

N,N-diisopropylcarboxylic Acid Amide Complexes of Thorium(IV) and Uranium(IV) N-Thiocyanates; the Crystal Structure of Tetraisothiocyanato Tetrakis(N,N-diisopropylacetamide-O)-uranium(IV)

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The complexes $M(\text{NCS})_4 \cdot xL$ ($x = 2, M = \text{U}, L = \text{Me}_3\text{CCON}(\text{Pr}^i)_2(\text{dippva})$; $x = 3, M = \text{Th}, L = \text{Me}_2\text{-CHCON}(\text{Pr}^i)_2(\text{dipiba})$ and dippva , $M = \text{U}, L = \text{EtCON}(\text{Pr}^i)_2(\text{dippa})$, dipiba and dippva ; $x = 4, M = \text{Th}, L = \text{MeCON}(\text{Pr}^i)_2(\text{dipa})$, dippa and dipiba , $M = \text{U}, L = \text{dipa}$, dippa) and the solvates $M(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$ ($M = \text{Th}, \text{U}$) have been prepared. Their i.r. and u.v.–visible ($M = \text{U}$ only) spectra are reported. The crystal and molecular structure of $\text{U}(\text{NCS})_4(\text{dipa})_4 \cdot \text{CH}_2\text{Cl}_2$ has been determined by the heavy-atom method from X-ray diffractometer data and refined by least squares to R 0.029 for 1135 independent reflections. The crystal is tetragonal, space group $P4_21c$, with $Z = 2$, $a = 15.663(4)$ and $c = 10.512(3)$ Å. The coordination geometry about the 8-coordinate uranium atom is dodecahedral with the N atoms of the NCS groups occupying the dodecahedral A sites and the 'dipa' O atoms the B sites. The bonding distances for U–O and U–N are 2.363(8), and 2.444(11) Å respectively.

Complexes of thorium(IV) and uranium(IV) N-thiocyanates with N,N-dialkylcarboxylic acid amides are commonly of the stoichiometry $M(\text{NCS})_4 \cdot 4L$ when the amide ligand is sterically undemanding ($L = \text{MeCONMe}_2$, $M = \text{Th}$ [1], U [2]; $L = \text{EtCONMe}_2$, $\text{Me}_2\text{CHCONMe}_2$, $M = \text{Th}$ [3], U [4]; $L = \text{EtCONEt}_2$, $M = \text{Th}$ [3]) whereas with the bulkier amide ligand, $\text{Me}_3\text{CCONMe}_2(\text{dmpva})$, tris complexes $M(\text{NCS})_4 \cdot 3\text{dmpva}$ ($M = \text{Th}$ [3], U (acetone solvate) [4]) are obtained.

The ligand $\text{Me}_2\text{CHCONMe}_2(\text{dmiba})$ appears to be borderline as regards bulk, for $\text{U}(\text{NCS})_4 \cdot 4\text{dmiba}$ readily loses ligand to form $[\text{U}(\text{NCS})_4(\text{dmiba})_3]$, an example of pentagonal bipyramidal 7-coordination of uranium(IV) [4], whereas with the larger thorium(IV) ion the complex $\text{Th}(\text{NCS})_4 \cdot 4\text{dmiba}$ could not be degraded to $\text{Th}(\text{NCS})_4 \cdot 3\text{dmiba}$ under similar conditions [3]. It was therefore of interest to extend the preliminary investigations [3, 4] on the effects of steric crowding in amide complexes of actinide(IV) N-thiocyanates to the more bulky N,N-diisopropylamides.

Experimental

All the complexes were prepared and handled under a dry nitrogen atmosphere in glove-boxes. Thorium [5] and uranium [6] tetrachlorides, the complexes $\text{ThCl}_4 \cdot 3L$ [7] ($L = \text{MeCON}(\text{Pr}^i)_2(\text{dipa})$, $\text{EtCON}(\text{Pr}^i)_2(\text{dippa})$, $\text{Me}_2\text{CHCON}(\text{Pr}^i)_2(\text{dipiba})$), $\text{ThCl}_4 \cdot 2\text{dippva}$ [7] ($\text{dippva} = \text{Me}_3\text{CCON}(\text{Pr}^i)_2$) and the amides used as ligands [7] were prepared by published methods. Spectroscopic measurements and the drying of solvents were carried out as described previously [3, 7, 8].

Preparations

(a) $\text{Th}(\text{NCS})_4 \cdot 4\text{dippa}$. The stoichiometric quantity of solid $\text{K}[\text{CNS}]$ (0.46 g, 4.74 mmol) and a large excess of dippa (1.2 g, 7.64 mmol) were added to a stirred solution of $\text{ThCl}_4 \cdot 3\text{dippa}$ (1 g, 1.18 mmol) in tetrahydrofuran (15 cm^3). After stirring for 3 days, the supernatant was evaporated to dryness *in vacuo*. The white residue was dissolved in dichloromethane (10 cm^3), centrifuged and the super-

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TABLE I. Analytical Results (%).^a

