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40368-44-3; KAl₂Cl₇, 67757-79-3; CsAl₂Cl₇, 88453-50-3; CsGa₂Cl₇, 12331-25-8; Al₂Cl₆, 13845-12-0.

Supplementary Material Available: A table of frequencies for the NaAlCl₄-Al₂Cl₆ spectra, including assignments of Al₂Cl₆ bands, and a figure showing IR emission spectra of KMCl₄ (M = Al, Ga, In) (2 pages). Ordering information is given on any current masthead page.

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Lewis-Base Properties of Ortho Chlorines in Copper(II) 2,4,6-Trichlorophenolates, 4-Bromo-2,6-dichlorophenolates, and 2,6-Dichlorophenolates As Studied by ³⁵Cl Nuclear Quadrupole Resonance Spectroscopy

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Several 2,4,6-trichlorophenolates of copper(II) for which X-ray crystallography has revealed weak ("secondary") bonding interactions of the metal and ortho chlorine have been studied by variable-temperature ³⁵Cl NQR. To aid in NQR frequency assignments, analogous 4-bromo-2,6-dichlorophenolates and 2,6-dichlorophenolates have also been synthesized and studied. The secondary-bonding chlorines have NQR frequencies from 0.8 to 2.2 MHz lower than those of the corresponding non-secondary-bonding ortho chlorines. Analysis of these figures using Townes-Dailey theory with some additional assumptions suggests the transfer or polarization of about 0.06 electron from Cl to (or toward) Cu. This figure is compared with corresponding data of T. L. Brown on electron transfer from the nitrogen donor atom of pyridine in its complexes. The NQR frequency lowerings are greater for the complexes *trans*-CuL₂(chlorophenolate)₂ (L = monodentate nitrogen ligand) than for *cis*-CuL'(chlorophenolate)₂ (L' = bidentate chelating nitrogen ligand). Anomalous temperature dependence of the NQR frequencies of the secondary-bonding chlorines is noted.

Introduction

Although the organic derivatives of most of the nonmetals (amines, phosphines, ethers and alcohols, sulfides and mercaptides, etc.) act as ligands in metal complexes, it is commonly presumed that the halocarbons are incapable of donating any of their unshared electron density to metal ions, even though the gas-phase basicity (proton affinity) of CH₃Cl is greater than that of, for example, CO.^{1,2} But there are cases in which a halocarbon has been found with its halogen atom apparently coordinated to a metal ion: the metal-halogen distance is within the sum of van der Waals radii of the metal and halogen atoms but is beyond the sum of the respective covalent radii. This type of weak interaction is commonly called secondary bonding.³⁻⁷ Its significance could be great in that the presence of weakly bonded ligands is often very desirable in catalysis by metal compounds.^{8,9}

Secondary bonding of a simple halocarbon to a metal compound has only been reported a few times.¹⁰⁻¹⁶ It is much

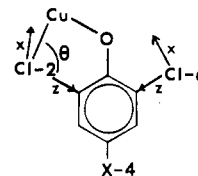
more likely if the halogen and the metal are present in the same organometallic molecule⁵⁻⁷ or if the halocarbon has another, stronger donor atom positioned so as to produce a chelating ligand.¹⁷ Of the crystallographically characterized examples of the latter class,¹⁸⁻²⁷ the largest number are 2,4,6-trichlorophenolates,²¹⁻²⁷ especially of copper(II).²³⁻²⁷ In each of the latter complexes one of the ortho chlorines of each

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Table I. Chlorine 3p Orbital Populations and Contributions to the Electric Field Gradient

orbital (on Cl no.)	population	population restated	contribution to $e^2 Qq_{zz}$
$3p_z$ (6)	$2 - \sigma$	$2 - \sigma$	$e^2 Qq_p$
$3p_y$ (6)	$2 - \pi$	$2 - \pi$	$-e^2 Qq_p/2$
$3p_x$ (6)	2	2	$-e^2 Qq_p/2$
$3p_z$ (2)	$2 - \sigma + \sigma_{pol}$	$2 - \sigma + \alpha\delta$	$e^2 Qq_p$
$3p_y$ (2)	$2 - \pi + \pi_{pol}$	$2 - \pi + \beta\delta$	$-e^2 Qq_p/2$
$3p_x$ (2)	$2 - \delta$	$2 - \delta$	$-e^2 Qq_p/2$

