Crystal Structure, Infrared and ^{31}P Nuclear Magnetic Resonance Studies of Complexes of Tris(2,4,6-trimethoxyphenyl)phosphine with Mercury(II) Halides†

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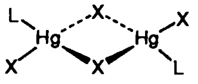
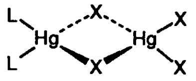
The ^{31}P NMR spectra of 1 : 1 solutions of tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) and mercury(II) halides HgX_2 (X = Cl, Br or I) in acetonitrile reveal the presence of the ionic complexes $[HgX(tmpp)]^+$ and $[Hg(tmpp)_2]^{2+}$. The amount of the first of these two species relative to the second increases from X = Cl to I. The solids which crystallize from tmpp–HgX_2 solutions in acetonitrile contain mixtures of ionic compounds which contain both of these cationic complexes. The first species was identified in the solid state by the observation of ν(HgX) bands in the far-IR spectra. In the X = Cl case, crystals of the complex $[Hg(tmpp)_2]^{2+}[Hg_2Cl_6]^{2-}$ were isolated from the solid product and the structure of this complex was determined by single-crystal X-ray diffraction [monoclinic, $C2/c$, a = 32.767(5), b = 11.500(2), c = 23.814(4) Å, β = 133.57(1)°, Z = 4 formula units; R = 0.047 for 3461 'observed' reflections]. The cation has C_2 symmetry and the mercury atom environment in this ion is dominated by a close association with the phosphorus atoms of the two attached ligands in a quasi-linear P–Hg–P array, but significant deviations from linearity arise, presumably because of contacts with the methoxy oxygen atoms [Hg–P 2.389(5) Å, P–Hg–P 166.51(9)°]. The Hg···O contacts involving the nearest *ortho*-methoxy oxygen atoms on the three phenyl groups in each ligand are 2.726(9), 2.938(7), 3.044(9) Å. The $[Hg_2Cl_6]^{2-}$ anions have a structure of C_i symmetry in which two mercury atoms with tetrahedral $HgCl_4$ co-ordination are linked by sharing two bridging Cl atoms. The structural parameters for this anion are similar to those found previously for this species in compounds with other cations. The far-IR spectra of the solids obtained from the other mercury halides reveal the presence of $[Hg_2X_6]^{2-}$ species in these compounds also. For X = I, the product is predominantly $[HgI(tmpp)]_2[Hg_2I_6]$.

Mercury(II) halides HgX_2 (X = Cl, Br or I) form a wide variety of complexes HgX_2L_n with tertiary phosphine ligands L,[1–31] and the structure and bonding in these compounds has been studied by X-ray diffraction,[4–16] vibrational spectroscopy,[7–10,12,17–20] and NMR spectroscopy.[20–31] The predominant stoichiometries are 1 : 1 and 2 : 1 (n = 1 or 2), although several examples of complexes with lower ligand to HgX_2 ratios have been reported.[1] The 2 : 1 complexes $[HgX_2L_2]$ have mononuclear pseudo-tetrahedral structures.[4,7,11,14] The structural chemistry of the 1 : 1 complexes is more diverse, and dimers,[5,8,10,12,13,15,16] tetramers,[5] and infinite-chain polymers[6] have been characterized. The dimeric complexes $[Hg_2X_4L_2]$ can adopt a centrosymmetric structure (**A**) or a non-centrosymmetric structure (**B**), depending on the nature of the ligand L.



A



B

Of these, the most commonly observed is the centrosymmetric structure **A**, structure **B** being found with ligands such as PPr_3 and PBu_3, and for X = I.[15,23,27] With the more basic and sterically less demanding ligands PMe_3 and PEt_3, chain-polymer structures are observed.[6]

Tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) is a very basic but very sterically hindered phosphine ligand,[32] and the small number of co-ordination complexes of this ligand which have been reported to date all have unusual co-ordination geometries.[33–35] The present study of its complexes with mercury(II) halides was carried out in order to determine whether new structural types occur with a ligand of greater base strength and steric bulk than those used heretofore. The study was also prompted by our attempts to prepare complexes of the type $[HgX(tmpp)]^+$, which are valence isoelectronic with the corresponding neutral copper(I) and silver(I) complexes [CuX(tmpp)] and [AgX(tmpp)].[33,34] It proved not to be possible to prepare these species by the method developed to prepare the corresponding triphenylphosphine complexes $[HgX(PPh_3)]^+$,[36] but it was found that the ionic species $[HgX(tmpp)]^+$ were generated, together with $[Hg(tmpp)_2]^{2+}$ in the reaction between tmpp and HgX_2. The characterization of these species by ^{31}P NMR and vibrational spectroscopy, and single-crystal X-ray diffraction, is reported here.

