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Structure of Bis[bis(η -cyclopentadienyl)tantalum(V)bis(μ -methanethiolato)]-platinum(0) Hexafluorophosphate

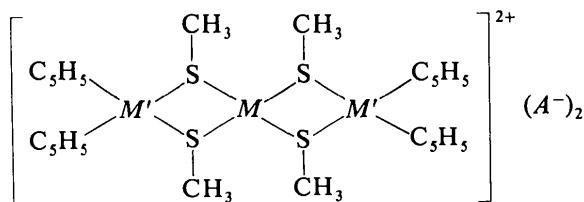
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Abstract. $[(\eta\text{-C}_5\text{H}_5)_2\text{Ta}(\mu\text{-SCH}_3)_2\text{Pt}(\mu\text{-SCH}_3)_2\text{Ta}(\eta\text{-C}_5\text{H}_5)_2](\text{PF}_6)_2$, $\text{C}_{24}\text{H}_{32}\text{PtS}_4\text{Ta}_2^{2+} \cdot 2\text{PF}_6^-$, $M_r = 1295$, monoclinic, $P2_1/c$, $a = 16.44$ (1), $b = 12.65$ (1), $c = 17.94$ (1) Å, $\beta = 97.8$ (1)°, $U = 3699$ Å³, $Z = 4$, $D_c = 2.32$ Mg m⁻³, Mo $K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 4.47$ mm⁻¹. The complex formally contains Ta^V and Pt⁰. The Pt atom has a tetrahedral coordination and the short Pt–Ta contacts (2.788 and 2.809 Å) correspond to metal–metal bonds.

Introduction. The complex $\text{Ta}(\eta\text{-C}_5\text{H}_5)_2(\text{SCH}_3)_2$ reacts with $\text{Pt}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ to give a diamagnetic trinuclear complex (I) isolated as the hexafluorophosphate salt (Sigantor, 1977).



(Ia) $M = \text{Pt}$, $M' = \text{Ta}$, $A = \text{PF}_6$

(Ib) $M = \text{Ni}$, $M' = \text{Nb}$, $A = \text{BF}_4$

(Ic) $M = \text{Ni}$, $M' = \text{Mo}$, $A = \text{BF}_4$

The electronic structure and the formal valence of the metals in these trinuclear complexes depend on the

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nature of the metals (Douglas & Green, 1972; Prout, Critchley & Rees, 1974). For (Ib) the short Ni–Nb distance (2.78 Å) corresponds to a metal–metal bond, in contrast to the Ni–Mo non-bonded contact in (Ic) which is much longer (3.39 Å). Moreover, the coordination of the Ni atom is tetrahedral in (Ib) and square-planar in (Ic). Complex (Ic) has been described as a $d^2-d^8-d^2$ system, but for (Ib) the favoured system was considered to be $d^0-d^{10}-d^0$. A $d^1-d^8-d^1$ system could also be proposed for (Ib) with Ni^{II} in tetrahedral coordination (for a complete discussion, see Prout, Critchley & Rees, 1974). The determination of the structure of (Ia) could clarify the situation, because tetrahedral coordination for Pt^{II} is unknown, and all attempts to make it have resulted in the stepped square-planar configuration found in (Ic).

The crystals were supplied by Dr M. L. H. Green and Mr N. Sigantor. A small red-orange crystal (approximately 0.2 × 0.2 × 0.4 mm) was mounted on a Nonius CAD-4F diffractometer, and Mo $K\alpha$ radiation from a graphite monochromator was used. Cell dimensions and the orientation matrix were obtained by least squares from the setting angles of 25 reflexions. The intensities of reflexions, $\theta < 20^\circ$, were measured by an $\omega/2\theta$ scan, with a variable scan rate and an ω -scan angle of $(1.80 + 0.35 \tan \theta)^\circ$. Lorentz and polarization corrections were applied to the 1228 reflexions with $I > 3\sigma(I)$ which were used in subsequent calculations. No corrections were made for absorption. The structure was solved by Patterson and Fourier techniques and refined by least squares with a large-block approximation. Because the locations of the

