Solid-State ^{199}Hg MAS NMR and Vibrational Spectroscopic Studies of Dimercury(I) Compounds

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The solid-state ^{199}Hg MAS NMR spectra of Hg_2X_2 (X = Cl, SCN, NCO, CH_3CO_2, CF_3CO_2) have been measured, and the infrared and Raman spectra of these compounds have been recorded and analyzed to further characterize them and to assist in the interpretation of the NMR data. Spinning-sideband analysis has been used to determine the ^{199}Hg shielding anisotropy and asymmetry parameters $\Delta\sigma$ and η from the solid-state ^{199}Hg MAS NMR spectra. In contrast to the case of the corresponding mercury(II) compounds, the shielding anisotropy is found to be relatively insensitive to the nature of the X group. This is consistent with the view that the electronic environment of the Hg atom in the mercury(I) compounds is dominated by the Hg−Hg bond. The changes in the ^{199}Hg shielding parameters from the mercury(II) to the corresponding mercury(I) compounds, as well as the changes in these parameters in the mercury(I) compounds with changes in X, can be interpreted in terms of variations in the local paramagnetic contribution to the shielding tensor.

Introduction

With the recent developments that have taken place in high-resolution NMR techniques for solids,[1−10] there has been increasing interest in the solid-state NMR spectra of heavy-metal nuclei.[4,5] Until recently, there were very few solid-state NMR studies involving ^{199}Hg, but in the past few years, there has been a considerable increase in the number of such investigations.[4,5,11−22] A recent review of this topic showed that very nearly all of these studies involved compounds of mercury-(II), the most common oxidation state of mercury in its compounds.[22] There are, however, a number of mercury compounds involving oxidation states lower than (+II), the most common of which are those involving mercury(I).[23−25] All known mercury(I) compounds contain the dimeric mercurous unit Hg_2^{2+}, and these compounds are notable for being among the earliest characterized examples of discrete metal−metal bonded species.[25] They are generally two-coordinate, forming linear or near-linear species of the type X−Hg−Hg−X or $[L-Hg-Hg-L]^{2+}$. The results of earlier studies suggested a dependence of the Hg−Hg bond length on the nature of the axially bound ligand (X^- or L),[26] but results from subsequent single-crystal X-ray studies have shown Hg−Hg distances in the narrow range 2.48−2.54 Å, with no obvious correlation between this parameter and the electronic properties of the ligands.[25,26] A simple view of the bonding in these systems is that the Hg−Hg bond is formed predominantly by overlap of the mercury 6s orbitals and that the ligands form dative bonds via the Hg 6p orbitals.[19] According to this view, the Hg−Hg bonding would contribute only to the diamagnetic shielding, whereas the metal−ligand bonding would contribute to the paramagnetic shielding of the Hg nucleus, so that a study of the ^{199}Hg shielding tensor for a variety of dimercury(I)

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complexes should yield information about the bonding in these systems, some aspects of which are still only poorly understood.[27]

To date, there has been only one report on the Hg shielding tensor in a mercury(I) compound. This involved a static single-crystal ^{199}Hg NMR study of mercury(I) nitrate dihydrate, and the tensor components were analyzed in terms of the simple bonding model described above, involving predominantly 6s−6s overlap for the Hg−Hg bonds and bonding of the two H_2O ligands with the Hg 6p orbitals.[19] This is not consistent with the view that the Hg atoms in linear mercury(I) compounds use sp hybrid orbitals, analogous to the generally accepted situation in linear mercury(II) complexes.[25,27] Also, in the analysis of these results, the presence of occupied metal−ligand π and π^* orbitals was assumed, but molecular orbital calculations show that π contributions to the bonding in mercury(I) compounds are rather insignificant.[27] If, as is proposed in the above model,[19] the Hg shielding tensor is dominated by contributions from the metal−ligand bonding, this tensor should show a significant dependence on the nature of the axial ligand, as has been found in the case of linear mercury(II) compounds.[20,22] In the present study, we have carried out ^{199}Hg MAS NMR studies of a range of mercury(I) compounds Hg_2X_2 (X = Cl, SCN, NCO, OAc, tfa; OAc = acetate, tfa = trifluoroacetate) with a view to investigating this point and to providing more information about the bonding in such compounds.

Experimental Section

Materials. Commercial samples of mercury(I) chloride, Hg_2Cl_2 (RDH), mercury(I) acetate, $Hg_2(OAc)_2$ (BDH), and mercury(I) nitrate dihydrate, $Hg_2(NO_3)_2 \cdot 2H_2O$ (BDH) were used without further purification.

Preparation of Compounds. (a) Mercury(I) Thiocyanate, $Hg_2(SCN)_2$. A solution of potassium thiocyanate (0.78 g, 8.0 mmol) in water (10 mL) was added, with stirring, to a solution of mercurous nitrate (2.24 g, 4.0 mmol) in water (10 mL) acidified with concentrated HNO_3 (0.4 mL). The product separated from the mixture as a fine, grayish-white precipitate, which was collected by vacuum filtration, washed several times with distilled water, and dried in the air. Despite the claim that the product obtained by this method is light sensitive,[23,28] the compound appears to be stable indefinitely under ambient conditions.

