

## Preparation and Crystal Structure of $\text{Na}_4[\text{Hg}_4(\mu\text{-Cl})_4\{\text{P}(\text{O})(\text{OEt})_2\}_8]\cdot 6\text{H}_2\text{O}^\dagger$

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The title complex was obtained from an aqueous solution containing  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]$  and  $\text{NaCl}$ . The crystal and molecular structure has been determined by single-crystal X-ray diffraction. The molecular structure consists of discrete, eight-membered, centrosymmetric, nearly square  $(\text{Hg}-\text{Cl})_4$  rings with the mercury atoms positioned in the corners  $\text{Hg}-\text{Cl}$  (mean) 2.853 Å;  $\text{Cl}-\text{Hg}-\text{Cl}$  (mean) 89.7,  $\text{Hg}-\text{Cl}-\text{Hg}$  (mean) 166.0°. Two  $\text{P}(\text{O})(\text{OEt})_2$  ligands are co-ordinated to each mercury atom. The  $\text{Hg}-\text{P}$  bonds are nearly perpendicular to the ring  $[\text{Hg}-\text{P}$  (mean) 2.402 Å,  $\text{P}-\text{Hg}-\text{P}$  (mean) 165.7°].

The mercury atom in bis(dialkyl phosphonato-*P*)mercury compounds develops a considerable Lewis acidity. This is evident from relatively close phosphoryl oxygen-mercury contacts in the crystal structure of  $[\text{Hg}\{\text{P}(\text{O})(\text{OMe})_2\}_2]^1$  and the corresponding formation of dimers in solution,<sup>2</sup> as well as from the existence of co-ordination compounds  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]^{2-n}(\text{PR}_3)_n$  (e.g.  $\text{R} = \text{Bu}$  or  $\text{Ph}$ )<sup>3-5</sup> and  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]^{2-n}(n = 3 \text{ or } 4)$ .<sup>6</sup> We report here on  $\text{Na}_4[\text{Hg}_4(\mu\text{-Cl})_4\{\text{P}(\text{O})(\text{OEt})_2\}_8]$  representing a further example of a co-ordination compound of  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]$  and the first mixed phosphonato-*P* mercurate.

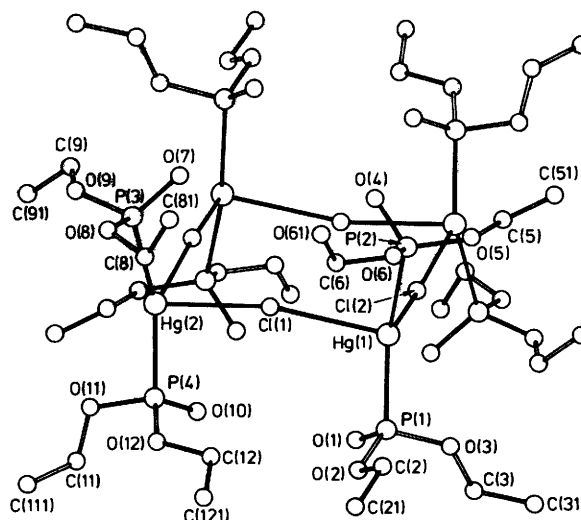
### Results and Discussion

Colourless crystals of the analytical composition  $\text{Na}[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2\text{Cl}]\cdot 1.5\text{H}_2\text{O}$  were isolated from an aqueous solution of  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]$  and  $\text{NaCl}$  (1:1). The crystal and molecular structure was determined using X-ray diffraction techniques. The fractional atomic co-ordinates and selected distances and angles are listed in Tables 1 and 2. The structure analysis reveals that the complex exists as discrete tetramers in the solid state (Figure 1): four mercury and four chlorine atoms form eight-membered  $(\text{Hg}-\text{Cl})_4$  heterocycles. The rings lie on crystallographically imposed centres of symmetry and are nearly square.