Complex	M ^b	C	H	N	S	Cl
Th(NCS) ₄ ·4dipa	22.9(22.4)	41.4(41.7)	6.7(6.6)	10.7(10.8)	11.8(12.4)	
Th(NCS) ₄ ·4dipa·CH ₂ Cl ₂	20.1(20.7)	39.7(39.6)	6.3(6.2)	10.1(10.0)	11.3(11.4)	5.9(6.3)
U(NCS) ₄ ·4dipa	23.0(22.8)	41.0(41.5)	6.9(6.5)	10.0(10.7)	12.2(12.3)	—
U(NCS) ₄ ·4dipa·CH ₂ Cl ₂	21.0(21.1)	39.7(39.4)	6.5(6.2)	10.0 (9.9)	11.4(11.4)	5.3(6.3)
Th(NCS) ₄ ·4dippa	21.4(21.2)	43.9(44.0)	7.0(7.0)	10.1(10.3)	11.6(11.7)	
U(NCS) ₄ ·4dippa	21.9(21.7)	43.4(43.7)	7.2(6.9)	10.4(10.2)	11.2(11.7)	
U(NCS) ₄ ·3dippa	25.2(25.3)	39.4(39.5)	6.1(6.1)	10.2(10.4)	14.0(13.6)	
Th(NCS) ₄ ·4dipiba	19.8(20.2)	46.0(46.0)	7.6(7.3)	9.8 (9.8)	11.8(11.2)	
Th(NCS) ₄ ·3dipiba	24.2(23.7)	41.5(41.8)	6.5(6.4)	10.0(10.0)	12.6(13.1)	
U(NCS) ₄ ·3dipiba	23.8(24.2)	41.8(41.5)	6.7(6.4)	9.9(10.0)	12.7(13.0)	
Th(NCS) ₄ ·3dippva	22.7(22.8)	41.5(43.6)	6.5(6.8)	9.4 (9.6)	12.7(12.6)	
U(NCS) ₄ ·3dippva	21.4(23.2)	43.4(43.3)	7.0(6.7)	10.0 (9.6)	11.9(12.5)	
U(NCS) ₄ ·2dippva	27.6(28.3)	36.1(37.1)	5.5(5.5)	8.8(10.0)	14.1(15.2)	

^aCalculated values are given in parentheses. ^bM = Th or U.

nant was evaporated to dryness *in vacuo*. The white solid product was washed with n-pentane (3 × 3 cm³) and vacuum dried (8 h). Yield, 81%.

(b) U(NCS)₄·3dipiba was prepared from UCl₄ as in (a) except that the final product was an oil, which solidified on trituration with n-pentane. Yield, *ca.* 68%.

Th(NCS)₄·4dipiba (from ThCl₄·3dipiba; yield, 69%); Th(NCS)₄·3dippva (from ThCl₄·2dippva; yield, 36%), U(NCS)₄·3dippva (from UCl₄; yield, *ca.* 40%) and U(NCS)₄·4dippa (from UCl₄; yield, *ca.* 55%) were prepared in the same way.

(c) Th(NCS)₄·4dipa was prepared from ThCl₄·3dipa as in (a) except that the oily residue left on vacuum evaporation of the reaction supernatant was dissolved in MeCO₂Et (6 cm³) and filtered. The very small amount of solid which separated on standing overnight was discarded and the supernatant was evaporated *in vacuo* to 2–3 cm³, when colourless crystals of the product separated. After standing for 1 h to complete crystallisation, the supernatant was decanted and the crystals were washed with n-pentane (3 × 2 cm³), then vacuum dried. Yield, *ca.* 50%.

(d) U(NCS)₄·4dipa·CH₂Cl₂ was prepared from UCl₄ as in (a) except that the product was recrystallised by dissolution in dichloromethane (5 cm³), followed by addition of n-pentane until the solution became cloudy. The crystals of the complex which separated on standing were washed with n-pentane (3 × 3 cm³) and vacuum dried (5 h). Yield, *ca.* 75%. Th(NCS)₄·4dipa·CH₂Cl₂ was prepared from ThCl₄·3dipa in the same way, except that the product crystallised from dichloromethane on standing without addition of n-pentane. Yield, *ca.* 55%.

(e) U(NCS)₄·4dipa was obtained by heating U(NCS)₄·4dipa·CH₂Cl₂ at 50 °C/10⁻² Torr for 8 h.

(f) U(NCS)₄·3dippa was prepared by dissolving U(NCS)₄·4dippa (0.4 g, 0.36 mmol) in dichloromethane (5 cm³), followed by addition of n-pentane until the solution became cloudy. Dark green crystals of the complex separated on standing (10 d). These were washed with n-pentane (3 × 3 cm³) and vacuum dried (5 h). Yield, *ca.* 30%. Th(NCS)₄·3dipiba was prepared from Th(NCS)₄·4dipiba in the same way. Yield, *ca.* 59%.

(g) U(NCS)₄·2dippva was obtained by dissolving U(NCS)₄·3dippva (0.5 g, 0.49 mmol) in dichloromethane (5 cm³). After centrifugation, the supernatant was vacuum evaporated to an oily residue, which solidified on trituration with n-pentane. The dissolution/evaporation/trituration process was repeated three times to yield the pale green complex, which was washed with n-pentane (2 × 3 cm³) and vacuum dried (8 h). Yield, *ca.* 40%.

