Dioxin Precursors: NQR Studies of Group 1 and Related 2,6-Dichlorophenolate and 2,4,6-Trichlorophenolate Salts *

G. Wulfsberg, K. Shadid, and B. Farris
Dept. of Chemistry, Middle Tennessee State University, Murfreesboro, TN 37132, USA

J. Monn, T. Bonner, and J. Yanisch
Dept. of Chemistry, St. John's University, Collegeville, MN, USA

Al. Weiss
Institut für Physikalische Chemie PCIII, Technische Hochschule, D-6100 Darmstadt, Germany

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The ^{81}Br and ^{35}Cl NQR spectra of anhydrous Group 1, tetraalkylammonium, and thallium(I) 2,6-dichlorophenolates, 2,4,6-trichlorophenolates, and 4-bromo-2,6-dichlorophenolates were searched for evidence of solid-state cation-organochlorine interactions that might, for example, be (in part) responsible for the difference in the thermal decomposition reactions of these salts (to give the supertoxic environmental pollutants, the polychlorinated dibenzodioxins) versus those of the corresponding Group 11 chlorophenolate complexes, which do not decompose to dioxins.

For cations ranging in size from tetraethylammonium to potassium, the total range of ^{35}Cl NQR frequencies in 2,6-dichlorophenolate and 2,4,6-trichlorophenolate salts is only 1.401 MHz, which, although larger than the 0.7 MHz range likely in molecular chlorocarbons, is smaller than in individual chlorophenolates of copper(I) and silver(I) (up to 2.0 MHz). In sodium and thallium(I) 2,4,6-trichlorophenolates substantially large frequency shifts (ca. 2.0 MHz) occur, to higher frequencies for the para-chlorines and lower frequencies for the ortho-chlorines (Na only). These disappear even in closely related compounds and show a pattern that seems unrelated to the decomposition products of the chlorophenolates.

Key words: Chlorophenolates, Nuclear quadrupole resonance, Dioxin.

Introduction

Chlorophenolate salts such as sodium 2,4-dichlorophenolate and sodium 2,4,5-trichlorophenolate are industrially important intermediates in the manufacture of herbicides and biocides such as 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), Silvex, and hexachlorophene. Of immense concern in recent years has been the side-reaction of such salts at high temperatures to eliminate NaCl and produce the teratogenic toxins, the dioxins [1]. Among the dioxins, 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD or simply "dioxin") shows lethal effects at extraordinarily low levels in animal tests. Heating silver or copper trichlorophenolates produces poly(2,6-dichlorophenylene oxides) [2, 3]; dioxin is not produced. Possibly Group 1 cation-*ortho*-organochlorine interactions [4] may be involved in directing elimination of *ortho*-rather than *para*-chlorines when dioxins are formed. Using NQR spectroscopy, we can study the degree to which various +1 cations influence the solid-state electronic distribution in chlorophenolate ions.

In this work we study chlorophenolates of the Group 1 metal ions Na^+ through Cs^+, and of Tl^+, NH_4^+, and the tetramethylammonium and tetraethylammonium ions. For safety and other technical reasons, we have studied, not the precursor of 2,3,7,8-TCDD itself, the 2,4,5-trichlorophenolate anion, but the presumably quite similar 2,4,6-trichlorophenolate ($OPhCl_3^-$), 2,6-dichlorophenolate ($OPhCl_2^-$), and 4-bromo-2,6-dichlorophenolate ($OPhCl_2Br^-$) ions. The presence of only one non-chlorine donor atom in anhydrous chlorophenolate salts, and that in a some-

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Reprint requests to Dr. Gary Wulfsberg, Department of Chemistry, Box 405, Middle Tennessee State University, Murfreesboro, TN 37132, USA.

what sterically hindered position, almost ensures that there must be cation-organochlorine contacts involving these very large metal cations [5]; there are 3.26-Å K–Cl contacts in the monohydrated potassium salts of the 2-chloro-4-nitrophenolate ion [6] and of the herbicide 2,4-D [7], despite the presence of many more (four) oxygen donor atoms per metal ion. A recent crystallographic database search found eight other structures involving K^+-organochlorine contacts of 3.26 Å and up [8].