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F atoms around P(2) and most of the C atoms of the cyclopentadienyl rings were associated with groups of diffuse peaks in difference syntheses, bond lengths and angles for the two anions and the cyclopentadienyl rings were constrained by Waser's (1963) method. Only the Pt and Ta atoms were refined with anisotropic temperature factors. Each reflexion was assigned a weight $w = 1/\sum_{r=1}^n A_r T_r(X)$ where n is the number of

coefficients, A_r , for a Chebyshev series, T_r is the polynomial function and X is $|F_o|/|F_o(\max.)|$. Three coefficients, A_r , were used with values 8.0, 10.8 and 4.3 (Rollett, 1965). The final R was 0.118 ($R_w = 0.142$). Calculations were performed on the Oxford University ICL 1906A and the London University CDC 7600 computers with the Oxford CRYSTALS package (Carruthers, 1975). The final positional parameters are given in Table 1.* Table 2 lists some interatomic distances and interbond angles with their e.s.d.'s calculated from the variance-covariance matrix.

Table 1. Fractional atomic coordinates and temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)
Pt	0.2255 (3)	0.1444 (4)	0.0377 (3)	*
Ta(1)	0.1865 (3)	0.3428 (4)	0.0905 (3)	*
Ta(2)	0.2637 (3)	-0.0574 (4)	-0.0130 (3)	*
S(1)	0.172 (2)	0.080 (3)	-0.083 (2)	0.041 (9)
S(2)	0.314 (2)	0.029 (2)	0.110 (2)	0.027 (8)
S(3)	0.116 (2)	0.172 (2)	0.110 (2)	0.030 (6)
S(4)	0.300 (2)	0.296 (3)	0.014 (2)	0.035 (6)
P(1)	-0.072 (2)	0.263 (2)	-0.238 (2)	0.039 (9)
P(2)	0.483 (2)	-0.270 (3)	0.172 (2)	0.06 (1)
F(11)	0.025 (5)	0.253 (8)	-0.210 (6)	0.13 (4)
F(12)	-0.058 (5)	0.375 (6)	-0.266 (5)	0.12 (4)
F(13)	-0.169 (4)	0.275 (6)	-0.261 (4)	0.08 (3)
F(14)	-0.089 (4)	0.152 (5)	-0.209 (4)	0.07 (2)
F(15)	-0.075 (6)	0.303 (6)	-0.157 (5)	0.13 (4)
F(16)	-0.067 (6)	0.222 (7)	-0.316 (4)	0.12 (4)
F(21)	0.560 (6)	-0.352 (8)	0.187 (6)	0.16 (5)
F(22)	0.506 (6)	-0.267 (8)	0.090 (5)	0.16 (5)
F(23)	0.535 (8)	-0.168 (9)	0.190 (6)	0.19 (6)
F(24)	0.465 (8)	-0.274 (9)	0.252 (5)	0.17 (6)
F(25)	0.430 (7)	-0.364 (8)	0.151 (6)	0.24 (8)
F(26)	0.404 (5)	-0.194 (7)	0.159 (6)	0.11 (3)
C(1)	0.141 (4)	0.459 (6)	-0.015 (4)	0.03 (1)
C(2)	0.095 (5)	0.366 (6)	-0.024 (3)	0.03 (1)
C(3)	0.044 (4)	0.362 (6)	0.033 (4)	0.03 (1)
C(4)	0.064 (4)	0.449 (6)	0.080 (4)	0.03 (1)
C(5)	0.126 (5)	0.507 (4)	0.052 (4)	0.03 (1)
C(6)	0.187 (5)	0.440 (6)	0.205 (4)	0.05 (2)
C(7)	0.193 (5)	0.335 (7)	0.228 (4)	0.04 (2)
C(8)	0.267 (5)	0.295 (5)	0.209 (5)	0.05 (2)
C(9)	0.307 (4)	0.376 (7)	0.176 (5)	0.05 (2)
C(10)	0.259 (5)	0.467 (5)	0.175 (5)	0.05 (2)
C(11)	0.329 (5)	0.011 (6)	-0.115 (4)	0.05 (2)
C(12)	0.378 (5)	0.033 (5)	-0.047 (5)	0.05 (2)
C(13)	0.410 (4)	-0.062 (7)	-0.017 (4)	0.05 (2)
C(14)	0.374 (5)	-0.144 (5)	-0.063 (5)	0.05 (2)
C(15)	0.325 (5)	-0.098 (5)	-0.124 (4)	0.05 (2)
C(16)	0.212 (5)	-0.229 (5)	-0.035 (4)	0.03 (1)
C(17)	0.259 (4)	-0.224 (5)	0.036 (4)	0.03 (1)
C(18)	0.215 (5)	-0.167 (6)	0.084 (3)	0.03 (1)
C(19)	0.145 (4)	-0.124 (6)	0.039 (4)	0.03 (1)
C(20)	0.144 (4)	-0.161 (6)	-0.035 (4)	0.03 (1)
C(21)	0.067 (5)	0.06 (1)	-0.080 (7)	0.04 (1)
C(22)	0.419 (5)	0.093 (8)	0.115 (6)	0.028 (9)
C(23)	0.144 (7)	0.093 (8)	0.193 (5)	0.03 (3)
C(24)	0.276 (7)	0.335 (9)	-0.087 (4)	0.032 (6)

