Crystal and Molecular Structures of Novel Polynuclear Complex Halogeno-anions Containing Mercury and Platinum or Palladium: $[Et_4N]_2Hg_2PtCl_8$, $[Et_4N]_2Hg_3PtCl_{10}$ and $[Et_4N]_2Hg_3PdCl_{10}$

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Summary The crystal structure of $[Et_4N]_2Hg_2PtCl_8$ contains centrosymmetric trinuclear anions linked by chloride bridges involving the terminal HgCl bonds; in $[Et_4N]_2Hg_3MCl_{10}$ (M = Pd or Pt) the same type of trinuclear anions are linked by the HgClM bridging chlorine atoms *via* linear $HgCl_2$ units.

Trihalogenomercurates of alkali metal cations are polymeric and the tendency to associate extends also to certain tetra-alkylammonium salts,[1] but only in the case of the unusual $[(Ph_3AsO)_2H]_2[Hg_2Br_6]$ is a discrete dimeric anion formed.[2] On the other hand, trihalogenopalladates(II) and trihalogenoplatinates(II) exist only as binuclear compounds $[R_4N]_2[M_2Cl_6]$ (M = Pd or Pt).[3,4] It was therefore of interest to attempt the synthesis of halogeno-anions containing palladium or platinum halogen-bridged to mercury, particularly in view of the differing stereochemical preferences of these metals.

Interaction of aqueous solutions of K_2PtCl_4 with $[Et_4N]_2HgCl_4$ (1 : 1), $[Et_4N]HgCl_3$ and $[Et_4N]Cl$ (1 : 1 : 1), or $HgCl_2$ and $[Et_4N]Cl$ (1 : 1 : 2), followed by slow evaporation afforded either $[Et_4N]_2Hg_2PtCl_8$ (I) or $[Et_4N]_2Hg_3PtCl_{10}$ (II) depending on the concentration of the solutions. From K_2PdCl_4 + $HgCl_2$ + $2[Et_4N]Cl$ in water, the only complex which could be isolated was $[Et_4N]_2Hg_3PdCl_{10}$ (III). In an attempt to deduce the structures of these compounds, we studied their far-i.r. spectra in the ν(HgCl) and ν(PdCl) or ν(PtCl) regions, but the results were confusing. We therefore undertook full structure determinations of all three complexes prepared.

Crystals of $C_{16}H_{40}N_2Hg_2PtCl_8$ (I) are monoclinic; a = 10·43(2), b = 9·80(2), c = 15·12(3) Å, β = 91·0(1)°; space group $P2_1/c$; D_m = 2·39 g cm^{-3}, D_c = 2·45 g cm^{-3} for

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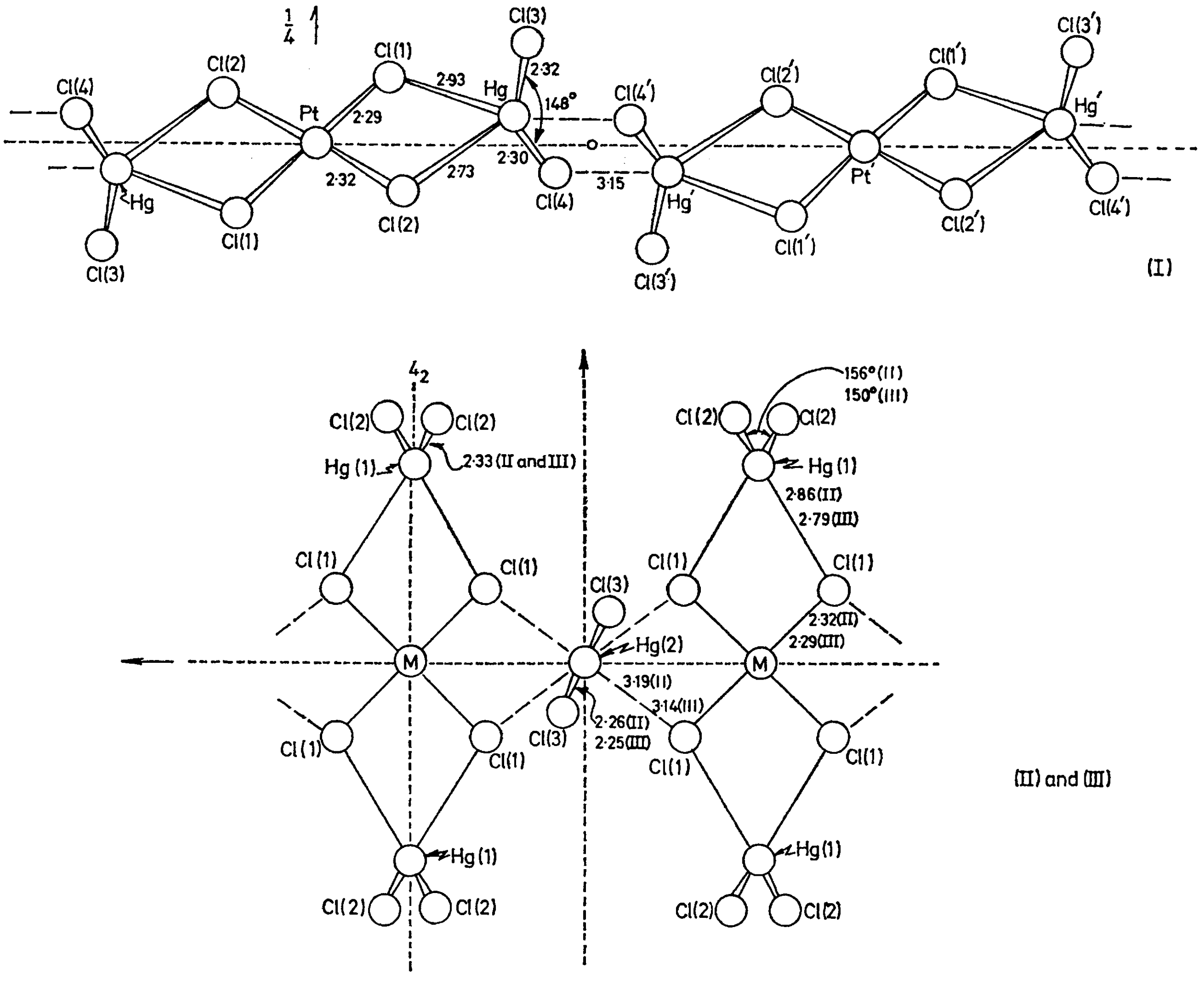