Metal-chlorine interactions in the Group 1 chlorophenolates presumably are electrostatic in nature. Silver(I) and copper(I) ions coordinate readily [9] to chlorophenolate *ortho*-chlorines, producing large (1.5–2.0 MHz) ^{35}Cl NQR low-frequency shifts for those chlorines; it is by no means obvious whether these M–Cl interactions (secondary bonding) [10] are principally electrostatic or covalent. Since Cu^+ and Ag^+ are similar in size and charge to the smaller Group 1 cations, the results can be compared to determine whether electrostatic interactions alone could suffice to produce 2-MHz frequency shifts.

Experimental

Elemental analyses were performed by Galbraith-Laboratories, Knoxville, TN, and by Midwest Microlabs, Indianapolis, IN, and are tabulated in Table 1. The infrared spectra of all compounds were examined carefully in the 3000–3500 cm^{-1} region for water. In some cases acid-base titrations were used to determine the equivalent weights of the salts, as an additional check for water of hydration. Later water was determined directly using a Mettler DL-18 Karl-Fischer titrator with Hydranal titrant; the reagents were periodically checked by determining the percent water present in sodium tartrate dihydrate. Solid-state UV-visible spectra (mineral oil mulls) were recorded on a Cary 17 instrument, and are shown in Table 2. The ^{35}Cl NQR spectra were measured on a Decca NQR spectrometer using Zeeman modulation at 77 K, 195 K, and 273 K. ^{81}Br NQR spectra were obtained at room temperature on a Wilks NQR-1 A spectrometer. NQR frequencies (in MHz) are tabulated in Tables 3 and 4, followed by the signal-to-noise ratio for each signal (in parentheses) and the lowering of that frequency when measured at 273 K [in brackets].

Table 1. Analytical data for new compounds.

Compound	%C[a]	%H	H_2O by IR?	Other[b]
$NaOPhCl_2$	38.96 (38.06)	1.63 (1.77)	No	Eq. wt. 185.0 (184.6) %H_2O 0.00 (0.27)
$KOPhCl_2$	35.84 (34.21)	1.50 (1.73)	No	Eq. wt. 201.1 (202.5)
$RbOPhCl_2 \cdot 1/2\ H_2O$	28.10 (27.84)	1.57 (1.35)	weak	
$CsOPhCl_2$	24.44 (24.31)	1.02 (1.47)	Yes	
$TlOPhCl_2$	19.67 (19.59)	0.83 (0.86)	No	%Cl 19.35 (19.45) %H_2O 0.00 (0.27)
$Me_4NOPhCl_2 \cdot 1/4\ H_2O$	49.91 (50.12)	6.49 (7.13)	Yes	
$Et_4NOPhCl_2$	57.54 (56.60)	7.93 (8.06)	Yes	
NH_4OPhCl_2	40.02 (39.29)	3.92 (3.91)		%N 7.78 (8.41)
$NaOPhCl_3$	32.84 (33.19)	0.92 (1.12)	No	Eq. wt. 219.4 (222.1)
$KOPhCl_3$	30.60 (29.36)	0.86 (0.95)	vw	Eq. wt. 235.5 (228.6) %H_2O 0.00 (0.00)
$RbOPhCl_3$	25.56 (25.63)	0.72 (0.95)	Yes	%H_2O 0.00 (0.15)
$CsOPhCl_3$	21.88 (22.05)	0.61 (0.78)	No	%H_2O 0.00 (1.11)
$TlOPhCl_3$	17.98 (17.93)	0.50 (0.49)	No	%Cl 26.54 (26.32)
$Me_4NOPhCl_3 \cdot 1/2\ H_2O$	42.96 (42.61)	5.41 (5.36)	Yes	
$Et_4NOPhCl_3$	51.47 (51.24)	6.79 (6.88)	No	
NH_4OPhCl_3	33.60 (33.66)	2.82 (2.85)		
$NaOPhCl_2Br$	27.31 (26.15)	0.76 (1.11)		%Na 8.71 (8.79)
$TlOPhCl_2Br$	16.19 (14.33)	0.45 (0.76)	No	%Tl 45.90 (44.18)

