The *X*-Ray Crystal Structure Determination of Tetraphenylarsonium Tris(η^5-cyclopentadienyl)di-isothiocyanatouranate(IV)†

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffraction data. The compound crystallises in space group $P\bar{1}$, with a = 15.570(7), b = 13.727(5), c = 9.082(4) Å, α = 94.8(1), β = 104.9(1), γ = 99.6(1)°, and Z = 2. The structure was solved by Patterson and Fourier methods; full-matrix least-squares refinement based on 3 584 reflections gave a final R value of 0.053. The co-ordination about the uranium atom in the anion $[U(cp)_3(NCS)_2]^-$ (cp = cyclopentadienyl) is a trigonal bipyramid with three π-bonded cp rings in the equatorial plane (U–ring centre distances 2.48, 2.49, and 2.50 Å) and two nitrogen-bonded thiocyanate groups in the axial positions (U–N 2.46 and 2.50 Å). The As–C distances in the cation $[AsPh_4]^+$ range from 1.873 to 1.886 Å and the C–As–C angles fall in the range 106.5—111.9°. The structure is discussed in conjunction with information available for $[U(cp)_3(NCS)(NCCH_3)]$ and $[U(cp)_3(NCCH_3)_2]_2[UO_2Cl_4]\cdot 2L$ (L = buta-1,3-diene).

The preparation of the first mononuclear, negatively charged, five-co-ordinate tris-cyclopentadienyl actinide(IV) complexes, $[M(cp)_3X_2]^-$ (M = U, Np, or Pu; X = NCS) and $[U(cp)_3XY]^-$ (X = NCS, Y = NCO), has recently been reported.[1] Spectrophotometric evidence suggested trigonal bipyramidal co-ordination for the metal atom in the uranium complexes, with which the neptunium and plutonium analogues were shown to be isostructural by *X*-ray powder diffraction data, as in the known structure of $[U(cp)_3(NCS)(NCCH_3)]$.[2] This has now been confirmed by the determination of the structure of $[AsPh_4][U(cp)_3(NCS)_2]$. The detailed co-ordination within the anion $[U(cp)_3(NCS)_2]^-$ is compared with similar information for the neutral complex $[U(cp)_3(NCS)(NCCH_3)]$ [2] and the cation $[U(cp)_3(NCCH_3)_2]^+$.[3]

Experimental

The complex $[AsPh_4][U(cp)_3(NCS)_2]$ was prepared as described earlier [1] and recrystallised from acetonitrile. A single crystal of approximate dimensions 0.03 × 0.04 × 0.1 mm, mounted in a glass capillary, was used for data collection.

Crystal Data.—$C_{41}H_{35}AsN_2S_2U$, M = 932.8, Triclinic, space group $P\bar{1}$, a = 15.570(7), b = 13.727(5), c = 9.082(4) Å, α = 94.8(1), β = 104.9(1), γ = 99.6(1)°, U = 1 835.4 Å^3, Z = 2, D_c = 1.69 g cm^{-3}, $F(000)$ = 904, μ(Mo-K_α) = 52.3 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Data Collection and Structure Refinement.—*X*-Ray intensity data were collected on a four-circle Philips PW1100 automated diffractometer with graphite monochromated Mo-K_α radiation. The unit cell was determined on the basis of 25 strong reflections found by mounting the crystal at random and varying the orientation angles φ and χ in the range of 120° each, with the detector position varying between θ = 6° and θ = 10°. For the determination of precise lattice parameters 20 strong reflections with $9 \leqslant \theta \leqslant 14°$ were considered. Integrated intensities of hkl reflections with $l \geqslant 0$ and $3 \leqslant \theta \leqslant 25°$ were measured using the θ—2θ scan method with a scan speed of 0.03° s^{-1}, scan width 1.2°, and two background counts of 20 s at each end of the scans. Of the 6 949 reflections thus considered, 3 584 having a net intensity greater than 3σ (σ = standard error based on counting statistics) were used in the structure determination and refinement. The intensities of three standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The intensity data were corrected for Lorentz and polarization effects and for absorption following the method of North *et al.*[4]

The positions of the uranium and arsenic atoms were determined from a three-dimensional Patterson function. The Fourier-difference synthesis phased with the heavy-atom positions allowed the location of some of the lighter atoms including the two NCS groups. A further Fourier-difference synthesis showed all the missing non-hydrogen atoms. At this point the R factor was 0.152. Full-matrix least-squares refinement was carried out. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors; w = 1 showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to $|F_o|$ and to $(\sin\theta)/\lambda$. Anisotropic thermal parameters were introduced for all the non-hydrogen atoms except those belonging to the phenyl rings, which were refined as rigid groups and restricted to their normal geometry (D_{6h} symmetry, C–C = 1.395 Å) using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen atom contributions were used as fixed atoms in calculated positions (d_{C-H} = 0.95 Å and B_{iso} = 7 Å^2).

