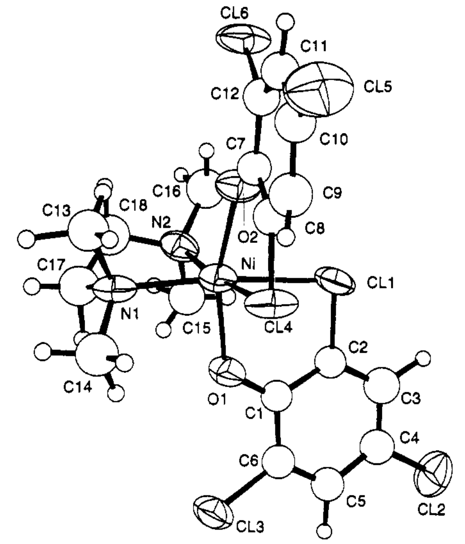

Figure 1. Molecular structure of Ni(tcp-*O*,*Cl*)$_2$(TMED).

Preformed nickel halide complexes Ni(diphos)Cl$_2$ (Strem) and Ni(Ph$_3$P)$_2$Br$_2$[27] were substituted as reactants in procedure a. (c) Aqueous hydrated nickel nitrate or zinc nitrate was reacted with aqueous NaOC$_6$H$_2$Cl$_2$X and ligand to precipitate the zinc or hydrated nickel complex (method 1 of Bullock[24]), which was dried in an Abderhalden vacuum apparatus at 110 °C. Usually the product was then recrystallized from acetone/heptane, but recrystallization of Ni(tcp)$_2$(py)$_2$ gave crystals of either the green tris(pyridine) adduct Ni(tcp)$_2$(py)$_3$ or the blue hydrate Ni(tcp)$_2$(py)$_2$(H$_2$O)$_4$, as both of these compounds are considerably less soluble than the desired bis(pyridine) complex. Ni(tcp)$_2$(py)$_3$ was subsequently synthesized rationally by recrystallization of Ni(tcp)$_2$(py)$_2$(H$_2$O)$_4$ from organic solvents containing an excess of pyridine; Ni(tcp)$_2$(py)$_2$ was analytically pure without recrystallization.

Larger quantities of yellow-green crystalline anhydrous Ni(tcp)$_2$(TMED), including the sample for the X-ray structure, were prepared by procedure d, given in the Experimental Section. The literature[7,25] syntheses of the methoxo-bridged nickel(II) chlorophenolate [Ni(OMe)(MeOH)(tcp)]$_4$ presented, difficulties when we tried to synthesize [Ni(OMe)(MeOH)(tcp)]$_4$, [Ni(OMe)(MeOH)(Brdcp)]$_4$, and [Ni(OMe)(MeOH)(dcp)]$_4$; the reaction given in the Experimental Section, which uses NaOCH$_3$ as an alternate source of methoxide ion, proved successful.

Difficulties were experienced with the syntheses of the products containing phosphine ligands. Only Ni(tcp)$_2$(diphos)$_{1?}$ could be isolated in a seemingly pure state, 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;[28] the rate of this reaction is evidently dramatically enhanced in chlorophenolate complexes. The compound Ni(tcp)$_2$(Ph$_3$P)$_{2?}$ was obviously impure when isolated and gave no NQR spectrum, while Ni(dcp)$_2$(Ph$_3$P)$_2$ 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.

Molecular Structures. Figures 1 and 2 show the structures of Ni(tcp-*O*,*Cl*)$_2$(TMED) and Ni(tcp)$_2$(py)$_3$, and Table VI gives important bond distances and angles for the two compounds.

The tcp ligands are chelated to the nickel in Ni(tcp)$_2$(TMED), 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(tcp-*O*,*Cl*)$_2$(TMED), in which the oxygens are cis and chlorines trans.[8] The Ni–Cl distances, 2.586(2) and 2.637(2) Å, are somewhat longer than the usual octahedral Ni–terminal chloride distance, 2.441 Å,[17] 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.[17] The C–Cl–Ni angles, 93.9(2) and 94.8(2)°, fall within