FIGURE. Structure of the $[Hg_2MCl_8]^{2-}$ anions in $[Et_4N]_2Hg_2PtCl_8$ (I), $[Et_4N]_2Hg_3PtCl_{10}$ (II) and $[Et_4N]_2Hg_3PdCl_{10}$ (III), showing long bonding interactions. All distances are in Å.

$Z = 2$. The intensities of 888 independent reflections (Mo-K_α radiation) were estimated visually and block diagonal least-squares refinement (all atoms except hydrogen) has given an R-value of 0·073.

Isomorphous crystals of $C_{16}H_{40}N_2Hg_3PtCl_{10}$ (II) and $C_{16}H_{40}N_2Hg_3PdCl_{10}$ (III) are tetragonal. For (II), $a =$ 8·71(2), $c =$ 22·81(5) Å; $D_m =$ 2·62 g cm^{-3}, $Z = 2$, $D_c =$ 2·71 g cm^{-3}. For (III), $a =$ 8·65(2), $c =$ 22·71(5) Å; $D_m =$ 2·51 g cm^{-3}, $Z = 2$, $D_c =$ 2·59 g cm^{-3}. The structures based on 428 (II) or 329 (III) independent visually estimated reflections (Mo-K_α radiation) have been refined in space group $P4_2/mmc$ (metal and halogen atoms only) to R-values of 0·12 (II) and 0·13 (III).‡

The common feature of all three complexes is the trinuclear anionic unit $[Hg_2MCl_8]^{2-}$ as shown in the Figure [M = Pt for (I) and (II), or M = Pd for (III)]. The anion in (I) is centrosymmetric and the anions in (II) and (III) have *mmm* symmetry. Bond lengths and angles in the MCl_2HgCl_2 units of these compounds (Figure) are comparable with those recently reported[5] for the binuclear neutral complex $(PhMe_2P)_2PtCl_2HgCl_2$.

The main differences between the structures of (I) and (II) or (III) are found in the long intermolecular bonds. In structure (I) the anions are linked to each other by bonds from *terminal* chlorine atoms [Hg–Cl(4') = 3·15(2) Å] to form polymeric zig-zag chain anions $[Hg_2PtCl_8]_n^{2n-}$. In structures (II) and (III) there are no such direct links between the anionic units, the closest contact between them being the Hg(1)–Hg(1') distance of 3·51(1) Å (II) or 3·48(1) Å (III) [these give a direct measure of the van der Waals' radius for mercury(II) as 1·75 Å]. In these structures the anionic units are linked sideways by bonds from their four *bridging* chlorine atoms to linear $HgCl_2$ groups (at special positions ½00, ½0½). The four crystallographically equiva-

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‡ The higher R-values for (II) and (III) arise because the metal atoms lie on the c-axis at intervals of almost exactly $c/6$ and thus only contribute to reflections where $l = 6n$; hence the missing carbon and nitrogen atoms contribute a relatively large amount to reflections where $l \neq 6n$. Without location of the light atoms the actual space group is not unambiguous, but the geometry of the anionic species is certain.

lent distances Hg(2)–Cl(1) are 3·19(3) Å for (II) or 3·14(3) Å for (III); this gives these mercury atoms characteristic distorted octahedral co-ordination. Effectively, polymeric anionic chains $[Hg_3MCl_{10}]_n^{2n-}$ are formed (M = Pd or Pt), half of which are parallel to the crystallographic *a* axis and the other half parallel to the *b* axis. The stoicheiometric addition of $HgCl_2$ as a linear $HgCl_2$ unit is clearly shown by the appearance of an intense $\nu_{as}(HgCl_2)$ i.r. band at *ca.* 371 cm^{-1}, close to the value observed (374 cm^{-1})[6] for crystalline $HgCl_2$ (which has a similar distorted octahedral Hg environment). The recently described compound $(Me_3P)_2PtCl_2(HgCl_2)_2$ shows an analogous strong i.r. band at 376 cm^{-1},[7] which suggests a structure closely related to that of the $[Hg_3MCl_{10}]_n^{2n-}$ anions reported here rather than the chain extended $(Me_3P)_2PtCl_2HgCl_2HgCl_2$ structure proposed.[7]

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