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^{35}Cl NQR AS A METHOD OF DETECTING POSSIBLE CHLORINE–METAL COORDINATION IN ORGANOMERCURY DERIVATIVES OF CHLOROCARBONS*

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Summary

The ^{35}Cl NQR spectra of *trans*-2-chlorovinylmercuric chloride, four trichloromethylmercurials and several pentachlorocyclopentadienylmercurials have been studied as a function of temperature. The NQR spectra of these compounds show several unexpectedly low frequencies, which usually are less shifted by temperature changes than the corresponding normal frequencies in the same compounds. Such phenomena were previously observed in inorganic compounds such as $SbCl_3$ and shown to be associated with intermolecular metal–chlorine coordination. As X-ray studies have also shown relatively close organochlorine–mercury contacts indicating probable coordination in four of the organomercurials studied, it is proposed that organochlorine coordination may explain the low NQR frequencies observed in these four and many of the other compounds studied. Hence under certain circumstances, it is suggested that low NQR frequencies and small temperature effects may be used to predict the presence of organochlorine coordination in organomercury compounds.

Introduction

Organic compounds of the Group V and the Group VI elements are very important as ligands for metals, but few instances are known in which organic derivatives of the Group VII elements, the halogens, act as ligands. Some reported examples are an adduct of hexachlorocyclopentadiene with aluminum chloride [1], a dichloromethane complex, $PtCl_5(CH_2Cl_2)^-$ [2], and cobalt(II) and nickel(II) complexes of some 2-halophenyltriazene 1-oxides [3]. A halogen atom in the organic part of an organometallic molecule can, if the metal is coordinatively unsaturated, act as a ligand to the metal atom in the same molecule (intramolecular) or to a

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metal atom in an adjacent molecule (intermolecular coordination). Intramolecular coordination by halogen has been treated in a recent review [4], which discussed the difficulties in detecting such coordination. Probably the most unambiguous case, since it is supported by X-ray crystallographic data, is an Sn···Br interaction in 4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyldimethyltin bromide [5]. Intermolecular coordination, suspected in several mercury compounds, is best documented by the crystal structure of *trans*-2-chlorovinylmercuric chloride [6], in which short intermolecular Hg···Cl distances are noted.

Nuclear quadrupole resonance (NQR) spectroscopy of halogen nuclei has proved useful in detecting intermolecular coordination in many covalent metal halides [7, 8], and should be equally applicable to organometallic derivatives of halocarbons [9]. We have now applied NQR to the study of coordination in chlorocarbon derivatives of mercury.

NQR spectra have previously been recorded for the following types of mercurials: pentachlorocyclopentadienyl-[10], trichloromethyl-[11, 12], trichloroacetato-[11, 13], pentachlorophenyl-[14], *cis*- and *trans*-chlorovinyl-[15], trichlorovinyl-[16], 2,6-dichlorophenoxy- and thiophenoxy-[17] and *p*-chlorophenylmercurials [18]. In many of these spectra unusual features were noted and ascribed to intramolecular interactions of chlorine and mercury; however, the descriptions of these interactions were often vague and inconsistent. The interactions could be either intermolecular or intramolecular coordination or interactions involving the C—Cl σ orbital. In this paper the consequences of intermolecular coordination will be discussed, and data compared with the predictions. Intramolecular coordination will be mentioned briefly, but interactions involving the C—Cl σ orbital (which give different effects in NQR spectra) will be discussed in the following paper [19].

Experimental

NQR spectra were recorded on a Decca Radar NQR Spectrometer using the following slush baths to obtain the indicated temperatures (K): liquid nitrogen (77), isopentane (113), n-pentane (144), carbon disulfide (163), toluene (178), dry ice—isopropanol (195), carbon tetrachloride (248), and ice water (273). Temperatures of the baths were checked to ±1° by running the spectrum of $KClO_3$ [20]. For most runs spectra were recorded at three to five temperatures, including ambient temperature, which varied between 301 and 313 K. Spectra were recorded over the range 35.0-40.0 MHz using Zeeman modulation, and were sometimes checked by running with frequency modulation and sideband suppression. Decca frequencies are estimated to be accurate to ±0.007 MHz. Due to low intensities, the spectrum of α-C_5Cl_5HgCl was recorded on a Wilks NQR-1A spectrometer, with frequencies calibrated with a Northeastern Engineering frequency counter. Several runs under slightly different conditions gave different interference patterns of sidebands, allowing identification of main bands with an accuracy of about ±0.03 MHz.

Spectra obtained on the Decca instrument were then plotted as a function of temperature in the manner of Fig. 1 in order to determine whether any lines crossed, then $\Delta\nu_T$ was evaluated for each line and reported in Table 2. In the event that spectra at ambient temperatures could not be obtained (as for liquid samples), the available data from at least three temperatures were fitted to an equation of form $\nu = \nu_0(1 + bT + c/T)$ [30]. Values of ν_0, b and c were obtained, then $\Delta\nu_T = \nu_{304} - \nu_{77} = (304 - 77)b\nu_0 + (1/304 - 1/77)c\nu_0$ was calculated. If spectra at intermediate temperatures were not available, the absence of phase transitions or line crossings could not be assured, so vinylic, etc. frequencies were averaged at 77 K and at ambient temperature, and their difference reported in Table 3.

Non-mercurial pentachlorocyclopentadienyls were prepared according to published methods given for $C_5Cl_5C(CH_3)_3$ [21], $C_5Cl_5C_2H_5$ [22], $C_5Cl_5CH_2C_6H_5$ [21], C_5Cl_5H [22]. $C_5Cl_5CCl_3$ [23], and C_5Cl_5Br [24]. $(C_5Cl_5)_2$ was obtained from R.M. Smith. α and β modifications of C_5Cl_6 were crystallized as described in the literature [25]. The modifications of $C_5Cl_5C_2H_5$ are reported here for the first time; the metastable α form was obtained by immersing a vial of liquid $C_5Cl_5C_2H_5$ in dry ice—isopropanol. The initial glass soon gave crystals. The stable β form was obtained by slow crystallization of the liquid in a freezer at −18°.

The preparation and analysis of most of the pentachlorocyclopentadienylmercurials have been reported previously [10]. Benzyl(pentachlorocyclopentadienyl)mercury was prepared as follows: 1.15 g (3.0 mmol) dibenzylmercury (Alfa Inorganics) and 0.82 g (3.0 mmol) mercuric chloride were stirred for 2 h in 25 ml ether. Crystals of benzylmercuric chloride separated. 1.43 g (6.0 mmol) C_5Cl_5H was added; the mixture was cooled to −80° with stirring, and 1.40 g (5.6 mmol) thallous ethoxide was slowly added. After being stirred 20 min the solution was warmed to 0° and filtered from TlCl. The filtered solution was pot-to-pot distilled at 0°, and treated with 25 ml heptane. The grayish solid that formed was recrystallized from 40 ml 8/1 pentane/ether. Large colorless crystals formed (0.60 g, 20%), but they were contaminated with dark material, hence were not submitted for analysis. The product is rather unstable, but did give an NQR spectrum, and was characterized as a benzyl and C_5Cl_5Hg compound by its IR and UV spectra.

$(C_5Cl_5)_2Hg \cdot 2$ THF was crystallized from THF, and was analyzed by pumping on a weighed sample until constant weight was achieved. Calculated weight loss (theoretical % THF) = 17.19%; found = 17.05%. The new adducts $C_5Cl_5HgBr \cdot$ diglyme, $C_5Cl_5HgCl \cdot$ triglyme, and $C_5Cl_5HgBr \cdot$ triglyme were crystallized from excess polyether/heptane, and were analyzed by Galbraith Laboratories. Found: C, 20.58; H, 2.33; Hg, 31.05. $C_5Cl_5HgBr \cdot C_6H_{14}O_3$ calcd.: C, 20.26; H, 2.16; Hg, 30.77%. Found: C, 23.79; H, 2.57; Hg, 30.98. C_5Cl_6Hg. $C_8H_{18}O_4$ calcd.: C, 23.96; H, 2.78; Hg, 30.79%. Found: C, 22.23; H, 2.73; Hg 28.76. $C_5Cl_5HgBr \cdot C_8H_{18}O_4$ calcd.: C, 22.43; H, 2.61; Hg, 28.82%.

