New Amide Complexes of Uranium(IV) Thiocyanate; the Crystal Structure of Tetraisothiocyanatotris(*NN*,2-trimethylpropionamide-*O*)-uranium(IV)

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The complexes $U(NCS)_4{\cdot}xL$ [$x = 4$, L = $EtCONMe_2$ (dmpa) or $Me_2CHCONMe_2$ (dmiba); $x = 3$, L = $Me_2CHCONMe_2$] and $U(NCS)_4{\cdot}3Me_3CCONMe_2{\cdot}MeCOMe$ have been prepared and their u.v.–visible and i.r. spectra are reported. The crystal and molecular structure of $[U(NCS)_4(dmiba)_3]$ has been determined by the heavy-atom method from *X*-ray diffractometer data and refined by least squares to *R* 0.083 for 1 816 independent reflections. The crystal is monoclinic, space group $P2_1/a$, with $Z = 4$, $a = 21.195(9)$, $b = 15.155(8)$, $c = 11.204(6)$ Å, and $\beta = 102.99(10)°$. The co-ordination geometry about the seven-co-ordinate uranium atom is pentagonal bipyramidal with two NCS groups in the axial positions, an unusual geometry for uranium(IV) species. The average bonding distances for U–O and U–N are 2.30 and 2.38 Å respectively.

THE only recorded amide complex of tetraisothiocyanatouranium(IV) appears to be [1] $U(NCS)_4{\cdot}4MeCONMe_2$. Since the stoicheiometry of the amide complexes formed by the tetrachloride, $UCl_4{\cdot}xL$, varies with the bulk of the ligands, which depends on the substituents R and R′ of the amides $RCONR'_2$ ($x = 2$ for [2] $Me_2CHCONMe_2$, and $Me_3CCONMe_2$, 2.5 for [3,4] $MeCONMe_2$ and [5] $Ph_2CHCONMe_2$, and 3 for [5] MeCONMePh or $PhCONMe_2$), it was of interest to investigate the behaviour of $U(NCS)_4$ with a series of amides derived from $CH_3CON(CH_3)_2$ by replacement of protons of the acetyl group by methyl groups. This led to the isolation of the four new complexes reported in this paper, which also includes the crystal and molecular structure of one of them.

EXPERIMENTAL

All the complexes were prepared and handled under a dry nitrogen atmosphere in glove-boxes. Uranium tetrachloride [6] and the amide ligands [2] were prepared by published methods. Spectroscopic measurements and the drying of solvents were carried out as described previously.[2]

Preparations.—(*a*) $U(NCS)_4{\cdot}4$dmpa (dmpa = $EtCONMe_2$). Solid K[CNS] (1.655 g, 17.03 mmol) was added to a solution of UCl_4 (1.617 g, 4.26 mmol) in tetrahydrofuran (thf) (50 cm³). After stirring for 2 h, dmpa (4 g, 40 mmol) was added and the mixture was stirred for 24 h. The supernatant was evaporated to dryness under vacuum, leaving a grey-green residue which was washed with toluene–pentane (3 × 5 cm³, 1 : 2 v/v) and then dissolved in dichloromethane. After centrifugation, the supernatant was evaporated to small volume (*ca.* 5 cm³) under vacuum and the toluene–pentane mixture was added to precipitate the *product*, which was washed with toluene–pentane (3 × 5 cm³) and dried *in vacuo* (8 h). Yield 50%.

(*b*) $U(NCS)_4{\cdot}4$dmiba (dmiba = $Me_2CHCONMe_2$). As (*a*), except that the *product* from the reaction in thf was not washed with the toluene–pentane mixture at the final stage. Yield 50%.

(*c*) $U(NCS)_4{\cdot}3$dmiba. This compound was obtained by adding toluene–pentane (1 : 2 v/v) to a solution of $U(NCS)_4{\cdot}4$dmiba in dichloromethane until a cloudiness developed. Dichloromethane was then added dropwise to clear the solution, which was then left to crystallise. The *product* was dried *in vacuo* (8 h). Yield 10%. If an excess of the toluene–pentane mixture was added, the yield increased to 50% but the product was not well crystalline.

