Actinide Structural Studies. Part 17.† The Crystal and Molecular Structures of Four Uranyl(VI) Complexes with *N,N*-Dialkyldithiocarbamate Ligands‡

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The synthesis and crystal structures are reported of four dithiocarbamates of general formula $[NR_4][UO_2(dtc)_3]$: [**1**; R = Et, dtc = *N*-tetramethylenedithiocarbamate ($C_4H_8NCS_2$)], *R* = 0.040 for 3 970 observed [$I/\sigma(I) \geqslant 3.0$] reflections; [**2**; R = Et, dtc = *N*-pentamethylenedithiocarbamate ($C_5H_{10}NCS_2$)], *R* = 0.057 for 5 729 reflections; [**3**; R = Et, dtc = *N,N*-dimethyldithiocarbamate (Me_2NCS_2)], *R* = 0.054 for 3 722 reflections; [**4**; R = Me, dtc = *N,N*-diethyldithiocarbamate (Et_2NCS_2)], *R* = 0.049 for 3 192 reflections. All four complexes exhibit hexagonal bipyramidal geometry about the central uranium atom, involving three bidentate dithiocarbamate molecules co-ordinated in the equatorial plane of the uranyl ion. The U–O(UO_2^{2+}) bond lengths are in the range 1.734(11)—1.862(12) Å. The U–S distances are almost equal in all the complexes [2.946(2) Å mean]. The equatorial planes show significant puckering to accommodate the six sulphur atoms [maximum deviation 0.32(5) Å]. Intra-ligand S • • • S distances (ligand bite) are in the range 2.856(4)—2.891(4) Å and inter-ligand distances are in the range 2.911(4)—3.109(4) Å.

Complexes involving U-S(ligand) bonds are less common than those which utilise U-O and U-N bonds, a consequence of steric and redox factors which lead to reduced stability. Most of the complexes reported involve dithiocarbamates or other S-chelates which form four-membered chelate rings.

Dithiocarbamate complexes of uranium(VI) were first reported by Delepine in 1908[1] and several dioxouranium(VI) bis(dithiocarbamate) complexes with a neutral donor ligand occupying the fifth equatorial site have been described by Malatesta.[2] The preparation of compounds of general formula $UO_2(R_2NCS_2)_2$[3] and the compound $KUO_2(Et_2NCS_2)_3$ have also been reported.[4] A variety of dialkylammonium tris(dithiocarbamate) salts were produced, (*a*) during early attempts to prepare the uranium(IV) salts, from uranium tetrachloride, the dialkylammonium salts of the reagents, and dry solvents,[5] and (*b*) as a product in the reaction between uranyl nitrate and the sodium salt of the dithiocarbamate ligand.[6] The brightly coloured solutions formed when UO_2^{2+} is treated with dithiocarbamate ligands have been used in the colorimetric determination of uranium[7,8] and the quantitative precipitation of UO_2^{2+} with dithiocarbamates under acid conditions has also been reported.[9,10]

Structural data on uranium(VI) dithiocarbamates are very limited. Only one crystal structure has been reported, a preliminary communication for the complex $[NMe_4]$-$[UO_2(Et_2NCS_2)_3]$ which involves six sulphur atoms of the diethyldithiocarbamate ligand co-ordinated to UO_2^{2+} in the equatorial plane.[11] This showed that the dithiocarbamate ligands were each co-ordinated through both sulphur atoms rather than as the double salt $[UO_2(Et_2NCS_2)]^+$-$[UO_2(Et_2NCS_2)_3]^-$ previously suggested for these complexes from polarographic studies.[12] However, the ethyl carbon atoms were not refined, and the final *R* value was only 0.14. A series of complexes of general formula $UO_2(dtc)_2 \cdot L$ (dtc = general dithiocarbamate; L = Ph_3PO, Ph_3AsO, or Me_3NO) has been produced by reaction of L with the stoicheiometric amount of $K[UO_2(dtc)_3]$ in acetone.[13-15] Unlike the tris(dithiocarbamate) complexes, the sulphur atoms are virtually coplanar.

Most investigations into dithiocarbamate complexes of uranium have involved i.r. spectral studies of ν_3(O–U–O),[16] ν(C–S), and ν(C–N).[17,18] Correlation of these values with the structural data reveals that the greater the donor ability of the monodentate ligand (*i.e.* the stronger the uranium–ligand bond), the lower is the stretching frequency of the uranyl group (weaker U=O bond). In an attempt to increase the amount of structural information available for U-S species, the synthesis and structural determination of four dithiocarbamates of uranium(VI) was undertaken and is described here. Three of these, dioxotris(*N*-tetramethylenedithiocarbamato)uranate(VI) (**1**), dioxotris(*N*-pentamethylenedithiocarbamato)uranate(VI) (**2**), and tris(*N,N*-dimethyldithiocarbamato)dioxouranate(VI) (**3**), were isolated as the tetraethylammonium salts. The fourth, tetramethylammonium tris(*N,N*-diethyldithiocarbamato)dioxouranate(VI) (**4**), was the same as that originally examined by Bowman and Dori.[11] It was re-examined to confirm their results and improve the precision.

Experimental

Preparation.—Compounds (**1**)—(**3**) were prepared by the method described by Graziani *et al.*[13] The required amine (30 mmol) was added dropwise with stirring to a cooled solution containing carbon disulphide (30 mmol) and potassium hydroxide (30 mmol) in water (8 cm^3), producing the potassium salt of the dithiocarbamate ligand. After 30 min the clear yellow solution obtained was added slowly to a solution of uranyl acetate dihydrate (10 mmol) in water (150 cm^3). The colour immediately became dark red and $K[UO_2(dtc)_3] \cdot H_2O$ precipitated as a dark red powder. The compound was collected and washed with diethyl ether. Metathesis with the stoicheiometric amount of tetraethylammonium chloride in acetone yielded ruby red crystals of compounds (**1**)—(**3**) which were suitable for structure determination. Initial attempts to obtain (**4**) by this method did not lead to the desired product, but gave what appears to be an O_2-bridged species. This has not yet been fully characterised. However, an alternative route involving the addition of 0.01 mol dm^{-3} uranyl nitrate (100 cm^3) to a solution containing sodium *N,N*-diethyldithiocarbamate (5 g) and potassium nitrate (5 g) was successful. Metathesis using tetramethylammonium chloride then gave red crystals of (**4**). Analytical and i.r. data for each complex are given in Table 1.

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† Part 16, N. W. Alcock, D. J. Flanders, and M. Pennington, *Acta Crystallogr., Sect. C*, 1988, **44**, 1664.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Crystal data and data collection conditions, analytical (%) and i.r. data (cm^{-1})

Compound	**(1)**	**(2)**	**(3)**	**(4)**
Formula	$C_{23}H_{44}N_4O_2S_6U$	$C_{26}H_{50}N_4O_2S_6U$	$C_{17}H_{38}N_4O_2S_6U$	$C_{19}H_{42}N_4O_2S_6U$
M	838.36	881.10	760.91	788.54
D_c/g cm^{-3}	1.743	1.547	1.756	1.687
Z	4	4	16	4
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
a/Å	17.322(4)	11.498(2)	20.613(11)	19.103(6)
b/Å	18.287(4)	16.938(4)	22.443(4)	17.288(8)
c/Å	10.228(3)	22.596(5)	24.879(6)	9.432(3)
α/°	90.0	81.33(2)	90.0	90.0
β/°	99.68(2)	85.08(2)	90.0	90.0
γ/°	90.0	77.89(1)	90.0	90.0
U/Å^3	3 194(1)	3 781(1)	11 510(12)	3 104(2)
Systematic absences	$h0l: l \neq 2n$ $0k0: k \neq 2n$	None	$0kl: l \neq 2n$ $h0l: h \neq 2n$ $hk0: k \neq 2n$	$0kl: k + l \neq 2n$ $h0l: h \neq 2n$
Space group	$P2_1/c$	$P\bar{1}$	$Pbca$	$Pna2_1$
Crystal size/mm	0.38 × 0.18 × 0.17	0.18 × 0.32 × 0.39	0.13 × 0.51 × 0.32	0.15 × 0.45 × 0.23
Max. transmission factor	0.64	0.63	0.82	0.53
Min. transmission factor	0.53	0.55	0.49	0.46
Scan range about $K_{\alpha_1} - K_{\alpha_2}$/°	$-1.1/+1.1$	$-1.0/+1.0$	$-1.0/+1.0$	$-1.10/+1.10$
Reflections: collected	6 037	10 279	9 548	3 192
observed [$I/\sigma(I) \geqslant 3.0$]	3 970	5 729	3 722	2 231
Weighting constant, g	0.0007	0.0018	0.0022	0.0018
R (final)	0.040	0.057	0.054	0.049
R' (final)	0.042	0.061	0.057	0.050
Max. on final diff. Fourier/e Å^{-3}	1.89	2.02	1.26	1.79
Min. on final diff. Fourier/e Å^{-3}	-0.67	-1.04	-1.06	-2.16
Max δ/σ (final cycle)	0.08	0.69	0.62	0.27
No. of parameters	325	525	439	312
C (found)	32.15	35.20	26.25	28.70
(expected)	32.95	35.45	26.85	28.95
H (found)	5.15	5.55	4.95	5.25
(expected)	5.30	5.70	5.05	5.35
N (found)	6.80	6.30	7.55	6.30
(expected)	6.70	6.35	7.35	7.10
ν(O–U–O)	915	915	910	875
ν(C–S)	100	1 050	1 000	1 000
ν(C–N)	1 490	1 500	1 500	1 470