**Figure 1.** The 4-X-substituted 2,6-dichlorophenolate ligand, symbolized in this paper by OPhX, in which X = H (2,6-dichlorophenolate), Cl (2,4,6-trichlorophenolate), or Br (4-bromo-2,6-dichlorophenolate). Labeling of axes at Cl-2 (the secondary-bonding chlorine) and Cl-6 is shown; the y axes are perpendicular to the plane of the ligand. In the complexes $CuL_2(OPhX)_2$, L_2 represents two of the monodentate ligands quinoline (quin), pyridine (py), imidazole (imid), 1-methylimidazole (NMI), and ammonia (NH_3) or one of the bidentate chelating ligands N,N,N',N' -tetramethyl-1,2-diaminoethane (TMED), 1,2-diaminoethane (en), 2,2'-bipyridyl (bpy), and 1,10-phenanthroline (phen).

2,4,6-trichlorophenolate group is coordinated to Cu, at a distance that is less than the sum of the van der Waals radii of Cu and Cl, 320 pm,²⁸ and is near the sum of the covalent radius of Cl and the "axial" covalent radius of Cu,²⁹ 289 pm.

The copper(II) 2,4,6-trichlorophenolates have been studied (1) as model compounds for the metal-binding site in transferrins and lactoferrins in which copper is bound to (phenolic) tyrosine groups,^{21,24,30,31} (2) with regard to possible metal bonding to thyroxine,³² (3) because of the catalytic function of copper ions in the oxidative coupling of phenols to produce useful polymers,³³⁻³⁷ and (4) with respect to magnetic coupling of copper(II) ions in polynuclear trichlorophenolates.^{22,26,27,35,38-41} In addition, copper(II) is involved in catalyzing a number of otherwise notoriously difficult nucleophilic aromatic substitution reactions of ortho-substituted aryl halides.^{42,43} Coordination of the halogen to the metal atom has been suggested as part of the mechanisms of these reactions.⁴²⁻⁴⁷ Characterization of the nature and degree of Lewis basicity of chlorocarbons would clearly be relevant to these proposed mechanisms. This work extends our previous study of mercury 2,6-dichlorophenolates^{48,49} and a concurrent

study of cobalt(II) chlorophenolates.⁵⁰

Use of NQR To Study Secondary Bonding

Interactions of a weak Lewis base such as a chlorocarbon are difficult to characterize: they may be too weak to perceptibly affect many spectroscopic measurements. Even the X-ray crystallographic data may be difficult to interpret, as secondary-bonding distances vary continuously upward through difficult-to-define sums of van der Waals radii.⁴ Organohalogen nuclear quadrupole resonance (NQR) frequencies, being determined mainly by the imbalance in the populations of the valence p orbitals of halogens,^{51,52} are highly sensitive to secondary bonding.^{48,49,53-55} As in our previous work, we will treat the secondary bonding as covalent bonding, using the Townes-Dailey theory,⁵¹ although this does not exclude the alternate hypothesis that it is electrostatic in nature.

For the crystallographically characterized chlorophenolates,²¹⁻²⁷ our calculations (supplementary material) show that the internuclear angles about the secondary-bonding ortho chlorine are all very close to 90°, which suggests that unhybridized 3p orbitals are used by the chlorine for the secondary bonding. Since there is π bonding of each chlorine to the phenolate ring, the secondary-bonding chlorine (which we designate Cl-2) has unknown populations for all three 3p orbitals. The other ortho chlorine (Cl-6) has two electrons in its $3p_x$ orbital, but the populations of the other two orbitals are unknown. (See Figure 1 for the axis system.) These populations are summarized in Table I. Here σ represents the C-Cl σ bond order, π represents the C-Cl π bond order, σ_{pol} and π_{pol} represent the number of electrons by which the σ and π bonds are polarized toward Cl by the metal atom, and δ represents the metal-chlorine secondary bond order (or the effects of polarization of the 3p electrons to higher orbitals by the metal ion).