Experimental

Preparation of Compounds.—The compound tris(2,4,6-trimethoxyphenyl)phosphine (tmpp) was prepared according to the procedure outlined in the literature[32] by the reaction of $P(OPh)_3$ and (2,4,6-trimethoxyphenyl)lithium in diethyl ether, followed by recrystallization of the solid product from ethanol. Phosphorus-31 NMR studies were carried out on acetonitrile solutions of tmpp and HgX_2 in a 1 : 1 mole ratio by dissolving tmpp (0.041 g, 0.077 mmol) and HgX_2 (0.077 mmol) in CH_3CN–CD_3CN (2 : 1, *ca.* 2.5 cm^3). Solutions containing tmpp and HgX_2 in mole ratios greater or less than 1 : 1 were prepared by dissolving solid tmpp or HgX_2 in the 1 : 1 solutions. Solid

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

complexes for single-crystal X-ray diffraction and vibrational spectroscopic studies were crystallized from acetonitrile solutions containing tmpp and HgX_2 in a 1:2 mole ratio by adding a solution of tmpp (0.081 g, 0.152 mmol) in CH_3CN (0.3 cm^3) to a suspension of HgX_2 (0.304 mmol) in CH_3CN (0.3 cm^3). The tmpp container was rinsed with a further quantity (0.4 cm^3) of CH_3CN which was then added to the reaction mixture. Crystals of the product began to form immediately (colourless, X = Cl or Br, pale yellow, X = I). After crystallization was complete, the product was collected by vacuum filtration. In the case of the X = Cl or Br complexes, the ^{31}P NMR spectra of the acetonitrile solutions of tmpp and HgX_2, and the X-ray crystal structure (X = Cl) and vibrational spectroscopic studies of the solid products indicate that these products are mixtures of the ionic complexes $[HgX(tmpp)]_2[Hg_2X_6]$ and $[Hg(tmpp)_2][Hg_2X_6]$ {Found: C, 32.5; H, 3.2. Calc. for 1:1 mixture of $[HgCl(tmpp)]_2[Hg_2Cl_6]$ ($C_{54}H_{66}Cl_8Hg_4O_{18}P_2$) and $[Hg(tmpp)_2][Hg_2Cl_6]$ ($C_{54}H_{66}Cl_6Hg_3O_{18}P_2$): C, 32.9; H, 3.4. Found: C, 28.6; H, 2.9. Calc. for 1:1 mixture of $[HgBr(tmpp)]_2[Hg_2Br_6]$ ($C_{54}H_{66}Br_8Hg_4O_{18}P_2$) and $[Hg(tmpp)_2][Hg_2Br_6]$ ($C_{54}H_{66}Br_6Hg_3O_{18}P_2$): C, 28.1; H, 2.9%}. For the X = I case, the ^{31}P NMR and vibrational spectra indicate that $[HgI(tmpp)]_2[Hg_2I_6]$ is the predominant species {Found: C, 21.6; H, 2.1. Calc. for $[HgI(tmpp)]_2[Hg_2I_6]$ ($C_{54}H_{66}Hg_4I_8O_{18}P_2$): C, 22.5; H, 2.3%}.

Structure Determination.—A crystal suitable for X-ray crystal structure determination was selected from the product of the tmpp–$HgCl_2$ reaction.

A unique data set was measured at ≈295 K within the limit $2\theta_{max} = 50°$ using an Enraf–Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; 2θ–θ scan mode) yielding 5719 independent reflections, 3461 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement. Analytical absorption corrections were applied. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals on $|F|$ at convergence were $R = 0.047$, $R' = 0.046$ [statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral-atom complex scattering factors were employed,[37] computation using the XTAL 3.0 program system.[38] Pertinent results are quoted in Fig. 1 and in Tables 1 and 2.

Crystal/refinement data for $[Hg(tmpp)_2][Hg_2Cl_6]$. $C_{54}H_{66}Cl_6Hg_3O_{18}P_2$, $M = 1879.6$, monoclinic, space group $C2/c$ (C_{2h}^6, no. 15), $a = 32.767(5)$, $b = 11.500(2)$, $c = 23.814(4)$ Å, $\beta = 133.57(1)°$, $U = 6501$ Å^3, D_c ($Z = 4$) = 1.92 g cm^{-3}, $F(000) = 3400$, $\mu_{Mo} = 71$ cm^{-1}, specimen 0.34 × 0.26 × 0.10 mm, $A^*_{min,max} = 2.09, 5.24$.