Table 2. Comparison of the averaged values for salient bond lengths (Å), angles (°), and out-of-plane puckering (Å) around the central uranium atom

	Compound			
	(1)	**(2)**	**(3)**	**(4)**
U–O	1.755(5)	1.755(11)	1.768(13)	1.798(11)
U–S	2.947(2)	2.926(6)	2.935(7)	2.923(4)
S • • • S (Bite)	2.897(5)	2.873(1)	2.898(7)	2.887(6)
S • • • S (Intermolecular)	3.017(4)	2.991(2)	3.029(7)	3.014(5)
C_α–S	1.688(8)	1.702(20)	1.694(23)	1.707(6)
O–U–O	178.3(3)	179.2(5)	179.0(8)	177.2(5)
S–U–S (Bite)	58.7(1)	58.8(1)	59.1(2)	59.0(1)
S–U–S (Intermolecular)	61.5(1)	61.5(2)	61.9(2)	62.1(2)
S–C_α–S	117.4(8)	115.0(10)	118.6(13)	115.1(9)
S Puckering (max.)	0.31(5)	0.43(5)	0.56(5)	0.62(4)
Angle O–O line/S_6 plane	89.0(4)	89.5(4)	88.0(4)	89.5(5)

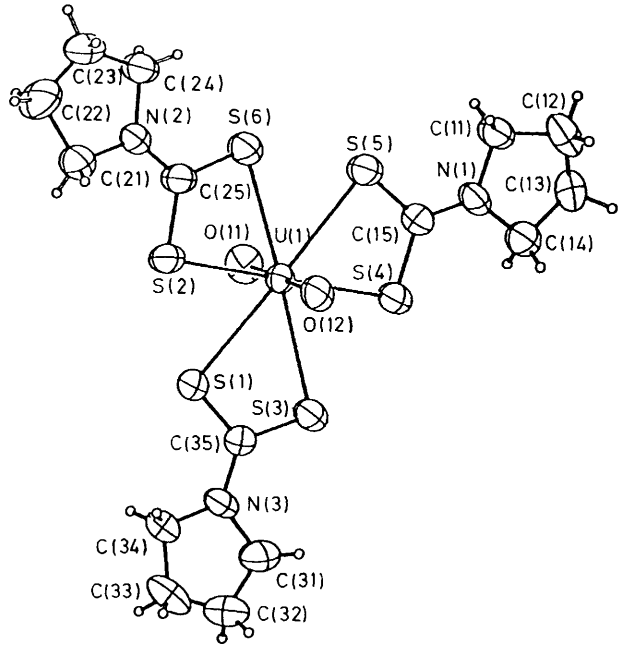

Figure 1. View of the anion of compound (**1**), showing the atomic numbering scheme

Data Collection and Structure Refinement.—Data were collected with a Syntex $P2_1$ four-circle diffractometer. Background intensities were measured at each end of the scan for 0.25 of the scan time. Scan speed was 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan. Three standard reflections which were monitored every 197 reflections showed slight decreases during the data collection; the data were rescaled for this. Unit-cell dimensions and standard deviations were

Table 3. Atom co-ordinates (× 10^4) for compound (**1**) (with standard deviations in parentheses)

Atom	x	y	z	Atom	x	y	z
U(1)	7 249.3(3)	3 861.7(2)	2 385.9(2)	C(21)	9 834(12)	3 956(5)	—286(6)
O(11)	5 727(6)	3 937(3)	1 754(4)	C(22)	9 955(14)	3 567(6)	−1 067(7)
O(12)	8 758(6)	3 783(3)	3 037(4)	C(23)	10 083(11)	2 810(5)	−892(6)
S(1)	7 637.5(28)	5 417.1(13)	2 134.2(14)	C(24)	9 285(9)	2 666(5)	−244(5)
S(2)	8 746.1(29)	4 350.2(13)	1 176.8(15)	C(25)	8 750(9)	3 498(5)	811(5)
S(3)	6 538.5(29)	5 008.8(13)	3 497.9(15)	C(31)	6 618(13)	6 697(5)	3 835(6)
S(4)	5 820.9(28)	3 365.3(12)	3 615.8(15)	C(32)	6 979(15)	7 439(6)	3 869(7)
S(5)	6 727.9(26)	2 300.6(12)	2 591.1(15)	C(33)	7 449(15)	7 623(6)	3 182(8)
S(6)	8 136.4(29)	2 814.7(13)	1 284.0(16)	C(34)	7 550(11)	6 981(5)	2 692(5)
N(1)	5 639(7)	1 936(4)	3 840(4)	C(35)	7 077(8)	5 682(4)	2 943(5)
N(2)	9 237(8)	3 381(4)	130(4)	C(41)	2 904(12)	4 391(7)	4 008(7)
N(4)	2 082(7)	5 043(4)	3 619(4)	C(42)	2 181(13)	3 656(6)	3 905(8)
N(3)	7 068(8)	6 405(4)	3 136(4)	C(43)	2 972(12)	5 738(6)	3 668(8)
C(11)	5 850(10)	1 163(4)	3 678(6)	C(44)	3 553(13)	5 970(7)	4 491(7)
C(12)	5 515(10)	778(5)	4 396(6)	C(45)	1 482(13)	4 879(7)	2 754(7)
C(13)	4 590(11)	1 290(5)	4 713(6)	C(46)	2 587(14)	4 675(8)	2 260(8)
C(14)	5 053(10)	2 042(5)	4 543(5)	C(47)	928(12)	5 149(7)	4 071(9)
C(15)	6 035(8)	2 468(4)	3 395(5)	C(48)	220(14)	5 866(7)	3 876(11)

Table 4. Atomic co-ordinates (× 10^4) for compound (**2**) (with standard deviations in parentheses)

