Crystal Structure and Vibrational Spectroscopic Studies of the Complexes [$HgX(NO_3)(C_5H_5N)$] (X = Cl, Br or I)†

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The structures of the complexes [$HgX(NO_3)(py)$] (py = pyridine, X = Cl or Br) have been determined by single-crystal X-ray diffraction analysis. Both complexes crystallize in the orthorhombic space group *Pnam* with one-half of the formula unit comprising the asymmetric unit of the structure. The mercury atom environments are dominated by close associations with the halide and pyridine nitrogen atoms in a quasi-linear array with nitrate oxygen contacts about the mercury in a 'plane' normal to N–Hg–X. The structural parameters for the N–Hg–X units are Hg–X 2.261(6) and 2.379(3), Hg–N 2.04(2) and 2.08(2) Å and N–Hg–X 177.0(5) and 176.1(4)° for X = Cl or Br respectively. The nitrate moieties link the mercury atoms in a two-dimensional polymeric array. The mean nearest-neighbour Hg···O distances in the two compounds are 2.99 and 3.02 Å respectively. The infrared and Raman spectra yield ν(HgX) 359 and 264 cm^{-1} (IR, Raman), ν(HgN) 160 and 158 cm^{-1} (Raman) for X = Cl or Br respectively. For the corresponding X = I compound the vibrational spectra suggest the presence of $[Hg(py)_2]^{2+}$ and molecular HgI_2 units in the solid, the latter giving rise to bands due to the symmetric and antisymmetric ν(HgI) modes at 154 (Raman) and 214 cm^{-1} (IR) respectively. The vibrational spectra of the 4-methylpyridine (4Me-py) complexes [$HgX(NO_3)(4Me\text{-}py)$] (X = Cl, Br or I) suggest that these all contain $[HgX(4Me\text{-}py)]^+$ units with ν(HgX) 343, 251 and 218 (IR, Raman), ν(HgN) 201, 187 and 162 cm^{-1} (Raman) for X = Cl, Br or I respectively.

Complexes of the type [HgX(Y)L] (L = tertiary phosphine or arsine; X = Cl, Br or I; Y = NO_3 or BF_4) have been known for some time.[1–3] We have recently shown by X-ray crystallography that the complexes [$HgX(NO_3)(PPh_3)$] contain $[HgX(PPh_3)]^+$ cations with weakly interacting NO_3^- anions, and that the ^{31}P cross polarization magic angle spinning (CP MAS) NMR spectra of these compounds show an unusual splitting due to coupling of the phosphorus nucleus to the quadrupolar ^{201}Hg nucleus.[4] To date, this phenomenon has been observed only in mercury complexes of the type $[HgX(PPh_3)]^+$ which contain nearly linear, two-co-ordinate P–Hg–X entities, although a similar splitting involving spin–spin coupling to quadrupolar ^{197}Au occurs in the ^{31}P CP MAS NMR spectra of the isoelectronic gold complexes [$AuX(PPh_3)$].[4] Linear two-co-ordination is common in gold(I) chemistry, where it is sometimes associated with unexpectedly short gold–gold contacts perpendicular to the axis of the digonal bonds,[5–12] but is less frequently encountered in mercury(II) complexes. In order completely to characterize further examples of this unusual bonding situation in mercury compounds, we have undertaken further X-ray crystallographic and spectroscopic studies of complexes of the type [$HgX(NO_3)L$].

In the present study the structures of [$HgX(NO_3)(py)$] (py = pyridine; X = Cl or Br) have been determined by single-crystal X-ray diffraction methods, and the results are correlated with the bonding information obtained from the infrared and Raman spectra of these and some related complexes.

Experimental

Preparation of Compounds.—Halogenopyridinemercury(II) *nitrates*, [$HgX(NO_3)(py)$] (X = Cl or Br). These were prepared by a previously described method[3] which involves the reaction between pyridine, HgX_2 and $Hg(NO_3)_2$ in a 2:1:1 mole ratio in a suitable solvent (glacial acetic acid or ethanol). The X = I analogue could not be prepared by this method because red HgI_2 does not dissolve in the reaction mixture. The following alternative method was therefore used. To a hot, stirred suspension of [$HgX_2(py)_2$][13] (1.0 mmol) in ethanol (20 cm^3) was added a solution of $Hg(NO_3)_2\cdot H_2O$ (0.34 g, 1.0 mmol) in water (3 cm^3) and concentrated HNO_3 (0.2 cm^3). The products separated immediately as white, microcrystalline solids which were collected by vacuum filtration, washed with ethanol (10 cm^3), and air-dried. The melting points and IR spectra of the X = Cl or Br products were identical to those prepared by the previously described method.[3] The X = I product, white solid, m.p. 158–162 °C (Found: C, 13.0; H, 1.6; N, 5.8. Calc. for $C_5H_5HgIN_2O_3$: C, 12.8: H, 1.1; N, 6.0%), was contaminated with a small amount of red HgI_2. A product which gave an identical m.p. and IR spectrum, but which was entirely free HgI_2, was obtained by carrying out the reaction at room temperature. [$^2H_5$]Pyridine analogues of the X = Cl or Br complexes were prepared by using a half-scale version of the first method above (with ethanol as solvent) by using C_5D_5N (0.84 g, 1.0 mmol) instead of pyridine. The X = I complex was prepared by using a reduced scale version of the second method above by using [$HgI_2(C_5D_5N)_2$] (0.10 g, 0.16 mmol) instead of the corresponding pyridine complex.