(*d*) $U(NCS)_4{\cdot}3Me_3CCONMe_2{\cdot}MeCOMe$. As (*a*) except that acetone was used in place of thf; the supernatant from the primary reaction was evaporated to *ca.* 5 cm³ under vacuum and the complex was then precipitated by addition of toluene–pentane (1 : 2 v/v). The precipitate was washed with the toluene–pentane mixture (3 × 5 cm³), dissolved in dichloromethane, and the supernatant evaporated to dryness under vacuum. After washing with the toluene-pentane mixture (3 × 5 cm³), the *product* was dried *in vacuo* (8 h). Yield 30%. The analytical results are given in Table 2.

Single-crystal Data Collection.—Green prismatic crystals of $U(NCS)_4{\cdot}3$dmiba were obtained by recrystallisation from a mixture of dichloromethane, toluene, and pentane. They are very sensitive to atmospheric moisture and were therefore mounted in thin-walled Lindemann glass capillaries in an inert-atmosphere glove-box.

Preliminary survey photographs, taken by both Weissenberg and precession methods, showed a monoclinic unit cell with the systematic absences $h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$. These are consistent with the space group $P2_1/a$. The crystal was mounted in a random orientation on a four-circle Philips PW1100 automated diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ 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 reflections with $8 \leqslant \theta \leqslant 15°$ were used.

Crystal Data.—$C_{22}H_{39}N_7O_3S_4U$, $M = 815.9$, Monoclinic, $a = 21.195(9)$, $b = 15.155(8)$, $c = 11.204(6)$ Å, $\beta = 102.99(10)°$, $U = 3\,506.7$ Å³, $D_c = 1.54$ g cm⁻³, $Z = 4$, $F(000) = 1\,600$, μ(Mo-K_α) = 47.2 cm⁻¹, space group $P2_1/a$.

Integrated intensities for hkl reflections with k and $l \geqslant 0$ and $3 \leqslant \theta \leqslant 25°$ were measured using the θ—2θ scan method with a scan speed of 1.80° min⁻¹, a scan width of 1.20°, and two background counts of 10 s at each end of the scan.

The intensities of 6 758 reflections were recorded; two reflections monitored at regular intervals showed only the deviations from their mean intensities predicted by counting statistics. Integrated intensities were corrected for Lorentz and polarisation effects and for absorption following the method proposed by North *et al.*[7]

Structure Determination.—The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Published scattering factors were used for neutral S, O, N, and C [8] atoms and for U; [9] the anomalous terms for uranium were taken from published data.[10]

With phasing based only on the uranium atoms the discrepancy factor, calculated as $\Sigma|F_o| - |F_c|/\Sigma F_o$, was 0.29. Three cycles of unit weight and individual isotropic refinement of the 37 non-hydrogen atoms decreased R to 0.15.

Anisotropic thermal parameters were applied first to the uranium atom only. A difference-Fourier map calculated at this point showed disorder in the proximity of the sulphur atoms. Efforts to resolve the disorder into a double set of discrete atoms failed and so they were refined with anisotropic thermal parameters. Hydrogen atoms were not observed and not included in the refinement. In the final stage of the refinement the weighting scheme used was $w = [3.9142/\sigma^2(F)] + 0.000\,755F^2$ which showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to $|F_o|$ and to $(\sin\theta)/\lambda$.

The final R factor was 0.083 for 1 816 data where $I \geqslant 2.5\sigma(I)$. The value of R_w $[=\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]$ was 0.078.

Table 1 contains final atomic positional parameters for all non-hydrogen atoms with their estimated standard deviations derived from the last cycle of least squares. The final observed and calculated structure-factor amplitudes and the thermal parameters are available as Supplementary Publication No. SUP 23149 (14 pp.).*