Atom	x	y	z	Atom	x	y	z
U(1)	526.4(6)	2 647.6(4)	8 718.8(2)	C(41)	2 463(7)	246(10)	2 772(7)
U(2)	2 041.5(7)	1 710.8(4)	3 865.1(3)	C(42)	1 936(18)	−211(15)	1 862(8)
S(1)	−1 548(5)	1 927(3)	9 243(2)	C(43)	2 622(25)	95(16)	1 321(10)
S(2)	551(4)	1 578(3)	9 914(2)	C(44)	3 817(23)	−575(18)	1 224(9)
S(3)	393(4)	3 794(3)	7 539(2)	C(45)	4 497(21)	−748(19)	1 789(9)
S(4)	−1 684(6)	3 210(5)	8 110(3)	C(46)	3 810(22)	−1 007(14)	2 284(10)
S(5)	2 624(5)	3 341(4)	8 216(2)	C(51)	−684(17)	3 158(11)	4 045(7)
S(6)	2 757(5)	2 126(4)	9 323(2)	C(52)	−2 621(18)	3 972(12)	3 666(7)
S(7)	3 512(6)	188(3)	3 295(2)	C(53)	−2 829(20)	4 903(12)	3 371(8)
S(8)	1 240(5)	1 065(3)	2 825(2)	C(54)	−3 073(25)	5 581(13)	3 778(11)
S(9)	−411(5)	2 432(3)	3 531(2)	C(55)	−2 078(20)	5 387(14)	4 228(9)
S(10)	431(5)	3 028(3)	4 537(2)	C(56)	−1 959(21)	4 441(13)	4 516(9)
S(11)	2 996(5)	2 421(3)	4 814(2)	C(61)	4 365(16)	1 721(10)	4 734(7)
S(12)	4 529(6)	1 067(3)	4 168(2)	C(62)	5 075(21)	2 219(14)	5 618(10)
O(1)	129(11)	3 608(8)	9 084(5)	C(63)	5 952(24)	2 857(17)	5 480(12)
O(2)	950(10)	1 676(6)	8 354(4)	C(64)	7 155(21)	2 308(13)	5 427(9)
O(3)	2 488(11)	2 589(7)	3 344(4)	C(65)	7 309(19)	1 684(15)	4 926(11)
O(4)	1 571(12)	843(7)	4 393(4)	C(66)	6 407(20)	1 093(13)	5 041(9)
N(11)	−1 389(12)	902(7)	10 305(5)	C(71)	2 677(23)	1 249(18)	6 487(9)
N(21)	−1 747(14)	4 437(11)	7 126(6)	C(72)	2 986(25)	1 461(18)	7 079(10)
N(31)	4 400(14)	3 101(10)	8 940(6)	C(73)	1 549(22)	68(12)	6 967(9)
N(41)	2 626(14)	−343(10)	2 362(7)	C(74)	2 492(26)	−680(16)	6 824(14)
N(51)	−1 690(14)	3 807(9)	4 100(6)	C(75)	1 366(22)	725(14)	5 886(7)
N(61)	5 228(15)	1 657(10)	5 113(7)	C(76)	265(21)	381(14)	5 798(8)
N(71)	1 501(14)	927(9)	6 506(5)	C(77)	461(23)	1 605(15)	6 718(9)
N(81)	9 885(16)	3 734(10)	1 247(6)	C(78)	397(32)	2 483(19)	6 259(11)
C(11)	−853(16)	1 395(9)	9 894(6)	C(81)	9 400(46)	2 925(27)	1 691(18)
C(12)	−800(16)	448(11)	10 864(7)	C(82)	8 787(46)	4 535(30)	1 498(20)
C(13)	−1 533(20)	719(14)	11 398(8)	C(83)	8 504(61)	3 076(40)	2 038(26)
C(14)	−2 725(23)	494(14)	11 414(7)	C(84)	8 089(37)	4 082(23)	1 945(16)
C(15)	−3 357(18)	921(12)	10 814(8)	C(85)	8 414(50)	3 550(33)	557(22)
C(16)	−2 558(15)	700(10)	10 282(7)	C(86)	8 905(33)	4 349(20)	862(14)
C(22)	−3 051(21)	4 587(14)	7 169(8)	C(87)	8 468(47)	3 940(32)	397(21)
C(23)	−3 506(23)	4 439(16)	6 590(10)	C(88)	10 346(49)	4 321(31)	684(21)
C(24)	−3 116(27)	5 081(15)	6 106(9)	C(89)	11 118(43)	3 143(28)	868(19)
C(21)	−1 089(19)	3 824(11)	7 546(7)	C(90)	11 560(44)	3 766(28)	460(18)
C(25)	−1 745(23)	4 903(17)	6 052(9)	C(91)	10 374(33)	4 282(21)	1 664(14)
C(26)	−1 250(21)	5 014(13)	6 608(7)	C(92)	10 541(47)	3 148(30)	1 791(19)
C(31)	3 391(16)	2 906(10)	8 838(7)	C(93)	11 033(47)	3 819(31)	2 151(21)
C(32)	5 012(21)	3 697(14)	8 519(8)	C(94)	11 547(47)	3 761(30)	1 986(20)
C(33)	5 152(21)	4 510(14)	8 787(11)	C(01)	5 076(41)	2 698(26)	2 133(18)
C(34)	5 729(23)	4 200(15)	9 411(10)	C(02)	5 254(44)	2 810(28)	2 697(19)
C(35)	5 122(23)	3 534(13)	9 806(11)	C(03)	4 414(42)	2 097(28)	2 106(18)
C(36)	5 043(18)	2 760(12)	9 488(9)	O(5)	5 699(35)	2 858(22)	1 766(16)

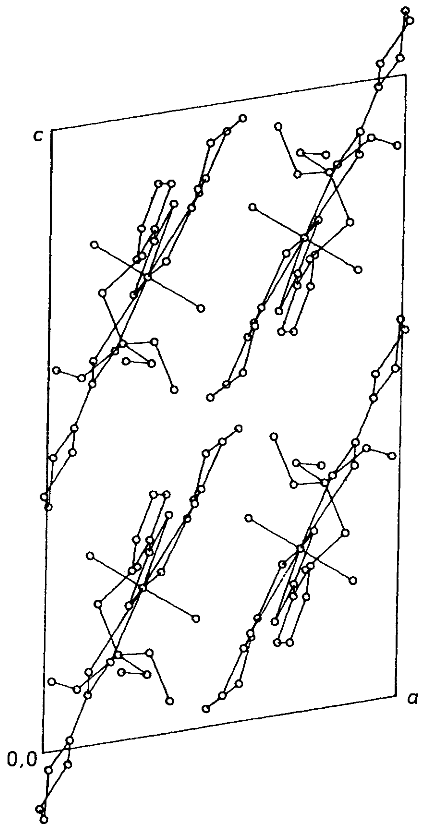

Figure 2. Packing diagram for compound (**1**)

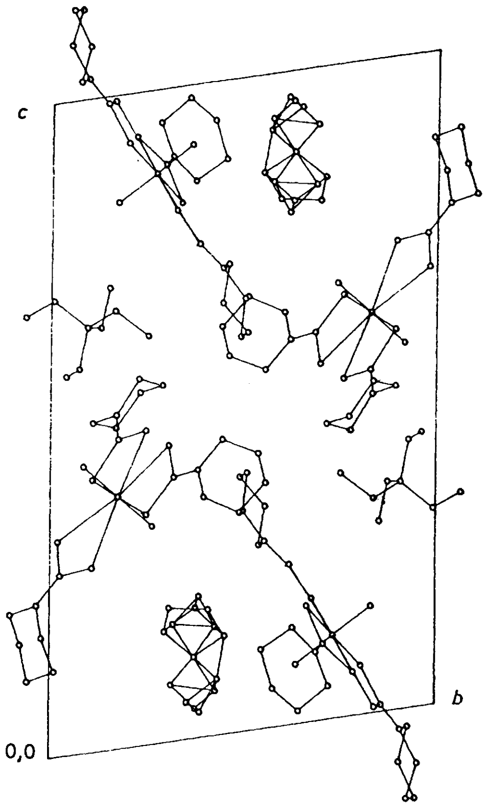

Figure 4. Packing diagram for compound (**2**)

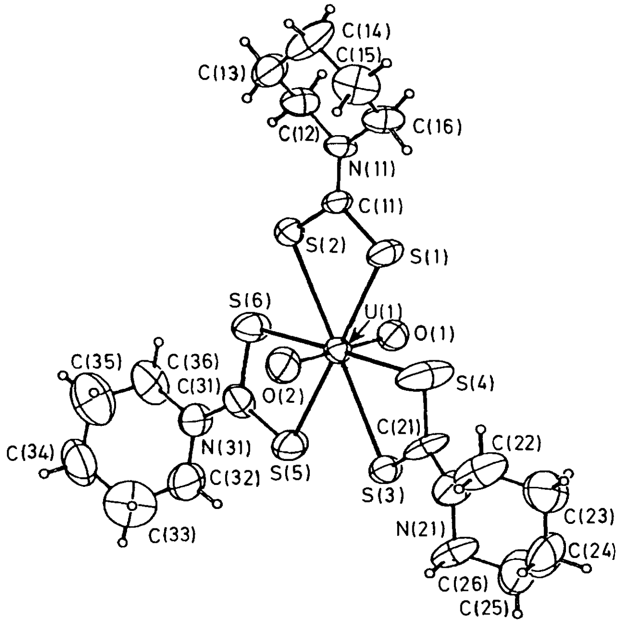

Figure 3. View of one anion of compound (**2**), showing the atomic numbering scheme

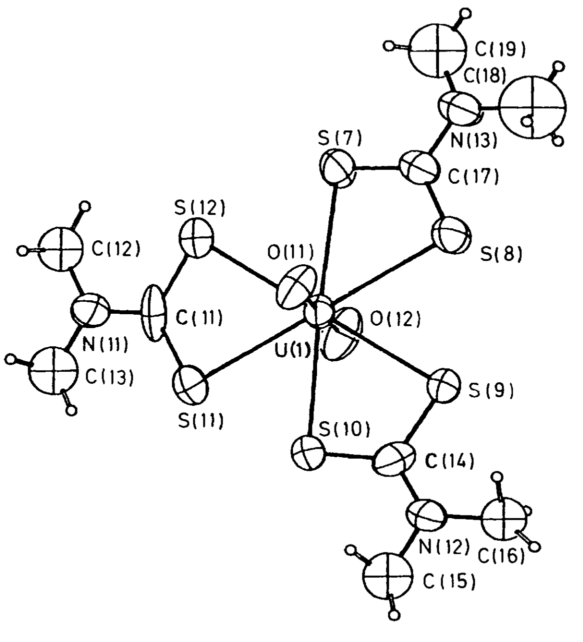

Figure 5. View of one anion of compound (**3**), showing the atomic numbering scheme

obtained by least-squares fit to 15 high-angle reflections ($20 \leqslant 2\theta \leqslant 25$). Maximum 2θ was 50° [40° for (**3**)]. Observed reflections [$I/\sigma(I) \geqslant 3.0$] were corrected for Lorentz, polarisation and absorption effects, the last by the analytical method, with ABSCOR[19] for (**1**) and by Gaussian methods for (**2**)—(**4**). The crystals of (**3**) were relatively weakly diffracting, and the proportion of observed reflections is lower than for the other compounds. The crystal data and data collection conditions for each compound are given in Table 1.

