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Structure of Tris(1—3-η-indenyl)iodouranium

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Abstract. [$U(C_9H_7)_3I$], $M_r = 710{\cdot}40$, monoclinic, $P2_1/c$, $a = 14{\cdot}454$ (5), $b = 10{\cdot}416$ (6), $c = 18{\cdot}156$ (3) Å, $\beta = 128{\cdot}87$ (6)°, $V = 2128$ (4) Å^3, $Z = 4$, $D_x = 2{\cdot}217$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 86{\cdot}786$ cm^{-1}, $F(000) = 1312$, $T = 295$ (1) K, $R = 0{\cdot}049$ for 1877 reflections [$I \geq 3\sigma(I)$]. The title compound is not isostructural with its Cl and Br analogues although the geometry of the coordination polyhedron about the U is identical in the three derivatives. The U atom is surrounded by three indenyl rings and one iodide atom in an approximately tetrahedral configuration. As for [$U(C_9H_7)_3Cl$] and [$U(C_9H_7)_3Br$] the orientation of the indenyl rings and the shorter bonds observed between the U atom and the three non-bridging C atoms from the five-membered ring of each indenyl moiety suggest a trihapto character of the metal–carbon bonding.

Introduction. Since the synthesis of uranocene (Streitwieser & Muller-Westerhoff, 1968) and its characterization (Zalkin & Raymond, 1969; Avdeef, Raymond, Hodgson & Zalkin, 1972), research on organometallic compounds of the tetravalent actinides has greatly increased. Nevertheless few structural data have been reported on organoactinide complexes of the indenide ligand [$U(C_9H_7)_3Cl$: Burns & Laubereau (1971); $U(C_9H_7)Br_3.C_4H_8O.OP(C_6H_5)_3$: Meunier-Piret, Germain, Declercq & Van Meerssche (1980); $Th(C_{12}H_{13})_3Cl$: Spirlet, Rebizant & Goffart (1982); $U(C_9H_7)Cl_3.2C_4H_8O$: Rebizant, Spirlet & Goffart (1983); $U(C_{12}H_{13})_3Cl$: Meunier-Piret & Van Meerssche (1984); $U(C_9H_7)Br_3.2C_4H_8O$: Rebizant, Spirlet & Goffart (1985); $U(C_9H_7)_3Br$: Spirlet, Rebizant & Goffart (1987)] and very few iodo complexes of uranium(IV) are known. The only U^{IV}—I bond length reported so far is that of UI_4 (Levy, Taylor & Waugh, 1980). The present work has been undertaken to provide further insight into actinide–C π bonding with an example of interaction between uranium(IV) and the indenide ligand in the presence of iodine ion rather than chlorine or bromine ion.

Experimental. Compound synthetized as described elsewhere (Goffart, Fuger, Gilbert, Hocks & Duyckaerts, 1975) and recrystallized from pentane. Selected specimen (0·26 × 0·30 × 0·20 mm) sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation using θ–2θ scans. Cell parameters refined by least squares from angle data of 25 reflections in range $6 < 2\theta < 30°$. Space group unequivocally established from systematic absences. Data collected in range $4 \leq 2\theta \leq 46°$, h −21→21, k 0→25, l −18→18; 6089 reflections collected, averaged to 2957 unique reflections ($R_{\text{int}} = 0{\cdot}03$), 1877 with $I \geq 3\sigma(I)$ used in refinement. Intensities of three standard reflections measured at 30 min intervals, anisotropic decay correction applied (total decay 1·6%). Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors range from 57·62 to 99·98%). Structure solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/\text{Lp}$ where A, the ignorance factor, is 0·08. The use of anisotropic thermal parameters resulted in non-positive values for several C atoms, so only the

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thermal motions of the U and I atoms were treated anisotropically. Inclusion of H atoms in calculated positions leads to a worse agreement between observed and calculated structure factors. The best R factors were obtained omitting H atoms and using a cutoff of $3\sigma(I)$.

A secondary-extinction coefficient refined to $g = 2{\cdot}7 \times 10^{-8}$ $\{F_c = F_c/[1 + g(F_c)^2\mathrm{Lp}]\}$. $R = 0{\cdot}049$, $wR = 0{\cdot}089$, $S = 1{\cdot}998$. Final $(\Delta/\sigma)_{\max} = 0{\cdot}02$. Maximum and minimum heights in final difference Fourier map 2·69 and $-2{\cdot}56$ e Å^{-3} (near the U position). Atomic factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. The structure consists of discrete molecules of $[\mathrm{U(C_9H_7)_3I}]$ which are illustrated in Fig. 1 together with the atomic numbering scheme. Final atomic coordinates are given in Table 1;* selected interatomic distances and angles are listed in Table 2.