(b) Mercury(I) Cyanate, $Hg_2(NCO)_2$. A solution of potassium cyanate (1.2 g, 14.8 mmol) in water (10 mL) was added, with stirring, to a solution of mercurous nitrate (2.8 g, 5 mmol) in water (10 mL) acidified with concentrated HNO_3 (0.5 mL). The product separated from the mixture as a fine, grayish-white precipitate, which was collected by vacuum filtration, washed several times with distilled water, and dried in the air. Anal. Calcd for $C_2Hg_2N_2O_2$: C, 4.95; H, 0.0; N, 5.77. Found: C, 4.8; H, 0.0; N, 5.6. The compound gradually turns a darker gray upon standing under ambient conditions over a period of several months.

(c) Mercury(I) Trifluoroacetate, $Hg_2(tfa)_2$. This was prepared as a white crystalline solid by a literature method.[29]

Spectroscopy. Carbon-13 and mercury-199 magic-angle-spinning spectra were obtained at 75.43 and 53.65 MHz, respectively, using a Varian Unity Plus 300 spectrometer. A 7.0 mm o.d. silicon nitride rotor with Vespel end-caps was used for all spectra, with spin rates in the range 8−11 kHz. Although measurements were nominally made at ambient probe temperature (ca. 25 °C), it is likely that the fast spinning used for the ^{199}Hg spectra resulted in substantially elevated temperatures (ca. 45 °C).[30] The carbon-13 spectra were recorded with direct polarization (sometimes referred to as single-pulse excitation). A recycle delay of 5 s was used, and 15 000 transients were collected (100 transients in the case of the acetate). Mercury-199 spectra were recorded with direct polarization (1 μs 12° pulses as judged via cross polarization for a sample of $[Hg(dmso)_6][O_3SCF_3]_2$). Centerband signals were located by varying the spinning rate. Recycle delays of 3 s with ca. 20 000 transients were required to obtain acceptable spectra. Spinning-sideband intensities were analyzed to yield values of the shielding tensor components by an iterative computer program written in house.[31] The fitting procedure used a minimum of 13 sidebands plus the centerband and was carried out for spinning rates in the range 8000−11 000 Hz. Accuracy was limited by the high noise levels and by the fact that the spectra required baseline correction. Errors in the shielding tensor parameters were calculated by a published method.[32] These are statistical in nature and may underestimate the true errors, which would also have systematic and experimental reproducibility contributions. The principal components σ_{11}, σ_{22}, and σ_{33} of the ^{199}Hg shielding tensor are defined such that

$$|\sigma_{33} - \sigma_{iso}| \geq |\sigma_{11} - \sigma_{iso}| \geq |\sigma_{22} - \sigma_{iso}| \quad (1)$$

where σ_{iso} is the isotropic, or scalar, shielding constant, related to the principal components of the shielding tensor by

$$\sigma_{iso} = (1/3)(\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (2)$$

and measured as

$$\sigma_{iso} - \sigma_r = -\delta_{iso} \quad (3)$$

where δ_{iso} is the isotropic chemical shift (the centerband shift) and σ_r is the shielding constant for the reference compound. Chemical shifts were referenced using replacement samples of adamantane ($\delta_C = 38.4$ ppm for the CH_2 carbon on the tetramethylsilane scale) and $[Hg(dmso)_6][O_3SCF_3]_2$ ($\delta_{Hg} = -2313$ ppm[33] on the dimethylmercury scale).

Infrared spectra were recorded with 4 cm^{-1} resolution at room temperature as Nujol mulls between KBr plates on a Perkin-Elmer Spectrum 1000 Fourier transform infrared spectrometer. Far-infrared spectra were recorded with 2 cm^{-1} resolution at room temperature as pressed polythene disks on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 line/mm wire mesh beam splitter, a mercury lamp source, and a pyroelectric triglycine sulfate detector. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a cooled photomultiplier (RCA C31034A) detector. The 514.5 nm exciting line from a Spectra-Physics model 2016 argon ion laser was used.

Results and Discussion

Vibrational Spectroscopy. Little is known about the properties of the mercury(I) pseudohalides $Hg_2(SCN)_2$ and $Hg_2(NCO)_2$.[23−25] We have therefore recorded the infrared and Raman spectra of these compounds to obtain information about their structures. The low-wavenumber vibrational spectra are shown in Figures 1 and 2, and the band assignments for all of the fundamental vibrational modes are given in Table 1. A comparison of selected vibrational frequencies for HgX_2[34−36] and Hg_2X_2[25,36] is given in Table 2.