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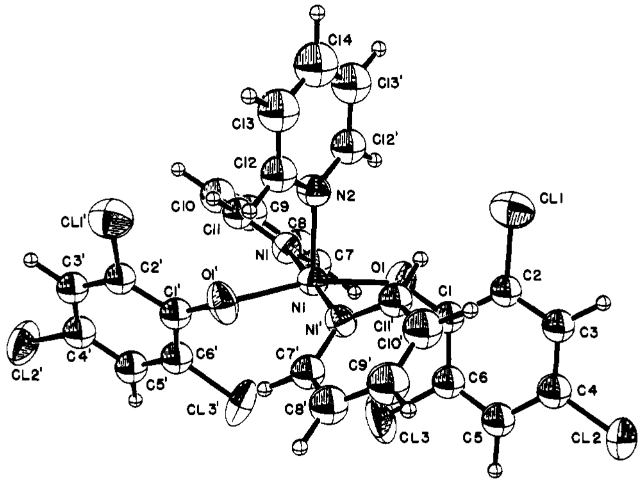


Figure 2. Molecular structure of Ni(tcp-*O*)$_2$(py)$_3$.

Table VI. Selected Distances (Å) and Angles (deg) for Ni(tcp-*O,Cl*)$_2$(TMED) and Ni(tcp-*O*)$_2$(py)$_3$

	Ni(tcp-*O,Cl*)$_2$(TMED)		
Ni–N(1)	2.099(5)	Ni–O(2)	1.959(4)
Ni–O(1)	1.961(4)	Ni–Cl(4)	2.637(2)
Ni–Cl(1)	2.586(2)	O(1)–C(1)	1.308(7)
Ni–N(2)	2.095(6)	O(2)–C(7)	1.304(7)
Ni–O(1)–C(1)	125.3(4)	N(1)–Ni–O(2)	99.8(2)
Ni–O(2)–C(7)	125.1(4)	N(2)–Ni–O(2)	93.6(2)
C(2)–Cl(1)–Ni	94.8(2)	Cl(1)–Ni–O(1)	79.4(1)
C(8)–Cl(4)–Ni	93.9(2)	Cl(1)–Ni–N(2)	92.1(2)
O(1)–Ni–O(2)	161.2(2)	Cl(1)–Ni–O(2)	87.5(1)
N(1)–Ni–Cl(1)	172.6(1)	Cl(1)–Ni–Cl(4)	88.8(1)
N(2)–Ni–Cl(4)	172.1(1)	Cl(4)–Ni–O(1)	87.6(1)
O(1)–Ni–N(1)	93.7(2)	Cl(4)–Ni–O(2)	78.6(1)
O(1)–Ni–N(2)	100.2(2)	Cl(4)–Ni–N(1)	93.4(2)
N(1)–Ni–N(2)	86.7(2)		
	Ni(tcp-*O*)$_2$(py)$_3$		
Ni–N(1)	2.074(4)	O(1)–C(1)	1.312(7)
Ni–N(2)	2.052(7)	Ni–Cl(3)	3.441(2)
Ni-O(1)	2.014(4)		
N(1)–Ni–N(2)	91.5(1)	N(2)–Ni–O(1)	97.9(1)
N(1)–Ni–O(1)	88.0(2)	Ni–O(1)–C(1)	130.4(4)

the range of angles observed for intermolecular C–Cl···M contacts.[13,30]

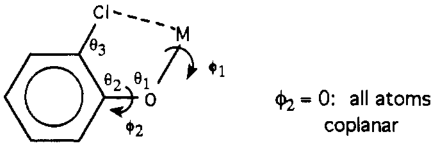
The five-coordinate complex Ni(tcp)$_2$(py)$_3$ lies on a crystallographic 2-fold symmetry axis, and the geometry about the nickel is best described as a distorted square pyramid with one of the pyridine ligands occupying an axial position. The closest Ni···Cl contacts are to two symmetry-related Cl(3) atoms below the base of the pyramid; the distance of 3.441(2) Å is at the van der Waals contact limit[29] 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.

Bullock and Hobson measured the magnetic susceptibilities and visible spectra of the hydrated and anhydrous nitrogen-ligand nickel(II) 2,4,6-trichlorophenolates[24] 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(tcp)$_2$(TMED) shows that the reason for the lower crystal field splitting is due to coordination of two organochlorines rather than two water molecules.

Structural Parameters Defining Secondary Bonding. The Cambridge Crystallographic Database (1991 version)[32] was searched for structures containing transition metals bonded to the oxygen of an *o*-chlorophenolate moiety. Chlorinated catechols and 8-hydroxyquinolines were eliminated from the group since their propensity toward *O,O*- or *O,N*-chelation eliminates the possibility of intramolecular M···Cl interactions. The search resulted in 22 complexes[4–13,33–40] displaying the full range of behavior from bonding to nonbonding organochlorine. Structural parameters are given in Table I of the supplementary material.

