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## Structure of Diaquadibromobis(tetrahydrofuran)dilithium–Tetrakis(methyleneoxydiphenylphosphinato)dimercury(II), $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$

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**Abstract.** Diaqua-1 $\kappa$ O;2 $\kappa$ O-dibromo-3 $\kappa$ Br;4 $\kappa$ Br-tetrakis- $\mu$ -[methyleneoxodiphenylphosphato(1-)]-1 $\kappa$ O:3 $\kappa$ C;1 $\kappa$ O:4 $\kappa$ C;2 $\kappa$ O:3 $\kappa$ C;2 $\kappa$ O:4 $\kappa$ C-bis(tetrahydrofuran)-1 $\kappa$ O;2 $\kappa$ O-dilithiumdimercury,  $[\text{Li}_2\text{Hg}_2(\text{C}_{13}\text{H}_2\text{OP})_4\text{Br}_2(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})_2]$ ,  $M_r = 1615.9574$ , triclinic,  $P\bar{1}$ ,  $a = 10.253$  (3),  $b = 12.765$  (3),  $c = 13.407$  (3) Å,  $\alpha = 63.42$  (2),  $\beta = 82.38$  (2),  $\gamma = 80.80$  (2)°,  $V = 1545.4$  (6) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.74$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 63.92$  cm<sup>-1</sup>,  $F(000) = 788.0$ ,  $T = 293$  K,  $R = 0.0303$ ,  $wR = 0.0358$  for 3240 reflections with  $F_o^2 > 3\sigma(F_o^2)$  and 352 variables. The structure consists of two  $\text{Hg}[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]_2$  units, which bridge between two  $\text{Li}^+$  cations to form a 16-membered cycle. There is a  $\text{Br}^-$  anion weakly associated with each Hg atom. The coordination geometry around each  $\text{Li}^+$  cation is approximately tetrahedral, involving one water and one tetrahydrofuran ligand at each cation, in addition to an O atom from each of the two bridging  $\text{Hg}[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]_2$  units.

**Introduction.** The synthesis of the methyleneoxydiphenylphosphinate ( $\text{mop}^-$ ) ligand,  $\text{CH}_2\text{P}(\text{O})\text{Ph}_2^-$ , and its characterization as the triphenyltin complex were reported 29 years ago (Seyferth, Welch & Heeren, 1964). Crystallographic investigations of complexes of mop have been limited. We have structurally characterized the mercury(II) complexes  $[\{\text{Hg}[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]_2\}_2\text{BrLi}]_n$  (Fackler & Kresinski, 1991) and now report the structure of  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ .

**Experimental.** Crystals of  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$  were obtained upon slow evapor-

ation of solvent from a concentrated solution of  $[\{\text{Hg}[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]_2\}_2\text{BrLi}]_n$  (Fackler & Kresinski, 1991) in 50:50  $\text{CH}_2\text{Cl}_2$ :0.1%  $\text{H}_2\text{O}$  in tetrahydrofuran. A crystal measuring approximately  $0.2 \times 0.3 \times 0.5$  mm was mounted in a random orientation on a glass fiber using cyanoacrylate adhesive. The crystal started to decay rapidly once data collection was complete. Decay was slight during data collection (< 5%). Unit-cell parameters were determined using 25 reflections between  $25 < 2\theta < 30^\circ$ , and the crystal symmetry and axial dimensions were confirmed using axial photographs. Data were collected at room temperature using Wyckoff scanning technique in bisecting geometry on a Nicolet *R3m/E* diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation. A total of 4412 data ( $0 \leq h \leq 12$ ,  $-14 \leq k \leq 14$ ,  $-15 \leq l \leq 15$ ) were measured with  $4 \leq 2\theta \leq 45^\circ$ . The scan range was  $1^\circ$  and the scan rate variable ( $3\text{--}30^\circ \text{ min}^{-1}$ ). Three standards (244, 411 and 110) were measured every 97 reflections; data were corrected for slight standard decay, Lorentz and polarization effects. An empirical absorption correction was applied on the basis of five azimuthal scans; maximum and minimum transmissions were 0.951 and 0.678. The data were merged to give 3240 unique reflections. Data processing was carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1986). The position of the Hg atom was determined by direct methods. The remaining non-H-atom positions were determined using difference Fourier syntheses. Scattering factors, including terms for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

All non-H atoms were refined anisotropically. C-bonded H atoms were placed in idealized positions