Bis(trichloromethyl)mercury and trichloromethylmercuric chloride were prepared as described by Logan [26], but CCl_3HgBr prepared by this or similar routes failed to give an NQR spectrum. Phenyl(trichloromethyl)mercury was prepared [27] and reacted with one equivalent of mercuric bromide in acetone; phenylmercuric bromide precipitated and was filtered off. Evaporation gave CCl_3HgBr which was recrystallized from acetone. The NQR of this compound was investigated only up to 144 K, as at that temperature most line intensities were becoming very low. *Trans*-2-Chlorovinylmercuric chloride was prepared as described by Nesmeyanov [28].

Theory

According to the Townes and Dailey approximation [29a], the NQR frequency of a covalent single-bonded chlorine atom can be expressed in terms of the populations N_x, N_y and N_z of its p_x, p_y and p_z orbital, where the z direction is taken as the direction of the covalent bond (eqn. 1). If this organochlorine

$$\nu \approx \frac{109.746}{2}\left(\frac{N_x + N_y}{2} - N_z\right) \tag{1}$$

atom now coordinates to a metal atom and donates[†] an amount of electron density Δ_x from its p_x orbital and Δ_y from its p_y orbital, these orbital populations will be diminished to $N_x - \Delta_x$ and $N_y - \Delta_y$ respectively. As a result of the bridging action the C—Cl bond may also lengthen and become more ionic, with N_z increasing to $N_z + \Delta_z$. Substituting these numbers in eqn. 1, we obtain the frequency of the organic halogen after it enters into the coordinative interaction[*]. The shift of the NQR frequency caused by coordination of the chlorine ($\Delta\nu_{\text{coord}}$) can be obtained by subtraction (eqn. 2). Hence we ascertain that coordination of an organohalogen should cause a decrease of its frequency[**].

$$\Delta\nu_{\text{coord}} = \frac{109.746}{2}\left(-\frac{\Delta_x + \Delta_y}{2} - \Delta_z\right) \tag{2}$$

The temperature dependence [30] of the NQR frequency, $\Delta\nu_T$, may also be affected by intermolecular coordination. As the lattice expands with increasing temperature, the interacting chlorine and metal atoms will find themselves, on the average, further apart, and thus will interact less, causing a smaller $\Delta\nu_{\text{coord}}$ at the higher temperature. Organochlorine frequencies normally decrease with increasing temperature, but the reduction in $\Delta\nu_{\text{coord}}$ should counteract this tendency to some extent, making $\Delta\nu_T$ less negative than it would otherwise have been. Knowing what $\Delta\nu_T$ would otherwise have been provides a difficulty, however, in view of the multiplicity of factors which affect $\Delta\nu_T$. Hence we will examine actual $\Delta\nu_T$ data in cases of known and suspected intermolecular coordination to see to what extent it does correlate with the first criterion of low NQR frequency[***].

[†] *Note added in proof* T. B. Brill [37] has pointed out that NQR effects such as those presented in this paper may be explained, not only by the covalent electron-transfer implied in this discussion, but also by an electrostatic polarization of chlorine electrons by mercury. Hence, although a chlorine—mercury interaction is suggested by the NQR data, this does not indicate whether the coordinative interaction is predominantly ionic or covalent.

[*] It is assumed that the coordinative interaction does not cause the asymmetry parameter to exceed about 0.2; nor in this qualitative treatment of a weak interaction will we attempt to redefine the x, y and z axes of the coordinating chlorine.

[**] If the chlorine had been engaging in π bonding to carbon before coordination but this π bonding was eliminated upon coordination, then eqn. 2 would read

$$\Delta\nu_{\text{coord}} = \frac{109.746}{2}\left(\frac{\Delta_x + \Delta_y}{2} - \Delta_z + \frac{\pi}{2}\right) \tag{2a}$$

[***] For early transition-metal halides with intermolecular coordination, the opposite NQR criteria (higher frequencies, more-negative $\Delta\nu_T$ values) have been proposed [33]. This results from the substantial π-bonding and strong coordination present in these systems.

Other factors could cause low NQR frequencies accompanied by less-negative $\Delta\nu_T$ values: (1) The frequency of an organochlorine nucleus may be lowered by interaction with a substituent atom bound to the same carbon atom which has lone pairs of electrons (O, F [29b], Cl, Br, S [31]. The effects on $\Delta\nu_T$ values seem not to have been studied. (2) If the chlorine is π-bonded to carbon, this will lower the frequency as compared to a similar, non-π-bonded chlorine. Raising the temperature may [29c] also disrupt this π-bonding, producing a similar less negative $\Delta\nu_T$. (3) Phase changes can produce frequency changes of about ±1% (±0.35 to ±0.5 MHz) [30] due to changing crystal field effects, with various changes in $\Delta\nu_T$. (4) Free rotation of the organochlorine group in the crystal can produce a very low NQR frequency, but with an extremely negative $\Delta\nu_T$ [30]. More frequently occurring would be a particularly low torsional frequency for the group, with similar but less extreme effects on the NQR spectrum. (5) Hydrogen bonding to chlorine could also lower the chlorine frequency and give it a less negative $\Delta\nu_T$. These hypotheses (Table 4) will also be considered.

A useful third criterion for detecting organochlorine coordination would be the appearance of a substantial asymmetry parameter. However, measurements of asymmetry parameters of NQR signals are experimentally difficult and have not been attempted here.

Results and Discussion

In Table 1 are presented the ^{35}Cl NQR spectra at 77 K of a series of chlorinated organomercurials and, as model compounds, some organic derivatives of the pentachlorocyclopentadienyl group. Those frequencies which seem anomalously low, and hence may indicate chlorine—metal coordination, are indicated by the superscript *b*. Table 2 presents data for selected compounds indicating the shift of each frequency on warming the sample from 77 K to 304 K. (In some cases this shift is extrapolated.) For some of the compounds spectra were obtained only at 77 K and at ambient temperature (about 304 K). Under these circumstances the behaviors of individual frequencies could not be distinguished, so the average frequency shifts for all similar chlorine atoms in the compound are reported in Table 3.

Let us first consider the verified cases of coordinative interactions. Among inorganic examples only $SbCl_3$ [9] will be mentioned here. The shortest intermolecular Cl—Sb distance is 3.41 Å, shorter than the sum of the van der Waals radii, 4.0 Å. (These chlorines are also more distant from their own antimony atom, 2.36 versus 2.30 Å for the other chlorine.) The non-coordinating chlorine shows its NQR frequency at 20.912 MHz at 77 K, with $\Delta\nu_T$ of —0.493 MHz, and an asymmetry parameter of 0.057. The coordinating chlorines show a lower frequency, 19.304 MHz, which has a less negative $\Delta\nu_T$, —0.125 MHz, and a larger asymmetry parameter of 0.153. As was pointed out by Chihara and coworkers [8], all the NQR consequences of coordination are as expected in $SbCl_3$.