* Anisotropic temperature factors ($\times 10^3$)

$$\{T = \exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2klb^* c^* U_{23} + \dots)]\}$$

	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Pt(1)	9 (3)	28 (3)	37 (4)	-2 (3)	-12 (2)	3 (2)
Ta(1)	22 (3)	14 (3)	45 (4)	-7 (3)	-18 (3)	7 (3)
Ta(2)	6 (3)	18 (3)	39 (4)	1 (3)	-12 (2)	-1 (2)

Discussion. The failure to grow better crystals has led to a structure less well defined than the authors would have liked, but the chemical problem is solved without ambiguity. The asymmetric unit contains one trinuclear cation and two anions in general positions. The cation (1a) is shown in Fig. 1. The geometry is the same as that described for the Nb-Ni-Nb complex (1b) and must be interpreted as a $d^0-d^{10}-d^0$ system with donor bonds from the Pt atom to the Ta atoms. So the preferred structure of (1b), with a Ni⁰ atom, is confirmed.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34349 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected interatomic distances (Å) and bond angles (°)

Pt-Ta(1)	2.788 (7)	Pt-Ta(2)	2.809 (8)
Pt-S(1)	2.37 (3)	Ta(1)-S(3)	2.49 (3)
Pt-S(2)	2.33 (3)	Ta(1)-S(4)	2.54 (3)
Pt-S(3)	2.38 (3)	Ta(2)-S(1)	2.52 (3)
Pt-S(4)	2.35 (3)	Ta(2)-S(2)	2.51 (3)
S(1)-C(21)	1.76 (7)	S(3)-C(23)	1.80 (7)
S(2)-C(22)	1.89 (7)	S(4)-C(24)	1.86 (7)
Ta(1)-C(1)	2.43 (6)	Ta(2)-C(11)	2.41 (7)
Ta(1)-C(2)	2.40 (7)	Ta(2)-C(12)	2.35 (7)
Ta(1)-C(3)	2.43 (7)	Ta(2)-C(13)	2.41 (7)
Ta(1)-C(4)	2.40 (7)	Ta(2)-C(14)	2.40 (7)
Ta(1)-C(5)	2.36 (7)	Ta(2)-C(15)	2.40 (7)
Ta(1)-C(6)	2.40 (7)	Ta(2)-C(16)	2.34 (6)
Ta(1)-C(7)	2.46 (7)	Ta(2)-C(17)	2.30 (6)
Ta(1)-C(8)	2.43 (7)	Ta(2)-C(18)	2.44 (7)
Ta(1)-C(9)	2.37 (7)	Ta(2)-C(19)	2.42 (7)
Ta(1)-C(10)	2.39 (7)	Ta(2)-C(20)	2.35 (6)
S(1)-Pt-S(2)	115 (1)	Pt-S(1)-Ta(2)	70 (1)
S(1)-Pt-S(3)	109 (1)	Pt-S(2)-Ta(2)	71 (1)
S(1)-Pt-S(4)	105 (1)	Pt-S(3)-Ta(1)	70 (1)
S(2)-Pt-S(3)	104 (1)	Pt-S(4)-Ta(1)	69 (1)
S(2)-Pt-S(4)	108 (1)	C(21)-S(1)-Pt	106 (4)
S(3)-Pt-S(4)	115 (1)	C(21)-S(1)-Ta(2)	113 (4)
Ta(1)-Pt-Ta(2)	178.8 (3)	C(22)-S(2)-Pt	105 (3)
S(3)-Ta(1)-S(4)	105 (1)	C(22)-S(2)-Ta(2)	114 (4)
S(1)-Ta(2)-S(2)	104 (1)	C(23)-S(3)-Pt	104 (4)
		C(23)-S(3)-Ta(1)	121 (4)
		C(24)-S(4)-Pt	110 (4)
		C(24)-S(4)-Ta(1)	113 (4)

