

Positional parameters and the equivalent values of the anisotropic displacement parameters for the non-H atoms are given in Table 1.* Bond lengths, bond angles, torsion angles, least-squares planes, dihedral angles and possible hydrogen bonds are given in Table 2.

Related literature. The title compound was structurally characterized in order to rationalize its poor reactivity with excess cyanide (Frommer & Lippert, 1990). This reaction has been studied with regard to differences of cisplatin-nucleobases adducts removal from DNA (Raudaschl-Sieber & Lippert, 1985). We have previously postulated that a fixed head-tail orientation of two bases carrying exocyclic oxygens adjacent to the Pt binding site successfully prevents ligand substitution by CN⁻. The present crystal structure confirms this assumption and strongly suggests that the single set of 1-MeC resonances in the ¹H NMR spectra (D₂O) of the title compound up to 348 K is due to a single rotamer (head-tail) rather than to rapid ligand rotation. While the CH₃ groups of the tmeda ligand further increase the steric bulk for rotation of 1-MeC (Reily & Marzilli, 1986)

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53594 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(tmeda = *N,N,N',N'*-tetramethylethylenediamine), these groups are not inherently responsible for the non-reactivity of the title compound towards CN⁻. Neither (tmeda)PtCl₂ nor [(tmeda)Pt(py)₂](ClO₄)₂ display similar behaviour. Rather, all ligands undergo rapid substitution by CN⁻. We have also characterized the latter compound by X-ray analysis [orthorhombic, *P*2₁2₁2₁, *a* = 10.936 (3), *b* = 13.000 (3), *c* = 16.985 (4) Å, *V* = 2415 (1) Å³, *Z* = 4], but the present refinement (*R* = 0.073), because of unreasonable displacement parameters is not satisfactory.

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Structure of Tris(η^5 -cyclopentadienyl)uranium Iodide

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Abstract. [U(C₅H₅)₃]I, *M_r* = 560.22, orthorhombic, *P*2₁2₁2₁, *a* = 8.109 (3), *b* = 13.346 (3), *c* = 13.626 (3) Å, *V* = 1475 (1) Å³, *Z* = 4, *D_x* = 2.523 g cm⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 124.9 cm⁻¹, *F*(000) = 1000, *T* = 295 (1) K, *R* = 0.037 for 902 observed unique reflections [*I* ≥ 1.5σ(*I*)]. The title compound is not isostructural with its bromide,

chloride or fluoride analogues. The four halide derivatives exhibit, however, identical coordination polyhedra about the U atom. This atom is surrounded by three η^5 -covalently bonded cyclopentadienyl rings and by one iodide atom in a distorted tetrahedral configuration.

Experimental. [U(C₅H₅)₃]I was prepared from uranium iodide and potassium cyclopentadienide in

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
U	0.4632 (1)	-0.01239 (5)	0.05539 (6)	2.12 (1)
I	0.5497 (3)	-0.1217 (1)	-0.1352 (1)	5.52 (4)
C(1)	0.167 (3)	0.084 (2)	0.078 (2)	4.0 (5)
C(2)	0.173 (3)	0.059 (2)	-0.022 (2)	5.0 (6)
C(3)	0.162 (3)	-0.041 (2)	-0.037 (2)	4.4 (5)
C(4)	0.148 (3)	-0.082 (2)	0.053 (2)	5.6 (6)
C(5)	0.154 (3)	-0.014 (2)	0.125 (2)	4.8 (6)
C(6)	0.519 (3)	0.185 (2)	0.091 (2)	4.4 (5)
C(7)	0.505 (3)	0.180 (2)	-0.007 (2)	4.6 (6)
C(8)	0.620 (4)	0.131 (2)	-0.053 (2)	6.4 (7)
C(9)	0.735 (3)	0.094 (2)	0.027 (2)	5.4 (7)
C(10)	0.677 (3)	0.133 (2)	0.111 (2)	4.4 (6)
C(11)	0.497 (3)	-0.203 (2)	0.139 (2)	5.0 (6)
C(12)	0.434 (3)	-0.141 (2)	0.209 (2)	5.4 (6)
C(13)	0.554 (3)	-0.067 (2)	0.237 (2)	5.0 (5)
C(14)	0.694 (3)	-0.088 (2)	0.180 (2)	5.8 (7)
C(15)	0.651 (4)	-0.170 (2)	0.112 (2)	6.3 (7)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) in $[\text{U}(\text{C}_5\text{H}_5)_3]\text{I}$, *e.s.d.*'s are given in parentheses