Halogeno(4-*methylpyridine*)*mercury*(II) *nitrates*, [$HgX(NO_3)(4Me\text{-}py)$] (X = Cl or Br). These were prepared by a modification of the first method above (with ethanol as solvent), by using 4-methylpyridine instead of pyridine. For the X = Br case a reasonably pure product was obtained only if the reaction was carried out at room temperature. For X = Cl the product is a white solid, m.p. 230–232 °C (Found: C, 18.4; H, 1.9; N, 7.1.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

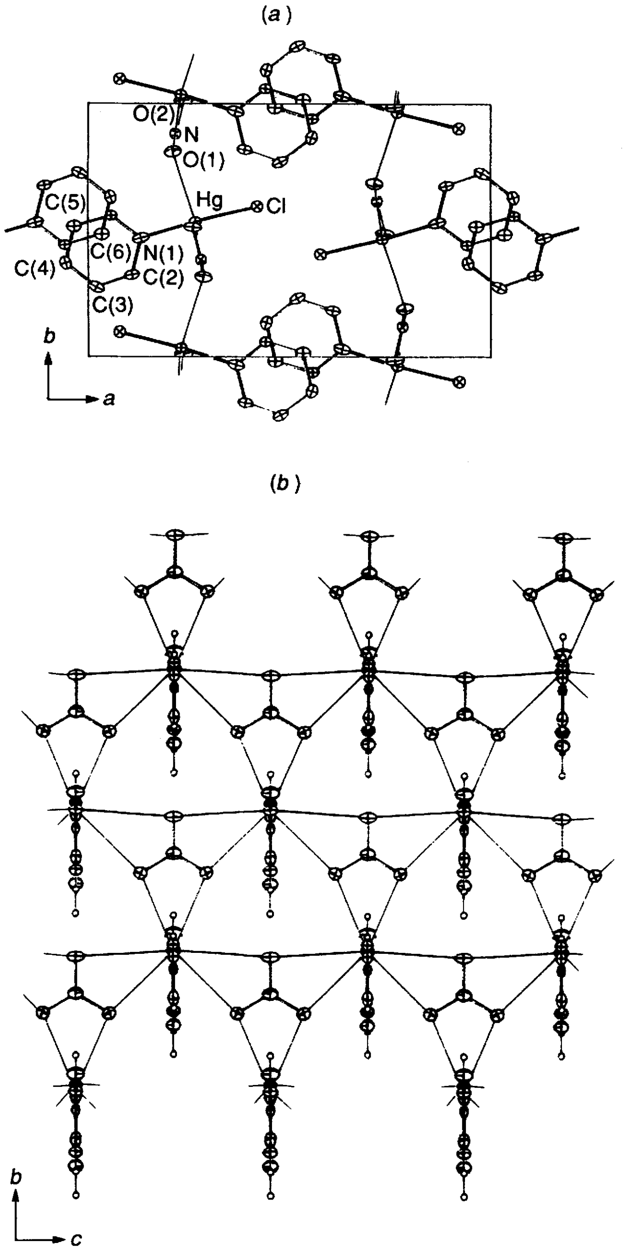

Fig. 1 (*a*) Unit-cell contents in [HgCl(NO$_3$)(py)] projected down *c*. (*b*) Projection of the extended network down *a*; 20% thermal ellipsoids are shown for the non-hydrogen atoms

Calc. for $C_6H_7ClHgN_2O_3$: C, 18.4; H, 1.8; N, 7.2%). For X = Br, white solid, m.p. 204–207 °C (Found: C, 17.3; H, 1.7; N, 6.7. Calc. for $C_6H_7BrHgN_2O_3$: C, 16.5; H, 1.6; N, 6.4%). The X = I compound was prepared by a method analogous to that described above for the corresponding pyridine complex. It is a white solid, m.p. 174–177 °C, which could not be obtained free of red HgI_2.

Structure Determinations.—Recrystallization of [HgX(NO$_3$)(py)] (X = Cl or Br) from glacial acetic acid yielded colourless crystals which were small and not particularly well formed. The crystals used in the X-ray structure determination were cleaved from twinned material and were poorly shaped, resulting in less-than-optimum absorption corrections. The X = I complex could not be recrystallized without decomposition to red HgI_2, so no structure determination was carried out for this compound.

Unique data sets were measured at ≈295 K within the limit $2\theta_{max} = 55°$ using an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; 2θ–θ scan mode) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after solution of the structures by the heavy-atom method and analytical absorption correction (the two structures are isomorphous, orthorhombic, space group *Pnam*, D_{2h}^{16}, no. 62, $Z = 4$). Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted at convergence; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral atom complex scattering factors were employed,[14] computation using the XTAL 3.0 program system.[15] Pertinent results are shown in Fig. 1 and Tables 1–3.