The position of the uranium atom in each case was deter-

Table 5. Atomic co-ordinates (× 10^4) for compound (**3**) (with standard deviations in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	−267.0(4)	2 539.0(3)	4 791.1(3)	C(19)	−2 754(15)	2 103(12)	3 796(15)
U(2)	7 472.1(5)	−140.4(3)	2 151.4(3)	C(21)	6 081(11)	−357(9)	1 355(10)
S(1)	8 157(4)	209(3)	3 231(3)	C(22)	5 517(14)	−727(10)	448(10)
S(2)	8 900(3)	−304(3)	2 234(3)	C(23)	4 860(13)	−324(10)	1 261(13)
S(3)	8 262(3)	−366(3)	1 092(3)	C(24)	7 425(12)	353(9)	3 574(9)
S(4)	6 806(3)	−489(3)	1 071(3)	C(25)	6 786(16)	709(12)	4 411(14)
S(5)	6 059(4)	−72(3)	2 050(3)	C(26)	8 037(15)	719(11)	4 458(14)
S(6)	6 734(4)	191(3)	3 209(3)	C(27)	8 964(11)	−441(8)	1 466(10)
S(7)	−1 633(3)	2 222(3)	4 639(3)	C(28)	10 138(13)	−602(10)	1 538(12)
S(8)	−987(3)	2 772(3)	3 678(3)	C(29)	9 575(15)	−650(10)	568(11)
S(9)	460(3)	2 830(3)	3 735(3)	N(31)	4 881(10)	1 339(7)	2 689(8)
S(10)	1 089(3)	2 856(3)	4 881(3)	C(31)	4 747(14)	1 011(10)	2 146(11)
S(11)	430(4)	2 274(3)	5 906(3)	C(32)	4 616(16)	1 326(11)	1 582(14)
S(12)	−982(4)	2 233(3)	5 860(3)	C(33)	4 317(17)	1 713(13)	2 858(14)
O(11)	−509(8)	3 193(5)	4 992(7)	C(34)	3 644(19)	1 370(14)	2 953(16)
O(12)	−52(10)	1 876(6)	4 597(7)	C(35)	5 026(15)	924(10)	3 222(13)
O(21)	7 405(9)	−802(5)	2 423(7)	C(36)	5 105(18)	1 199(12)	3 806(16)
O(22)	7 534(10)	526(6)	1 875(7)	C(37)	5 408(16)	1 782(12)	2 616(13)
N(11)	−297(10)	1 836(7)	6 768(8)	C(38)	6 072(19)	1 496(12)	2 486(16)
N(12)	1 700(9)	3 117(7)	3 874(8)	N(41)	2 308(14)	1 158(11)	4 986(13)
N(13)	−2 190(11)	2 378(11)	3 607(10)	C(40)	3 254(45)	904(34)	5 507(43)
N(21)	5 512(10)	−475(7)	1 040(8)	C(41)	2 985(39)	779(28)	4 948(36)
N(22)	7 419(13)	583(8)	4 136(8)	C(42)	3 107(56)	1 253(38)	4 750(47)
N(23)	9 517(8)	−555(7)	1 213(8)	C(43)	2 240(33)	1 780(24)	4 286(28)
C(11)	−266(15)	2 085(8)	6 222(9)	C(45)	1 551(54)	811(39)	4 627(43)
C(12)	−882(12)	1 665(10)	7 030(11)	C(46)	1 211(46)	1 171(34)	4 559(39)
C(13)	276(14)	1 715(11)	7 083(12)	C(47)	2 141(69)	1 003(54)	5 751(63)
C(14)	1 155(12)	2 926(9)	4 152(10)	C(50)	2 458(43)	1 601(29)	4 643(33)
C(15)	2 290(14)	3 182(11)	4 193(12)	C(51)	2 083(37)	782(27)	4 620(31)
C(16)	1 748(13)	3 176(10)	3 229(11)	C(52)	2 062(35)	1 423(29)	5 383(33)
C(17)	−1 634(12)	2 463(10)	3 947(11)	C(54)	2 111(53)	1 270(43)	6 077(47)
C(18)	−2 203(22)	2 641(15)	3 014(16)				

Table 6. Atomic co-ordinates (× 10^4) for compound (**4**) (standard deviations in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
U(1)	2 413.1(2)	7 168.5(3)	2 500.0	C(14)	2 964(13)	3 945(11)	3 120(29)
S(1)	3 143(2)	5 683(2)	2 799(7)	C(15)	3 357(14)	3 651(14)	1 907(32)
S(2)	1 676(2)	5 704(2)	2 068(5)	C(21)	928(10)	8 153(10)	1 539(18)
S(3)	1 071(3)	7 228(3)	1 046(7)	C(22)	−275(10)	8 131(11)	613(24)
S(4)	1 610(2)	8 597(3)	2 384(8)	C(23)	−211(14)	8 188(18)	−933(28)
S(5)	3 119(2)	8 608(2)	3 309(7)	C(24)	182(11)	9 317(13)	1 869(29)
S(6)	3 792(2)	7 145(3)	3 931(6)	C(25)	187(25)	9 901(16)	816(37)
O(1)	2 789(7)	7 249(7)	834(11)	C(31)	3 878(8)	8 134(10)	3 818(22)
O(2)	2 051(5)	7 090(7)	4 327(14)	C(32)	5 128(10)	8 076(13)	4 385(25)
N(11)	2 357(7)	4 395(7)	2 633(45)	C(33)	5 207(13)	8 029(14)	5 899(27)
N(21)	309(8)	8 526(9)	1 312(18)	C(34)	4 502(12)	9 366(13)	3 997(33)
N(31)	4 473(7)	8 478(8)	4 056(17)	C(35)	4 686(11)	9 630(13)	2 517(34)
N(1)	2 533(7)	5 956(7)	7 604(52)	C(1)	2 906(11)	5 580(13)	8 776(34)
C(11)	2 399(8)	5 175(8)	2 580(41)	C(2)	1 873(13)	6 287(23)	8 036(28)
C(12)	1 699(10)	3 950(10)	2 566(35)	C(3)	2 831(21)	6 715(21)	7 214(35)
C(13)	1 333(14)	3 887(15)	3 957(30)	C(4)	2 434(17)	5 498(14)	6 365(27)

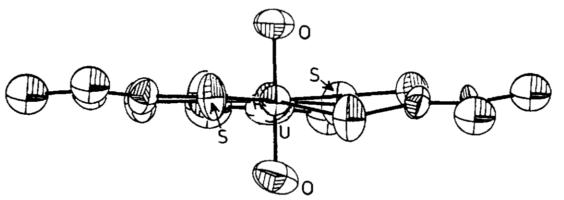

Figure 6. Side view of one anion of compound (**3**), showing pucker of S atoms

mined from a three-dimensional Patterson map. In compounds (**2**) and (**3**) two independent uranium atoms were located. Lighter atoms were found by successive Fourier syntheses, and refined with anisotropic thermal parameters except in (**3**), where only the uranium, sulphur, nitrogen, and oxygen atoms were refined anisotropically. The disordered cation carbon atoms, and a 0.5 occupancy solvent acetone molecule in (**2**) were refined isotropically. In both (**2**) and (**3**), one of the independent cations has its carbon atoms disordered over two sites. Hydrogen atoms were inserted at calculated positions with fixed isotropic thermal parameters (U = 0.07 Å^2). A weighting scheme of the form $w = 1/[\sigma^2(F) + g(F^2)]$ was applied to all complexes and shown to be satisfactory by weight analysis. Final *R* factors and the weighting constants are given in Table 1.