A reasonable structural criterion for a bonding interaction is that the observed M···Cl distance be less than 1.0 Å greater than the normal distance[17] between the metal and chloride ion; this criterion will be discussed in more detail below. By this criterion, 14 *o*-chlorophenolate complexes, including Ni(tcp)$_2$(TMED), contain bonded organochlorine[5–13,33–35] and eight, including Ni(tcp)$_2$(py)$_3$, do not[4,36–40] (note that [(C$_6$H$_5$)$_4$P][Fe(tcp)$_4$)] was originally thought to exhibit secondary bonding interactions[4]). The fact that there is a continuous range of distances, including some just at the borderline, shows the advantages of techniques such as NQR to determine the extent of the bonding. The Ni···Cl distances in Ni(tcp)$_2$(TMED) are among the shortest known, both in an absolute sense and with respect to normal M^{n+}–Cl^- distances. Only [Ni(OMe)(MeOH)(tcp)]$_4$ has shorter distances involving chlorines in chlorophenolate complexes, 2.483–2.530 Å.[7]

The ligands display conformational flexibility about the C–O bond (ϕ_2), and the ligand can twist either to avoid metal–chlorine contacts or to maximize them. Rotation about the C–O bond takes the nickel out of the ring plane and increases the Ni–Cl distance; ϕ_2 is generally >60° in complexes with nonbonded ortho chlorines and <60° in complexes with short M···Cl distances. For a fixed value of ϕ_2, the M···Cl distance can be increased by expanding the the angles θ_1, θ_2, and θ_3; θ_1 is especially variable and can reach values above 140° in some complexes.[36–40] The torsion angle ϕ_1 varies the position of the tcp ligand plane with respect to other ligands but does not change the M···Cl distance.



The C′–Cl distance for the secondary bonded chlorines is not significantly lengthened in comparison to other C–Cl distances, even in the complexes with the shortest M′–Cl distances. This is perhaps not surprising, given the fact that the chlorine is using a second pair of electrons for the additional bonding and is not sharing a single pair between three centers.

NQR Spectra. The ^{35}Cl NQR data recorded at 77 K for the compounds in this study are reported in Table II. Frequencies are given in megahertz, followed by the signal-to-noise ratio for

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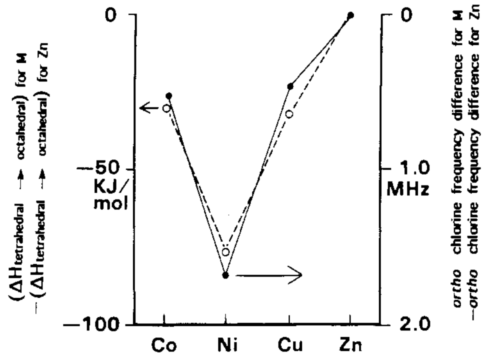

Figure 3. Average ^{35}Cl NQR frequency difference of coordinated *o*-Cl (Cl-2) and noncoordinated *o*-Cl (Cl-6) as a function of the metal ion, compared to Zn as a reference (solid line, right scale), and OSSE (octahedral site stabilization energy) for conversion of tetrahedral to octahedral complexes, as a function of the metal ion, compared to Zn as a reference (broken line, left scale). (The quantitative measure of the OSSE used in ΔH for the reaction $MCl_4^{2-} + 6H_2O \rightarrow M(H_2O)_6^{2+} + 4Cl^-$.)

each line (in parentheses) and by the lowering of that frequency when recorded at 273 K [in brackets].[41] Spectra were also generally recorded at 195 K and sometimes at other temperatures to detect crossings of frequencies. Frequency assignments for the tcp derivatives $Ni(tcp)_2(TMED)$, $Ni(tcp)_2(py)_2$, and $Ni(tcp)_2(py)_3$ were confirmed by preparing the analogous derivatives $Ni(Br\text{-}dcp)_2(TMED)$, $Ni(Br\text{-}dcp)_2(py)_2$, and $Ni(Br\text{-}dcp)_2(py)_3$, for which the frequencies assigned to the para chlorines disappeared while those assigned to the ortho chlorines were but slightly altered.

