

Information on Structure and Basicity from the Nuclear Quadrupole and Infrared Spectra of Mercuric Halide Adducts of Polyethers and a Crown Ether^{1a}

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The halogen NQR frequencies and Hg-Cl ir stretching frequencies of the mercuric halide adducts of the polyethers $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_{n-1}\text{R}$ ($\text{R} = \text{CH}_3$ or $(\text{CH}_3)_3\text{C}$, $n = 2-5,7$) and the crown ether $(\text{CH}_2\text{CH}_2\text{O})_6$ have been recorded and analyzed in terms of the number of oxygen donor atoms per mercury atom n and the number of intermolecular halogen-mercury interactions present in the adducts, as judged by molecular models and published crystal structures. It is found that each Cl-Hg intermolecular interaction lowers the ^{35}Cl NQR frequency by 0.7-1.5 MHz; the factor n has a smaller effect of -0.6 MHz per donor atom. If these factors are first taken into account, the NQR frequencies or Hg-Cl stretching frequencies of HgX_2 adducts of oxygen Lewis bases can then give information on the relative basicity of the oxygen base or reveal any unusual coordination environment of the mercury. Several examples of the latter are discussed, including mercuric bromide-triglyme, which shows a phase transition between monomer and dimer forms, and HgCl_2 itself, which should be used only with caution as a reference point in solid-state ir or NQR studies.

Introduction

The chlorine, bromine, and iodine nuclear quadrupole resonance (NQR) spectra of many derivatives of the mercury halides have been studied, including the mercuric halides themselves,² the adducts of the mercuric halides with organic Lewis bases (usually having oxygen donor atoms),³⁻⁹ the complex chloro anions of mercury,¹⁰ and various organo-mercury halides.¹¹⁻¹⁸ Related quadrupole coupling constants have also been obtained by Mössbauer¹⁹ and microwave²⁰⁻²¹ spectroscopy. But the interpretation of these NQR frequencies is complex due to the many factors which may affect the halogen directly or modify the mercury-halogen covalent bond. An incomplete listing of the factors previously suggested would include (1) the inductive effect of the Q substituent in QHgCl , (2) the electron-donating effect of each donor atom in a Lewis base adduct, (3) the number of donor atoms about mercury, (4) any weak coordinate-covalent or Sternheimer²² interaction of the halogen itself with mercury atom(s) in other molecules, and (5) any partial mercury-halogen triple bonding. As an apparent consequence of this number of factors, the NQR frequencies of ^{35}Cl bonded to mercury occur over the wide range of 8 to more than 23 MHz, and their detailed interpretation remains unclear.

In this paper we report a study of the 1:1 adducts of HgCl_2 , HgBr_2 , and HgI_2 with the following polyethers $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_{n-1}\text{R}$: glyme, gly ($\text{R} = \text{CH}_3$, $n = 2$); diglyme, digly ($\text{R} = \text{CH}_3$, $n = 3$); diglytbu ($\text{R} = (\text{CH}_3)_3\text{C}$, $n = 3$); triglyme, trigly ($\text{R} = \text{CH}_3$, $n = 4$); tetraglyme, tetragly ($\text{R} = \text{CH}_3$, $n = 5$); and the cyclic (crown) ether 18-crown-6, $(\text{CH}_2\text{CH}_2\text{O})_6$. (Only the combination glyme + HgI_2 failed to give an isolable adduct.) In addition we studied the 2:1 hexaglyme adducts $2\text{HgX}_2 \cdot \text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_3$, where $\text{X} = \text{Cl}$, Br , and I .

Experimental Section

Mercuric halides were analytical reagent grade and were used without further purification. Polyethers, used without further purification, were obtained from the Aldrich Chemical Co., except for diglytbu (diethylene glycol di-*tert*-butyl ether), from Dow Chemical Co., and hexaglyme (hexagly; 2,5,8,11,14,17,20-heptaohexacosane), from Schuchardt, Munich. Adducts were prepared by either or both of two methods: (1) the mercuric halide was dissolved in an excess of hot polyether and cooled; (2) stoichiometric quantities of polyether and mercuric halide were combined in hot ethanol, and the solution was cooled. Mercury was determined iodometrically by the Rupp method, using gelatin as a protective colloid.²³ For analysis, the adducts of the higher ethers were rinsed three times with Skelly B and then vacuum-dried to constant weight; satisfactory analyses were obtained. For the diglyme adducts, the coordinated polyether was too readily lost, so that air-drying was used; consequently results for

Hg were about 1% low. For HgBr_2 -gly, glyme was determined by weight loss on prolonged exposure to air. For HgCl_2 -18-crown-6, it was necessary to add detergent to the reaction mixture to obtain sufficient solubility of the sample for the Rupp method. HgBr_2 -18-crown-6 gave very low analysis by the Rupp method even with prolonged digestion with detergent, while HgI_2 -18-crown-6 was so insoluble that it gave no detectable mercury. However, excellent carbon-hydrogen analyses were obtained for these three adducts. All analytical data are reported in Table 1 of the supplementary material.