The mercury atoms are positioned in the corners. Two phosphonato-ligands are co-ordinated *via* phosphorus to each mercury atom; the mercury-phosphorus bonds are nearly perpendicular to the ring. All (eight) phosphoryl oxygen atoms are directed towards the centre of the ring. The environment around mercury is a very distorted tetrahedron resembling that of  $[\text{HgCl}_2(\text{PETe}_3)_2]$ .<sup>7</sup> The  $\text{Hg}-\text{Cl}$  bonds in the ring are very similar in length. Their separations are considerably less than the sums of the van der Waals radii (3.3 Å) but are very long compared with those of  $\text{HgCl}_2$  (2.25 Å). Mercury-chlorine distances of 2.8 Å were reported for the  $\text{Hg}-\text{Cl}-\text{Hg}$  bridges in  $\text{K}_2[\text{HgCl}_4]\cdot \text{H}_2\text{O}$ <sup>8</sup> and 2.88–3.11 Å for  $\text{Na}[\text{Hg}(\text{CN})_2\text{Cl}]\cdot \text{H}_2\text{O}$ .<sup>9</sup> The chlorine atoms form two approximately collinear bonds to mercury  $[\text{Hg}-\text{Cl}-\text{Hg}$  (mean) 166.0°]; the mercury

**Table 1.** Selected bond lengths (Å) and angles (°) (non-hydrogen atoms) with estimated standard deviations in parentheses

$\text{Hg}(1)-\text{P}(1)$	2.399(7)	$\text{Hg}(2)-\text{P}(3)$	2.409(8)
$\text{Hg}(1)-\text{P}(2)$	2.405(8)	$\text{Hg}(2)-\text{P}(4)$	2.395(7)
$\text{Hg}(1)-\text{Cl}(1)$	2.874(7)	$\text{Hg}(2)-\text{Cl}(1)$	2.863(7)
$\text{Hg}(1)-\text{Cl}(2)$	2.820(7)	$\text{Hg}(2)-\text{Cl}(2')$	2.855(6)
$\text{P}(1)-\text{O}(1)$	1.489(20)	$\text{Na}(1)-\text{O}(1w)$	2.383(25)
$\text{P}(1)-\text{O}(2)$	1.611(14)	$\text{Na}(1)-\text{Cl}(1)$	2.921(7)
$\text{P}(1)-\text{O}(3)$	1.585(17)	$\text{Na}(1)-\text{Cl}(2)$	2.766(7)
$\text{Hg}(1)-\text{Cl}(1)-\text{Hg}(2)$	165.0(4)	$\text{Cl}(1)-\text{Hg}(2)-\text{Cl}(2')$	88.9(2)
$\text{Hg}(1)-\text{Cl}(2)-\text{Hg}(2)$	167.1(4)	$\text{P}(1)-\text{Hg}(1)-\text{P}(2)$	166.6(2)
$\text{Cl}(1)-\text{Hg}(1)-\text{Cl}(2)$	90.4(2)	$\text{P}(3)-\text{Hg}(2)-\text{P}(4)$	164.8(2)



**Figure 1.** Molecular structure of  $[\text{Hg}_4(\mu\text{-Cl})_4\{\text{P}(\text{O})(\text{OEt})_2\}_8]^{4-}$

<sup>†</sup> Tetrasodium tetra- $\mu$ -chloro-octakis(diethyl phosphonato-*P*)tetramercurate(4-) hexahydrate.