The title compound is not isostructural with the corresponding Cl and Br derivatives $[\mathrm{U(C_9H_7)_3Cl}$: Burns & Laubereau (1971) and $\mathrm{U(C_9H_7)_3Br}$: Spirlet, Rebizant & Goffart (1987)]. However, in the molecule the coordination and the geometry around U are identical with that observed for the Cl and Br analogues. The I and the five-membered rings of the three indenyl moieties are arranged in an approximate tetrahedron about U. The extent of deviation of the structure from a regular tetrahedron is shown by the angles between the U—I direction and the U–centre of ring (designated as ind. I, ind. II and ind. III) directions (Table 2). The average I—U—ind. angle of 99·3° and the average ind.—U—ind. angle of 117·5° agree well with the corresponding mean values of 100·7 and 116·6° for $\mathrm{U(C_9H_7)_3Cl}$ and 100·8 and 116·6° for $\mathrm{U(C_9H_7)_3Br}$. Such an agreement is also observed with the corresponding mean values of 100 and 117° respectively reported for a series of organometallic complexes of U with the general formula $\mathrm{U(C_5H_5)_3}R$ (Perego, Cesari, Farina & Lugli, 1976). The distances from the U atom to the centre of the rings ind. I, ind. II and ind. III are respectively 2·47 (2), 2·52 (2) and 2·48 (2) Å.

The five- and six-membered portions of the indenyl rings are almost planar although each indenyl ring as a whole exhibits significant deviations from planarity. An average bending of about 7° occurs between the five- and the six-membered ring portions. This bending would result from steric hindrance between the bulky ligands around the U atom. Indeed there appear to be

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (e.s.d.'s in parentheses)*

	x	y	z	B_{eq}*/B_{iso}(Å^2)
U	0·22883 (6)	0·78742 (6)	0·25298 (4)	2·91 (2)
I	0·3520 (1)	0·5916 (2)	0·21655 (7)	4·63 (4)
C1	0·454 (1)	0·865 (2)	0·363 (1)	3·6 (4)
C2	0·385 (1)	0·973 (1)	0·3377 (8)	1·6 (3)
C3	0·340 (2)	0·976 (2)	0·388 (1)	4·4 (4)
C4	0·389 (1)	0·832 (2)	0·5204 (9)	3·0 (4)
C5	0·453 (2)	0·729 (2)	0·573 (1)	4·2 (4)
C6	0·520 (2)	0·657 (3)	0·561 (2)	6·8 (6)
C7	0·531 (2)	0·686 (3)	0·493 (2)	6·7 (6)
C8	0·453 (1)	0·795 (2)	0·431 (1)	3·4 (4)
C9	0·388 (2)	0·868 (2)	0·449 (1)	5·1 (5)
C10	0·177 (2)	0·542 (2)	0·288 (1)	5·1 (5)
C11	0·206 (2)	0·630 (2)	0·354 (1)	4·1 (4)
C12	0·121 (2)	0·723 (2)	0·323 (1)	4·3 (4)
C13	−0·104 (3)	0·719 (3)	0·145 (2)	7·8 (8)
C14	−0·161 (3)	0·650 (4)	0·065 (2)	10 (1)
C15	−0·113 (2)	0·557 (3)	0·051 (2)	7·7 (7)
C16	0·005 (1)	0·503 (2)	0·117 (1)	4·0 (4)
C17	0·069 (1)	0·566 (2)	0·205 (1)	3·2 (4)
C18	0·024 (2)	0·678 (2)	0·219 (1)	4·6 (5)
C19	0·035 (2)	0·919 (3)	0·117 (1)	5·5 (5)
C20	0·053 (2)	0·819 (3)	0·076 (2)	7·0 (7)
C21	0·146 (2)	0·836 (3)	0·071 (2)	6·9 (6)
C22	0·290 (2)	1·036 (3)	0·118 (2)	7·8 (8)
C23	0·296 (1)	1·158 (2)	0·146 (1)	3·8 (4)
C24	0·244 (2)	1·205 (2)	0·173 (2)	5·9 (6)
C25	0·161 (2)	1·142 (2)	0·175 (1)	5·1 (5)
C26	0·131 (1)	1·017 (2)	0·1389 (8)	1·8 (3)
C27	0·190 (1)	0·958 (2)	0·111 (1)	3·2 (4)

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

Table 2. *Selected distances (Å) and angles (°) with e.s.d.'s in parentheses*

U–I 3·041 (1)