^{35}Cl NQR spectra were measured at 77 K and at ambient temperature (ca. 304 K) on a Decca Radar NQR spectrometer with Zeeman modulation and are accurate to ± 0.005 MHz. ^{79}Br , ^{81}Br , and ^{127}I ($\pm 1/2 \leftrightarrow \pm 3/2$) frequencies were recorded on a Wilks NQR-1A spectrometer at room temperature, which was measured with a thermometer and held relatively constant by means of an air stream directed at the coil and sample. The sidebands present in these spectra may conceal some slightly split doublet signals. Some halogen NQR signals might also have been missed due to unfavorable relaxation times, which would of course alter the structural interpretation. Frequencies were calibrated using external reference samples of HgBr_2 and KBrO_3 ; bromine frequencies were interpolated to ± 0.3 MHz, while most iodine frequencies were extrapolated to ± 0.7 MHz. Solid-state ir spectra ($1400-250\text{ cm}^{-1}$) were obtained as Nujol mulls on polyethylene sheets between CsI plates and were found to be very similar to the results obtained by Iwamoto.²⁴ Solution ir spectra ($429-250\text{ cm}^{-1}$) were obtained in benzene solution in 2-mm polyethylene cells on a Perkin-Elmer Model 457 ir spectrometer. Framework molecular models were used to assess geometrical constraints.

Hypotheses and Theory

In this series of adducts many of the five factors mentioned in the Introduction can be controlled: (1) the substituent on mercury is always Cl, Br, or I; (2) all oxygen donor atoms should be of similar basicity; and (5) any mercury-halogen triple-bonding character (which is often not considered important in any case) should be nearly constant for each halogen. Hence only two important variable factors remain.

In the 1:1 adducts factor 3, the number of donor atoms about mercury (which we will symbolize by n), would equal the number of oxygen atoms in the polyether, if the polyether adopts a completely chelating conformation. Iwamoto²⁴ has shown by x-ray crystallography that this is so for the adducts HgCl_2 -tetragly and HgCl_2 -tetraglyet ($\text{R} = \text{CH}_3\text{CH}_2$, $n = 5$), and he has analyzed the ir spectra of the polyether ligands in the HgCl_2 and HgBr_2 adducts of glyme, diglyme, and triglyme,²⁴ to show that their conformations are similar. Iwamoto's x-ray data²⁴ on the above and more complex polyether-mercuric chloride adducts show Hg...O distances of 2.66-2.96 Å and O-Hg-O angles of 59-64°. These are substantially the same as the K...O distances and O-K-O angles found²⁵ in the especially stable crown ether adducts of

Table I. Intermolecular Interactions Predicted in Polyether Adducts Using Molecular Models

Compd	CN- (Hg) ^a	CN- (X ₁)	CN- (X ₂)	State of aggregation
HgBr ₂ , yellow HgI ₂ ^b	6	3	3	Layer polymer
HgBr ₂ ·THF ^b	6	2	3	Layer polymer
HgCl ₂ · 2CH ₃ OH ^b	6	2	2	Linear polymer
HgCl ₂ ·diox ^b	6	2	2	Linear polymer cross-linked by dioxane
HgX ₂ ·gly	6	2	2	Puckered linear polymer
HgX ₂ ·digly	6	1	2	Dimer
HgX ₂ ·diglytbu	5 or 6	1 2	1 or 2	Monomer or dimer
HgX ₂ ·trigly	6 or 7	1 2	1 or 2	Monomer or dimer
HgBr ₂ ·2diox ^b	6	1	1	Monomer cross-linked by dioxane in two dimensions
HgCl ₂ ·tetragly ^b	7	1	1	Monomer
HgX ₂ · 18-crown-6	8	1	1	Monomer
2HgCl ₂ · hexaglyet ^b	7	1	2	Monomer with two HgCl ₂ units

^a CN(Hg) is the coordination number of mercury; CN(X₁) and CN(X₂) are the coordination numbers of halogen atoms 1 and 2.

^b From the crystal structure (see text for references).

18-crown-6 and K⁺. As we also observe the ir spectra of the crown ether ligand in the HgX₂ and K⁺ adducts to be very similar, we take as our working hypothesis that, in general, in the above adducts each polyether oxygen atom is coordinated to mercury and that the ligand is completely chelating.

Factor 4, the number of weak intermolecular halogen-mercury interactions, was then assessed using molecular models with the Hg...O distances and O-Hg-O angles just cited,²⁴ conventional²⁶ Hg and halogen covalent radii, van der Waals radii, etc. (There is dispute as to the value of the Hg van der Waals radius, but within the limits of reliability of our molecular models this uncertainty would not affect our conclusions.) From the models the number of possible intermolecular contacts of each halogen atom were determined for each adduct; this number plus 1 for the shorter covalent Hg-X bond gives the predicted halogen coordination numbers CN(X₁) and CN(X₂) shown in Table I. (In some cases the steric fits were too tight to predict the presence or absence of a certain intermolecular contact, given the simple nature of our models; two numbers are then listed for CN(X) in Table I.) The predicted coordination number of the mercury atom (CN(Hg)) is then given by eq 1. Although these compounds

$$\text{CN(Hg)} = n + \text{CN(X}_1) + \text{CN(X}_2) \quad (1)$$

generally show the expected²⁶ pseudooctahedral coordination about mercury, the small 59–64° bite of the OCH₂CH₂O chelate allows the possibility of seven-coordination and even hexagonal-bipyramidal eight-coordination, in some of the adducts (Table I), while the large size of the *tert*-butyl groups in HgX₂·diglytbu might cause five-coordination. The prediction for HgCl₂·tetragly is, of course, confirmed by the x-ray structure;²⁴ the listed coordination numbers for the mercuric halides themselves^{27–29} and for HgBr₂·THF,³⁰ HgCl₂·2C-H₃OH,³¹ HgCl₂·diox³² (diox = dioxane), and HgBr₂·2diox³³ result from x-ray structures.