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0.96 Å from their parent atoms, with isotropic thermal parameters equal to 1.2 times  $U_{iso}$  of their parent atoms. No attempt was made to find or otherwise model the H atoms of the water molecule. Refinement was based on  $F$  with weights of the form  $w^{-1} = \sigma^2(F_o) + g(F_o^2)$ ;  $g = 0.0005$ . Convergence to conventional discrepancy indices of  $R = 0.0303$  and  $wR = 0.0358$  (GOF = 1.043) was obtained using 352 variable parameters and 3240 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The H atoms were removed and re-inserted at 1.2 times the new  $U_{iso}$  of their parent atoms for the last stages of refinement. The largest shift/e.s.d. in the last least-squares cycle was 0.009; the maximum and minimum residual electron densities in the final Fourier map were in the range  $\pm 0.57 \text{ e } \text{Å}^{-3}$ . A view of the title complex is shown in Fig. 1. Table 1 contains atomic positions and their associated equivalent isotropic thermal parameters. Table 2 contains bond lengths and angles.\*

**Discussion.** The only other crystal structure reported containing the  $[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]^-$  ligand is that of  $\{[\text{Hg}[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]_2\text{BrLi}]_n\}$  (Fackler & Kresinski, 1991), although other ( $sp^3$ )C—P=O-containing structures are known (Lin, Kao, Feng, Wu, Lee &

\* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55859 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1029]

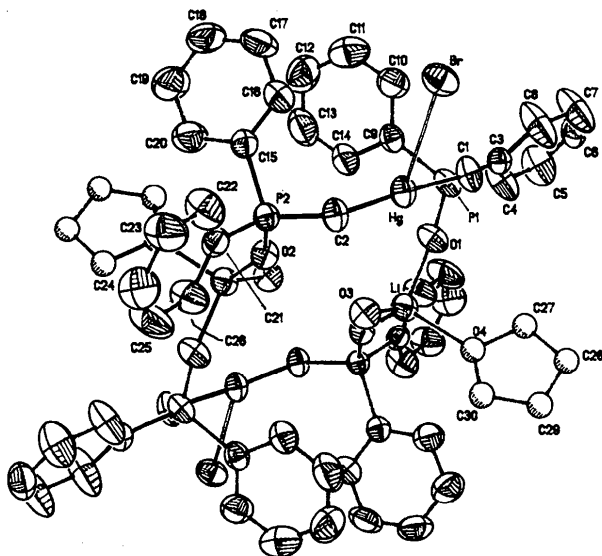


Fig. 1. A perspective view of  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ . H atoms are omitted and tetrahydrofuran ligand atoms are represented by spheres of arbitrary radii, for clarity. Thermal ellipsoids have been drawn at 40% probability.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
Hg	3845 (1)	3714 (1)	580 (1)	42 (1)
Br	6657 (1)	2356 (1)	532 (1)	60 (1)
P(1)	2082 (2)	2264 (2)	2773 (2)	44 (1)
P(2)	2850 (2)	4753 (2)	-1955 (1)	37 (1)
O(1)	1035 (5)	3258 (4)	2568 (4)	54 (2)
O(2)	1481 (4)	5032 (4)	-1566 (4)	42 (2)
O(3)	1247 (5)	5645 (4)	248 (4)	51 (2)
O(4)	802 (6)	5619 (5)	2613 (5)	75 (3)
C(1)	3657 (7)	2712 (7)	2325 (6)	53 (4)
C(2)	4010 (6)	4802 (6)	-1156 (5)	43 (3)
C(3)	2071 (7)	1284 (6)	4241 (5)	41 (3)
C(4)	931 (8)	1165 (8)	4892 (7)	76 (4)
C(5)	854 (10)	418 (8)	6015 (7)	80 (5)
C(6)	1911 (10)	-234 (7)	6529 (7)	65 (4)
C(7)	3041 (11)	-125 (10)	5937 (8)	107 (6)
C(8)	3131 (10)	630 (10)	4795 (7)	102 (6)
C(9)	1836 (7)	1424 (6)	2053 (5)	43 (3)
C(10)	2701 (9)	467 (7)	2053 (7)	66 (5)
C(11)	2448 (11)	-113 (8)	1476 (9)	85 (6)
C(12)	1379 (12)	219 (9)	864 (8)	86 (6)
C(13)	527 (11)	1138 (9)	878 (8)	86 (5)
C(14)	734 (9)	1747 (7)	1450 (7)	69 (4)
C(15)	3116 (7)	3329 (6)	-1996 (6)	42 (3)
C(16)	3958 (9)	2401 (7)	-1353 (7)	66 (4)
C(17)	4027 (10)	1305 (8)	-1379 (8)	76 (5)
C(18)	3293 (10)	1177 (7)	-2073 (8)	76 (5)
C(19)	2492 (10)	2105 (8)	-2744 (9)	83 (6)
C(20)	2385 (9)	3186 (7)	-2695 (8)	73 (5)
C(21)	3228 (7)	5827 (6)	-3370 (5)	43 (3)
C(22)	4404 (9)	5695 (8)	-3926 (7)	71 (4)
C(23)	4741 (10)	6564 (8)	-4973 (7)	78 (5)
C(24)	3916 (11)	7539 (8)	-5453 (7)	84 (5)
C(25)	2778 (11)	7694 (8)	-4924 (8)	87 (5)
C(26)	2409 (8)	6833 (7)	-3869 (7)	67 (4)
C(27)	1380 (17)	4936 (11)	3667 (9)	149 (9)
C(28)	1864 (18)	5716 (14)	3981 (14)	177 (12)
C(29)	1650 (26)	6841 (14)	3093 (15)	278 (17)
C(30)	1100 (11)	6757 (9)	2219 (8)	94 (6)
Li	344 (11)	4857 (10)	1709 (10)	45 (5)

