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Structure of Tris(η-methylcyclopentadienyl)(trimethylphosphine)uranium(III), $[\mathrm{U(CH_3C_5H_4)_3\{P(CH_3)_3\}}]$

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Abstract. $M_r = 551{\cdot}5$, monoclinic, Cc, $a = 13{\cdot}949\,(5)$, $b = 9{\cdot}280\,(4)$, $c = 16{\cdot}194\,(6)$ Å, $\beta = 104{\cdot}09\,(4)°$, $V = 2033\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}801\,(3)$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 76{\cdot}4$ cm^{-1}, $F(000) = 1052$, $T = 296$ K, $R = 0{\cdot}024$ for 1568 reflections ($F^2 > 2\sigma$). The structure consists of U-centered monomolecular units in which the U atom is coordinated in a pentahapto fashion to three cyclopentadiene rings and to the P atom of the trimethylphosphine molecule. The average U—C distance is 2·79 ±0·06 Å and the U—P distance is 2·972 (6) Å.

Introduction. We are currently studying the relative affinity of Lewis bases toward $\mathrm{(CH_3C_5H_4)_3U}$. Interligand contacts influence the ability of a ligand to coordinate to a metal ion and must be considered when comparing ligand basicities. As part of this study we report here the X-ray structure of $\mathrm{(CH_3C_5H_4)_3U\{P(CH_3)_3\}}$.

Experimental. Red, air-sensitive needles of the phosphine complex were prepared by reacting $\mathrm{UCl_3}$ (Andersen, 1979) with $\mathrm{Na(CH_3C_5H_4)}$ in tetrahydrofuran (THF), adding $\mathrm{P(CH_3)_3}$, and crystallizing from pentane at 253 K. Crystals were sealed inside quartz capillaries because of their reactivity in the atmosphere, and no measured density is reported for the same reason. Crystal 0·15 × 0·23 × 0·38 mm with 9 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 31 reflections, $20° < 2\theta < 27°$; analytical absorption correction, range 2·78 to 3·41; max. $(\sin\theta)/\lambda = 0{\cdot}60$ Å^{-1}, h −16 to 16, k 0 to 11, l −19 to 19; three standard reflections, <2% variation in intensities from average, intensities adjusted accordingly; 3650 data, 1798 unique (including 230, $F^2 < 2\sigma$), $R_{\rm int} = 0{\cdot}029$; structure solved by Patterson and Fourier methods, refined on F, 207 parameters, non-methyl H atoms in calculated positions with isotropic thermal parameters, methyl H atoms not included, anisotropic thermal parameters for non-hydrogen atoms, ring C—C and C—$\mathrm{CH_3}$ bond distances restrained; $R = 0{\cdot}033$ for 1798 reflections (0·024 for 1568 for which $F^2 > 2\sigma$), $wR = 0{\cdot}032$, $S = 1{\cdot}07$; $w = [\sigma(F)]^{-2}$, $p = 0{\cdot}05$ in calculation of $\sigma(F^2)$; max. $(\Delta/\sigma) = 0{\cdot}08$; max. correction for extinction 3% of F, $F_{\rm corr} = F_{\rm obs}(1 + 4{\cdot}0 \times 10^{-8}I)$; max. and min. of ΔF synthesis 0·34 and −0·37 e Å^{-3}; atomic f for neutral U, P and C, and spherical bonded H from *International Tables for X-ray Crystallography* (1974); local unpublished programs and *ORTEP* (Johnson, 1965).

In an effort to determine the absolute configuration of the molecule, the full unaveraged data set was used to refine both enantiomorphic structures, but the results showed no significant differences in the R factors for the two structures. The Friedel pairs of selected reflections with large differences were investigated, but again there was no significant correlation with the observed data. On the assumption that the crystal was twinned with both enantiomers present in equal amounts, the data were averaged. The f'' term of the anomalous dispersion was set to zero, and the f' term was applied as usual.

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The cyclopentadienyl rings suffered considerable thermal motion. The C atoms in the ring were not well resolved resulting in unrealistic C—C bond lengths and slow convergence of the least-squares refinements, and it was necessary to apply distance restraints (Waser, 1963) to the atoms of the methylcyclopentadiene ligands [1·40 (2) for C—C and 1·52 (2) Å for C—CH_3].

Discussion. Atomic parameters are listed in Table 1.* A view of the molecule is shown in Fig. 1.

The complex $(CH_3C_5H_4)_3U\{P(CH_3)_3\}$ is monomolecular in the crystalline state and consists of a U atom coordinated to the three methylcyclopentadienyl groups in a pentahapto bonding mode and to the P atom of the trimethylphosphine molecule in a distorted tetrahedral arrangement; the angles about the U atom are given in Table 2. The U atom is 2·972 (6) Å from the P atom and 2·51 to 2·54 Å from the least-squares planes of the cyclopentadienyl (Cp) rings; the average U—C distance is 2·79 ±0·06 Å. There are no observed close contacts between the phosphine ligand and the Cp rings.