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

Spectroscopy.—Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as pressed polythene discs on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 6.25 μm mylar film beam splitter, a mercury lamp source and a TGS detector. Solution ^{31}P-{^1H} NMR spectra were obtained at room temperature on a Bruker AM-400 spectrometer at a frequency of 161.98 MHz. Chemical shifts were referenced to 85% H_3PO_4 *via* trimethylphosphite (δ = 139.2).

Results and Discussion

The single-crystal X-ray diffraction, ^{31}P NMR, and vibrational spectroscopic results to be discussed in more detail below indicate that tmpp and HgX_2 interact in CH_3CN solution to form the cationic species $[HgX(tmpp)]^+$ and $[Hg(tmpp)_2]^{2+}$ with $[Hg_2X_6]^{2-}$ counterions. The complexes $[HgX(tmpp)]_2[Hg_2X_6]$ (=$2HgX_2\cdot$tmpp) and $[Hg(tmpp)_2][Hg_2X_6]$ (=$3HgX_2\cdot$2tmpp) correspond to HgX_2:tmpp mole ratios of 2 and 1.5 respectively. In order to try to obtain crystals of the first of these two compound types, solids were crystallized from solutions of HgX_2 and tmpp in a 2:1 mole ratio in CH_3CN. However, the analytical and vibrational spectroscopic data indicate that the solids obtained when X = Cl or Br contain both of these compound types, and only in the X = I case is the first predominant. In the X = Cl case, the presence of $[Hg(tmpp)_2][Hg_2Cl_6]$ in the product was confirmed by an X-ray crystal structure determination carried out on a crystal selected from it.

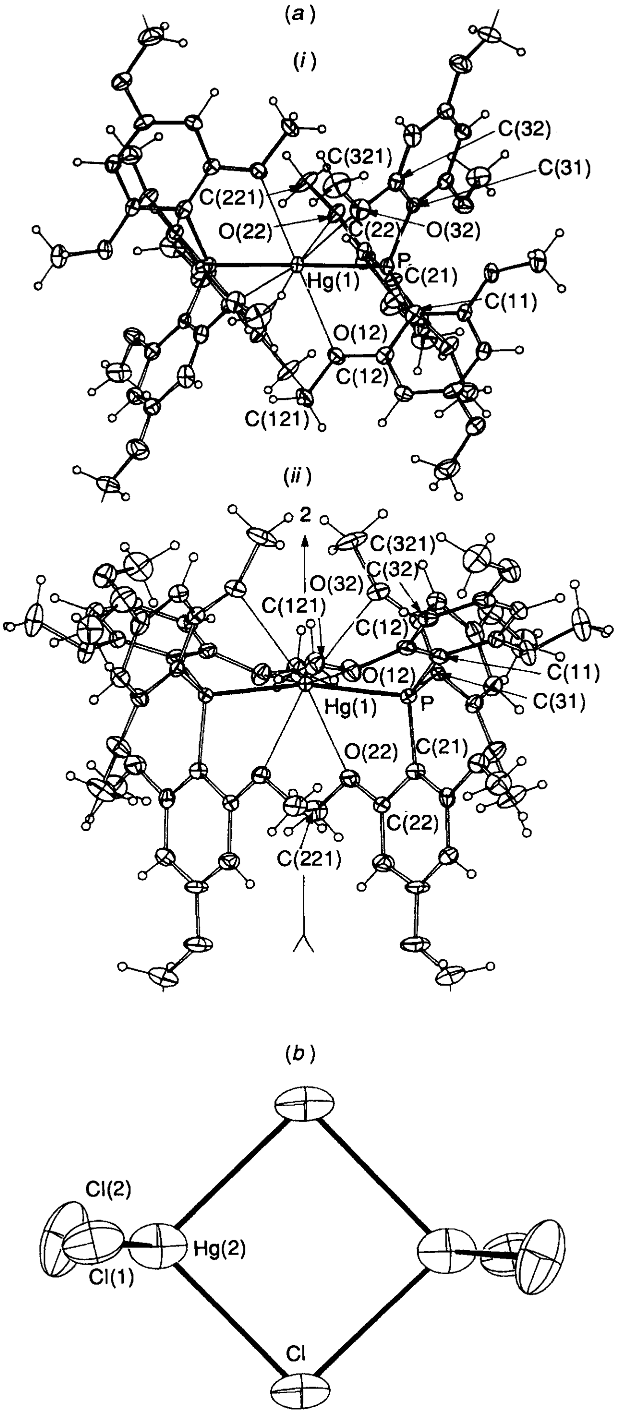


Fig. 1 The structure of $[Hg(tmpp)_2][Hg_2Cl_6]$. (*a*) The cation projected (*i*) down and (*ii*) normal to the two-fold axis. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. (*b*) The anion, projected normal to the central Hg_2Cl_2 plane