The analytical results are given in Table I.

Single Crystal Data Collection

Green prismatic crystals of U(NCS)₄(dipa)₄·CH₂Cl₂ were obtained by recrystallization 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. The crystal was mounted in a random orientation on a four-circle Philips PW1100 automated diffractometer with graphite monochromated MoK_α radiation (λ = 0.7107 Å). The unit cell was determined on the basis of 25 strong reflections

TABLE II. Fractional Coordinates ($\times 10^4$) with e.s.d.s in Parentheses.

	x/a	y/b	z/c	K
U	0	0	0	0.25
Cl(1)	-929(6)	7(9)	4620(9)	0.5
N(1)	26(8)	1484(4)	-718(6)	
C(1)	75(8)	2109(5)	-1256(9)	
S(1)	89(4)	3003(2)	-2036(4)	
N(2)	-2206(4)	468(5)	-2511(7)	
O(1)	-922(3)	22(7)	-1779(5)	
C(2)	-1687(6)	-139(6)	-2156(8)	
C(3)	-1931(8)	-1072(7)	-2186(16)	
C(4)	-3117(7)	359(7)	-2839(12)	
C(5)	-3660(6)	-17(16)	-1762(11)	
C(6)	-3264(8)	-105(16)	-4125(11)	
C(7)	-1894(7)	1376(7)	-2496(14)	
C(8)	-2278(11)	1823(9)	-1326(13)	
C(9)	-2056(10)	1854(9)	-3725(14)	
C(10)	0	0	5000	0.25

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 $8 \leq \theta \leq 15^\circ$ were used.

Crystal Data

$C_{37}H_{70}Cl_2O_4N_8S_4U$, $M = 1128.2$, tetragonal, space group $P4_21c$, $a = 15.663(4)$, $c = 10.512(3)$; $D_c = 1.38 \text{ Mg m}^{-3}$, $Z = 2$, $F(000) = 1140$, $\mu(\text{MoK}\alpha) = 32.8 \text{ cm}^{-1}$.

Integrated intensities for hkl reflections with h k and $l \geq 0$ and $3 \leq \theta \leq 25^\circ$ were measured using the $\theta-2\theta$ scan method with a scan speed of $1.80^\circ \text{ min}^{-1}$,

scan width of 1.20° and two background counts of 10 s at each end of the scan.

The intensities of 3508 reflections were recorded which merged (internal $R = 0.02$) gave 1748 unique reflections and 1135 were considered observed having $I \geq 3\sigma(I)$; two reflections 0 2 4 and 5 4 3 monitored at regular intervals showed only the deviations from their mean intensities predicted by counting statistics. Integrated intensities were corrected for Lorentz and polarization effects and for absorption following the published method [9].

Structure Determination

The structure was solved by conventional Patterson, Fourier and least-squares refinement techniques. Published scattering factors were used for neutral U, S, O, N and carbon atoms [10]; the anomalous terms for uranium were taken from published data [11].

The uranium atom lies on a crystallographic $\bar{4}$ axis and, consequently, this is the symmetry imposed on the $U(\text{NCS})_4(\text{dipa})_4$ molecule, the asymmetric unit being formed by a quarter of an uranium atom, one NCS and one depa ligands.

With phasing based only on the uranium atoms the discrepancy factor, calculated as $\Sigma(|F_o| - |F_c|)/\Sigma F_o$, was 0.27. A few cycles of unit weight and individual isotropic refinement of 14 non-hydrogen atoms decreased R to 0.09.

Anisotropic thermal parameters were applied to all non hydrogen atoms. A difference Fourier map calculated at this point showed the position of the CH_2Cl_2 molecule with the carbon atom lying on a 4 crystallographic axis. This implies a statistical disposition of the chlorine and hydrogen atoms. The chlorine (in a general position) was introduced with an occupancy factor of 0.5 as a consequence of the two

TABLE III. Anisotropic and Isotropic Thermal Parameters ($\times 10^3$) with e.s.d.s in Parentheses.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	24.7(2)	24.7(2)	36.1(2)	—	—	—
N(1)	58(4)	31(3)	49(4)	50(3)	-13(7)	-1(7)
C(1)	35(5)	38(4)	54(4)	9(4)	5(6)	-9(5)
S(1)	97(3)	59(2)	115(3)	47(2)	-10(4)	-12(3)
N(2)	36(4)	42(4)	40(4)	-5(3)	-11(4)	9(3)
O(1)	35(3)	43(3)	45(3)	-4(6)	-9(2)	-2(5)
C(2)	48(5)	36(7)	37(4)	-4(4)	-14(4)	6(4)
C(3)	72(8)	34(6)	94(11)	0(7)	-25(8)	-17(6)
C(4)	38(6)	77(7)	67(7)	0(6)	-16(6)	0(5)
C(5)	39(5)	107(9)	107(9)	30(18)	2(5)	-7(9)
C(6)	77(8)	113(14)	76(7)	-10(11)	-36(6)	-12(11)
C(7)	54(7)	38(6)	60(7)	6(6)	-14(6)	8(4)
C(8)	112(11)	60(8)	61(7)	-18(7)	11(8)	-5(7)
C(9)	97(10)	64(8)	69(7)	20(6)	-1(7)	10(8)
C(10)	264(36)					
Cl(1)	123(3)					

possible alternative positions which mirrored each other. Carbon and chlorine of the CH_2Cl_2 molecule were refined isotropically.