This model converged at a final R 0.053. A difference-Fourier map calculated at this point was practically featureless except for a few peaks of *ca.* 0.8 e Å^{-3} in the proximities of the uranium and arsenic positions.

The anomalous dispersion terms [5] for U and As were taken

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† *Supplementary data available* (No. SUP 23439, 25 pp.): observed and calculated structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U	2 259(0)	112(0)	4 253(1)				
As	7 407(1)	4 123(1)	1 710(2)				
S(1)	4 839(3)	3 283(4)	5 640(6)				
S(2)	−244(3)	−3 055(4)	3 807(6)				
N(1)	3 462(10)	1 630(11)	4 608(18)				
N(2)	1 097(10)	−1 394(11)	3 973(18)				
C(1)	4 035(11)	2 320(13)	5 050(19)				
C(2)	537(11)	−2 080(13)	3 900(19)				
C(3)	685(12)	801(20)	3 583(29)	H(31)	33	67	428
C(4)	617(13)	191(16)	2 214(30)	H(41)	21	−43	183
C(5)	1 232(15)	660(10)	1 559(23)	H(51)	134	40	64
C(6)	1 697(12)	1 558(17)	2 497(27)	H(61)	216	203	229
C(7)	1 339(13)	1 611(15)	3 701(27)	H(71)	153	215	152
C(8)	3 136(17)	−256(22)	2 089(28)	H(81)	314	25	143
C(9)	2 477(18)	−1 084(25)	1 868(30)	H(91)	196	−126	101
C(10)	2 711(15)	−1 585(14)	3 103(38)	H(101)	236	−219	323
C(11)	3 539(14)	−1 059(17)	4 046(29)	H(111)	386	−124	499
C(12)	3 774(12)	−243(15)	3 399(27)	H(121)	431	25	379
C(13)	1 979(16)	742(17)	7 066(22)	H(131)	153	114	704
C(14)	1 833(14)	−277(16)	6 958(21)	H(141)	127	−71	687
C(15)	2 651(13)	−595(15)	6 993(20)	H(151)	275	−126	689
C(16)	3 308(13)	237(15)	7 182(23)	H(161)	394	28	731
C(17)	2 917(19)	1 077(18)	7 229(22)	H(171)	320	176	732
C(18)	6 458(6)	3 010(7)	1 360(9)				
C(19)	5 988(6)	2 790(7)	2 445(9)	H(19)	615	320	341
C(20)	5 275(6)	1 969(7)	2 114(9)	H(20)	496	182	285
C(21)	5 032(6)	1 369(7)	697(9)	H(21)	455	81	47
C(22)	5 503(6)	1 589(7)	−388(9)	H(22)	534	118	−135
C(23)	6 215(6)	2 410(7)	−57(9)	H(23)	654	256	−80
C(24)	8 370(7)	3 665(7)	1 166(10)				
C(25)	8 744(7)	2 926(7)	1 920(10)	H(25)	853	268	273
C(26)	9 437(7)	2 556(7)	1 488(10)	H(26)	969	205	200
C(27)	9 757(7)	2 925(7)	303(10)	H(27)	23	267	1
C(28)	9 383(7)	3 664(7)	−451(10)	H(28)	960	392	−126
C(29)	8 689(7)	4 034(7)	−20(10)	H(29)	843	454	−53
C(30)	7 011(6)	5 094(6)	488(12)				
C(31)	6 211(6)	4 878(6)	−708(12)	H(31)	586	422	−96
C(32)	5 925(6)	5 629(6)	−1 542(12)	H(32)	538	548	−236
C(33)	6 438(6)	6 596(6)	−1 180(12)	H(33)	624	711	−175
C(34)	7 238(6)	6 811(6)	16(12)	H(34)	759	747	26
C(35)	7 525(6)	6 060(6)	849(12)	H(35)	807	621	166
C(36)	7 746(6)	4 725(7)	3 757(12)				
C(37)	8 578(6)	4 695(7)	4 777(12)	H(37)	899	435	445
C(38)	8 805(6)	5 171(7)	6 282(12)	H(38)	937	515	698
C(39)	8 200(6)	5 677(7)	6 768(12)	H(39)	836	600	779
C(40)	7 368(6)	5 707(7)	5 748(12)	H(40)	696	605	608
C(41)	7 141(6)	5 231(7)	4 243(12)	H(41)	657	525	355

into account in the refinement. Atomic scattering factors for U and As were taken from ref. 6, for the other non-hydrogen atoms from ref. 7, and for the hydrogen atoms from ref. 8. Data processing and computation were carried out using the SHELX 76 programs package.[9] The final positional parameters are listed in Table 1.