Let us restate each bond population as some fraction of the secondary bond order:

$$\sigma_{pol} = \alpha\delta \quad \pi_{pol} = \beta\delta \quad (1)$$

Then the populations can be expressed as shown in the third

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column of Table I. The last column of Table I gives the contribution per electron of each orbital to the quadrupole coupling constant e^2Qq_{zz} at each chlorine, where e^2Qq_p is the contribution from one 3p electron. These contributions can be summed up as

$$\begin{aligned} e^2Qq_{zz} \text{ for Cl-6} &= e^2Qq_p[(\pi/2) - \sigma] \\ e^2Qq_{zz} \text{ for Cl-2} &= e^2Qq_p[(\pi/2) - \sigma + \delta(1/2 + \alpha - (\beta/2))] \end{aligned} \quad (2)$$

The ^{35}Cl NQR frequency is related to the quadrupole coupling constant by the expression

$$\nu(^{35}\text{Cl}) = \frac{e^2Qq_{zz}}{2} [1 + (\eta^2/3)]^{1/2} \quad (3)$$

The asymmetry parameter η lies between 0 and 1 and cannot be measured with our instruments. But measurements of it in halophenols⁵⁶⁻⁶² (in which one halogen is engaged in hydrogen bonding, a form of secondary bonding) show it to be generally less than 0.16. This has a negligible effect in eq 3, so that we can obtain for the NQR frequencies

$$\nu(\text{Cl-6}) \cong \frac{e^2Qq_p}{2} [(\pi/2) - \sigma] \quad (4)$$

$$\nu(\text{Cl-2}) \cong \frac{e^2Qq_p}{2} [(\pi/2) - \sigma + \delta(1/2 + \alpha - (\beta/2))] \quad (5)$$

The frequency difference between Cl-6 and Cl-2 may finally be derived, with use of -109.746 MHz for e^2Qq_p .⁵¹

$$\nu(\text{Cl-6}) - \nu(\text{Cl-2}) \cong 54.873\delta[1/2 + \alpha - (\beta/2)] \quad (6)$$

Since we have one equation in three unknowns, it is necessary to make some assumptions about the values of the fractional bond polarizations α and β :

(a) In our previous study⁵⁵ of secondary bonding in mercury and antimony halide complexes, we found $\alpha \cong 1/3$. However, electrons in carbon-chlorine bonds ought to be less polarizable than those in metal-chlorine bonds. Consistent with this view, we find the average C-Cl bond lengthening upon secondary bond formation to be much smaller (1.3 ± 1.3 pm, supplementary material) than the Cu-Cl bond lengthening upon secondary bond formation in copper(II) chloro dimers⁶³ (2.8 pm). Polarization of the C-Cl σ and π bonds should each tend to reduce the C-Cl bond order and lengthen the bond. Since the bond lengthening is not significant, we presume that the fractional bond polarizations α and β are each considerably less than $1/3$.

(b) We would expect the π electrons to be more polarizable than the σ C-Cl bond electrons. Should the corresponding polarization parameter β be twice α , the term $\alpha - \beta/2$ becomes zero and drops out of eq 6. This is unlikely to be exactly the case, but the fact that α and β have opposite signs further

justifies our assumption that $\alpha - \beta/2$ is small compared to the term $1/2$ in eq 6.

With this approximation, eq 6 then becomes

$$\delta \cong \frac{\nu(\text{Cl-6}) - \nu(\text{Cl-2})}{27.436} \quad (7)$$

It should be noted (as pointed out by a reviewer) that Townes-Dailey treatments such as this rely for their success on the assumption that the Sternheimer effect⁵¹ is the same in the organochlorine as in the chlorine atom (from which e^2Qq_p comes). This seems to be approximately true in covalent chlorides but does not hold in ionic chlorides.⁵¹ As there is undoubtedly a substantial partial positive charge on Cu in these complexes, the Cu-Cl secondary bond may well be partially ionic, and part of the frequency difference of Cl-6 and Cl-2 may be due to Sternheimer polarization of chlorine core orbitals rather than valence electron donation or polarization. Until this effect can be evaluated more precisely, eq 7 is best used for comparative purposes rather than for the obtention of absolute values of numbers of electrons donated.

