Structure and Stereochemistry in *f*-Block Complexes of High Co-ordination Number. Part 2.[1] The [M(unidentate ligand X)$_4$(unidentate ligand Y)$_4$] System: Crystal Structure * of Tetrakis(hexamethylphosphoramide)tetrakis(isothiocyanato)uranium(IV)

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The crystal structure of the title compound [$U^{IV}(NCS)_4\{OP(NMe_2)_3\}_4$] has been determined from *X*-ray diffraction data at 295 K, the structure being refined by least squares to a residual of 0.059 for 7 356 ' observed ' reflections. Crystals are monoclinic, space group *P*2/*c*, with a = 25.06(1), b = 21.50(1), c = 22.64(1) Å, β = 117.94(3)°, and Z = 8. The structure comprises discrete molecules of the complex, all of which have eight-co-ordinate uranium atoms lying on crystallographic two-fold symmetry axes, with U–O ranging from 2.276(13) to 2.357(10) Å and U–N from 2.410(15) to 2.526(17) Å. The stereochemistry and relative stability of the different isomers of [M(unidentate ligand X)$_4$(unidentate ligand Y)$_4$] have been examined by repulsion theory.

For those complexes in which eight unidentate ligands are bound to a central atom, two stereochemistries are expected: the square antiprism and the triangular dodecahedron.[2] The square antiprism is slightly more stable but in situations where the metal–ligand effective bond-length ratio *R*(X/Y) differs appreciably from unity the dodecahedron may become favoured, and this is particularly so for [M(unidentate ligand X)$_4$(unidentate ligand Y)$_4$], where equal numbers of two distinctly different ligand types are employed. For [$ThCl_4(Ph_2SO)_4$], dodecahedral stereochemistry is observed;[3] Th–Cl, 2.75_7—2.75_9 Å, is much longer than Th–O, 2.4_6 Å, but the ' effective bond lengths ' are in the reverse order and in consequence the chlorine atoms occupy the B sites. On the other hand, thiocyanato-complexes have been reported with both stereochemistries. Dodecahedral structures have been reported for $K_4[Nd(NCS)_4(H_2O)_4][NCS]_3$,[4] $K_4[Eu(NCS)_4(H_2O)_4][NCS]_3$,[4] and [$Th(NCS)_4\{OC(NMe_2)_2\}_4$],[5] but square-antiprismatic structures for [$U(NCS)_4(OPMe_3)_4$],[6] [$U(NCS)_4(OPPh_3)_4$],[7] and 2 [$U(NCS)_4(H_2O)_4$]·3(18-crown-6)·$6H_2O$·2MeBuCO.[8] However, the structures are either not known with sufficient precision or are too distorted to allow an accurate comparison with calculated structures. Accordingly, a further complex has been examined and is reported in this work, [$U(NCS)_4\{OP(NMe_2)_3\}_4$].

Experimental

A preparation of [$U(NCS)_4\{OP(NMe_2)_3\}_4$] has been described previously.[9]

In the present work, hexamethylphosphoramide (hmpa) (0.6 cm^3, 3.6 mmol) was added to a solution of uranium tetrachloride (0.3 g, 0.8 mmol) in dry acetone (30 cm^3); to this was added an acetone solution (10 cm^3) of potassium thiocyanate (0.3 g, 3.1 mmol). The precipitated potassium chloride was filtered off, and the acetone removed from the filtrate under reduced pressure. The green residue was dissolved in the minimum of ethyl acetate and left to stand overnight whereupon green crystals of the complex were obtained. All operations were carried out in a nitrogen atmosphere; the crystals appeared stable in the air once formed, and a capillary was not found necessary for data collection.

The thorium analogue was prepared in a similar manner.

Crystallography.—For general details of procedure, *etc.* the reader is referred to the preceding paper.[1]

Crystal data. $C_{28}H_{48}N_{16}O_4P_4S_4U$, M = 1 083.1, Monoclinic, space group *P*2/*c*, (C^4_{2h}, no. 13), a = 25.06(1), b = 21.50(1), c = 22.64(1) Å, β = 117.94(3)°, U = 10 776(64) Å^3, Z = 8, D_c = 1.33 g cm^{-3}, $F(000)$ = 4 800, μ_{Mo} = 31.8 cm^{-1}, prism dimensions 0.20 × 0.17 × 0.17 mm, $2\theta_{max.}$ = 50°, N = 19 027, N_o = 7 356, R = 0.059, R' = 0.068.

Abnormal features. In spite of being extensive, the data were rather weak and the resulting residual rather high.