Among organometallic compounds one of the best documented cases of organochlorine coordination is in *trans*-ClCH=CHHgCl, for which an X-ray crystallographic study has been done [6]. There are three crystallographically-nonequivalent molecules per unit cell. The organochlorine atom of one molecule has no mercury neighbors. From the published data [6] we calculate that

(continued on p. 310)

TABLE 1

^{35}Cl NQR SPECTRA OF ORGANOCHLORINES IN MERCURIALS AT 77 K

Compound	Frequencies MHz (S/N)					
	Line 1	Line 2	Line 3	Line 4	Line 5	Line 6
A. Trans-2-Chlorovinyl- and Trichloromethylmercurials						
ClCH=CHHgCl [a]	31.751(3) [b]	32.412(3) [b]	33.456(3)			
ClCH=CHHgBr [a]	33.246					
$(CCl_3)_2Hg$ [c]	37.037(12) [b]	37.681(12) [b]	36.675(13)			
CCl_3HgCl [c]	37.622(11) [b]	37.973(14) [b]	39.048(4)	39.176(5)		
CCl_3HgBr [c]	37.602(4) [b]	37.887(5) [b]	38.811(2)	39.037(2)		
$CCl_3HgC_6H_5$	36.210(5) [b]	36.293(4) [b]	36.335(4) [b]	36.609(6) [b]	36.675(5) [b]	37.125(5)
	Line 1, 6	Line 2, 7	Line 3, 8	Line 4, 9	Allylic lines (5, 10)	
B. Pentachlorocyclopentadienylmercury compounds						
1. α-$(C_5Cl_5)_2Hg$	36.261(3) [b]	36.687(5)	36.753(3)	[c]	38.863(4)	
	36.343(3) [b]	36.738(5)	36.914(7) [c]	37.061(3)	39.058(4)	
2. β-$(C_5Cl_5)_2Hg$ [d]	36.015(3) [b]	36.071(4)	36.162(3)	36.347(4)	37.773(3) [b]	
3. γ-$(C_5Cl_5)_2Hg$	36.431(7) [b]	36.700(13)	36.812(12)	36.882(12)	38.240(6) [b]	
	36.569(5) [b]	36.925(11)	36.980(5)	36.995(8)	38.364(6) [b]	
4. $(C_5Cl_5)_2Hg \cdot 2THF$	36.433(2)	36.559(2)	[c]	36.680(3)	37.713(2) [b]	
	36.523(2)	36.620(2) [c]	36.628(3)	36.698(2)	37.778(2) [b]	
5. $(C_5Cl_5)_2Hg \cdot 5/3$ glyme	36.120(5) [c]	36.419(3)	36.555(6) [e]	36.696(6) [a]	38.316(3)	
	[c]	36.482(3)	[c]	[c]	38.471(3)	
	36.194(3)	36.500(4) [c]	36.605(3)	36.880(3)	38.652(3)	
	36.342(3)	[c]	36.628(3)	36.927(3)	38.782(3)	
6. α-C_5Cl_5HgCl [f]	35.47(5) [b]	36.12(5)	[c]	36.49(5) [c]	38.44(9)	
	35.61(7) [b]	36.22(9) [c]	36.31(4)	[c]	38.70(7)	
7. β-C_5Cl_5HgCl	36.788(3)		37.147(2)		39.177(4)	
	36.884(4)		37.159(4)		39.233(2)	
	36.962(4)		37.188(8) [c]		39.266(4)	
	36.983(2)		[a]		39.322(2)	
	37.014(3)	[g]	37.222(4)	[g]	39.378(2)	
	37.057(5)		37.270(5)		39.447(3)	
	37.078(4)		37.376(3)		39.577(3)	
	37.098(5)		37.412(5)		39.693(2)	
8. γ-C_5Cl_5HgCl	35.722(3) [b]	36.975(5)	37.109(4)	37.154(5)	37.919(3) [b]	
	35.895(3) [b]	37.054(6)	37.118(5)	37.300(4)	38.439(3) [b]	
9. C_5Cl_5HgBr	35.842(4) [b]	36.936(8)	37.079(5)	37.154(5)	37.832(3) [b]	
	35.997(4) [b]	37.054(5)	37.121(8)	37.280(7)	38.476(4) [b]	

10. $C_5Cl_5HgCl \cdot$ glyme	36.197(9) [b?]	36.562(6)	[c]	36.771(9) [c]	38.489(6)
	36.288(7) [b?]	36.615(10) [c]	36.738(5)	[c]	38.912(6)
11. $C_5Cl_5HgBr \cdot$ glyme	36.302(5) [b?]	36.541(6)	36.608(7)	[c]	38.437(5)
	36.362(5) [b?]	36.602(sh)	36.745(9) [c]	36.784(8)	38.870(5)
12. $C_5Cl_5HgCl \cdot$ diglyme	36.543(12)	36.570(10)	36.592(9)	36.613(10)	38.364(12)
13. $C_5Cl_5HgBr \cdot$ diglyme	36.369(6)	36.517(7)	36.593(5)	36.688(5)	38.406(5)
14. $C_5Cl_5HgCl \cdot$ triglyme	36.518(4)	36.591(6) [e]	36.649(5) [c]	36.692(5) [e]	38.631(3)
	36.557(4)	[c]	[c]	[c]	38.852(3)
15. $C_5Cl_5HgBr \cdot$ triglyme	36.397(3)	36.578(2)	36.689(3)	36.774(3)	38.687(2)
16. $C_5Cl_5HgCl \cdot 1/2$ THF	36.571(10) [b?]	36.926(9)	36.971(9)	37.237(8)	38.406(5) [b]
	36.807(9)	36.934(sh)	37.025(8)	37.287(8)	39.394(6)
17. $C_5Cl_5HgCl \cdot HgCl_2$	36.247(7) [b, e]	37.160(5)	37.198(3)	37.421(7)	37.565(3) [b]
	[b, e]	37.181(3)	37.268(5)	37.458(7)	37.672(6) [b]
18. $C_5Cl_5HgBr \cdot HgBr_2$	36.275(sh) [b]	37.072(2)	37.29(2)	37.348(3)	37.694(3) [b]
	36.284(4) [b]	37.189(3)	37.31(2)	37.377(3)	37.768(3) [b]
19. $C_5Cl_5HgC_6H_5$	36.212(9)	36.265(8)	36.737(10)	36.865(9)	37.350(6) [b]
20. $C_5Cl_5HgCH_2C_5H_5$	35.76(3)	35.98(3)	36.25(4)	36.48(3)	37.61(5) [b?]
	35.89(3)	36.13(3)	36.47(3)	36.84(3)	37.77(2) [b?]
C. Organic pentachlorocyclopentadienes					
$C_5Cl_5C(CH_3)_3$	37.018(35)	[g]	36.935(35)	[g]	37.031(15)
α-$C_5Cl_5C_2H_5$	36.275(44)	36.734(44)	36.436(74)	36.874(72)	37.174(23)
β-$C_5Cl_5C_2H_5$	36.286(13)	36.961(13)	36.754(17)	37.101(17)	36.861(10)
$C_5Cl_5CH_2C_6H_5$	36.422(20)	36.565(22)	36.895(21)	37.171(25)	37.709(18)
C_5Cl_5H	36.887(9)	36.928(12)	36.951(5)	37.090(9)	38.019(8)
$(C_5Cl_5)_2$	37.469(13)	37.483(7)	37.055(16)	37.131(16)	39.365(11)
	37.750(13)	38.007(15)	37.287(14)	37.387(12)	39.826(11)
$C_5Cl_5CCl_3$	37.907(27)	[g]	37.085(27)	[g]	39.430(13)
	39.759(12) [h]	40.762(22) [h]			
C_5Cl_5Br	37.59(3)	37.67(4)	37.00(3)	37.26(2)	39.26(2)
α-C_5Cl_6 [i]	37.283(10)	37.464(10)	36.953(9)	37.279(6)	38.813(7)
					39.082(10)
β-C_5Cl_6 [i]	37.351(8)	37.379(8)	36.970(7)	37.061(6)	39.072(8)
	37.461(10)	37.656(8)	37.108(7)	37.303(8)	39.092(8)

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[a] Data from ref. 16. [b] Assigned to a coordinating chlorine. Question mark indicates quite uncertain assignment. [c] Also reported in ref. 12. [d] Data recorded at 248 K. [e] Coincidence of two lines. [f] Data from ambient termperature, recorded on Wilks NQR-1A spectrometer. [g] Crystallographic equivalence of the two sides of the C_5Cl_5 ring reduces the number of observed vinylic frequencies. [h] Frequencies of trichloromethyl chlorines. [i] Data from ref. 26.

