Chemistry of the Uranyl Group. Part IV.[1] Preparation and Properties of Triphenyl-phosphine and -arsine oxide Complexes of Uranyl Dithioacetate and Dithiobenzoate, and the Structure of Bis(dithioacetato)dioxo(triphenylphosphine oxide)uranium(VI)

By **G. Bombieri,*** **U. Croatto,** and **E. Forsellini,** Laboratorio di Chimica e Technologia dei Radioelementi del C.N.R., 35100 Padova, Italy
B. Zarli, Istituto di Chimica Generale dell'Università di Padova, Via Loredan 4, Padova, Italy
R. Graziani, Facoltà di Chimica Industriale, Università di Venezia, Venezia, Italy

Monomeric complexes of formula $UO_2(MeCS_2)_2L$ and $UO_2(PhCS_2)_2L$ (L = Ph_3PO and Ph_3AsO) have been synthesized and characterized. The crystal structure of $UO_2(MeCS_2)_2(Ph_3PO)$ has been determined from three-dimensional counter data by Patterson and electron-density syntheses and refined by least-squares to R 0·077 for 3924 reflections. The crystals are monoclinic, space-group $P2_1/c$, with a = 16·728 Å, b = 11·001 Å, c = 15·678 Å, β = 113° 29′, Z = 4. The uranium(VI) atom is in a seven-co-ordinate, pentagonal-bipyramidal environment. The linear uranyl group is perpendicular to the equatorial plane in which four sulphur atoms of two dithioacetate groups and the oxygen atom of the ligand occupy the corners of an irregular pentagon.

PREVIOUS research [2,3] on complexes of uranyl nitrate or acetate with triphenylphosphine (or triphenylarsine) oxide indicated that the co-ordination to the uranyl group is affected by the different anionic ligands used. In fact the complexes of formula $UO_2(NO_3)_2(L)_2$ (where L = Ph_3PO or Ph_3AsO) are six-co-ordinate species with

---

[1] Part III, R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, **9**, 2116.

[2] C. Panattoni, R. Graziani, U. Croatto, B. Zarli, and G. Bombieri, *Inorg. Chim. Acta*, 1968, **2**, 43.

[3] C. Panattoni, R. Graziani, G. Bandoli, B. Zarli, and G. Bombieri, *Inorg. Chem.*, 1969, **8**, 320.

respect to the uranyl ion, the two nitrato-groups behaving exclusively as chelate ligands.[2] However when uranyl acetate is used, two types of compounds are obtained of formula $UO_2(AcO)_2(L)_2$ and $[UO_2(AcO)_2(L)]_2$ respectively, the former six-co-ordinate with a configuration quite similar to the nitrato-complexes, and the latter dimeric acetato-bridged, each uranyl group in the molecule being five-co-ordinate.[3]

We have prepared uranyl compounds with the neutral bases L and sulphur-containing anionic ligands. Recently the properties of the diethyl dithiocarbamate (dtc) complexes of the type $UO_2(dtc)_2(L)$ have been reported.[1] These are monomeric five-co-ordinate species with a quite different configuration from the acetato-analogues.[3]

In principle, the same molecular structures as those determined for the acetato-compounds, would be expected for complexes with sulphur-donor bidentate ligands. Surprisingly, we were unable to prepare dtc complexes of this type. To provide a more direct comparison with known compounds of uranyl acetate, novel uranyl dithioacetate (dtac) complexes were prepared and we here report the crystal structure of one of them, *i.e.* $UO_2(MeCS_2)_2(Ph_3PO)$. In addition dithiobenzoate (dtb) derivatives were synthesized. The reaction are as follows:

TABLE 1

Some physical data for the compounds

Compounds	Λ_M [a]	M [b]	$\nu_{as}(UO_2)$ [c]	$\nu(X - O)$ [c]	Band maxima [d]
$UO_2(S_2CMe)_2(Ph_3PO)$	7	550(730)	918	1132, 1120	25·0(2500), 30·0sh(10,700), 33·1(17,500)
$UO_2(S_2CPh)_2(Ph_3PO)$	9	665(854)	920	1137, 1123	28·0sh(7300), 32·2(21,200)
$UO_2(S_2CMe)_2(Ph_3AsO)$	11	615(774)	910	882	26·3(2100), 31·0sh(8800), 33·3(10,400)
$UO_2(S_2CPh)_2(Ph_3AsO)$	12	740(898)	912	862, 858	27·5sh(12,000), 32·2(39,000)