Hydrogen atoms were not observed and not included in the refinement. In the final stage of the refinement the weighting scheme used was $w = 2.7842/\sigma^2(F_o) + 0.000611(F_o)^2$ 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 0.029 for 1135 data where $I \geq 3\sigma(I)$. $R_w (= \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ was 0.030.

Table II contains final atomic positional parameters for all non hydrogen atoms with their e.s.d.s derived from the last cycle of least-squares and Table III anisotropic and isotropic thermal parameters. The listing of the final observed and calculated structure factor amplitudes are available as supplementary material.

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 [12].

Results and Discussion

The Complexes

The solid complexes $\text{M}(\text{NCS})_4 \cdot 4\text{L}$ ($\text{M} = \text{Th}$, $\text{L} = \text{MeCON}(\text{Pr}^i)_2(\text{dipa})$, $\text{EtCON}(\text{Pr}^i)_2(\text{dippa})$, $\text{Me}_2\text{CHCON}(\text{Pr}^i)_2(\text{dipiba})$; $\text{M} = \text{U}$, $\text{L} = \text{dippa}$) and $\text{M}(\text{NCS})_4 \cdot 3\text{L}$ ($\text{M} = \text{Th}$, $\text{L} = \text{Me}_3\text{CCON}(\text{Pr}^i)_2(\text{dippva})$; $\text{M} = \text{U}$, $\text{L} = \text{dipiba}$, dippva) were obtained by addition of an excess of the ligand in tetrahydrofuran solution to the solution resulting from the reaction of $\text{ThCl}_4 \cdot 3\text{L}$ or UCl_4 in the same solvent with the stoichiometric quantity of potassium thiocyanate, followed by evaporation of the supernatant to dryness under vacuum. In most cases the residue was an oil which

was dissolved in ethyl acetate and left to crystallise after evaporation to small volume ($\text{Th}(\text{NCS})_4 \cdot 4\text{dipa}$) or which solidified on trituration with *n*-pentane ($\text{Th}(\text{NCS})_4 \cdot 4\text{dipiba}$, $\text{Th}(\text{NCS})_4 \cdot 3\text{dippva}$, $\text{U}(\text{NCS})_4 \cdot 4\text{dippa}$, $\text{U}(\text{NCS})_4 \cdot 3\text{L}$ with $\text{L} = \text{dipiba}$, dippva). $\text{Th}(\text{NCS})_4 \cdot 4\text{dippa}$, which remained as a solid on evaporation of the reaction supernatant, was purified by dissolution in dichloromethane and subsequent vacuum evaporation. The solvates $\text{M}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$ ($\text{M} = \text{Th}$, U) resulted from crystallisation of the crude products from dichloromethane. The presence of the solvent molecule was confirmed by ^1H -nmr spectroscopy, using d^6 -acetone ($\text{Th}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$; shifts downfield of TMS, 1.38 ppm (doublet), 48H of $-\text{CH}(\text{CH}_3)_2$; 2.43 ppm (singlet), 12H of CH_3CO ; 4.08 ppm (multiplet), 8H of $\text{CH}(\text{CH}_3)_2$; 5.52 ppm (singlet), 2H of CH_2Cl_2). In the ^1H -nmr spectrum of $\text{U}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$ the resonance due to the $-\text{CH}(\text{CH}_3)_2$ protons had split into two broad singlets (shifts, 0.78 and 1.91 ppm, both 24H), and the shifts for CH_3CO (5.69 ppm, broad singlet, 12H) and $-\text{CH}(\text{CH}_3)_2$ (5.25 ppm, 8H, broad multiplet) were noticeably greater than those in the spectrum of the thorium analogue, presumably due to pseudocontact effects arising in the case of the paramagnetic uranium(IV) compound. The shift for CH_2Cl_2 (5.48 ppm, 2H, singlet) was almost identical to that observed for the thorium compound. The infrared spectra of the two dichloromethane solvates were almost identical to those of the parent compounds (Table IV) apart from an additional feature at about 740 cm^{-1} which may be due to $\nu(\text{CCl})$ of CH_2Cl_2 . $\text{U}(\text{NCS})_4 \cdot 4\text{dipa}$ was obtained by heating the solvate at $50^\circ\text{C}/10^{-2} \text{ Torr}$. $\text{Th}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$ appears to be more stable with respect to decomposition than the unsolvated product, crystals of which become pale yellow after 14 days.

The i.r. spectra (Table IV) of the complexes as solid mulls indicate that all of the ligand is strongly

TABLE IV. The Infrared Spectra of the Complexes (cm^{-1}), (a) Nujol mull, (b) CH_2Cl_2 solution, (c) thf solution.