Table 1. *Atomic parameters*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
U	$\frac{1}{4}$	0·33828 (3)	$\frac{1}{4}$	2·90
P	0·2795 (5)	0·1759 (6)	0·4124 (4)	4·88
C(1)	0·3866 (17)	0·6528 (20)	0·3706 (14)	6·75
C(2)	0·3884 (18)	0·5525 (23)	0·2977 (13)	6·69
C(3)	0·4381 (15)	0·4213 (27)	0·3031 (14)	8·11
C(4)	0·4393 (14)	0·3757 (16)	0·2249 (12)	4·08
C(5)	0·3819 (12)	0·4671 (18)	0·1635 (12)	5·11
C(6)	0·3564 (17)	0·5789 (22)	0·2077 (11)	7·01
C(7)	0·1118 (18)	0·5983 (26)	0·0735 (15)	8·32
C(8)	0·1035 (13)	0·5246 (18)	0·1569 (12)	5·65
C(9)	0·1227 (19)	0·5741 (17)	0·2414 (17)	6·30
C(10)	0·0919 (16)	0·4650 (26)	0·2921 (14)	10·62
C(11)	0·0536 (16)	0·3444 (20)	0·2398 (15)	5·87
C(12)	0·0494 (13)	0·3974 (21)	0·1572 (14)	5·85
C(13)	0·1536 (25)	0·274 (3)	0·0135 (15)	9·08
C(14)	0·1978 (16)	0·1897 (27)	0·0916 (1)	11·26
C(15)	0·1437 (12)	0·1244 (16)	0·1435 (11)	5·37
C(16)	0·2094 (12)	0·0493 (16)	0·2061 (12)	6·54
C(17)	0·3030 (12)	0·0713 (17)	0·1946 (12)	7·00
C(18)	0·2964 (13)	0·1650 (17)	0·1271 (10)	5·66
C(19)	0·3336 (25)	0·275 (5)	0·5188 (20)	10·53
C(20)	0·3698 (19)	0·0282 (21)	0·4288 (15)	9·42
C(21)	0·1669 (16)	0·0940 (29)	0·4345 (18)	9·23

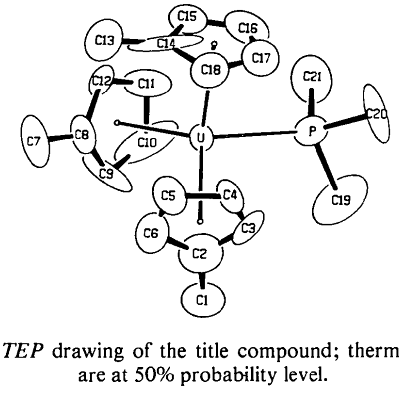

Fig. 1. *ORTEP* drawing of the title compound; thermal ellipsoids are at 50% probability level.

Table 2. *Selected distances* (Å) *and angles* (°)

U—P	2·972 (6)	U—C(14)	2·847 (23)
U—C(2)	2·748 (23)	U—C(15)	2·805 (15)
U—C(3)	2·668 (22)	U—C(16)	2·797 (15)
U—C(4)	2·789 (19)	U—C(17)	2·795 (16)
U—C(5)	2·834 (16)	U—C(18)	2·756 (15)
U—C(6)	2·856 (20)	U—Cp_1*	2·51
U—C(8)	2·817 (17)	U—Cp_2	2·51
U—C(9)	2·800 (21)	U—Cp_3	2·54
U—C(10)	2·728 (21)	P—C(19)	1·933 (26)
U—C(11)	2·704 (21)	P—C(20)	1·837 (18)
U—C(12)	2·889 (17)	P—C(21)	1·857 (20)
P—U—Cp_1	112·7	Cp_2—U—Cp_3	106·0
P—U—Cp_2	109·7	C(19)—P—C(20)	97 (2)
P—U—Cp_3	96·7	C(19)—P—C(21)	101 (2)
Cp_1—U—Cp_2	119·4	C(20)—P—C(21)	104 (2)
Cp_1—U—Cp_3	109·8		

* Cp_1, Cp_2 and Cp_3 represent the centers of atom groups C(2)–C(6), C(8)–C(12) and C(14)–C(18) respectively.

