Some Oxygen-donor Di-*N*-thiocyanato–thorium(IV) and –uranium(IV) Bis[hydrotris(pyrazol-1-yl)borate] Complexes

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Di-*N*-thiocyanato–thorium(IV) and –uranium(IV) bis[hydrotris(pyrazol-1-yl)borate] complexes, $M(NCS)_2[HB(pz)_3]_2 \cdot xL$ [pz = $C_3H_3N_2$; x = 1, M = Th, L = tetrahydrofuran (thf); M = U, L = thf, $MeCONMe_2$, PMe_2PhO, $PMePh_2O$, or PPh_3O; x = 2, M = Th, L = $MeCONMe_2$, PMe_3O, PMe_2PhO, $PMePh_2O$, or PPh_3O; M = U, L = PMe_3O; x = 1.5, M = Th, L = $P(NMe_2)_3O$], $Th(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2$ and $U(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2 \cdot thf$ (3,5Me$_2$-pz = 3,5-dimethylpyrazol-1-yl) have been prepared. The i.r. and u.v.–visible spectra [uranium(IV) complexes only] of these compounds are reported and the effects of steric crowding on the possible bonding arrangements of the hydrotris(pyrazol-1-yl)borate ligands are discussed in terms of a cone angle factor approach to steric crowding about the metal centres in these complexes.

Unsolvated dihalogenouranium(IV) hydrotris(pyrazol-1-yl)-borates such as $UCl_2[HB(pz)_3]_2$ (pz = $C_3H_3N_2$) are easily obtained,[1] but the only recorded complexes of this type of compound with oxygen-donor ligands are $UCl_2[HB(pz)_3]_2 \cdot$dma,[2] $UX_2[HB(3,5Me_2\text{-}pz)_3]_2 \cdot$thf (X = Cl or Br)[2] and $ThCl_3[HB(pz)_3] \cdot$dma·thf (dma = *NN*-dimethylacetamide, thf = tetrahydrofuran).[3] Replacement of halogen by the smaller *N*-thiocyanate group should provide additional space for neutral ligands to enter the co-ordination sphere, and it was therefore of interest to attempt to prepare a series of complexes of the type $M(NCS)_2[HB(pz)_3]_2 \cdot xL$ for M = Th and U, and to correlate the results by applying the cone angle factor approach to steric crowding which was described briefly in a recent paper.[4]

Results and Discussion

Preparation of the Complexes.—The di-*N*-thiocyanato-complexes $M(NCS)_2[HB(pz)_3]_2 \cdot xL$ were obtained by evaporating the filtrate from the reaction of the anhydrous metal tetrachloride in thf with stoicheiometric quantities of $K[HB(pz)_3]$ and KNCS in the presence of an excess of the ligand where appropriate. Free ligand was removed from the oily products by washing them with a mixture of thf and n-pentane or with n-pentane alone.

The thorium compound formed bis-complexes except with L = thf (x = 1) and tdpo [tris(dimethylamino)phosphine oxide; x = 1.5], whereas the uranium analogue formed 1 : 1 complexes except with L = tmpo (trimethylphosphine oxide; x = 2). Repeated crystallisation of the last from thf appears to lead to disproportionation to $U(NCS)_3[HB(pz)_3] \cdot 2$tmpo. The hydrotris(3,5-dimethylpyrazol-1-yl)borate complexes, $Th(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2$ and $U(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2 \cdot$thf were prepared in the same way as $Th(NCS)_2[HB(pz)_3]_2 \cdot$thf. All of the thorium compounds are white and their uranium(IV) analogues are green.