Having predicted the factors which will influence the frequencies of these compounds, we expect, according either to the Townes-Dailey approximation³⁴ or to considerations of the Sternheimer effect³⁴ that (a) increasing CN(Hg) should, by pushing or polarizing electrons toward the halogen, lower the halogen NQR frequency and (b) increasing CN(X₁) or CN(X₂) should, by removing electrons from the p_x (and perhaps p_y) orbitals of the halogen or by polarizing the np_x

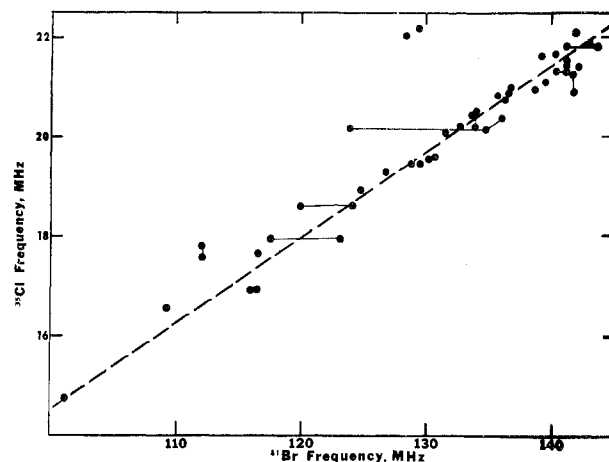


Figure 1. Correlation of ³⁵Cl vs. ⁸¹Br NQR frequencies of pairs of compounds QHgX·donor. Individual points are listed in the supplementary material.

and np_y orbitals to increasing (n + 1)p_x and (n + 1)p_y character, also lower the NQR frequency of the halogen involved.

Relationships among the Different Spectroscopic Measurements

In order to understand how the ³⁵Cl NQR data relate to the ⁸¹Br data, we noted the observation of Brill⁷ that many chlorine and bromine NQR frequencies in analogous adducts of the same Lewis base show excellent correlations and thus are reasonably certain to have the same general structural features. In Figure 1 we have plotted all available^{2–18} pairs of ³⁵Cl and ⁸¹Br NQR frequencies taken at the same temperature for mercury chloride and bromide derivatives having the same empirical formula (except for chlorine and bromine). Most points do indeed fall near a common straight line, including compounds such as γ-C₅Cl₅HgX and C₅Cl₅HgX·gly, which are strongly suspected of being isostructural.³⁵ Falling far from the line are HgX₂ and *trans*-ClCH=CHHgX, which are known *not* to be isostructural.^{26,36,37} Points connected by bars in Figure 1 show different multiplicities in their Cl and Br NQR frequencies and hence clearly are not exactly isostructural. The least-squares fit of all points in Figure 1 gives a line of slope 0.156, in reasonable agreement with the ratio of atomic quadrupole coupling constants³⁴ of ³⁵Cl and ⁸¹Br, 0.171.

We propose that, if the point for a mercuric chloride-mercuric bromide derivative falls a distance of more than 2% of the chlorine or bromine frequency from the line of Figure 1 (the justification of 2% will be presented later), the bromide and chloride should be suspected not only of being crystallographically nonisostructural but also of having some molecular dissimilarities, such as differences in n, CN(X), or CN(Hg). Eliminating these points from the correlation gives a new line described by eq 2; the correlation coefficient im-

$$\nu(^{35}\text{Cl}) = 0.165\nu(^{81}\text{Br}) - 1.800 \quad (2)$$

proves from 0.922 to 0.964.

A similar comparison of ⁸¹Br and ¹²⁷I frequencies can be carried out, with somewhat less satisfactory results, since ⁸¹Br and ¹²⁷I have different spins. Therefore their NQR frequencies depend in a different way on their quadrupole coupling constants and asymmetry parameters. Using all available literature data we obtain the correlation

$$\nu(^{81}\text{Br}) = 0.800\nu(^{127}\text{I}) - 0.002 \quad (3)$$

The slope expected, ignoring the asymmetry parameter and the different polarizabilities of the halogens, is 0.935. De-

