Some Substituted Urea Complexes of Thorium(IV) and Uranium(IV) *N*-Thiocyanates

Abdul Ghany M. Al-Daher and Kenneth W. Bagnall*
Chemistry Department, The University of Manchester, Manchester M13 9PL

The complexes $M(NCS)_4 \cdot xL$ [$x = 4$, M = Th or U, L = $(MePhN)_2CO$; M = Th, L = $(Me_2N)(Et_2N)CO$ or $(Et_2N)_2CO$; M = U, L = $(Me_2N)_2CO$; $x = 3$, M = U, L = $(Me_2N)_2CO$, $(Me_2N)(Et_2N)CO$, $(Et_2N)_2CO$, or $(MePhN)_2CO$] and $U(NCS)_4 \cdot 2(MePhN)_2CO \cdot 2MeCN$ have been prepared. Their i.r. and near i.r.–visible spectra [uranium(IV) complexes only] are reported and their stoicheiometries are discussed briefly in terms of a cone-packing model.

The only recorded substituted urea complex of thorium(IV) or uranium(IV) *N*-thiocyanate appears to be $[Th(NCS)_4(tmu)_4]$ [tmu = $(Me_2N)_2CO$], in which the co-ordination polyhedron is a slightly distorted dodecahedron.[1] It was therefore of interest to prepare the analogous uranium(IV) complex, as well as complexes of both *N*-thiocyanates with the bulky substituted ureas $(Me_2N)(Et_2N)CO$ (dedmu), $(MePhN)_2CO$ (dmdpu), and $(Et_2N)_2CO$ (teu), and to correlate the stoicheiometries of the complexes so obtained by applying the cone-angle approach to steric crowding described in recent papers.[2,3]

Results and Discussion

Preparation of the Complexes and Steric Considerations.—The complexes were prepared by treating the metal tetrachloride [$U(NCS)_4 \cdot 4tmu$, $U(NCS)_4 \cdot 4dmdpu$, or $U(NCS)_4 \cdot 3dedmu$] or the corresponding complex of the tetrachloride [$Th(NCS)_4 \cdot 4dmdpu$ or $Th(NCS)_4 \cdot 4dedmu$] with the stoicheiometric amount of potassium thiocyanate and an excess of the ligand in tetrahydrofuran (thf), followed by vacuum evaporation of the supernatant to dryness and either crystallisation from a mixture of dichloromethane and n-pentane or grinding the residue under n-pentane [$Th(NCS)_4 \cdot 4dedmu$ or $U(NCS)_4 \cdot 3dedmu$]. The complex $U(NCS)_4 \cdot 3dedmu$ was also crystallised from a mixture of ethyl acetate and n-pentane. The complexes $Th(NCS)_4 \cdot 4teu$ and $U(NCS)_4 \cdot 3teu$ were prepared in the same way from the tetrachlorides, with the final crystallisation from a mixture of toluene and n-pentane [$Th(NCS)_4 \cdot 4teu$] or by grinding under 2-methylbutane [$U(NCS)_4 \cdot 3teu$]. In the last two preparations the stoicheiometric amount of teu was used, for the products could not be induced to crystallise when an excess of the ligand was present. The remaining complexes were prepared from uranium tetrachloride using methyl cyanide [$U(NCS)_4 \cdot 3tmu$ or $U(NCS)_4 \cdot 2dmdpu \cdot 2MeCN$] or dichloromethane [$U(NCS)_4 \cdot 3dmdpu$] as solvent in place of thf: the reaction was very slow in the latter case because of the low solubility of the reactants in dichloromethane. These three complexes were finally crystallised from a mixture of dichloromethane and n-pentane.

All of the complexes were soluble in thf, dichloromethane, and ethyl acetate, but less soluble in toluene and insoluble in n-pentane or 2-methylbutane. The tris complexes were more hygroscopic and [uranium(IV) compounds] more air-sensitive than the tetrakis complexes.