Crystal/refinement data for [HgX(NO$_3$)(py)] (=$C_5H_5XHgN_2O_3$). X = Cl, $M = 377.2$, $a = 14.281(5)$, $b = 9.156(5)$, $c = 6.305(1)$ Å, $U = 824.4$ Å^3. $D_c = 3.04$ g cm^{-3}, $F(000) = 680$, $\mu_{Mo} = 183$ cm^{-1}, specimen 0.19 × 0.29 × 0.25 mm, $A^*_{min,max} = 6.84, 25.8$, $N = 1030$, $N_o = 821$, $R = 0.054$, $R' = 0.065$.

X = Br, $M = 421.6$, $a = 14.399(6)$, $b = 9.365(4)$, $c = 6.326(2)$ Å, $U = 853.0$ Å^3, $D_c = 3.28$ g cm^{-3}, $F(000) = 752$, $\mu_{Mo} = 219$ cm^{-1}, specimen 0.24 × 0.30 × 0.33 mm, $A^*_{min,max} = 11.5, 36.4$, $N = 1071$, $N_o = 781$, $R = 0.050$, $R' = 0.052$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Spectroscopy.—Infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed KBr discs on a Digilab FTS-60 Fourier-transform spectrometer employing an uncooled deuteriotriglycine sulfate detector. Far-infrared (FIR) spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed Polythene discs on a Digilab FTS-60 Fourier-transform spectrometer employing an FTS-60V vacuum optical bench with mylar film beam splitters of thickness 6.25 μm (100–450 cm^{-1}) or 25 μm (40–120 cm^{-1}), a mercury lamp source and a triglycine sulfate detector. Raman spectra were excited with 100 mW of argon-ion 514.5 nm radiation using a Coherent model 52 laser, and were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer.

Results and Discussion

Syntheses.—The complexes [HgX(NO$_3$)L] (X = Cl, Br or I; L = py or 4Me-py) can be prepared by the reaction between L, HgX_2 and $Hg(NO_3)_2$ in a suitable solvent. In a previously reported study of the corresponding L = PPh_3 complexes[4] it was shown by ^{31}P NMR spectroscopy that a symmetrization equilibrium (1) exists in solution. The unsymmetrical complex

$$2[\mathrm{HgX(NO_3)L}] \rightleftharpoons [\mathrm{Hg(NO_3)_2L_2}] + \mathrm{HgX_2} \quad (1)$$

on the left is the major species present in this case, although there is a definite shift in the equilibrium to the right from X = Cl to X = I. A similar situation apparently exists for the L = py or 4Me-py cases, as the difficulty of obtaining pure [HgX(NO$_3$)L] increases from X = Cl to X = I so that the X = I products are usually contaminated with red HgI_2. It was significantly more difficult to obtain pure X = Br or I products for L = 4Me-py than for L = py (see Experimental section). This suggests that the above equilibrium lies further to the right for L = 4Me-py than for L = py.

X-Ray Structure Determinations.—The results of the single-crystal X-ray studies of the two complexes with L = py, X = Cl or Br are consistent with their formulation as [HgX(NO$_3$)(py)]; they are isomorphous, crystallizing in an orthorhombic, space group *Pnam*, cell with one-half of the formula unit comprising the asymmetric unit of the structure. The structure of the chloride is shown in Fig. 1, and the non-hydrogen interatomic distances and interbond angles are given in Tables 2 and 3. The mercury atom environments are dominated by close associ-

Table 1 Non-hydrogen atom coordinates for $[HgX(NO_3)(py)]$

	X = Cl		X = Br	
Atom	*x*	*y*	*x*	*y*
Hg	0.268 50(7)	0.535 72(8)	0.267 72(6)	0.534 37(9)
X	0.421 9(4)	0.596 6(7)	0.428 2(2)	0.594 8(2)
N(1)	0.132(2)	0.470(2)	0.130(1)	0.467(2)
C(2)	0.109(2)	0.321(2)	0.111(2)	0.322(2)
C(3)	0.021(2)	0.272(2)	0.021(2)	0.278(2)
C(4)	−0.056(2)	0.367(3)	−0.051(2)	0.370(2)
C(5)	−0.035(2)	0.516(2)	−0.032(1)	0.515(2)
C(6)	0.058(2)	0.559(2)	0.059(1)	0.553(2)
N	0.218(1)	0.882(2)	0.222(1)	0.876(2)
O(1)	0.212 0(9)	0.812(1)	0.211 8(7)	0.809(1)
O(2)	0.238(1)	1.013(2)	0.235(1)	1.011(1)

For all atoms except O(1), z = 0.25; for O(1), z = 0.079(2) or 0.077(2) (chloride or bromide).

Table 2 Non-hydrogen interatomic distances (Å) for $[HgX(NO_3)(py)]$

	X = Cl	X = Br
Hg–X	2.261(6)	2.379(3)
Hg–N(1)	2.04(2)	2.08(2)
Hg–O(1)	2.87(1)	2.91(1)
Hg–O(2^{I})	3.161(1)	3.171(1)
Hg–O(1^{I})	2.93(1)	2.97(1)
N–O(1)	1.25(1)	1.27(1)
N–O(2)	1.23(3)	1.28(2)

Symmetry operation: I $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$.