[a] Calculated percentage listed first, followed by percentage found (in parentheses).

[b] Eq. wt. = equivalent weight by acid-base titration; %H_2O by Karl Fischer titration.

Table 2. UV spectral data (λ_{max} in nm).

Cation or R group	2,4,6-Trichlorophenolate	2,6-Dichlorophenolate	4-Chlorophenolate	Phenolate
(State)	Solid	Solid	Glyme[a]	Glyme[a]
CH_3	287.5 (liq)			
H	288		283	274
p-RHg[b]	299	298		
NH_4	324			
Li			307	296.5
Na	324; 315[c]	314		
K	318	308		
Cs			327	317.5
Tl	323; 316[c] 295[d]	310	283	275

[a] Glyme = in solution in 1,2-dimethoxyethane; data from A. G. Lee, J. Chem. Soc. A, **1971,** 2007.

[b] R = p-dimethylaminophenyl.

[c] In solution in methanol.

[d] In solution in 1,2-dimethoxyethane.

Sodium, potassium, rubidium, and cesium salts were prepared by the neutralization and azeotropic drying method of Hunter [11], often with the distillation being done under reduced pressure to avoid excessive heating of the product. Cesium 2,4,6-trichlorophenolate was also prepared by an alternate route, which apparently produced a different crystal form. Cesium iodide (3.82 g, 14.7 mmol) was dissolved in 80 mL dry methanol; 5.88 g (14.7 mmol) $TlOPhCl_3$ was added; the mixture was stirred overnight. The precipitated TlI was filtered off, and the volume of the solution was reduced until crystals formed, which were dried under house vacuum for 5 days. The infrared spectrum showed no water or organic solvent; Karl-Fischer titration gave 1.1% water, corresponding to 0.2 mol H_2O per mole of salt. The acetone solvate of $NaOPhCl_3$ was obtained by dissolving $NaOPhCl_3$ in anhydrous acetone and placing the solution under house vacuum overnight. Large crystals which effloresced readily were obtained; their composition was inferred from their weight gain.

Tetramethyl- and tetraethylammonium salts were prepared similarly from commercial solutions of tetramethyl- or tetraethylammonium hydroxide in water or methanol, omitting the toluene. The solvents were distilled off under reduced pressure, leaving oils which sometimes crystallized upon cooling, but which in any event were allowed to sit in a vacuum desiccator over phosphorus pentoxide, where the crystalline crusts that formed were broken up until complete solidification had occurred. The product was filtered in a glove bag, rinsed with hexane, and again dried in the desiccator. Only for the tetraethylammonium salts was complete dryness suggested by the infrared spectra; the elemental analyses and IR spectra of the tetramethylammonium salts suggested that they were half- or quarter-hydrates. Their NQR spectra were quite similar to those of the tetraethylammonium salts, so possibly the water was merely surface contamination or the result of handling during analysis [12].

Thallium [13] and ammonium salts are of quite limited solubility in water or in organic solvents and crystallize in anhydrous form; NH_4OPhCl_3 was prepared by placing a benzene solution of 2,4,6-trichlorophenol and a beaker of concentrated aqueous ammonia inside a bell jar which contained solid NaOH as a desiccant. After two hours the thick precipitate in the benzene solution was filtered off in a glove bag and washed with benzene. Single crystals of thallium 2,4,6-trichlorophenolate were grown by refluxing for 12 hours a mixture of 5 mL ethanol and 50 mL water in which 0.99 g (5.0 mmol) 2,4,6-trichlorophenol, 1.33 g (5.0 mmol) thallium(I) nitrate, and 0.60 g (10.0 mmol) urea were dissolved; very long, very thin needles resulted. $TlOPhCl_2Br$ decomposed upon attempted crystallization by these methods, so the elemental analysis was of unrecrystallized precipitate.