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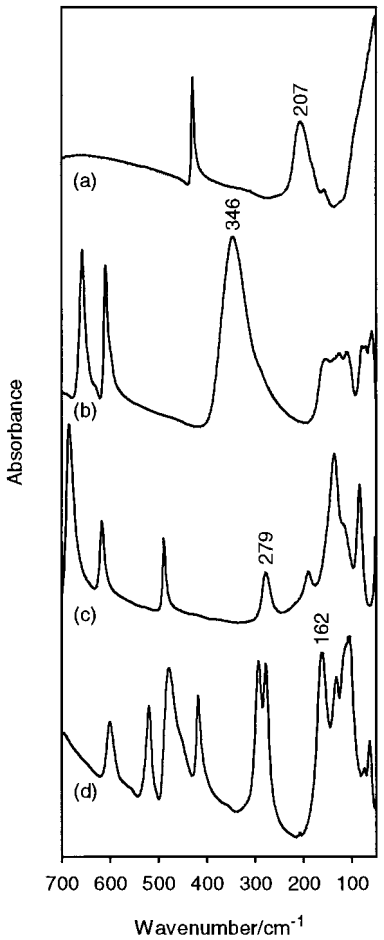

Figure 1. Far-IR spectra of Hg_2X_2: (a) X = SCN; (b) X = NCO; (c) X = OAc; (d) X = tfa. Bands assigned to ν(HgX) are labeled with their wavenumbers.

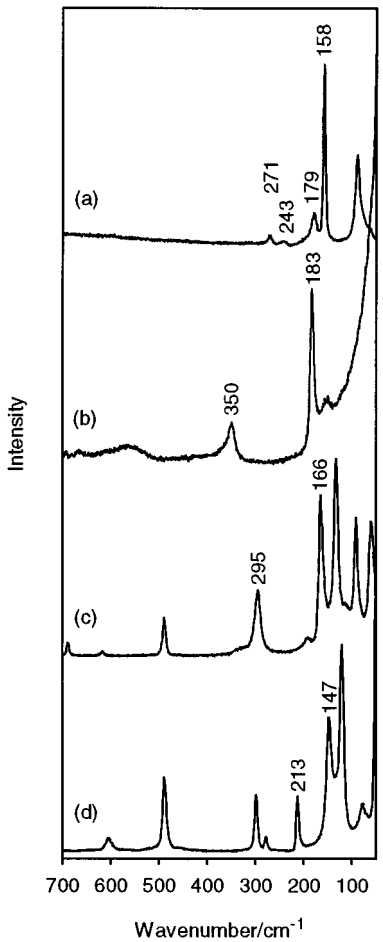

Figure 2. Low-wavenumber Raman spectra of Hg_2X_2: (a) X = SCN; (b) X = NCO; (c) X = OAc; (d) X = tfa. Bands assigned to ν(HgX) and ν(HgHg) are labeled with their wavenumbers.

The positions of the ν(CN), ν(CS), and δ(SCN) bands in the vibrational spectra of $Hg_2(SCN)_2$ are generally consistent with the presence of terminally S-bound thiocyanate groups.[37] The vibrational spectra are readily interpreted in terms of a linear S−Hg−Hg−S structure, analogous to that of the corresponding halides.[26] In particular, the observation of noncoincident bands in the Raman and IR spectra for the symmetric and antisymmetric Hg−S stretching vibrations, ν_s(HgS) and ν_a(HgS), respectively, with ν_s(HgS) > ν_a(HgS), follows the pattern observed for the ν(HgX) modes in Hg_2X_2;[25] see the data for X = Cl in Table 2. This is the reverse of the situation ν_s(HgX) < ν_a(HgX), which is observed for the corresponding mercury(II) species HgX_2, this change being due to coupling of ν_s(HgX) with the low-frequency ν(HgHg) mode in the mercury(I) species. The ν(HgHg) mode in $Hg_2(SCN)_2$ is assigned to a strong Raman band at 158 cm^{-1}, although a Raman band of medium intensity at 179 cm^{-1} may also be due to this mode. Strong splitting of the ν(HgHg) band was previously observed for other mercury(I) complexes and was attributed to factor group effects.[25] Other evidence for factor group effects in the Raman spectrum of $Hg_2(SCN)_2$ is the presence of two ν(CN) bands (2131, 2113 cm^{-1}) and two ν(HgS) bands (271, 243 cm^{-1}). However, the essential absence of bands that are coincident in the IR and Raman spectra suggests a centrosymmetric structure. The only counterindicator to this conclusion is the possible presence of a very weak IR band at 157 cm^{-1}, which is almost coincident with the strong ν(HgHg) Raman band at 158 cm^{-1}. However, on balance, the vibrational spectra generally support a centrosymmetric structure

Table 1. Assignments of the Bands (cm^{-1}) in the Vibrational Spectra of $Hg_2(SCN)_2$ and $Hg_2(NCO)_2$

$Hg_2(SCN)_2$		$Hg_2(NCO)_2$		
IR	R	IR	R	assignt[a]
2144 vs	2131 m	2251 w, sh	2165 w	ν(CN)
	2113 w	2200 vs, sh	2120 w	
		2164 vs		
		2126 s, sh		
		2077 w, sh		
884 m	802 w	1378 vw	1356 w	ν(CE)
		1353 vw	1294 w	
		1291 vw		
		1266 vw		
430 s		659 m	693 vw	δ(ECN)
		611 m	668 vw	
			565 m, br	
207 s	271 w	346 s	350 m	ν(HgX)
	243 w			
	179 m			ν(HgHg)?
157 vw	158 s		183 s	ν(HgHg)
53 s	89 s	154 w	152 m	δ(HgHgX)
		138 w, sh		
		127 w		
		111 w		
		79 w		lattice
		73 w		
		59 w		

[a] E = O or S; X = S or N.