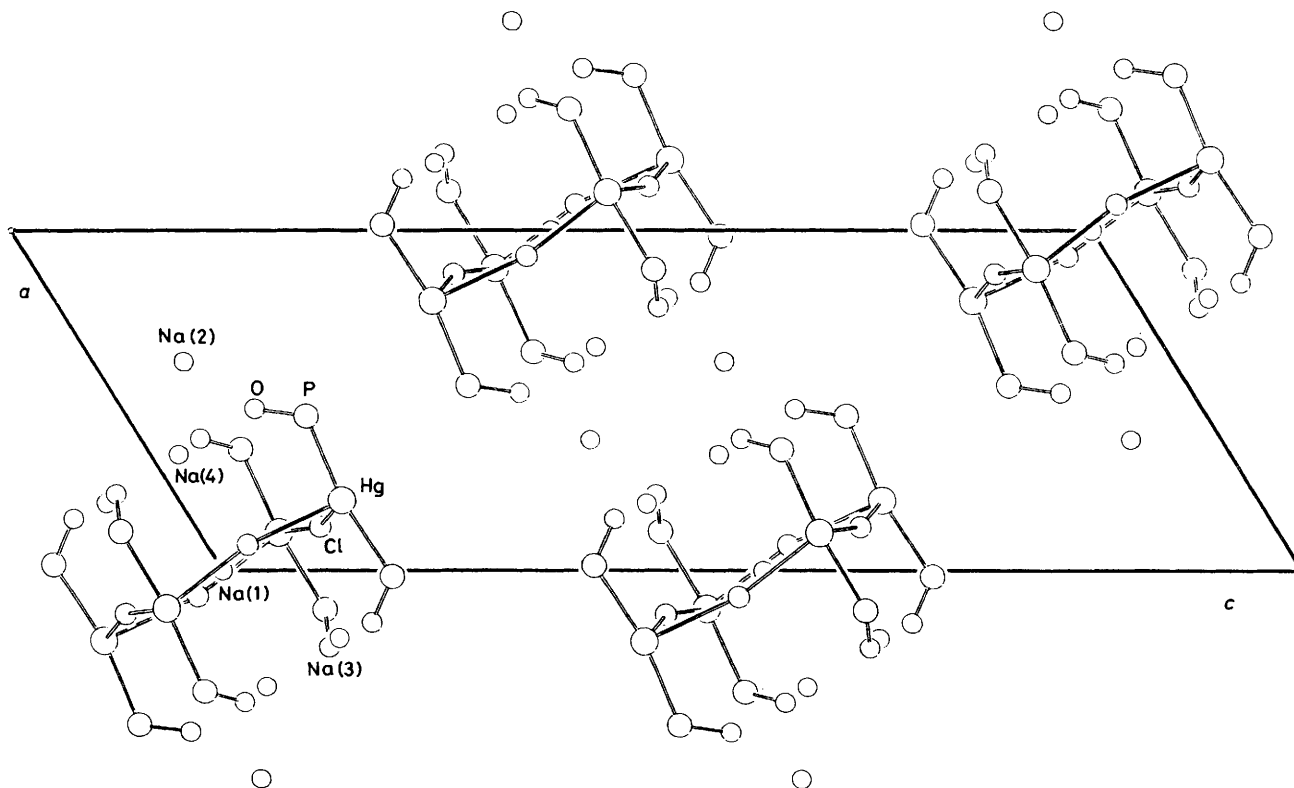
Supplementary data available (No. SUP 56164, 12 pp.): full atomic co-ordinates and thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

atoms form two essentially right-angled bonds to two chlorine atoms  $[\text{Cl}-\text{Hg}-\text{Cl}$  (mean) 89.7°]. The  $\text{Hg}-\text{P}$  bond length is very similar to that observed in  $[\text{Hg}\{\text{P}(\text{O})(\text{OMe})_2\}_2]$  (2.41 Å)<sup>1</sup> and  $[\text{HgCl}_2(\text{PETe}_3)_2]$  (2.39 Å).<sup>7</sup> The  $\text{P}-\text{Hg}-\text{P}$  bond angle deviates from the diagonal geometry as a consequence of the co-