Table II. NQR Frequencies of Polyether Adducts and Related Compounds

Compd	$^{35}\text{Cl}(77\text{ K})$	$^{35}\text{Cl}^a$	$^{81}\text{Br}^a$	$^{79}\text{Br}^a$	$^{127}\text{I}^a$
HgX_2^b	22.522	22.050	128.4 ^c	153.74	159.95
	22.874	22.230	129.4 ^c	154.86	161.82
$\text{HgX}_2\cdot\text{THF}$	19.272 ^d	19.628 ^e	130.22 ^e		
	20.584 ^d	21.014 ^e	136.74 ^e		
$\text{HgX}_2\cdot\text{diox}^f$		20.454	133.70 ^c	160.03	172.77
$\text{HgCl}_2\cdot 2\text{CH}_3\text{OH}^e$		20.052			
		20.205			
$\text{HgX}_2\cdot\text{gly}^g$	21.325 (74)	21.137 (12)	139.5 (69)	167.1 (81)	
$\text{HgX}_2\cdot\text{digly}$	21.094 (7)	20.957 (7)	138.7 (50)	165.9 (27)	
	22.287 (9)	21.846 (7)	143.1 (50)	171.1 (22)	175.5 (19)
$\text{HgX}_2\cdot\text{diglytbu}$	21.880 (7)	21.400 (5)	140.3 (4)	167.8 (2)	175.5 (4)
	22.593 (8)	22.116 (5)	142.0 (5)	169.5 (4)	176.6 (4)
					178.6 (6)
$\alpha\text{-HgX}_2\cdot\text{trigly}$	22.144 (19)	21.603 (11)	141.7 ⁱ	168.7 ^h	
$\beta\text{-HgX}_2\cdot\text{trigly}$			139.3 ^{i,j}	165.5 ^j	170.4 (3)
			142.9 ^{i,j}	171.0 ^j	175.0 (3)
$\text{HgX}_2\cdot 2\text{diox}^f$	21.21	21.15	142.08 ^c	170.07	
$\text{HgX}_2\cdot\text{tetragly}$	21.084 (5)	20.869 (7)	141.7 (63)	169.9 (60)	174.3 (31)
	21.488 (5)	21.213 (7)			
$\text{HgX}_2\cdot 18\text{-crown-6}$	20.590 (5)	20.231 (3)	132.9 (9)	158.9 (6)	163.0 (9)
$2\text{HgX}_2\cdot\text{hexagly}$		20.215 (1.5)	133.1 (6)	159.2 (3)	174.9 (4)
		20.468 (1.5)			
		20.966 (3)	136.5 (10)	163.1 (3)	176.4 (2)

^a Frequencies in MHz, at room temperature (297–304 K) unless otherwise indicated. Signal-to-noise ratios (S/N) in parentheses. ^b Data from ref 2 and 6. ^c Computed using $Q(^{79}\text{Br})/Q(^{81}\text{Br}) = 1.197$. ^d Data from ref 4. ^e Data from ref 7. ^f Data from ref 9. ^g $\text{HgCl}_2\cdot\text{gly}$ data, 77 K, agree with ref 4, while ref 8 gives 21.80 MHz, 77 K. ^h ^{81}Br data have been reported for $\text{HgBr}_2\cdot\text{gly}$ at 77 K: 140.40 and 141.23 MHz in ref 4; 141.19 and 143.75 MHz in ref 8. $\text{HgI}_2\cdot\text{gly}$ (77 K) in ref 8 is assigned 180.06 MHz. ⁱ At 312 K; $S/N = 3$ for β -form ^{79}Br lines and 8 for α -form ^{79}Br line. ^j At 308 K; $S/N = 25$ for β -form ^{81}Br lines and 4 for α -form ^{81}Br line. ^k At 302 K; $S/N = 70$ for β -form ^{81}Br lines and 25 for β -form ^{79}Br line; α -form lines absent.

viations of greater than 2% from this correlation may suggest molecular dissimilarities or (if the iodine frequency is too high) an asymmetry parameter of the order of 0.17 or higher.

In comparing ^{35}Cl and ^{81}Br NQR results on mercury halides and their adducts, it must be remembered that the structure of HgCl_2 ²⁷ is quite different from that of the isostructural pair HgBr_2 ²⁸ and yellow HgI_2 ²⁹. Consequently the point in Figure 1 corresponding to HgCl_2 vs. HgBr_2 shows the greatest deviation from eq 2 of any pair of compounds. From Figure 1 one may predict that if HgCl_2 had the HgBr_2 structure, it would have room-temperature frequencies of 19.3 and 19.4 MHz, rather than the observed 22.05 and 22.23 MHz. From its crystal structure HgBr_2 clearly has $\text{CN}(\text{Hg}) = 6$ and $\text{CN}(\text{X}_1) = \text{CN}(\text{X}_2) = 3$. But the crystal structure of HgCl_2 , which is frequently misinterpreted²⁶ as indicating $\text{CN}(\text{Hg}) = 6$, is quite difficult to interpret. In a sense $\text{CN}(\text{Hg}) = 8$ and $\text{CN}(\text{X}) = 4$, since there are three³¹ pairs of intermolecular $\text{Hg}\cdots\text{Cl}$ contacts. Two of these intermolecular distances, 3.54 and 3.40 Å, slightly exceed the sum of conventional van der Waals radii, 3.30 Å, while the third distance, 3.23 Å, is only slightly under the sum.³¹ All may be under the sum of revised van der Waals radii. Hence $\text{CN}(\text{Hg})$ is uncertain in HgCl_2 ; for purposes of reference in our discussion we use the 19.3- and 19.4-MHz frequencies of a hypothetical HgCl_2 which is isostructural with HgBr_2 and has $\text{CN}(\text{Hg}) = 6$.

In his work on the chloro anions of mercury, Scaife¹⁰ noted a good correlation between the $\text{Hg}-\text{Cl}$ stretching frequencies and NQR frequencies for the compounds he was studying. We find that the same correlation can be applied even more successfully to these frequencies in the polyether adducts of HgCl_2 and $\text{C}_5\text{Cl}_5\text{HgCl}$,¹⁶ the combined correlation is shown in Figure 2. This suggests an opportunity to extend this study to dissolved adducts, which cannot be studied by NQR, and it suggests that the same factors which determine the NQR frequencies of the solids may determine the more readily accessible ir stretching frequencies.

