

Table 6. Average values of selected interatomic distances in confacial-bioctahedral dimers of Nb and Ta (Å)

THT tetrahydrothiophene; <i>b</i> bridging; <i>t</i> terminal.						
	<i>M-M</i>	<i>M-X_b</i>	<i>M-X_t</i>	<i>M-L_b</i>	<i>M-L_t</i>	References
(I) Nb ₂ Br ₆ (THT) ₃	2.728 (5)	2.626 [10]*	2.534 [6]	2.487 [32]	2.632 [41]	Templeton <i>et al.</i> (1978)
(II) Ta ₂ Br ₆ (THT) ₃	2.710 (2)	2.633 [8]	2.516 [3]	2.393 [3]	2.624 [3]	Templeton <i>et al.</i> (1978)
(III) Ta ₂ Cl ₆ (THT) ₃	2.681 (1)	2.503 [5]	2.366 [2]	2.390 [11]	2.629 [7]	Cotton & Najjar (1981)
(IV)† Ta ₂ Cl ₆ (SMe ₂) ₃	2.691 (1)	2.498 [20]	2.370 [5]	2.378 (5)	2.618 (5)	Cotton & Najjar (1981)
(V) Ta ₂ Cl ₆ (μ-SMe ₂)(Me ₂ N) ₃ P ₁₂	2.704 (1)	2.500 [7]	2.347 [3]	2.400 [3]	2.726 [3]	Cotton, Falvello & Najjar (1982)
(VI)† Ta ₂ Cl ₆ (μ-(Bu ^t C) ₂)(THF) ₂	2.677 (1)	2.489 [7]	2.344 [17]	2.315 [10]‡	2.282 (8)	Cotton & Hall (1980)
(VII) Ta ₂ Cl ₆ (μ-SMe ₂)(THF) ₂	2.6695 (5)	2.494 [1]	2.368 [1]	2.370 [1]	2.229 [10]	This work
(VIII) Nb ₂ Cl ₆ (μ-SMe ₂)(THF) ₂	2.684 (2)	2.489 [2]	2.375 [5]	2.406 [1]	2.234 [1]	This work

* Numbers in square brackets are variances, obtained from the expression $[(\sum \Delta_i^2)/(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmetic mean and *n* is the total number of values averaged.

† Molecules of (IV) and (VI) reside on crystallographic symmetry elements *m* and *C₂*, respectively.

‡ Bridging C≡C group perpendicular to the *M-M* axis.

(b) Little variation in the *M-S_b* distances for different donors *trans* to *S_b* indicates a negligible *trans* effect.

(c) While the *M-X_b* distance is longer than the *M-X_t* one, the opposite is true for metal-sulfur bonds.

(d) In contrast to *M-L* bonds the *M-M* separation is more responsive to the nature of the ligands. It appears that Ta=Ta double bonds are shorter than those between niobium atoms in identical environments. This may arise from relativistic effects, which play a significant role with tantalum, but a more specific explanation can only be provided by theoretical MO calculations.

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Structure of Tetrakis[dimethyl(phenyl)phosphine]mercury(II) Decachloro-μ-oxo-ditantalate(V), [Hg{P(CH₃)₂(C₆H₅)₂}₄][Ta₂Cl₁₀O]

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Abstract. *M_r* = 1485.65, orthorhombic, *Pbcn*, *a* = 4799.5 Å³, *Z* = 4, *D_x* = 2.056 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 84.077 cm⁻¹, *F*(000) = 2800.0, *T* = 295 K, *R* = 0.0472 for 1991 observed reflections. The compound consists of [Hg(PMe₂Ph)₄]²⁺ and

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[Ta₂OCl₁₀]²⁻ ions. The former is the first structurally characterized homoleptic phosphine complex of Hg^{II}. It has a crystallographic twofold symmetry with an average Hg—P distance of 2.537 [10] Å and P—Hg—P angles in the range 102.4 (2) to 111.9 (1)°. The anion consists of two TaCl₅O octahedra sharing the oxygen apex with Ta—O—Ta = 180°, Ta—O = 1.878 (1), Ta—Cl(*trans* to O) = 2.395 (4) and Ta—Cl(*cis*) ranging from 2.332 (4) to 2.358 (4) Å.