Complex		$\nu(\text{CO})$	$\Delta\nu(\text{CO})$	$\nu(\text{CN})$
$\text{Th}(\text{NCS})_4 \cdot 4\text{dipa}$	a	1548(s)	85	2018(s)
	b	1553(s), 1630(vw,sh)	80,3	2035(s)
	c	1547(s), 1633(m)	86,0	2020(s)
$\text{Th}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$	a	1545(s)	88	2032(s)
	b	1549(s), 1621(vw,sh)	84,12	2030(s)
	c	1544(s), 1632(m)	89,1	2012(s)
$\text{U}(\text{NCS})_4 \cdot 4\text{dipa}$	a	1546(s)	87	2025(s)
	b	1555(s), 1626(vw)	78,7	2020(s)
	c	1550(s), 1637(m)	83, (-4)	2000(s)
$\text{U}(\text{NCS})_4 \cdot 4\text{dipa} \cdot \text{CH}_2\text{Cl}_2$	a	1543(s)	90	2033(s)
	b	1551(s), 1623(vw,sh)	82,10	2020(s)
	c	1554(s), 1632(m)	79,1	2010(s)

(continued on facing page)

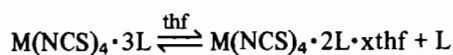
TABLE IV. (continued)

Complex		$\nu(\text{CO})$	$\Delta\nu(\text{CO})$	$\nu(\text{CN})$
Th(NCS) ₄ ·4dippa	a	1539(s)	95	2034(s)
	b	1537(s), 1622(w,sh)	97,12	2022(s)
	c	1530(s), 1628(m)	104,6	2008(s)
U(NCS) ₄ ·4dippa	a	1536(s)	98	2036(s)
	b	1542(s), 1628(w)	92,6	2008(s), 2043(s,sh)
	c	1539(s), 1634(s)	95,0	2000(s)
U(NCS) ₄ ·3dippa	a	1541(s)	93	2012(s), 2050(s,sh)
	b	1550(s)	84	2005(s)
	c	1536(s), 1632(m)	98,2	2000(s)
Th(NCS) ₄ ·4dipiba	a	1534(s)	97	2039(s)
	b	1532(s), 1620(m)	99,11	2015(s)
	c	1533(s), 1632(s)	98, (-1)	2010(s)
Th(NCS) ₄ ·3dipiba	a	1538(s)	93	2002(shsh), 2018(s), 2042(s,sh)
	b	1541(s)	90	2010(s), 2044(s,sh)
	c	1537(m), 1632(s)	94, (-1)	2005(s)
U(NCS) ₄ ·3dipiba	a	1536(s)	95	2018(s), 2052(s,sh)
	b	1534(s)	97	2002(s)
	c	1535(s), 1634(s)	96, (-3)	1990(s)
Th(NCS) ₄ ·3dippva	a	1531(s)	99	2008(s), 2032(s)
	b	1530(s), 1621(w)	100,9	2015(s)
	c	1629(s)	1	2010(s)
U(NCS) ₄ ·3dippva	a	1529(s), 1594(m)	101,36	2010(s)
	b	1533(m), 1625(m)	98,5	2000(s)
	c	1631(s)	(-1)	2005(s)
U(NCS) ₄ ·2dippva	a	1535(s)	95	1954(s), 1980(s), 2020(s,sh)
	b	1528(s), 1615(vw)	102,15	1980(s), 2005(s,sh)
	c	1628(s)	2	2022(s)

s = strong; m = medium; w = weak; v = very; sh = shoulder.

bonded to the metal atom except in the case of U(NCS)₄·3dippva, the i.r. spectrum of which shows that both weakly and strongly bonded ligand is present. The i.r. spectra of M(NCS)₄·4L (M = Th, U; L = dipa, dippa; M = Th, L = dipiba) and U(NCS)₄·xdippva (x = 2 or 3) in dichloromethane and thf solutions all show the presence of both strongly bonded and free ligand, suggesting that the environment of the metal atom in these complexes is overcrowded. Dissolution of U(NCS)₄·4dippa and Th(NCS)₄·4dipiba in dichloromethane, followed by addition of n-pentane until the solution became cloudy, led to the crystallisation of the corresponding tris complexes. U(NCS)₄·2dippva was obtained from the tris complex by dissolution in dichloromethane and vacuum evaporation of the supernatant to an oily residue which solidified on trituration with n-pentane, the complete cycle being repeated three times. The ready degradation of Th(NCS)₄·4dipiba and U(NCS)₄·4dippa to the tris complexes, and of U(NCS)₄·3dippva to the bis compound, an unusual stoichiometry for a uranium(IV) N-thiocyanate complex, certainly indicates overcrowding about the metal atom arising from the secondary effects of the branched chain substituents in the ligands.

Although the dichloromethane solution i.r. spectra of the tris complexes, M(NCS)₄·3L (M = Th, U, L = dipiba; M = U, L = dippa) do not show any sign of ligand dissociation, their spectra in thf show that free ligand is present, presumably resulting from displacement of the ligand by the solvent:



In the cases of the three dippva complexes, all of the ligand appears to be displaced in thf solution (Table IV).