In the i.r. spectra of these complexes (Table 1) the shifts observed for ν(CO) (L = dma) and ν(PO) [L = tmpo, dmppo (PMe_2PhO), mdppo ($PMePh_2O$), tppo (PPh_3O), and tdpo] are similar in magnitude to those observed for the corresponding complexes with the tetrachlorides [dmppo, mdppo (Th or U);[5] tppo (Th[6] or U[7]); tdpo (Th[8] or U[9]); dma (Th[10] or U[11])] except for the tmpo compounds for which the shift is only about half of that observed[12] for $MCl_4 \cdot 6$tmpo (M = Th or U). The B–H stretching mode appears at 2 455—2 480 cm^{-1} in the i.r. spectra of the $HB(pz)_3$ complexes and at 2 550 cm^{-1} in those of the $HB(3,5Me_2\text{-}pz)_3$ compounds. The C–N stretching mode appears at 2 020—2 050 cm^{-1}, which is consistent with nitrogen-bonding in thiocyanates,[13] and the intensity of this feature in each case was relatively high, which also suggests that the thiocyanate groups are nitrogen-bonded.[14,15] The C–S feature in the i.r. spectra of N-bonded thiocyanates is usually observed at 760—880 cm^{-1} as against 700 cm^{-1} for S-bonded thiocyanates,[16,17] but this feature could not be identified owing to interference from modes arising from the organic ligands.

The principal features of the u.v.–visible spectra (solid reflectance and solution in thf) are very similar to those reported for $[U(\eta\text{-}C_5H_5)X_3L_2]$ (X = Cl,[18] Br,[18] or NCS[4]) and are consistent with a low symmetry, high co-ordination number ($\geqslant 8$) environment for the uranium(IV) centre.

The ^1H n.m.r. spectra of the compounds $M(NCS)_2[HB(pz)_3]_2 \cdot$thf (M = Th or U) in CD_2Cl_2 indicate that both $HB(pz)_3$ groups are tridentate [H(3), τ 2.2, doublet (Th) and −12.5 p.p.m. (U); H(5), τ 2.55, doublet (Th) and H(5) + B–H, 2.4 p.p.m. (U); H(4), τ 3.8, triplet (Th) and 6.9 p.p.m. (U)], which would suggest nine-co-ordination for the metal atoms if the thf molecule is bonded. The thf resonances [H(1),H(4) and H(2),H(3), τ = 6.25 and 8.1 (Th), 5.25 and 8.00 p.p.m. (U) respectively] do not resolve this point.

In an attempt to determine whether the $HB(pz)_3$ groups are bidentate or tridentate in the other complexes, the cone angle factor (c.a.f.) approach to steric crowding[4] was applied to them. The calculated values of Σ(c.a.f.) for 17 uranium(IV) compounds of known structure indicated[4] that the average value was 0.80 (σ = 0.03) and that for values of Σ(c.a.f.) lower than 0.77, secondary crowding, such as that caused by bulky groups R in the phosphine oxides PR_3O (*e.g.* R = Ph or NMe_2), was necessary to achieve the formation of a stable complex. The average value of the c.a.f. calculated for 20 thorium(IV) complexes was also found to be 0.80 (σ = 0.04).[19] As a first-order approximation for these complexes, the values of the c.a.f. for bidentate and tridentate $HB(pz)_3$ groups were calculated to be 0.19 and 0.28 respectively; the average values for the neutral amide and phosphine oxide donor ligands were 0.10 for thorium and 0.11 for uranium,[4] and for thf the value was 0.09 for both elements. The value for the NCS group[4] was taken to be 0.11.

The calculated values of Σ(c.a.f.) for all possibilities of bonding for the $HB(pz)_3$ groups are summarised in Table 2. These calculations suggest that in the complexes $M(NCS)_2[HB(pz)_3]_2 \cdot L$ (L = dma or PR_3O) it is most likely that one $HB(pz)_3$ group is bidentate and the other tridentate, making the co-ordination number eight [Σ(c.a.f.) = 0.80 for the uranium(IV) compounds]. The value of Σ(c.a.f.) for the thorium(IV) and uranium(IV) thf complexes would be 0.78 on