[a] In $ohm^{-1}\ cm^2\ mol^{-1}$. [b] Calc. values are in parentheses. [c] In cm^{-1}; X = P or As. [d] Frequencies in kK with molar extinction coefficients in parentheses; sh = shoulder.

$$UO_2(NO_3)_2,6H_2O + 2K(dtac) \xrightarrow{MeOH} UO_2(dtac)_2 + 2KNO_3\downarrow + 6H_2O$$

$$UO_2(dtac)_2 + L \longrightarrow UO_2(dtac)_2(L)\downarrow$$

$$UO_2(OAc)_2 2H_2O + 2Hdtb + L \longrightarrow UO_2(dtb)_2(L) + 2H_2O + 2HOAc$$

EXPERIMENTAL

Materials.—Dithioacetic acid was synthesized by the method of ref. 4, and dithiobenzoic acid by the method of ref. 5.

Bis(dithioacetato)dioxo(triphenylphosphine oxide)uranium(VI).—To a solution of uranyl nitrate hexahydrate (500 mg, 1 mM) in methanol (10 ml) was added with stirring dithioacetic acid (0·15 ml, 2 mM). The resulting bright red solution was neutralized with potassium hydroxide (112 mg, 2 mM) in methanol (10 ml). The crystalline precipitate of potassium nitrate was filtered off. To the filtrate was added triphenylphosphine oxide (280 mg, 1 mM) in methanol and the orange-red complex was precipitated. It was washed with methanol, dried *in vacuo*, and recrystallized from acetone as brilliant orange-red crystals (suitable for *X*-ray diffraction analysis), m.p. 165—170 °C (decomp.) (Found: C, 36·2; H, 2·9; S, 17·5; U, 32·4. $C_{22}H_{21}O_3PS_4U$ requires C, 36·2; H, 2·9; S, 17·5; U, 32·6%).

Bis(dithioacetato)dioxo(triphenylarsine oxide)uranium(VI).—This was prepared similarly from triphenylarsine oxide (320 mg, 1 mM) and recrystallized from acetone as orange-yellow needles, m.p. 175—180 °C (decomp.) (Found: C, 34·3; H, 2·8; S, 16·0; U, 31·0. $C_{22}H_{21}AsO_3S_4U$ requires C, 34·0; H, 2·7; S, 16·5; U, 30·8%).

Bis(dithiobenzoato)dioxo(triphenylphosphine oxide)uranium(VI).—To a solution of uranyl acetate dihydrate (425 mg, 1 mM) in methanol (30 ml) was added dithiobenzoic acid (308 mg, 2 mM). To the filtered deep red solution were added triphenylphosphineoxide (280 mg, 1 mM) in methanol with stirring. The complex which was precipitated was washed with methanol, dried *in vacuo*, and recrystallized from dichloromethane–acetone as red crystals, m.p. 198—200 °C (decomp.) (Found: C, 44·5; H, 2·8; S, 14·5; U, 28·6. $C_{32}H_{25}O_3PS_4U$ requires C, 45·0; H, 2·9; S, 15·0; U, 27·9%).

Bis(dithiobenzoato)dioxo(triphenylarsine oxide)uranium(VI). This was prepared similarly from triphenylarsine oxide (320 mg, 1 mM) as orange-yellow crystals, m.p. 215—217 °C (decomp.) (Found: C, 42·8; H, 2·7; S, 14·4; U, 25·8. $C_{32}H_{25}AsO_3S_4U$ requires C, 42·7; H, 2·8; S, 14·2; U, 26·5%).

Physical Measurements.—Molar conductivities at 25° were measured on 10^{-3}M solutions in nitromethane with an LKB 3216 B conductivity bridge. Molecular weights were determined at 37° for *sym*-dichloroethane solutions with a Mechrolab 302 vapour pressure osmometer. I.r. spectra were recorded (4000—400 cm^{-1}) on a Perkin-Elmer 337 grating i.r. spectrophotometer for Nujol mulls between potassium bromide plates. Room-temperature u.v. spectra for *sym*-dichloroethane solutions were recorded (15—35 kK) with a Beckman DK 2A spectrophotometer and 1 cm quartz cells. The results are summarized in Table 1.