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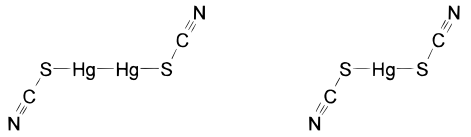
Table 2. Comparison of Selected Vibrational Frequencies (cm^{-1}) for HgX_2 and Hg_2X_2

	HgX_2				Hg_2X_2				
X	ν_a(HgX)	ν_s(HgX)	δ(XHgX)	ref	ν_a(HgX)	ν_s(HgX)	ν(HgHg)	δ(HgHgX)	ref
Cl	370	315	106	34	252	277	167	139, 109	25
SCN	309, 313	270	85	35	207	243, 271	179, 158	89, 53	*a*
NCO	425	358		*b*	346	350	183	154−111	*a*
OAc	314	279		36	279	295	166		36, *a*
tfa					162	213	147		*a*

[a] This work. [b] For the $Hg(NCO)_2$ units in $K_2[Hg_3(NCO)_8]$; ref 21.

which, given the nonlinear M−S−C geometry that normally occurs in S-bonded thiocyanate complexes,[38] would have local C_{2h} symmetry (structure **I**). This closely resembles the structure of the corresponding mercury(II) complex (structure **II**).[39]



The vibrational spectra of the cyanate compound $Hg_2(NCO)_2$ are more complex than those of the thiocyanate discussed above, splitting of the bands due to the vibrations of the coordinated NCO groups being observed in both the IR and Raman spectra (see Table 1). It has been claimed that ν(CO) increases relative to the free-ion value (ca. 1250 cm^{-1})[37] upon bonding via the N atom,[40] and this is observed in the present complex, with bands due to this mode occurring in the range 1260−1380 cm^{-1}. Neither the structure nor the vibrational spectra of the corresponding mercury(II) compound have been reported to date, but the complex $K_2[Hg_3(NCO)_8]$ has been shown to contain $Hg(NCO)_2$ molecules in its lattice, with terminal N-bound cyanate groups and nonlinear Hg−N−C angles of ca. 130°, forming an approximately C_{2h} structure.[41] The ν(HgN) frequencies listed in Table 2 for $Hg(NCO)_2$ are those assigned to this species in $K_2[Hg_3(NCO)_8]$.[21] The presence of the dimercury unit in $Hg_2(NCO)_2$ is confirmed by the observation of a strong ν(HgHg) band in the Raman spectrum at 183 cm^{-1} (Figure 2). This is at the upper end of the range of previously determined ν(HgHg) frequencies (110−190 cm^{-1})[25] and is comparable to the value of 185 cm^{-1} reported for Hg_2F_2.[25] It is also close to the value of ν(HgHg) = 181 cm^{-1} reported for the N-bonded mercury(I) complex of *N*,*N*′-diacetylhydrazine: $[Hg_2N(COCH_3)N(COCH_3)]_n$.[25]

The ν(HgN) bands of $Hg_2(NCO)_2$ are observed at about 350 cm^{-1} (Figures 1 and 2). The IR-active antisymmetric mode, ν_a(HgN), shows a substantial decrease in frequency relative to that of the corresponding mercury(II) complex, and this decrease is similar in magnitude to those observed for Hg_2Cl_2 and $Hg_2(SCN)_2$ (Table 2). This reflects a substantial weakening of the Hg−X bond in Hg_2X_2 relative to that in HgX_2. The frequency of the Raman-active symmetric mode, ν_s(HgN), for $Hg_2(NCO)_2$ is almost the same as that of the IR-active antisymmetric mode, ν_a(HgN). For the series Hg_2X_2 (X = Cl, Br, I), ν_s(HgX) is greater than ν_a(HgX) (in contrast to the situation for HgX_2), but the difference between these decreases along this series. The reason for these observations is that the Hg−X and Hg−Hg coordinates are strongly coupled, because the ν_s(HgX) and ν(HgHg) modes have the same symmetry and similar frequencies and the degree of coupling increases as ν_s(HgX) decreases. In the X = NCO case, ν_s(HgX) is higher than for the halides mentioned above, so that the degree of coupling is reduced to the point where ν_s(HgN) is approximately equal to ν_a(HgN) (Table 2). This near-coincidence is therefore proposed to be "accidental", but this and other possible coincidences between the IR and Raman spectra (Table 1) do not allow the definite conclusion of a centrosymmetric structure for the compound. However, the other features of the vibrational spectra discussed above strongly support a structure with a linear or near-linear N−Hg−Hg−N arrangement, and it is equally clear that the crystal structure is not isomorphous with that of $Hg_2(SCN)_2$.