TABLE 1

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

Atom	*x*	*y*	*z*
U	1 295(1)	1 973(1)	2 347(1)
N(1)	493(15)	2 384(20)	617(29)
C(1)	124(20)	2 581(26)	−256(40)
S(1)	−409(7)	2 864(12)	−1 405(12)
N(2)	509(14)	2 213(23)	3 590(29)
C(2)	297(18)	2 469(26)	4 367(36)
S(2)	−26(6)	2 807(10)	5 425(11)
N(3)	1 732(16)	901(26)	1 257(31)
C(3)	2 009(24)	526(36)	769(46)
S(3)	2 398(7)	−97(11)	−124(18)
N(4)	2 052(16)	1 589(23)	4 106(35)
C(4)	2 242(21)	1 378(31)	5 036(47)
S(4)	2 600(10)	1 074(14)	6 445(14)
O(1)	1 400(11)	3 412(16)	3 002(21)
C(11)	1 210(17)	4 162(27)	3 424(37)
C(12)	774(23)	4 769(32)	2 515(44)
C(13)	1 013(22)	4 772(32)	1 304(44)
C(14)	60(21)	4 469(28)	2 307(37)
N(11)	1 378(15)	4 297(23)	4 639(31)
C(15)	1 126(19)	5 085(29)	5 175(36)
C(16)	1 788(20)	3 652(29)	5 408(38)
O(2)	713(11)	695(17)	2 338(22)
C(21)	372(19)	32(26)	2 546(32)
C(22)	721(21)	−651(31)	3 442(43)
C(23)	1 361(25)	−967(36)	3 262(48)
C(24)	827(32)	−210(49)	4 667(66)
N(21)	−221(15)	−36(22)	1 974(30)
C(25)	−486(21)	633(33)	1 083(43)
C(26)	−618(22)	−807(34)	2 191(41)
O(3)	2 067(12)	2 634(17)	1 464(22)
C(31)	2 578(18)	2 600(23)	1 001(33)
C(32)	3 206(21)	2 645(30)	1 823(40)
C(33)	3 204(19)	3 131(33)	2 976(39)
C(34)	3 427(23)	1 706(33)	2 169(44)
N(31)	2 417(18)	2 595(23)	−240(33)
C(35)	3 018(25)	2 510(34)	−747(45)
C(36)	1 765(24)	2 588(32)	−1 019(45)

The calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Interuniversitario, Italia Nord Orientale using the SHELX 76 program package.[11]

RESULTS AND DISCUSSION

The Complexes.—The solid complexes $U(NCS)_4{\cdot}4L$ with L = dmpa ($EtCONMe_2$) or dmiba ($Me_2CHCONMe_2$) were obtained by addition of an excess of the ligand (U : L *ca.* 1 : 9) to the solution resulting from the reaction of uranium tetrachloride with the stoicheiometric quantity of potassium thiocyanate in tetrahydrofuran, followed by evaporation to dryness under vacuum. The complex with dmpa was purified by dissolution in dichloromethane after washing with a mixture of toluene and pentane (1 : 2 v/v), but this purification treatment led to an appreciable loss of the ligand in the case of the complex with dmiba. The analytical results (Table 2) also indicate a slight deficit of ligand content for this complex even when the purification treatment is omitted. However, the i.r. spectra of both tetrakis complexes as solid mulls (Table 3) indicate that all of the ligand is bonded to the uranium atom, but in solution in dichloromethane the i.r. spectrum of the dmiba complex indicates the presence of both free and bonded ligands, which suggests that the environment of the uranium atom in $U(NCS)_4{\cdot}4$dmiba is overcrowded. Dissolution of this last complex in dichloromethane and addition of a mixture of toluene and pentane to the solution leads to crystallisation of the tris complex, $U(NCS)_4{\cdot}3$dmiba, confirming that the tetrakis complex loses ligand in solution. With the even more bulky ligand, $Me_3CCONMe_2$, there was no evidence for the formation of a tetrakis complex, and only the solvated tris complex, $U(NCS)_4{\cdot}3Me_3CCONMe_2{\cdot}MeCOMe$, was obtained. It is not clear from the i.r. spectrum whether the acetone molecule is bonded to the uranium, but this seems unlikely.

The i.r. spectrum of the complex $U(NCS)_4{\cdot}4$dmpa in dichloromethane does not show any evidence for free ligand, but the presence of free ligand was observed in the i.r. spectrum of this complex in solution in co-ordinating solvents such as thf although such dissociation appears to be limited.

The shifts in the C=O stretching vibration of the ligand on complexation are similar to those observed in analogous complexes of uranium tetrachloride,[2] indicating bonding *via* the carbonyl oxygen atom. The C–N stretching mode appears at *ca.* 2 020 cm^{-1} in the i.r. spectra of all of the complexes, which is on the borderline for distinguishing between sulphur and nitrogen bonding in thiocyanates,[12] although the relatively high intensity of this feature in each case suggests that the thiocyanate groups are nitrogen bonded.[13,14] The C–S feature in the