Systematic absences for compound (**4**) gave a choice of two possible space groups, *Pna*2$_1$ and *Pnam*: density calculations were consistent with four molecules per cell. If the space group is *Pnam*, then the molecule would be planar, with the uranium and

Table 7. Principal bond lengths (Å) and angles (°) (standard deviations in parentheses)

Compound (**1**)

U(1)–O(11)	1.752(6)	U(1)–O(12)	1.758(6)	S(2)···S(6)	2.889(3)	S(1)–C(35)	1.672(9)
U(1)–S(1)	2.915(2)	U(1)–S(2)	2.934(3)	S(3)–C(35)	1.708(9)	S(2)–C(25)	1.681(9)
U(1)–S(3)	3.018(3)	U(1)–S(4)	2.923(3)	S(4)–C(15)	1.707(9)	S(4)···S(5)	2.891(4)
U(1)–S(5)	2.937(2)	U(1)–S(6)	2.952(3)	S(6)–C(25)	1.674(9)	S(5)–C(15)	1.693(9)
S(1)···S(3)	2.880(4)						
O(11)–U(1)–O(12)	178.7(3)	O(11)–U(1)–S(1)	87.6(2)	S(2)–U(1)–S(6)	58.8(1)	S(3)–U(1)–S(6)	175.3(1)
O(12)–U(1)–S(1)	92.8(2)	O(11)–U(1)–S(2)	92.6(2)	S(4)–U(1)–S(6)	121.0(1)	S(5)–U(1)–S(6)	61.9(1)
O(12)–U(1)–S(2)	88.6(2)	S(1)–U(1)–S(2)	59.7(1)	U(1)–S(1)–S(3)	62.8(1)	U(1)–S(1)–C(35)	94.7(3)
O(11)–U(1)–S(3)	93.4(2)	O(12)–U(1)–S(3)	85.8(2)	S(3)–S(1)–C(35)	32.0(3)	U(1)–S(2)–S(6)	60.9(1)
S(1)–U(1)–S(3)	58.0(1)	S(2)–U(1)–S(3)	117.0(1)	U(1)–S(2)–C(25)	91.2(3)	S(6)–S(2)–C(25)	30.5(3)
O(11)–U(1)–S(4)	88.8(2)	O(12)–U(1)–S(4)	89.9(2)	U(1)–S(3)–S(1)	59.2(1)	U(1)–S(3)–C(35)	90.4(3)
S(1)–U(1)–S(4)	120.6(1)	S(2)–U(1)–S(4)	178.6(1)	S(1)–S(3)–C(35)	31.2(3)	U(1)–S(4)–S(5)	60.7(1)
S(3)–U(1)–S(4)	63.1(1)	O(11)–U(1)–S(5)	89.5(2)	U(1)–S(4)–C(15)	92.1(3)	S(5)–S(4)–C(15)	31.6(3)
O(12)–U(1)–S(5)	90.0(2)	S(1)–U(1)–S(5)	177.2(1)	U(1)–S(5)–S(4)	60.2(1)	U(1)–S(5)–C(15)	91.9(3)
S(2)–U(1)–S(5)	120.6(1)	S(3)–U(1)–S(5)	122.0(1)	S(4)–S(5)–C(15)	31.9(3)	U(1)–S(6)–S(2)	60.3(1)
S(4)–U(1)–S(5)	59.1(1)	O(11)–U(1)–S(6)	89.1(2)	U(1)–S(6)–C(25)	90.7(3)	S(2)–S(6)–C(25)	30.6(3)
O(12)–U(1)–S(6)	91.7(2)	S(1)–U(1)–S(6)	118.1(1)				

Compound (**2**)

U(1)–S(1)	2.913(5)	U(1)–S(2)	2.929(4)	S(2)–C(11)	1.700(19)	S(3)···S(4)	2.856(8)
U(1)–S(3)	2.948(4)	U(1)–S(4)	2.900(6)	S(3)–C(21)	1.693(23)	S(4)–C(21)	1.647(18)
U(1)–S(5)	2.904(6)	U(1)–S(6)	2.913(6)	S(5)···S(6)	2.863(6)	S(5)–C(31)	1.695(17)
U(1)–O(1)	1.734(12)	U(1)–O(2)	1.750(10)	S(6)–C(31)	1.718(17)	S(7)···S(8)	2.880(8)
U(2)–S(7)	2.946(5)	U(2)–S(8)	2.958(5)	S(7)–C(41)	1.739(20)	S(8)–C(41)	1.675(17)
U(2)–S(9)	2.922(5)	U(2)–S(10)	2.926(5)	S(9)···S(10)	2.876(8)	S(9)–C(51)	1.681(17)
U(2)–S(11)	2.922(5)	U(2)–S(12)	2.926(6)	S(10)–C(51)	1.728(19)	S(11)···S(12)	2.891(7)
U(2)–O(3)	1.765(10)	U(2)–O(4)	1.773(11)	S(11)–C(61)	1.714(16)	S(12)–C(61)	1 704(17)
S(1)···S(2)	2.873(7)	S(1)–C(11)	1.737(14)				
S(1)–U(1)–S(2)	58.9(1)	S(1)–U(1)–S(3)	119.5(1)	S(10)–U(2)–O(3)	92.3(3)	S(11)–U(2)–O(3)	88.9(4)
S(2)–U(1)–S(3)	176.9(1)	S(1)–U(1)–S(4)	61.3(2)	S(12)–U(2)–O(3)	88.7(4)	S(7)–U(2)–O(4)	85.3(4)
S(2)–U(1)–S(4)	119.6(2)	S(3)–U(1)–S(4)	58.4(2)	S(8)–U(2)–O(4)	93.9(4)	S(9)–U(2)–O(4)	90.6(4)
S(1)–U(1)–S(5)	178.8(1)	S(2)–U(1)–S(5)	119.9(1)	S(10)–U(2)–O(4)	86.8(4)	S(11)–U(2)–O(4)	90.9(4)
S(3)–U(1)–S(5)	61.7(1)	S(4)–U(1)–S(5)	120.0(2)	S(12)–U(2)–O(4)	92.0(4)	O(3)–U(2)–O(4)	179.0(5)
S(1)–U(1)–S(6)	119.8(1)	S(2)–U(1)–S(6)	61.3(1)	U(1)–S(1)–S(2)	60.8(1)	U(1)–S(1)–C(11)	93.7(6)
S(3)–U(1)–S(6)	120.6(1)	S(4)–U(1)–S(6)	178.6(2)	S(2)–S(1)–C(11)	32.9(6)	U(1)–S(2)–S(1)	60.3(1)
S(5)–U(1)–S(6)	59.0(1)	S(1)–U(1)–O(1)	92.5(4)	U(1)–S(2)–C(11)	93.9(4)	S(1)–S(2)–C(11)	33.7(4)
S(2)–U(1)–O(1)	86.3(3)	S(3)–U(1)–O(1)	91.2(3)	U(1)–S(3)–S(4)	59.9(1)	U(1)–S(3)–C(21)	90.6(5)
S(4)–U(1)–O(1)	89.0(4)	S(5)–U(1)–O(1)	87.7(4)	S(4)–S(3)–C(21)	30.8(5)	U(1)–S(4)–S(3)	61.6(2)
S(6)–U(1)–O(1)	90.1(4)	S(1)–U(1)–O(2)	88.1(4)	U(1)–S(4)–C(21)	93.2(8)	S(3)–S(4)–C(21)	31.7(7)
S(2)–U(1)–O(2)	93.5(3)	S(3)–U(1)–O(2)	89.0(3)	U(1)–S(5)–S(6)	60.7(2)	U(1)–S(5)–C(31)	92.9(7)
S(4)–U(1)–O(2)	91.8(4)	S(5)–U(1)–O(2)	91.7(4)	S(6)–S(5)–C(31)	33.2(6)	U(1)–S(6)–S(5)	60.4(2)
S(6)–U(1)–O(2)	89.1(4)	O(1)–U(1)–O(2)	179.1(5)	U(1)–S(6)–C(31)	92.1(6)	S(5)–S(6)–C(31)	32.7(6)
S(7)–U(2)–S(8)	58.4(1)	S(7)–U(2)–S(9)	119.9(2)	U(2)–S(7)–S(8)	61.0(1)	U(2)–S(7)–C(41)	92.8(5)
S(8)–U(2)–S(9)	62.2(1)	S(7)–U(2)–S(10)	172.0(1)	S(8)–S(7)–C(41)	31.8(5)	U(2)–S(8)–S(7)	60.6(1)
S(8)–U(2)–S(10)	121.1(1)	S(9)–U(2)–S(10)	58.9(1)	U(2)–S(8)–C(41)	93.8(6)	S(7)–S(8)–C(41)	33.2(6)
S(7)–U(2)–S(11)	119.8(2)	S(8)–U(2)–S(11)	174.6(1)	U(2)–S(9)–S(10)	60.6(2)	U(2)–S(9)–C(51)	93.3(7)
S(9)–U(2)–S(11)	120.2(1)	S(10)–U(2)–S(11)	61.5(1)	S(10)–S(9)–C(51)	33.0(6)	U(2)–S(10)–S(9)	60.5(1)
S(7)–U(2)–S(12)	60.9(2)	S(8)–U(2)–S(12)	118.1(1)	U(2)–S(10)–C(51)	92.1(6)	S(9)–S(10)–C(51)	32.0(5)
S(9)–U(2)–S(12)	177.3(1)	S(10)–U(2)–S(12)	120.7(2)	U(2)–S(11)–S(12)	60.4(2)	U(2)–S(11)–C(61)	92.5(6)
S(11)–U(2)–S(12)	59.2(1)	S(7)–U(2)–O(3)	95.6(3)	S(12)–S(11)–C(61)	32.2(6)	U(2)–S(12)–S(11)	60.3(2)
S(8)–U(2)–O(3)	86.3(4)	S(9)–U(2)–O(3)	88.6(4)	U(2)–S(12)–C(61)	92.6(6)	S(11)–S(12)–C(61)	32.4(6)