Results and Discussion

Figure 1 shows the stereochemistry of the $[U(cp)_3(NCS)_2]^-$ anion and $[AsPh_4]^+$ cation and the atom numbering scheme. The relevant interatomic distances and bond angles are given in Tables 2 and 3, respectively, and the significant best mean planes in the structure are shown in Table 4. The packing of the ionic units viewed down *c* is shown in Figure 2.

The co-ordination around the uranium atom is a trigonal bipyramid, comprising three π-bonded η^5-cyclopentadienyl rings, the centres of which form the equatorial plane of the bipyramid, and two axially co-ordinated thiocyanate groups which are bonded *via* the nitrogen atoms. This arrangement is similar to those in the neutral complex $[U(cp)_3(NCS)(NCCH_3)]$[2] and in the cationic group $[U(cp)_3(NCCH_3)_2]^+$.[3] Selected bond distances and angles for the three species are compared in Table 5, from which it is seen that the average U–C and U–M (M = ring centre) distances and the M–U–M′ angles are very similar. These values are also comparable to those reported for tetrahedral compounds of the type $[U(cp)_3X]$ (X = halogen or aryl group); for example, in $[U(cp)_3F]$, U–C = 2.74 Å and the average M–U–M′ angle is 117°.[10] Thus the conversion from four-co-ordinate tetrahedral geometry to five-co-ordinate trigonal bipyramidal geometry, at least for the presently known *trans* thiocyanates and methyl cyanide adducts of the latter class, involves little change in the steric arrangement of the $U(cp)_3{}^+$ nucleus. Indeed, the main change on the evidence available appears to be a small increase in the average M–U–M′ angle from *ca.* 117° to *ca.* 120°. This undoubtedly explains the ease with which five-co-ordinate actinide(IV) compounds of the types $[M(cp)_3X_2]$ and

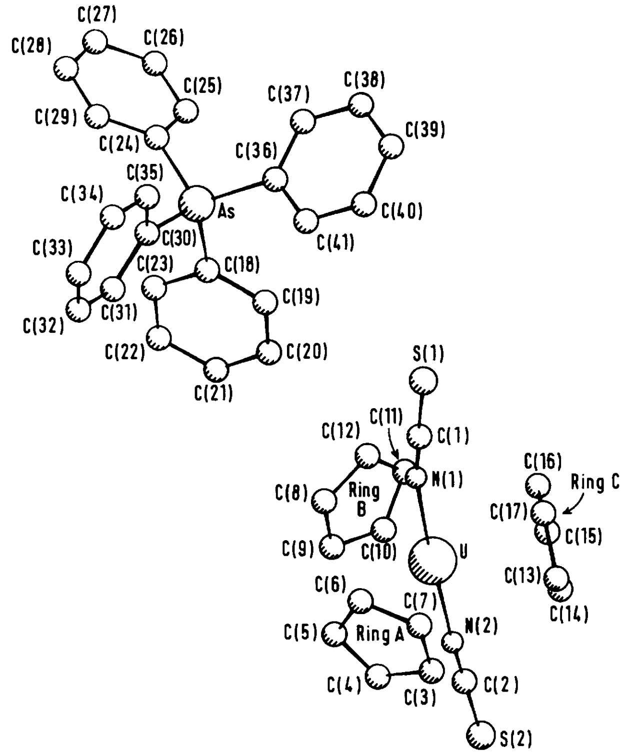

Figure 1. The $[U(cp)_3(NCS)_2]^-$ anion and $[AsPh_4]^+$ cation showing the atomic numbering system

Table 2. Interatomic distances (Å) with e.s.d.s in parentheses

U–N(1)	2.50(1)	N(1)–C(1)	1.15(2)	C(1)–S(1)	1.61(2)
U–N(2)	2.46(1)	N(2)–C(2)	1.16(2)	C(2)–S(2)	1.63(2)