The thorium analogue, [$Th(NCS)_4\{OP(NMe_2)_3\}_4$], has an isomorphous *P*2/*c* unit cell with a = 25.03(1), b = 21.44(1), c = 22.58(1) Å, and β = 117.87(4)°.

Discussion

The structure determination confirms the stoicheiometry to be [$U(NCS)_4\{OP(NMe_2)_3\}_4$] (see Figures 1 and 2 and Tables 1—3).

The unit cell is of considerable interest. The *P*2/*c* cell contains eight molecules; of these, four half molecules, each in an independent molecule which lies on a two-fold axis, comprise the asymmetric unit. The structure contains strong suggestions of pseudosymmetry, clearly visible in Figure 1: a pseudo-hexagonal array is developed from the nearness of β to 120°, while a pseudo-orthorhombic array may also be seen. This is further developed in the molecular geometries. Although all molecules have broadly the same stereochemistry, the four elements comprising the asymmetric unit may be divided into two sets of closely conforming molecular geometry, namely molecules 1 and 2 and 3 and 4 (Table 2). (Atom labelling within each molecule is organised so as to maintain correspondence between apparently equivalent co-ordinating atoms.)

Within each molecule, the stereochemistry conforms most nearly to a square antiprism; each square face contains two oxygen and two nitrogen atoms, with atoms of the same type *trans* to each other. Consideration of the detailed geometries shows that, whereas the atoms of the two faces of the square antiprism in molecules 1 and 2 exhibit relatively minor deviations from those planes, the deviations in molecules 3

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* *Supplementary data available* (No. SUP 23432, 51 pp.): thermal parameters, ligand geometries, structure factor amplitudes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