Results and Conclusions

In Table II are presented the NQR spectra which we measured for the mercuric halide-polyether adducts, together

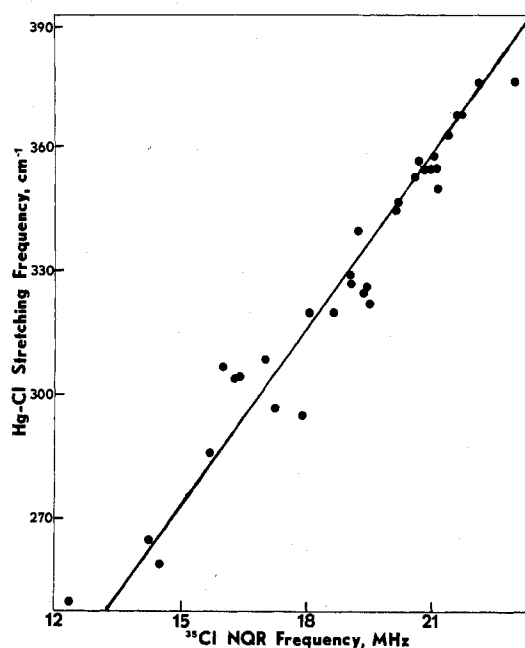


Figure 2. Correlation of $\text{Hg}-\text{Cl}$ ir stretching frequencies vs. 300 K ^{35}Cl NQR frequencies for selected mercurials ($\text{HgCl}_2\cdot\text{donor}$, $\text{HgCl}_n^{(n-2)-}$, $\text{C}_5\text{Cl}_5\text{HgCl}\cdot\text{donor}$).

with previously known data for several other adducts of known crystal structures.^{30–33} The frequencies for ^{35}Cl are plotted in Figure 3 with square points as a function of the number of oxygen donor atoms, n . $\text{HgCl}_2\cdot\text{hexagly}$ and $\text{HgCl}_2\cdot\text{diglytbu}$ are omitted, while the $n = 1$ point represents $\text{HgCl}_2\cdot\text{THF}$ (THF = tetrahydrofuran) and the $n = 0$ points represent the real and the hypothetical values for HgCl_2 . (A similar curve can be drawn for the ^{81}Br or ^{79}Br NQR data, but for ^{127}I the results are different.)

Table III presents the solid-state and benzene solution data for the ir $\text{Hg}-\text{Cl}$ stretching frequency. The solid-state ir data correlate well with the ^{35}Cl NQR frequencies of these

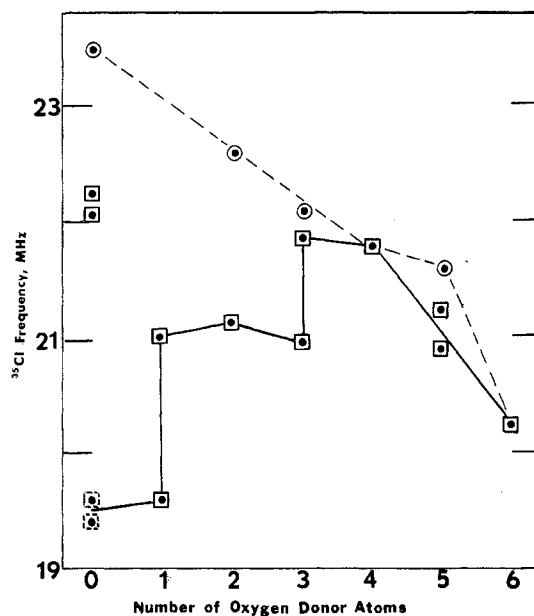


Figure 3. ^{35}Cl NQR frequencies of selected polyether adducts of HgCl_2 vs. the number of oxygen donor atoms n . Solid line connects solid-state NQR frequencies; broken line connects points derived from solution ir data using Figure 2.

Table III. Hg-Cl Stretching Frequencies of Adducts^a

Adduct	Solid	Soln ^b
HgCl_2	373	393
HgCl_2 ·gly	355	380
HgCl_2 ·digly	363	374
HgCl_2 ·diglytbu	368	368
HgCl_2 ·trigly	368	369
HgCl_2 ·tetragly	358	367
HgCl_2 ·18-crown-6	347	344
2HgCl_2 ·hexagly	353	367

^a Frequencies in cm^{-1} . ^b In benzene solution; all spectra also showed lines at 393 cm^{-1} attributed to free HgCl_2 .

compounds, as indicated in Figure 2, but when the ^{35}Cl NQR frequencies of the two chlorines are split, as for $n = 1$ and $n = 3$, there is still only one $\nu(\text{Hg}-\text{Cl})$ apparent. The solution ir data are quite different, however, and selected values (converted via Figure 2 from cm^{-1} to MHz) are plotted in Figure 3 with circles.

The solution spectra suggest a relatively smooth drop in $\nu(\text{Hg}-\text{Cl})$ as n increases from 0 to 6 (with a minor deviation for $n = 5$, which will be discussed in the section on applications). This corresponds to the drop in NQR frequency expected from increasing factor 3, the number of donor atoms n about mercury. Evidently, then, factor 4, the number of intermolecular interactions, is constant (or smoothly changing) in this series of adducts in solution. Evidence of weak dimeric association of HgCl_2 in benzene has been reported;³⁸ however molecular weight determinations in benzene solution (Galbraith Laboratories) suggest a monomeric formulation for HgCl_2 ·diglytbu (calcd mol wt 490, found 494) and HgCl_2 ·trigly (calcd mol wt 450, found 448). Also, the solid-state data for HgCl_2 ·tetragly fit this curve, and HgCl_2 ·tetragly is known²⁴ to be monomeric in the solid state.