Introduction. The title compound is obtained as a byproduct during the synthesis of [TaCl₄(PMe₂Ph)₂] (Cotton, Duraj & Roth, 1984). The crystallization of the major product by addition of toluene to the postreaction solution consistently afforded material contaminated with a small amount of colorless crystals. Preliminary examination indicated that they contain heavy elements and therefore a complete structural characterization was carried out. The compound was found to be ionic and composed of discrete [Ta₂OCl₁₀]²⁻ anions and [Hg(PMe₂Ph)₄]²⁺ cations. The former ion has been described previously (Cotton & Najjar, 1981). Its presence in small amounts in the highly reactive TaCl_x—phosphine system is not surprising, especially since commercially obtained reactants were used as received. The cation is a representative of rare homoleptic [Hg(phosphine)₄]²⁺ species. A number of mercury—phosphine complexes have been characterized crystallographically (Alyea, Dias, Ferguson & Khan, 1979; Aurivillius & Wendel, 1976; Bell, Dee, Goggin, Goldstein, Goodfellow, Jones, Kessler, McEwan & Nowell, 1981; Bell, Goldstein, Jones & Nowell, 1980; Buergi, Fischer, Kunz, Parvez & Pregosin, 1982; Falth, 1976), most of them being neutral species of the type [HgX₂L_n].

Synthesis and characterization of [Hg(PR₃)₄]²⁺ in solution has been described (Schmidbaur & Rathlein, 1973; Colton & Dakternieks, 1981) but no structural data concerning any tetraphosphinemercury(II) cation seem to be available.

Experimental. The reaction was carried out as described previously (Cotton *et al.*, 1984). PMe₂Ph (1.8 ml) and a drop of mercury were added to a suspension of TaCl₅ (1.5 g) and Mg turnings (0.15 g) in 19 ml of CH₂Cl₂. The mixture was stirred for three days and then filtered. A dark-green solution was obtained and its volume was reduced to *ca* 5 ml under vacuum. A layer of toluene (10 ml) was placed on top of the CH₂Cl₂ solution. Slow interdiffusion of the layers afforded highly crystalline orange [TaCl₄(PMe₂Ph)₂] (1.3 g) and white, leaflike crystals of [Hg(PMe₂Ph)₄]-[Ta₂OCl₁₀] (10–20 mg).

Triangular prismatic crystal, 0.3 × 0.3 × 0.1 mm, CAD-4 diffractometer. Graphite-monochromated Mo K α radiation; unit-cell dimensions from exact goniometer settings of 25 reflections, 20 < 2 θ < 28°;

Table 1. *Positional and equivalent isotropic thermal parameters for [Hg(PMe₂Ph)₄][Ta₂OCl₁₀]*