Experimental Section

The compounds were, in general, prepared either by the method given in the crystallographic paper or by one of the two methods described by Harrod.³⁴ $\text{Cu}(\text{quin})_2(\text{OPhH})_2$, obtained by the reaction of $\text{Cu}(\text{py})_2(\text{OPhH})_2$ with 2 mol of quinoline, was obtained only after a crop of unreacted starting material had been removed and then only after the mother liquor had been in a refrigerator for a few months. All samples gave satisfactory elemental analyses for C, H, and N; these were performed by Galbraith Laboratories, Knoxville, TN, or by Midwest Microlabs, Indianapolis, IN. Infrared spectra were recorded to 200 cm^{-1} on a Perkin-Elmer 427 IR spectrometer and were compared with spectra of chlorophenolate salts and ligands to confirm presence of the appropriate ligands and absence of H_2O . Additional bands in the Cu-O and Cu-N stretching regions were observed but could not reliably be assigned. The charge-transfer UV band in the visible region was recorded in toluene solution on a Cary 17E spectrophotometer. NQR spectra were recorded on a Decca NQR spectrometer using Zeeman modulation at temperatures of 77 K (liquid- N_2 bath), 195 K (solid- CO_2 /isopropyl alcohol bath) and 273 K (ice-water bath) and then at additional temperatures if needed to clarify assignments or if phase transitions appeared. These temperatures were achieved with organic solvent slush baths or with a Endocal heating/cooling bath (range -22 to $+100$ °C) connected to a variable-temperature NQR probe (design of A. Weiss). Probe temperatures were then measured with an iron-constantan thermocouple connected to a Omega Digicor digital thermometer. The accuracy of the NQR frequency measurements is ± 0.007 MHz, but two frequencies within 0.025 MHz of each other cannot generally be resolved due to overlapping of sidebands.

Results and Discussion

Table II presents the ^{35}Cl NQR frequencies of the copper 2,4,6-trichlorophenolates in this study. As expected, there is one ^{35}Cl NQR frequency for each crystallographically distinct Cl in each of the four compounds of known crystal structure.²³⁻²⁶

Examination of the data shows that the majority—usually two-thirds—of the ^{35}Cl NQR frequencies fall in the usual 35–36-MHz range, while the rest fall significantly lower in frequency. Some frequency differences are expected due to the "crystal field effect", but Weiss⁶⁴ found that this could produce, in 99% of all cases, no greater than a 0.7-MHz splitting of the NQR frequencies of chemically equivalent aromatic chlorines. The ranges of frequencies found in these compounds greatly exceed this figure.

One problem is that the chlorines in a 2,4,6-trichlorophenolate are not all chemically equivalent, even in the absence of secondary bonding. Thus one could perhaps attribute the

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Table II. ³⁵Cl NQR Spectra and Charge-Transfer Spectra of 2,4,6-Trichlorophenolates and 4-Bromo-2,6-Dichlorophenolates

compd	<i>n</i> ^b	higher NQR freq, ^{a,c} MHz		lower NQR freq, ^a Cl-2	ν_{CT} , nm ^d
		Cl-4	Cl-6		
Cu(TMED)(OPhCl) ₂ , phase I ^e		35.750 (5) (0.337) 35.668 (6) (0.355) 35.547 (4) (0.291)	35.384 (5) (0.278) 35.322 (3) (0.293) 35.276 (3) (0.297)	34.582 (3) (0.327) 34.325 (5) (0.252) 34.248 (5) (0.227)	
Cu(TMED)(OPhCl) ₂ , phase II ^f	9	35.102 ^g (3) (0.233) <i>g</i> (0.233) 34.980 (2) (0.225)	34.924 (2) (0.249) 34.812 ^g (2) (0.175) <i>g</i> (0.175)	34.067 (3) (0.241) 33.873 ^g (2) (0.150) <i>g</i> (0.185)	493
Cu(TMED)(OPhBr) ₂			35.535 (3) (0.506) 35.469 (2) (0.440) 35.379 (4) (0.473)	34.679 (4) (0.573) 34.444 (3) (0.484) 34.245 (3) (0.409)	487
[Cu(OCH ₃)(quin)(OPhCl)] ₂ [Cu(OCH ₃)(quin)(OPhBr)] ₂	3	35.476 (5) (0.530) 226.8 (8) ^h	34.944 (5) (0.320) 34.964 (8) (0.346)	33.755 (6) (0.427) 33.731 (9) (0.431)	
Cu(py) ₂ (OPhCl) ₂ Cu(py) ₂ (OPhBr) ₂	3	35.635 (47) (0.467) 228.0 (22) ^h 226.5 (26) ^h	35.805 (46) (0.412) 36.033 (9) (0.528) 35.726 (10) (0.517)	33.654 (37) (0.310) 34.123 (9) (0.347) 33.728 (10) (0.370)	450 434
Cu(imid) ₂ (OPhCl) ₂ ·H ₂ O Cu(en)(OPhCl) ₂ ·H ₂ O	3	35.552 (4) (0.819) 35.734 (6) (0.803) 35.573 (6) (0.474)	35.447 (9) (0.528) 35.430 (6) (0.777) 35.355 (7) (0.530)	34.004 (5) (0.475) 34.724 (9) (0.518) 34.262 (7) (0.494)	430 ⁱ
Cu(bpy)(OPhCl) ₂ , phase I ^j		35.962 (14) 35.461 (13)	35.226 (39) ^g <i>g</i>	<i>g</i> 33.863 (13)	491
Cu(bpy)(OPhCl) ₂ , phase II ^k		35.747 (2) (0.755) <i>l</i> (0.469)	<i>l</i> (0.527) 35.024 (4) (0.628)	34.785 (3) (0.582) 34.082 (3) (0.332)	497
Cu(phen)(OPhCl) ₂		35.616 (12) (0.514) 35.425 (12) (0.600)	35.351 (12) (0.786) 35.261 (12) (0.582)	35.149 (12) (0.642) 34.033 (12) (0.394)	