U—C(1)	2.75 (2)	I—U—Cp.I	100.9 (6)
U—C(2)	2.75 (3)	I—U—Cp.II	101.3 (6)
U—C(3)	2.78 (3)	I—U—Cp.III	100.0 (6)
U—C(4)	2.72 (3)	Cp.I—U—Cp.II	114.5 (7)
U—C(5)	2.69 (2)	Cp.I—U—Cp.III	116.4 (7)
U—C(6)	2.72 (2)	Cp.II—U—Cp.III	119.0 (8)
U—C(7)	2.73 (2)		
U—C(8)	2.73 (3)		
U—C(9)	2.65 (3)		
U—C(10)	2.72 (3)		
U—C(11)	2.81 (2)		
U—C(12)	2.72 (2)		
U—C(13)	2.69 (3)		
U—C(14)	2.72 (3)		
U—C(15)	2.70 (4)		
U—I	2.059 (2)		
U—Cp.I*	2.467 (3)		
U—Cp.II	2.435 (3)		
U—Cp.III	2.449 (3)		

* Cp.I denotes centroid of ring 1 [C(1), C(2), C(3), C(4), C(5)]; Cp.II denotes centroid of ring 2 [C(6), C(7), C(8), C(9), C(10)]; Cp.III denotes centroid of ring 3 [C(11), C(12), C(13), C(14), C(15)].

tetrahydrofuran as described by Fischer, von Ammon & Kanellakopoulos (1970). Extraction followed by recrystallization with *n*-pentane yields dark brown prismatic single crystals. The selected specimen (0.30 × 0.25 × 0.20 mm) was sealed in a thin-walled glass capillary under an inert atmosphere. X-ray diffraction data were measured with an Enraf-Nonius CAD-4 X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation and θ -2 θ scans. The unit-cell dimensions were determined from 25 reflections in the range $5 \leq 2\theta \leq 23^\circ$. The space group was established from systematic absences. Intensity data were collected in the range $2 \leq 2\theta \leq 23^\circ$, h 0 → 10, k 0 → 16, l 0 → 16: 2304 unique reflections were collected, 902 of which were considered

observed [$I \geq 1.5\sigma(I)$] and used in refinement. The intensities of three standard reflections were measured at 30 min intervals. An anisotropic decay correction was applied to the measured intensities (total decay 1.39%). The intensities were corrected for Lorentz-polarization effects. Empirical absorption corrections were also applied using the program *DIFABS* (Walker & Stuart, 1983); the min. and max. transmission coefficients were 0.8558 and 1.1831. The structure was solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$: $w = 1/[(F_o)^2]$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I) + (A/I)^2]^{1/2}/Lp$, where the ignorance factor $A = 0.06$. Anisotropic thermal parameters were used for the U and I atoms. H atoms in calculated positions were included in the final structure-factor calculation with an individual isotropic temperature factor for each H atom equal to that of the attached C atom. A secondary-extinction coefficient refined to a value of $g = 9.2 \times 10^{-8} \{F_c = F_c/[1 + g(F_c^2 Lp)]\}$. The refinement converged to $R = 0.037$, $wR = 0.042$. $S = 1.12$, $(\Delta/\sigma)_{\text{max}} = 0.001$. $\Delta\rho$ in final difference Fourier map was within +1.05 and -1.07 e \AA^{-3} (around U atom). Atomic factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were from the Enraf-Nonius (1986) *SDP* system. Atomic coordinates and isotropic temperature factors are given in Table 1* with selected bond distances and angles in

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53562 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

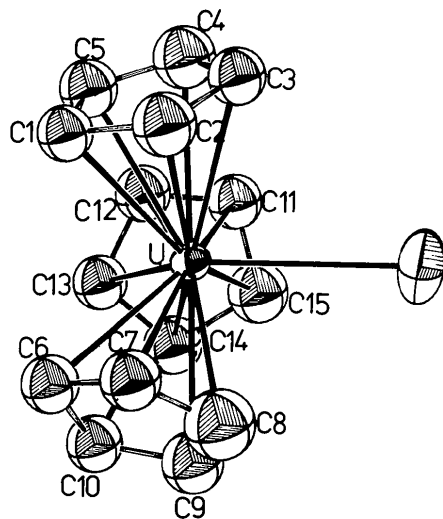


Fig. 1. The molecular structure of $[\text{U}(\text{C}_5\text{H}_5)_3]\text{I}$. Thermal ellipsoids are at the 50% probability level.