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Ta	0.11713 (5)	-0.03569 (3)	0.00659 (4)	3.60 (1)
Cl(1)	0.2670 (3)	-0.0801 (3)	0.0144 (3)	5.6 (1)
Cl(2)	0.1722 (3)	0.0870 (2)	0.0023 (3)	4.5 (1)
Cl(3)	0.1108 (3)	-0.0294 (3)	0.1368 (3)	5.7 (1)
Cl(4)	0.1255 (4)	-0.0421 (3)	-0.1240 (3)	6.1 (1)
Cl(5)	0.0684 (4)	-0.1613 (2)	0.0107 (4)	7.3 (2)
O	0.000	0.000	0.000	4.6 (4)
Hg	0.000	-0.32597 (4)	0.250	3.23 (2)
P(1)	-0.1229 (3)	-0.2466 (2)	0.1953 (3)	3.6 (1)
P(2)	0.0655 (3)	-0.4154 (2)	0.1536 (3)	3.8 (1)
C(11)	-0.223 (1)	-0.2612 (7)	0.248 (1)	4.1 (4)
C(12)	-0.293 (1)	-0.3054 (9)	0.220 (1)	5.3 (5)
C(13)	-0.365 (1)	-0.3219 (9)	0.266 (1)	6.0 (5)
C(14)	-0.369 (1)	-0.296 (1)	0.338 (1)	6.3 (6)
C(15)	-0.302 (1)	-0.252 (1)	0.366 (1)	6.1 (5)
C(16)	-0.226 (1)	-0.233 (1)	0.323 (1)	4.9 (4)
C(17)	-0.102 (1)	-0.1436 (8)	0.1972 (9)	3.9 (4)
C(18)	-0.150 (1)	-0.266 (1)	0.099 (1)	5.1 (5)
C(21)	0.001 (1)	-0.4999 (8)	0.147 (1)	3.7 (3)
C(22)	-0.093 (1)	-0.4917 (9)	0.139 (1)	4.6 (4)
C(23)	-0.146 (1)	-0.555 (1)	0.134 (1)	5.7 (5)
C(24)	-0.110 (1)	-0.625 (1)	0.143 (1)	5.6 (5)
C(25)	-0.019 (2)	-0.6338 (9)	0.154 (1)	7.2 (6)
C(26)	0.036 (1)	-0.5707 (9)	0.153 (1)	5.2 (5)
C(27)	0.067 (1)	-0.381 (1)	0.057 (1)	5.7 (5)
C(28)	0.180 (1)	-0.447 (1)	0.173 (1)	6.0 (5)

systematic absences *Ok*l, *k* ≠ 2*n*, *h*0*l*, *l* ≠ 2*n* and *hk*0, *h* + *k* ≠ 2*n*, indicated *Pbcn*; 4690 unique reflections measured, 4 < 2 θ < 50°; 1991 with *I* > 3 σ , 0 ≤ *h* ≤ 17, 0 ≤ *k* ≤ 21, 0 ≤ *l* ≤ 21; three intensity standards checked at 1 h intervals showed 42.5% decay over 41.1 h exposure; empirical absorption correction using ψ scans for seven reflections with Eulerian angle near 90°, each reflection measured at 10° intervals from 0 to 360°; minimum and maximum absorption correction 0.6948 and 0.9987; position of Ta atom derived by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), remaining atoms found by iterative application of least-squares refinement and difference Fourier maps; H atoms not located; *F*_{obs} corrected for Lorentz, polarization, absorption and decay, and used for refinement of positions, with anisotropic temperature factors and scale factor; 228 parameters, final *R* = 0.0472, *wR* = 0.0517, *w* = 1/ σ^2 (*I*_o), *S* = 1.316, *A*_{max}/ σ = 0.05, four largest peaks in final difference Fourier map with density 2.3–3.3 e Å⁻³ located < 1.2 Å from metal atoms, others below 0.86 e Å⁻³; atomic scattering factors and *f*', *f*'' values from *International Tables for X-ray Crystallography* (1974). All calculations performed with Enraf–Nonius (1981) *SDP* on the VAX 11/80 computer at the Department of Chemistry, Texas A&M University.

Table 2. Selected bond distances (Å) and angles (°) in $[\text{Hg}(\text{PMe}_2\text{Ph})_4][\text{Ta}_2\text{OCl}_{10}]$

Hg—P(1)	2.527 (4)	Ta—Cl(3)	2.332 (4)
Hg—P(2)	2.547 (4)	Ta—Cl(4)	2.341 (5)
Ta—Cl(1)	2.395 (4)	Ta—Cl(5)	2.358 (4)
Ta—Cl(2)	2.341 (3)	Ta—O	1.878 (1)
P(1)—Hg—P(1)'	111.8 (2)	Cl(2)—Ta—Cl(4)	89.7 (2)
P(1)—Hg—P(2)	111.9 (1)	Cl(2)—Ta—Cl(5)	177.4 (2)
P(1)—Hg—P(2)'	109.2 (1)	Cl(2)—Ta—O	90.8 (1)
P(2)—Hg—P(2)'	102.4 (2)	Cl(3)—Ta—Cl(4)	179.3 (2)
Cl(1)—Ta—Cl(2)	88.7 (1)	Cl(3)—Ta—Cl(5)	90.1 (2)
Cl(1)—Ta—Cl(3)	89.8 (2)	Cl(3)—Ta—O	90.5 (1)
Cl(1)—Ta—Cl(4)	89.5 (2)	Cl(4)—Ta—Cl(5)	90.1 (2)
Cl(1)—Ta—Cl(5)	88.7 (2)	Cl(4)—Ta—O	90.3 (1)
Cl(1)—Ta—O	179.5 (1)	Cl(5)—Ta—O	91.8 (1)
Cl(2)—Ta—Cl(3)	90.1 (2)	Ta—O—Ta'	180.00