Table 3 Non-hydrogen interbond angles (°) for $[HgX(NO_3)(py)]$

	X = Cl	X = Br
X–Hg–N(1)	177.0(5)	176.1(4)
X–Hg–O(1)	93.2(3)	93.4(2)
X–Hg–O(2^{I})	92.6(4)	91.6(3)
X–Hg–O(1^{I})	94.6(3)	94.1(2)
N(1)–Hg–O(1)	89.6(5)	90.2(5)
N(1)–Hg–O(2^{I})	87.3(4)	88.1(3)
N(1)–Hg–O(1^{I})	83.3(4)	83.1(4)
O(1)–Hg–O(2)	71.1(4)	71.5(3)
O(1)–Hg–O(2^{I})	115.1(4)	115.5(3)
O(1)–Hg–O(1^{I})	155.5(3)	156.5(3)
O(1)–Hg–O(1^{II})	44.1(3)	44.1(3)
O(1)–Hg–O(1^{III})	112.2(3)	113.2(3)
O(2^{I})–Hg–O(2^{IV})	171.7(5)	172.1(3)
O(2^{I})–Hg–O(1^{III})	131.6(4)	130.5(3)
O(1^{I})–Hg–O(2^{I})	41.4(4)	42.1(3)
O(1^{I})–Hg–O(1^{III})	90.3(3)	88.4(3)
Hg–N(1)–C(2)	121(1)	119(1)
Hg–N(1)–C(6)	125(1)	124(1)
O(1)–N–O(2)	120.8(9)	120.3(8)
O(1)–N–O(1^{I})	118(1)	119(1)
O(2)–N–O(1^{II})	120.8(9)	120.3(8)
Hg–O(1)–N	96(1)	94.6(9)
Hg–O(1)–Hg^{V}	148.9(4)	149.6(4)
N–O(1)–Hg^{V}	104.3(9)	103.8(9)
Hg–O(2^{IV})–Hg^{VI}	171.7(6)	172.1(5)
Hg–O(2^{IV})–N^{IV}	93.3(3)	93.7(2)

Symmetry operations: I $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; II $x, y, \frac{1}{2} + z$; III $\frac{1}{2} - x, y - \frac{1}{2}, z$; IV $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; V $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; VI $x, y, z - 1$.

ations with the halide and pyridine nitrogen atoms in a quasi-linear array with nitrate oxygen contacts about the mercury in a 'plane' normal to N–Hg–X. In this respect the structures closely resemble those of the analogous complexes with L = PPh_3 which have been described previously;[4] in the latter, in various ways, the nitrate species interact with the mercury atoms by three long Hg···O contacts in the range 2.5–2.9 Å, bridging them in one-dimensional polymeric arrays. In the present complexes, presumably because of the smaller bulk of the planar pyridine ligand, the interactions of the mercury with the nitrate groups, although still long, are more extensive so that a two-dimensional polymeric array is formed, dominated by parallel mirror planes (parallel to *ab*) in which all atoms (except for a pair of nitrate oxygens which are symmetrically disposed to either side of it) lie. This gives rise to a structure in which there are six long Hg···O contacts in the range 2.8–3.2 Å. The mean nearest-neighbour Hg···O distances in the two compounds are 2.99 and 3.02 Å, significantly longer than those in the PPh_3 complexes (2.70 and 2.75 Å for X = Cl or Br respectively).[4] This is not necessarily indicative of a weaker total Hg···O interaction for the pyridine relative to the PPh_3 complex since the number of nearest-neighbour Hg···O contacts for the pyridine complexes is twice that for the PPh_3 complexes. The N–Hg–X angles [177.0(5) and 176.1(4)° for X = Cl or Br] show a considerably smaller degree of distortion from linearity than do the P–Hg–X angles in $[HgX(NO_3)(PPh_3)]$ [158.44(6) and 166.05(4)° for X = Cl or Br]. This is probably a consequence of the considerably more symmetrical arrangement of Hg···O contacts in the case of the pyridine complexes. The nitrate groups in these complexes are not significantly distorted from planarity and, within the accuracy of the structure determination, are hardly distorted from three-fold symmetry (O–N–O angles all close to 120°).

The metal–ligand bond lengths in the $[HgX(py)]^+$ units are Hg–X 2.261(6) and 2.379(3) Å and Hg–N 2.04(2), 2.08(2) Å for X = Cl or Br respectively. The Hg–X bond lengths are significantly shorter than those in $[HgX(NO_3)(PPh_3)]$: Hg–X 2.328(2) and 2.4386(8) Å for X = Cl or Br respectively.[4] This is an indication of the greater *trans* influence of PPh_3 compared with pyridine. The Hg–X bond lengths are also significantly shorter than those in gas-phase HgX_2 (2.28 and 2.40 Å for X = Cl or Br),[16] indicating that the *trans* influence of X^- is greater than that of pyridine.