In cone-angle terms (see ref. 2), tmu provides almost the same degree of secondary crowding as the amide $Me_2CHCONMe_2$ (dmiba) for which the complexes $U(NCS)_4 \cdot 3dmiba$ and $M(NCS)_4 \cdot 4dmiba$ (M = Th or U) have been reported, although $Th(NCS)_4 \cdot 3dmiba$ could not be obtained.[4,5] The same pattern was observed in this work with tmu, in which $U(NCS)_4 \cdot 4tmu$ could be isolated only when a large excess of tmu was used. Similarly, the tetrakis complexes, $Th(NCS)_4 \cdot 4L$, were the only products obtained with L = teu, dedmu, and dmdpu. Although $U(NCS)_4 \cdot 4dmdpu$ was isolated, $U(NCS)_4 \cdot 3dmdpu$ and the solvate $U(NCS)_4 \cdot 2dmdpu \cdot 2MeCN$ were easily obtained by using the stoicheiometric quantities of the ligand in the preparations and the tris complexes $U(NCS)_4 \cdot 3L$ were the only products isolated with L = teu and dedmu.

The tris complexes could not be prepared by recrystallisation of $U(NCS)_4 \cdot 4tmu$ or $U(NCS)_4 \cdot 4dmdpu$ from a mixture of dichloromethane and n-pentane, even though the i.r. spectra of these complexes in dichloromethane solution (Table 1) showed the presence of free ligand resulting from dissociation. Similarly, the attempted degradation of the tetrakis complexes, $Th(NCS)_4 \cdot 4L$ (L = teu, dedmu, or dmdpu), by repeated recrystallisation from mixtures of dichloromethane and n-pentane or toluene and n-pentane (L = teu) were unsuccessful. The tris complexes, $Th(NCS)_4 \cdot 3L$, would, however, be very much 'undercrowded' in cone-angle terms,[2] with Σc.a.f. = 0.70 as against 0.80 for the tetrakis complexes (c.a.f. = cone-angle factor); the corresponding values of Σc.a.f. for the uranium(IV) complexes are 0.74 and 0.84 respectively, which are nearer the values observed for the 'stable' regions [thorium(IV) complexes,[3] 0.80 ± 0.04 and uranium(IV) complexes,[2] 0.80 ± 0.03]. The formation of the methyl cyanide solvate, $U(NCS)_4 \cdot 2dmdpu \cdot 2MeCN$ (Σc.a.f = 0.81), presumably results from the dissociation of the slightly undercrowded tris complex, $U(NCS)_4 \cdot 3dmdpu$, in the presence of a large excess of methyl cyanide, coupled with the low solubility of this solvate in methyl cyanide.

Infrared Spectra.—The shifts in the carbonyl-stretching features of the ligands (Table 1) are comparable with those observed for the analogous complexes of thorium and uranium tetrachlorides.[6,7] The spectra of the tetrakis complexes, $M(NCS)_4 \cdot 4L$ (M = Th, L = teu, dedmu, or dmdpu; M = U, L = tmu or dmdpu), in solution in dichloromethane and in tetrahydrofuran showed that some free ligand was present, which indicates some dissociation or (in thf) replacement of the bulky ligands by solvent molecules. The presence of free ligand was also observed in the spectra of the tris complexes, $U(NCS)_4 \cdot 3L$ (L = tmu, teu, or dedmu), in tetrahydrofuran, but no dissociation appeared to occur in dichloromethane solution.

The C–N stretching mode appears at 1 900—2 052 cm^{-1} in the i.r. spectra of the complexes, which is on the borderline for distinguishing between sulphur and nitrogen bonding in thiocyanates;[8] however, this feature is of relatively high intensity in the spectra of all of the complexes, which suggests that the thiocyanate groups are nitrogen bonded.[9,10] The C–S feature in the i.r. spectra of nitrogen-bonded thiocyanates usually appears between 760 and 880 cm^{-1} as against 700 cm^{-1} for sulphur-bonded thiocyanates,[11,12] but this feature could not be identified owing to interference from features arising from the organic ligands.

