SOME COMPLEXES OF CYCLOPENTADIENYL THORIUM(IV) AND URANIUM(IV) CHLORIDES AND URANIUM(IV) *N*-THIOCYANATE WITH NEUTRAL DONOR LIGANDS

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Summary

Complexes of cyclopentadienyl thorium(IV) chloride $Th(cp)Cl_3 \cdot xL$ ($cp \equiv \eta^5 \cdot C_5H_5$) (x = 2, $L \equiv tetrahydrofuran$ (thf); x = 3, $L \equiv CH_3CN$), Th(CH₃cp)Cl₃·2thf and the uranium(IV) compounds U(cp)Cl₃·2L (with $L \equiv P(CH_3)_3O$, $P(CH_3)_2C_6H_5O$ (dmppo) and $PCH_3(C_6H_5)_2O$ (mdppo)) as well as the uranium(IV) *N*-thiocyanato complexes U(cp)(NCS)₃·3L (with $L \equiv$ dmppo and mdppo) have been prepared. The IR and UV-visible spectra (uranium(IV) complexes only) of these compounds are reported and their stoichiometries are discussed in terms of the steric crowding about the metal atom using a cone packing model.

1. Introduction

Complexes of cyclopentadienyl thorium(IV) trihalides of composition Th(cp)X₃L_y (cp $\equiv \eta^5$ -C₅H₅) (with y = 2, X \equiv Br, L \equiv tetrahydrofuran (thf) and $X \equiv Cl$, $L \equiv P(C_6H_5)_3O$ (tppo); y = 2.5, $X \equiv Cl$, $L \equiv thf$, $CH_3CON(CH_3)_2$ (dma) and $X \equiv Cl$ or Br, $L \equiv (CH_3)_3 CON(CH_3)_2$ (dmpva); y = 3.5, $X \equiv Br$, $L \equiv dma$), Th(cp)Br₃(tppo)₂(thf) and Th(cp)Cl₃(dma)_{1.5}(napy) (napy = 1,8naphthyridine) have been reported previously [1]. Analogous uranium(IV) complexes U(cp)X₃L_y have been recorded for y = 1, $X \equiv Cl$, $L \equiv 1,2$ -dimethoxyethane [2] and $X \equiv Cl$ or Br, $L \equiv (C_6H_5)_2(O)PCH_2CH_2P(O)(C_6H_5)_2$ [3] and for y = 2, $X \equiv Cl$ or Br, $L \equiv dmpva$ or tppo [3] and $X \equiv Cl$, $L \equiv dma$ [3], thf [4] and $P(N(CH_3)_2)_3O$ (tdpo) [5]. In the structures of $[U(cp)Cl_3]$ - $(tdpo)_2$ [5] and $[U(cp)Cl_3(tppo)_2] \cdot thf$ [6] the oxygen donor ligands occupy cis positions in an octahedral arrangement about the uranium atom, assuming that the C_5H_5 ring occupies one vertex. Analogous uranium(IV) N-thiocyanato compounds $U(cp)(NCS)_3L_2$ are known only for the bulky ligands tppo, tdpo, dmpva and $(CH_3)_2$ CHCON $(CH_3)_2$ [7]. It was therefore of interest to attempt the preparation of similar N-thiocyanato complexes with the less bulky phosphine oxides $P(CH_3)_2C_6H_5O$ (dmppo) and $PCH_3(C_6H_5)_2O$ (mdppo), together with the corresponding cyclopentadienyl trichloride complexes, and to investigate the possible formation of complexes of the type $Th(cp)Cl_3L_x$ with the relatively small ligands thf and CH_3CN , and then to correlate the results using the cone packing model described briefly in a recent paper [7].

2. Experimental details

2.1. Materials

ThCl₄ [8] and UCl₄ [9], U(cp)Cl₃·2thf [4] and the phosphine oxide ligands [10] were prepared by the published methods. All the experimental work, including the drying of solvents and the handling of the air- and moisture-sensitive products, was carried out as described previously [4, 11, 12].

2.2. Physical measurements

IR and UV-visible spectra were obtained as described previously [13].