The low-wavenumber vibrational spectra of mercury(I) acetate and trifluoroacetate are shown in Figures 1 and 2. The structure of $Hg_2(OAc)_2$ has not been reported to date, but that of the trifluoroacetate $Hg_2(tfa)_2$ shows the presence of discrete molecules of C_2 symmetry, with monodentate trifluoroacetate groups bound to the dimercury unit to give a near-linear O−Hg−Hg−O array with Hg−Hg−O = 166.6°.[42] The vibrational spectra of the acetate complex have been interpreted on the basis of a similar model.[36] The frequencies of the ν(HgO) and ν(HgHg) modes for these two compounds are given, together with those for the ν(HgO) modes of mercury(II) acetate, in Table 2. The present results for $Hg_2(OAc)_2$ are essentially in agreement with the previous report, the main difference being the observation of a single ν_a(HgO) IR band at 279 cm^{-1} (Figure 1), rather than the previously reported doublet at 268, 283 cm^{-1}.[36] The occurrence of multiple strong bands below 200 cm^{-1} renders the assignment of ν(HgHg) less certain than in the case of the halides or pseudohalides; this situation is found for several other mercury(I) complexes with oxygen-donor ligands.[25] In accordance with the previous study of the acetate,[36] we assign the strong band of highest frequency below 200 cm^{-1} to ν(HgHg) for both compounds (Table 2). The mutual exclusion of the ν(HgO) bands between the IR and the Raman spectra (Table 2) implies the presence of a centrosymmetric O−Hg−Hg−O arrangement, as is found in the crystal structure of $Hg_2(tfa)_2$.[42]

Mercury-199 MAS NMR Spectra. The solid-state ^{199}Hg MAS NMR spectra of Hg_2Cl_2 and $Hg_2(OAc)_2$ are shown in Figure 3. As with other mercury complexes that show large ^{199}Hg shielding anisotropy, the spectra consist of a centerband flanked by a number of spinning sidebands.[22] The chemical shift and shielding parameters obtained from a spinning-sideband analysis of these spectra, and of the spectra of the other compounds studied in this work, are compared with the previously reported data for $Hg_2(NO_3)_2 \cdot 2H_2O$[19] in Table 3. Apart from the spectra of the compounds discussed in the previous section, the spectrum of dimercury(I) sulfate, Hg_2SO_4, was also recorded. This compound has been shown to contain infinite

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Table 3. ^{199}Hg Chemical Shifts and Shielding Tensor Parameters from Solid-State ^{199}Hg NMR Spectra

compound	$\sigma_{11} - \sigma_r$/ppm	$\sigma_{22} - \sigma_r$/ppm	$\sigma_{33} - \sigma_r$/ppm	δ_{iso}/ppm	$\Delta\sigma$/ppm	η	ref
Hg_2Cl_2	−396(39)	−53(36)	3598(39)	−1050	3822(58)	0.14(3)	*a*
$Hg_2(SCN)_2$	−157(30)	219(25)	2988(37)	−1017	2957(56)	0.19(2)	*a*
$Hg_2(NCO)_2$	−498(54)	10(43)	3735(75)	−1082	3979(112)	0.19(2)	*a*
$Hg_2(OAc)_2$	326(57)	326(57)	3699(20)	−1450	3374(30)	0.00(5)	*a*
$Hg_2(tfa)_2$	507(38)	508(38)	3931(13)	−1649	3423(20)	0.00(3)	*a*
Hg_2SO_4	505(87)	606(87)	3544(13)	−1552	2988(34)	0.05(9)	*a*
$Hg_2(NO_3)_2 \cdot 2H_2O$[b]	435.2	496.7	3669.3	−1533.7	3203	0.03	19
$HgCl_2$	282(27)	573(26)	4019(26)	−1625	3592(37)	0.12(2)	20
$Hg(SCN)_2$	81(23)	428(21)	3390(24)	−1300	3135(37)	0.17(2)	21
$Hg(OAc)_2$	1859	1947	3685	−2497	1782	0.07	18

[a] This work. [b] Static single-crystal measurement.

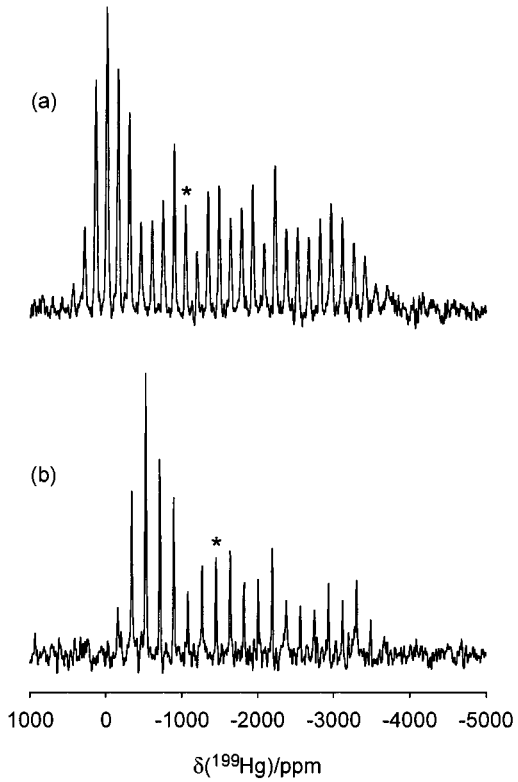

Figure 3. 53.6 MHz ^{199}Hg MAS NMR spectra of (a) Hg_2Cl_2 (spinning rate ν_s = 8000 Hz) and (b) $Hg_2(OAc)_2$ (ν_s = 10000 Hz). Baseline corrections and line broadening (500 Hz) were applied prior to plotting. The centerband is indicated by the asterisk.