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2

Analytical results (%) *

Complex	U	C	H	N	S
$U(NCS)_4 \cdot 4EtCONMe_2$	27.3 (27.2)	33.0 (33.0)	5.1 (5.1)	12.8 (12.8)	14.7 (14.7)
$U(NCS)_4 \cdot 4Me_2CHCONMe_2$	25.0 (25.6)	35.5 (36.1)	5.5 (5.6)	10.6 (12.0)	13.0 (13.8)
$U(NCS)_4 \cdot 3Me_2CHCONMe_2$	29.7 (29.2)	32.7 (32.4)	4.9 (4.8)	12.0 (12.0)	14.9 (15.7)
$U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$	25.5 (26.0)	35.1 (36.7)	5.5 (5.6)	10.7 (10.7)	14.1 (14.0)

* Calculated values are given in parentheses.

i.r. spectra of *N*-bonded thiocyanates usually lies between 760 and 880 cm^{-1}, as against 700 cm^{-1} for *S*-bonded thiocyanate,[15,16] but this feature is usually weak and is often difficult to identify when organic ligands are present.[12] In the i.r. spectra of the amide complexes, weak to medium features were observed in the region 720—760 cm^{-1}, but these could not be assigned to the C–S mode with certainty to provide additional confirmatory evidence for *N*-bonded thiocyanate groups.

TABLE 3

Infrared spectra (cm^{-1}) [a] of the complexes

Compound	ν(C=O) [b]	$\Delta\nu$(C=O) [b]
$U(NCS)_4 \cdot 4EtCONMe_2$	1 600	45
$U(NCS)_4 \cdot 4Me_2CHCONMe_2$	1 590	40
	ca. 1 630, 1 590 [c]	0, 40 [c]
$U(NCS)_4 \cdot 3Me_2CHCONMe_2$	1 590	40
$U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$	1 590, 1 570	40, 60

[a] Solid mulled in Nujol; all complexes are grey-green. [b] Amide C=O. [c] Solution in CH_2Cl_2.

The u.v.–visible spectra (solid reflectance and dichloromethane solution) of the two tetrakis amide complexes and of $U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$ are illustrated in Figure 1; these spectra are consistent with the presence of high (>6) co-ordinate uranium(IV) species (bands at 1 130 nm in the solid and at 1 150—1 180 nm in the solution spectra). The spectrum of $U(NCS)_4 \cdot 4dmiba$ in solution is essentially that of the tris complex. The solution u.v.–visible spectrum of $U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$ shows a weak additional band at 1 050 nm which may indicate a dissociation in solution of the form (1). However, we have been unable to confirm this.

$$2\,U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe \rightleftharpoons U(NCS)_4 \cdot 2Me_3CCONMe_2 + U(NCS)_4 \cdot 4Me_3CCONMe_2 + 2\,MeCOMe \quad (1)$$

Crystal-structure Results.—Two perspective views of the molecule, which include the atom-numbering scheme, are presented in Figure 2 and the crystal packing, viewed along the *c* axis, is shown in Figure 3. Selected bond distances and angles are listed in Table 4.