Indenyl group I		Indenyl group II		Indenyl group III	
U–C1	2·66 (2)	U–C10	2·85 (2)	U–C19	2·67 (2)
–C2	2·61 (1)	–C11	2·64 (2)	–C20	2·57 (2)
–C3	2·74 (2)	–C12	2·63 (2)	–C21	2·77 (2)
–C8	2·80 (2)	–C17	2·98 (1)	–C26	2·89 (1)
–C9	2·89 (2)	–C18	2·85 (2)	–C27	2·89 (1)

I–U–ind. I	99·8 (4)	I–U–ind. III	101·4 (6)	ind.I–U–ind.III	117·2 (8)
I–U–ind. II	96·6 (4)	ind. I–U–ind. II	117·8 (7)	ind.II–U–ind.III	117·4 (8)

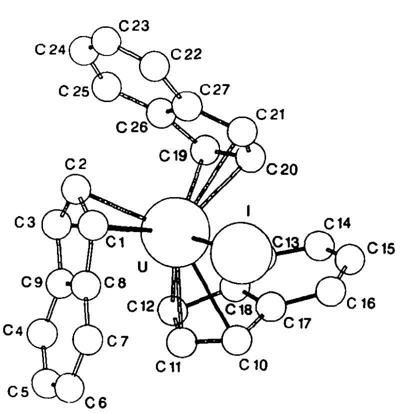

Fig. 1. View of the molecular structure.

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* Lists of structure amplitudes, anisotropic thermal parameters, intramolecular contact distances and a fuller list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51062 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

several short intramolecular non-bonded contacts in the coordination sphere,* the shortest being three C···C contacts between C13 and C19 3·16 (3), C2 and C26 3·18 (2) and C18 and C19 3·18 (3) Å.

The U—I bond length of 3·041 (1) Å is not much shorter than the sum of the ionic radii of U^{4+} and $I^- = 3·16$ Å and is to be compared with the U—I (bridging) distances 3·08 (2) and 3·11 (2) Å and the U—I (terminal) distances 2·92 (2) Å in UI_4 (Levy, Taylor, & Waugh, 1980).

The U—C distances reported in Table 2 show that the closest approaches are, in each case, to the three non-bridging atoms of the five-membered rings. The lengthening of the U—C distances to the bridging C atoms in comparison with the U—C bond lengths to the non-bridging C atoms cannot be ascribed solely to steric factors, since short intramolecular contacts involve both the non-bridging C atoms and the bridging ones. It results also from electronic factors, the negative charge of the indenyl anion residing primarily on the non-bridging C atoms. These observations confirm the conclusions reported for $U(C_9H_7)_3Cl$ (Burns & Laubereau, 1971) and for $U(C_9H_7)_3Br$ (Spirlet, Rebizant & Goffart, 1987) suggesting trihapto actinide—C π bonding with the indenyl ligands.

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* See deposition footnote.

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Structure of 3,4-Ethylenedithio-3′,4′-propylenedithio-2,2′,5,5′-tetrathiafulvalenium Tetraiodoindate(III)

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Abstract. 4,5-Ethylenedithio-4′,5′-trimethylenedithio-2,2′-bi-1,3-dithiolylidenium tetraiodoindate(III), $C_{11}H_{10}S_8^+.InI_4^-$, $M_r = 121·1$, monoclinic, $P2_1/c$, $a = 6·920$ (2), $b = 12·176$ (5), $c = 30·421$ (8) Å, $\beta = 92·17$ (2)°, $V = 2561$ (1) Å^3, $Z = 4$, $D_x = 2·648$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 6·309$ mm^{-1}, $F(000) = 1860$, $T = 296$ K. The first crystal-structure determination of a cation-radical salt containing the new unsymmetrical donor 3,4-ethylenedithio-3′,4′-propylenedithio-2,5,2′,5′-tetrathiafulvalene (EPT) is reported. The electrocrystallization of EPT with $[N(C_4H_9)_4][InI_4]$ yields a charge-transfer salt in which EPT cations and InI_4^- anions are present in a 1:1 ratio. The structure consists of dimerized stacks of EPT donor cations segregated by InI_4^- anions, forming one-dimensional chains of EPT cations oriented along the *a*-axis direction. Within each dimeric unit the EPT donors are separated by a distance of 3·29 (2) Å. Side-by-side intermolecular S···S contacts between individual EPT donors range from 3·522 (3) to 3·688 (4) Å, the shortest of which involve the S atoms of the six- and seven-atom ethylene and propylene rings. Convergence to conventional R values of $R = 0·080$ and $wR = 0·044$ was obtained using 238 variable parameters and 4512 averaged reflections ($R_{\text{int}} = 0·031$).

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