**Table 2.** Fractional atomic co-ordinates for non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Hg(1)	0.206 26(9)	0.617 72(6)	0.150 37(3)	O(7)	-0.225(2)	0.300(1)	0.055(6)
P(1)	0.455 5(6)	0.614 9(4)	0.166 2(2)	O(8)	-0.072(2)	0.184(1)	0.131 2(7)
P(2)	-0.016 9(7)	0.642 9(4)	0.153 3(2)	O(9)	-0.188(2)	0.141(1)	0.036 5(8)
Cl(1)	0.128 2(7)	0.438 2(4)	0.115 1(3)	O(10)	0.388(2)	0.333(1)	0.055 4(6)
O(1)	0.477(2)	0.573(1)	0.122 6(6)	O(11)	0.377(2)	0.166 6(9)	0.069 7(6)
O(2)	0.572(2)	0.569(1)	0.225(6)	O(12)	0.483(2)	0.264(1)	0.152 0(6)
O(3)	0.503(2)	0.715(1)	0.175 4(7)	C(8)	0.008(4)	0.240(2)	0.183(1)
O(4)	-0.152(2)	0.597(1)	0.108 1(6)	C(81)	-0.087(4)	0.275(2)	0.195(1)
O(5)	-0.040(2)	0.745(1)	0.157 0(6)	C(9)	-0.261(6)	0.137(4)	-0.016(2)
O(6)	0.014(2)	0.620(1)	0.213 6(6)	C(91)	-0.193(5)	0.074(3)	-0.038(2)
C(2)	0.571(3)	0.603(2)	0.274(1)	C(11)	0.518(3)	0.147(2)	0.071(1)
C(21)	0.684(3)	0.558(2)	0.323(1)	C(111)	0.583(6)	0.069(3)	0.101(2)
C(3)	0.619(4)	0.752(3)	0.170(2)	C(12)	0.527(3)	0.345(2)	0.183(1)
C(31)	0.658(5)	0.845(3)	0.189(2)	C(121)	0.644(3)	0.332(2)	0.240(1)
C(5)	-0.097(4)	0.797(2)	0.103(1)	Na(1)	0.000 00	0.500 00	0.000 00
C(51)*	-0.161(8)	0.877(3)	0.098(3)	Na(2)	0.615(2)	0.567(1)	0.084 3(7)
C(6)	0.035(8)	0.529(3)	0.230(3)	Na(3)	-0.198(2)	0.454(1)	0.069 1(6)
C(61)	-0.036(5)	0.503(3)	0.257(2)	Na(4)	0.342(2)	0.611(1)	0.025 9(7)
Hg(2)	0.111 54(9)	0.263 76(6)	0.073 86(4)	O(1w)	0.236(2)	0.485(1)	0.006 6(8)
P(3)	-0.114 7(7)	0.225 7(4)	0.072 2(3)	O(2w)	0.541(2)	0.674(1)	0.030 9(8)
P(4)	0.356 9(6)	0.263 9(4)	0.086 5(2)	O(3w)	0.643(2)	0.436(1)	0.092 8(8)
Cl(2)	0.076 0(8)	0.671 2(4)	0.037 7(3)				

\* Alternative co-ordinates -0.024(8), 0.863(3), 0.116(3) (partial occupancy caused by crystallographic disorder).



**Figure 2.** Projection down *b*; only the Na, Hg, Cl, P, and phosphoryl O atoms are shown

ordination of two chlorine atoms.<sup>7,10</sup> The value is nearly identical to that in  $[\text{Hg}\{\text{P}(\text{O})(\text{OMe})_2\}_2]$  ( $165.9^\circ$ )<sup>1</sup> and even larger than that in  $[\text{HgCl}_2(\text{PEt}_3)_2]$  ( $158.5^\circ$ ).<sup>7</sup> The P=O length and the mean P-O bond length are in good agreement with those found in  $[\text{Hg}\{\text{P}(\text{O})(\text{OMe})_2\}]^1$  and  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}\text{Cl}]^2$ .