The bond lengths in the essentially two-co-ordinate $[HgBr(py)]^+$ complex can be compared with those in $[HgBr_2(py)_2]$ which has a pseudo-tetrahedral four-co-ordinate geometry with Hg–Br 2.478(3) and 2.483(3), Hg–N 2.38(2) and 2.39(2) Å, Br–Hg–Br 141.2(1)° and N–Hg–N 90.7(7)°.[13] The above results show that, on going from the two- to the four-co-ordinate geometry, the Hg–N bond length increases by 14%, whereas the Hg–Br distance increases by only 4%. The basis for this difference is the strong preference exhibited by Hg^{II} for linear two-co-ordination and for co-ordination to Br^- rather than to pyridine. In $[HgBr(py)]^+$, pyridine is involved in the primary two-co-ordinate environment because there are no other more basic ligands available. In $[HgBr_2(py)_2]$ there is a distortion from tetrahedral co-ordination which reflects a preference for the formation of the two-co-ordinate Br–Hg–Br unit. Thus, upon addition of pyridine and a Br^- ligand to $[HgBr(py)]^+$ to form $[HgBr_2(py)_2]$, the strongly co-ordinated pyridine ligand is displaced from the primary two-co-ordinate environment by Br^- to yield an $HgBr_2$ unit which is distorted from linearity by weaker Hg–N interactions. The large increase in the Hg–N bond length is a consequence of this displacement of the pyridine ligand from the primary two-co-ordinate environment about the Hg atom. The situation is different for the corresponding X = Cl complexes because the structure of $[HgCl_2(py)_2]$ is different from that of the bromo analogue. This complex is a chloride-bridged polymer of square-planar $HgCl_4$ units with two pyridine ligands occupying the *trans*-octahedral sites about the Hg atom.[13] In this case, the primary two-co-ordinate environment is N–Hg–N, with Hg–N 2.266(6) Å. This Hg–N distance is nevertheless still significantly longer than those in the $[HgX(py)]^+$ species, presumably because the interaction with the equatorial Cl ligands in $[HgCl_2(py)_2]$ is greater than that with the NO_3^- groups in the $[HgX(py)]^+$ salts.

Vibrational Spectra.—The far-infrared spectra of $[HgX(NO_3)(py)]$ are shown in Fig. 2. These show sharp, intense,

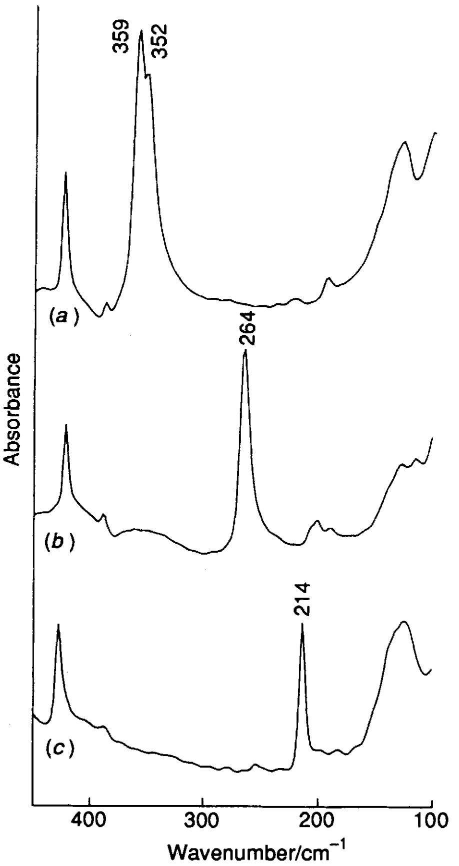

Fig. 2 Far-infrared spectra of [HgX(NO$_3$)(py)]; X = Cl (*a*), Br (*b*) or I (*c*). Bands due to ν(HgX) are labelled with their wavenumbers

halogen-sensitive bands at 359, 264 and 214 cm^{-1} (X = Cl, Br or I) which can readily be assigned as ν(Hg–X) modes. In the case of the chloride complex, this band has a shoulder at 352 cm^{-1} which can be assigned to the heavier chlorine isotope, ^{37}Cl.[4,17] Assignments of the ν(Hg–X) wavenumbers for these and for some related complexes are given in Table 4. The present assignments for X = Cl or Br are supported by the monotonic increase in ν(HgX) with decreasing Hg–X bond length which is observed for the compounds listed. Such a relationship has been observed previously for a wide range of mercury halide complexes, and the present results fit in very well with the correlations reported there.[19]

The Raman spectra in the range 50–1100 cm^{-1} are shown in Fig. 3. The spectra for the X = Cl and Br complexes show ν(HgX) bands at 360 and 265 cm^{-1} respectively which are almost exactly the same as the wavenumbers of the corresponding bands in the FIR spectra. This result is consistent with the crystal structures of these complexes, which contain [HgX(py)]$^+$ units with approximately C_{2v} symmetry, and for which a single ν(HgX) mode of A$_1$ symmetry (IR and Raman active) is expected. The Raman spectrum of the X = I complex, however, shows a very strong band at 154 cm^{-1}, with no trace of a band corresponding to ν(HgI) 214 cm^{-1} in the FIR. Likewise, there is no band in the FIR spectrum which corresponds to the very strong Raman band at 154 cm^{-1}. This complete mutual exclusion between the IR and Raman spectra is not consistent with the presence of [HgI(py)]$^+$ units in the complex.

