Preparation, Properties, and Crystal Structure of Acetonedi-isothiocyanato-dioxobis(triphenylphosphine oxide)uranium(VI)

By **Gabriella Bombieri,* Eleonora Forsellini, and Giovanni De Paoli**, Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy
David Brown * and Tze Chung Tso, Chemistry Division, A.E.R.E. Harwell, Oxfordshire OX11 0RA

The title compound is obtained by the interaction of uranyl(VI) chloride, potassium thiocyanate, and triphenylphosphine oxide in acetone–methanol mixtures, and by treatment of $[UO_2(NCS)_2(PPh_3O)_2]$ with acetone at room temperature. The structure of this compound has been determined by single-crystal *X*-ray diffraction methods from diffractometer data and refined to a final *R* value of 0.047. It crystallises in space group $Pna2_1$ with a = 17.667(8), b = 9.112(5), c = 25.275(12) Å, and Z = 4. The seven-co-ordinate uranium atom is at the centre of a pentagonal bipyramid, the axis of which is defined by a linear uranyl(VI) group (U–O 1.78 and 1.70 Å). Bond distances to the coplanar equatorial atoms are U–N 2.44 (× 2), U–O(PPh_3) 2.36 and 2.38, and U–O(CMe_2) 2.56 Å.

ACTINOID thiocyanates have not been extensively studied and in particular there is a paucity of structural data.[1,2] During our investigations of the structures of quadrivalent uranium chloro- and thiocyanato-complexes[3-6] a new uranyl(VI) complex, $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$, was obtained accidentally during the recrystallisation of an old sample of the uranium(IV) complex $[U(NCS)_4(PPh_3O)_4]$. We now report the direct preparation of this uranyl(VI) compound together with details of the structure determination by means of which it was initially identified.

EXPERIMENTAL

Preparation of $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$.—An excess of potassium thiocyanate (0.5 g) was added to uranyl(VI) chloride (*ca.* 1.5 g) in an acetone–methanol mixture (10 cm³). Following removal of the precipitated KCl by centrifugation, triphenylphosphine oxide (0.86 g) was added to the solution. The bright yellow insoluble *product* was isolated, washed with acetone, and vacuum dried at room temperature {Found: U, 23.7; NCS, 11.6. $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$ requires U, 23.8; NCS, 11.6%}. When the reaction was performed in methanol or ethanol alone the product was $[UO_2(NCS)_2(PPh_3O)_2]$ as previously reported.[7] Treatment of this with acetone at room temperature provided an alternative route to $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$.

Analysis.—Uranium was weighed as U_3O_8 following ignition of the hydrated oxide formed on addition of carbonate-free aqueous ammonia to the solid. Thiocyanate, which remained in the ammoniacal supernatant, was weighed as silver thiocyanate, after precipitation from the acidified solution.

Physical Studies.—Infrared spectra (650—4 000 cm^{-1}) were recorded for samples mounted as mulls in Nujol using an Infrascan spectrophotometer.

Single-crystal Data Collection.—Yellow, air-stable, prismatic crystals were obtained by recrystallisation from acetone.

Preliminary survey photographs, taken by both Weissenberg and precession methods, showed an orthorhombic unit cell with the following systematic absences: $0kl$ for $k + l = 2n + 1$ and $h0l$ for $l = 2n + 1$. These are consistent with the space groups *Pnam* and $Pna2_1$; the latter was chosen and confirmed by the subsequent successful refinement.

The crystal was mounted in a random orientation on a four-circle Philips PW 1100 automated diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 7 Å). The unit cell was determined on the basis of 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 positions varying between $\theta = 6$ and 10°. For the determination of precise lattice parameters 25 strong reflections with $8 \leqslant \theta \leqslant 15°$ were used.

Crystal Data.—$C_{41}H_{36}N_2O_5P_2S_2U$, M = 1 000.8, Orthorhombic, a = 17.667(8), b = 9.112(5), c = 25.275(12) Å, U = 4 069 Å³, Z = 4, D_c = 1.63 g cm^{-3}, $F(000)$ = 1 960, space group $Pna2_1$, μ(Mo-K_α) = 40.1 cm^{-1}.