The centre of the (Hg-Cl)<sub>4</sub> ring is occupied by a sodium atom whose position resembles that in a 'crown ether.' The

mean of the Na-Cl distances is 2.843 Å, compared with 2.820 Å in rock salt. The co-ordination sphere of sodium is completed by two water oxygen atoms at 2.38 Å giving a distorted octahedral environment. Besides this sodium and oxygen atom [Na(1) and O(1w)] there were found five further peaks attributable to sodium or water oxygen atoms [Na(2)—Na(4), O(2w), O(3w)] in the asymmetric unit. The allocation of the

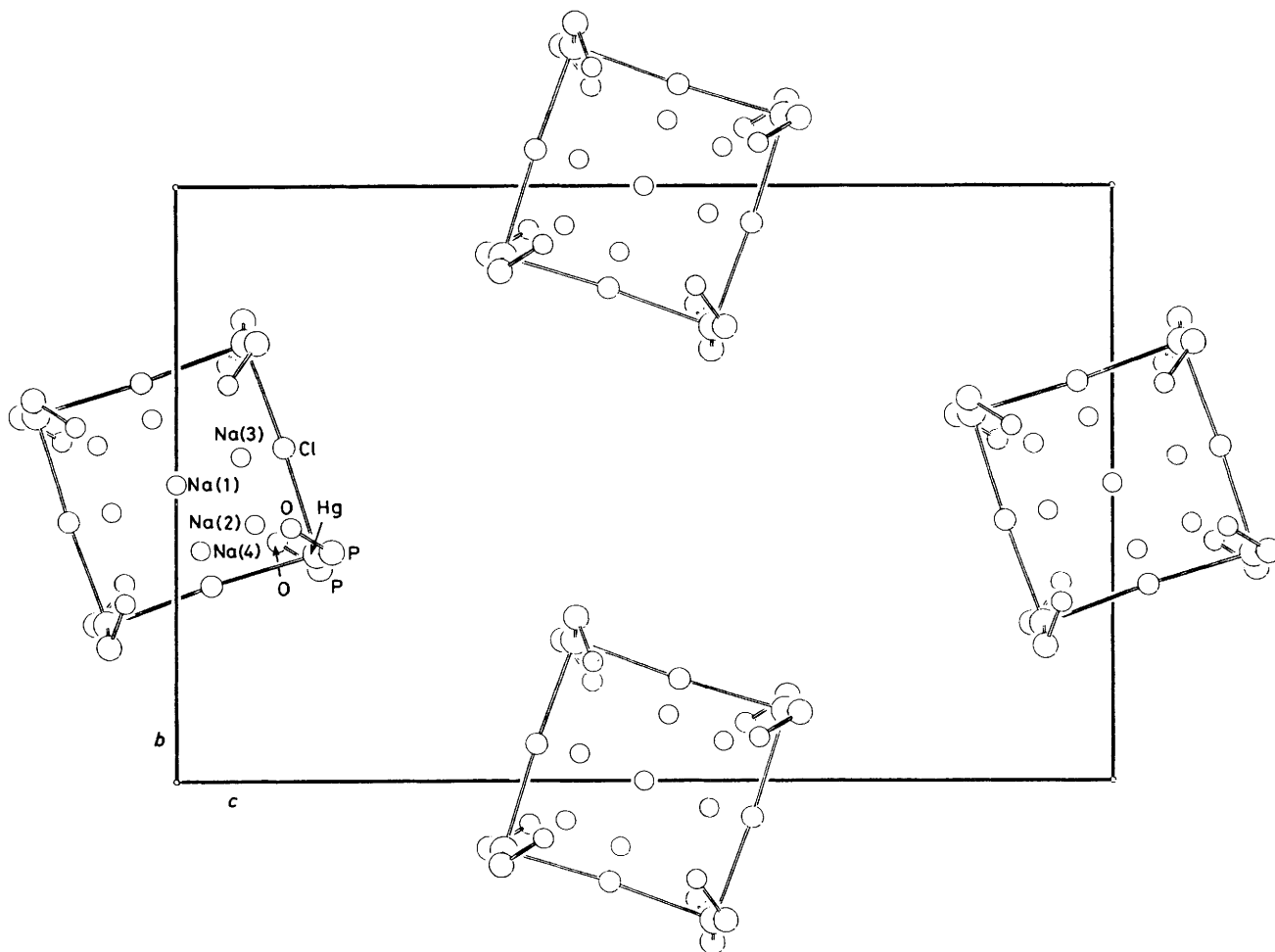


Figure 3. Projection down  $a$ , only the Na, Hg, Cl, P, and phosphoryl O atoms are shown