TABLE 2

CHANGES ($\Delta\nu_T$) IN INDIVIDUAL NQR FREQUENCIES BETWEEN 77 K AND 304 K

Compound	Line 1, 6	Line 2, 7	Line 3, 8	Line 4, 9	(Allylic) Line 5, 10
$ClCH{=}CHHgCl$ [a]	−0.51 [b]	−0.67 [b]	−0.77		
$(CCl_3)_2Hg$	−0.83 [b]	−0.87 [b]	−1.05		
CCl_3HgBr [a]	−1.14 [b]	−0.97 [b]	[c]	−1.26	
CCl_3HgCl [a]	−1.15 [b]	−0.94 [b]	−1.82	−1.19	
CCl_3HgCl [d]	−0.40 [b]	−0.30 [b]	−0.65	−0.38	
$CCl_3HgC_6H_5$	−0.82 [b]	−0.95 [b]	−0.85 [b]	−1.03 [b]	−0.88 [b]
	−1.10				
β-$(C_5Cl_5)_2Hg$ [e]	−0.17 [b]	−0.23	−0.23	−0.26	−0.20 [b]
γ-$(C_5Cl_5)_2Hg$ [a]	−0.54 [b]	−0.78	−0.95	−1.11	−0.66 [b]
	−0.66 [b]	−0.97	−0.87	−0.99	−0.75 [b]
γ-C_5Cl_5HgCl	−0.55 [b]	−0.62	−0.93	−0.75	−0.40 [b]
	−0.68 [b]	−0.69	−0.71	−0.75	−0.63 [b]
$C_5Cl_5HgCl \cdot$ glyme [f]	−0.70 [b?]	−0.74	−1.12	−0.83	−0.60
	−1.01 [b?]	−0.75	−0.80	−1.08	−0.57
$C_5Cl_5HgBr \cdot$ glyme [f]	−0.64 [b?]	−0.72	−1.05	−0.84	−0.58
	−1.01 [b?]	−0.78	−0.84	−0.93	−0.61
$C_5Cl_5HgCl \cdot$ diglyme	−0.93	−0.94	−0.82	−0.94	−0.70
$C_5Cl_5HgC_6H_5$	−0.74	−0.79	−0.93	−0.90	−0.68 [b]
$C_5Cl_5C(CH_3)_3$	−0.78		−0.74		−0.50
α-$C_5Cl_5C_2H_5$ [a]	−1.18	−1.14	−1.18	−1.17	−0.94
β-$C_5Cl_5C_2H_5$ [a]	−0.70	−0.70	−0.81	−0.66	−0.64
$C_5Cl_5CH_2C_6H_5$	−0.60	−0.57	−0.60	−0.59	−0.39
C_5Cl_5H [a]	−0.90	−0.79	−0.80	−0.74	−0.72
$(C_5Cl_5)_2$	−0.84	−0.53	−0.74	−0.83	−0.50
	−0.60	−0.80	−0.70	−0.73	−0.55
$C_5Cl_5CCl_3$	−0.70		−0.62		−0.63
α-C_5Cl_6 [c]	−1.08	−1.24	−0.78	−1.01	−1.01; −1.01
β-C_5Cl_6 [a]	−0.73	−0.85	−0.74	−0.57	−0.87; −0.71
	−0.72	−0.81	−0.80	−0.77	−0.86; −0.83

[a] Frequencies for these compounds were not observed at 304 K· $\Delta\nu_T$ was extrapolated to 304 K as described in the experimental section solely to allow comparison of data with data from different compounds. [b] Assigned to coordinating chlorines. Question mark indicates uncertain assignment. [c] Intensity of this line too low to allow observation above 77 K. [d] Change in NQR frequency between 77 and 163 K (data not extrapolated). [e] Change in NQR frequency between 248 and 304 K (data not extrapolated). [f] $\Delta\nu_T$ was extrapolated to 304 K as described earlier, and the extrapolation confirmed to ±0.03 MHz by observing the room temperature spectrum on the Wilks spectrometer.

the second organochlorine atom has two mercury neighbors* at distances of 3.71 and 3.88 Å; the remaining organochlorine has a neighbor at 3.40 Å and a distant mercury neighbor at 4.03 Å. In contrast, *trans*-ClCH=CHHgBr has a structure [33] with only one type of molecule per unit cell, having no organochlorine—mercury distances of less than 4.46 Å. Comparison of the spectra of these two mercurials should provide a good example of the effects in NQR spectroscopy of organochlorine—metal coordination.

The ^{35}Cl NQR spectrum of *trans*-ClCH=CHHgBr [15] shows the expected

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* Although the conventional sum of van der Walls radii of mercury and chlorine is 3.30 Å, there is some ambiguity in and doubt about the van der Waals radius of mercury [33]. Furthermore, the radius of the $6p_x$ and $6p_y$ orbitals are not counted in these radii, since they are formally "unoccupied". These diffuse orbitals, when used, will extend outward some unknown distance beyond the Van der Waals radius.

TABLE 3

AVERAGE CHANGES OF NQR FREQUENCIES FOR COMPOUNDS STUDIED ONLY AT 77 AND 304 K, AND MEANS AND STANDARD DEVIATIONS FOR ALL COMPOUNDS

Compound	Average change in frequency ($\Delta\nu_T$) between 77 and 304 K for:			
	coordinating vinylic chlorine	normal vinylic chlorine	coordinating allylic chlorine	normal allylic chlorine
α-$(C_5Cl_5)_2Hg$	−0.42	−0.74		−0.63
$C_5Cl_5HgCl \cdot THF$		−0.73	−0.49	−0.78
$C_5Cl_5HgCl \cdot HgCl_2$	−0.46	−0.69	−0.41	
$C_5Cl_5HgBr \cdot HgBr_2$	−0.34	−0.6	−0.23	
C_5Cl_5HgBr	−0.66	−0.78	−0.54	
M and SD[a] for C_5Cl_5 mercurials	−0.52 ± 0.13	−0.79 ± 0.10	−0.51 ± 0.16	−0.66 ± 0.08
M and SD for C_5Cl_5 organic derivatives		−0.80 ± 0.18		−0.69 ± 0.21
M and SD[a] for CCl_3 mercurials			−0.96 ± 0.10	−1.22 ± 0.21

[a] Mean and standard deviation of average $\Delta\nu_T$ values, including compounds in Table 2.

single line, at 33.246 MHz. This can be considered to be a "normal" frequency. The NQR spectrum of *trans*-ClCH=CHHgCl [15] (at 77 K in the C—Cl region) shows three lines due to the three nonequivalent molecules in the unit cell (Table 1). By comparison Pakhomov and Kitaigorodskii [6] assigned the frequency of 33.456 MHz to the non-coordinating, "normal" organic chlorine, and the other two frequencies, 32.413 MHz and 31.751 MHz to the two coordinating organic chlorines; as expected, these occur at lower frequencies. We have measured the NQR spectrum of *trans*-ClCH=CHHgCl at 144 K and 195 K in order to check the effects of coordination on the temperature dependencies, $\Delta\nu_T$, of these frequencies*. The non-coordinating chlorine shows the most negative temperature dependency, as predicted (Table 2).