Wang, 1986; Bowen, Duesler, Payne & Campana, 1982). In assigning bonds in  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ , comparisons were made with bond lengths in the above structures, as well as with P=O and P—O lengths in  $[\{\text{C}_5(\text{CH}_3)_5\}\text{ReI}(\text{CO})\{\text{P}(\text{O})(\text{OCH}_3)_2\}]$  (Einstein, Rickard, Klahn & Leiva, 1991), P—C lengths in  $\text{Ph}_3\text{P}=\text{CH}_2$  (Burt, 1969), and bond lengths between Hg, C and P in the several known examples of Hg complexes of the  $[\text{CH}_2\text{P}(\text{S})\text{Ph}_2]^-$  ligand (Wang & Fackler, 1989, 1990). The rather short P—C(methylene) distances in  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$  deserve comment. The  $[\text{CH}_2\text{P}(\text{O})\text{Ph}_2]^-$  ligand may be thought of as having its negative charge delocalized onto the O atom and the methylene group. Alternatively, an ylidic resonance contributor may be invoked, viz.  $[\text{CH}_2\text{P}^+(\text{O}^-)\text{Ph}_2]$ . Thus, the bond order between the P atom and the C and O atoms may be expected to be anything between 1 and 2. In  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ , the average P—C(methylene) distance is 1.734 (5) Å, while the average P—C(phenyl) distance is 1.806 (4) Å. This shortness of the P—C( $sp^3$ ) bond distance, especially as compared to a P—C( $sp^2$ )(phenyl) bond, may be understood as implying some degree of

Table 2. Bond lengths (Å) and angles (°)