Integrated intensities for hkl reflections with $h,k,l \geqslant 0$ and $3 \leqslant \theta \leqslant 25°$ were measured using the θ—2θ scan method with a scan speed of 1.80° min^{-1}, scan width of 1°, and two background counts of 10 s at each end of the scan. The intensities of 3 601 reflections were recorded. Two reflections monitored at regular intervals showed only the deviations from their mean intensities predicted by counting statistics. The standard deviations for the background-corrected intensities were calculated from: $\sigma(I) = [CT + (t_c/t_b)^2 (B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are background counts each obtained in time $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$. A value of 0.04 was assigned to the factor p in the formula to calculate $\sigma(I)$ to allow for other errors. The values of I and $\sigma(I)$ were corrected for Lorentz and polarisation effects and an absorption correction was applied according to the method proposed by North *et al.*[8] The crystal dimensions were 0.08 × 0.15 × 0.24 mm. 1 848 Reflections with intensities $I > 3\sigma(I)$ were employed for the structure determination.

Structure Determination.—The uranium atoms were located in a sharpened three-dimensional Patterson synthesis. Subsequent refinement and difference-Fourier syntheses revealed the positions of all the expected atoms except the hydrogens and those of the acetone ligand. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimised with the weights w equal to unity; $|F_o|$ and $|F_c|$ are, respectively, the observed and calculated structure-factor amplitudes. The atomic scattering factors for uranium were taken from ref. 9, for the other non-hydrogen atoms from ref. 10, and for the hydrogen atoms from ref. 11. The effects of anomalous dispersion were included in F_c, values of $\Delta f'$ and $\Delta f''$ for U being taken from ref. 12. After a few initial least-squares refinements in which all atoms were assigned variable isotropic vibrational parameters, except the uranium atom which was allowed to vibrate anisotropically, the R value

$(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.059. A subsequent difference-Fourier synthesis revealed the position of an acetone molecule attached to the uranium atom in the equatorial plane. The introduction of this ligand and the subsequent least-squares refinement gave $R = 0.055$. Throughout the refinement process the phenyl rings were treated as rigid groups (symmetry D_{6h}; C–C 1.395 Å). At this point hydrogen atoms belonging to the phenyl rings were introduced at calculated positions (assuming C–H 0.95 Å and C–C–H 120°) and assigned isotropic temperature factors equal to those of the carbon atoms to which they were attached. Two final cycles of full-matrix least-squares refinement, in which the uranium atoms and those co-ordinated to it [O(1), O(2), O(3), O(4), O(5), N(1), and N(2)] were allowed anisotropic temperature factors while the remaining atoms had isotropic temperature factors, lowered R to 0.047, which was considered as final since at this stage the ratios of the parameter shifts to standard deviations were <0.1. A final difference Fourier did not show any significant residual electron density. All data processing and computations were carried out using the SHELX 76 program package.[13]

TABLE 1

Infrared spectral results (cm^{-1})

	$[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$	$[UO_2(NCS)_2(PPh_3O)_2]$
ν(C–N)	2 020s, 1 990w (sh)	2 075m, 2 035 (sh), 2 022s, 1 995w (sh)
ν(C=O)	1 667m	
Δν(C=O)	43	
ν(P=O)	1 123s, 1 067s	1 129s, 1 067s
Δν(P=O)	67, 123	63, 123
ν(UO_2^{2+})	923s, 918 (sh)	925s, 918s

s = Strong, m = medium, sh = shoulder.

RESULTS AND DISCUSSION

The addition of potassium thiocyanate to uranyl(VI) chloride in methanol, ethanol, or a methanol–acetone mixture results in the precipitation of KCl and the formation of deep red supernatants. As reported previously[7] the complex $[UO_2(NCS)_2(PPh_3O)_2]$ precipitates on addition of a small excess of triphenylphosphine oxide to the ethanol solution. The same product also crystallises from methanol but the new complex $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$ is obtained from the methanol–acetone mixture. This is a yellow solid which, like $[UO_2(NCS)_2(PPh_3O)_2]$, is moderately soluble in methanol, ethanol, ethyl acetate, benzene, chloroform, and methylene dichloride. Unlike this complex, however, it fails to dissolve in methyl cyanide and carbon tetrachloride; both compounds are insoluble in isopentane and water.