Intermolecular organochlorine—mercury contacts have also been detected in trichloromethylmercuric bromide [11]. The unit cell of CCl_3HgBr contains two nonequivalent molecules. In each molecule the trichloromethyl chlorines are split into an equivalent pair and an unique chlorine. Our calculations from the published data [11] show that the chlorine atoms in each equivalent pair have single near mercury neighbors, at a distance of 3.43 in one molecule and 3.69 Å in the other, whereas neither unique chlorine has a mercury neighbor. The compound CCl_3HgCl is isomorphous with CCl_3HgBr [11], and short intermolecular Cl···Hg distances have also been proposed [12] for $(CCl_3)_2Hg$ on the basis of unpublished X-ray data.

The pattern of frequencies reported for these compounds [11] at 77 K (Table 1) is entirely consistent with the pattern expected for intermolecular coordination. The centrosymmetric molecule $(CCl_3)_2Hg$ gives three frequencies [11]; two of these fall at much lower frequencies than the third, suggesting inter-

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* The NQR signals were too weak to be observed above 195 K, so the frequencies were extrapolated mathematically to 304 K. $\Delta\nu_T$ is taken as the frequency at 304 K less the frequency at 77 K.

molecular coordination. Both CCl_3HgBr and CCl_3HgCl show two lines of doubled intensity at low frequencies, which clearly are attributable to the two pairs of organochlorines engaged in intermolecular coordination. At higher frequencies each compound shows two lines of unit intensity, which are assignable to the unique, non-coordinating chlorine in each trichloromethyl group. The splitting between the high and low frequencies, 0.9 to 1.5 MHz, is larger* than one would expect from simple nonequivalence of the crystal lattice sites of the unique and paired chlorines**.

The NQR frequencies of CCl_3HgCl, CCl_3HgBr and $(CCl_3)_2Hg$ were measured at different temperatures and $\Delta\nu_T$ values computed (Table 2). As predicted, the low-frequency lines in the CCl_3HgBr and $(CCl_3)_2Hg$ spectra also showed less negative values of $\Delta\nu_T$. The results for CCl_3HgCl, however, do not completely meet the prediction, as the two lowest frequencies show the smallest and third-smallest negative $\Delta\nu_T$ values over the experimental temperature range 77-163 K (when extrapolated to 304 K the behavior is normal). Above 163 K the frequencies of one of the two distinct trichloromethyl groups in CCl_3HgCl (lines 1 and 3 in Table 1; see also Fig. 1) disappear, possibly due to free rotation of this trichloromethyl group [35]. As seen in Table 2 and Fig. 1, lines 1 and 3 show anomalously large negative $\Delta\nu_T$ values, presumably due to their much lower torsional frequency (ca. 95 cm^{-1} calculated [30] from the NQR spectrum for this CCl_3 group versus ca. 146 cm^{-1} for the less freely-rotating group). This low-temperature torsional motion apparently counteracts the effect of intermolecular coordination on the $\Delta\nu_T$ value of line 1, causing a failure of the prediction for CCl_3HgCl, and almost causing a failure for line 1 of CCl_3HgBr.

Before finally proposing intermolecular coordination, one should rule out the systematic applicability of the other causes of low frequencies or less-negative $\Delta\nu_T$ values (see Theory section and Table 4). Hypotheses 1, 2 and 5 are clearly inapplicable to CCl_3HgX. The NQR data indicate that any phase transitions which might be present produce at best negligible frequency changes. Free rotation and a low torsional frequency appear to be present, but by themselves cannot account for the observed pattern of frequencies and $\Delta\nu_T$ values.

In summary, for the eight cases of intermolecular coordination found by X-ray crystallography in the compounds just discussed, we find eight corresponding unusually low NQR frequencies, thus demonstrating the potential value of this test for intermolecular coordination in organometallic compounds. Seven

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* In a study of chemically-equivalent chlorines bound to benzene rings, Weiss [30] found that, of 265 such frequencies, 264 (99.6%) fell within a range of ±0.350 MHz, or ±1.0% of the NQR frequency. This can be taken as a likely outer limit to the effects of nonequivalent lattice sites in ring compounds. Furthermore, 94.7% of the frequencies fell within a range of ±0.250 MHz (±0.7% of the frequency). For aliphatic compounds a larger crystal field splitting is possible, but has not been quantified.

** Semin and coworkers [11, 12] attributed this splitting not to the intermolecular coordination that they detected, but to an intramolecular hyperconjugative interaction. As evidence they cited the fact that the unique trichloromethyl chlorines in CCl_3HgBr are 0.06 Å closer to the mercury atom of the same molecule than are the paired chlorines. We will discuss their mechanism in a subsequent paper [19]; for the present we wish to point out that the splitting can be explained by intermolecular coordination. The 0.06 Å difference in intermolecular Hg--Cl distances can also be explained by the bridging of the paired chlorines; an identical difference in Sb--Cl distances is found in $SbCl_3$ [8].

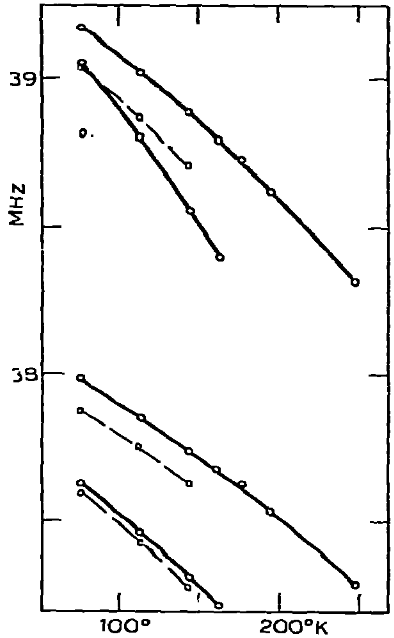

Fig. 1. Variable-temperature NQR spectra of organic chlorines in CCl_3HgX (X = Cl, Br). Frequencies for CCl_3HgCl are connected by heavy solid lines, those for CCl_3HgBr (not studied above 144 K) are connected by light broken lines.

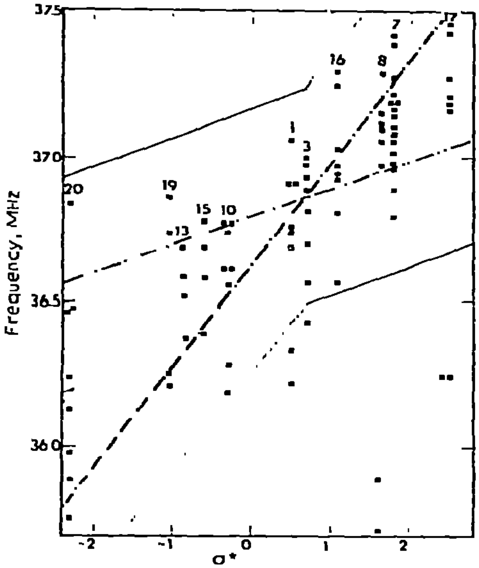

Fig. 2. 77 K NQR frequencies of vinylic chlorines of selected pentachlorocyclopentadienylmercurials as a function of σ^* of the mercury group. Numbers on the figure identify the spectra from Table 1. The line (——) represents the mean frequencies of 1,4-vinylic chlorines in organic RC_5Cl_5 compounds as a function of $\sigma^*(R)$; the line (—··—) represents the mean frequencies of the 2,3-vinylic chlorines in organic RC_5Cl_5 compounds; the solid lines represent the maximum ±1% deviations in these frequencies expected from normal variations in the electric field within the crystal lattice.

or eight (depending on the temperature range) of these unusually low frequencies also have the least-negative $\Delta\nu_T$ values for their compounds. Hence we observe that the $\Delta\nu_T$ test can fail, but if in a series of NQR spectra, most of the anomalously low NQR frequencies also have the least-negative $\Delta\nu_T$ values, we propose that there is a high probability that many or most of the compounds in the series do indeed possess intermolecular coordination.