While there are a number of similar trivalent lanthanoid structures in the literature [$(C_5H_5)_3$-$Gd(OC_4H_8)$ (Rogers, Bynum & Atwood, 1980), $(C_5H_5)_3Y(OC_4H_8)$, $(C_5H_5)_3La(OC_4H_8)$ (Rogers, Atwood, Emad, Sikora & Rauch, 1981), and $(C_5H_5)_3$-$Nd(CNC_6H_{11})$ (Burns & Baldwin, 1976)], there is currently only one related trivalent U compound, $(C_5H_5)_3U(OC_4H_8)$, structurally characterized (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983). The average U to cyclopentadiene ring distance is 2·52 ±0·02 Å in both $(CH_3C_5H_4)_3U\{P(CH_3)_3\}$ and $(C_5H_5)_3U(OC_4H_8)$. In the trimethylphosphine complex, the average Cp—U—P angle is 106 ±9°, and the average Cp—U—Cp angle, 112 ±7°. This compares to 99 ±3° for the Cp—U—O angle and 118 ±2° for the Cp—U—Cp angle in the tetrahydrofuran complex, and reflects the sterically more demanding nature of the phosphine ligand relative to tetrahydrofuran.

In comparison to three U^{III} alkylphosphine structures described in the literature, the U^{III}—P distance in $(CH_3C_5H_4)_3U\{P(CH_3)_3\}$, 2·972 (6) Å, is significantly shorter than the U—P distances of 3·211 (8) and 3·092 (8) Å in $\{(CH_3C)_5\}_2UH\{(CH_3)_2PCH_2$-$CH_2P(CH_3)_2\}$ (Duttera, Fagan, Marks & Day, 1982), 3·057 (9) and 3·139 (9) Å in $U(BH_4)_3\{(CH_3)_2$-$PCH_2CH_2P(CH_3)_2\}_2$ (Wasserman, Moody & Ryan, 1984), and 3·085 (3) and 3·174 (3) Å in $U(CH_3BH_3)_3$-$\{(CH_3)_2PCH_2CH_2P(CH_3)_2\}_2$ (Brennan, Shinomoto, Zalkin & Edelstein, 1984).

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, deviations from least-squares planes, distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42123 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Tetrakis[2(1*H*)-pyridinethione-*S*]copper(I) Perchlorate–2-Pyridinethione (1/2), $[Cu(C_5H_5NS)_4]ClO_4.2(C_5H_5NS)$

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Abstract. $M_r = 830{\cdot}0$, triclinic, $P\bar{1}$, $a = 10{\cdot}269\ (1)$, $b = 11{\cdot}988\ (1)$, $c = 15{\cdot}982\ (2)$ Å, $\alpha = 95{\cdot}19\ (1)$, $\beta = 106{\cdot}53\ (2)$, $\gamma = 101{\cdot}23\ (1)°$, $V = 1827{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}508$, $D_m = 1{\cdot}495$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}0244$ mm^{-1}, $F(000) = 852$, room temperature, final $R = 0{\cdot}048$ for 2150 independent non-zero reflexions. The structure consists of isolated $Cu(C_5H_5NS)_4^+$ ions connected to the ClO_4^- ions through N—H···O hydrogen bonds. The non-coordinated 2-pyridinethione molecules are also connected to the ions through N—H···O hydrogen bonds. The Cu atom in the complex ion is surrounded by four S atoms in a distorted tetrahedral coordination, Cu—S range 2·273 (3)–2·480 (3) Å.

Introduction. Metal complexes of 2-pyridinethiol have attracted considerable attention mainly because of their relevance to certain biological systems (Evans & Wilkinson, 1974; Cotton, Fanwick & Fitch, 1978) and, to a lesser extent, due to the ability of 2-pyridinethiol to act as a uni- or bidentate or as a bridging ligand (Fletcher & Skapski, 1972). Of particular interest are complexes of Cu^I since the stereochemistry of this metal with soft ligands is very flexible. We report here the crystal structure of the title complex, TPTCP. Magnetic measurements, showing the compound to be diamagnetic, indicated that copper is in the +1 oxidation state.

Experimental. Yellow crystals prepared by treating copper perchlorate with 2-pyridinethiol in alcohol solution, m.p. 403 K, D_m measured by flotation in CCl_4/CH_2Cl_2, measured crystal $0{\cdot}55 \times 0{\cdot}43 \times 0{\cdot}15$ mm, Philips PW 1100 computer-controlled four-circle single-crystal diffractometer, cell parameters and standard deviation by least-squares analysis of measured θ angles of the 25 strongest reflexions, intensity statistics indicated $P\bar{1}$, Nb-filtered Mo $K\alpha$, ω–2θ scan, scan width $\Delta\omega = (1{\cdot}0+0{\cdot}35\tan\theta)°$, three standard reflexions without significant intensity variation, 3425 reflexions measured, $\theta = 2$–$20°$ (max. hkl range = ±9, ±11, 15), 2150 unique reflections with $I > 2\sigma(I)$, no absorption correction; direct methods with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977), 29 non-H atoms located on E

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