remaining three sodium atoms per ring (*i.e.* twice the asymmetric unit) requires the occupancy of only half of the positions Na(2), Na(3), Na(4), Na(2'), Na(3'), and Na(4'). The only modes of occupancy leading to reasonable Na–Na distances are Na(2), Na(3'), Na(4') or Na(2'), Na(3), Na(4). These three sodium atoms are located below or above the (Hg–Cl)<sub>4</sub> rings (Figures 2 and 3). The structural effect is the formation of chains parallel to the  $a$  axes, consisting of translated ring molecules held together by the sodium atoms in between. An alternating sequence of the two occupancy modes, *e.g.* [ring/Na(2), Na(3'), Na(4')/ring/Na(2'), Na(3), Na(4)]<sub>*n*</sub> along the cell direction  $a$  would mean that the observed cell is actually a supercell. Since no additional reflections could be detected, we suggest that there is crystallographic disorder with a statistical sequence of the occupancy modes Na(2), Na(3'), Na(4') and Na(2'), Na(3), Na(4) in the cell direction  $a$ . The sodium atoms Na(2)–Na(4) are co-ordinated by chlorine, water oxygen, and phosphoryl oxygen atoms.

Eight-membered (Hg–E)<sub>4</sub> ring systems were also reported for E = Se in the crystal structure of [Hg<sub>4</sub>(μ–SeEt)<sub>4</sub>Cl<sub>4</sub>(py)<sub>4</sub>] (py = pyridine)<sup>11</sup> and for E = P in solutions of various compounds [Hg<sub>4</sub>(μ–PR<sub>2</sub>)<sub>4</sub>L<sub>4</sub>].<sup>12–14</sup> It is interesting to note that the structural principle of the title compound, *i.e.* a (Hg–X)<sub>4</sub> ring (X = halogen) and terminal phosphorus ligands is just inverse to that of the complex [Hg<sub>4</sub>{μ–P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>}<sub>4</sub>X<sub>8</sub>]<sup>4–</sup> (C<sub>6</sub>H<sub>11</sub> = cyclohexyl)<sup>14</sup> involving a (Hg–P)<sub>4</sub> ring and terminal halogen atoms co-ordinated to mercury.

The addition of sodium chloride to an aqueous solution of

Table 3. N.m.r. data\* in aqueous solution (0.25 mol dm<sup>-3</sup>)

Compound	$\delta(^{199}\text{Hg})$	$^1J(^{199}\text{Hg}-^{31}\text{P})$	$\delta(^{31}\text{P})$
[Hg{P(O)(OEt) <sub>2</sub> }] <sub>2</sub>	1 032	7 521	107.0
Na[Hg{P(O)(OEt) <sub>2</sub> }] <sub>2</sub> Cl	1 194	7 718	107.5

\* Chemical shifts in p.p.m. to high frequency of aqueous Hg(ClO<sub>4</sub>)<sub>2</sub> (2 mmol HgO per cm<sup>3</sup> 60% HClO<sub>4</sub>) or 85% H<sub>3</sub>PO<sub>4</sub>; coupling constants are in Hz.