Dissolution of $[UO_2(NCS)_2(PPh_3O)_2]$ in acetone at room temperature provides an alternative route to $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$, which rapidly deposits as a fine solid. Although hydrates such as $[UO_2(NCS)_2L_2(OH_2)]$ (L = urea or dimethylformamide) are known,[14] this appears to be the first example of a uranyl(VI) thiocyanate complex containing two different organic ligands. However, it is likely that other complexes could be prepared by treatment of $[UO_2(NCS)_2(PPh_3O)_2]$ with relatively small organic ligands of insufficient donor strength to displace the triphenylphosphine oxide. The failure of the alcohol ligands to co-ordinate is probably due to the fact that relative to acetone, for example, they are weak donors.

Comparison of the i.r. spectra of the uranyl(VI) complexes with those of the ligands permits the assignments shown in Table 1. Weak bands at 840 cm^{-1} in the spectra, the region associated[15-17] with ν(C–S) for nitrogen-bonded NCS groups and the first harmonic of the NCS deformation frequency for a *S*-bonded group, cannot be assigned on account of ligand bands in this region of the spectrum of PPh_3O. The positions of the ν(C–N) vibrations and their high relative intensities are indicative[15,18,19] of nitrogen-bonded thiocyanate groups; this is confirmed by the structural results described below for $[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$. The Δν(P=O) values are similar to those reported previously for quadrivalent actinide complexes.[20]

Crystal Structure.—Final positional parameters are given in Table 2 with their standard deviations estimated from the inverse matrix. Observed and calculated structure factors and thermal parameters are contained in Supplementary Publication No. SUP 22626 (14 pp.).* Selected interatomic distances and angles are given in Table 3. The Figure shows the unit-cell contents viewed down the *b* axis.

As in the case of many uranyl(VI) complexes the seven-co-ordinated uranium atom is at the centre of a pentagonal bipyramid. Two isothiocyanato-, two triphenylphosphine oxide molecules, and one acetone molecule are co-ordinated in the plane perpendicular to the uranyl(VI) group, which defines the axis of the bipyramid. This is linear, and perpendicular to the equatorial plane where the five atoms which constitute it are coplanar, but the two U–O bond lengths are different [U–O(1) 1.78(2) and U–O(2) 1.70(2) Å]. Such differences are not unusual, occurring, for example, in $[UO_2(saldien)]$[21] where the difference between the two lengths is also 0.08 Å [H_2saldien = *NN*-bis(salicylidene)-3-azapentane-1,5-diamine].

The values of the U–OP bond distances [2.36(2)—2.38(2) Å] are greater than those in $[UO_2Cl_2(PPh_3O)_2]$ [2.300(8) Å] but are comparable with those in other uranyl(VI) compounds as shown in Table 4. However, the two independent values of the U–O–P angles are