Table 1 Non-hydrogen atom coordinates for $[Hg(tmpp)_2][Hg_2Cl_6]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	1/2	0.219 38(5)	3/4	C(241)	0.578 8(6)	−0.385(1)	0.697 1(9)
P	0.519 9(1)	0.195 0(2)	0.671 3(2)	C(25)	0.579 8(5)	−0.137 7(9)	0.700 2(7)
C(11)	0.583 8(4)	0.275 1(9)	0.714 8(7)	C(26)	0.575 0(4)	−0.016 7(9)	0.696 2(6)
C(12)	0.624 1(4)	0.290 8(8)	0.793 3(6)	O(26)	0.615 0(3)	0.053 2(6)	0.710 9(5)
O(12)	0.611 9(3)	0.242 9(6)	0.833 3(4)	C(261)	0.668 9(5)	0.010(1)	0.752 3(8)
C(121)	0.652 0(5)	0.255(1)	0.916 0(7)	C(31)	0.460 5(4)	0.246 6(8)	0.573 9(6)
C(13)	0.673 8(4)	0.347 9(9)	0.829 5(6)	C(32)	0.436 4(5)	0.354 2(9)	0.565 2(7)
C(14)	0.682 8(4)	0.386 9(8)	0.783 7(7)	O(32)	0.461 9(3)	0.410 9(6)	0.634 3(5)
O(14)	0.730 4(3)	0.445 4(7)	0.813 3(5)	C(321)	0.435 6(6)	0.516(1)	0.630 3(9)
C(141)	0.773 0(6)	0.467(1)	0.895 1(9)	C(33)	0.390 6(5)	0.396 3(9)	0.494 8(7)
C(15)	0.644 4(5)	0.367 6(9)	0.704 7(7)	C(34)	0.367 2(5)	0.333(1)	0.429 9(7)
C(16)	0.594 9(4)	0.310 6(8)	0.669 9(6)	O(34)	0.320 6(4)	0.379 3(8)	0.359 8(5)
O(16)	0.554 8(3)	0.285 2(7)	0.592 7(4)	C(341)	0.291 1(5)	0.315(1)	0.292 7(7)
C(161)	0.554 3(6)	0.345(1)	0.539 4(9)	C(35)	0.388 3(5)	0.223(1)	0.434 9(6)
C(21)	0.528 4(4)	0.039 5(8)	0.673 9(6)	C(36)	0.437 0(5)	0.184 1(9)	0.510 1(7)
C(22)	0.486 6(4)	−0.028 7(8)	0.658 5(6)	O(36)	0.462 2(3)	0.083 6(7)	0.518 9(4)
O(22)	0.441 7(3)	0.027 6(6)	0.637 6(5)	C(361)	0.430 1(6)	−0.008(1)	0.464 4(8)
C(221)	0.396 9(5)	−0.038(1)	0.621 0(8)	Hg(2)	0.773 68(3)	−0.155 71(6)	0.964 62(4)
C(23)	0.489 9(5)	−0.149 7(9)	0.660 6(7)	Cl	0.683 0(2)	−0.277 8(4)	0.898 3(2)
C(24)	0.537 1(5)	−0.201 1(8)	0.681 8(7)	Cl(1)	0.746 7(2)	0.038 5(3)	0.955 8(3)
O(24)	0.536 3(4)	−0.319 3(6)	0.683 0(6)	Cl(2)	0.826 9(2)	−0.232 8(4)	0.940 6(4)

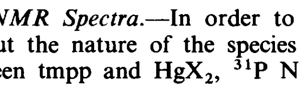
Table 2 Selected bond lengths (Å) and angles (°) for $[Hg(tmpp)_2]$-$[Hg_2Cl_6]$

Cation		Anion	
Hg–P	2.389(5)	Hg(2)–Cl′	2.620(5)
Hg · · · O(12)	2.726(9)	Hg(2)–Cl(1)	2.357(4)
Hg · · · O(22)	2.938(7)	Hg(2)–Cl(2)	2.35(1)
Hg · · · O(32)	3.044(9)	Hg(2) · · · Hg(2′)	3.682(2)
		Hg(2)–Cl	2.614(4)
P–Hg–P″	166.51(9)	Cl′–Hg(2)–Cl(1)	103.6(2)
P–Hg · · · O(12)	67.9(2)	Cl′–Hg(2)–Cl(2)	109.7(2)
P–Hg · · · O(22)	63.6(3)	Cl–Hg(2)–Cl′	90.6(2)
P–Hg · · · O(32)	62.5(2)	Cl(1)–Hg(2)–Cl(2)	129.1(2)
P–Hg · · · O(12″)	113.5(2)	Cl(1)–Hg(2)–Cl	104.8(2)
P–Hg · · · O(22″)	105.6(3)	Cl(2)–Hg(2)–Cl	112.1(2)
P–Hg · · · O(32″)	129.2(3)	Hg(2)–Cl–Hg(2′)	89.4(1)

Symmetry operations: ′ $1.5 - x, -0.5 - y, 2 - z$; ″ $1 - x, y, 1.5 - z$.