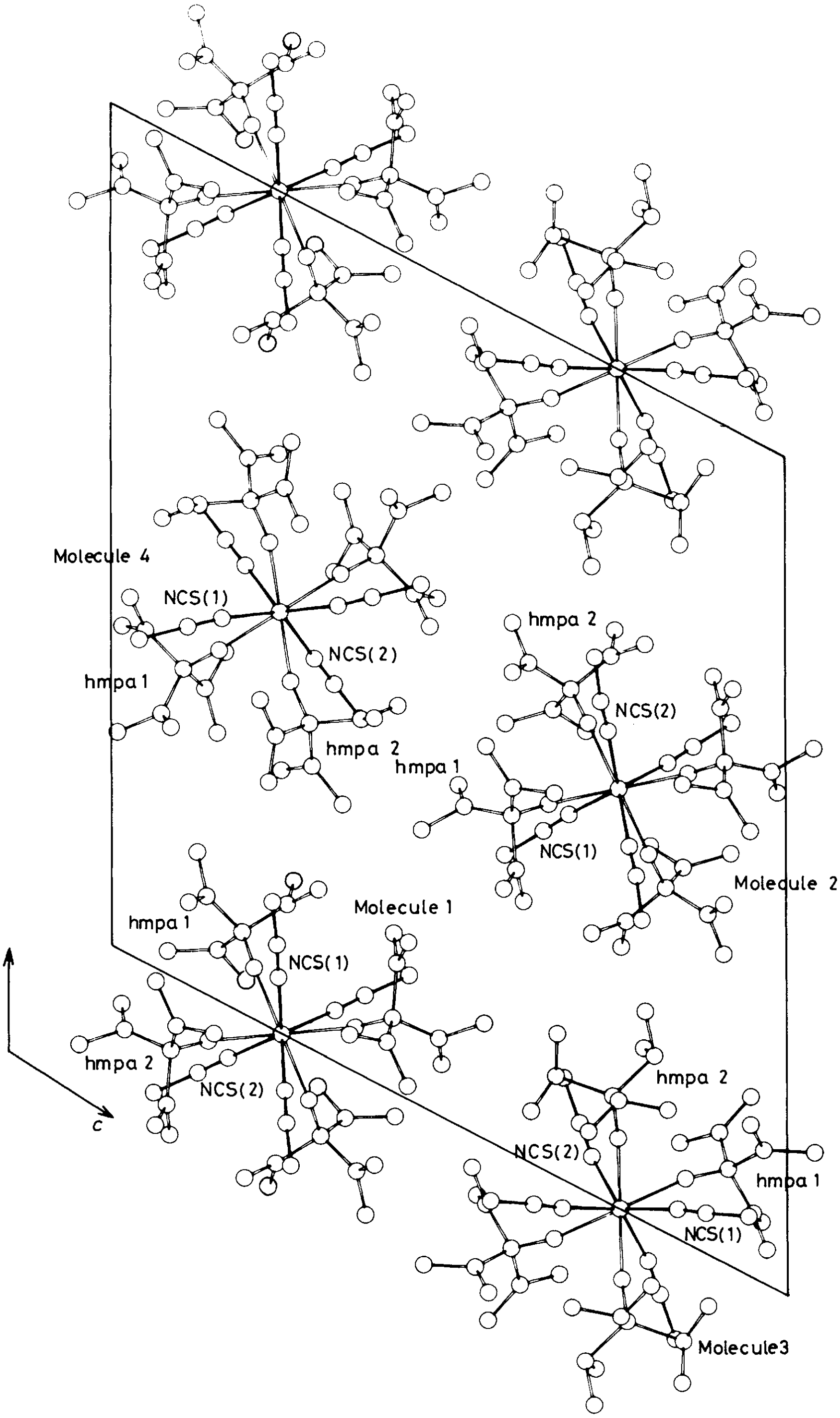
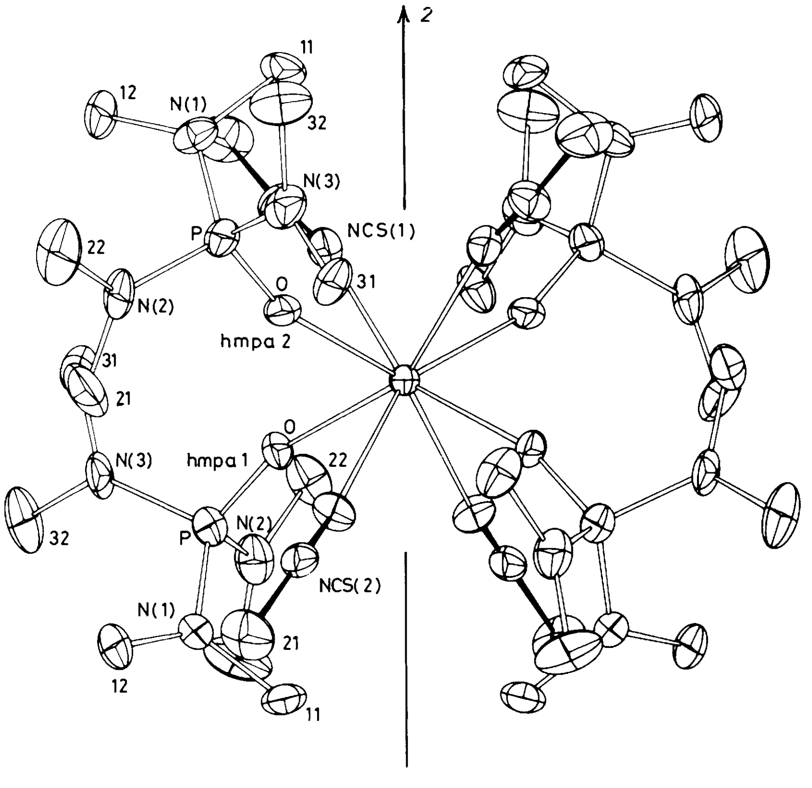


Figure 1. Unit-cell contents projected down *b*. Only the lower half of the unit cell is shown

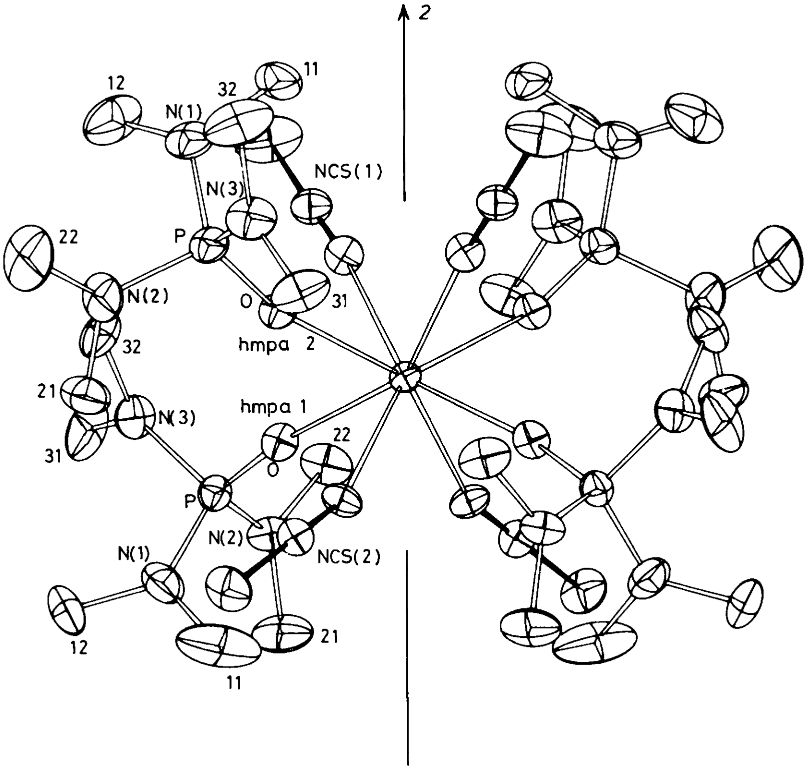
and 4 are more substantial and indicative of distortion towards the dodecahedral conformation.