The solid-state NQR spectra, in contrast, show a peculiar "double-step function" until $n = 4$, after which they behave much as do the solution ir spectra. For $n = 4, 5$, and 6 (i.e., HgCl_2 ·trigly, HgCl_2 ·tetragly, and HgCl_2 ·18-crown-6) a monomeric formulation is suggested, as was hypothesized in Table I. The diglyme, glyme, and THF adducts behave differently; in Table I these adducts had been predicted to have (or possibly to have) $\text{CN}(\text{X}_1)$ or $\text{CN}(\text{X}_2)$ greater than 1, i.e.,

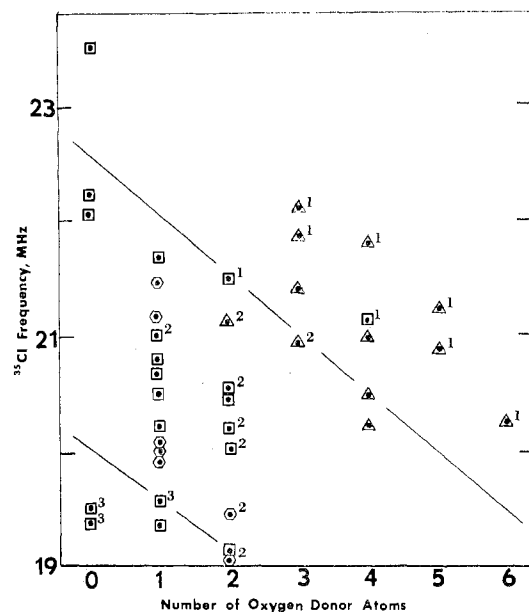


Figure 4. Donor atom table: all reported ^{35}Cl NQR frequencies of HgCl_2 adducts of oxygen donors vs. most likely number of oxygen donor atoms n . Superscripts give $\text{CN}(\text{X})$ when known or deduced via molecular models; Δ , polyether adducts; \odot , N -oxide or S -oxide adducts; \square , other adducts.

to have intermolecular interactions. The diglyme ($n = 3$) and THF ($n = 1$) adducts were predicted to have $\text{CN}(\text{X}_1) \neq \text{CN}(\text{X}_2)$; it is these adducts which show large splittings in their ^{35}Cl NQR spectra. Furthermore comparison of Table I and Figure 3 shows that (for n less than 5, i.e., mercury pseudo-octahedrally coordinated) if a particular chlorine is predicted to have $\text{CN}(\text{X}) = 3$, its frequency is about 19.6 MHz; if $\text{CN}(\text{X}) = 2$, then its frequency is about 21.0 MHz; and if $\text{CN}(\text{X}) = 1$, then its frequency is about 21.7 MHz. (For ^{81}Br these figures are 128–130, 136–139, and 142–143 MHz, respectively.) For higher numbers of intermolecular interactions the frequency is lower, as previously predicted.

Hence this work tends to support the suggestion of Bryukhova et al.¹⁸ that the factor of intermolecular interactions, which was formerly often overlooked, is very important in determining the NQR frequencies of mercury halides and their derivatives. We thus suggest that each additional $\text{Hg}\cdots\text{Cl}$ interaction lowers the ^{35}Cl NQR frequency by 0.7–1.5 MHz, while (from the slope of the dashed line in Figure 3) each additional polyether donor atom lowers the ^{35}Cl frequency by only about 0.6 MHz.

Hence we propose that from the NQR data for an adduct of unknown structure and the postulated value for n (from analytical data), possible structures of the adduct can be derived. In Figure 4 all reported^{4–9} ^{35}Cl NQR data at room temperature of HgCl_2 adducts of organic oxygen bases are plotted as a function of n . For compounds of known structure, $\text{CN}(\text{X})$ is indicated beside each point. Two lines of slope -0.6 MHz/unit of n are drawn in to separate the approximate regions of differing $\text{CN}(\text{X})$. $\text{CN}(\text{Hg})$ can then be computed using eq 1. The boundaries are diffuse, however, because these adducts do not all possess oxygen donor atoms of equal basicity. Hence, in a given n column, the relative position within a given $\text{CN}(\text{X})$ region should indicate relative basicity (although crystal field variations must be taken into account).

In the $n = 2$ column most of the data correspond to known crystal structures and so can be discussed particularly well. In this column the known x-ray and NQR data are as follows: HgCl_2 ·cyclohexanedione,³⁹ 21.51 MHz;⁹ HgCl_2 ·gly, 21.137 MHz (this work); HgCl_2 ·diox,³² 20.454 MHz;⁹ HgCl_2 ·2C-H₃OH,³¹ 20.205 and 20.052 MHz;⁷ HgCl_2 ·py- N -O (possessing

Table IV. Possible Structural Interpretations of Literature NQR Data^a for HgX₂ (X = Cl, Br) Adducts