X-Ray Crystal Structure Determination.—$[Hg(tmpp)_2][Hg_2Cl_6]$ crystallizes in the monoclinic space group *C*2/*c* with one half of the formula unit comprising the asymmetric unit of the structure. The structure of the cation is shown in Fig. 1(*a*), and the structural parameters which define the mercury environments in the cation and anion are given in Table 2. The cation has C_2 symmetry, and the mercury atom environment in this ion is dominated by a close association with the phosphorus atoms of the two attached ligands in a quasi-linear P–Hg–P array. Significant deviations from linearity arise, presumably because of contacts with the methoxy oxygen atoms. The structural parameters for the P–Hg–P units are Hg–P 2.389(5) Å, P–Hg–P 166.51(9)°. These can be compared with the corresponding parameters Hg–P 2.451(1) Å, P–Hg–P 131.76(3)° in $[Hg(NO_3)_2(PPh_3)_2]$.[30] In this latter complex, the P–Hg–P entity is strongly bent due to the presence of two nitrate ions in the mercury co-ordination sphere, and Hg–P is longer, in keeping with the higher co-ordination number. The Hg · · · O contacts involving the nearest *ortho*-methoxy oxygen atoms on the three phenyl groups in each ligand are 2.726(9), 2.938(7), 3.044(9) Å. These can be compared with the Hg · · · O contacts of 2.507(4), 2.790(4) Å involving the co-ordinated nitrate groups in $[Hg(NO_3)_2(PPh_3)_2]$.[30] The closest contact is significantly longer in the tmpp complex, consistent with the greater P–Hg–P angle and the shorter Hg–P distance in this complex. The Hg–P distance is similar in magnitude to those observed in $[HgX(NO_3)(PPh_3)]$ [2.372(1)–2.402(2) Å] (X = Cl, Br or I) which contain nearly linear P–Hg–X units with P–Hg–X bond angles in the range 158.44(6)–166.17(5)°, and only weakly co-ordinated nitrate units.[36] These results suggest that the steric bulk of the tmpp ligands forces the Hg atom to adopt a nearly linear two-co-ordinate geometry, slightly modified by secondary interactions with the *ortho*-methoxy oxygen atoms. The $[Hg_2Cl_6]^{2-}$ anions have a structure of C_i symmetry in which two mercury atoms with tetrahedral $HgCl_4$ co-ordination are linked by sharing two bridging Cl atoms. The structural parameters for this anion are similar to those found previously for this species in compounds with different cations.[39]

The present complex has the same stoichiometry as complexes of the type $[Hg_3X_6L_2]$ which have been reported for other phosphine ligands,[1] and for which structures similar to **A** and **B** above for $[Hg_2X_4L_2]$ can be postulated. The structure of the isomer corresponding to **B** is given by **C**.



C

The structure of the present complex can be regarded as a limiting case of **C** in which the high basicity and steric bulk of L precludes any interaction of the attached Hg atom with the neighbouring halogen atoms, so that the complex separates completely into $[HgL_2]^{2+}$ and $[Hg_2X_6]^{2-}$ units.

Solution ^{31}P *NMR Spectra.*—In order to obtain further information about the nature of the species formed in the interaction between tmpp and HgX_2, ^{31}P NMR spectra of mixtures of these two compounds dissolved in CH_3CN were obtained. The spectra of 1 : 1 mixtures consisted of signals from two species, each of which showed a single central line due to species which contain the non-magnetic isotopes of Hg, together with satellites which are assigned to $^1J(^{199}Hg^{31}P)$ coupling (^{199}Hg, 16.84% natural abundance, nuclear spin $I = \frac{1}{2}$). The ^{31}P NMR parameters for one of these species are strongly halogen-dependent, and are assigned to the species $[HgX(tmpp)]^+$. The parameters for the other species are almost completely halogen-independent, and are assigned to the species $[Hg(tmpp)_2]^{2+}$. The $\delta(^{31}P)$ and $^1J(^{199}Hg^{31}P)$ values for these species are given in Table 3. The assignment of the signals with halogen-dependent parameters to $[HgX(tmpp)]^+$ is supported by comparison of the $^1J(^{199}Hg^{31}P)$ values with those of