Compound (**3**)

U(1)–S(7)	2.944(7)	U(1)–S(8)	2.963(7)	S(1)–C(24)	1.732(25)	S(2)···S(3)	2.885(9)
U(1)–S(9)	2.897(6)	U(1)–S(10)	2.912(7)	S(2)–C(27)	1.763(23)	S(3)–C(27)	1.683(23)
U(1)–S(11)	2.960(6)	U(1)–S(12)	2.917(7)	S(4)···S(5)	2.876(10)	S(4)–C(21)	1.656(24)
U(1)–O(11)	1.761(14)	U(1)–O(12)	1.763(15)	S(5)–C(21)	1.715(23)	S(6)–C(24)	1.694(25)
U(2)–S(1)	2.935(7)	U(2)–S(2)	2.978(7)	S(7)···S(8)	2.882(9)	S(7)–C(17)	1.666(25)
U(2)–S(3)	2.936(7)	U(2)–S(4)	2.919(7)	S(8)–C(17)	1.653(25)	S(9)···S(10)	2.883(9)
U(2)–S(5)	2.926(7)	U(2)–S(6)	2.937(7)	S(9)–C(14)	1.728(25)	S(10)–C(14)	1.652(24)
U(2)–O(21)	1.761(14)	U(2)–O(22)	1.776(16)	S(11)–C(11)	1.667(30)	S(12)–C(11)	1.724(30)
S(7)–U(1)–S(8)	58.4(2)	S(7)–U(1)–S(9)	117.8(2)	S(5)–U(2)–S(6)	62.0(2)	S(1)–U(2)–O(21)	91.7(5)
S(8)–U(1)–S(9)	61.3(2)	S(7)–U(1)–S(10)	177.3(2)	S(2)–U(2)–O(21)	85.9(6)	S(3)–U(2)–O(21)	98.4(5)
S(8)–U(1)–S(10)	119.1(2)	S(9)–U(1)–S(10)	59.5(2)	S(4)–U(2)–O(21)	88.4(5)	S(5)–U(2)–O(21)	90.1(6)
S(7)–U(1)–S(11)	120.1(2)	S(8)–U(1)–S(11)	178.2(2)	S(6)–U(2)–O(21)	86.7(5)	S(1)–U(2)–O(22)	88.7(6)
S(9)–U(1)–S(11)	119.8(2)	S(10)–U(1)–S(11)	62.3(2)	S(2)–U(2)–O(22)	94.5(7)	S(3)–U(2)–O(22)	81.7(6)
S(7)–U(1)–S(12)	62.8(2)	S(8)–U(1)–S(12)	119.5(2)	S(4)–U(2)–O(22)	91.2(6)	S(5)–U(2)–O(22)	89.4(7)
S(9)–U(1)–S(12)	179.0(2)	S(10)–U(1)–S(12)	119.9(2)	S(6)–U(2)–O(22)	93.3(6)	O(21)–U(2)–O(22)	179.5(10)

Table 7 (*continued*)

Compound (**3**)							
S(11)–U(1)–S(12)	59.4(2)	S(7)–U(1)–O(11)	90.4(6)	U(2)–S(1)–C(24)	90.6(8)	U(2)–S(2)–S(3)	60.1(2)
S(8)–U(1)–O(11)	83.9(6)	S(9)–U(1)–O(11)	97.2(5)	U(2)–S(2)–C(27)	92.3(8)	S(3)–S(2)–C(27)	32.3(7)
S(10)–U(1)–O(11)	90.2(6)	S(11)–U(1)–O(11)	97.2(6)	U(2)–S(3)–S(2)	61.5(2)	U(2)–S(3)–C(27)	95.5(8)
S(12)–U(1)–O(11)	83.5(5)	S(7)–U(1)–O(12)	87.8(7)	S(2)–S(3)–C(27)	34.0(8)	U(2)–S(4)–S(5)	60.7(2)
S(8)–U(1)–O(12)	95.8(6)	S(9)–U(1)–O(12)	84.4(6)	U(2)–S(4)–C(21)	92.6(8)	S(5)–S(4)–C(21)	32.0(8)
S(10)–U(1)–O(12)	91.7(7)	S(11)–U(1)–O(12)	83.0(6)	U(2)–S(5)–S(4)	60.4(2)	U(2)–S(5)–C(21)	91.1(8)
S(12)–U(1)–O(12)	94.9(6)	O(11)–U(1)–O(12)	178.0(8)	S(4)–S(5)–C(21)	30.8(8)	U(2)–S(6)–C(24)	91.3(8)
S(1)–U(2)–S(2)	60.9(2)	S(1)–U(2)–S(3)	117.3(2)	U(1)–S(7)–S(8)	61.1(2)	U(1)–S(7)–C(17)	90.7(9)
S(2)–U(2)–S(3)	58.4(2)	S(1)–U(2)–S(4)	179.3(2)	S(8)–S(7)–C(17)	29.6(9)	U(1)–S(8)–S(7)	60.5(2)
S(2)–U(2)–S(4)	118.5(2)	S(3)–U(2)–S(4)	62.1(2)	U(1)–S(8)–C(17)	90.3(9)	S(7)–S(8)–C(17)	29.9(2)
S(1)–U(2)–S(5)	121.7(2)	S(2)–U(2)–S(5)	175.4(2)	U(1)–S(9)–S(10)	60.5(2)	U(1)–S(9)–C(14)	91.2(8)
S(3)–U(2)–S(5)	120.0(2)	S(4)–U(2)–S(5)	59.0(2)	S(10)–S(9)–C(14)	30.7(8)	U(1)–S(10)–S(9)	60.0(2)
S(1)–U(2)–S(6)	60.0(2)	S(2)–U(2)–S(6)	120.0(2)	U(1)–S(10)–C(14)	92.2(9)	S(9)–S(10)–C(14)	32.3(9)
S(3)–U(2)–S(6)	174.5(2)	S(4)–U(2)–S(6)	120.7(2)	U(1)–S(11)–C(11)	90.3(8)	U(1)–S(12)–C(11)	90.6(8)
Compound (**4**)							
U(1)–S(1)	2.928(4)	U(1)–S(2)	2.918(4)	S(2)–C(11)	1.724(18)	S(1)–C(11)	1.681(16)
U(1)–S(3)	2.909(5)	U(1)–S(4)	2.902(4)	S(3)–C(21)	1.681(18)	S(3) · · · S(4)	2.866(7)
U(1)–S(5)	2.924(4)	U(1)–S(6)	2.960(5)	S(5) · · · S(6)	2.890(6)	S(4)–C(21)	1.710(19)
U(1)–O(1)	1.734(11)	U(1)–O(2)	1.862(12)	S(6)–C(31)	1.714(17)	S(3)–C(31)	1.732(17)
S(1) · · · S(2)	2.886(6)						
S(1)–U(1)–S(2)	59.2(1)	S(1)–U(1)–S(3)	119.7(1)	S(4)–U(1)–O(2)	84.3(4)	S(5)–U(1)–O(2)	89.5(4)
S(2)–U(1)–S(3)	62.6(1)	S(1)–U(1)–S(4)	175.3(2)	S(6)–U(1)–O(2)	84.7(3)	O(1)–U(1)–O(2)	177.2(5)
S(2)–U(1)–S(4)	118.2(1)	S(3)–U(1)–S(4)	59.1(1)	U(1)–S(1)–S(2)	60.2(1)	U(1)–S(1)–C(11)	92.3(5)
S(1)–U(1)–S(5)	119.8(1)	S(2)–U(1)–S(5)	172.9(2)	S(2)–S(1)–C(11)	32.5(6)	U(1)–S(2)–S(1)	60.6(1)
S(3)–U(1)–S(5)	119.9(1)	S(4)–U(1)–S(5)	62.2(1)	U(1)–S(2)–C(11)	91.8(5)	S(1)–S(2)–C(11)	31.6(5)
S(1)–U(1)–S(6)	61.4(1)	S(2)–U(1)–S(6)	118.8(1)	U(1)–S(3)–S(4)	60.3(1)	U(1)–S(3)–C(21)	92.7(6)
S(3)–U(1)–S(6)	178.4(1)	S(4)–U(1)–S(6)	119.9(1)	S(4)–S(3)–C(21)	32.6(6)	U(1)–S(4)–S(3)	60.6(1)
S(5)–U(1)–S(6)	58.8(1)	S(1)–U(1)–O(1)	87.7(4)	U(1)–S(4)–C(21)	92.4(6)	S(3)–S(4)–C(21)	32.0(6)
S(2)–U(1)–O(1)	98.2(4)	S(3)–U(1)–O(1)	86.3(4)	U(1)–S(5)–S(6)	61.2(1)	U(1)–S(5)–C(31)	93.3(6)
S(4)–U(1)–O(1)	96.7(4)	S(5)–U(1)–O(1)	88.7(4)	S(6)–S(5)–C(31)	32.8(6)	U(1)–S(6)–S(5)	60.0(1)
S(6)–U(1)–O(1)	92.6(4)	S(1)–U(1)–O(2)	91.4(4)	U(1)–S(6)–C(31)	92.5(6)	S(5)–S(6)–C(31)	33.2(6)
S(2)–U(1)–O(2)	83.5(4)	S(3)–U(1)–O(2)	96.4(3)				