Table 1. Infrared spectra (cm^{-1}) of the complexes

Complex	ν(BH)	ν(CN)	ν(CO)	$\Delta\nu$(CO) *	ν(PO)	$\Delta\nu$(PO) *
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot thf}$	2 480	2 030	—	—	—	—
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot thf}$	2 470	2 030	—	—	—	—
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2dma}$	2 480	2 040	1 600	50	—	—
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot dma}$	2 470	2 040	1 600	50	—	—
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2tmpo}$	2 475	2 050	—	—	1 092	73
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot 2tmpo}$	2 460	2 030	—	—	1 120	45
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2dmppo}$	2 455	2 040	—	—	1 090	85
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot dmppo}$	2 460	2 020	—	—	1 065	110
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2mdppo}$	2 460	2 040	—	—	1 085	85
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot mdppo}$	2 460	2 030	—	—	1 065	105
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2tppo}$	2 460	2 030	—	—	1 070	120
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot tppo}$	2 460	2 020	—	—	1 065	125
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 1.5tdpo}$	2 460	2 040	—	—	1 065	140
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot tdpo}$	2 470	2 030	—	—	1 050	155
$\mathrm{Th(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2}$	2 550	2 020	—	—	—	—
$\mathrm{U(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2\cdot thf}$	2 560	2 030	—	—	—	—

* Shift in ν(CO) or ν(PO) on complexation.

Table 2. Calculated values of Σ(c.a.f.) (metal ion co-ordination numbers in parentheses)

Complex	Both $\mathrm{HB(pz)_3}$ groups bidentate	Both $\mathrm{HB(pz)_3}$ groups tridentate	One bidentate and one tridentate $\mathrm{HB(pz)_3}$ group
$\mathrm{M(NCS)_2[HB(pz)_3]_2\cdot thf}$ (M = U or Th)	0.69 (7) *	0.87 (9) *	0.78 (8) *
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2L}$ (L = dma, tmpo, dmppo, mdppo, or tppo)	0.80	0.98 (10)	0.89 (9)
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot L}$ (L = dmppo, mdppo, tppo, or tdpo)	0.71 (7)	0.89 (9)	0.80 (8)
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot dma}$	0.70 (7)	0.88 (9)	0.79 (8)
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot 2tmpo}$	0.81 (8)	1.00 (10)	0.91 (9)

* Assuming that the thf molecule is bonded to the metal atom. If it is not, the values are 0.60, 0.78, and 0.69 respectively for the three cases, left to right.

Table 3. Analytical data * (%) and yields of complexes

Complex	Metal	C	H	N	S	P	B	Yield (%)
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot thf}$	27.4 (27.4)	33.7 (34.0)	3.5 (3.3)	23.1 (23.1)	7.3 (7.6)	—	2.3 (2.6)	60
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot thf}$	28.5 (28.0)	32.1 (33.8)	3.0 (3.3)	22.4 (23.0)	7.6 (7.5)	—	—	50
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2dma}$	24.0 (24.5)	35.3 (35.4)	4.1 (4.0)	23.3 (23.6)	6.8 (6.8)	—	2.3 (2.3)	60
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot dma}$	28.2 (27.5)	31.7 (33.2)	3.3 (3.4)	22.3 (24.2)	6.7 (7.4)	—	—	30
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2tmpo}$	23.9 (24.2)	32.0 (32.6)	3.9 (4.0)	20.2 (20.5)	6.3 (6.7)	5.9 (6.5)	2.1 (2.3)	68
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot 2tmpo}$	25.4 (24.7)	32.9 (32.4)	3.7 (3.9)	20.3 (20.3)	6.8 (6.6)	—	—	50
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2dmppo}$	20.7 (21.5)	39.6 (40.0)	4.1 (3.9)	17.6 (18.1)	5.5 (5.9)	5.3 (5.7)	2.0 (2.0)	63
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot dmppo}$	24.8 (25.5)	35.5 (36.0)	3.5 (3.3)	20.3 (21.0)	6.7 (6.9)	3.3 (3.3)	—	58
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2mdppo}$	18.6 (19.2)	45.3 (45.8)	4.0 (3.8)	15.6 (16.3)	4.8 (5.3)	4.5 (5.1)	1.8 (1.8)	60
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot mdppo}$	23.5 (23.9)	39.6 (39.8)	3.6 (3.3)	18.9 (19.7)	6.1 (6.4)	3.0 (3.1)	—	55
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 2tppo}$	17.0 (17.4)	50.4 (50.5)	4.0 (3.8)	14.2 (14.7)	4.5 (4.8)	4.5 (4.7)	—	60
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot tppo}$	22.1 (22.5)	42.4 (43.1)	3.5 (3.3)	17.9 (18.5)	5.6 (6.1)	2.7 (2.9)	—	56
$\mathrm{Th(NCS)_2[HB(pz)_3]_2\cdot 1.5tdpo}$	22.1 (22.3)	32.8 (33.4)	4.5 (4.5)	23.8 (24.9)	5.9 (6.1)	4.3 (4.5)	2.3 (2.1)	55
$\mathrm{U(NCS)_2[HB(pz)_3]_2\cdot tdpo}$	24.6 (24.8)	32.5 (32.6)	4.4 (4.0)	21.3 (24.8)	7.2 (6.7)	—	—	50
$\mathrm{Th(NCS)_2[HB(3,5Me\text{-}pz)_3]_2}$	24.9 (24.6)	41.3 (40.8)	4.8 (4.7)	20.5 (20.8)	7.3 (6.8)	—	2.2 (2.3)	53
$\mathrm{U(NCS)_2[HB(3,5Me_2\text{-}pz)_3]_2\cdot thf}$	22.3 (23.3)	41.6 (42.4)	5.3 (5.1)	19.0 (19.2)	5.7 (6.3)	—	—	25