Table 1. Infrared spectral data (cm^{-1}) for the complexes

	Nujol mull			Dichloromethane solution			Tetrahydrofuran solution		
Complex	ν(CO)	Δν(CO)	ν(CN)	ν(CO)	Δν(CO)	ν(CN)	ν(CO)	Δν(CO)	ν(CN)
$U(NCS)_4 \cdot 3tmu$	1 557s,br	80	1 998s, 2 020s (sh), 2 046s	1 562s	75	2 010s, 2 042m (sh)	1 558s, 1 648w	79, −11	2 000s
$U(NCS)_4 \cdot 4tmu$	1 570s (sh)	67	2 021s (sh), 2 039s	1 567s (sh), 1 633m	70, 4	2 022s, 2 042m (sh)	1 558s (sh), 1 640m	79, −3	2 000s
$Th(NCS)_4 \cdot 4teu$	1 525s	115	2 043s	1 520s, 1 625m	120, 15	2 020s	1 518s, 1 636s	122, 4	2 000s
$U(NCS)_4 \cdot 3teu$	1 532s (sh)	108	2 002s, 2 020s (sh), 2 041m (sh)	1 528s (sh)	112	1 995s, 2 004s (sh)	1 522s (sh), 1 640m	118, 0	1 990s
$Th(NCS)_4 \cdot 4dedmu$	1 545s (sh)	98	2 032s	1 544s (sh), 1 630w	99, 13	2 012s	1 543s (sh), 1 639m	100, 4	2 010s
$U(NCS)_4 \cdot 3dedmu$	1 552s (sh)	91	1 999s, 2 048m (sh)	1 557s (sh)	86	2 000s	1 559s, (sh), 1 653m	84, −10	2 020s
$Th(NCS)_4 \cdot 4dmdpu$	1 539s	105	1 982m (sh), 2 021s	1 530s, 1 640w	114, 4	2 017s	1 540s, 1 641s	104, 3	2 005s
$U(NCS)_4 \cdot 2dmdpu \cdot 2MeCN$	1 520s (sh)	124	2 015s, 2 052s (sh)	1 518s (sh)	126	2 015s	1 535s,br, 1 650s	109, −6	2 000s
$U(NCS)_4 \cdot 3dmdpu$	1 524s (sh)	120	1 985s, 2 005s (sh), 2 040m (sh)	1 520s (sh)	124	1 985s	1 523s,br, 1 643s	121, 1	1 998s
$U(NCS)_4 \cdot 4dmdpu$	1 537s,br	107	2 033s, 2 038s (sh)	1 520s, 1 642w	124, 2	2 000s	1 517s,br, 1 643w	127, 1	1 990s

s = Strong, m = medium, w = weak, br = broad, and sh = shoulder.

Table 2. Principal features (600—2 200 nm) of the near i.r.–visible spectra of the complexes $U(NCS)_4 \cdot xL$

Complex	Solid reflectance	Solution in dichloromethane	Solution in thf
$U(NCS)_4 \cdot 3tmu$	660m, 890m, 1 080m (sh), 1 132s, 1 428m, 1 605m	675s, 905m, 1 135s, 1 425m, 1 600m	690s, 915w, 1 152s, 1 520m,br
$U(NCS)_4 \cdot 4tmu$	665s, 900w, 1 052m (sh), 1 130s, 1 555m,br	675s, 900m, 1 145s, 1 420m, 1 595m	685s, 910w, 1 040m (sh), 1 150s, 1 535m,br
$U(NCS)_4 \cdot 3teu$	663m, 890s, 1 085s (sh), 1 134s, 1 422m, 1 565m	680s, 920m, 1 150s, 1 450m, 1 620m	690s, 925w, 1 060m (sh), 1 160s, 1 530m
$U(NCS)_4 \cdot 3dedmu$	652m, 890s, 1 085m (sh), 1 135s, 1 425m, 1 590m	665s, 900m, 1 135s, 1 430m, 1 595m	665s, 900m, 1 145s, 1 520m,br
$U(NCS)_4 \cdot 2dmdpu \cdot 2MeCN$	670s, 905m, 1 065m (sh), 1 135s, 1 495s	690s, 930m, 1 155s, 1 425m,br, 1 620m	690s, 925w, 1 070m (sh), 1 160s, 1 515m,br
$U(NCS)_4 \cdot 3dmdpu$	685m, 920m, 1 140s, 1 450m, 1 640m	665s, 915m, 1 145s, 1 455m, 1 620m	680s, 915w, 1 040m (sh), 1 155s, 1 420m,br
$U(NCS)_4 \cdot 4dmdpu$	680s, 905m, 1 050m (sh), 1 135s, 1 580m,br	680s, 925m, 1 150s, 1 470m, 1 620m	675s, 910w, 1 035m (sh), 1 155s, 1 515m