^a Frequencies measured at 77 K, followed by signal-to-noise ratios at 77 K in the first parentheses and the change in the NQR frequency on cooling from 273 to 77 K in the second parentheses. ^b *n* = number of crystallographically distinct chlorines in the asymmetric unit of the unit cell, according to the crystallographic studies.²³⁻²⁶ ^c Since in most cases the set of higher frequencies come within 0.7 MHz of each other, they cannot definitively be assigned to Cl-4 (para chlorine) and Cl-6 (noncoordinated ortho chlorine). The "assignments" given here are considered only slightly more probable than other possible assignments. ^d Charge-transfer absorption, measured in toluene solution. ^e The phase stable at 77 K. The change in the NQR frequency is measured for cooling from 195 to 77 K. ^f The room-temperature phase. Frequencies given were measured at 252 K; the change in the NQR frequency is measured for cooling from 320 to 252 K. ^g Overlapping signals. ^h ⁸¹Br NQR frequencies (±0.6 MHz) measured at ca. 308 K on a Wilks NQR-1A spectrometer. ⁱ Measured in acetone solution. ^j The phase stable at 77 K. ^k The phase stable above 77 K and metastable at 77 K. ^l Overlapping with the 35.461-MHz signal of phase I.

Table III. ³⁵Cl NQR and Charge-Transfer Spectra of 2,6-Dichlorophenolates

compd	higher (Cl-6) freq, ^a MHz	lower (Cl-2) freq, ^a MHz	ν_{CT} , nm ^d
Cu(TMED)(OPhH) ₂ , phase I ^b	34.534 (4) 34.368 (4)	33.214 (4) 33.080 (6)	
Cu(TMED)(OPhH) ₂ , phase II ^c	34.243 (16) (0.335)	32.998 (15) (0.277)	480
Cu(py) ₂ (OPhH) ₂ , phase I	34.900 (15) (0.825) 34.500 (15) (0.886)	33.280 (15) (0.515) 33.221 (15) (0.486)	434
Cu(py) ₂ (OPhH) ₂ , phase II	34.825 (26) (0.764) 34.772 (22) (0.672)	33.216 (25) (0.447) 33.154 (23) (0.339)	
Cu(bpy)(OPhH) ₂	34.711 (25) (0.728) 34.628 (25) (0.892)	33.704 (25) (1.026) 33.582 (25) (0.904)	471
Cu(phen)(OPhH) ₂	34.612 (11) (0.522) 34.468 (13) (0.451)	33.758 (13) (0.566) 32.753 (11) (0.392)	494
Cu(NMI) ₂ (OPhH) ₂ Cu(NH ₃) ₂ (OPhH) ₂ Cu(quin) ₂ (OPhH) ₂	34.538 (12) (0.442) 34.445 (14) (0.391) 34.784 (6) (0.527) 34.699 (6) (0.637)	32.859 (10) (0.394) 33.021 (16) (0.440) 33.986 (4) (0.664) 32.992 (4) (0.456)	426