The C–N stretching mode of the thiocyanate group appears at 2036 to 2000 cm⁻¹ in the i.r. spectra of all of the complexes; the relatively high intensity of this feature in every case suggests that the thiocyanate groups are N-bonded [13, 14], although the observed frequency of this mode is on the borderline for distinguishing between S- and N-bonding in thiocyanates. The frequency of the C–S feature in the i.r. spectra of N- and S-bonded thiocyanates is usually between 760 and 880 cm⁻¹, and at 700 cm⁻¹ respectively [16, 17], but this feature is usually weak and is often difficult to identify in the presence of organic ligands [15], as was found in this work.

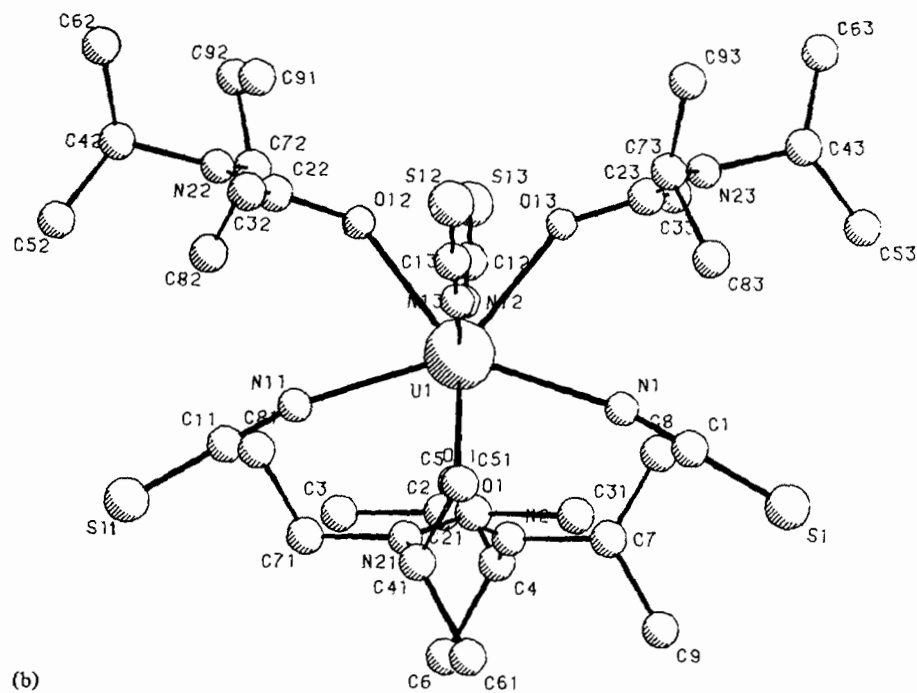
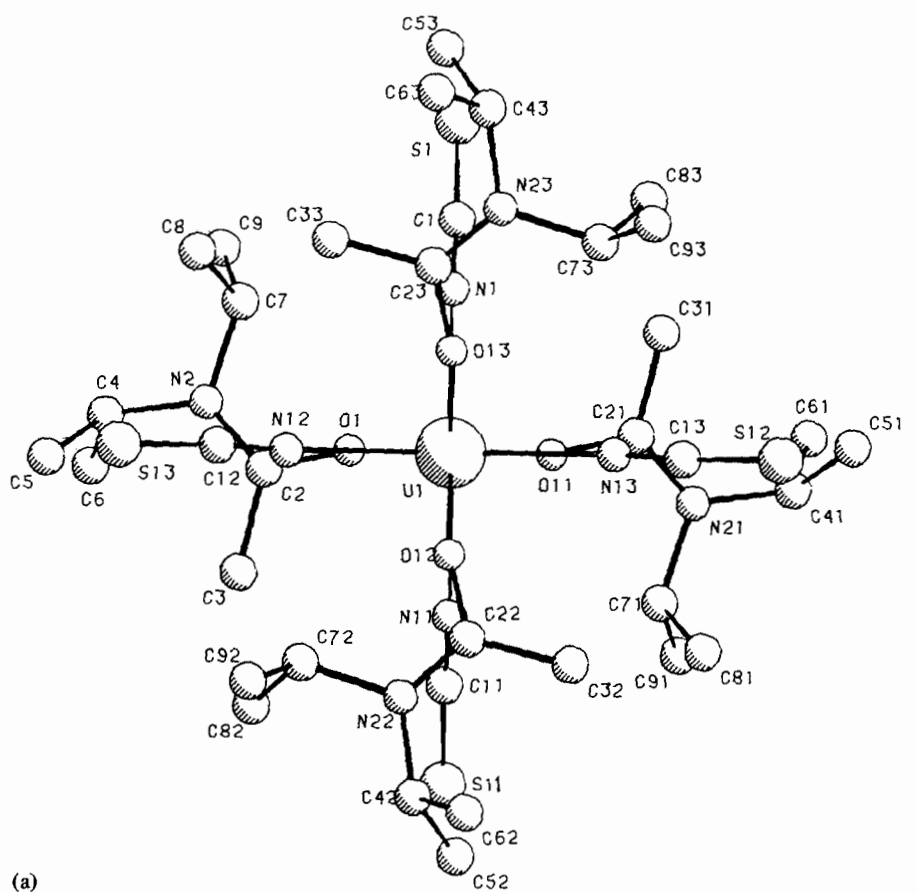


Fig. 1. Two views of the molecular structure of $U(NCS)_4(dipa)_4$, one normal to the $\bar{4}$ axis (a) and one (b) down a showing the U dodecahedral coordination polyhedron (the second figure in the atom numbering scheme indicates the symmetry relations: $1 -x, -y, z; 2 -y, x, -z; 3 y, -x, -z$).