<i>n</i>	CN(Hg)	Compds fitting this pattern	Cl splitting ^b	Br splitting ^b
1	6	A. CN(X ₁) = 2, CN(X ₂) = 3 HgX ₂ ·acetophenone, HgX ₂ ·THF	1.476, 1.386	7.24, 6.52
1	4 ^{c,d}	B. CN(X ₁) = 1, CN(X ₂) = 2 HgX ₂ ·benzophenone	0.943	2.91 ^c
1 or 2 ^c	4 or 5 ^c	HgX ₂ ·γ-pic-N-O, HgCl ₂ ·DMSO, HgBr ₂ ·py-N-O	1.401, 1.109	9.78 9.18
3	6	HgX ₂ ·digly, HgCl ₂ ·diglytbu ^c	0.889, 0.716	4.4
4	7	HgBr ₂ ·trigly-β, 2HgX ₂ ·hexagly ^c	0.498, 0.751	3.6, 3.4
0	2 ^d	C. CN(X ₁) = CN(X ₂) HgCl ₂ ·C ₃ Cl ₃ , HgCl	0.01-0.15	
0	4	HgCl ₂	0.200	
0	6	HgBr ₂		0.95
1	5	HgBr ₂ ·benzophenone ^c		2.91
2	4	HgCl ₂ ·cyclohexanedione	0	
2	6	HgX ₂ ·gly, HgX ₂ ·diox, HgCl ₂ ·benzoquinone, HgCl ₂ ·2CH ₃ OH, HgCl ₂ ·py-N-O, HgCl ₂ ·DMSO (77 K), HgCl ₂ ·DMF, HgCl ₂ ·dimethylpyrone, HgBr ₂ ·2(phenoxathiin)	0, 0 0, 0.153 0.439, 0.384 0.248, 0	0, 0 1.27
3	5	HgX ₂ ·diglytbu, ^c 2HgX ₂ ·hexagly ^{c,e}	0.716, 0	1.7, 0
4	6	2HgX ₂ ·hexagly, ^{c,e} HgX ₂ ·trigly-α, HgX ₂ ·2diox, HgBr ₂ ·tetragly	0.253, 0 0	0, 0 0, 0
5	7	HgCl ₂ ·tetragly	0.34	
6	8	HgX ₂ ·18-crown-6	0	0

^a Literature data from ref 4-9 and 16 and from this work. ^b Differences in frequencies (in MHz) between two lines of the NQR spectrum for ³⁵Cl or ⁸¹Br. ^c Alternate interpretations also possible. ^d Not counting possible additional coordination by organic π systems or organic chlorines. ^e NQR data for one of two inequivalent HgX₂ molecules in the unit cell.

bridging *N*-oxide groups, therefore two oxygen donor functions per mercury),⁴⁰ 19.461 and 19.022 MHz.⁷ The cyclohexanedione adduct is highest in frequency because its CN(X) = 1; in all others CN(X) = 2. The order of frequencies then suggests that the basicities should fall in the order glyme < dioxane ~ methanol < pyridine *N*-oxide. The greater basicity of pyridine *N*-oxide is reasonable in terms of the partial negative charge on oxygen. The apparent low basicity of glyme may result from the small O-Hg-O bond angles. This (approximately) 60° angle is not optimal for overlap with the mercury 6p orbitals. This result can also be seen in the *n* = 4 column. The flat lines in the left part of Figure 3 also suggest that the basicity toward mercury of glyme oxygen is about equal to the basicity of chloride covalently bonded to mercury, since replacement of one donor atom with the other does not alter the frequency.

Given the data needed to use Figure 4 and a preconception of the relative basicity of the oxygen donor atoms, it is then possible to predict the structure, or a few alternate structures, for an adduct. Since mercuric halide adducts of oxygen-donor ligands usually have a pseudooctahedral structure,²⁶ one would generally expect CN(X₁) ≠ CN(X₂) and hence large splittings for odd values of *n*. For even values of *n* one would generally expect CN(X₁) = CN(X₂) structures and small NQR splittings. The known NQR data are used to predict possible structures in Table IV. Of particular interest are compounds which are predicted to have CN(Hg) ≠ 6. These are the compounds likely to have unusual features of special interest to crystallographers.

Finally, it is useful to examine the magnitudes of the splittings of the NQR frequencies in these adducts. Among the adducts with CN(X₁) ≠ CN(X₂), it appears that larger splittings are observed for adducts of *N*-oxide and *S*-oxide ligands, probably due to the larger point charges present. Omitting these ligands, we note that the splittings seem to be larger for CN(X₁) = 2, CN(X₂) = 3 (1.4-1.5 MHz for ³⁵Cl and 6.5-7.2 MHz for ⁸¹Br) than for CN(X₁) = 1, CN(X₂) = 2 (0.5-0.9 MHz for ³⁵Cl and 2.9-4.5 MHz for ⁸¹Br), although there are not many examples of each type. This does not necessarily mean that there is any meaningful difference

in the splittings of the quadrupole coupling constants, however, since the frequency also depends on the asymmetry parameter

$$\nu(^{35,37}\text{Cl or }^{79,81}\text{Br}) = \frac{e^2 Q q}{2} (1 + \eta^2/3)^{1/2} \quad (4)$$

For CN(X) = 1 there should be substantially no asymmetry parameter. Since there is no threefold or higher symmetry axis for the halogen if CN(X) = 2 or 3, there would be an asymmetry parameter in these cases, which by (4) would raise the frequency slightly and reduce the splitting observed between CN(X) = 1 and CN(X) = 2.

It follows from the use of Figure 4 that the largest splittings must be associated with the assignment of CN(X₁) ≠ CN(X₂), but there appear to be few splittings of intermediate magnitude (0.45-0.8 MHz for ³⁵Cl and 2-4 MHz for ⁸¹Br). These few cases occur in adducts where the intermolecular interactions may be sterically hindered. Hence, except for these cases, it may be possible to distinguish large splittings due to intermolecular interactions from small splittings due to crystallographic inequivalence of halogens in adducts in which CN(X₁) = CN(X₂). These crystallographic splittings (omitting *N*-oxides and the uncertain intermediate cases) appear to range from 0 to 0.4 MHz for ³⁵Cl and from 0 to 2.9 MHz for ⁸¹Br, i.e., about 2% of the NQR frequency. This small splitting, if confirmed by structural studies of the intermediate cases, would seem to suggest the absence of any great ionic contributions to the lattice electric field gradient and therefore to the bonding in the mercuric halides themselves or to the mercury-ligand bonding.