Crystal Structure of $UO_2(dtac)_2(Ph_3PO)$

The space-group was determined from precession and Weissenberg photographs. Unit-cell parameters, determined initially from films, were subsequently refined with counter data by use of a least-squares program.

Crystal Data.—$C_{22}H_{21}O_3PS_4U$, $M = 730·5$, Monoclinic, $a = 17·728 \pm 0·005$, $b = 11·001 \pm 0·004$, $c = 15·678 \pm 0·005$ Å, $\beta = 113° 29' \pm 5'$, $U = 2650$ Å^3, $D_m = 1·84$ (by flotation), $Z = 4$, $D_c = 1·83$; $F(000) = 1392$. Space-group $P2_1/c$. Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 250·1 cm^{-1}.

Intensity Data.—Because of the larger absorption coefficient a crystal specimen was ground into a sphere and mounted about [001]. A total of 3924 independent reflections were collected with a computer-controlled

---

[4] J. Houben and H. Pohl, *Ber.*, 1907, **40**, 1303.

[5] J. Houben, *Ber.*, 1906, **39**, 3224.

Siemens four-circle automatic diffractometer by use of the θ—2θ scan and the five-point measuring procedure. Intensities were measured up to $\theta_{\text{max.}}$ 60°. They were corrected for absorption for a spherical specimen,[6] assuming μR 3·2. Atomic form factors were taken from ref. 7, and a correction for the real part of the anomalous dispersion was applied to the uranium atom.

The calculations were performed with an IBM 360/44 computer, with programs of refs. 8 and 9.

TABLE 2

Atomic positional ($\times 10^4$) and thermal parameters, with estimated standard deviations in parentheses

	x	y	z	$B/\text{Å}^2$
U	2595(1)	450(1)	1502(1)	*
S(1)	957(4)	1550(6)	434(4)	*
S(2)	2039(4)	2479(5)	2268(4)	*
S(3)	3938(5)	907(9)	3270(5)	*
S(4)	4050(5)	−1143(7)	2119(6)	*
P	2271(3)	−1611(4)	−513(3)	*
O(1)	2079(13)	−415(19)	1987(12)	*
O(2)	3089(13)	1334(19)	998(12)	*
O(3)	2187(10)	−815(14)	202(9)	*
C(1)	1148(18)	2490(19)	1331(18)	*
C(2)	441(22)	3438(25)	1274(27)	*
C(3)	4471(18)	−245(33)	3061(16)	*
C(4)	5439(27)	−518(44)	3709(46)	*
C(5)	1315(13)	−1407(20)	−1604(14)	4·8(3)
C(6)	1264(15)	−202(21)	−2380(15)	5·3(4)
C(7)	517(18)	−2018(25)	−3171(18)	6·5(5)
C(8)	−184(15)	1296(22)	−3126(16)	5·5(4)
C(9)	−123(19)	−669(27)	−2367(20)	6·6(5)
C(10)	630(15)	−763(22)	−1556(15)	5·2(4)
C(11)	3223(11)	−1311(17)	−744(12)	4·2(3)
C(12)	3222(17)	−410(21)	−1343(18)	5·9(5)
C(13)	3917(26)	−75(39)	−1470(26)	8·9(8)
C(14)	4691(29)	−733(41)	−1028(28)	9·4(9)
C(15)	4769(20)	−1763(30)	−419(21)	7·5(6)
C(16)	3963(18)	−1944(26)	−308(18)	6·5(5)
C(17)	2316(11)	−3443(15)	−162(11)	3·6(3)
C(18)	2434(13)	−4102(19)	−697(13)	4·6(3)
C(19)	2473(18)	−5356(23)	−503(20)	6·3(5)
C(20)	2384(19)	−5562(23)	362(20)	6·3(5)
C(21)	2214(18)	−4638(23)	917(19)	6·2(5)
C(22)	2183(17)	−3415(24)	673(18)	6·3(5)