−SO_4−Hg−Hg−SO_4−Hg−Hg− chains with a nearly linear Hg−Hg−O angle of 164.9°.[43] The spectrum of $Hg_2(NCO)_2$ was of significantly poorer quality than those of the other dimercury(I) compounds in Table 3, and this accounts for the somewhat greater errors in the shielding parameters for this compound. An attempt to record the spectrum of dimercury(I) *o*-phthalate, $Hg_2(OOC)_2C_6H_4$, resulted in a spectrum that was not of sufficient quality to allow analysis. Of all the compounds examined, this is the only one for which the two Hg atoms in the dimercury(I) unit are inequivalent.[44] An attempt was also made to record the spectrum of dimercury(I) dibromide, Hg_2Br_2. As in the case of the corresponding mercury(II) compound $HgBr_2$,[20] this was unsuccessful. A possible reason for this is that unresolved coupling to the ^{79}Br, ^{81}Br nuclei causes severe broadening of the ^{199}Hg signals. A similar effect is probably responsible for the significantly greater line width in the ^{199}Hg spectrum of Hg_2Cl_2 compared with that of $Hg_2(OAc)_2$ (Figure 3). The greater magnetic and quadrupole moments of ^{79}Br, ^{81}Br relative to ^{35}Cl, ^{37}Cl would result in still broader lines for Hg_2Br_2.

The shielding anisotropy is defined as

$$\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{11} + \sigma_{22}) \quad (4)$$

and the departure of the shielding tensor from axial symmetry is described by the asymmetry parameter

$$\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso}) \quad (5)$$

We recently showed that anisotropic ^{199}Hg shielding parameters can be interpreted on the basis of the expressions which have been derived for the local paramagnetic contribution to the shielding.[22] Within the average excitation energy (AEE) approximation, the expressions for the principal components of the local paramagnetic shielding tensor, for the case where the shielding is due to electron density in the valence p orbitals only and the local symmetry is sufficiently high that cross terms in the charge density matrix are zero, are

$$\sigma_{xx} = (n_y + n_z - n_y n_z)\sigma_p \quad (6)$$

$$\sigma_{yy} = (n_x + n_z - n_x n_z)\sigma_p \quad (7)$$

$$\sigma_{zz} = (n_x + n_y - n_x n_y)\sigma_p \quad (8)$$

where n_x, n_y, n_z are the populations of the Hg $6p_x$, $6p_y$, $6p_z$ orbitals, respectively, and σ_p is a constant relating to the contribution of the valence *n*p orbitals to the shielding:

$$\sigma_p = -\mu_0 e^2 h^2 \langle r^{-3} \rangle_{np} / 4\pi m^2 \Delta E \quad (9)$$

Here μ_0 is the permeability constant, *e* is the electronic charge, *m* is the electron rest mass, ΔE is the average excitation energy, and $\langle r^{-3} \rangle_{np}$ is the expectation value of r^{-3} for the valence *n*p electron.[45,46] The average, or isotropic, local paramagnetic shielding derived from the above is

$$\sigma_{iso} = (1/3)[2n_x + 2n_y + 2n_z - n_x n_y - n_y n_z - n_x n_z]\sigma_p \quad (10)$$

In both HgX_2 and Hg_2X_2, the Hg atoms are involved in σ-bonding, which mainly concerns the Hg 6s and $6p_z$ orbitals (the *z* axis lies along the linear axis of the molecules). Thus, the only nonzero orbital population in eqs 6−8 is the Hg $6p_z$ population n_z (=*n*). This yields $\sigma_{xx} = \sigma_{yy} = n\sigma_p$; $\sigma_{zz} = 0$. Since σ_p is negative (eq 9), this yields $\sigma_{zz} > \sigma_{xx} = \sigma_{yy}$. If it is assumed

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(46) Jameson, C. J.; Gutowsky, H. S. *J. Chem. Phys.* **1964**, *40*, 1714.

that the diamagnetic contributions to the shielding are isotropic, and so contribute equally to all three principal components of the shielding tensor, the above relationship should also hold for the total shielding constants. Defining the principal axes of the shielding tensor according to eq 1 yields the relationship $\sigma_{33} > \sigma_{11} = \sigma_{22}$. Inspection of the results for HgX_2 and Hg_2X_2 in Table 3 shows that the experimental values correspond closely to this relationship; the small deviations from equality of σ_{11} and σ_{22} in the solid-state data are due to small deviations from axial symmetry in the primary and/or secondary bonding interactions. Substitution of the above expressions for the shielding tensor components for linear HgX_2 into eq 4 yields $\Delta\sigma = -n\sigma_p$. Since σ_p is negative (eq 9), $\Delta\sigma$ is positive. Thus $\Delta\sigma$ is proportional to the $6p_z$ population n which, in turn, is proportional to the σ-donor strength of the ligand, and so a strong σ-donor ligand, such as Cl^-, will result in a greater n than will a weaker σ-donor, such as OAc^-. Therefore $\Delta\sigma$ is predicted to be greater for $HgCl_2$ than for $Hg(OAc)_2$, and the results in Table 3 show that this prediction is confirmed. The same relationship is observed for the mercury(I) compounds Hg_2Cl_2 and $Hg_2(OAc)_2$, but the difference is much smaller than for the corresponding mercury(II) compounds. The shielding anisotropy for Hg_2Cl_2 is only slightly greater than that for $HgCl_2$, whereas the value for $Hg_2(OAc)_2$ is about twice as great as that for $Hg(OAc)_2$ This result is difficult to reconcile with the previously expressed view that the shielding anisotropy is dominated by the mercury−ligand bonding.[19] If this were the case, then $\Delta\sigma$ for $Hg_2(OAc)_2$ should only be approximately half the value for $Hg(OAc)_2$, since there is only one Hg−O bond for each Hg atom in the former, compared to two in the latter.