Table 2. An *ORTEP* illustration (Johnson, 1976) of the molecular structure is given in Fig. 1.

Related literature. Structures of tris(cyclopentadienyl)halogenouranium complexes $[\text{U}(\text{C}_5\text{H}_5)_3]\text{X}$ have previously been reported in the literature for $\text{X} = \text{F}, \text{Cl}$ and Br [Ryan, Penneman & Kanellakopoulos (1975); Wong, Yen & Lee (1965) and Spirlet, Rebizant, Apostolidis, Andreotti & Kanellakopoulos (1989) for $\text{X} = \text{F}, \text{Cl}$ and Br , respectively]. With the present structure analysis of the iodine derivative the series is completed. Although the pseudo-tetrahedral coordination geometry about the U atom is almost identical in the four compounds, they all exhibit different packing arrangements. None is isostructural with another. The U—C bond distances range from 2.65 (3) to 2.80 (2) Å; the U—I bond length of 3.059 (2) Å is comparable to that of 3.041 (1) Å

observed in $\text{U}(\text{C}_5\text{H}_7)_3\text{I}$ (Rebizant, Spirlet, Van Den Bossche & Goffart, 1988).

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Structure of 2,3,4- μ_3 -Chloro-1,2,3;1,3,4;1,2,4-tri- μ_3 -sulfido-tris[(tri-phenylphosphine)copper](sulfidotungsten)(3 Cu—W).0.5-Propanol

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Abstract. $[\{\text{WCu}_3\text{S}_3\text{Cl}\}(\text{S})\{\text{P}(\text{C}_6\text{H}_5)_3\}_3] \cdot 0.5(\text{CH}_3)_2\text{CHOH}$, $M_r = 1355.1$, triclinic, $P\bar{1}$, $a = 13.181$ (10), $b = 20.327$ (12), $c = 12.005$ (6) Å, $\alpha = 93.35$ (5), $\beta = 116.10$ (4), $\gamma = 74.57$ (6)°, $V = 2777$ (3) Å³, $Z = 2$, $D_x = 1.62$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.710690$ Å, $\mu = 35.59$ cm⁻¹, $F(000) = 1346$, $T = 296$ K, $R = 0.071$ for 3892 observed unique reflections, $I \geq 3\sigma(I)$. The structure contains discrete molecules with a distorted cubane-like cluster core ($\text{WCu}_3\text{S}_3\text{Cl}$) [three Cu...Cl distances are 2.794 (8), 2.668 (7) and 2.696 (7) Å; W=S 2.134 (8) Å]; mean Cu—S 2.417 (7), W—Cu 2.832 (3), W—(μ_3 -S) 2.246 (7) Å. The W atom has a tetrahedral coordination from four S atoms, and the PPh_3 ligands complete tetrahedral geometry at each Cu atom. One solvent molecule of propanol disorders near the origin of the unit cell.

Experimental. Crystals of the title compound were obtained by the reaction of PPh_3 , CuCl and $(\text{NH}_4)_2\text{WS}_4$ in a mixed solution of CH_2Cl_2 /

$(\text{CH}_3)_2\text{CHOH}$. The yellow crystal measured $0.30 \times 0.05 \times 0.30$ mm and was mounted in a random orientation on a glass fibre. Data were collected using a RIGAKU AFC5R diffractometer [CONTROL software (Molecular Structure Corporation, 1986)] using Mo $K\alpha$ radiation at ca 296 K. Cell constants were obtained by least-squares analysis of 20 diffraction maxima ($24 < 2\theta < 35^\circ$), $\omega/2\theta$ scan, scan speed varied between 2, 4, and 8° min^{-1} (in ω) on the basis of SEARCH intensity, the scan width is $(1.523 + 0.35 \tan \theta)^\circ$, maximum $2\theta = 50^\circ$ ($0 \leq h \leq 16$, $-24 \leq k \leq 24$, $-14 \leq l \leq 14$). Maximum $(\sin \theta)/\lambda = 0.5946$ Å⁻¹. Of the 10241 reflections that were collected, 9772 were unique. Three standard reflections were measured periodically, only random deviations were observed. Intensity was defined as $C - 1/2(t_c/t_b)(b_1 + b_2)$, where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of the background, b_1 = high-angle background counts and b_2 = low-angle background counts; the intensity error $\sigma(F^2) = [C + 1/4(t_c/t_b)^2(b_1 + b_2) + (pI)^2]^{1/2}$, where I is the intensity

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