* Anisotropic thermal parameters ($\times 10^4$) in the form:

$$T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})].$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	48(1)	73(1)	50(1)	−6(1)	21(1)	−1(1)
S(1)	61(3)	118(5)	80(3)	17(3)	19(2)	3(4)
S(2)	80(4)	100(5)	80(4)	−9(3)	39(3)	−21(3)
S(3)	68(3)	194(9)	82(4)	−14(5)	13(3)	−27(5)
S(4)	62(3)	145(7)	108(5)	21(4)	26(3)	10(5)
P	48(2)	77(4)	51(2)	−1(2)	20(2)	0(2)
O(1)	92(11)	168(21)	41(10)	34(14)	44(9)	−25(13)
O(2)	101(12)	151(22)	51(10)	12(14)	58(9)	−23(12)
O(3)	63(7)	92(11)	48(7)	−12(8)	14(6)	7(7)
C(1)	94(15)	75(16)	92(16)	2(13)	63(14)	−1(13)
C(2)	81(15)	98(23)	147(25)	6(16)	41(17)	−8(19)
C(3)	66(12)	252(43)	41(10)	−45(19)	20(9)	−12(16)
C(4)	71(19)	215(63)	206(56)	10(25)	−29(28)	48(44)

Determination of the Structure and Refinement.—The uranium co-ordinates were easily obtained from the Patterson function and refined by least-squares. A subsequent electron-density difference synthesis clearly showed the positions of the sulphur, phosphorus, and oxygen atoms, together with those of some carbon atoms. Refinement reduced R to 12·9%. A further difference Fourier synthesis revealed the remaining atom positions. Isotropic refinement was then continued until R was 10·2%, the Cruickshank weighting scheme being used. Anisotropic thermal parameters were then introduced for the uranium, phosphorus, sulphur, and oxygen atoms, and for the carbon atoms of the dithioacetate groups. Full-matrix least-squares refinement with the same weighting scheme reduced R to the final value of 7·7%. Changes in parameter values in the last cycle were $< 0·2\sigma$.

No hydrogen atoms were included in the calculation.

The final co-ordinates and vibration parameters are given in Table 2 together with their estimated standard deviations derived from the least-squares calculations. Bond distances and bond angles are given in Table 3.

TABLE 3

Bond distances and angles with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

U–O(1)	1·66(2)	S(3)–C(3)	1·66(3)
U–O(2)	1·66(2)	S(4)–C(3)	1·68(3)
U–O(3)	2·34(1)	C(3)–C(4)	1·56(6)
U–S(1)	2·85(1)	P–O(3)	1·47(2)
U–S(2)	2·86(1)	P–C(5)	1·84(2)
U–S(3)	2·84(1)	P–C(11)	1·80(2)
U–S(4)	2·84(1)	P–C(17)	1·77(2)
S(1)–C(1)	1·67(1)		
S(2)–C(1)	1·63(3)	Mean C–C(Ph) *	1·396, σ 0·02
C(1)–C(2)	1·55(4)		

(*b*) Bond angles (°)

O(1)–U–O(2)	179(1)	U–S(3)–C(3)	87(1)
O(1)–U–O(3)	92(1)	U–S(4)–C(3)	87(1)
O(1)–U–S(1)	88(1)	U–O(3)–P	159(1)
O(1)–U–S(2)	87(1)	S(1)–C(1)–S(2)	124(2)
O(1)–U–S(3)	90(1)	S(1)–C(1)–C(2)	119(2)
O(1)–U–S(4)	91(1)	S(2)–C(1)–C(2)	117(2)
O(2)–U–O(3)	88(1)	S(3)–C(3)–S(4)	124(2)
O(2)–U–S(1)	91(1)	S(3)–C(3)–C(4)	122(3)
O(2)–U–S(2)	93(1)	S(4)–C(3)–C(4)	115(3)
O(2)–U–S(3)	91(1)	O(3)–P–C(5)	109(1)
O(2)–U–S(4)	90(1)	O(3)–P–C(11)	114(1)
S(1)–U–S(2)	61(1)	O(3)–P–C(17)	110(1)
S(2)–U–S(3)	73(1)	C(5)–P–C(11)	108(1)
S(3)–U–S(4)	62(1)	C(5)–P–C(17)	109(1)
S(4)–U–O(3)	81(1)	C(11)–P–C(17)	108(1)
O(3)–U–S(1)	82(1)		
U–S(1)–C(1)	87(1)	Mean C–C–C(Ph) *	120°, σ 2°
U–S(2)–C(1)	88(1)		

* The standard deviations of the mean are calculated from $[\Sigma_i\Delta_i{}^2{}_4 m(M - 1)]^{\frac{1}{2}}$. The estimated standard deviations of the carbon–carbon distances are *ca.* 0·04 Å and those for the angles in the phenyl groups *ca.* 3°.