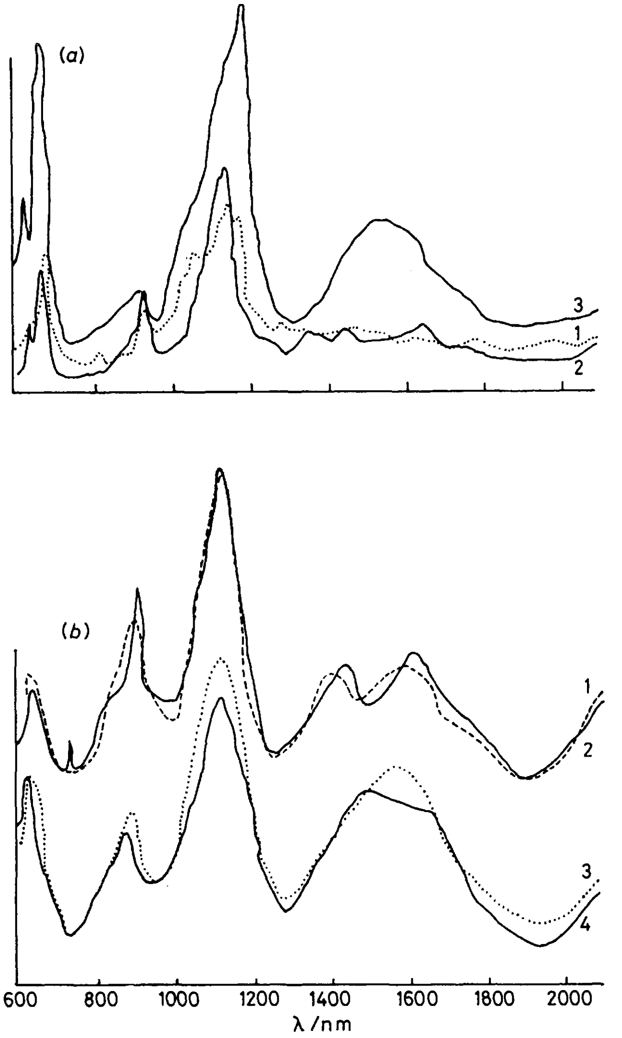

FIGURE 1 Ultraviolet–visible spectra of the complexes. (*a*) Solutions of: $U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$ (in CH_2Cl_2) (1); $[U(NCS)_4(dmiba)_3]$ (in thf) (2); $U(NCS)_4 \cdot 4dmpa$ (in thf) (3). The spectrum of $U(NCS)_4 \cdot 4dmiba$ in thf is the same as (2) owing to dissociation. (*b*) Solid reflectance: $U(NCS)_4 \cdot 3Me_3CCONMe_2 \cdot MeCOMe$ (1); $[U(NCS)_4(dmiba)_3]$ (2); $U(NCS)_4 \cdot 4dmpa$ (3); $U(NCS)_4 \cdot 4dmiba$ (4). Spectra (1) and (2) have been moved upwards to eliminate superimposition

The structure consists of discrete $[U(NCS)_4(dmiba)_3]$ molecules separated by van der Waals contacts. The central uranium atom is seven-co-ordinated in a slightly distorted pentagonal-bipyramidal structure. Two isothiocyanato-groups occupy axial positions and the other two, together with three dmiba ligands co-ordinated through the oxygen atoms, are located in the pentagonal plane. The five atoms in the equatorial plane deviate slightly from ideal planarity. The equation of the best mean plane in direct space is $10.7886X - 4.1395Y + 7.6295Z - 2.3474 = 0$ and the deviations (Å) of the atoms from this plane are N(2) 0.025, N(3) 0.017, O(1) 0.041, O(2) −0.082, O(3) −0.091, and U 0.024. The O $\cdots$ N and O $\cdots$ O contact distances in the plane range from 2.72 to 2.80 Å.