Results

Simple crystalline 2,4,6-trichlorophenolates of several Group 1, 2, and related cations (such as NH_4^+) have been known for over 150 years [14]. These salts are normally hydrates, in which any hydrogen bonding to the chlorophenolate oxygen [15] or chlorine atoms could cause a substantial alteration of the chlorine NQR frequencies (note the large differences in the NQR spectra of anhydrous versus hydrated $KOPhCl_3$ and $NaOPhCl_3$ in Table 3). Hence we have prepared anhydrous salts by azeotropic removal of the water of hydration [11] or by the reaction of a slurry of the Group 1 metal iodide with the thallium(I) chlorophenolate in a dry organic solvent under a dry atmosphere in Schlenkware, followed by filtration of the insoluble TlI, and concentration of the solvent. Although we also wished to prepare crystalline anhydrous Group 2 chlorophenolates, the hydrated salts were insoluble and difficult to dehydrate, and when prepared anhydrous were not crystalline. The ammonium chlorophenolates, although anhydrous and

Table 3. ^{35}Cl NQR frequencies (MHz at 77 K) of Group 1 and related 2,6-dichlorophenolates[a].

Compound, Ref.	Frequencies, MHz			
$HOPhCl_2$[b]	35.856	[0.356]	35.304	[0.504]
NH_4OPhCl_2	34.341 (8)	[0.416]	32.971 (9)	[0.389]
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$TlOPhCl_2$	33.333 (12)	[0.493]	33.165 (12)	[0.473]
$NaOPhCl_2$	33.137 (4)	[0.282]	32.612 (4)	[0.208]
$NaOPhCl_2$[c]	33.148		32.631	
$KOPhCl_2$	33.621 (24)	[0.595]	33.540 (16)	[0.514]
$RbOPhCl_2 \cdot 1/2\,H_2O$	33.266 (9)	[0.408]	32.553 (6)	[0.466]
$CsOPhCl_2$	33.488 (14)	[0.465]	32.796 (3)	[0.475]
	33.408 (10)	[0.471]	32.655 (5)	[0.475]
$(CH_3)_4NOPhCl_2$	33.786 (10)	[0.849]	33.004 (8)	[0.669]
	33.439 (8)	[0.727]	32.720 (8)	[0.654]
$(C_2H_5)_4NOPhCl_2$	33.403 (11)	[0.677]	33.215 (12)	[0.502]

[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.

[b] T. A. Babushkina, A. P. Zhukov, L. S. Kobrina, G. K. Semin, and G. G. Yakobson, Sib. Chem. J. **12**, 588 (1969); Engl. trans. of Izv. Sib. Otdel. Akad. Nauk SSSR, Ser. Chem. Sci. **12**, 93 (1969).

[c] Ref. [21].

Table 4. 77 K ^{35}Cl and room-temperature ^{81}Br NQR frequencies (MHz) of Group 1 2,4,6-trichlorophenolates and related compounds [a].