Although the bond lengths appear rather variable, their precision is not high, U–O ranging between 2.28(1) and 2.36(1) Å; the range of U–O distances observed in eight-co-ordinate uranium(IV) complexes has been discussed in the preceding paper,[1] and the present values are not exceptional. No other U^{IV}–O(phosphoramide) distances appear to have been determined in eight-co-ordination but in six-co-ordinate $[UCl_4\{OP(NMe_2)_3\}_2]$ [10] U–O is shorter as might be expected, 2.23(1) Å. In $[U(NCS)_4(OPMe_3)_4]$ and $[U(NCS)_4(OPPh_3)_4]$ U–O are 2.31(2), 2.33(1) Å and 2.30—2.36(2) Å respectively; the present values are in good agreement with these.

A variety of U^{IV}–NCS distances has been determined in eight-co-ordination. In $[U(NCS)_4(OPMe_3)_4]$ [6] and $[U(NCS)_4(OPPh_3)_4]$,[7] U–N are 2.46(2), 2.47(2) Å and 2.40(4)—2.54(3) Å respectively. In the square-antiprismatic isomer of $[U(NCS)_8]^{4-}$ U^{IV}–NCS are 2.38(3), 2.46(3) Å,[11] while in the cubic isomer U–N is 2.38(1) Å.[12] In $[U(NCS)_4(H_2O)_4]$, U–N ranges from 2.38(2) to 2.42(1) Å.[8] In the present compound,



Molecule 2



Molecule 4

Figure 2. Single molecules of $[U(NCS)_4\{OP(NMe_2)_3\}_4]$ (molecules 2 and 4) projected through the centres of the square faces of the square-antiprismatic geometry. The direction of the *b* axis is also shown