Although pentagonal-bipyramidal geometry is the rule

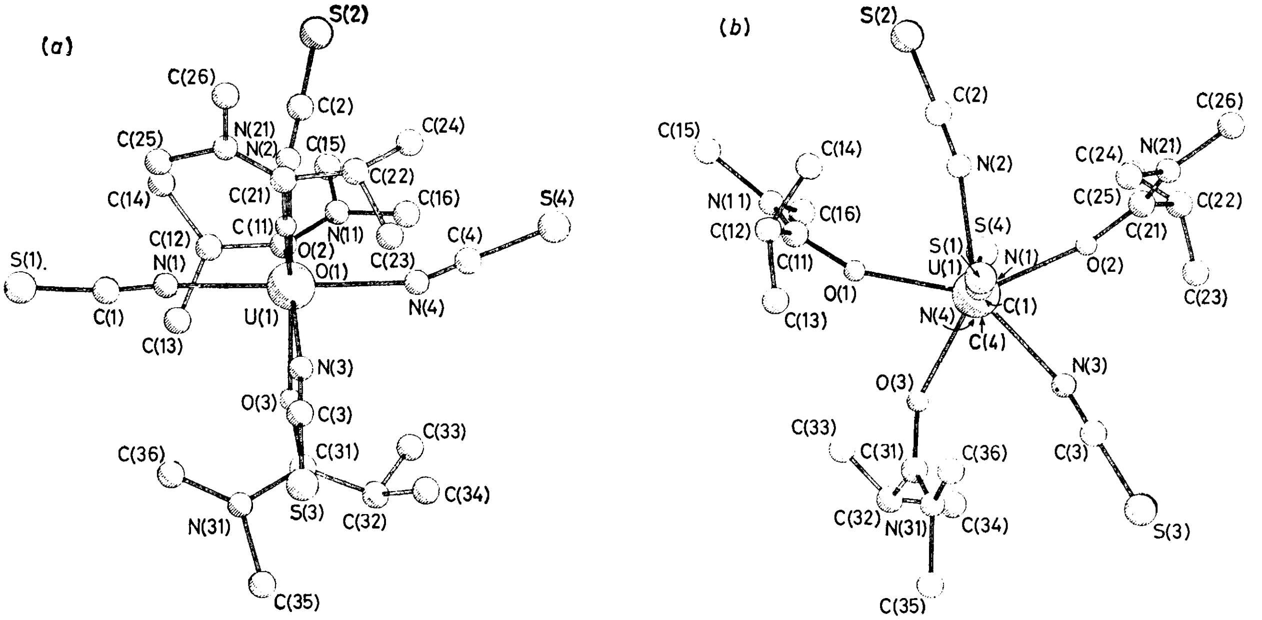

FIGURE 2 Two perspective views of the molecular structure of $[U(NCS)_4(dmiba)_3]$, one normal to the SCN–U–NCS axis (*a*) and one down that axis (*b*), with the numbering scheme of the atoms

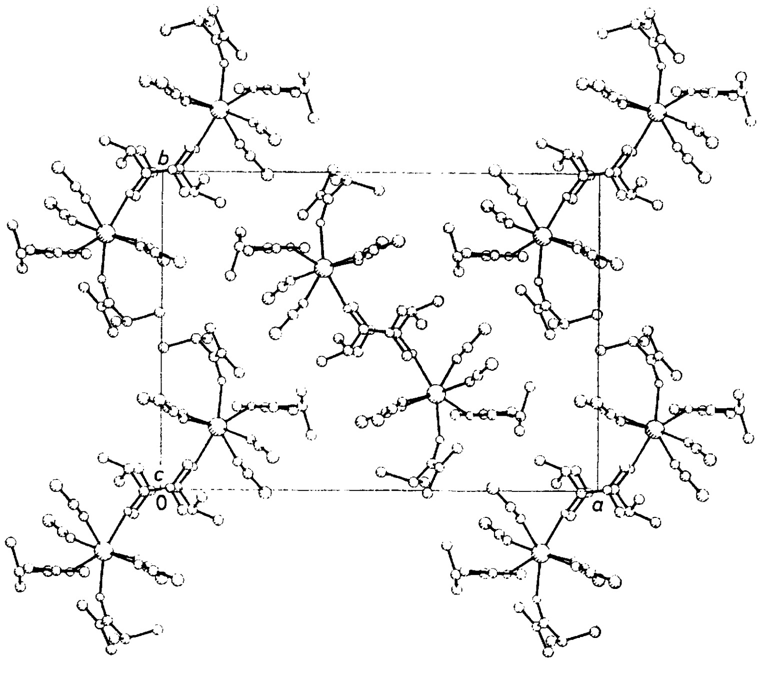

FIGURE 3 Crystal packing diagram for $[U(NCS)_4(dmiba)_3]$ viewed along the *c* axis

for seven-co-ordinated uranium(VI) compounds containing the linear O=U=O group which provides the axis of the structure, this co-ordination geometry is very unusual in uranium(IV) compounds and, to our knowledge, the structure of $[U(NCS)_4(dmiba)_3]$ is the first example of this geometry in a mononuclear compound. The only other example of this co-ordination number and geometry is in the structure of [17] UBr_4, which is a bromine-bridged polymer. One other example of seven-co-ordinate uranium(IV) is the cation $[UCl(OPMe_3)_6]^{3+}$, the co-ordination polyhedron of which can be described either as a distorted monocapped trigonal antiprism or as a distorted monocapped octahedron.[18]

The average of the four independent U–N bond distances is 2.38 Å which is close to the values reported for other isothiocyanatouranium(IV) complexes {$Cs_4[U(NCS)_8]$,[19] 2.42 Å, square antiprismatic geometry; $[NEt_4]_2[U(NCS)_8]$,[20] 2.38 Å, cubic geometry; and