Compound, Ref.	Cl-4, Br-4	Cl-6, Cl-2	Cl-6, Cl-2
$HOPhCl_3$ [b]	35.300 [0.336]	36.771 [0.404]	35.403 [0.420]
$HOPhCl_2Br$ [c]	230.3 (100)	36.540	35.907
		36.480	35.826
NH_4OPhCl_3	35.120 (6) [0.437]	34.943 (6) [0.430]	34.311 (7) [0.344]
$NaOPhCl_3 \cdot H_2O$	34.177 (2)	33.992 (3)	33.820 (2.5)
	34.087 (2)	33.906 (4)	33.616 (2)
$KOPhCl_3 \cdot 1/2\ H_2O$	36.087 (2)	35.758 (2)	
$CsOPhCl_3$ [e]	36.27 (2)	34.76 (2)	34.39 (2)
	35.65 (2)	34.48 (2)	33.88 (2)
	35.12 (2)	34.41 (2)	33.39 (2)
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$TlOPhCl_3$	35.895 (4) [0.346]	33.997 (3) [0.367]	33.717 (5) [0.387]
$TlOPhCl_2Br$	225.0 (12)	34.187 (8) [0.360]	34.010 (7) [0.387]
$NaOPhCl_3$	36.051 (4) [0.43]	33.675 (3.5) [0.49]	33.098 (2.5) [0.39]
$NaOPhCl_3$ [e]	35.94 (3)	33.58 (3)	33.05 (3)
$NaOPhCl_2Br$	222.7 (16)	33.940 (4) [0.317]	33.730 (5) [0.307]
$NaOPhCl_3 \cdot$ acetone	35.381 (15) [0.828]	34.341 (14) [0.730]	34.108 (17) [0.928]
$KOPhCl_3$	34.192 (7) [0.342]	34.140 (7) [0.399]	33.863 (5) [0.348]
$KOPhCl_3$ [f]			
$RbOPhCl_3$	34.378 (2) [0.442]	34.293 (4) [0.458]	33.921 (3) [0.396]
$CsOPhCl_3$ [g]	35.110 (3) [0.333]	34.479 (8) [0.454]	34.291 (5) [0.460]
$CsOPhCl_3$ [h]	34.820 (2)	34.082 (2)	33.847 (2)
	34.475 (2)	33.975 (2)	33.709 (2)
$(CH_3)_4NOPhCl_3$	34.925 (7) [0.643]	34.285 (7) [0.610]	33.932 (6) [0.543]
$(C_2H_5)_4NOPhCl_3$	34.657 (5) [0.506]	33.966 (5) [0.498]	33.932 (5) [0.596]

[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 arbitrarily listed under the Cl-4 column.

[b] D. Biedenkapp and Al. Weiss, J. Chem. Phys. **49**, 3933 (1968).

[c] ^{35}Cl data from T. A. Babushkina, A. P. Zhukov, L. S. Kobrina, G. K. Semin, and G. G. Yakobson, Sib. Chem. J. **12,** 588 (1969); Engl. trans. of Izv. Sib. Otdel. Akad Nauk SSSR, Ser. Chem. Sci. **12,** 93 (1969); D. N. Kravtsov, A. P. Zhukov, T. A. Babushkina, E. V. Bryukhova, L. S. Golovchenko, and G. K. Semin, Bull. Acad. Sci. USSR, Div. Chem. Sci. **1972,** 1655; Engl. trans. of Izv. Akad. Nauk SSSR, Ser. Khim. **1972,** 1710.

[d] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear Quadrupole Resonance in Chemistry, Jerusalem: Israel Program for Scientific Translations, 1975, p. 487.

[e] W. Pies, Dr.-Ing. Dissertation, Technische Hochschule Darmstadt, Darmstadt **1978,** p. 277. The cesium salt was student-prepared, so we have listed it with the hydrated salts.

[f] W. Pies, op cit.; measured only at 301 K (33.76, 33.63, and 33.43 MHz; frequencies similar to ours measured at 273 K.

[g] Sample prepared in aqueous solution by neutralization.

[h] Sample prepared in acetone from CsI and $TlOPhCl_3$; spectrum too weak to be observed reliably at 273 K.

crystalline, must also be presumed to involve hydrogen bonding to the anion. The thallium(I) salts crystallize from water-containing solutions in anhydrous form.