2.3. Preparative methods

(a) Th(cp)Cl₃·2thf was prepared by treating ThCl₄ (0.39 g, 1.04 mmol) in thf (25 cm³) with the stoichiometric amount of freshly sublimed Tl(cp) (0.28 g, 1.06 mmol). After stirring overnight the supernatant was vacuum evaporated to a small volume, when the product separated as a white solid which was washed with cold dry thf (5 cm³) and then vacuum dried for 8 h. The yield was about 45%. The results of analysis showed 42.2% Th, 28.2% C, 3.6% H and 19.9% Cl. ThC₁₃H₂₁Cl₃O₂ requires 42.4% Th, 28.5% C, 3.8% H and 19.5% Cl. Th(CH₃cp)Cl₃·2thf was prepared in the same way. The yield was about 55%. The results of analysis showed 41.1% Th, 28.9% C, 4.2% H and 18.1% Cl. ThC₁₄H₂₃Cl₃O₂ requires 41.3% Th, 29.9% C, 4.1% H and 19.0% Cl.

(b) $U(cp)Cl_3 \cdot 2tmpo \ (tmpo \equiv P(CH_3)_3O)$ was prepared by adding the stoichiometric quantity of tmpo (0.31 g, 3.37 mmol), dissolved in thf (10 cm³), to a solution of $U(cp)Cl_3 \cdot 2thf$ (0.923 g, 1.67 mmol) in the same solvent (30 cm³). After stirring for 30 min the supernatant was vacuum evaporated to half-volume. The product crystallized out on standing overnight and was washed with cold thf (2 × 5 cm³), then vacuum dried (6 h). The yield was about 65%. The results of analysis showed 40.1% U, 22.2% C, 4.1% H, 18.3% Cl and 10.9% P. UC₁₁H₂₃Cl₃O₂P₂ requires 40.1% U, 22.2% C, 3.9% H, 17.9% Cl and 10.5% P.

The following complexes were prepared in the same way.

(1) The yield of U(cp)Cl₃·2dmppo was 60% and the results of analysis showed 32.7% U, 33.9% C, 3.8% H, 15.6% Cl and 8.9% P. $U_{21}H_{27}Cl_3O_2P_2$ requires 33.2% U, 35.1% C, 3.8% H, 14.8% Cl and 8.9% P.

(2) The yield of $U(cp)Cl_3 \cdot 2mdppo$ was 72%. The results of analysis showed 28.3% U, 44.2% C, 4.0% H, 11.7% Cl and 7.3% P. $UC_{31}H_{31}Cl_3O_2P_2$ requires 28.3% U, 44.2% C, 3.7% H, 12.6% Cl and 7.4% P.

(c) $Th(cp)Cl_3 \cdot 3CH_3CN$ was prepared as in (a) but with CH_3CN as the solvent. The yield was 65%. The results of analysis showed 45.2% Th, 24.2% C, 2.8% H, 8.3% N and 19.3% Cl. $ThC_{11}H_{14}N_3Cl_3$ requires 44.1% Th, 25.1% C, 2.7% H, 8.0% N and 20.2% Cl.

(d) $U(cp)(NCS)_3$ · 3dmppo was prepared by treating UCl_4 (0.48 g, 1.26 mmol) in thf (25 cm³) with the stoichiometric quantity of freshly sublimed Tl(cp) (0.34 g, 1.28 mmol); after stirring for 12 h, the stoichiometric amount of KNCS (0.37 g, 3.8 mmol) was added followed, after 1 h stirring, by an excess of dmppo (0.69 g, 4.48 mmol). After stirring for 12 h, the supernatant was vacuum evaporated to dryness and the oily residue was solidified by washing several times with a 1:1 (by volume) mixture of thf and *n*-pentane. The green product was vacuum dried for 8 h. The yield was 36%. The results of analysis showed 24.4% U, 40.2% C, 4.1% H, 4.3% N, 10.4% P and 9.3% S. $UC_{32}H_{38}N_3O_3P_3S_3$ requires 25.3% U, 40.9% C, 4.0% H, 4.5% N, 9.9% P and 10.2% S. $U(cp)(NCS)_3$ ·3mdppo was prepared in the same way. The yield was 68%. The results of analysis showed 21.0% U, 49.5% C, 3.9% H, 3.6% N, 8.1% P and 7.8% S. $UC_{47}H_{44}N_3O_3P_3S_3$ requires 21.2% U, 50.1% C, 3.9% H, 3.7% N, 8.3% P and 8.5% S.