Application to pentachlorocyclopentadienylmercurials

The application of these criteria can be demonstrated in a series of mercurials, the pentachlorocyclopentadienylmercurials [10], for which no X-ray crystallographic data exist. Let us consider first the vinylic chlorines (positions 1, 2, 3 and 4 on the cyclopentadiene ring). These chlorines actually consist of two chemically distinct groups, the 1,4-chlorines and the 2,3-chlorines, whose NQR frequencies are very similar. However, as the non-chlorine substituent in the 5 position varies from electron-accepting to electron-donating, the adjacent 1,4-chlorines will be affected inductively more than the distant 2,3-chlorines. Hence with many substituents there will be a splitting of the vinylic chlorine frequencies which is not due to coordination or other unusual effects.

To determine the expected behavior of the 1,4-, 2,3- and 5- (allylic) chlorines, a series of organic derivatives RC_5Cl_5 were prepared, and their NQR spectra were recorded (Table 1). Where possible the observed frequencies were assigned to 5-, 1,4- and 2,3-chlorines. Functions were then derived relating these frequencies to the Taft polar substituent constant σ^* of the R group*. The functions for the 1,4-chlorine and 2,3-chlorine frequencies of RC_5Cl_5 compounds are plotted in Fig. 2. These frequencies can of course experience a crystallographic splitting of ±1% [11, 24] so that the expected range of frequencies (in the absence of chlorine coordination) is indicated by the solid outer lines of Fig. 2.

The 77 K vinylic frequencies of some of the pentachlorocyclopentadienylmercurials were next plotted in Fig. 2 as a function of σ^* of the mercuri group**. Many frequencies for the mercury compounds deviate significantly from the values expected for vinylic chlorine (from the RC_5Cl_5 data) and all of the deviations are to lower frequency, as expected for Cl···Hg coordination.

In all we find ten vinylic frequencies, in α- and γ-C_5Cl_5HgCl, C_5Cl_5HgBr and $C_5Cl_5HgX \cdot HgX_2$ (X = Cl, Br), which are more than 0.75 MHz lower than expected; such large shifts are quite unlikely to be due to crystal-lattice effects. These large shifts are observed for highly electron-withdrawing (high σ^*) substituents only. This is reasonable according to our model, for the highly electronegative bromo and chloro substituents should cause the *6p* orbitals of mercury to contract, making them better able to coordinate organochlorine ligands***. Of these compounds, only γ-C_5Cl_5HgCl has been studied at more than two temperatures; its lowest vinylic frequency shows the least-negative $\Delta\nu_T$ value, but its other unusually low frequency has a quite negative $\Delta\nu_T$ value. (As in CCl_3HgX, the two distinct C_5Cl_5HgCl molecules in the unit cell may be quite different, since the infrared spectra of γ-C_5Cl_5HgCl (and C_5Cl_5HgBr) show closely-spaced doublets for each absorption expected in the 250-1600 cm^{-1} range. This in turn might reasonably lead to two quite different torsional frequencies, hence quite different $\Delta\nu_T$ values to add to the effect on $\Delta\nu_T$ of intermolecular coordination.) C_5Cl_5HgBr and $C_5Cl_5HgX \cdot HgX_2$ (X = Cl, Br) have been studied at two temperatures, and their low vinylic frequencies do show less-negative average $\Delta\nu_T$ values than their normal vinylic frequencies (Table 3). Again we are observing that, for these compounds, a less-negative $\Delta\nu_T$ is usually, but not always, associated with an unusually low NQR frequency.

Among compounds with intermediate σ^* we found ten cases of slightly low (0.30-0.75 MHz) vinylic frequencies, in α-, β- and γ-$(C_5Cl_5)_2Hg$, $C_5Cl_5HgCl \cdot$ ½THF, and $C_5Cl_5HgX \cdot$ glyme (X = Cl, Br). Many of these frequencies fell just within ±1% of the expected value, so that the alternate hypothesis of crystal-lattice effects is quite plausible. In such ambiguous cases, the $\Delta\nu_T$ values may be especially valuable. Of the nine slightly low frequencies studied at two or more temperatures, seven possessed least-negative $\Delta\nu_T$ values; statistically we would have expected 2.25. Hence it seems probable that some very weak organochlorine coordination exists in this series of compounds, but clearly without further information

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* Details of assignment and derivation of the functions are given in the following paper [19].

** The σ^* values of mercuri groups are calculated, tabulated and discussed in ref. 13.

*** The fact that Cl and Br are less bulky than the other substituents on mercury may also facilitate coordination.

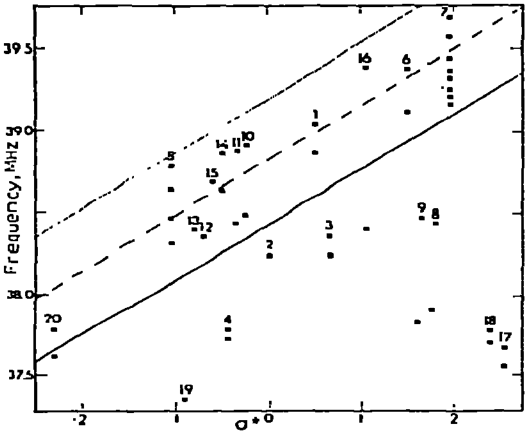

Fig. 3. 77 K NQR frequencies of allylic chlorines of pentachlorocyclopentadienylmercurials as a function of σ^* of the mercuri group. Numbers identify the spectra from Table 1 The dotted line (— · —) represents the mean of these frequencies (excluding those proposed to be shifted by coordination): the solid lines represent the maximum ±1% deviation expected from the crystal lattice effect. Spectra 2 and 6 are estimated from room temperature data by subtracting average $\Delta\nu_T$ values (Table 3).

we cannot specify with certainty in which individual compounds organochlorine coordination occurs.

In Fig. 3 the frequencies of the allylic chlorines of the pentachlorocyclopentadienylmercurials are plotted as a function of σ^* of the mercuri group. A majority of the frequencies fall within ±1% of the line which is drawn in Fig. 3. As these frequencies include the glyme, diglyme and triglyme adducts, in which coordination of organochlorines should be least likely [12], it is proposed that the frequencies within ±1% of this line are due to non-coordinating allylic chlorines*.

As among the vinylic frequencies, a sizeable number of allylic frequencies are observed to fall at significantly lower frequencies than expected from the line of Fig. 3, while none occur at significantly higher frequencies. Furthermore, (except for $C_6H_5HgC_5Cl_5$) the points which are at very low frequencies occur in the region of high σ^*. Hence coordination of allylic chlorines can be proposed in these cases of low frequencies.

The $\Delta\nu_T$ data for these allylic chlorines, however, is quite difficult to use. An "internal reference" of non-coordinating allylic chlorine atom(s) should be present to use the $\Delta\nu_T$ criterion, because extraneous variations in $\Delta\nu_T$ values from compound to compound are likely due to differing torsional frequencies. Unfortunately, none of the compounds with apparent allylic coordination have a reliable "internal reference" of non-coordinating allylic frequencies**. However,

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* The frequencies of non-coordinating allylic chlorines in mercurials are generally quite different from the allylic frequencies in organic pentachlorocyclopentadienes, this difference, the so-called "alpha effect", will be discussed in a separate paper [19].

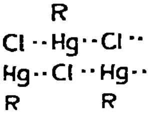
** $C_5Cl_5HgCl \cdot \frac{1}{2}THF$ (point 16 in Fig. 3) would appear to be such a case, and indeed shows the expected less-negative $\Delta\nu_T$ for the lower frequency. However, the stoichoimetry of this compound suggests a structure such as $C_5Cl_5HgCl \cdot (C_5Cl_5HgCl \cdot THF)$, in which the allylic chlorines are chemically different. In the cases of γ-C_5Cl_5HgCl and C_5Cl_5HgBr (points 8 and 9, Fig. 3), it appears from the low frequency criterion that one allylic chlorine is much more strongly coordinated than the other in each compound. The lower frequency chlorines again show less negative $\delta\nu_T$ values.

if the average $\Delta\nu_T$ is taken for all significantly low allylic frequencies in Fig. 3, we find this average (—0.51 ± 0.16 MHz) to be less negative than the average $\Delta\nu_T$ for "normal" allylic frequencies in mercurials (—0.66 ± 0.08) or RC_5Cl_5 compounds (—0.69 ± 0.21).