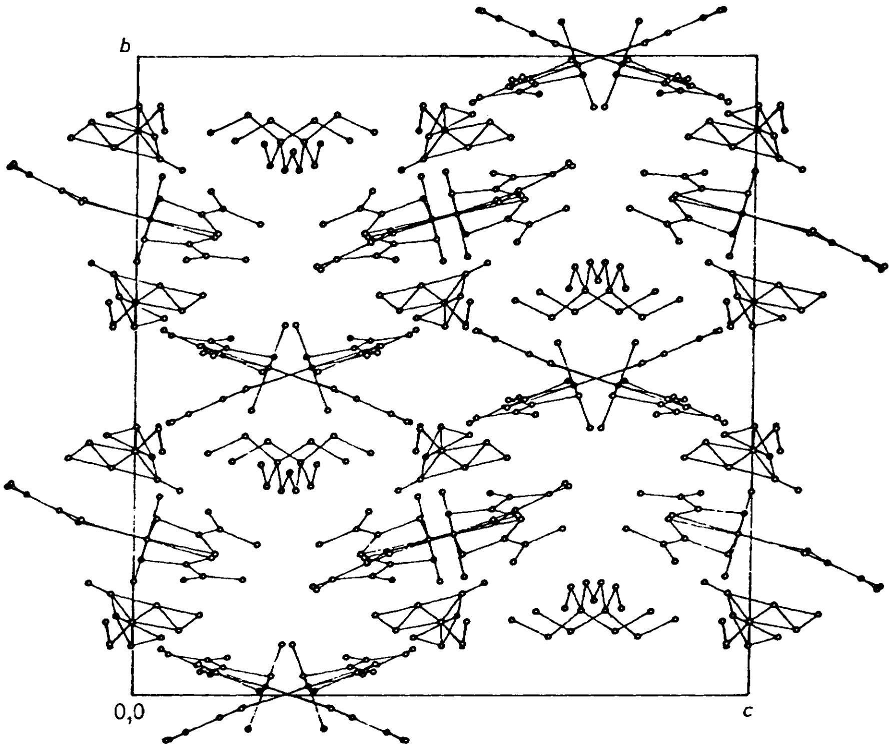

Figure 7. Packing diagram for compound (**3**)

Table 8. Deviations (Å) from planes (defined by atoms listed) and angles (°) between planes and lines. Plane (1) comprises the six S atoms of each complex, (2)—(4) are the S_2CN units of the three individual dithiocarbamates in each complex; none departs significantly from planarity. For compounds (**2**) and (**3**), molecules 1 and 2 contain U(1) and U(2) respectively. Planes 2—4 have successively numbered S atoms, from the lowest up

		Compound					
			(**2**)		(**3**)		
Plane	Atoms	(**1**)	Mol. 1	Mol. 2	Mol. 1	Mol. 2	(**4**)
1	S(1)	−0.17	−0.12	−0.25	0.16	−0.23	0.19
	S(2)	0.11	0.12	0.18	−0.28	0.22	−0.30
	S(3)	0.14	−0.05	0.20	0.28	−0.23	0.32
	S(4)	−0.06	0.08	−0.15	−0.17	0.24	−0.24
	S(5)	0.01	0.06	0.08	0.05	−0.24	0.12
	S(6)	−0.03	−0.10	0.12	−0.05	0.24	−0.10
Angles between planes							
1–2		6.3	5.5	8.9	8.0	10.5	13.9
1–3		6.3	10.4	7.7	11.6	9.3	14.5
1–4		6.3	15.0	3.8	6.8	15.1	13.2
2–3		6.0	15.1	1.9	19.5	13.9	25.3
2–4		4.2	9.8	7.5	1.8	19.7	1.0
3–4		94	22.6	5.8	18.0	24.3	25.0
Angles between planes and O···O line							
1		89.0	89.4	89.3	88.0	86.6	89.5
2		83.0	80.5	83.9	83.0	81.9	77.5
3		83.9	81.6	80.3	77.5	82.4	75.5
4		82.7	85.6	74.8	84.5	72.6	77.2

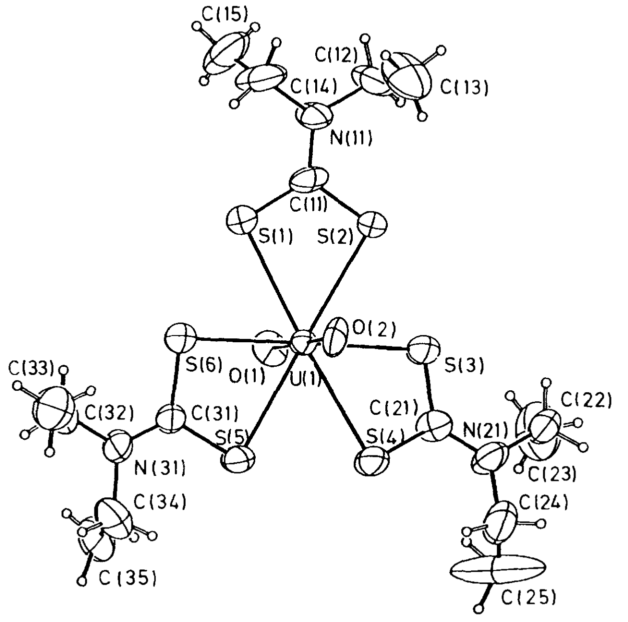

Figure 8. View of the anion of compound (**4**), showing the atomic numbering scheme

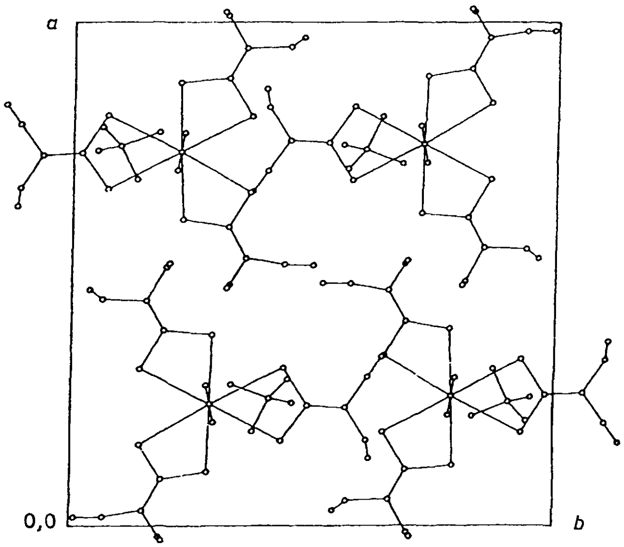

Figure 9. Packing diagram for compound (**4**)

sulphur atoms lying on a mirror plane. In view of the steric interactions that this would introduce in the equatorial plane, this seemed unlikely and $Pna2_1$ was selected. The position of the uranium atom was determined from a three-dimensional Patterson map. The positions of the lighter non-hydrogen atoms were determined from successive Fourier difference syntheses with caution, to allow for atoms generated by false symmetry. Refinement gave a final $R = 0.049$. This successful refinement confirms the space group selection. A centrosymmetric model with half-occupancy ligand molecules disordered about the mirror plane was also tested but could not be refined beyond $R = 0.12$.