$[HgX(PPh_3)]^+$ in the same solvent.[36] The values for the X = I complexes are almost identical, while those for X = Br, Cl are 9 and 15% higher respectively in the tmpp complexes. The assignment of the signals with halogen-independent parameters to $[Hg(tmpp)_2]^{2+}$ was verified by recording the spectrum of $[Hg(tmpp)_2][NO_3]_2$ in CH_3CN. This gave a signal with $\delta(^{31}P) = -30.62$, $^1J(^{199}Hg^{31}P) = 5212$ Hz. In the solutions containing tmpp and HgX_2 in a 1:1 mole ratio, the relative amounts of $[HgX(tmpp)]^+$ and $[Hg(tmpp)_2]^{2+}$ are dependent on X. For X = Cl, these two species are present in approximately equal amounts, but the proportion of $[Hg(tmpp)_2]^{2+}$ decreases from 50 to about 13% from X = Cl to I. The proportion of $[Hg(tmpp)_2]^{2+}$ is increased by addition of further tmpp in accordance with equilibrium (1). However, the position

$$[HgX(tmpp)]^+ + tmpp \rightleftharpoons [Hg(tmpp)_2]^{2+} + X^- \quad (1)$$

of equilibrium in the 1:1 mixtures appears to be unaffected by the addition of excess of HgX_2. Thus, a solution of $HgCl_2$ and tmpp in the ratio 2:1 gave a spectrum essentially the same as that for the ratio 1:1. This indicates that equilibrium (2)

$$[Hg(tmpp)_2]^{2+} + HgX_2 \rightleftharpoons 2[HgX(tmpp)]^+ \quad (2)$$

lies well to the left. In agreement with this, it was found that addition of $HgCl_2$ to a solution of $[Hg(tmpp)_2][NO_3]_2$ in CH_3CN resulted in no signal due to $[HgX(tmpp)]^+$, and it was found not to be possible to prepare $[HgX(tmpp)][NO_3]$ by this method, despite the fact that the corresponding PPh_3 complexes can be prepared in an analogous reaction.[36]

The complexes $[HgX(tmpp)]^+$ which have been detected in this study are valence isoelectronic with the corresponding neutral copper(I) and silver(I) complexes [CuX(tmpp)] and [AgX(tmpp)].[33,34] The ^1J(MP) values measured from the ^{31}P NMR spectra of the X = Cl species are compared in Table 4. In order to compare these coupling constants more directly, the effect of the different magnetic moments of the metal nuclei has been eliminated by dividing by the magnetogyric ratio γ of the metal nucleus concerned (the γ value which was used for the copper nucleus is the weighted mean of those for the naturally occurring isotopes ^{63}Cu, ^{65}Cu since separate signals for the two isotopes were not resolved in the solid-state NMR spectra from which the coupling constants are measured). This yields a reduced coupling constant J_r which is essentially the magnitude of the magnetic field at the metal nucleus which is induced by the magnetic moment of the phosphorus nucleus by means of the Fermi contact interaction between the nuclei and the electrons in the M–P bond. Since this arises from the Fermi contact interaction, it depends on the contributions of the phosphorus and the metal valence s orbitals to the M–P bonds. The complexes which are compared in Table 4 have the same ligand, so the phosphorus s-orbital contribution should be similar in all cases. Thus, the values of J_r should be a reflection of the metal valence s-orbital density at the metal nucleus. The results in Table 4 show that this quantity increases progressively from the copper(I) to the mercury(II) complex, in accordance with the expectation that metal s-electron density should increase with increasing atomic mass, and also with increasing nuclear charge. The factor by which J_r increases from Ag to Hg is greater than that from Cu to Ag because both influences mentioned above are operating in the former case.

Vibrational Spectra.—The presence of $[HgX(tmpp)]^+$ and $[Hg_2X_6]^{2-}$ species in the solid products crystallized from 2:1 solutions of HgX_2 and tmpp in CH_3CN was confirmed by their far-infrared spectra, which are shown in Fig. 2. The analytical data for the product from the X = I reaction indicate that this consists mainly of a compound of 2:1 HgX_2:tmpp stoichiometry. The solution ^{31}P NMR results (see above) show that the predominant tmpp-containing species in solution is $[HgI(tmpp)]^+$. The presence of this species in the solid product is confirmed by its far-IR spectrum (Fig. 2). The sharp band at 178

Table 3 Solution (CH_3CN) ^{31}P NMR parameters for complexes formed between tmpp and mercury(II) halides