3. Results and discussion

3.1. The complexes

The uranium(IV) complexes $U(cp)Cl_3 \cdot 2PR_3O$ ($R_3 \equiv CH_3(C_6H_5)_2$, $(CH_3)_2C_6H_5$ and $(CH_3)_3$) were obtained as green solids by addition of the stoichiometric quantity of the phosphine oxide to a thf solution of U(cp)- $Cl_3 \cdot 2$ thf. The complexes crystallized from the supernatant on evaporation to small volume. The attempted preparation of the analogous thorium(IV) complexes in the same way yielded precipitates of variable analytical composition, the IR spectra of which did not show any features assignable to the C_5H_5 group. These products presumably result from disproportionation of the expected complexes Th(cp)Cl_3 \cdot xPR_3O to the relatively insoluble [10] thorium tetrachloride complexes and Th(cp)_3Cl, which would remain in solution, but this could not be confirmed.

Th(cp)Cl₃·2thf was prepared by the reaction of ThCl₄ in thf with the stoichiometric quantity of Tl(cp), a route previously reported [1] to yield Th(cp)Cl₃·2.5thf, which suggests that the additional thf in the latter was only loosely held and was removed in this work by the more prolonged vacuum drying of the product. The white complexes Th(CH₃cp)Cl₃·2thf and Th(cp)Cl₃·3CH₃CN were obtained in the same way as Th(cp)Cl₃·2thf, using thf and CH₃CN respectively as the solvents for the preparation.

The N-thiocyanate complexes $U(cp)(NCS)_3 \cdot 3PR_3O$ ($R_3 \equiv (CH_3)_2C_6H_5$ and $CH_3(C_6H_5)_2$) were prepared from the tetrachloride in thf by reaction with the stoichiometric quantities of Tl(cp) and KNCS, followed by addition of an excess of the phosphine oxide and evaporation of the supernatant to dryness. The oily residue solidified on repeated washing with a 1:1 mixture of thf and *n*-pentane. This procedure failed to yield identifiable products with tmpo, and the corresponding reactions with $ThCl_4$ were also unsuccessful.

Application of the cone angle factor (CAF) approach to steric crowding [7] in the bis phosphine oxide complexes $U(cp)Cl_3 \cdot 2R_3PO$ ($R_3 \equiv (CH_3)_3$, $(CH_3)_2C_6H_5$ and $CH_3(C_6H_5)_2$ indicated that the probable value of ΣCAF was about 0.8, on the basis of the known structure of $[U(cp)Cl_3(tppo)_2]$. thf [6], while the values for the tris complexes $U(cp)(NCS)_3 \cdot 3R_3PO$ ($R_3 \equiv$ $(CH_3)_2C_6H_5$ and $CH_3(C_6H_5)_2$ were approximately 0.84, both sets of values being close to the range (0.80 ± 0.03 [7]) found for stable uranium(IV) complexes of known structure. The probable values of ΣCAF for $Th(cp)Cl_3 \cdot 2thf$, $Th(CH_3cp)Cl_3 \cdot 2thf$ and $Th(cp)Cl_3 \cdot 3CH_3CN$ are approximately 0.77, 0.83 and 0.85 respectively, close to the average value (0.80 ± 0.04 [14]) for thorium(IV) complexes of known structure. The values of ΣCAF for the complexes $Th(cp)Cl_3 \cdot 2R_3PO$ and $Th(cp)(NCS)_3 \cdot 3R_3PO$ would be expected to be about 0.79 and 0.80 respectively, and it is rather surprising that complexes of this type could not be obtained, particularly since $Th(cp)Cl_3 \cdot 2tpop$ [1] is known.

3.2. UV-visible spectra

The solid reflectance spectra of the complexes $U(cp)Cl_3 \cdot 2L$ ($L \equiv tmpo$, dmppo and mdppo) are very similar to each other (Table 1) and are almost identical with their spectra in CH₃CN solution and with the corresponding spectra of known complexes of this composition (*e.g.* with $L \equiv tppo$ [3]). However, the solid reflectance spectra of the *N*-thiocyanate complexes $U(cp)(NCS)_3 \cdot 3L$ ($L \equiv$ dmppo and mdppo) differ markedly from those of the chloride compounds, with new, relatively strong, bands in the regions at 995 nm (L = mdppo) and 1500 nm (both ligands) while the bands between 1230 and 1280 nm and around 1940 - 1990 nm observed in the spectra of the chloride compounds are absent in the spectra of the *N*-thiocyanates. The thf solution spectra, however, are less clear cut.