Applications

Of particular interest are cases where CN(X₁) + CN(X₂) + *n* do not seem to add up to a coordination number of 6 for mercury. Several such cases turned up in this study. One such case is the series of adducts HgX₂·diglytbu (X = Cl, Br, I). The molecular models suggest that the bulky *tert*-butyl groups hinder each other in the possible dimer with CN(Hg) = 6, unless the *tert*-butyl groups adopt an axial configuration, in which case they bump the lone pairs of the halogen (especially chlorine). Use of Figure 3 and its Br and I equivalents suggests

that $CN(Hg) = 5$ for HgX_2 -diglytbu ($X = Br, I$). For $X = Cl$, however, the data are uncertain: there is a substantial (but smaller than expected) splitting of the ^{35}Cl frequencies, which might suggest formation of a dimer. However, there is no appreciable difference in temperature dependence,³⁵ and the identical natures of the solid-state and solution ir spectra suggest the same degree of aggregation in both (which is monomeric, in solution).

The triglyme adducts also show some very interesting results. According to the models, the coordinated trigly ligand occupies virtually the same volume as the diglytbu ligand but of course has one more donor atom. Hence the same two possibilities, but with $CN(Hg)$ being 1 higher and NQR frequencies presumably being lower, exist. $HgCl_2$ -trigly has only one NQR frequency, so both chlorines must have $CN(X) = 1$. HgI_2 -trigly, however, has two substantially split frequencies in the proper range to suggest $CN(X_1) = 1$, $CN(X_2) = 2$, $CN(Hg) = 7$. Most interesting is the compound $HgBr_2$ -trigly, which shows a phase transition just above room temperature. At 302 K the NQR spectrum indicates the compound to be isostructural with the iodide adduct, with two frequencies and a dimeric structure. At 308 K these two lines begin to fade and a new line grows in between the two. At 312 K only the new frequency remains, at a value which indicates the same structure as the chloride monomer.

The tetraglyme adducts show an irregularity; Iwamoto²⁴ reported that the bromide adduct was *not* isostructural with the chloride adduct, and our NQR frequencies confirm this: both the bromide and iodide give only one signal which is too high to correspond to that of the chloride. In fact the spectra do correspond with the monomeric form of HgX_2 -trigly ($X = Cl, Br$), which suggests the possibility that the effective number of donor atoms in the bromide and iodide adducts is only 4. The infrared spectra of the tetraglyme ligand in the bromide and iodide are virtually superimposable, but there are some small differences between these ir spectra and that of the chloride. Hence there may be a different conformation of the ligand in which one oxygen is not coordinated to mercury, or the two end oxygens are each weakly coordinated. The high $Hg-Cl$ stretching frequency of $HgCl_2$ -tetragly in solution suggests that the same thing may happen to the chloride adduct in solution.

Some data, of course, have more than one quite satisfactory explanation. Such is the case for $2HgX_2$ -hexagly, which has not yet been discussed. For these compounds n is computed to be 3.5, which could mean $n = 3$ for one mercury and $n = 4$ for the other. This gives one satisfactory interpretation, featuring one five-coordinate mercury. On the other hand, Iwamoto has done the x-ray structure²⁴ of the very closely related complex $2HgCl_2 \cdot C_2H_5(OCH_2CH_2)_6OC_2H_5$ and found the central oxygen to be bridging, both $CN(Hg)$ values being 7. Assuming this for the $HgCl_2$ and $HgBr_2$ adducts also gives a satisfactory fit to Figure 4. Other distributions of the available donor atoms also gave satisfactory fits but on examination with molecular models proved sterically impossible.

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Registry No. $HgCl_2$ -gly, 59187-92-7; $HgBr_2$ -gly, 59187-94-9; $HgCl_2$ -digly, 59187-71-2; $HgBr_2$ -digly, 59187-72-3; HgI_2 -digly, 59187-73-4; $HgCl_2$ -diglytbu, 59187-74-5; $HgBr_2$ -diglytbu, 59187-75-6; HgI_2 -diglytbu, 59187-76-7; $HgCl_2$ -trigly, 40237-14-7; $HgBr_2$ -trigly, 59187-77-8; HgI_2 -trigly, 59187-78-9; $HgCl_2$ -tetragly, 40802-28-6;

$HgBr_2$ -tetragly, 59187-79-0; HgI_2 -tetragly, 59187-64-3; $HgCl_2$ -18-crown-6, 59187-80-3; $HgBr_2$ -18-crown-6, 59187-81-4; HgI_2 -18-crown-6, 59187-82-5; $2HgCl_2$ -hexagly, 59187-83-6; $2HgBr_2$ -hexagly, 59187-84-7; $2HgI_2$ -hexagly, 59187-85-8; ^{35}Cl , 13981-72-1; ^{81}Br , 14380-59-7; ^{79}Br , 14336-94-8; ^{127}I , 7553-56-2.

Supplementary Material Available: A listing of analytical data and melting points of these adducts and complete data for correlations of ^{35}Cl , ^{81}Br , and ^{127}I NQR frequencies (3 pages). Ordering information is given on any current masthead page.

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