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20278 (6 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The analysis shows that the geometry of the co-ordination polyhedron in the molecule is a slightly irregular pentagonal bipyramid. Two dithioacetate groups are chelated to the central atom. The four

---

* For details of Supplementary publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full-size copies).

[6] 'International Table for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[7] F. H. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[8] A. Immirzi, *Ricerca sci.*, 1968, 850.

[9] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Huber, 1966, NCR Crystallography Programs for the IBM/360 System, World List of Crystallographic Computer Programs.

sulphur atoms lie in the equatorial plane and the fifth atom is the oxygen of the triphenylphosphine oxide. The uranyl group is linear and normal to this plane. In Figure 1 a perspective view of the molecule is shown with the numbering scheme used, and in Figure 2 the structure is viewed in projection along [010]. All distances and angles in the molecule are as expected and compare well with the corresponding ones found in the isomorphous pair $UO_2(Et_2NCS_2)_2(Ph_3AsO)$ and $UO_2(Et_2NCS_2)_2(Ph_3PO)$ whose structures were determined by *X*-ray analysis from photographic data (Table 4). It appears that the substitution of NEt_2 by a methyl group in the chelated ligands has no detectable influence on the bonding of the co-ordinated atoms.

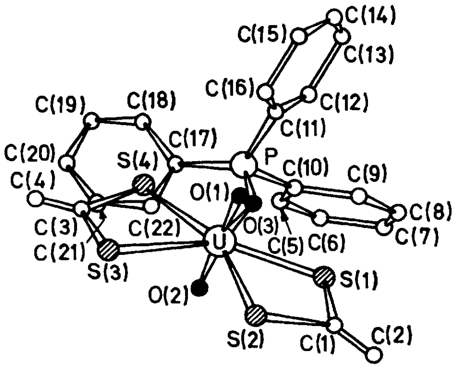


FIGURE 1 A perspective view of the molecule

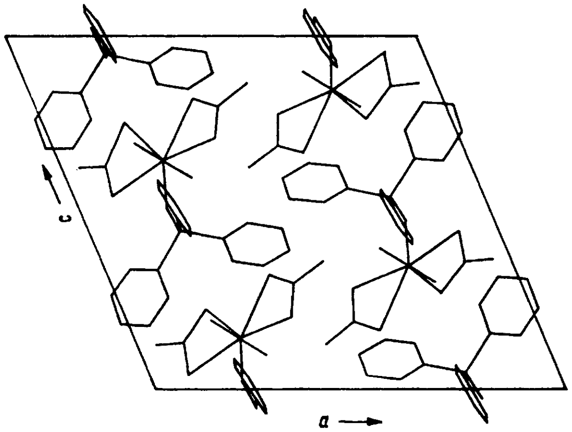


FIGURE 2 Projection of the structure along [010]

The U–S distances [mean 2·85(1) Å] are similar to the Np–S distances [mean 2·87 Å] in $[Et_4N][Np(dtc)_4]$,[10] and to the Th–S distances [mean 2·87 Å] in $Th(dtc)_4$,[11] but they are larger by *ca.* 0·05 Å than the U–S distance [mean 2·80(1) Å] in $[Me_4N][UO_2(dtc)_3]$.[12] The S–S distances across the 'bite' of the chelate molecule [2·91(1) and 2·94(1) Å] are similar to the analogous distances in the neptunium and thorium compounds (2·93 and 2·73 Å respectively) but differ considerably from the corresponding value of *ca.* 3·35 Å in $[Me_4N][UO_2(dtc)_3]$. In the last-named complex however steric factors are dominant and could be responsible for the observed differences. The S–S approach for the adjacent dtac molecules [3·41(1) Å] is slightly shorter than the sum of the van der Waals radii[13] (3·7 Å). However this has no detectable influence on the co-ordinated atoms since the two dithioacetate molecules and the ligand oxygen atom as well as the uranium atom are coplanar within experimental error.