Thallium(I) is considerably more electronegative than the Group 1 cations, hence its chlorophenolates may not be ionic: thallium(I) 2,4,6-tris(trifluoromethyl)phenolate is a dimeric molecule with bridging phenolate oxygen atoms [16]. In an attempt to clarify the solid-state bonding type of the thallium(I) chlorophenolates, we compared their infrared spectra down to 250 cm^{-1} to those of the undoubtedly-ionic Group 1 salts. No extra band was found which could possibly be attributed to a Tl–O stretching frequency; we observed Hg–O stretching frequencies around 500 cm^{-1} in the covalent organomercury(II) chlorophenolates. Similarly, the first UV band of both the solid thallium and the Group 1 2,4,6-trichlorophenolates (a ring $\pi-\pi^*$ transition) appears at 318–324 nm, in contrast to covalent organomercury, hydrogen, and organic trichlorophenolates, in which the band appears at 288–300 nm [17]. The NQR spectra of the thallium salts closely resemble those of the sodium salts, adding some further support to the tentative conclusion that the thallium chlorophenolates are ionic. In the hopes of clarifying this and other bonding questions via a crystal structure determination, we attempted to grow single crystals of thallium(I) 2,4,6-

trichlorophenolate by homogeneous precipitation from aqueous solution using ammonia from slowly hydrolyzing urea, the phenol, and a thallium salt, or by slow cooling of a solution in hot toluene. Both gave rise to extraordinarily long, paper-thin needles which were unsuitable for X-ray crystallography. Determination of the crystal structure of the anhydrous sodium salt $NaOPhCl_3$ would also have been desirable but seemed infeasible, as only tiny needle-like crystals were obtained.

Discussion

Electrostatic effects of the cations on organochlorines should be minimized in the tetraalkylammonium salts, since these cations must be fairly distant from the anions, have no empty orbitals, and are not so likely to act as concentrated point charges. The frequency spread in the six NQR signals from tetraalkylammonium, 2,6-dichlorophenolates is only 1.07 MHz, not so much greater than that found in molecular lattices [18]. The spread in the 2,4,6-trichlorophenolates is only 0.99 MHz, and this spread also includes the frequencies of the chemically-distinct *para*-chlorines.

The cations in the Cs^+, Rb^+, and K^+ chlorophenolates are somewhat smaller and have more localized charges. Nonetheless the NQR frequency range expands only to 1.233 MHz, from the lowest frequency in $RbOPhCl_2$ to the highest in $(CH_3)_4NOPhCl_2$. The frequency range in the 2,4,6-trichlorophenolates is 1.401 MHz, found in the two modifications of $CsOPhCl_3$. Several studies of the effect of varying cations on ^{35}Cl NQR frequencies of chloro anions have been made in the salts A_2MCl_6 (M = Pt, Sn, Te, Re; $A = K^+$, Rb^+, Cs^+, $(CH_3)_4N^+$) [19]; increasing the size of the cation A causes the ^{35}Cl NQR frequency of the anion to increase over a range of 0.87 MHz (M = Pt), 1.21 MHz (M = Te, Re), or 1.61 MHz (M = Sn). Our results for chlorophenolates fall within this range. The accepted interpretation of the NQR frequency shifts in A_2MCl_6 is that they are not due to cation effects per se, but to variations in the degree of anion-anion repulsion as the lattice parameters change. A number of other types of anions have NQR frequencies which do not vary systematically with changes in the cation. This appears to be true for the chlorophenolates.