	$[HgX(tmpp)]^+$		$[Hg(tmpp)_2]^{2+}$	
X	δ	$^1J(^{199}Hg^{31}P)$/Hz	δ	$^1J(^{199}Hg^{31}P)$/Hz
Cl	−30.21	9190	−30.70	5217
Br	−26.62	8405	−30.84	5219
I	−24.59	6839	−30.76	5275

Table 4 Comparison of ^1J(MP) from ^{31}P NMR spectra of isostructural copper(I), silver(I) and mercury(II) complexes with tmpp

Complex	Metal nucleus M	Magnetogyric ratio $\gamma/10^7$ T^{-1} s^{-1}	^1J(MP)/ Hz	$10^6 J_r$/ T^a	Ref.
$[CuCl(tmpp)]^b$	$^{63,65}Cu$	7.247^c	2040	28	31
[AgCl(tmpp)]	^{109}Ag	−1.250	821	66	34
$[HgCl(tmpp)]^+$	^{199}Hg	4.815	9190	191	*d*

[a] $J_r = |J/\gamma|$. [b] From solid-state ^{31}P cross-polarisation magic angle spinning (CP MAS) NMR spectrum. [c] The weighted mean of the values for the two isotopes was used in this case (see text). [d] This work.

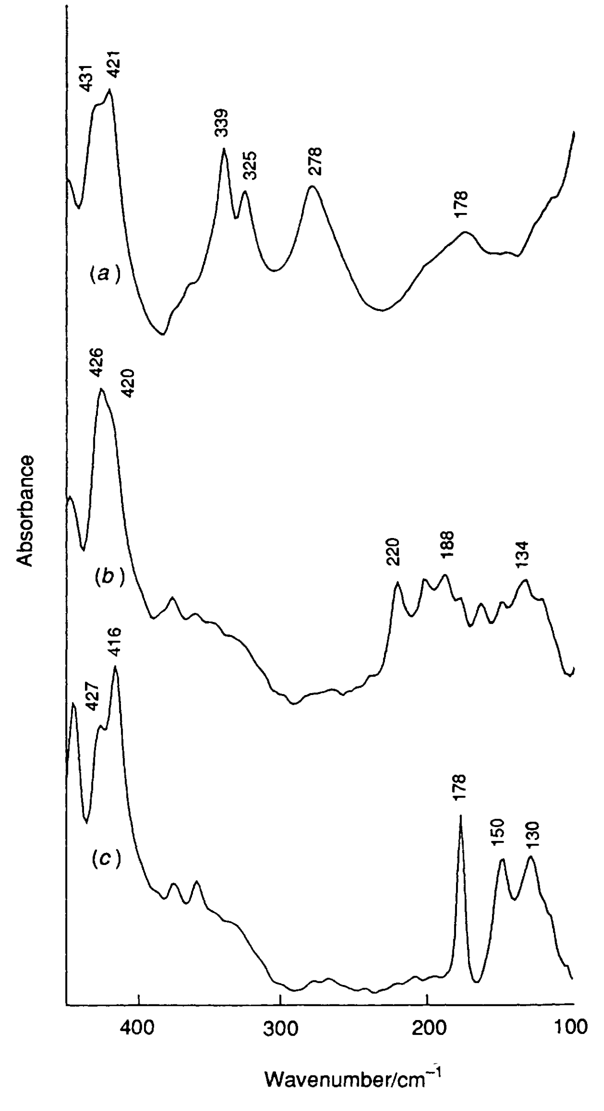


Fig. 2 Far-infrared spectra of solid products of the reaction of tmpp with HgX_2 in a 1:2 mole ratio; X = Cl (*a*), Br (*b*) or I (*c*)

Table 5 Values of ν(HgX) (cm^{-1}) for $[HgXL]^+$ species

L	X = Cl	Br	I	Ref.
PPh_3	322	231	189	36
tmpp	339, 325	220	178	This work
PMe_3	319	205	166	40

Table 6 Vibrational bands (wavenumbers/cm^{-1}) assigned to $[Hg_2X_6]^{2-}$ species in tmpp–HgX_2 reaction products and in $[NR_4]_2[Hg_2X_6]$

Species	tmpp–HgX_2	$[NR_4]_2[Hg_2X_6]$*	Assignment
$[Hg_2Cl_6]^{2-}$	278	290, 275	$\nu(HgCl_t)$
	178	198, 161	$\nu(HgCl_{br})$
$[Hg_2Br_6]^{2-}$	202, 188, 178	194, 181	$\nu(HgBr_t)$
	164, 150, 134	154,135	$\nu(HgBr_{br})$
$[Hg_2I_6]^{2-}$	150, 130	148, 135	$\nu(HgI_t)$
		107, 92	$\nu(HgI_{br})$