^a Frequencies measured at 77 K, followed by signal-to-noise ratios at 77 K in the first parentheses and the change in the NQR frequency on cooling from 273 to 77 K in the second parentheses. ^b The phase stable at 77 K. ^c The phase stable from 152 to 294 K. Frequencies given were measured at 152 ± 1 K, the change in the NQR frequency is measured for cooling from 273 to 152 ± 1 K. ^d Charge-transfer spectra, measured in toluene solution.

low frequencies to the chemically distinct para chlorines. These frequencies are too low to be reasonable for such chlorines, however.⁶⁵ This also could not explain why, in Cu(phen)(OPhCl)₂ and both phases of Cu(bpy)(OPhCl)₂, only one-sixth of the NQR frequencies are significantly lower than the others. We suggest instead that, in the latter compounds, the Cl-2 of only one of the two 2,4,6-trichlorophenolate rings engages in secondary bonding, producing (probably) five-coordinate copper. Precedent for this exists.²¹

In order to clarify the assignment of the low-frequency NQR signals, we also synthesized 4-bromo-2,6-dichlorophenolates corresponding to the 2,4,6-trichlorophenolates of known structure and, although this is a greater electronic alteration,

a number of 2,6-dichlorophenolates (Table III). The ³⁵Cl NQR spectra of the 4-bromo-2,6-dichlorophenolates retain the low frequencies while losing half the set of high frequencies found in the spectra of the 2,4,6-trichlorophenolates; a similar pattern is found in the spectra of the 2,6-dichlorophenolates. Hence, the low frequencies must be assigned to ortho chlorines; as they are too low for normal ortho chlorines,⁶⁵ they must be assigned to the secondary-bonding Cl-2's.

Since the frequencies of Cl-4 and Cl-6 generally fall together within a range of 0.7 MHz, they cannot be reliably distinguished in the 2,4,6-trichlorophenolates. Hence, when we look at frequency differences in the trichlorophenolates, we must compute the difference between the mean of the Cl-4 and Cl-6 frequencies and the Cl-2 frequency. In any reasonable model of secondary bonding, the shorter the metal-chlorine bond

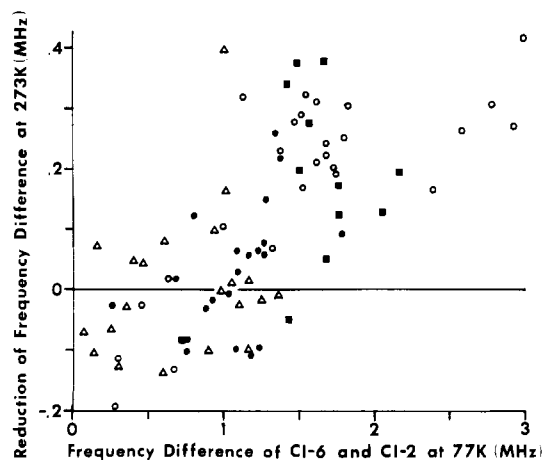


Figure 2. Reduction of NQR frequency splittings at 273 K (computed as $[\bar{\nu}(\text{Cl-6}) - \nu(\text{Cl-2})]_{T=273\text{K}} - [\bar{\nu}(\text{Cl-6}) - \nu(\text{Cl-2})]_{T=77\text{K}}$) vs. the NQR frequency splitting at 77 K. Circles (●) represent data for copper(II) complexes of chelating ligands; squares (■) represent copper(II) complexes of monodentate ligands; open circles (○) represent cobalt(II) complexes,⁵⁰ open triangles (Δ) represent mercurial compounds, phenols, and anisoles.⁴⁸

distance is, the greater this difference should be. We find this to be the case.⁵⁰

There is no apparent dependence of the frequency difference on the pK_b of the nitrogen ligand(s) in the complexes, but we note that the difference is substantially less (1.06 ± 0.36 MHz) with the chelating ligands than with the monodentate ligands (1.60 ± 0.35 MHz). The intense O-to-Cu charge-transfer absorptions of these compounds also occur at substantially lower energy with chelating than with monodentate ligands³⁰ (Tables II and III). Unusual features were noted in the structure determination of $\text{Cu}(\text{TMED})(\text{OPhCl})_2$ ²³ which would be expected to alter the Cu-O and Cu-Cl bonding.