The [HgX(py)]$^+$ units in [HgX(NO$_3$)(py)] are expected to give rise to a single ν(HgN) band in the IR and Raman spectra. Bands which have been assigned to ν(HgN) modes have been observed in the spectra of [HgX$_2$(py)$_2$] (X = Br or I),[18,20] and the wavenumbers of these and the corresponding ν(HgX) wavenumbers are listed in Table 4. In order to obtain additional support for these assignments we recorded the FIR and Raman spectra of [HgBr$_2$(C$_5$D$_5$N)$_2$] and the results are also given in Table 4. The bands assigned as ν(HgBr) show only a small downward shift in wavenumber, whereas those assigned as ν(HgN) show a significantly greater downward shift, as expected for an increase of 5 units in the mass of the pyridine ligand. The fact that the ν(HgBr) bands are also affected by the increase in mass of the pyridine indicates that there is some mixing of the Hg–Br coordinates with the Hg–N coordinates for the modes concerned. It was noted above that the Hg–N bond lengths in [HgX(NO$_3$)(py)] are shorter than those in [HgX$_2$(py)$_2$]. If a monotonic relationship exists between ν(HgN) and the Hg–N bond length then the ν(HgN) wavenumbers for [HgX(NO$_3$)(py)] should lie above the range 112–145 cm^{-1} found for [HgX$_2$(py)$_2$]. There are no strong bands present in the FIR spectra in this region (Fig. 2) which could be definitely assigned to such modes. However, the Raman spectra for the X = Cl or Br complexes (Fig. 3) show bands at 160 and 158 cm^{-1} respectively which can be thus assigned. This situation is similar to that observed previously for [HgX(NO$_3$)(PPh$_3$)], for which bands assigned as ν(HgP) occur at 164 and 161 cm^{-1} (X = Cl or Br) in the Raman spectrum, but not in the FIR.[4] The above assignments for [HgX(NO$_3$)(py)] (X = Cl or Br) are supported by the results for [HgX(NO$_3$)(C$_5$D$_5$N)] (Table 4); the bands assigned as ν(HgX) undergo a very small downward shift in wavenumber (*ca.* 2 cm^{-1}), whereas those assigned as ν(HgN) show a considerably greater downward shift (*ca.* 10 cm^{-1}). In this respect, too, the X = I complex behaves completely differently from the X = Cl or Br compounds; neither the IR band at 214 cm^{-1} nor the Raman band at 154 cm^{-1} shows a significant shift on deuteriation.

A possible explanation for the anomalous behaviour of the X = I complex is suggested by the structures of the 1:1 adducts of pyridine with gold(I) halides. These might have been expected to contain the two-co-ordinate species [AuX(py)], which are isoelectronic with the [HgX(py)]$^+$ entities characterized for X = Cl or Br in the present study. However, these compounds have been shown to be ionic [Au(py)$_2$]$^+$[AuX$_2$]$^-$ (X = Cl or I) in the solid state, with short Au $\cdots$ Au distances between the anion and cation [3.249(3) and 2.990(1) Å for X = Cl or I respectively].[6] An analogous structure for the mercury complexes would contain [Hg(py)$_2$]$^{2+}$ and HgX$_2$ units. This clearly does not occur for X = Cl or Br, but the vibrational spectroscopic results discussed above for the X = I case are entirely consistent with such a structure. Thus, the Raman band at 154 cm^{-1} and the IR band at 214 cm^{-1} can be assigned to the symmetric and antisymmetric stretching modes ν_1 and ν_3 of the linear centrosymmetric HgI$_2$ molecule. The corresponding values for HgI$_2$ in the vapour phase are ν_1 158 and ν_3 237 cm^{-1}.[21,22] Red HgI$_2$, the stable phase at ambient temperature, has an infinite layer structure which does not contain identifiable HgI$_2$ molecules.[23] Yellow HgI$_2$, the stable solid phase at temperatures above 126 °C, does contain HgI$_2$ molecules which are arranged in layers with weak secondary Hg $\cdots$ I interactions between the molecules.[23] The HgI$_2$ molecules in this environment yield ν_1 141, ν_3 202 cm^{-1}.[24,25] The wavenumbers observed in the present case thus lie between those for vapour-phase HgI$_2$ and those for HgI$_2$ molecules in the yellow phase of the solid. This seems reasonable for the structure postulated, since the HgI$_2$ molecules would be separated from each other by the [Hg(py)$_2$]$^{2+}$ and NO$_3$$^-$ ions which are also present. These latter species contain atoms which would act less effectively as bridging atoms than do the iodine atoms which bridge neighbouring molecules in yellow HgI$_2$. Since these bridging interactions are the main cause of the downward shift of the ν(HgI) wavenumbers relative to the vapour-phase values, a reduction in the extent of these interactions would be expected to yield ν(HgI) wavenumbers which are higher than those of yellow HgI$_2$, as is observed experimentally. The proposed structure also provides a simple

Table 4 Vibrational wavenumbers (cm^{-1}) for [HgX(NO$_3$)(py)] and some related complexes