Discussion of individual compounds

$(C_5Cl_5)_2Hg$ and derivatives. Three distinct phases of $(C_5Cl_5)_2Hg$ are known [10]. From their NQR spectra, γ-$(C_5Cl_5)_2Hg$ and β-$(C_5Cl_5)_2Hg$, the low and high temperature forms respectively, seem closely related. Both show evidence of Cl···Hg coordination involving two allylic and two vinylic chlorines, giving mercury an average coordination number of six. In contrast α-$(C_5Cl_5)_2Hg$, which does not convert to the β or γ form by temperature alone, shows evidence of coordination of two vinylic chlorines per molecule only, giving mercury an average coordination number of four. Models of these compounds indicate that access to the mercury atom is sterically restricted, so that it is not surprising that all of these apparent coordinative interactions are relatively weak (as indicated by the relatively small shifts to low frequency). Apparently these coordinative interactions are completely broken up in the adduct with 1,2-dimethoxyethane (glyme), as no low frequency lines appear in the spectrum of this adduct.

C_5Cl_5HgX and derivatives. Three distinct phases of C_5Cl_5HgCl are known, each differing in the number and types of apparent organochlorine coordination. α-C_5Cl_5HgCl is the high temperature and β-C_5Cl_5HgCl the low temperature form of the yellow variety, while the cream-colored γ form is obtained separately [10]. Organomercuric halides are usually associated in the solid state in a linear antiparallel motif (A) [18, 22], which gives each mercury a coordination number of



$$\begin{array}{l} \text{R} \\ \text{Cl}\cdots\text{Hg}\cdots\text{Cl}\cdots \\ \text{Hg}\cdots\text{Cl}\cdots\text{Hg}\cdots \\ \text{R}\qquad\text{R} \end{array}$$

(A)

four. In α-C_5Cl_5HgCl one vinylic chlorine appears to be coordinated per C_5Cl_5HgCl unit. In the β form, despite the incredible complexity of its spectrum (which indicates eight crystallographically-distinct molecules per unit cell), there is no noncrystallographic splitting of the NQR signal, hence no detectable organochlorine coordination. In the γ form of C_5Cl_5HgCl and in C_5Cl_5HgBr there are apparently two vinylic and two allylic chlorines coordinated for each pair of C_5Cl_5HgX units. Hence there is a probable average coordination number for mercury of four in the β form, five in the α form, and six in the γ form (assuming linear association of RHgX units). Very close similarities exist in the spectra of γ-C_5Cl_5HgX, $C_5Cl_5HgX \cdot$ glyme and $C_5Cl_5HgX \cdot HgX_2$, which suggest that X = Cl compounds are isostructural with the corresponding X = Br derivatives. The weakly coordinating ether tetrahydrofuran apparently does not break up all of the organochlorine coordination in the adduct $C_5Cl_5HgCl \cdot \frac{1}{2}$THF, and some very weak coordination may exist in the glyme adducts; but judging from the NQR spectra all organochlorine coordination is eliminated in the diglyme and triglyme adducts.

The very large differences in the frequencies of some of the chlorines of these three phases of the same compound, C_5Cl_5HgCl, strongly suggest that inductive mechanisms are not responsible for the frequency shifts observed. Inter- or intra-molecular coordination of a fairly weak nature provides the simplest hypothesis to explain these differences, as well as their gradual disappearance in the polyether adducts.

Conclusions

In the study of pentachlorocyclopentadienylmercurials we observed 199 NQR frequencies. Of the 156 vinylic resonances, none deviated to significantly higher frequencies, ten deviated to much lower ($>$ 0.75 MHz) frequencies than expected, and ten showed slightly lower (0.30-0.75 MHz) frequencies than expected. Of these 20 frequencies, three were not studied by variable-temperature NQR, seven showed less-negative $\Delta\nu_T$ values than did any normal-frequency vinylic chlorines in the same compound and phase, seven showed lower average $\Delta\nu_T$ values on the basis of incomplete NQR studies at only two temperatures, and three failed to show less-negative $\Delta\nu_T$ values. Hence there appears to be a statistical association of less-negative $\Delta\nu_T$ values with low NQR frequencies among these vinylic chlorines. By way of contrast, in the study of 44 vinylic chlorine resonances of organic pentachlorocyclopentadienes, no deviations to significantly lower frequencies were observed [19]. If we arbitrarily consider the lowest frequency in each of the nine compounds or phases studied at different temperatures, we find that three of these nine low frequencies have least-negative $\Delta\nu_T$ values, as compared to a random expectation of 2.5. Hence in the organic pentachlorocyclopentadienes, in which coordination is impossible, there are no unusually low frequencies and only random association of lowest frequencies with least-negative $\Delta\nu_T$ values.

Among the 43 allylic resonances observed, none showed significantly higher frequencies than expected, thirteen showed much lower frequencies and four showed slightly lower frequencies. Comparison of $\Delta\nu_T$ values for low-frequency and normal-frequency allylic chlorines in the same compound could not be made, but the overall average $\Delta\nu_T$ for the 17 low allylic frequencies was less negative than the average $\Delta\nu_T$ for normal-frequency allylic chlorines. Corresponding data for trichloromethyl- and chlorovinyl- mercurials were summarized earlier in this paper.

In Table 4 we summarize the hypotheses developed in the theory section which might explain these observations. (This list is, of course, not exhaustive.) The first and fifth hypotheses are generally not applicable to the compounds in this study. Hypothesis 2 is inapplicable to trichloromethyl or allylic chlorines; it seems unlikely to apply to just one-fourth the vinylic chlorines in a C_5Cl_5 ring (in none of the mercurials do more than this fraction show the low frequencies). Undetected phase changes are possible, especially for the compounds listed in Table 3; but they are very unlikely by themselves to produce 0.75-2 MHz shifts to lower frequencies. The smaller (0.30-0.75 MHz) shifts found in 16 cases (including $CCl_3HgC_6H_5$) could be so explained, but it is improbable that phase changes would always produce shifts to lower frequencies, usually of one-fourth the allylic chlorines, and usually making $\Delta\nu_T$ less negative. Free rotation and low torsional frequencies appear to be a complicating factor in CCl_3HgX and perhaps a few other cases, but their expected effect on $\Delta\nu_T$ is

TABLE 4

POSSIBLE HYPOTHESES TO EXPLAIN UNUSUALLY LOW NQR FREQUENCIES WHICH HAVE LESS NEGATIVE $\Delta\nu_T$ VALUES THAN EXPECTED.

Hypothesis	Approximate magnitude of shift to lower frequency (MHz)	Effect on $\Delta\nu_T$
1a. α-Substituent of F, N or O	1-4	unknown
1b. α-Substituent of Cl, Br or S	< 1	unknown
2. π-Bonding disrupted by higher temperature	< 2	less negative than expected
3. Phase changes	± 0.4	
4a. Free rotation	4 in $C_2H_4Cl_2$ [30]	very much more negative
4b. Low torsional frequencies	< 1	more negative than expected
5. Hydrogen bonding	< 1	less negative than expected
6a. Weak intermolecular coordination	0.75-2	less negative than expected
6b. Very weak intermolecular coordination	0.3-0.75	less negative than expected
7. Intramolecular coordination	< 2	unknown-expect (often none)

the opposite to that observed. (Free rotation could occur in C_5Cl_5HgX in the form of fluxional motion of the cyclopentadienyl ring [36], but this would affect all of the frequencies; we found no evidence for any fluxional behavior in any of these cyclopentadienylmercurials on the NQR time scale).