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 2

Fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
U	2 537(1)	330(1)	2 500
O(1)	2 238(11)	2 196(19)	2 493(16)
O(2)	2 833(8)	−1 451(17)	2 494(11)
O(3)	1 722(11)	−209(30)	1 785(9)
O(4)	2 710(9)	421(22)	3 433(6)
O(5)	3 858(12)	1 246(22)	2 758(8)
N(1)	1 335(13)	−401(39)	2 889(11)
N(2)	3 295(14)	766(34)	1 711(11)
S(1)	92(7)	−1 072(15)	3 501(5)
S(2)	4 285(7)	878(16)	860(5)
P(1)	1 237(4)	−907(8)	1 384(3)
P(2)	2 819(4)	1 434(8)	3 884(3)
C(37)	840(15)	−708(32)	3 148(11)
C(38)	3 732(17)	796(35)	1 382(13)
C(39)	4 537(18)	804(39)	2 777(13)
C(40)	5 124(2)	1 893(40)	2 977(14)
C(41)	4 785(18)	−597(40)	2 591(16)
C(1)	1 367(9)	−64(23)	755(8)
C(2)	2 110(9)	130(23)	581(8)
C(3)	2 251(9)	851(23)	105(8)
C(4)	1 650(9)	1 378(23)	−198(8)
C(5)	907(9)	1 184(23)	−24(8)
C(6)	766(9)	463(23)	452(8)
C(7)	1 441(13)	−2 826(28)	1 331(7)
C(8)	1 611(13)	−3 592(28)	1 794(7)
C(9)	1 718(13)	−5 108(28)	1 778(7)
C(10)	1 655(13)	−5 858(28)	1 299(7)
C(11)	1 484(13)	−5 092(28)	836(7)
C(12)	1 378(13)	−3 576(28)	852(7)
C(13)	257(12)	−722(22)	1 573(9)
C(14)	−12(12)	572(22)	1 801(9)
C(15)	−733(12)	692(22)	1 942(9)
C(16)	−1 265(12)	−482(22)	1 855(9)
C(17)	−996(12)	−1 775(22)	1 628(9)
C(18)	−235(12)	−1 895(22)	1 487(9)
C(19)	2 627(8)	3 316(20)	3 720(7)
C(20)	3 171(8)	4 187(20)	3 472(7)
C(21)	2 988(8)	5 605(20)	3 309(7)
C(22)	2 260(8)	6 153(20)	3 393(7)
C(23)	1 716(8)	5 282(20)	3 641(7)
C(24)	1 899(8)	3 864(20)	3 805(7)
C(25)	2 209(11)	891(19)	4 416(8)
C(26)	2 178(11)	1 760(19)	4 870(8)
C(27)	1 779(11)	1 275(19)	5 313(8)
C(28)	1 412(11)	−80(19)	5 302(8)
C(29)	1 442(11)	−949(19)	4 849(8)
C(30)	1 841(11)	−463(19)	4 405(8)
C(31)	3 778(12)	1 328(19)	4 151(9)
C(32)	4 161(12)	2 460(19)	4 410(9)
C(33)	4 873(12)	2 205(19)	4 630(9)
C(34)	5 203(12)	819(19)	4 591(9)
C(35)	4 821(12)	−313(19)	4 332(9)
C(36)	4 109(12)	−58(19)	4 113(9)
H(2)	2 520	−229	788
H(3)	2 757	984	−14
H(4)	1 746	1 869	−523
H(5)	497	1 543	−231
H(6)	260	330	571
H(8)	1 654	−3 080	2 120
H(9)	1 834	−5 629	2 093
H(10)	1 727	−6 891	1 288
H(11)	1 441	−5 603	510
H(12)	1 262	−3 055	537
H(14)	323	1 371	1 860
H(15)	−956	1 573	2 097
H(16)	−1 783	−400	1 951
H(17)	−1 331	−2 574	1 569
H(18)	−52	−2 776	1 332
H(20)	3 666	3 814	3 415
H(21)	3 358	6 198	3 140
H(22)	2 135	7 119	3 282
H(23)	1 221	5 655	3 698
H(24)	1 529	3 271	3 973
H(26)	2 428	2 683	4 877
H(27)	1 759	1 867	5 622
H(28)	1 140	−110	5 604
H(29)	1 192	−1 871	4 841
H(30)	1 862	−1 055	4 096
H(32)	3 936	3 404	4 436
H(33)	5 133	2 976	4 806
H(34)	5 688	645	4 740
H(35)	5 046	−1 257	4 306
H(36)	3 849	−829	3 936

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Bond lengths

U–O(1)	1.78(2)	P(1)–O(3)	1.47(2)
U–O(2)	1.70(2)	P(2)–O(4)	1.48(2)
U–O(3)	2.36(2)	P(1)–C(1)	1.78(2)
U–O(4)	2.38(2)	P(1)–C(7)	1.79(3)
U–O(5)	2.56(2)	P(1)–C(13)	1.80(2)
U–N(1)	2.44(2)	P(2)–C(19)	1.80(2)
U–N(2)	2.44(2)	P(2)–C(25)	1.79(2)
N(1)–C(37)	1.13(3)	P(2)–C(31)	1.83(2)
C(37)–S(1)	1.63(3)	O(5)–C(39)	1.27(3)
N(2)–C(38)	1.13(4)	C(39)–C(40)	1.52(5)
C(38)–S(2)	1.64(3)	C(39)–C(41)	1.43(5)