		ν(HgX)		ν(HgN)	
Complex	X	IR	Raman	IR	Raman
[HgX(NO$_3$)(py)]	Cl	359, 352	360, 353	—	160
	Br	264	265	—	158
	I	214	154	—	—
[HgX(NO$_3$)(C$_5$D$_5$N)]	Cl	359, 351	359, 351	—	150
	Br	262	262	—	146
	I	214	155	—	—
[HgX(NO$_3$)(4Me-py)]	Cl	343, 335	343, 336	—	201
	Br	251	249	—	187
	I	218	215	—	162
[HgX$_2$(py)$_2$][a]	Cl[b]	313, 287	313, 282	—	—
	Br	217, 182	216, 182	141, 114	143, 112
	I	176, 145	173, 139	140, 125	121
[HgX$_2$(C$_5$D$_5$N)$_2$]	Br	214, 181	217, 183	135, 109	136, 108

[a] Ref. 18. [b] Solution in pyridine.

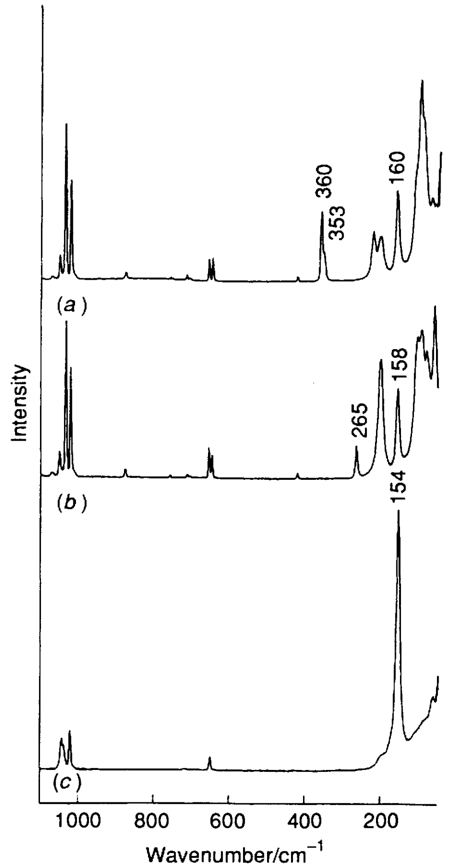

Fig. 3 Low-wavenumber Raman spectra of [HgX(NO$_3$)(py)]; X = Cl (*a*), Br (*b*) or I (*c*). Bands due to ν(HgX) and ν(HgN) are labelled with their wavenumbers

Table 5 Nitrate ν_3 band positions and splittings (cm^{-1}) for [HgX(NO$_3$)(py)] and [HgX(NO$_3$)(4Me-py)]

Complex	X	Wavenumber	Splitting
[HgX(NO$_3$)(py)]	Cl	1315, 1378	63
	Br	1317, 1382	65
	I	1298, 1383	85
[HgX(NO$_3$)(4Me-py)]	Cl	1303, 1338, 1374, 1395	92
	Br	1307, 1338, 1364, 1393	86
	I	1298, 1324, 1349, 1389	91

explanation for the invariance of the wavenumbers of the bands at 214 and 154 cm^{-1} on substitution of pyridine with C$_5$D$_5$N; the vibrating unit (the HgI$_2$ molecule) does not have a pyridine molecule directly co-ordinated to it. Further evidence for the presence of HgI$_2$ units in the structure was obtained from the FIR spectrum in the region below 100 cm^{-1}. This shows a single strong band at 46 cm^{-1} which can be assigned to the bending mode ν_2 of the HgI$_2$ molecule. This wavenumber is close to that observed for the yellow phase of solid HgI$_2$, which shows a partially resolved doublet at 40 and 52 cm^{-1} due to the ν_2 mode which is split by site-group and factor-group effects.[24] This postulated change in structure from one involving L–M–X units for X = Cl or Br to one involving L$_2$M and MX$_2$ units for X = I has a precedent in the 1:1 complexes of tetrahydrothiophene (tht) with gold(I) halides; the chloro and bromo compounds contain neutral [Au(tht)X] molecules, whereas the X = I compound consists of [Au(tht)$_2$]$^+$ and [AuI$_2$]$^-$ ions.[8,9]

In order to obtain data on related systems which might be used to check some of the above conclusions, and to study the effect of changing the base strength of the amine ligand, the complexes [HgX(NO$_3$)(4Me-py)] were prepared. Despite the greater difficulty experienced in synthesizing these compounds (see Experimental section), reasonable samples of all three members (X = Cl, Br or I) were obtained and their vibrational data are given in Table 4. The results for the X = Cl or Br complexes are similar to those obtained for the pyridine complexes, the X = I species follows the same pattern as those for the X = Cl or Br complexes, indicating that these all contain [HgX(4Me-py)]$^+$ units. The electron-releasing methyl group in 4Me-py results in this ligand having a greater base strength than that of pyridine itself, and this is reflected in previously reported thermochemical studies of the reaction of these ligands with HgX$_2$.[26] In the present study, these differences are manifested in the lower ν(HgX) and higher ν(HgN) wavenumbers for the 4Me-py relative to the pyridine complexes; the Hg–X bonds are weaker and the Hg–N bonds are stronger in the 4Me-py case as a result of the higher basicity of this ligand.