Table 1. Atomic co-ordinates for the complex $[U(NCS)_4\{OP(NMe_2)_3\}_4]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Molecule 1				Molecule 2			
U	0.000 00(—)	0.354 38(4)	0.250 00(—)	U	0.500 00(—)	0.122 46(4)	0.750 00(—)
Thiocyanate 1				Thiocyanate 1			
N	0.064 3(7)	0.439 1(6)	0.245 0(7)	N	0.437 8(7)	0.039 4(6)	0.676 7(7)
C	0.102 8(8)	0.467 1(8)	0.243 8(10)	C	0.403 2(9)	0.008 8(8)	0.638 8(9)
S	0.150 8(4)	0.512 1(4)	0.237 0(5)	S	0.350 7(3)	−0.038 7(3)	0.581 3(3)
Thiocyanate 2				Thiocyanate 2			
N	−0.061 2(7)	0.273 4(7)	0.171 0(7)	N	0.563 3(7)	0.206 2(7)	0.734 9(7)
C	−0.097 5(8)	0.247 1(8)	0.126 7(9)	C	0.593 3(9)	0.234 3(8)	0.723 6(10)
S	−0.148 6(3)	0.210 2(3)	0.060 8(3)	S	0.641 7(3)	0.275 8(3)	0.715 5(4)
Hexamethylphosphoramide 1				Hexamethylphosphoramide 1			
O	0.061 5(5)	0.312 5(5)	0.209 8(5)	O	0.438 8(5)	0.165 5(5)	0.646 4(5)
P	0.096 7(3)	0.265 9(2)	0.192 3(3)	P	0.402 0(3)	0.210 5(2)	0.591 8(2)
N(1)	0.059 9(6)	0.202 3(6)	0.155 6(7)	N(1)	0.436 0(7)	0.275 6(6)	0.593 7(7)
C(11)	0.040 9(10)	0.159 0(9)	0.194 3(11)	C(11)	0.454 5(9)	0.317 3(8)	0.654 9(9)
C(12)	0.027 4(10)	0.192 6(10)	0.081 9(10)	C(12)	0.468 0(11)	0.288 9(10)	0.553 9(11)
N(2)	0.157 6(7)	0.242 8(7)	0.259 3(7)	N(2)	0.340 0(7)	0.229 4(7)	0.597 8(7)
C(21)	0.190 5(10)	0.178 7(9)	0.268 0(11)	C(21)	0.309 4(9)	0.294 5(9)	0.579 3(12)
C(22)	0.194 5(9)	0.290 9(8)	0.305 2(9)	C(22)	0.307 1(9)	0.182 0(9)	0.608 9(10)
N(3)	0.117 3(7)	0.300 3(7)	0.139 5(8)	N(3)	0.382 6(7)	0.174 9(7)	0.521 1(6)
C(31)	0.097 4(12)	0.365 9(9)	0.113 4(13)	C(31)	0.404 9(13)	0.114 9(11)	0.512 9(12)
C(32)	0.164 3(9)	0.269 3(10)	0.127 2(10)	C(32)	0.329 5(11)	0.200 5(13)	0.458 4(10)
Hexamethylphosphoramide 2				Hexamethylphosphoramide 2			
O	−0.053 8(5)	0.395 9(5)	0.141 3(5)	O	0.559 0(5)	0.078 9(5)	0.705 0(5)
P	−0.087 8(3)	0.438 6(3)	0.086 0(3)	P	0.588 5(3)	0.031 8(2)	0.680 1(3)
N(1)	−0.090 4(10)	0.404 0(11)	0.018 4(9)	N(1)	0.553 0(7)	−0.034 3(6)	0.653 8(7)
C(11)	−0.063 7(12)	0.345 2(12)	0.012 8(14)	C(11)	0.548 3(9)	−0.076 8(7)	0.703 6(10)
C(12)	−0.137 1(17)	0.434 6(17)	−0.048 6(19)	C(12)	0.507 4(10)	−0.044 5(9)	0.583 0(9)
N(2)	−0.054 8(10)	0.508 4(8)	0.094 2(10)	N(2)	0.593 0(7)	0.063 6(7)	0.617 4(8)
C(21)	−0.016 2(17)	0.518 3(17)	0.061 6(18)	C(21)	0.575 0(13)	0.130 1(10)	0.595 2(11)
C(22)	−0.040 5(12)	0.548 2(13)	0.149 1(14)	C(22)	0.634 5(10)	0.036 1(12)	0.593 6(11)
N(3)	−0.155 2(10)	0.451 8(9)	0.079 4(10)	N(3)	0.653 5(7)	0.012 2(8)	0.739 7(8)
C(31)	−0.188 6(12)	0.399 3(11)	0.084 3(13)	C(31)	0.688 5(9)	0.062 1(10)	0.789 9(10)
C(32)	−0.186 8(13)	0.511 2(12)	0.063 1(14)	C(32)	0.687 0(10)	−0.050 0(10)	0.747 3(13)
Molecule 3				Molecule 4			
U	0.000 00(—)	0.124 70(4)	0.750 00(—)	U	0.500 00(—)	0.391 60(4)	0.250 00(—)
Thiocyanate 1				Thiocyanate 1			
N	0.035 2(7)	0.203 8(7)	0.835 4(7)	N	0.456 3(6)	0.472 4(6)	0.163 8(7)
C	0.048 3(9)	0.237 8(8)	0.878 3(9)	C	0.424 8(8)	0.496 1(8)	0.113 0(8)
S	0.070 1(4)	0.287 8(3)	0.941 9(3)	S	0.380 0(3)	0.530 0(3)	0.041 8(3)
Thiocyanate 2				Thiocyanate 2			
N	0.045 0(7)	0.045 3(7)	0.708 1(8)	N	0.465 6(6)	0.311 4(6)	0.301 0(6)
C	0.077 4(9)	0.022 3(8)	0.691 1(9)	C	0.447 5(8)	0.278 9(8)	0.329 7(9)
S	0.122 1(3)	−0.010 4(3)	0.667 5(3)	S	0.423 8(4)	0.234 5(3)	0.368 3(3)
Hexamethylphosphoramide 1				Hexamethylphosphoramide 1			
O	0.076 7(5)	0.081 7(5)	0.848 2(5)	O	0.417 0(5)	0.348 2(5)	0.160 5(5)
P	0.114 3(2)	0.048 3(2)	0.911 6(2)	P	0.372 5(3)	0.305 5(2)	0.107 4(3)
N(1)	0.152 8(8)	−0.006 9(7)	0.898 7(7)	N(1)	0.305 2(7)	0.339 4(8)	0.074 0(8)
C(11)	0.117 1(13)	−0.049 3(11)	0.840 3(11)	C(11)	0.295 0(10)	0.402 4(9)	0.088 0(11)
C(12)	0.215 2(10)	−0.027 2(12)	0.946 4(14)	C(12)	0.257 3(12)	0.314 1(15)	0.008 3(13)
N(2)	0.077 0(8)	0.020 3(8)	0.949 5(8)	N(2)	0.362 4(7)	0.236 5(7)	0.139 4(7)
C(21)	0.071 7(12)	−0.047 8(9)	0.961 6(13)	C(21)	0.418 5(10)	0.198 1(9)	0.170 2(11)
C(22)	0.041 5(10)	0.062 5(10)	0.969 6(11)	C(22)	0.317 9(12)	0.221 6(11)	0.157 5(14)
N(3)	0.159 2(7)	0.099 6(7)	0.964 6(8)	N(3)	0.395 1(8)	0.288 8(7)	0.051 6(7)
C(31)	0.180 7(11)	0.158 0(10)	0.945 1(11)	C(31)	0.422 9(11)	0.337 9(9)	0.028 5(10)
C(32)	0.187 3(11)	0.090 5(14)	1.040 8(10)	C(32)	0.386 2(13)	0.226 3(11)	0.016 6(12)