As–C(18)	1.882(9)	As–C(30)	1.886(10)
As–C(24)	1.873(12)	As–C(36)	1.874(10)

Ring A		Ring B		Ring C	
U–C(3)	2.72(2)	U–C(8)	2.72(3)	U–C(13)	2.79(2)
U–C(4)	2.77(2)	U–C(9)	2.73(3)	U–C(14)	2.77(2)
U–C(5)	2.79(2)	U–C(10)	2.74(2)	U–C(15)	2.71(2)
U–C(6)	2.76(2)	U–C(11)	2.79(2)	U–C(16)	2.71(2)
U–C(7)	2.71(2)	U–C(12)	2.77(2)	U–C(17)	2.76(2)
U–C (average)	2.75	U–C (average)	2.75	U–C (average)	2.75
U–M_A	2.49	U–M_B	2.50	U–M_C	2.48

Averages: U–C 2.75, C–C 1.38, U–M 2.49

M = Centre of a C_5H_5 ring.

$[M(cp)_3XY]$ (where X and Y are anionic or neutral ligands) are formed, subject, of course, to the proviso that M^{4+} should be sufficiently large and that the donor atom from X and Y should be suitably small to allow bonding without steric hindrance.

The two axial NCS groups in $[U(cp)_3(NCS)_2]^-$ are collinear [N(1)–U–N(2) = 178.4(5)°] and the average M–U–N angle is 90°, close to the values obtained for the other two species (Table 5). However, there are significant differences between the U–N bond lengths in the three trigonal bipyramidal units. Thus (Table 5) the U–N (thiocyanate) distance is 2.407(15) Å when it is *trans* to CH_3CN in $[U(cp)_3(NCS)(NCCH_3)]$ compared to the average U–NCS distance of 2.48(1) Å in $[U(cp)_3(NCS)_2]^-$, whilst the U–$NCCH_3$ bond length in the former complex is 2.678(16) Å compared with an average value of 2.60 Å in the cation $[U(cp)_3(NCCH_3)_2]^+$. The anionic ligand NCS^- is clearly co-ordinated more strongly to the Lewis acid U^{IV} than is the neutral ligand $NCCH_3$ and it also exerts a *trans* influence on the U–$NCCH_3$ bond in $[U(cp)_3(NCS)(NCCH_3)]$ as indicated by significant lengthening of the U–$NCCH_3$ distance in this complex relative to the average value in $[U(cp)_3(NCCH_3)_2]^+$.