Hg—Br	3.127 (1)	Hg—C(1)	2.105 (6)
Hg—C(2)	2.110 (6)	P(1)—O(1)	1.472 (5)
P(1)—C(1)	1.740 (7)	P(1)—C(3)	1.799 (6)
P(1)—C(9)	1.797 (10)	P(2)—O(2)	1.477 (4)
P(2)—C(2)	1.728 (8)	P(2)—C(15)	1.819 (9)
P(2)—C(21)	1.809 (6)	O(1)—Li	1.909 (11)
O(2)—Li <sub>a</sub>	1.883 (12)	O(3)—Li	1.939 (12)
O(4)—C(27)	1.436 (14)	O(4)—C(30)	1.377 (13)
O(4)—Li	1.997 (18)	C(3)—C(4)	1.348 (11)
C(3)—C(8)	1.341 (11)	C(4)—C(5)	1.375 (11)
C(5)—C(6)	1.319 (13)	C(6)—C(7)	1.304 (14)
C(7)—C(8)	1.397 (12)	C(9)—C(10)	1.390 (12)
C(9)—C(14)	1.377 (12)	C(10)—C(11)	1.357 (18)
C(11)—C(12)	1.354 (17)	C(12)—C(13)	1.355 (16)
C(13)—C(14)	1.367 (18)	C(15)—C(16)	1.359 (10)
C(15)—C(20)	1.363 (15)	C(16)—C(17)	1.406 (15)
C(17)—C(18)	1.349 (17)	C(18)—C(19)	1.349 (12)
C(19)—C(20)	1.397 (16)	C(21)—C(22)	1.360 (11)
C(21)—C(26)	1.356 (10)	C(22)—C(23)	1.386 (10)
C(23)—C(24)	1.330 (13)	C(24)—C(25)	1.318 (15)
C(25)—C(26)	1.397 (11)	C(27)—C(28)	1.415 (28)
C(28)—C(29)	1.402 (20)	C(29)—C(30)	1.417 (28)
Li—O(2a)	1.883 (12)		
Br—Hg—C(1)	89.2 (2)	Br—Hg—C(2)	92.6 (2)
C(1)—Hg—C(2)	176.9 (3)	O(1)—P(1)—C(1)	113.0 (3)
O(1)—P(1)—C(3)	110.2 (3)	C(1)—P(1)—C(3)	108.3 (3)
O(1)—P(1)—C(9)	111.3 (3)	C(1)—P(1)—C(9)	106.4 (4)
C(3)—P(1)—C(9)	107.5 (3)	O(2)—P(2)—C(2)	112.3 (3)
O(2)—P(2)—C(15)	112.7 (3)	C(2)—P(2)—C(15)	109.1 (3)
O(2)—P(2)—C(21)	11.05 (3)	C(2)—P(2)—C(21)	106.0 (3)
C(15)—P(2)—C(21)	105.8 (4)	P(1)—O(1)—Li	151.0 (5)
P(2)—O(2)—Li <sub>a</sub>	147.6 (6)	C(27)—O(4)—C(30)	107.5 (9)
C(27)—O(4)—Li	121.5 (8)	C(30)—O(4)—Li	126.8 (7)
Hg—C(1)—P(1)	111.4 (4)	Hg—C(2)—P(2)	117.5 (4)
P(1)—C(3)—C(4)	120.4 (5)	P(1)—C(3)—C(8)	125.7 (6)
C(4)—C(3)—C(8)	113.9 (7)	C(3)—C(4)—C(5)	123.1 (8)
C(4)—C(5)—C(6)	121.4 (8)	C(5)—C(6)—C(7)	117.5 (8)
C(6)—C(7)—C(8)	121.6 (9)	C(3)—C(8)—C(7)	122.4 (9)
P(1)—C(9)—C(10)	124.0 (7)	P(1)—C(9)—C(14)	118.5 (6)
C(10)—C(9)—C(14)	117.4 (9)	C(9)—C(10)—C(11)	120.3 (9)
C(10)—C(11)—C(12)	122.5 (10)	C(11)—C(12)—C(13)	117.1 (13)
C(12)—C(13)—C(14)	122.6 (11)	C(9)—C(14)—C(13)	120.0 (8)
P(2)—C(15)—C(16)	124.2 (8)	P(2)—C(15)—C(20)	117.0 (5)
C(16)—C(15)—C(20)	118.7 (9)	C(15)—C(16)—C(17)	120.3 (10)
C(16)—C(17)—C(18)	120.2 (8)	C(17)—C(18)—C(19)	119.8 (10)
C(18)—C(19)—C(20)	120.3 (11)	C(15)—C(20)—C(19)	120.6 (8)
P(2)—C(21)—C(22)	120.5 (5)	P(2)—C(21)—C(26)	121.3 (6)
C(22)—C(21)—C(26)	117.9 (6)	C(21)—C(22)—C(23)	120.5 (7)
C(22)—C(23)—C(24)	120.6 (9)	C(23)—C(24)—C(25)	120.0 (8)
C(24)—C(25)—C(26)	120.8 (8)	C(21)—C(26)—C(25)	120.2 (8)
O(4)—C(27)—C(28)	108.3 (10)	C(27)—C(28)—C(29)	106.0 (17)
C(28)—C(29)—C(30)	109.7 (17)	O(4)—C(30)—C(29)	107.6 (9)
O(1)—Li—O(3)	115.2 (7)	O(1)—Li—O(4)	100.9 (6)
O(3)—Li—O(4)	105.3 (6)	O(1)—Li—O(2a)	110.6 (6)
O(3)—Li—O(2a)	109.9 (6)	O(4)—Li—O(2a)	114.7 (7)

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## Structure of Dicarbonyl( $\eta^5$ -pentamethylcyclopentadienyl)iridium

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**Abstract.**  $[\text{Ir}(\text{CO})_2(\text{C}_{10}\text{H}_{15})]$ ,  $M_r = 383.45$ , monoclinic,  $P2_1/n$ ,  $a = 7.692(2)$ ,  $b = 10.565(1)$ ,  $c = 15.057(3)$  Å,  $\beta = 98.99(1)^\circ$ ,  $V = 1208.7(4)$  Å<sup>3</sup>,

multiple bonding therein; for example, it corresponds in length to the aromatic-type bond [1.72(2) Å] in  $[\text{Ph}_3\text{C}_5\text{H}_2\text{P}(\text{OCH}_3)_2]$  (Thewalt, 1969). However, the average P=O distance, 1.475(3) Å, is entirely consistent with the presence of a full double bond. A P—C bond order of more than one would necessitate a P atom with more than five bonds. Furthermore, the average Hg—C distance of 2.108(4) Å is typical of a full single bond. Ylidic ionic contributions undoubtedly contribute to the bond lengths observed in  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ .

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