* R = Bu, X = Cl or Br; R = Pr, X = I; data from ref. 39.

cm^{-1} is assigned as ν(HgI) of $[HgI(tmpp)]^+$. This is close to the value (189 cm^{-1}) observed in the corresponding PPh_3 complex.[36] The two broader bands at 150 and 130 cm^{-1} are assigned to the $[Hg_2I_6]^{2-}$ complex which is present as the counter ion. These wavenumbers compare well with the values previously reported for this species in $[NPr_4]_2[Hg_2I_6]$ (148, 135 cm^{-1}) and in $[NEt_4]_2[Hg_2I_6]$ (152, 135 cm^{-1}) which have been assigned as $\nu(HgI_t)$, the vibrations of the terminal Hg–I bonds.[39] The vibrations $\nu(HgI_{br})$ involving the bridging iodine atoms should occur at about 100 cm^{-1}, but are very weak and broad in the IR.[39] Another possible counter-ion which would maintain the overall 2:1 HgX_2:tmpp stoichiometry is the mononuclear $[HgI_3]^-$ species. The ν(HgI) vibrations of this species occur at 160 and 154 cm^{-1} in $[NBu_4][HgI_3]$,[39] and these do not agree very well with the wavenumbers observed in the tmpp complex. This complex is therefore formulated as $[HgI(tmpp)]_2[Hg_2I_6]$. The analytical data for the chloro and bromo complexes indicate that these are mixtures of $[HgX(tmpp)]_2[Hg_2X_6]$ and $[Hg(tmpp)_2][Hg_2X_6]$, and their far-IR spectra contain bands which can be assigned to ν(HgX) of $[HgX(tmpp)]^+$ and $[Hg_2X_6]^{2-}$ (Tables 5 and 6). The ν(HgX) wavenumbers in the cations are compared in Table 5 with those of the related $[HgXL]^+$ (L = PPh_3 or PMe_3) species. For the X = Br or I cases, the values for the tmpp complex lie between those of the other two. For the X = Cl case, two bands are observed, and both lie above the values for the other two complexes. It would be expected that the ν(HgX) wavenumbers in $[HgXL]^+$ would reflect the *trans* influence of the ligand L, as do the ν(AuX) values in [AuXL].[41] The *trans* influence is determined by the σ-donor strength of the ligand, and the results for the X = Br, I complexes in Table 5 indicate that the σ-donor strength for tmpp is intermediate between those for PPh_3 and PMe_3. The reason for the anomalous behaviour of the chloro complex is not understood at present. The ν(HgX) values assigned to the $[Hg_2X_6]^{2-}$ species in the tmpp–HgX_2 reaction products agree well with those previously reported for $[NBu_4]_2[Hg_2X_6]$[39] (Table 6). For the X = Cl, Br complexes, bands due to the bridging modes $\nu(HgX_{br})$ are seen as well as those due to the terminal modes $\nu(HgX_t)$. These assignments are verified in the X = Cl case by the identification by X-ray diffraction of $[Hg(tmpp)_2][Hg_2Cl_6]$ as one component of the reaction product (see above).

Conclusion

Other studies have demonstrated the ability of the tmpp ligand to displace halide ion from copper(I) or silver(I) halides to produce ionic complexes.[34,42,43] The present results for the mercury(II) halides provide further examples of this type of behaviour, and this contrasts with that of the less basic and less sterically hindered triphenylphosphine ligand, which only forms neutral adducts with HgX_2. However, the present results are similar to those reported previously for complexes of HgX_2 with the more basic ligand trimethylphosphine, PMe_3.[44] Thus, the structure of the 2:3 complex of PMe_3 with HgI_2 can be described as comprising of $[Hg(PMe_3)_2]^{2+}$ cations linked *via* weak Hg–I interactions to four $[HgI_3]^-$ anions which are themselves linked to form $[Hg_2I_6]^{2-}$ dimers.[44] This bears some similarity to the structure determined in the present study for $[Hg(tmpp)_2][Hg_2Cl_6]$, which is likewise an adduct of 2:3 stoichiometry. In the latter case, however, the steric requirements of the ligand preclude any interaction between the anion and the cation, whereas the presence of such interactions in the PMe_3 complex results in an overall structure consisting of a two-dimensional network of interlinked chains.[44]

Acknowledgements

We acknowledge support of this work by grants from the New Zealand University Grants Committee, the University of Auckland Research Committee, and the Australian Research Grants Scheme. We thank Dr. D. Camp and Dr. P. C. Healy for supplying the tmpp ligand.

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Received 4*th June* 1993; *Paper* 3/03194B