We have not yet discussed hypothesis 7, intramolecular coordination. In theory one would expect it to produce similar frequency shifts, but, as expansion of the crystal lattice with increasing temperature would have less effect on intramolecular coordination, one might expect no unusual $\Delta\nu_T$ values unless some thermally-activated torsional motion occurred which increased the average separation of the chlorine and mercury [29c]. However, variable-temperature NQR spectra of compounds known to contain intramolecular coordination are not yet available, so we do not, in this paper, attempt to draw any conclusions as to whether the organochlorine coordination being suggested is inter- or intramolecular. We hope to do studies in the future into possible ways of making the distinction by NQR.

Hence we conclude that for compounds with substantial low-frequency shifts, inter- or intra-molecular coordination of the organochlorine to mercury is the most likely explanation for these shifts. Most of these compounds show the less-negative $\Delta\nu_T$ values which are probable for intermolecular, and possible for intramolecular, coordination. For the compounds with slight low-frequency shifts, alternate hypotheses such as phase changes or simply crystal-field variations are possible, so that X-ray data would be essential to support proposals of organochlorine coordination, especially for a given compound. In cases where X-ray data are obtained, the NQR data can still be valuable, however. The van der Waals radius of mercury is still quite in doubt [34]; a correlation of non-bonded Hg···Cl distances from X-ray studies with NQR shifts of these chlorines could give information as to the distance at which the mercury and chlorine interact so little as to be undetectable by the very sensitive method of NQR.

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References

1 H.P. Fritz and L. Schafer, J. Organometal. Chem., 1(1964) 318.
2 P.M. Cook, L.F. Dahl and D.W. Dickerhoof, J. Amer. Chem. Soc., 94 (1972) 5511.
3 P.S. Zacharias and A. Chakravorty, Inorg. Chem., 10 (1971) 1961.
4 A.K. Prokof'ev, V.I. Bregadze and O. Yu. Okhlobystin, Russ. Chem. Rev., 39 (1970) 196.
5 F.P. Boer, J.J. Flynn, H.H. Freedman, S.V. McKinley and V.R. Sandel, J. Amer. Chem. Soc., 89 (1967) 5068.
6 V.I. Pakhomov and A.I. Kitaigorodskii, J. Struct. Chem., 7 (1966) 798.
7 T. Okuda, Y. Furukawa and H. Negita, Bull. Chem. Soc. Japan, 45 (1972) 2940, T Okuda, A. Nakao, M. Shiroyama and H. Negita, Bull. Chem. Soc. Japan, 41 (1968) 61.
8 H. Chihara, N. Nakamura and H. Okuma, J. Phys. Soc. Japan, 24 (1968) 306, M. Hashimoto, T. Morie and Y. Kato, Bull. Chem. Soc. Japan, 44 (1971) 1455.
9 M.G. Voronkov and V.P. Feshin, in F.C. Nachold and J.H. Zuckerman (Eds.), Determination of Organic Structures by Physical Methods, Vol. 5, Academic Press, New York, 1973, pp. 169-233.
10 G. Wulfsberg and R. West, J. Amer. Chem. Soc., 93 (1971) 4085; G. Wulfsberg, R. West and V.N.M. Rao, ibid., 95 (1973) 8658.
11 T.A. Babushkina, E.V. Bryukhova, F.K. Velochko, V.I. Pakhomov and G.K. Semin, J. Struct. Chem., 9 (1968) 153.
12 E.V. Bryukhova, F.K. Velichko and G.K. Semin, Bull. Acad. Sci. USSR, Chem. Ser., (1969) 880.
13 F.K. Velichko, L.A. Nikonova and G.K. Semin, Bull. Acad. Sci. USSR, Chem. Ser., (1967) 78.
14 V.I. Bregadze, T.A. Babushkina, O. Yu. Okhlobystin and G.K. Semin, Theor. Exper. Chem., 3 (1967) 325.
15 E.V. Bryukhova, T.A. Babushkina, M.V. Kashutina, O. Yu. Okhlobystin and G.K. Semin, Proc. Acad. Sci. USSR, 183 (1968) 1035.
16 G.K. Semin and V.I. Robas, cited in I.P. Biryukov, M.G. Voronkov and I A. Safin, Tables of Nuclear Quadrupole Resonance Frequencies, Israel Program for Scientific Translations, Jerusalem, 1969, p. 24.
17 D.N. Kravtsov, A.P. Zhukov, B.A. Faingor, El.M. Rokhlina, G.K. Semin and A.N. Nesmeyanov, Bull. Acad. Sci. USSR, Chem. Ser., (1968) 1161; D.N. Kravtsov, G.K. Semin, A.P. Zhukov, T.A. Babushkina and E.M. Rokhlina, Teor. Eksp. Khim., 9 (1973) 513.
18 A.N. Nesmeyanov, O. Yu. Okhlobystin, E.V. Bryukhova, V.I. Bregadze, D.N. Kravtsov, B.A. Faingor, L.S. Golovchenko and G.K. Semin, Bull. Acad. Sci. USSR, Chem. Ser., (1969) 1785.
19 G. Wulfsberg, J. Organometal. Chem. 86 (1974) 321.
20 A.D. Brodskii, V.I. Solov'ev and E.T. Shub, Tr. Inst. Gos. Kom. Stand., Mer Izmer. Prib. SSSR, 87 (1966) 44; Chem. Abstr., 67 (1967) 77744m.
21 V. Mark, R.E. Wann and H.C. Godt, Jr., Org. Syn., 43 (1963) 90.
22 E.T. McBee and D.K. Smith, J. Amer. Chem. Soc., 77 (1955) 389.
23 E.T. McBee, J.A. Bosoms and C.J. Morton, J. Org. Chem., 31 (1966) 768.
24 G. Wulfsberg and R. West, J. Amer. Chem. Soc., 94 (1972) 6069.
25 M. Hayek, D. Gill, I. Agranat and M. Rabinovitz, J. Chem. Phys. 47 (1967) 3680.
26 T.J. Logan, J. Org. Chem., 28 (1963) 1129.
27 T.J. Logan, Org. Syn., 46 (1966) 98.
28 A.N.Nesmeyanov and R. Kh. Freidlina, Izv. Akad. Nauk SSSR, Org. Khim. Nauk, (1945) 150.
29 (a) E.A.C. Lucken, Nuclear Quadrupole Coupling Constants, Academic Press, London, 1969, Ch. 7; (b) Ibid., Ch. 10; (c) Ibid., Ch. 13.
30 A. Weiss, Fortsch. Chem. Forsch. 30 (1972) 1.
31 E.N. Tsvetkov, G.K. Semin, D.I. Lobanov and M.I. Kabachnik, Theor. Exper. Chem., 4 (1968) 288.
32 P.A. Edwards and R.E. McCarley, Inorg. Chem., 12 (1973) 900.
33 G.Grdenic, Quart. Rev., 19 (1965) 303; L.G. Kuz'mina, N.G. Bokii, Yu. T. Struchkov, D.N. Kravtsov and L.S. Golovchenko, J. Struct. Chem., 14 (1973) 463; R.M. Barr, M. Goldstein, T.N.D. Hairs, M.McPartlin and A.J. Markwell, J.Chem. Soc., Chem. Comm., (1974) 221.
34 A.I. Kitaigorodskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1947) 259.
35 M. Hashimoto and K. Mano, Bull. Chem. Soc. Japan., 45 (1972) 706.
36 J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, Harper and Row, New York, 1972, p. 497-502.
37 T.B. Brill, J. Chem. Phys., 61 (1974) 424.