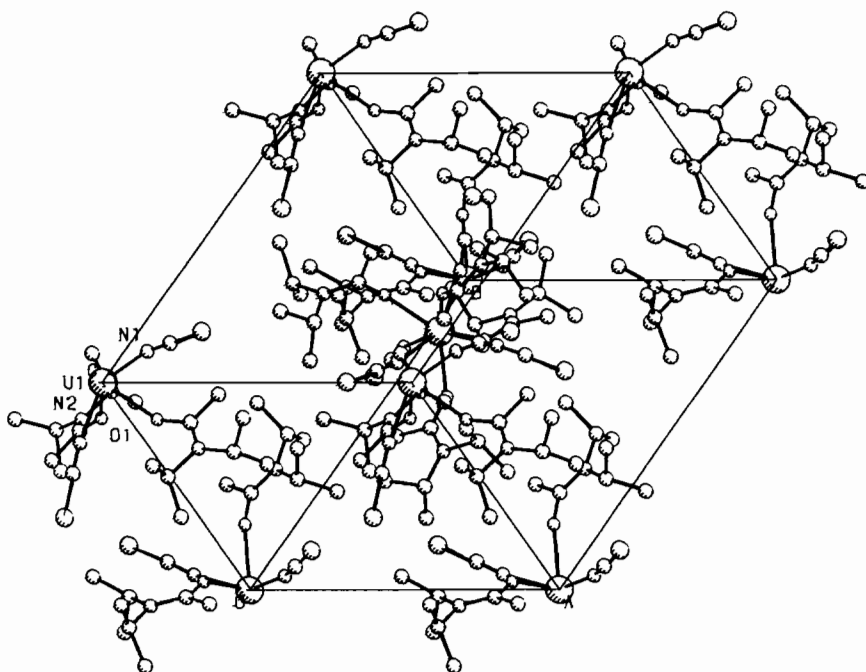
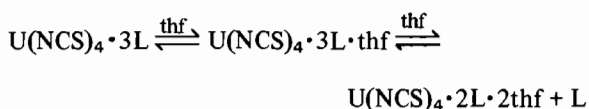


Fig. 2. Perspective view of the unit cell content (the CH_2Cl_2 molecules are omitted for the sake of clarity).

The solid reflectance and dichloromethane solution u.v.-visible spectra of $\text{U}(\text{NCS})_4 \cdot 2\text{dippva}$ are very similar and are typical of 6-coordinate uranium(IV), with the strongest feature appearing at 1990 nm (solid reflectance) and 2005 nm (solution). The solid reflectance spectra of all of the complexes $\text{U}(\text{NCS})_4 \cdot 3\text{L}$ are almost identical to their dichloromethane solution spectra and to the spectrum of $[\text{U}(\text{NCS})_4(\text{dmiba})_3]$ [4], with strong bands in the region 1085 to 1110 nm, and medium bands in the ranges 1412 to 1441 and 1580 to 1622 nm. The dichloromethane solution spectra of the complexes $\text{U}(\text{NCS})_4 \cdot 4\text{L}$ also indicate dissociation to the tris complex, and their solution i.r. spectra (see above) indicate the presence of free ligand but attempts to prepare $\text{U}(\text{NCS})_4 \cdot 3\text{dipa}$ and $\text{Th}(\text{NCS})_4 \cdot 3\text{dippa}$ from the tetrakis complexes by repeated recrystallisation were unsuccessful.

The solid reflectance spectra of the complexes $\text{U}(\text{NCS})_4 \cdot 4\text{L}$ were characteristic of 8-coordinate uranium(IV) with strong-bands around 1080 to 1095 and 1155 to 1170 nm. The spectra of all of the uranium(IV) complexes in thf solution were very similar to each other and to the reflectance spectra of the complexes $\text{U}(\text{NCS})_4 \cdot 4\text{L}$, suggesting that solvation and dissociation occur:



and



In all cases the i.r. spectra of thf solutions of the complexes exhibited features due to the presence of the free ligand L.

Crystal Structure Results

Two perspective views of the molecule, one along the $\bar{4}$ axis and the second down a , which include the atom numbering scheme, are presented in Fig. 1 and the crystal packing is shown in Fig. 2. Selected bond distances and angles are listed in Table V.