Calculations were performed using the SHELXTL system[20] on a Data General DG30 computer. Table 2 gives a comparison of the average values of salient bond lengths and angles. Final atomic co-ordinates are given in Tables 3—6. Bond lengths and angles are listed in Table 7. Details of least-squares planes are listed in Table 8. Views of the anions of compounds (**1**)—(**4**) and their unit cells are shown in Figures 1—9. A further view of (**3**) (Figure 6) directed along the U–C–N line of one Me_2NCS_2 group is also included to show the puckering of the sulphur atoms in the equatorial plane.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Discussion

All four complexes exhibit hexagonal bipyramidal co-ordination about the central uranium atom, involving three bidentate dithiocarbamate ligands in the equatorial plane and two axial oxygen atoms, this being the only stereochemistry that can accommodate the short, linear uranyl group.

The U–O(uranyl) bond lengths in the range 1.734(11)—1.862(12) Å are somewhat longer than the values found for other six-co-ordinated UO_2^{2+} species.[21] This may be due to the greater ligand–oxygen repulsion for U–S compared to U–O complexes. The U–S bonds for each complex are respectively 2.915(2)—3.018(3) in (**1**), 2.900(6)—2.958(5) in (**2**), 2.897(6)—2.978(7) in (**3**), and 2.902(4)—2.960(5) Å in (**4**). The bond lengths determined by Bowman and Dori lie below these ranges, U–O 1.69(5) and 1.72(4), U–S 2.80(1) Å, presumably a result of their failure to refine the structure fully. Indeed some of their quoted values (particularly the S–U–S bond angle) are clearly in error.

The uranyl bond angle varies from being essentially linear [179.5(10)°] to showing a slight deviation [177.2(5)°]. This 'linearity' seems to relate to the degree of puckering of the sulphurs in the equatorial plane, and a general trend which emerges for compounds (**1**)—(**3**) is that the greater the puckering, the closer the uranyl group approaches to linearity (illustrated in Table 2). Compound (**4**), however, does not fit this trend, with puckering above and below the equatorial plane of −0.30 [S(2)] to +0.32 [S(3)], *i.e.* 0.6 Å and an O–U–O(uranyl) angle of 177.2(5)°. This greater deviation may be associated with the presence of the smaller tetramethylammonium cation leading to increased interionic forces. In each compound, the sulphur atoms of the dithiocarbamate ligands define an almost perfect hexagon. Mean bite angles are slightly less than 60.0°, in the range 58.7(1)—59.1(2)°. Intra-ligand S • • • S distances within each compound are in the range 2.856(4)—2.891(4) Å. Inter-ligand S • • • S contacts are not much greater, 2.911(4)—3.109(6) Å. Both sets of distances are well within the sum of the van der Waals radii for two sulphur atoms, and the amount of puckering in these complexes is clearly insufficient to alleviate the equatorial strain. Comparison with the corresponding values for dithiophosphinate complexes is significant.[22] Here the bite angle is much larger [110.5(2) Å] than that encountered for the dithiocarbamate ligands. As a result, steric crowding in the equatorial plane prevents the co-ordination of three ligands and the sulphur atoms become less puckered (maximum value 0.15 Å). Both the intra-ligand and inter-ligand distances in these dithiophosphinate complexes approach more closely the sum of the van der Waals radii for two sulphur atoms. The complexes are co-ordinatively unsaturated, the fifth site of the pentagonal bipyramid being occupied by alcohol, triphenylphosphine oxide, or chloride.

In compound (**1**) the α-carbon atoms are displaced with respect to the mean equatorial plane: C(15) is above (+0.08), C(25) is below (−0.04), whilst C(35) is virtually coplanar (−0.0006 Å). The pyrrolidine rings are displaced in the same direction as the α-carbons with the exception of N(3)—C(33) which lies above the plane, with C(34) below. This is presumably a result of packing interactions. All the piperidine rings in compound (**2**) adopt the chair conformation with the chair out-of-plane displacement being 0.54 Å. In the first molecule of (**3**), all of the Me$_2$NC moieties are directed below the equatorial plane and away from O(11) (Table 8). In the second molecule the units are either directed above, below, or twisted about the mean plane. In compound (**4**), the α-carbon atoms C(11) and C(21) both lie below the mean equatorial plane defined by the six sulphur atoms (0.25 and 0.09 Å respectively) whilst the α-carbon C(31) lies 0.20 Å above. The positions of the carbon atoms of the ethyl groups of these ligands with respect to this plane is influenced by the extent of displacement of the sulphur atoms above or below the plane; *e.g.* S(2) lies further below this plane than S(1) does above, and carbon atoms C(11)—C(14) are all found below. Only C(15) of this ligand molecule is found above. A similar result is found for C(32)—C(35) which are found above with the exception of C(33). In the third dithiocarbamate ligand, the β-carbon atoms C(22) and C(24) both lie below the plane, but the terminal C atoms of the ethyl groups C(23) and C(25) are above the plane.

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References

1 M. Delepine, *Bull. Soc. Chim. Fr.*, 1908, **3**, 643.
2 L. Malatesta, *Gazz. Chim. Ital.*, 1939, **69**, 408.
3 R. G. Jones, E. Binschalder, G. A. Martin, jun., J. R. Thirtle, and H. Gilman, *J. Am. Chem. Soc.*, 1957, **79**, 4971.
4 R. A. Zingaro, *J. Am. Chem. Soc.*, 1956, **78**, 3568.
5 H. Albers and S. Lange, *Chem. Ber.*, 1952, **85**, 278.
6 S. Bonatti and M. Frazini, *Atti. Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Nat. Rend.*, 1966, **41**, 264.
7 C. J. Rodden, Analytical Chemistry of the Manhattan Project, McGraw-Hill, New York, 1950, p. 1070.
8 E. B. Sandell, Colorimetric Determination of Trace Metals, Interscience, New York, 1950, p. 603.
9 K. Gleu and R. Schwab, *Angew. Chem.*, 1950, **62**, 320.
10 I. D. Muzyka, E. D. Romanenko, and N. N. Tananaeva, *Russ. J. Inorg. Chem.*, 1966, **11**, 648.
11 K. Bowman and Z. Dori, *Chem. Commun.*, 1956, 636.
12 P. Zanello, A. Cinquanti, and G. Mazzocchin, *Inorg. Chim. Acta*, 1977, **21**, 195.
13 R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, *Inorg. Chem.*, 1970, **9**, 2116.
14 T. M. Siddal and C. F. Voisin, *J. Inorg. Nucl. Chem.*, 1972, **34**, 2078.
15 E. Forsellini, G. Bombieri, R. Graziani, and B. Zarli, *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 461.
16 S. M. Sinitsyna and N. M. Sinitsyn, *Russ. J. Inorg. Chem.*, 1965, **10**, 499.
17 J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature* (*London*), 1965, **177**, 1042.
18 J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suom. Kemistil B*, 1956, **29**, 75.
19 N. W. Alcock, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, pp. 271–278.
20 G. M. Sheldrick, SHELXTL User Manual, Nicolet Instrument Co., Madison, Wisconsin, 1981.
21 R. G. Denning, 'Properties of the UO$_2^{n+}$ (n = 1,2) Ions,' Gmelin suppl. vol. A6, Springer Verlag, Berlin, 1983.
22 A. E. Storey, F. Zonnevijle, and A. A. Pinkerton, *Inorg. Chim. Acta*, 1983, **75**, 103.

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