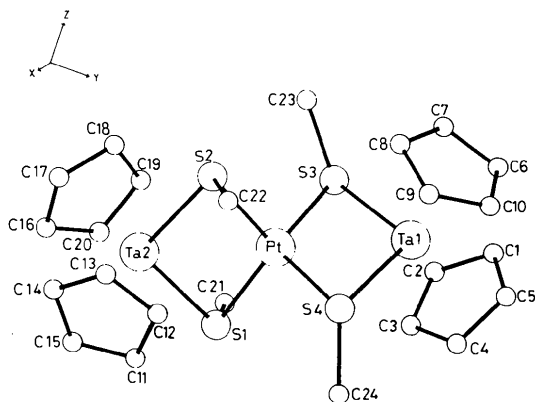


Fig. 1. The cation seen projected down the pseudo S_4 axis of the PtS₄ tetrahedron. The transformation matrix from crystal coordinates is

$$\begin{pmatrix} -0.216 & 0.919 & 0.331 \\ -0.041 & -0.347 & 0.937 \\ 0.976 & 0.189 & 0.113 \end{pmatrix}$$

The coordination of the Pt atom is an almost regular tetrahedron. The Pt and Ta atoms are in a linear arrangement, bridged by the methanethiolato ligands. The acute angles, Ta—S—Pt 70° (mean), and the short distances, Pt—Ta 2.798 Å (mean), are consistent with the criteria for metal—metal bonding (Dahl, Gil & Feltham, 1969). The bis(η -cyclopentadienyl)tantalum groups present the usual geometry described for bent

bis(η -cyclopentadienyl) metal complexes (Prout, Cameron, Forder, Critchley, Denton & Rees, 1974). The perpendicular distances from the Ta atoms to the rings are 2.09 Å for Ta(1)—C(1–5), 2.09 Å for Ta(1)—C(6–10), 2.08 Å for Ta(2)—C(11–15) and 2.04 Å for Ta(2)—C(16–20). These perpendiculars to the cyclopentadienyl rings meet the rings close (0.07 Å mean) to their centroids and make angles of 124.7° at Ta(1) and 129.4° at Ta(2). Also the TaS₂ plane is almost perpendicular to that defined by the normals to the cyclopentadienyl rings [87.4 and 86.6° respectively at Ta(1) and Ta(2)]. All the cyclopentadienyl rings are planar within experimental error and the C—C distances are in the range 1.39–1.42 Å.

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Pentadecacarbonyl(methoxyphosphinato)pentaosmium

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Abstract. C₁₆H₃O₁₆Os₅P, Os₅(CH₃OP)(CO)₁₅, monoclinic, *Cc*, $a = 15.990(5)$, $b = 9.762(3)$, $c = 16.965(5)$ Å, $\beta = 107.53(2)^\circ$, $U = 2525.2$ Å³, $Z = 4$, $D_c = 3.769$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 25.20$ mm⁻¹. The structure was refined to an R of 0.060 for 3310 unique observed diffractometer data. The Os atoms define a distorted square pyramid. The phosphinato ligand lies under the Os₄ basal plane with the P atom bonded to the four Os atoms. Each Os atom is also coordinated to three terminal CO ligands.

Introduction. The title compound was one of a number of pentanuclear clusters containing uncommon P donor

ligands isolated from the pyrolysis of Os₃(CO)₁₁-P(OCH₃)₃ (Fernandez, Johnson & Lewis, 1979). The crystal structure determination of this product was undertaken to establish the molecular geometry since the results of spectroscopic analysis were ambiguous. A preliminary report has appeared (Fernandez, Johnson, Lewis & Raithby, 1978).

Crystals were obtained as red tablets from ethyl acetate/hexane. 3647 intensities were measured in the range $3.0 < 2\theta < 60.0^\circ$ on a Syntex P2₁ four-circle diffractometer, with graphite-monochromated Mo $K\alpha$ radiation and a crystal $0.32 \times 0.32 \times 0.63$ mm. Lp and semi-empirical absorption corrections (based on