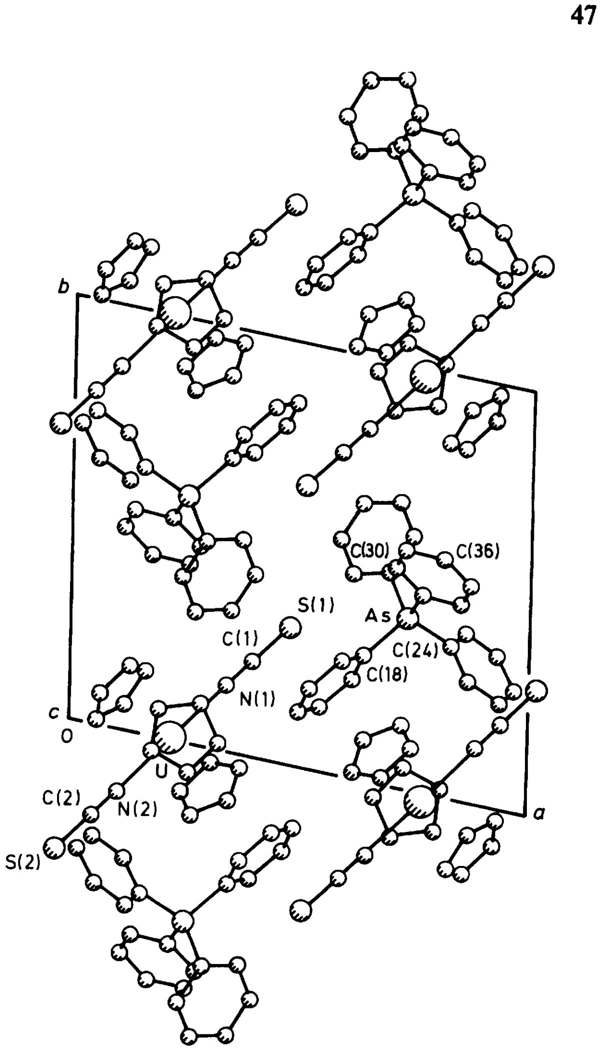

Figure 2. The unit-cell contents viewed down *c*

Table 3. Bond angles (°) with e.s.d.s in parentheses

U–N(1)–C(1)	168(1)	U–N(2)–C(2)	177(2)
N(1)–C(1)–S(1)	179(2)	N(2)–C(2)–S(2)	179(2)
N(1)–U–N(2)	178.4(5)		
C(18)–As–C(24)	106.7(4)	C(24)–As–C(36)	111.9(4)
C(18)–As–C(30)	109.4(4)	C(24)–As–C(30)	110.9(5)
C(18)–As–C(36)	111.4(4)	C(30)–As–C(36)	106.5(4)
M_A–U–M_B	118.8(1)	M_A–U–M_C	120.2(1)
M_B–U–M_C	121.0(1)		
N(1)–U–M_A	90.6(4)	N(2)–U–M_A	90.8(4)
N(1)–U–M_B	89.4(4)	N(2)–U–M_B	90.7(4)
N(1)–U–M_C	89.4(4)	N(2)–U–M_C	89.2(4)

Averages: C–C–C 108, M–U–M′ 120, N(1)–U–M′ 89.8, N(2)–U–M 90.2

In the $[AsPh_4]^+$ cation the As–C distances range from 1.873(12) to 1.886(10) Å whilst the C–As–C angles deviate

Table 4. Least-squares planes with deviations (Å) of the relevant atoms in square brackets. The equation of a plane in the direct space is given by $pX + qY + rZ = s$

		p	*q*	*r*	*s*
Plane 1.	C(3)—C(7) [C(3) 0.0, C(4) 0.002, C(5) −0.003, C(6) 0.003, C(7) −0.002]	10.4162	−8.9361	3.4518	1.2345
Plane 2.	C(8)—C(12) [C(8) −0.003, C(9) 0.009, C(10) −0.011, C(11) 0.009, C(12) −0.003]	11.5078	−7.8400	−5.5229	2.6596
Plane 3.	C(13)—C(17) [C(13) −0.01, C(14) 0.012, C(15) −0.01, C(16) 0.005, C(17) 0.003]	−1.0539	−1.0087	8.9049	6.0184
Plane 4.	M_A, M_B, M_C [U −0.01, S(1) 5.181, S(2) −5.248, N(1) 2.486, N(2) −2.467, C(1) 3.608, C(2) −3.620]	8.8547	9.7202	−1.2669	1.5800
Plane 5.	C(18)—C(23)	10.4823	−10.1097	2.4886	4.0647
Plane 6.	C(24)—C(29)	6.5058	7.4462	4.0711	8.6489
Plane 7.	C(30)—C(35)	11.7239	−3.5304	−7.2079	6.0700
Plane 8.	C(36)—C(41)	5.7733	11.1106	−4.3839	8.0746

Angles (°) between the planes

1—2	60.5	1—3	59.9	2—3	59.6
5—6	81.9	6—7	78.7	7—5	69.8
8—5	65.2	8—6	59.1	8—7	69.8

Table 5. Molecular parameters in trigonal bipyramidal U^{IV} complexes containing cyclopentadienyl ligands

		$[U(cp)_3(NCS)(NCCH_3)]$ (Ref. 2)	$[U(cp)_3(NCCH_3)_2]^+$ (Ref. 3)	$[U(cp)_3(NCS)_2]^-$ (This work)
(*a*) Distances (Å)				
	U-C	2.763	2.74	2.75
	U-$NCCH_3$	2.678(16)	2.61(2) 2.58(2)	
	U-NCS	2.407(15)		2.50(1) 2.46(1)
	U-M	2.484	2.47	2.49
	C-C(ring)	1.42	1.39	1.38
(*b*) Angles (°)				
	M-U-M′	119.9	119.9	120
	M-U-$NCCH_3$	87.8	89.2 90.9	
	M-U-NCS	92.2		89.8 90.2

M = Centre of a C_5H_5 ring.

somewhat from the ideal tetrahedral value, two being less than 109° [106.7(4) and 106.5(4)°], three larger [110.9(5), 111.4(4), and 111.9(4)°], and one close to the expected value [109.4(4)°]. Thus the interatomic interactions only influence the valence angles, as noted in other ionic compounds.[11]

Intermolecular contacts in the compound are not of particular significance.

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