Table 1 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hexamethylphosphoramide 2				Hexamethylphosphoramide 2			
O	0.083 5(5)	0.169 3(6)	0.747 4(6)	O	0.423 9(5)	0.433 1(5)	0.265 4(5)
P	0.130 2(3)	0.206 6(3)	0.739 0(3)	P	0.385 7(2)	0.465 3(2)	0.292 5(3)
N(1)	0.204 9(12)	0.184 7(12)	0.807 4(13)	N(1)	0.422 9(7)	0.491 4(6)	0.369 1(7)
C(11)	0.206 9(—)	0.110 2(—)	0.786 1(—)	C(11)	0.461 2(10)	0.446 3(8)	0.422 9(9)
C(12)	0.251 9(—)	0.211 1(—)	0.788 8(—)	C(12)	0.431 9(11)	0.555 3(9)	0.388 3(10)
N(2)	0.117 0(11)	0.179 3(11)	0.651 4(12)	N(2)	0.350 9(7)	0.524 4(7)	0.243 2(8)
C(21)	0.061 9(—)	0.221 3(—)	0.618 8(—)	C(21)	0.382 6(16)	0.565 4(10)	0.219 4(15)
C(22)	0.170 6(—)	0.229 4(—)	0.657 6(—)	C(22)	0.290 3(11)	0.539 3(12)	0.231 7(17)
N(3)	0.133 0(12)	0.277 9(13)	0.753 1(14)	N(3)	0.336 9(7)	0.415 2(7)	0.296 3(8)
C(31)	0.147 8(—)	0.300 2(—)	0.821 5(—)	C(31)	0.313 3(9)	0.361 9(9)	0.251 7(10)
C(32)	0.073 2(—)	0.310 4(—)	0.703 8(—)	C(32)	0.310 5(10)	0.423 5(11)	0.341 5(12)

Table 2. Uranium atom environments. In each matrix *r* is the uranium–ligand distance (Å). The other entries are the angles (°) subtended at U by the relevant ligand atoms. Primed atoms are generated by the intramolecular two-fold axis