3.3. IR spectra

In the IR spectra of the complexes (Table 2), the shifts in $\nu(PO)$ range from 73 cm⁻¹ (U(cp)Cl₃·2tmpo) to 105 cm⁻¹ (U(cp)(NCS)₃·3dmppo), similar to the shifts observed in the spectra of the uranium tetrachloride and tetra-*N*-thiocyanate complexes [10] with these ligands. The observed frequencies of $\nu(UCl)$ are low compared with those of the analogous uranium tetrachloride complexes [10], which are in the range from 252 to 260 cm⁻¹; the assignments of $\nu(ThCl)$, $\nu(Th-C_5H_5)$, $\nu(UCl)$ and $\nu(U-C_5H_5)$ are based on the frequency of the $\nu(U-C_5H_5)$ feature in the spectra of the complexes $U(cp)(NCS)_3 \cdot 3L$ (L = dmppo and mdppo) and they should be regarded as tentative. The frequency of the $\nu(CN)$ feature in the spectra of the *N*-thiocyanate complexes (2030 - 2040 cm⁻¹) is consistent with nitrogen bonding of the thiocyanate group [15], and the intensity of this feature is relatively high, which also suggests nitrogen-bonded thiocyanate [16, 17]. The C-S

TABLE 1

Principal features in the UV-visible spectra of the uranium(IV) complexes (900 - 2000 nm)

Complex	Solid reflectance (nm)	Solution (nm) 1080, 1170, 1270, 1425, 1975 ^a	
U(cp)Cl ₃ •2tmpo	1080 , 1230, 1395, 1680, 1940		
U(cp)Cl ₃ ·2dmppo	1070 , 1250, 1360, 1700, 1810, 1920	1100, 1180, 1275, 1420 , 1980 ^a	
U(cp)Cl ₃ ·2mdppo	1100 , 1280, 1410, 1710, 1820, 1990	1100 , 1180, 1280, 1420 , 1990 ^a	
U(cp)(NCS)3•3dmppo	1120 , 1500, 1630 (sh)	1120 , 1400, 1480, 1620 ^b	
U(cp)(NCS) ₃ ·3mdppo	99 5, 1140 , 1440, 1790	1150 , 1540 ^b	

sh, shoulder; the most intense bands are indicated by bold type. ^aIn CH_3CN . ^bIn thf.

TABLE 2

The IR spectra of the complexes

Complex	$\nu(PO)$ (cm ⁻¹)	$\Delta v(PO)$ (cm ⁻¹)	$\nu(CH)$ of C_5H_5 (cm ⁻¹)	v(MCl) (cm ⁻¹)	$\nu(M-C_5H_5)$ (cm ⁻¹)
Th(cp)Cl ₃ ·2thf			802 (s)	248 (s)	270 (s)
Th(CH ₃ cp)Cl ₃ ·2thf	_		795 (s)	248 (s)	260 (s)
$Th(ep)Cl_3 \cdot 3CH_3CN$	_		795 (s)	240 (m)	260 (m)
$U(cp)Cl_3 \cdot 2tmpo$	1090 (s)	73	782 (s)	230 (m)	252 (s)
U(cp)Cl ₃ ·2dmppo	1080 (s)	95	792 (s)	232 (s)	258 (s)
$U(cp)Cl_3 \cdot 2mdppo$	1095 (s)	80	790 (s)	238 (s)	258 (m)
U(cp)(NCS) ₃ ·3dmppo	1070 (s)	105	790 (s)	a	260 (s)
U(cp)(NCS) ₃ ·3mdppo	1092 (s)	83	795 (s)	b	255 (m)
	1082 (s)	93			. ,

s, strong; m, medium.

 $^{a}\nu(CN) = 2040 \text{ cm}^{-1}$ (s).

 $^{\rm b}\nu({\rm CN}) = 2030 \ {\rm cm}^{-1}$ (s).

mode, which should appear at 760 - 800 cm^{-1} in the IR spectra of nitrogenbonded thiocyanates or at 700 cm⁻¹ for sulphur-bonded thiocyanate [18, 19], could not be identified in the spectra because of interference from modes arising from the organic ligands.

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