The structure consists of discrete $\text{U}(\text{NCS})_4(\text{dipa})_4$ molecules and disordered CH_2Cl_2 molecules separated by Van der Waals contacts. The central uranium atom lies on the $\bar{4}$ crystallographic axis and the molecular symmetry is constrained to be 4. The U-coordination polyhedron is a regular dodecahedron with the dipa ligands in B sites and the isothiocyanate ligands in the A sites.

The U–N bond distance 2.444(11) Å is longer with respect to the U–O bond distance of 2.363(8) and theory would predict that in a dodecahedral structure N would occupy the A sites and O the B sites as a consequence of the longer U–N distance which in principle should prefer the more crowded positions of the polyhedron *i.e.* the A sites.

The shape parameters predicted for the most favourable polyhedron [18] are $\theta_A = 35.2$ and $\theta_B = 73.5^\circ$ where θ_A is the angle between the M–A bond vector and the $\bar{4}$ axis of the polyhedron and θ_B ,

TABLE V. Bond Lengths (Å) and Angles (°) with e.s.d.s in Parentheses.

(a) Lengths					
U–N(1)	2.444(11)	N(1)–C(1)	1.13(2)	C(1)–S(1)	1.62
U–O(1)	2.363(8)	O(1)–C(2)	1.29(2)	N(2)–C(4)	1.48(2)
N(2)–C(2)	1.30(2)	N(2)–C(7)	1.50(2)	C(7)–C(9)	1.52(3)
C(2)–C(3)	1.51(2)	C(7)–C(8)	1.54(3)	C(10)–Cl(1)	1.51(2)
C(4)–C(5)	1.53(3)	C(4)–C(6)	1.55(3)		
(b) Angles					
N(1)–U–N(11)	144.0(6)			O(1)–O–O(11)	75.4(4)
U–O(1)–C(2)	168(1)			N(1)–C(1)–S(1)	177(2)
U–O(1)–C(2)	144(1)			O(1)–C(2)–C(3)	116(2)
O(1)–C(2)–N(2)	122(2)			N(2)–C(2)–C(3)	123(2)
C(2)–N(2)–C(4)	126(1)			C(2)–N(2)–C(7)	119(1)
C(4)–N(2)–C(7)	115(1)			N(2)–C(4)–C(5)	114(2)
N(2)–C(4)–C(6)	114(2)			C(5)–C(4)–C(6)	112(2)
N(2)–C(7)–C(8)	108(2)			N(2)–C(7)–C(9)	114(2)
U–N(1)–C(1)	168(1)			C(8)–C(7)–C(9)	113(2)

the angle between the M–B bond vector and the $\bar{4}$ axis with a ratio of the lengths M–A/M–B = 1.03. Here the experimental values are respectively $\theta_A = 37.7^\circ$ and $\theta_B = 72.0^\circ$ very close to the theoretical ones, while the M–A/M–B ratio is 0.967, not in agreement with theory.

Exceptions to this rule are rather frequent; in some cases as in $\text{Th}(\text{NCS})_4(\text{tmu})_4$ [19], oxygen and nitrogen donor atoms are equally distributed between the A and B sites in spite of the significant difference between Th–O (2.36(1) Å) and Th–N (2.51(1) Å) bond lengths, while in $\text{ThCl}_4(\text{diphenyl sulphoxide})_4$ [20], as in the present case, the longer Th–Cl distances (2.758 Å) are in the B sites and the shorter Th–O (2.46 Å) in the A sites.

In addition the compounds $\text{U}(\text{NCS})_4(\text{tmpo})_4$ [21] and $\text{U}(\text{NCS})_4(\text{tppo})_4$ [22] adopt a square antiprismatic geometry with significant differences between the U–N and U–O bond lengths.

At this point it is important to reconsider the theory dealing with the predictions of the coordination polyhedra in the solid state as crystal packing forces can exert an unpredictable influence on the geometry adopted by a particular compound.

The U–N bond distance, 2.444(11) Å, is close to the values reported for other 8-coordinated isothiocyanato uranium(IV) complexes ($\text{Cs}_4\text{U}(\text{NCS})_8$) [23] (2.42 Å) and $\text{U}(\text{NCS})_4(\text{tmpo})_4$ [21] (2.465 Å) but is somewhat longer with respect to the average of 2.38 Å found in $\text{U}(\text{NCS})_4(\text{dmiba})_3$ [4] which presents a pentagonal bipyramidal geometry; also the U–O bond distance 2.363(8) Å is longer with respect to the average of 2.30 Å found in $\text{U}(\text{NCS})_4(\text{dmiba})_3$ [4].

The bond lengths and bond angles in the N-thiocyanato groups are as usual and the dipa ligand has the expected geometry, bond lengths and angles.

It is worthwhile to note that the less bulky dipa ligand allows the coordination of four neutral ligands around the uranium atom while with the dmiba ligand a pentagonal bipyramidal compound $\text{U}(\text{NCS})_4(\text{dmiba})_3$ is obtained with the coordination of only three neutral ligands (two additional methyl groups attached to the carbon bound to the CO group in the dmiba ligand cause more steric hindrance in the uranium coordination sphere than the additional C(5)H₃ C(6)H₃ C(8)H₃ C(9)H₃ methyl groups present in the dipa ligand).

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