Bond angles

O(1)–U–O(2)	179(2)	O(3)–P(1)–C(7)	111(1)
O(3)–U–N(1)	74(1)	O(3)–P(1)–C(13)	110(1)
N(1)–U–O(4)	74(1)	C(1)–P(1)–C(7)	109(1)
O(4)–U–O(5)	68(1)	C(1)–P(1)–C(13)	109(1)
O(5)–U–N(2)	70(1)	C(7)–P(1)–C(13)	108(1)
N(2)–U–O(3)	75(1)	O(4)–P(2)–C(19)	113(1)
U–N(1)–C(37)	168(3)	O(4)–P(2)–C(25)	109(1)
N(1)–C(37)–S(1)	176(3)	O(4)–P(2)–C(31)	112(1)
U–N(2)–C(38)	168(3)	C(19)–P(2)–C(25)	109(1)
C(38)–N(2)–S(2)	173(3)	C(19)–P(2)–C(31)	108(1)
U–O(3)–P(1)	166(2)	C(25)–P(2)–C(31)	105(1)
U–O(4)–P(2)	143(1)	O(5)–C(39)–C(40)	117(3)
O(3)–P(1)–C(1)	111(1)	O(5)–C(39)–C(41)	124(3)
O(3)–U–O(4)	147(1)	C(40)–C(39)–C(41)	119(3)
N(2)–U–N(1)	149(1)		

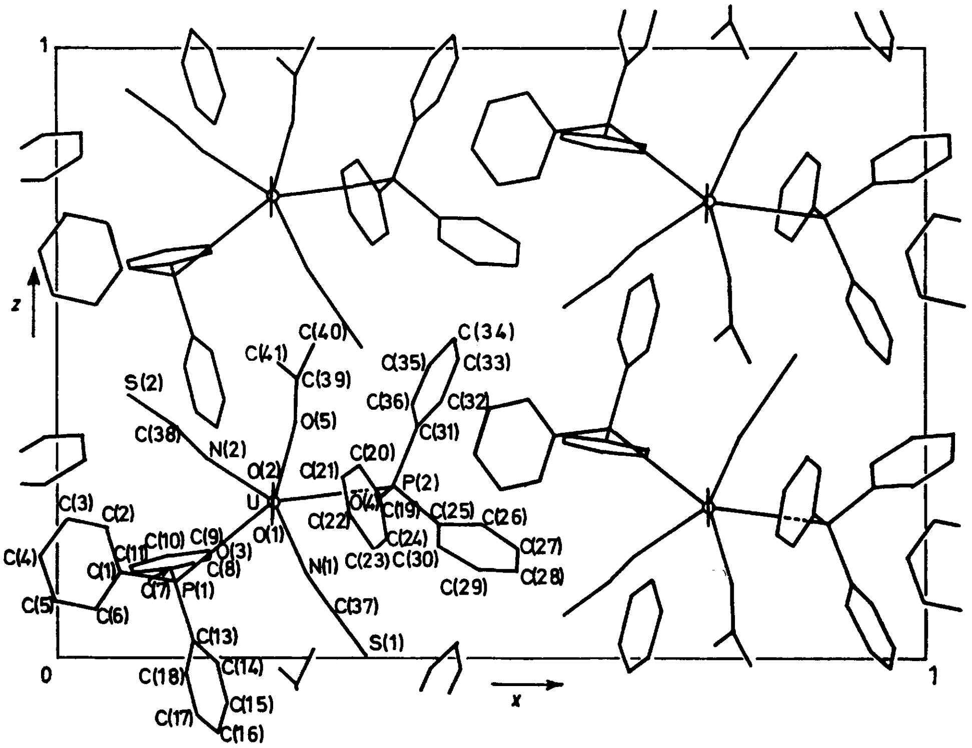
TABLE 4

Bond lengths (Å) and angles (°) reported for some uranium compounds containing the co-ordinated $OPPh_3$ group

Compound	U–OP/ Å	U–O–P/ °	Ref.
$[UO_2(NCS)_2(PPh_3O)_2(CH_3COCH_3)]$	2.36(2), 2.38(2)	166(2), 143(1)	Present work
$[UO_2(O_2CMe)_2(PPh_3O)_2]$	2.37(3)	142(1.5)	*a*
$[UO_2(S_2CNH_2)_2(PPh_3O)]$	2.30(2)	162(2)	*b*
$[UO_2(S_2CMe)_2(PPh_3O)]$	2.34(1)	159(1)	*c*
$[UO_2Cl_2(PPh_3O)_2]$	2.300(8)	158.7(6)	*d*
$[UCl_5(PPh_3O)]$	2.11(2)	163.7(1)	*e*
$[UCl_4(PPh_3O)_2]$	2.242(7)	165.1(5)	4