* Calculated values are given in parentheses.

this basis, assuming bonded thf, but the ^{1}H n.m.r. spectra (see above) indicate that both $\mathrm{HB(pz)_3}$ groups are tridentate [Σ(c.a.f.) = 0.87 if thf is bonded, 0.78 if not bonded], which would suggest that the thf is only held in the lattice. For the bis-complexes, the most likely bonding situation is for both of the $\mathrm{HB(pz)_3}$ groups to be bidentate [Σ(c.a.f.) = 0.80 for the thorium(IV) compounds and 0.81 for the uranium(IV) one], making the probable co-ordination number eight in all cases.

Experimental

The drying of solvents and the handling of air- and moisture-sensitive products was carried out as described previously.[1] $\mathrm{ThCl_4}$,[9] $\mathrm{UCl_4}$,[20] $\mathrm{K[HB(pz)_3]}$,[21] $\mathrm{K[HB(3,5Me_2\text{-}pz)_3]}$,[21] mdppo,[22] and tmpo [23] were prepared by published methods; dmppo was prepared from $\mathrm{PPhCl_2O}$ in the same way as tmpo; tdpo, dma (B.D.H., Ltd), and tppo (Aldrich Chemical Co.) were used as supplied. U.v.–visible spectra were recorded using a Cary 14 (solution) or Beckmann DK2A (solid reflectance) spectrophotometer. I.r. spectra (200—4 000 cm^{-1}) were obtained using a Perkin-Elmer 577 spectrometer and ^{1}H n.m.r. spectra were recorded using a 60-MHz Perkin-Elmer R12B or 300-MHz Varian SC300 instrument.

Preparations.—*(Dimethylphenylphosphine oxide)bis[hydrotris(pyrazol-1-yl)borato]di-isothiocyanatouranium*(IV),

$U(NCS)_2[HB(pz)_3]_2$·dmppo. Solid $K[HB(pz)_3]$ (0.672 g, 2.667 mmol) was added to a solution of UCl_4 (0.507 g, 1.334 mmol) in thf. After stirring for 72 h, dmppo (0.256 g, 1.662 mmol) and KNCS (0.259 g, 2.67 mmol) were added, and the mixture was stirred for a further 96 h. The supernatant was evaporated to dryness under vacuum and the oily residue was washed with a mixture of thf and n-pentane (1 : 1 v/v, 5 cm^3), then with n-pentane (5 cm^3), and finally with the thf–n-pentane mixture (3×5 cm^3). The solid product was then vacuum dried for 8 h. The other complexes reported here were prepared in the same way. Analyses were obtained as reported previously [1] (Table 3, which includes yields).

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