According to an approximate Townes–Dailey treatment,[15] the ^{35}Cl NQR frequency ν of a coordinated chlorophenolate ortho chlorine (Cl-2) is expected to be lower than that of the noncoordinated ortho chlorine (Cl-6):

$$\nu(\text{Cl-6}) - \nu(\text{Cl-2}) = \Delta\nu = 27.4 \times \text{no. of electrons transferred} \quad (1)$$

This equation is better used for qualitative comparisons (as of the effects of the four metals Co, Ni, Cu, and Zn) than for 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[13,15,16] 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 chlorines, Cl-2 and Cl-6. Figure 3 shows the average $\Delta\nu$ for the corresponding complexes $M(OPhX)_2L_n$ with the same ligands but different divalent metals: by far the greatest $\Delta\nu$ is found for M = Ni. If eq 1 is taken literally, then at least one-tenth of an electron is being transferred from chlorine to nickel in $Ni(tcp)_2(TMED)$, which is a small but not negligible bonding interaction. Using the previously-established correlation[15] between $\Delta\nu$ and M–Cl secondary bond distance, we predicted that the Ni–Cl bond distance in $Ni(tcp)_2(TMED)$ 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, in addition to steric energy terms, the octahedral site stabilization energy (OSSE) for the high-spin metal ion. In units appropriate for octahedral complexes, Dq_{oct}, this stabilization is $2.67Dq_{oct}$ for d^7, $8.45Dq_{oct}$ for d^8, $4.22Dq_{oct}$ for d^9, and zero for d^{10}; i.e., it is greatest for d^8 metal ions such as Ni^{2+}. As suggested by Figure 3, the $\Delta\nu$ 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 and the entropy advantages in liberating water. In Table II we also show the NQR data for two hydrates, $Ni(tcp)_2(TMED)(H_2O)_4$ and $Ni(tcp)_2(py)_2(H_2O)_4$: these show no low NQR frequencies characteristic of coordinated organochlorines.

The compounds $Ni(tcp)_2(diphos)_{1?}$ and $Ni(dcp)_2(diphos)_{1?}$ were of interest since the parent halides $Ni(diphos)X_2$ are diamagnetic and square planar, a geometry for which there is a strong crystal field stabilization energy and in which we would not anticipate there to be a strong driving force for organochlorine coordination. Both $Ni(tcp)_2(diphos)_{1?}$ and $Ni(dcp)_2(diphos)_{1?}$ 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 $Ni(tcp)_2(diphos)_{1?}$; 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.

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 $[Ni(OMe)(MeOH)(tcp)]_4$.[7] The cobalt(II) analogue[5] 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.[12] These data can also be rationalized by crystal field theory. The complexes would be five-coordinate (either square pyramidal or trigonal bipyramidal) without coordination of the organochlorine. For high-spin metal ions, the OSSE values as compared to those for a square pyramidal complex are $-2.86Dq_{oct}$ for d^7, $+2Dq_{oct}$ for d^8, and $-2.86Dq_{oct}$ for d^9, again favoring Ni^{2+}. The OSSE values as compared to those for a trigonal bipyramidal complex are $+2.56Dq_{oct}$ for d^7, $+5.57Dq_{oct}$ for d^8, and $-1.07Dq_{oct}$ for d^9, also favoring Ni^{2+}.

Note that although the OSSE favors octahedral coordination for $Ni(tcp)_2(py)_3$, the steric crowding would increase. Thus the nonpreferred five-coordinate geometry is preserved.

Unfortunately, we failed to fine the expected large ortho chlorine NQR $\Delta\nu$'s for nickel in the methoxo-bridged compounds, for which the very short Ni–Cl distances would lead one to anticipate a $\Delta\nu$ of perhaps 4 MHz. The methoxo compound of known structure ($[Ni(OMe)(MeOH)(tcp)]_4$) failed to give an NQR spectrum at all; from its structure twelve signals were anticipated. $[Ni(OMe)(MeOH)(Br\text{-}dcp)]_4$ gave only two high-frequency signals, while $[Ni(OMe)(MeOH)(dcp)]_4$ gave four. It is possible either that half of the observed signals are due to Cl-2 and half to Cl-6, in which case these analogues have no organochlorine coordination and are thus grossly not isostructural with the X = Cl compound, or that these represent two serious

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(41) We have previously found[14] 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 and zinc chlorophenolates $Zn(dcp)_2(py)_2$, $Ni(dcp)_2(TMED)$, $Ni(dcp)_2(py)_2$.