[a] C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320. [b] R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, **9**, 2116. [c] G. Bombieri, U. Croatto, E. Forsellini, B. Zarli, and R. Graziani, *J.C.S. Dalton*, 1972, 560. [d] G. Bombieri, E. Forsellini, and J. P. Day, *J.C.S. Dalton*, 1978, 678. [e] G. Bombieri, D. Brown, and C. Mealli, *J.C.S. Dalton*, 1976, 2025.

significantly different (Table 3). Thus, the U–O(3)–P(1) angle is 166(2)° whilst U–O(4)–P(2) is 143°. The former value is close to those reported for several uranium compounds containing co-ordinated triphenylphosphine oxide (Table 4) but the latter is significantly smaller than these with the exception of that for $[UO_2(O_2CMe)_2(PPh_3O)_2]$ (142°). The conformations of the two PPh_3O ligands are also different. Table 5 lists some



The unit-cell contents viewed down the *b* axis

significant least-squares planes for the compound. While the ligand unit O(3)–P(1)Ph_3 has angles between the phenyl rings of 85.2, 82.3, and 89.6°, close to the values registered in [$UO_2Cl_2(PPh_3O)_2$] and related compounds, those in the second ligand unit, O(4)–P(2)Ph_3, exhibit significant differences, being, respectively, 67.3, 56.6, and 86.6°. The asymmetry in the uranyl bond lengths and the differences in the angles between the phenyl rings of the O(4)–P(2)Ph_3 ligand suggest that some strain exists in the structure. Certain

TABLE 5

Least-squares planes with the deviations (Å) of the relevant atoms in square brackets. The equation of a plane in direct space is given by $PX + QY + RZ = S$

	P	*Q*	*R*	*S*
Plane (1): U, O(3), O(4), O(5), N(1), N(2)				
	−5.5734	8.6462	−0.2552	−1.1897
[U −0.003, O(3) 0.004, O(4) −0.044, O(5) 0.046, N(1) 0.025, N(2) −0.028, C(37) 0.029, S(1) 0.127, C(38) −0.237, S(2) −0.461, C(39) −0.715, C(40) −0.105, C(41) −2.060, P(1) −0.319, P(2) 0.759]				
	0.7926	7.9546	12.2757	0.9841
Plane (2): C(1), C(2), C(3), C(4), C(5), C(6)				
[C(1) 0.000, C(2) −0.000, C(3) 0.000, C(4) −0.000, C(5) 0.000, C(6) −0.000]				
Plane (3): C(7), C(8), C(9), C(10), C(11), C(12)				
	17.2457	1.2682	−4.2108	1.5663
[C(7) 0.000, C(8) 0.001, C(9) 0.000, C(10) −0.002, C(11) 0.003, C(12) −0.002]				
Plane (4): C(13), C(14), C(15), C(16), C(17), C(18)				
	3.7736	−3.3010	22.9312	3.9431
[C(13) −0.001, C(14) −0.006, C(15) 0.011, C(16) −0.008, C(17) 0.000, C(18) 0.004]				
Plane (5): C(19), C(20), C(21), C(22), C(23), C(24)				
	5.0533	3.2451	22.4842	10.7680
[C(19) −0.000, C(20) −0.000, C(21) 0.001, C(22) −0.000, C(23) −0.000, C(24) 0.001]				

TABLE 5 (*Continued*)

	P	*Q*	*R*	*S*
Plane (6): C(25), C(26), C(27), C(28), C(29), C(30)				
	14.6163	−4.0380	8.7249	6.7216
[C(25) 0.000, C(26) 0.000, C(27) −0.001, C(28) 0.000, C(29) 0.000, C(30) −0.000]				
Plane (7): C(31), C(32), C(33), C(34), C(35), C(36)				
	−7.5960	−2.4200	21.8100	5.8625
[C(31) 0.000, C(32) 0.000, C(33) 0.000, C(34) 0.000, C(35) −0.001, C(36) 0.001]				