Near I.r.–Visible Spectra.—The principal features in the near i.r.–visible spectra of the uranium(IV) complexes are summarised in Table 2. The solid reflectance and thf solution spectra of $U(NCS)_4 \cdot 4tmu$ and $U(NCS)_4 \cdot 4dmdpu$ are characteristic of high ($\geqslant 8$)-co-ordination-number uranium(IV) species and are similar to the spectra of the tris complexes in thf, which suggests that solvation and/or dissociation occurs (Scheme). Evidence in support of the second stage is provided by the i.r. spectra of the complexes in thf (see above). The spectra of these two complexes in dichloromethane are similar to those of the complexes $U(NCS)_4 \cdot 3L$ in that solvent, again indicating dissociation, and their i.r. spectra in dichloromethane (Table 1) also show the presence of both free and bonded ligand.

$$\underset{(\Sigma\text{c.a.f.} = 0.74)}{U(NCS)_4 \cdot 3L} \xrightleftharpoons{\text{thf}} \underset{(\Sigma\text{c.a.f.} = 0.82)}{U(NCS)_4 \cdot 3L \cdot thf} \xrightleftharpoons{\text{thf}} \underset{(\Sigma\text{c.a.f.} = 0.80)}{U(NCS)_4 \cdot 2L \cdot 2thf} + L$$

Scheme.

The spectra of the tris complexes in dichloromethane are very similar to their solid reflectance spectra and are almost identical to that of the known pentagonal-bipyramidal seven-co-ordinate complex[4] $[U(NCS)_4(dmiba)_3]$, and these compounds are almost certainly genuine seven-co-ordinate uranium(IV) species.

Experimental

All of the experimental work, including the drying of solvents and the handling of air- and moisture-sensitive starting materials and products, was carried out as described previously.[13] The compounds $ThCl_4$,[14] UCl_4,[15] $ThCl_4 \cdot 3dmdpu$,[6] and $ThCl_4 \cdot 3dedmu$[7] were prepared by the published methods; dmdpu (K. and K. Laboratories), tmu (B.D.H. Ltd.), and teu (Aldrich) were used as supplied, and dedmu was prepared by the standard method, reaction of diethylamine with dimethylcarbamoyl chloride. Infrared[16] and near i.r.–visible[17] spectra were obtained as described previously.

Preparations.—(*a*) $Th(NCS)_4 \cdot 4dmdpu$. An excess of dmdpu (0.65 g, 2.71 mmol) and the stoicheiometric amount of

Table 3. Analytical results (%)*

Complex	Metal	C	H	N	S	Yield (%)
$\mathrm{U(NCS)_4\cdot 3tmu}$	29.0 (29.1)	27.9 (27.7)	4.4 (4.4)	17.1 (17.0)	16.0 (15.6)	53
$\mathrm{U(NCS)_4\cdot 4tmu}$	25.1 (25.5)	30.6 (30.8)	5.2 (5.1)	17.5 (18.0)	13.3 (13.7)	66
$\mathrm{Th(NCS)_4\cdot 4teu}$	19.9 (20.1)	41.6 (41.7)	7.0 (6.9)	14.8 (14.6)	10.6 (11.1)	30
$\mathrm{U(NCS)_4\cdot 3teu}$	24.3 (24.1)	37.4 (37.7)	6.2 (6.1)	14.1 (14.2)	13.0 (13.0)	65
$\mathrm{Th(NCS)_4\cdot 4dedmu}$	21.6 (22.3)	36.6 (36.9)	6.2 (6.2)	15.9 (16.2)	12.1 (12.3)	72
$\mathrm{U(NCS)_4\cdot 3dedmu}$	27.0 (26.4)	33.2 (33.3)	5.5 (5.3)	15.4 (15.5)	14.3 (14.2)	80
$\mathrm{Th(NCS)_4\cdot 4dmdpu}$	16.3 (16.3)	53.8 (53.9)	4.4 (4.5)	11.9 (11.8)	8.8 (9.0)	55
$\mathrm{U(NCS)_4\cdot 2dmdpu\cdot 2MeCN}$	22.7 (23.1)	44.1 (44.1)	3.8 (3.7)	13.2 (13.6)	12.7 (12.4)	30
$\mathrm{U(NCS)_4\cdot 3dmdpu}$	20.4 (20.0)	49.1 (49.4)	4.0 (4.0)	11.7 (11.8)	10.5 (10.8)	80
$\mathrm{U(NCS)_4\cdot 4dmdpu}$	16.5 (16.6)	53.6 (53.7)	4.5 (4.5)	12.0 (11.7)	8.5 (9.0)	58