	r	O(2)	N(1)	N(2)	O(1′)	O(2′)	N(1′)	N(2′)
U(1)								
O(1)	2.309(14)	84.1(4)	72.5(5)	75.0(5)	134.1(4)	113.4(4)	151.2(5)	72.9(5)
O(2)	2.357(10)		74.9(4)	69.6(4)	113.4(4)	135.5(4)	72.7(5)	152.5(5)
N(1)	2.469(16)			133.5(6)	151.2(5)	72.7(5)	84.9(5)	111.0(5)
N(2)	2.452(13)				72.9(5)	152.4(5)	111.0(5)	89.5(4)
U(2)								
O(1)	2.311(10)	88.4(4)	72.2(4)	74.8(4)	132.8(4)	110.3(4)	153.2(5)	72.0(5)
O(2)	2.348(15)		75.2(5)	70.3(5)	110.3(4)	133.0(4)	70.8(5)	154.9(5)
N(1)	2.440(13)			132.2(6)	153.2(5)	70.8(5)	85.9(4)	111.8(5)
N(2)	2.526(17)				72.0(5)	154.9(5)	111.8(5)	89.1(6)
U(3)								
O(1)	2.342(10)	80.7(4)	71.8(4)	76.8(5)	133.5(4)	119.1(5)	150.3(5)	71.5(4)
O(2)	2.329(14)		74.6(6)	72.3(5)	119.1(5)	131.4(5)	71.6(5)	150.8(4)
N(1)	2.410(15)			137.3(5)	150.3(5)	71.6(5)	90.3(5)	104.0(6)
N(2)	2.469(18)				71.4(4)	150.8(4)	104.0(6)	92.4(6)
U(4)								
O(1)	2.314(9)	79.5(4)	72.9(4)	76.0(4)	132.4(3)	119.9(4)	149.9(5)	70.9(4)
O(2)	2.276(13)		75.6(5)	72.4(5)	119.9(4)	133.9(4)	72.2(5)	148.7(4)
N(1)	2.454(12)			138.6(5)	149.9(4)	72.2(5)	89.9(4)	104.4(5)
N(2)	2.446(16)				70.9(4)	148.7(4)	104.4(5)	90.3(5)

Table 3. Least-squares planes through square-antiprismatic faces of the molecules given in the form $pX + qY + rZ = s$, where the right-hand orthogonal Ångström frame (X,Y,Z) is defined with X parallel to a and Z in the ac plane. Atom deviations, δ, and σ (defining atoms) are in Å. Atoms (1,2,3,4) defining planes a,b are, respectively, O(1,2′),N(1,2′) and O(2,1′),N(2,1′) where a prime denotes the two-fold image

	Molecule 1		Molecule 2		Molecule 3		Molecule 4	
	a	b	a	b	a	b	a	b
10^4p	8 609	8 608	8 874	8 873	−5 263	−5 263	−4 169	−4 169
10^4q	0 056	−0 055	0 113	−0 113	0 239	−0 239	−0 050	0 050
10^4r	5 088	5 089	4 610	4 610	8 499	8 499	9 090	9 089
s	1.640	−1.116	9.645	12.31	18.34	15.53	−0.942	1.793
σ	0.065	0.065	0.03	0.03	0.18	0.18	0.20	0.20
δ (atom 1)	−0.06	0.06	0.03	−0.03	−0.16	0.16	0.18	−0.18
δ (atom 2)	−0.06	0.06	0.03	−0.03	−0.16	0.16	0.18	−0.18
δ (atom 3)	0.06	−0.06	−0.03	0.03	0.16	−0.16	−0.17	0.18
δ (atom 4)	0.06	−0.05	−0.03	0.03	0.16	−0.16	−0.18	0.17
δ (U)	−1.34	1.34	1.36	−1.36	−1.34	1.34	1.33	−1.33
a/b dihedral angle	0.6		1.3		2.7		0.6	

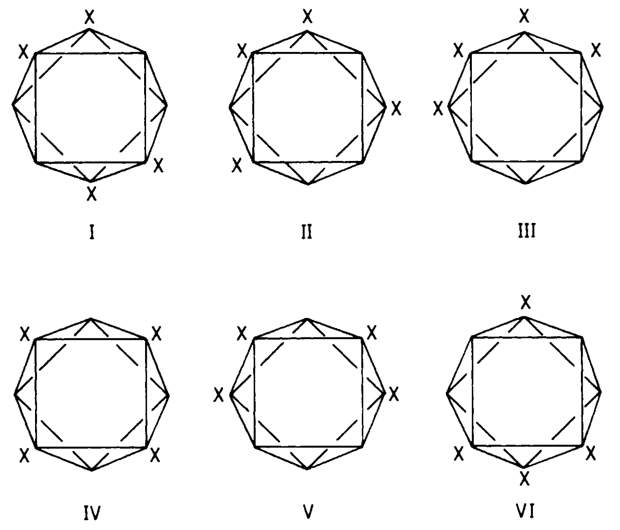


Figure 3. Square-antiprismatic isomers for [M(unidentate ligand $X)_4$(unidentate ligand $Y)_4$]