TABLE 4

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

(*a*) Bond distances

U–N(1)	2.36(3)	U–N(2)	2.43(3)	U–N(3)	2.34(3)	U–N(4)	2.32(3)
N(1)–C(1)	1.14(3)	N(2)–C(2)	1.13(3)	N(3)–C(3)	1.05(3)	N(4)–C(4)	1.08(4)
C(1)–S(1)	1.57(4)	C(2)–S(2)	1.58(3)	C(3)–S(3)	1.72(4)	C(4)–S(4)	1.66(4)
U–O(1)	2.30(2)	U–O(2)	2.29(2)	U–O(3)	2.32(2)		
O(1)–C(11)	1.33(3)	O(2)–C(21)	1.29(3)	O(3)–C(31)	1.30(3)		
N(11)–C(11)	1.34(3)	N(21)–C(21)	1.28(3)	N(31)–C(31)	1.36(3)		
N(11)–C(15)	1.49(4)	N(21)–C(25)	1.45(4)	N(31)–C(35)	1.51(4)		
N(11)–C(16)	1.46(4)	N(21)–C(26)	1.49(4)	N(31)–C(36)	1.46(4)		
C(11)–C(12)	1.52(4)	C(21)–C(22)	1.52(4)	C(31)–C(32)	1.44(4)		
C(12)–C(13)	1.55(5)	C(22)–C(23)	1.50(4)	C(32)–C(33)	1.49(4)		
C(12)–C(14)	1.55(4)	C(22)–C(24)	1.50(6)	C(32)–C(34)	1.52(4)		

(*b*) Angles

O(1)–U–N(2)	72.8(8)	N(2)–U–O(2)	72.1(8)	O(2)–U–N(3)	71.8(8)
N(3)–U–O(3)	71.2(8)	O(3)–U–O(1)	72.5(6)	N(1)–U–O(1)	90.7(7)
N(1)–U–N(2)	88.4(8)	N(1)–U–O(2)	86.1(7)	N(1)–U–N(3)	93.0(8)
N(1)–U–O(3)	89.0(7)	N(4)–U–O(1)	88.2(8)	N(4)–U–N(2)	89.0(9)
N(4)–U–O(2)	93.5(8)	N(4)–U–N(3)	89.4(9)	N(4)–U–O(3)	92.9(8)
N(4)–U–N(1)	177.4(9)	U–N(1)–C(1)	177(2)	U–N(2)–C(2)	159(2)
U–N(3)–C(3)	167(3)	U–N(4)–C(4)	159(3)	N(1)–C(1)–S(1)	177(3)
N(2)–C(2)–S(2)	178(3)	N(3)–C(3)–S(3)	175(4)	N(4)–C(4)–S(4)	175(4)
U–O(1)–C(11)	156(2)	U–O(2)–C(21)	168(2)	U–O(3)–C(31)	152(2)
O(1)–C(11)–C(12)	118(3)	O(2)–C(21)–C(22)	116(3)	O(3)–C(31)–C(32)	118(3)
O(1)–C(11)–N(11)	117(3)	O(2)–C(21)–N(21)	120(3)	O(3)–C(31)–N(31)	112(3)
C(11)–N(11)–C(15)	120(3)	C(21)–N(21)–C(25)	118(3)	C(31)–N(31)–C(35)	110(3)
C(11)–N(11)–C(16)	119(3)	C(21)–N(21)–C(26)	120(3)	C(31)–N(31)–C(36)	127(3)
C(15)–N(11)–C(16)	121(3)	C(25)–N(21)–C(26)	121(3)	C(35)–N(31)–C(36)	123(3)
C(11)–C(12)–C(13)	108(3)	C(21)–C(22)–C(23)	117(3)	C(31)–C(32)–C(33)	113(3)
C(11)–C(12)–C(14)	110(3)	C(21)–C(22)–C(24)	105(4)	C(31)–C(32)–C(34)	108(3)
C(13)–C(12)–C(14)	112(3)	C(23)–C(22)–C(24)	108(4)	C(33)–C(32)–C(34)	108(3)

[$U(NCS)_4(OPMe_3)_4$],[21] dodecahedral geometry, 2.465 Å} and for analogous dioxouranium(VI) compounds with the same pentagonal-bipyramidal geometry {[$UO_2(NCS)_5]^{3-}$, 2.45 Å [22] and [$UO_2(NCS)_2(OPPh_3)_2$(MeCOMe)],[23] 2.44 Å}. The average U–O bond lengths (2.30 Å) are comparable to the U–O distances in the seven-co-ordinated [$UCl(OPMe_3)_6]^{3+}$ cation [18] (2.26 Å) and eight-co-ordinated [$U(NCS)_4(OPMe_3)_4$] molecule [21] (2.32 Å). The bond lengths and bond angles in the isothiocyanato-groups are in close agreement with those reported in the structures quoted above. The dmiba ligand has the expected geometry, bond lengths, and angles.

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