* Calculated values in parentheses.

potassium thiocyanate (0.35 g, 3.64 mmol) were stirred with $\mathrm{ThCl_4\cdot 3dmdpu}$ (1.0 g, 0.91 mmol) in thf (10 $\mathrm{cm^3}$) for 3 d, after which the supernatant was vacuum evaporated to dryness. The oily residue was dissolved in dichloromethane (5 $\mathrm{cm^3}$) and n-pentane was added to the supernatant until it became cloudy. The colourless crystals of the *product* which separated on standing overnight were washed with n-pentane (3×3 $\mathrm{cm^3}$) and vacuum dried (8 h).

The complexes $\mathrm{U(NCS)_4\cdot 4tmu}$ and $\mathrm{U(NCS)_4\cdot 4dmdpu}$ were prepared from $\mathrm{UCl_4}$ in a similar manner, except that the cloudiness induced by addition of n-pentane to the dichloromethane solution was cleared by dropwise addition of the latter. The green *products* crystallised on standing overnight. The complexes $\mathrm{Th(NCS)_4\cdot 4dedmu}$, $\mathrm{U(NCS)_4\cdot 3teu}$, and $\mathrm{U(NCS)_4\cdot 3dedmu}$ were prepared in a similar manner from $\mathrm{ThCl_4\cdot 3dedmu}$ or $\mathrm{UCl_4}$, except that the dichloromethane solutions of the reaction products were vacuum evaporated to leave oily residues which solidified when ground under n-pentane [$\mathrm{Th(NCS)_4\cdot 4dedmu}$ or $\mathrm{U(NCS)_4\cdot 3dedmu}$] or 2-methylbutane [$\mathrm{U(NCS)_4\cdot 3teu}$]. After standing overnight under the hydrocarbon, the *products* were washed and dried as above.

(*b*) $\mathrm{U(NCS)_4\cdot 3dedmu}$. This complex was also prepared from $\mathrm{UCl_4}$ as in (*a*), but by dissolving the oily residue remaining from the vacuum evaporation of the thf supernatant in ethyl acetate (5 $\mathrm{cm^3}$); n-pentane was then added to the filtrate until the solution became cloudy and dark green crystals of the complex separated on standing overnight. These were then washed and dried as in (*a*).

(*c*) $\mathrm{Th(NCS)_4\cdot 4teu}$. This complex was prepared from $\mathrm{ThCl_4}$ as in (*a*) except that the stoicheiometric quantity of teu was used and the oily residue remaining after vacuum evaporation of the reaction supernatant was dissolved in toluene, followed by addition of n-pentane as in (*b*). Colourless crystals of the *complex* formed on standing and, after 3 d, these were separated and then washed and dried as in (*a*).

(*d*) $\mathrm{U(NCS)_4\cdot 3tmu}$. This dark green complex was prepared from $\mathrm{UCl_4}$ as in (*a*) but using methyl cyanide as solvent and with only a slight excess of tmu. Green $\mathrm{U(NCS)_4\cdot 2dmdpu\cdot 2MeCN}$ was obtained in the same way.

(*e*) $\mathrm{U(NCS)_4\cdot 3dmdpu}$. This complex was prepared from $\mathrm{UCl_4}$ as in (*a*) but using dichloromethane as the reaction medium and with the stoicheiometric quantity of dmdpu; after stirring for 3 weeks the dark green *product* was isolated as described in (*a*).

The analytical results are summarised in Table 3.

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