A simple explanation for the observed $\Delta\sigma$ values for the dimercury(I) compounds can be obtained by considering the dimercury(I) compounds to be linear mixed-ligand complexes YHgX where Y is the other X−Hg unit in the molecule. For each mercury atom, the Hg $6p_z$ orbital population consists of contributions from both the Y and X ligands. The Hg orbitals involved in the bonding must have some $6p_z$ character if the Hg−Hg bonding is to affect the $6p_z$ orbital populations. This would be the case if the orbitals involved were sp hybrids, as is normally assumed in the case of linear mercury compounds, although it should be recognized that this is a limiting case corresponding to the maximum possible degree of $6p_z$ orbital involvement. A theoretical study of several mercury compounds yielded equal $6p_z$ orbital populations of 0.40 for $HgCl_2$ and Hg_2Cl_2.[27] According to the model discussed above, this would result in equal $\Delta\sigma$ values for these two compounds, in good agreement with the experimental observations (Table 3). No calculations have been reported for corresponding carboxylate compounds, but for the fluorides, the $6p_z$ orbital population increases from 0.24 to 0.31 from HgF_2 to Hg_2F_2.[27] This indicates that the Hg−Hg bond in the dimercury(I) compound contributes more to the $6p_z$ orbital population than the Hg−X bond does. If this is the case, then this orbital population should be less sensitive to changes in X than it is in the corresponding mercury(II) compounds. According to the model for the paramagnetic shielding discussed above, this implies that the shielding anisotropy $\Delta\sigma$ should show a smaller X-dependence for the dimercury(I) compounds, in good agreement with the experimental observations (Table 3). Nevertheless, there is a significant dependence of $\Delta\sigma$ on X, and this is such that $\Delta\sigma$ decreases as the σ-donor strength of X^- decreases (e.g., from X = Cl to X = OAc). This can also be readily understood in terms of the model discussed above, since the weaker σ-donor donates less electron density to the Hg $6p_z$ orbital and thus produces a lower shielding anisotropy, $\Delta\sigma$. Compared to those for the other Hg_2X_2 compounds, $\Delta\sigma$ for $Hg_2(SCN)_2$ is unexpectedly low, and this point will be discussed further below.

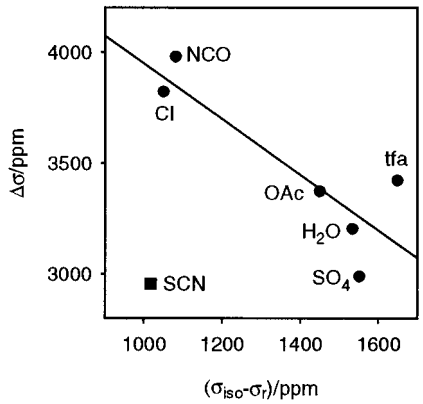

Figure 4. Plot of the shielding anisotropy $\Delta\sigma$ for Hg_2X_2 (X = Cl, NCO, OAc, tfa), Hg_2SO_4, and $Hg_2(NO_3)_2{\cdot}2H_2O$ (●) and for $Hg_2(SCN)_2$ (■) against the corresponding isotropic shielding constant $\sigma_{iso} - \sigma_r$.

The values of the asymmetry parameter η obtained for the mercury(I) compounds (Table 3) are all less than 0.2 (small values of η are difficult to determine accurately),[6,47] implying that the shielding tensor is almost axially symmetric in these compounds. This is as expected for a linear or near-linear X−Hg−Hg−X arrangement such as those observed in the structures of these systems or those deduced from the vibrational spectra (see above).

The isotropic shielding constants are obtained from the centerband shifts δ_{iso} (eq 2), values of which are listed in Table 3 for the compounds studied in the present work. The relationship of this parameter to the electronic structure of the complex is given by eq 10. For the linear HgX_2 and Hg_2X_2 cases, this yields $\sigma_{iso} = (2/3)n\sigma_p$, compared with the corresponding expression derived above for the shielding anisotropy $\Delta\sigma = -n\sigma_p$, so that a plot of $\Delta\sigma$ vs σ_{iso} should be linear, with a slope of −1.5. Such a plot for the various Hg_2X_2 compounds (excluding X = SCN) in Table 3 is shown in Figure 4. An approximately linear relationship is observed with a slope of -1.3 ± 0.4, and the compounds clearly fall into two separate groups: the halides and pseudohalides, with isotropic shieldings ($\sigma_{iso} - \sigma_r$) of about 1000 ppm, and the oxygen-donor ligands, with isotropic shieldings of about 1500 ppm. The decrease in $\Delta\sigma$ from the halide to the oxygen-donor ligands has been explained above in terms of the decrease in ligand σ-donor strength. The anomalously low $\Delta\sigma$ value for $Hg_2(SCN)_2$ was also mentioned above, and this results in the point for this compound lying well below the correlation line for the other compounds in Figure 4. Exactly the same kind of anomaly has been observed for the X = SCN compounds in a corresponding plot for HgX_2 and HgX(OAc) and was attributed to the presence of secondary bonding involving intermolecular interactions between the Hg atoms and the N atoms of the SCN groups on neighboring molecules.[20] It is interesting to note that this anomaly does not occur for $Hg_2(NCO)_2$, consistent with the fact that the cyanate group normally bonds via the N atom and not via the O atom.[38]