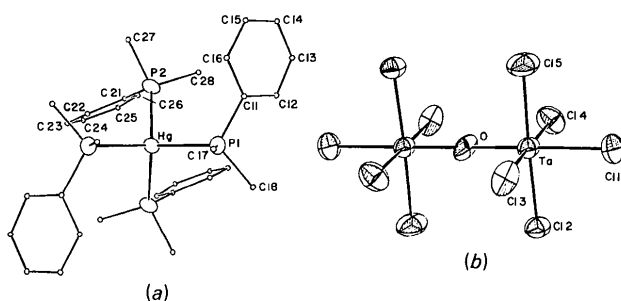


Fig. 1. (a) ORTEP (Johnson, 1976) drawing of the $[\text{Hg}(\text{PMe}_2\text{Ph})_4]^{2+}$ cation. Hg and P atoms are represented by their ellipsoids of thermal vibration drawn at 30% level. C atoms have been assigned arbitrarily small isotropic thermal parameters for the sake of clarity. A crystallographic twofold axis passing through Hg is almost perpendicular to the plane of the drawing. (b) ORTEP drawing of the $[\text{Ta}_2\text{OCl}_{10}]^{2-}$ anion. Thermal ellipsoids are drawn at 40% probability level. The O atom is positioned on a crystallographic inversion center which relates the halves of the ion.

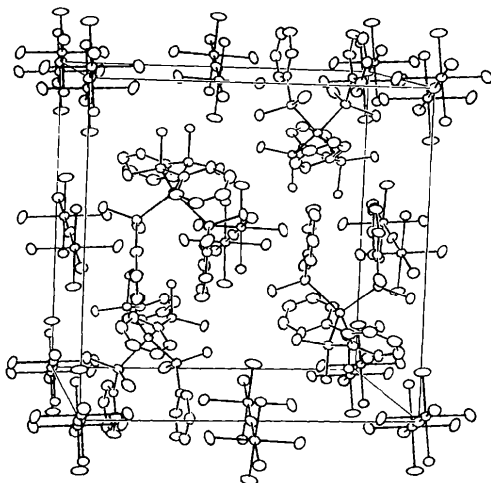


Fig. 2. A packing diagram of the unit cell.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Table 1. Important interatomic dimensions for both ions are listed in Table 2. Fig. 1 depicts the ions and defines the atomic-labeling scheme. The unit-cell packing is shown in Fig. 2.*

The Hg atom resides on a crystallographic twofold axis. Virtual symmetry of the coordination sphere is T_d . The $L\text{—Hg—}L'$ angles are within the range 102.4 (2) to 111.9 (1)° and their deviations from the tetrahedral angles are apparently in response to intermolecular packing forces. The average Hg—P bond length is equal to 2.537 [10] Å. This value falls within the range found in complexes of the type $[\text{Hg}X_2L_2]$ (Buergi *et al.*, 1982).

The central $\mu\text{—O}$ atom in the $[\text{Ta}_2\text{OCl}_{10}]^{2-}$ anion is positioned on a crystallographic inversion center. The Ta—X distances are, within the experimental error, identical to the values determined for the ion in $[\text{PMe}_2\text{Ph}]_2[\text{Ta}_2\text{OCl}_{10}]$ (Cotton & Najjar, 1981).

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* Lists of structure factors, bond distances and angles, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42094 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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