[Hg{P(O)(OEt)<sub>2</sub>}]<sub>2</sub> is accompanied by a high-frequency shift of the mercury-199 resonance (Table 3); corresponding results were obtained for the co-ordination of halide to HgX<sub>2</sub> or Hg(CN)<sub>2</sub> to produce HgX<sub>3</sub><sup>-</sup> or [Hg(CN)<sub>2</sub>X]<sup>-</sup>.<sup>15</sup> The co-ordination is also associated with a slight increase of the one-bond mercury–phosphorus coupling constant. A corresponding increase in  $^1J(^{199}\text{Hg}, ^{31}\text{P})$  is observed upon the addition of halide to [Hg(PR<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> to give [Hg(PR<sub>3</sub>)<sub>2</sub>X]<sup>+</sup>.<sup>16</sup> The position of  $\delta(^{31}\text{P})$  is virtually unaffected. The co-ordination of the halide ion is also indicated by a chlorine-35 relaxation time short enough to prevent the observation of a <sup>35</sup>Cl n.m.r. signal.<sup>17</sup> However, no evidence was found for the existence of oligomers being stable on the n.m.r. time-scale in keeping with the high kinetic lability of mercury–halogen bonds.<sup>18</sup>

Crystalline addition compounds may also be isolated from [Hg{P(O)(OEt)<sub>2</sub>}]<sub>2</sub> or [Hg{P(O)(OMe)<sub>2</sub>}]<sub>2</sub> with Group 1A,2A

(except for Be), or Group 2B (except for Hg which forms asymmetric compounds) metal halides (except for F) or pseudohalides.<sup>19</sup> Co-ordination compounds of  $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2\text{X}]$  are also formed.<sup>19</sup>

### Experimental

*Preparation of Tetrasodium Tetra- $\mu$ -chloro-octakis(diethyl phosphonato-P)tetramercurate(4-) Hexahydrate.*— $[\text{Hg}\{\text{P}(\text{O})(\text{OEt})_2\}_2]^{20}$  (237 mg, 0.5 mmol) and NaCl (29.2 mg, 0.5 mmol) were dissolved in  $\text{H}_2\text{O}$  ( $2\text{ cm}^3$ ). The solvent was evaporated at ambient temperature until the supersaturated solution started to crystallize. A clear solution was obtained upon heating to  $50^\circ\text{C}$ . The product crystallized upon slow cooling of the solution to room temperature. Yield 240 mg (86%), m.p.  $161\text{--}162^\circ\text{C}$  (decomp.) (Found: C, 17.2; H, 3.9. Calc. for  $\text{C}_{32}\text{H}_{92}\text{Cl}_4\text{Hg}_4\text{Na}_4\text{O}_{30}\text{P}_8$ : C, 17.2; H, 4.1%).

N.m.r. spectra were recorded on a multinuclear Bruker WP-80 spectrometer operating in the Fourier-transform mode; chemical analyses were obtained with a Heraeus EA 415 instrument.

*Crystal data.*— $\text{C}_{32}\text{H}_{92}\text{Cl}_4\text{Hg}_4\text{Na}_4\text{O}_{30}\text{P}_8$ ,  $M = 2241$ , monoclinic,  $a = 10.439(6)$ ,  $b = 15.22(1)$ ,  $c = 28.00(2)$  Å,  $\beta = 121.67(5)^\circ$ ,  $U = 3785.82$  Å<sup>3</sup> (by least-squares refinement on diffractometer angles of 12 automatically centred reflections,  $\lambda = 0.71069$  Å), space group  $P2_1/c$  (no. 14),  $Z = 2$ ,  $D_c = 1.97$  g  $\text{cm}^{-3}$ ,  $F(000) = 2152$ ,  $\mu(\text{Mo-K}\alpha) 86.4$   $\text{cm}^{-1}$ ,  $T = 225$  K.

*Data Collection and Processing.*—Syntex P3 diffractometer,  $\omega$ -scan mode,  $\omega$ -scan width =  $1.1^\circ$ ,  $2.2 \leq \omega \leq 29.3^\circ$   $\text{min}^{-1}$ , graphite-monochromated Mo- $K_\alpha$  radiation, 3057 unique reflections, 2646 reflections with  $I > 2\sigma(I)$ , the absorption correction was measured.

*Structure Analysis and Refinement.*—Direct methods (SHELXTL<sup>21</sup>), followed by full-matrix least-squares refinement. Hydrogen atoms were at calculated positions. Final  $R = 0.0426$ ,  $R' = 0.0572$ .

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