Angles (°) between the planes:

(2)–(3)	85.2	(2)–(4)	82.3	(3)–(4)	89.6
(2)–(5)	40.9	(3)–(5)	79.6	(4)–(5)	42.3
(5)–(6)	67.3	(2)–(6)	79.5	(3)–(6)	46.5
(4)–(6)	49.4	(7)–(5)	56.6	(7)–(6)	86.6
(7)–(2)	80.3	(7)–(3)	53.1	(7)–(4)	38.1

TABLE 6

Some intramolecular and intermolecular contacts ⩽ 3.7 Å with estimated standard deviations in parentheses

N(1) ··· O(3)	2.88(4)	C(32) ··· C(5′)	3.68(3)
O(3) ··· N(2)	2.92(3)	C(27) ··· C(17″)	3.63(3)
N(2) ··· O(5)	2.86(3)	O(1) ··· C(9‴)	3.18(3)
O(5) ··· O(4)	2.75(3)	O(1) ··· H(9‴)	2.34(3)
O(4) ··· N(1)	2.89(3)	O(2) ··· C(22^{IV})	3.31(3)
C(26) ··· C(12′)	3.57(3)	O(2) ··· C(21^{IV})	3.39(3)
C(27) ··· C(12′)	3.53(3)	C(34) ··· S(2^{V})	3.67(2)
C(27) ··· C(11′)	3.57(3)	H(34) ··· S(2^{V})	3.15(2)

Symmetry code:

I $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$
II $\frac{1}{2} + x, -y, -z$
III $x, 1 + y, z$
IV $x, -1 + y, z$
V $\frac{1}{2} + x, -y, 1 - z$

intermolecular contacts between two rings in adjacent molecules (see Table 6) could account for such distortions. Thus, the C(25)–C(30) ring and the C(7′)–C(12′) one facing it at $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$, present close contacts, suggesting the existence of some π interaction that could stabilise the whole structure and also cause the distortions encountered in the O(4)–P(2)Ph_3 ligand.

The U–N bond lengths, both 2.43(3) Å, compare favourably with those reported for $[dpsh]_3[UO_2(NCS)_5]$ [22] [dpsh = 2-(2-pyridylthio)pyridinium] as do the bond lengths and angles within the isothiocyanate groups.

[9/287 *Received*, *23rd February*, 1979]

REFERENCES

[1] K. W. Bagnall, ' The Actinide Elements,' Elsevier, Amsterdam, 1972.

[2] D. Brown, ' Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1974, vol. 5, p. 212.

[3] G. Bombieri, P. T. Moseley, and D. Brown, *J.C.S. Dalton*, 1975, 1520.

[4] G. Bombieri, D. Brown, and R. Graziani, *J.C.S. Dalton*, 1975, 1873.

[5] G. Bombieri, E. Forsellini, D. Brown, and B. Whittaker, *J.C.S. Dalton*, 1976, 735.

[6] G. Bombieri, E. Forsellini, G. De Paoli, and D. Brown, *J. Inorg. Nuclear Chem.*, 1979, **41**, 1315.

[7] F. A. Hart and J. E. Newbery, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1334.

[8] A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Cryst.*, 1968, **A24**, 351.

[9] ' International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1959, vol. 4, p. 101.

[10] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] R. F. Stewart, *J. Chem. Phys.*, 1965, **42**, 3175.

[12] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[13] G. Sheldrick, SHELX 76 Computing System, University of Cambridge, 1976.

[14] R. N. Shchelokov, I. M. Shul'gina, and I. I. Chernyaev, *Doklady Chem.*, 1966, **166/8**, 640.

[15] A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665.

[16] J. Lewis, R. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

[17] A. Turco and C. Pecile, *Nature*, 1961, **191**, 66.

[18] S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, 1962, **16**, 1447.

[19] C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

[20] Z. M. S. Al-Kazzaz, K. W. Bagnall, and D. Brown, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1501.

[21] M. N. Akhtar and A. J. Smith, *Acta Cryst.*, 1973, **B29**, 275.

[22] G. Bombieri, E. Forsellini, R. Graziani, and G. Pappalardo, *Transition Metal Chem.*, 1979, **4**, 70, and refs. therein.