When we include the somewhat more acidic [20] cations Na^+ and Tl^+, the NQR frequency range significantly enlarges to 3.0 MHz – but only in the 2,4,6-trichlorophenolates. This range expansion is principally due to unusually high frequencies in $NaOPhCl_3$ and $TlOPhCl_3$ (higher even than in the parent phenol), which are absent in $NaOPhCl_2$, $TlOPhCl_2$, $TlOPhCl_2Br$ and $NaOPhCl_2Br$, and so can be assigned to the *para*-chlorines. The total range of *para*-chlorine NQR frequencies in all of these salts thus is at least about 2.0 MHz. Bayle [21] noted an unusually high NQR frequency for the *para*-chlorine in sodium *p*-chlorophenolate (but not sodium *o*-chlorophenolate), and attributed it to a mesomeric effect of the unshared oxygen electron pair, which could reduce C–Cl π bond orders. This could raise the NQR frequency provided that there was not a corresponding drift of the C–Cl σ bond electrons, which may be unlikely at the remote *para* position.

Our data for a variety of cations suggest that this is not a general effect in solid Group 1 chlorophenolates; even in $NaOPhCl_3$ the effect is reduced upon formation of an acetone adduct. We also note that the ^{81}Br frequencies of the *para*-bromines in $NaOPhCl_2Br$ and $TlOPhCl_2Br$ are *not* higher than that of the parent phenol. Perhaps the mesomeric effect of electron donation of phenolate oxygen lone pairs is dependent on the position of nearby cations. Alternatively, in an ionic chlorophenolate lattice it may be that the *para*-chlorine or bromine sits adjacent to a Na^+ or Tl^+ ion, which in the right position could perhaps also selectively induce appropriate σ or π-electron polarizations. Since our attempts to grow crystallographic-quality crystals of $NaOPhCl_3$ and $TlOPhCl_3$ were unsuccessful, no decisive explanation of this phenomenon now seems possible.

The *ortho*-chlorines show unusually low frequencies in one case only, $NaOPhCl_3$; this feature disappears upon formation of an acetone adduct, or in $NaOPhCl_2Br$ or $NaOPhCl_2$. One frequency in $NaOPhCl_3$ is more than 1 MHz lower than in other Group 1 chlorophenolates, and expands the total range of "crystal field effects" for *ortho*-chlorines to 2 MHz, which is comparable to those found in the Group 11 (Cu(I) and Ag(I)) chlorophenolates. Hence we cannot rule out the possibility that the *ortho*-chlorine splittings we have been observing in the transition-metal chlorophenolates is primarily due to electrostatic interaction between the charge of the transition-metal ion and the electrons of the nearby *ortho*-chlorine. This effect appears much less frequently in the Group 1 chlorophenolates than in the

Group 11 and transition-metal chlorophenolates, so the Group 1 interaction evidently lacks the same energetic consequences.

The temperature dependence of NQR frequencies (i.e. the frequency difference between 273 K and 77 K, shown in brackets in Tables 3 and 4) is significantly less in the Group 1 metal chlorophenolates (0.415 MHz $\pm$ 0.073 MHz, $n = 32$) than in the tetraalkylammonium chlorophenolates (0.664 ± 0.127 MHz, $n = 15$) or of non-coordinated chlorines in the transition metal chlorophenolate complexes (0.320–1.130 MHz, with a much higher mean) [22]. Normally NQR frequencies fall with increasing temperature due to increasing librational motion of the NQR-active species; we suppose that the strong lattice forces present in the ionic compounds of the Group 1 metal ions resist large amplitudes of librational motion.

Finally, to return to the dioxin question, there is indeed some type of unusual polarization of the aromatic chlorine atoms in sodium 2,4,6-trichlorophenolate – but not in the salts of the other Group 1 cations or in the other chlorophenolates. The unusual polarization of *ortho*-chlorines is more common in the Cu(I) and Ag(I) chlorophenolates, which do *not* eliminate these chlorines to form dioxins. Hence it seems unlikely that these secondary bonding effects are common enough or energetic enough to affect the high-temperature decomposition of Group 1 chlorophenolates significantly. Although the study by NQR of the metal-halogen interactions in salts of these anions as the temperature of decomposition is approached would have been interesting, we have not carried out this study for safety reasons, even though recent research results indicate "dioxin" is not nearly as extraordinarily toxic to humans as it is to animals [23].

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