Carbon-13 MAS NMR Spectra. The ^{13}C MAS NMR parameters for Hg_2X_2 (X = SCN, NCO, OAc) are given in Table 4, together with those for HgX_2 (X = SCN, OAc). The ^{13}C

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Table 4. Solid-State ^{13}C NMR Parameters for Mercury Complexes

complex	carbon	$\delta(^{13}C)$/ppm	$\lvert^{n}J(^{199}Hg^{13}C)\rvert$/Hz	ref
$Hg(SCN)_2$	SCN	129.4		21
$Hg_2(SCN)_2$	SCN	129.9		*a*
$Hg_2(NCO)_2$	NCO	138.0		*a*
$Hg(OAc)_2$	CH_2	180.9	118 (^2J)	52
		176.8	156 (^2J)	
	CH_3	24.7	176 (^3J)	
		24.3	195 (^3J)	
$Hg_2(OAc)_2$	CH_2	181.4	<120 (^2J)	*a*
	CH_3	26.1	<150 (^3J)	

[a] This work.

spectra of $Hg(SCN)_2$ and $Hg(NCO)_2$ showed single lines, consistent with the proposed structures of these compounds (see Vibrational Spectroscopy section above). The ^{13}C chemical shift in $Hg_2(SCN)_2$ is very similar to that in $Hg(SCN)_2$, showing that the S-bound structure observed for $Hg(SCN)_2$[39] is also present in $Hg_2(SCN)_2$, in agreement with the results from the vibrational spectra discussed above. It has previously been shown that the ^{13}C chemical shifts of S- and N-bound thiocyanate are lower and higher than the value for ionic thiocyanate (134.0 ppm), respectively.[48,49] The shifts in both of the above complexes conform to this rule but are significantly greater than those in $[Au(SCN)_2]^-$ (116.3 ppm) or $[Hg(SCN)_4]^{2-}$ (124.8 ppm) and are higher than those observed for a range of other diamagnetic S-bound thiocyanate complexes,[48] while still remaining less than that for ionic thiocyanate. It has been claimed that the ^{13}C chemical shift of O-bound cyanate lies in the range 104−119 ppm, while that of N-bound cyanate occurs in the range 114−132 ppm.[50,51] The value observed in the present work for $Hg_2(NCO)_2$ significantly extends the upper limit of the N-bound range to 138 ppm. The values reported for a number of other N-bound cyanate complexes lie below the value for ionic cyanate (127.9 ppm),[48,50] and $Hg_2(NCO)_2$ is an unusual case in which the shift lies above this value.

The ^{13}C spectrum of $Hg_2(OAc)_2$ showed the expected signals due to the acetate ligand, but the long-range (^2J, ^3J) couplings to ^{199}Hg, which were observed in $Hg(OAc)_2$ (Table 4),[52] were not seen in the dimercury(I) compound. The signals showed a slight additional broadening near the baseline, and from the line widths in this region, the upper limits to the long-range couplings were estimated (Table 4). These are less than the values observed in the mercury(II) complex, which is surprising because a greater Hg 6s population would be expected in the dimercury(I) compound. This must be counteracted by the lower effective charge on the Hg atom and the weaker Hg−O bonding (reflected in the lower ν_a(HgO) value) in the dimercury(I) compound. In contrast to the situation for $Hg(OAc)_2$, where separate ^{13}C signals are seen for the two crystallographically inequivalent acetate groups in the molecule,[12,52] only single lines for each type of carbon atom are seen in the spectrum of $Hg_2(OAc)_2$, which is consistent with the centrosymmetric structure proposed for this compound (see Vibrational Spectroscopy section above).

Conclusion

The vibrational spectra of Hg_2X_2 (X = SCN, NCO, OAc) show that these compounds have structures similar to those of their halide and trifluoroacetate counterparts. In contrast to those for the corresponding mercury(II) compounds, the ^{199}Hg shielding anisotropies for a range of Hg_2X_2 compounds are found to be relatively insensitive to the nature of the X group. This implies that the electronic environment of the Hg atom in the mercury(I) compounds is dominated by the Hg−Hg bond, a view which is consistent with the fact that the Hg−Hg force constants determined from the vibrational frequencies of Hg_2X_2 are considerably greater than the Hg−X force constants.[25] A previous conclusion (based on the measured direction of the principal axis of the ^{199}Hg shielding tensor in $[Hg_2(OH_2)_2]^{2+}$) that the shielding tensor is dominated by contributions from metal−ligand bonding[19] is not verified by the results obtained for the greater range of compounds examined in the present study.

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