The crystal structures of [HgX(NO$_3$)(py)] (X = Cl or Br) show that the nitrate ions in these complexes are not very much distorted from D_{3h} symmetry (see above). Nevertheless, the sites occupied by these ions have lower than D_{3h} symmetry, and this is evident in the IR spectra of these complexes. The distortion from D_{3h} symmetry which generally occurs upon co-ordination of the nitrate ion results in a lifting of the degeneracy of the E′ vibrational modes of this ion.[27–29] The vibration which is most sensitive to this distortion is ν_3 (the E′ N–O stretching mode), which occurs at 1390 cm^{-1} in the IR spectrum of unco-ordinated nitrate.[21] For all three [HgX(NO$_3$)(py)] compounds, ν_3 is split into a doublet and the band positions and splittings are listed in Table 5. The splittings for the X = Cl and Br complexes are similar in magnitude, and are significantly smaller than those observed in the corresponding PPh$_3$ complexes (89 and 110 cm^{-1}).[4] This is consistent with the greater average Hg···O distances and the more symmetrical distribution of Hg atoms around the NO_3^- in the pyridine complexes. The nitrate ν_3 splitting pattern for the [HgX(NO_3)(4Me-py)] compounds is more complex than that for the pyridine complexes, four relatively sharp bands being observed instead of two broad bands. The overall splitting for the 4Me-py complexes is about 90 cm^{-1} for all three halides, whereas that for the $X = I$ complex is significantly greater than the $X = Cl$ or Br values for the pyridine complexes. This further highlights the unusual nature of the [HgI(NO_3)(py)] complex, providing additional evidence that the structure of this compound is different from that determined crystallographically for $X = Cl$ and Br.

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References

1 P. L. Goggin, R. J. Goodfellow, S. R. Haddock and J. G. Eary, *J. Chem. Soc., Dalton Trans.*, 1972, 647.
2 P. L. Goggin, R. J. Goodfellow, D. M. McEwan, A. J. Griffiths and K. Kessler, *J. Chem. Res.*, 1979, (*S*) 194.
3 G. A. Bowmaker and D. A. Rogers, *J. Chem. Res.*, 1984, (*S*) 158; (*M*) 1601.
4 L-J. Baker, G. A. Bowmaker, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1992, 989.
5 S. L. Lawton, W. J. Rohrbaugh and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 2227.
6 H.-N. Adams, W. Hiller and J. Strähle, *Z. Anorg. Allg. Chem.*, 1982, **485**, 81.
7 Y. Jiang, S. Alvarez and R. Hoffmann, *Inorg. Chem.*, 1985, **24**, 749.
8 S. Ahrland, B. Norén and Å. Oskarsson, *Inorg. Chem.*, 1985, **24**, 1330.
9 S. Ahrland, K. Dreisch, B. Norén and Å. Oskarsson, *Acta Chem. Scand., Ser. A*, 1987, **41**, 173.
10 J. Beck and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 95.
11 H. Schmidbaur, W. Graf and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 417.
12 S. Attar, W. H. Bearden, N. W. Alcock, E. C. Alyea and J. H. Nelson, *Inorg. Chem.*, 1990, **29**, 425.
13 A. J. Canty, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 15.
14 J. A. Ibers and W. C. Hamilton (Editors), *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
15 S. R. Hall and J. M. Stewart (Editors), *XTAL Users' Manual*, Version 3.0, Universities of Western Australia and Maryland, 1990.
16 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, p. 611.
17 D. R. Williamson and M. C. Baird, *J. Inorg. Nucl. Chem.*, 1972, **34**, 3393.
18 I. Persson, M. Sandström, P. L. Goggin and A. Mosset, *J. Chem. Soc., Dalton Trans.*, 1985, 1597.
19 L. V. Konovalov and K. A. Davarski, *J. Coord. Chem.*, 1986, **14**, 201.
20 R. M. Barr, M. Goldstein and W. D. Unsworth, *J. Cryst. Mol. Struct.*, 1974, **4**, 165.
21 W. Klemperer, *J. Chem. Phys.*, 1956, **25**, 1066.
22 R. J. H. Clark and D. M. Rippon, *J. Chem. Soc., Faraday Trans. 2*, 1973, 1496.
23 G. A. Jeffrey and M. Vlasse, *Inorg. Chem.*, 1967, **6**, 396.
24 Y. Marqueton, F. Abba, E.-A. Decamps and M.-A. Nusimovici, *C. R. Hebd. Acad. Sciences., Ser. B*, 1971, **272**, 1014.
25 R. P. Cooney, *Aust. J. Chem.*, 1974, **27**, 1555.
26 Y. Farhangi and D. P. Graddon, *Aust. J. Chem.*, 1973, **26**, 983.
27 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.
28 C. C. Addison, N. Logan, S. C. Wallwork and C. D. Garner, *Qt. Rev. Chem. Soc.*, 1971, **25**, 289.
29 L. I. Katzin, *J. Inorg. Nucl. Chem.*, 1962, **24**, 245.

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