Anomalous temperature dependences of the NQR frequencies are often found in complexes,^{66,67} so we also examined the NQR spectra of these compounds at temperatures higher than 77 K (Tables II and III). A secondary-bonding chlorine has often been found to have a less negative temperature dependence of its NQR frequency than an analogous terminal chlorine.^{48,49,53-55,68-72} This would produce, for Cl-6 and Cl-2 in these compounds, a temperature dependence of the frequency difference itself, such that the difference would be

reduced at a higher temperature. In Figure 2 we plot the reduction of the Cl-6/Cl-2 frequency difference at 273 K vs. the frequency difference at 77 K, for each Cl-2 in each chlorophenolate of copper(II) (this work), cobalt(II),⁵⁰ and mercury⁴⁸ and in the (hydrogen-bonded) chlorophenols themselves.⁴⁸ An interesting pattern emerges: large frequency differences (at 77 K) are reduced in magnitude at 273 K; small frequency differences are not (as an overall trend—some are slightly reduced, some are slightly increased). Although we previously discussed the latter trend,⁴⁸ the most common explanations of anomalous temperature dependences^{64,66} do not seem capable of explaining the change in this effect on going from small to large frequency differences. We hope, in future work, to investigate this point further.

Finally, applying eq 7 to the mean ortho-chlorine frequency difference (1.60 MHz) in copper(II) chlorophenolates with monodentate nitrogen ligands, we compute an apparent transfer of about 0.06 electron from chlorine to copper. Although, as we indicated previously, this number does not have absolute validity, it is interesting to compare it qualitatively with the data obtained by ¹⁴N NQR on complexes of pyridine by Rubenacker and Brown.^{73,74} (An exact comparison is not valid because the Sternheimer effects are different for nitrogen and chlorine.) Pyridine is a much stronger Lewis base than a chlorocarbon, so it is not surprising that the pyridine nitrogen normally donates much more than 0.06 electron.^{73,74} But a very comparable figure was obtained for the complexes of pyridine with the lithium ion, a weak Lewis acid. Thus, our NQR data suggest that, under favorable circumstances, chlorocarbons show weak Lewis basicity and can act as ligands, forming complexes not unlike those of the organic derivatives of the other nonmetals.

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Registry No. $\text{Cu}(\text{TMED})(\text{OPhCl})_2$, 22180-38-7; $\text{Cu}(\text{TMED})(\text{OPhBr})_2$, 51823-48-4; $[\text{Cu}(\text{OCH}_3)(\text{quin})(\text{OPhCl})_2]$, 73034-10-3; $[\text{Cu}(\text{OCH}_3)(\text{quin})(\text{OPhBr})_2]$, 88510-62-7; $\text{Cu}(\text{py})_2(\text{OPhCl})_2$, 22180-36-5; $\text{Cu}(\text{py})_2(\text{OPhBr})_2$, 14841-05-5; $\text{Cu}(\text{imid})_2(\text{OPhCl})_2$, 61127-51-3; $\text{Cu}(\text{en})(\text{OPhCl})_2$, 88510-63-8; $\text{Cu}(\text{bpy})(\text{OPhCl})_2$, 22180-40-1; $\text{Cu}(\text{phen})(\text{OPhCl})_2$, 22251-22-5; $\text{Cu}(\text{TMED})(\text{OPhH})_2$, 88510-64-9; $\text{Cu}(\text{py})_2(\text{OPhH})_2$, 88586-76-9; $\text{Cu}(\text{bpy})(\text{OPhH})_2$, 88510-65-0; $\text{Cu}(\text{phen})(\text{OPhH})_2$, 88510-66-1; $\text{Cu}(\text{NMI})_2(\text{OPhH})_2$, 88510-67-2; $\text{Cu}(\text{NH}_3)_2(\text{OPhH})_2$, 88510-68-3; $\text{Cu}(\text{quin})_2(\text{OPhH})_2$, 88510-69-4; ³⁵Cl, 13981-72-1.

Supplementary Material Available: A table of crystallographic data (from the literature, private communications, and our calculations) for organochlorines in metal 2,4,6-trichlorophenolate complexes (2 pages). Ordering information is given on any current masthead page.

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