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

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_{z^2} or $d_{x^2-y^2}$ orbital, which is directed straight at the coordinated organochlorine. So possibly our failure to observe NQR signals clearly attributable to the coordinated chlorines in $[Ni(OMe)(MeOH)(dcp)]_4$ or $[Ni(OMe)(MeOH)(Br\text{-}dcp)]_4$ (or, in the cases of $[Ni(OMe)(MeOH)(tcp)]_4$ or $Ni(tcp)_2(Ph_3P)_2$?, to any chlorines) is a result of excessively short chlorine relaxation times due to delocalization of unpaired nickel electrons into the chlorophenolate ligand.[44] We hypothesize that this problem does not occur in the other $Ni(OPhX)_2L_n$ compounds such as $Ni(tcp)_2(TMED)$ or in any of the cobalt compounds because these have longer M–Cl distances and hence probably less extensive delocalization of the unpaired electrons.

Some inconclusive support for this hypothesis is derived by comparing the apparent signal-to-noise ratios of the coordinated and the noncoordinated 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 noncoordinated chlorines. Fairly frequency in the nickel and cobalt chlorophenolates, however, there are great disparities in the apparent signal-to-noise ratios (although this does not occur, e.g., in $Ni(tcp)_2(TMED)$). This could result if the delocalization of the unpaired d_{z^2} or $d_{x^2-y^2}$ electron changed the relaxation times of the two types of ortho chlorines 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 line shapes, much less measurements of the spin–spin relaxation time T_2, this speculation would need verification with data from a pulse NQR spectrometer.

In Figure 4, 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.[17] The compound $Ni(tcp)_2(TMED)$ provides one of the points at the upper left (strong M–Cl interactions), while the compounds $Ni(tcp)_2(py)_3$ and $[(C_6H_5)_4P][Fe(tcp)_4]$ provide two points at the lower right (very weak or nonexistent M–Cl interactions). The addition of the last two points 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 4 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 dashed lines in Figure 4 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 II) to the noncoordinated chlorines (Cl-6) in $Ni(Br\text{-}dcp)_2(TMED)$ show a frequency spread of 1.101 MHz, well in excess of 0.7 MHz. However, the number of coordination compounds that show frequency 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 4 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).

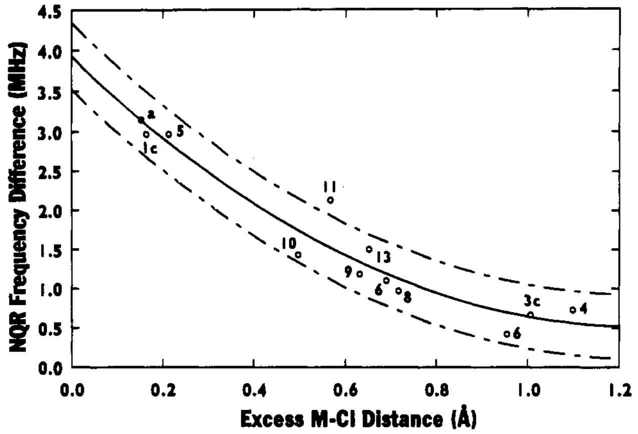

Figure 4. Average ^{35}Cl NQR frequency difference of coordinated *o*-Cl (Cl-2) and noncoordinated *o*-Cl (Cl-6) as a function of the excess M–Cl distance, defined as the observed M–Cl distance minus the normal M–Cl single-bond distance in octahedral complexes, from ref 17. The solid line is the best-fit curve, and the broken lines enclose the expected scatter (±0.35 MHz) in the frequency differences due to solid-state effects. Numbers/letters on points give literature references to the corresponding crystal structures, except for 1c = $Ni(tcp)_2(TMED)$, 3c = $Ni(tcp)_2(py)_3$ (this work), and a = $C_{13}H_8NCl_3Mo(CO)_3$. (R. Harrison, A. M. Arif, G.; Wulfsberg, R. Lang, T. Ju, G. Kiss, C. D. Hoff, and T. G. Richmond, manuscript submitted for publication.) NQR data are from refs 15 and 16 and this work.

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Supplementary Material Available: Figures showing the packing diagrams for $Ni(tcp)_2(TMED)$ and $Ni(tcp)_2(py)_3$, tables giving analytical data for all complexes, crystal data and details of the structure determination for $Ni(tcp)_2(TMED)$ and $Ni(tcp)_2(py)_3$, anisotropic displacement parameters, calculated hydrogen positions, bond distances and angles, and Cambridge Crystallographic Database information on distances, angles, and other structural parameters associated with secondary bonding of *o*-chlorophenolates (14 pages). Ordering information is given on any current masthead page.

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(44) 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.

(45) The compound $Ni(tcp)_2(py)_3$, for which there is a 1.0-Å excess bond distance and a 0.66-MHz $\Delta\nu$, 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.