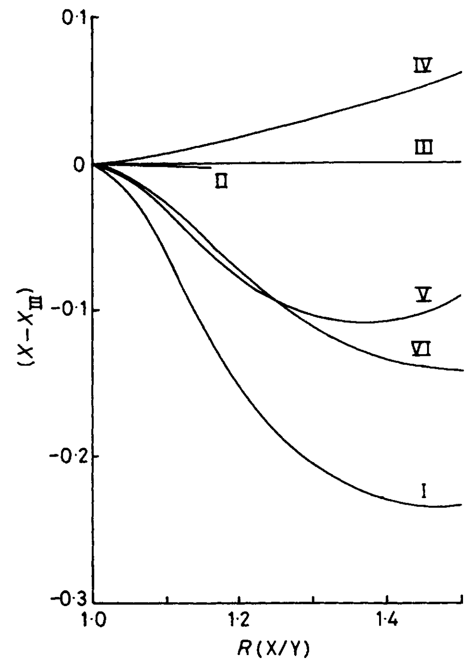


Figure 4. Repulsion-energy coefficients, *X*, of isomers I—VI relative to that of isomer III, for [M(unidentate ligand $X)_4$(unidentate ligand $Y)_4$], as a function of effective bond-length ratio *R*(X/Y)

[$U(NCS)_4\{OP(NMe_2)_3\}_4$], U–NCS range from 2.410(15) to 2.526(17) Å.

Stereochemistry of [M(unidentate ligand $X)_4$(unidentate ligand $Y)_4$].—Previous calculations[2] based on repulsion theory have established that for [M(unidentate ligand$)_8$] the square-antiprismatic structure is more stable than the dodecahedral structure, although the energy difference is not large. This is in agreement with the observation that most such compounds are square antiprismatic, although two are dodecahedral and there are one or two intermediate structures.

These calculations are now extended to complexes of the type [M(unidentate ligand $X)_4$(unidentate ligand $Y)_4$]. There are six ways in which the ligands can be arranged around a square antiprism, still retaining an element of symmetry (Figure 3). Isomers I—III have a C_2 axis as the only symmetry imposed in the calculations, V and VI have a mirror plane as the only imposed symmetry; IV contains both of these elements of symmetry, but the calculations show that only one of them needs to be imposed. Calculations have previously been reported for isomer I, with a four-fold inversion axis through the metal atom being imposed.[2] The results obtained were the same as in this work. As in [M(unidentate ligand$)_8$], all these square-antiprismatic isomers may readily distort towards dodecahedral structures.

The relative stability of each of these isomers and the range of existence as potential-energy minima are shown in Figure 4 as a function of the effective bond length ratio *R*(X/Y). These results were obtained using $n = 6$ in the energy expression; similar results were obtained for $n = 1$ and 12. It can be seen that for $R(X/Y) > 1.1$, isomer I, which at $R(X/Y) = 1.2$—1.5 is transformed into a dodecahedron with the X atoms in the sterically more hindered 'A' sites,[2] is significantly more stable.

The compound studied in this work [$U(NCS)_4(hmpa)_4$], has the isomer I structure. The experimental bond angles can be fitted against those calculated as a function of *R*(X/Y) to give $R(hmpa/NCS^-) = 1.1 \pm 0.1$. A similar procedure for [$ThCl_4(Ph_2SO)_4$][2] gives $R(Ph_2SO/Cl^-) \geqslant 1.2$, this value being typical of a mixture of halide ions and uncharged ligands co-ordinated to transition-metal ions.[2,13] It is therefore concluded that co-ordinated thiocyanate does not correspond to the short effective bond length characteristic of co-ordinated halide, $R(X^-/\text{uncharged ligand}) \approx 0.8$ [or $R(\text{uncharged ligand}/X^-) \approx 1.2$].

The observation that [$U(NCS)_4(OPMe_3)_4$][6] and [$Th(NCS)_4\{OC(NMe_2)_2\}_4$][5] are found as isomer II also implies that $R(NCS^-/\text{ligand}) \approx 1.0$, as isomer II exists as a discrete minimum and is of comparable stability to isomer I only for $R(X/Y) = 1.0$—1.1 (Figure 4). For isomer II there is little variation in bond angles with changing effective bond-length ratio and accurate values of $R(NCS^-/\text{ligand})$ cannot be obtained by this fitting procedure.

Less information can be obtained from other lanthanoid and actinoid complexes. Atomic co-ordinates have not yet been published for $[M(NCS)_4(H_2O)_4]^{x-}$ (M = Nd^{III},[4] Eu^{III},[4] or U^{IV} [8]) and accurate comparisons with calculated structures are not possible. The complex [$U(NCS)_4(OPPh_3)_4$] is significantly distorted from D_2 symmetry and it is again not possible accurately to fit calculated to experimental angular parameters.

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