TABLE 4

Comparison of bond distances in the analogous dithiocarbamate complexes

	$UO_2(dtc)_2$-(Ph_3AsO)[a]	$UO_2(dtc)_2$-(Ph_3PO)[b]	$UO_2(dtac)$-(Ph_3PO)[c]
U–S(1)	2·84(1)	2·85(1)	2·85(1)
U–S(2)	2·861()	2·86(1)	2·86(1)
U–S(3)	2·83(1)	2·84(1)	2·84(1)
U–S(4)	2·80(1)	2·84(1)	2·84(1)
U–O	2·30(2)	2·34(2)	2·34(1)
Mean S–C	1·69(4)	1·71(4)	1·66(3)
S(1)–U–S(2)	62·3(0·3)	61·9(0·3)	61(1)
S(2)–U–S(3)	73·8(0·3)	74·7(0·3)	73(1)
S(3)–U–S(4)	62·6(0·4)	62·6(0·4)	62(1)
S(4)–U–O	79·8(0·7)	78·4(0·6)	81(1)
O–U–S(1)	81·5(0·7)	82·5(0·6)	82(1)
U–O–As(or P)	159(1)	162(2)	159(1)

[a] Ref. 1. [b] Ref. 1. [c] Present work.

From the reaction of uranyl dithioacetate or dithiobenzoate with triphenylphosphine (or triphenylarsine) oxide, only compounds of the known[1] type UO_2X_2L (where X = dtac or dtb) were isolated (see Experimental section). There was no evidence for the formation of six-co-ordinate or bridged five-co-ordinate complexes.

Conductivity measurements showed that all four compounds were slightly dissociated in nitromethane (Table 1) and practically undissociated (0—2 mhos) in *sym*-dichloroethane. The complexes were shown to be monomeric in this solvent from molecular-weight determinations. However, values lower than the theoretical were observed at 37 °C, indicating that neutral particles had been lost, presumably molecules of ligand, to a greater extent for the phosphine oxide complexes than for the arsine analogues. A similar feature was also observed for the dtc complexes although more satisfactory values of molecular weights were obtained because of the lower experimental temperature (25 °C).[1]

The asymmetric stretching vibration bands of the uranyl ion (Table 1) are close to that of the diethyldithiocarbamato-analogues,[1] indicating that the central group is scarcely influenced by ligands which differ only in the substituent, *i.e.* Et_2N, Me, or Ph, in molecules most probably with the same configuration.

From the u.v. and visible spectra (Table 1) of $UO_2(dtac)_2(Ph_3PO)$ and $UO_2(dtac)_2(Ph_3AsO)$ the two charge-transfer bands expected for π(sulphur)–*f*(uranium) transitions[1] are found at 25 and 30·5 kK and at 26·3 and

---

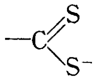
[10] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 786.

[11] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 423.

[12] K. Bowmann and Z. Dori, *Chem. Comm.*, 1968, 636.

[13] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.

31·3 kK respectively. The very intense band centred around 33·2 kK is ascribed to the dithioacetate groups. The first charge-transfer band of $UO_2(dtb)_2(Ph_3PO)$ is found at 28 kK and that for the arsine oxide analogue at 27·8 kK. However the second band of these complexes is apparently masked by the absorption due to the dithiobenzoate groups (32·2 kK), because of the u.v. shift of the charge-transfer transitions in the order of increasing frequencies: dtc < dtac < dtb.

All the observations are consistent with the chemical behaviour of the new compounds being similar to that of the diethyl dithiocarbamato-complexes. One conclusion from the present work is that, when the uranyl ion is bonded by  $-C(=S)S^-$ groups in complexes with neutral unidentate ligands, a discrete five-co-ordinate configuration should be preferred.

We thank Mrs. Milena Magnabosco and Franco Benetollo for assistance with data reduction.

[1/404 *Received, 29th March,* 1971]