SOME PHOSPHINE OXIDE COMPLEXES OF THORIUM(IV) AND URANIUM(IV) TETRACHLORIDE AND TETRA-*N*-THIOCYANATES

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Summary

The complexes $MCl_4 \cdot xL$ ($x = 2$, M ≡ U, L ≡ $P(CH_3)_2(C_6H_5)O$ (dmppo); $x = 2.5$, M ≡ U, L ≡ $PCH_3(C_6H_5)_2O$ (mdppo); $x = 3$, M ≡ Th and U, L ≡ mdppo; $x = 3.5$, M ≡ Th and U, L ≡ dmppo and mdppo) have been prepared. The IR and UV–visible (M ≡ U only) spectra of the complexes are reported, and some possible coordination arrangements for the tetrachloride complexes are discussed in terms of a cone angle factor approach to steric crowding about the metal atoms in these compounds.

1. Introduction

A variety of trimethylphosphine oxide (tmpo) complexes $MCl_4 \cdot x$tmpo have been recorded for M ≡ Th (with $x = 2$, 3 [1] or 6 [2]) and M ≡ U (with $x = 2$ [2 - 4], 3 [2, 3] or 6 [2, 4]), whereas only bis complexes $MCl_4 \cdot 2L$ appear to be formed with the bulkier triphenylphosphine oxide (tppo) for M ≡ Th [1, 5 - 7] and M ≡ U [3 - 5, 7, 8] and with PEt_2PhO (Et ≡ C_2H_5; Ph ≡ C_6H_5) and $PEtPh_2O$ for M ≡ Th [1] and U [3]. However, the 1:2 stoichiometry reported for the PEt_2PhO and $PEtPh_2O$ complexes is limited by the preparative methods used, namely chlorine oxidation in a hot ethanol solution containing the stoichiometric quantities of $ThCl_4$ and the phosphine [1] or the phosphonium salt $[PRR'_2H]_2UCl_6$ (R, R' ≡ Et or Ph) [3], although the bis complexes with $ThCl_4$ seem also to have been obtained by adding $ThCl_4$ to hot tetrahydrofuran (thf) containing an excess of the ligand [1]. Analogous complexes of the *N*-thiocyanates $M(NCS)_4 \cdot xL$ are known for L ≡ tmpo (with $x = 6$ for M ≡ Th and $x = 4$ for M ≡ U) and L ≡ tppo (with $x = 4$ for M ≡ Th and U) [9]. The structures of $UCl_4 \cdot 6$tmpo [10] and $UCl_4 \cdot 2$tppo [11] have been reported, the former being ionic $[UCl(tmpo)_6]^{3+}3Cl^-$, whereas the latter is a neutral *cis* octahedral complex, although an unstable *trans* octahedral isomer has also been reported [12]. It was therefore of interest to prepare complexes of the tetrachlorides and tetra-*N*-thiocyanates with the slightly less bulky alkaryl phosphine oxides PMe_2PhO (dmppo) (Me ≡ CH_3) and $PMePh_2O$ (mdppo) in order to examine the effects of the increasing bulk of the ligand in the series $PMe_xPh_{3-x}O$ (from $x = 0$ to $x = 3$).

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2. Experimental details

2.1. Materials

$ThCl_4$ [13], UCl_4 [14] and tmpo [15] were prepared by published methods and dmppo was prepared in the same way as tmpo using $PhPOCl_2$ (K and K Laboratories); mdppo was prepared by dequaternization of $MePh_3P^+I^-$ with sodium hydroxide [16]. The quaternary phosphonium salt was obtained by the standard method, reaction of PPh_3 with MeI in toluene. All the experimental work, including the drying of solvents and the handling of the air- and moisture-sensitive tetrahalides and complexes, was carried out as described previously [17, 18].

2.2. Physical measurements

IR and UV–visible spectra were obtained as described previously [19].

2.3. Preparative methods

(a) $UCl_4 \cdot 3$mdppo was prepared by adding an excess of mdppo (1.12 g, 5.18 mmol) to a solution of UCl_4 (0.48 g, 1.26 mmol) in thf (30 cm^3). The complex separated as a green solid on stirring overnight, was washed with thf (3×5 cm^3) and then vacuum dried (8 h). The yield was 72%. The results of analysis were as follows: 22.7% U, 45.4% C, 3.8% H, 13.7% Cl and 9.1% P. $UC_{39}H_{39}Cl_4O_3P_3$ requires 23.1% U, 45.5% C, 3.8% H, 13.8% Cl and 9.0% P.

The following complexes were prepared in a similar manner from thf.

(1) The yield of $ThCl_4 \cdot 5$tmpo was 85% and the results of analysis showed 27.3% Th, 22.0% C, 5.5% H, 17.4% Cl and 17.8% P. $ThC_{15}H_{45}Cl_4O_5P_5$ requires 27.8% Th, 21.6% C, 5.4% H, 17.0% Cl and 18.6% P.

(2) The yield of $UCl_4 \cdot 4$tmpo was 84% and the results of analysis showed 31.3% U, 19.8% C, 5.1% H, 18.6% Cl and 17.0% P. $UC_{12}H_{36}Cl_4O_4P_4$ requires 31.8% U, 19.3% C, 4.8% H, 18.9% Cl and 16.6% P.

(3) The yield of $2ThCl_4 \cdot 7$dmppo was 85% and the results of analysis showed 24.8% Th, 36.8% C, 4.4% H, 15.6% Cl and 11.5% P. $Th_2C_{56}H_{77}Cl_8O_7P_7$ requires 25.4% Th, 36.8% C, 4.25% H, 15.5% Cl and 11.9% P.

(4) The yield of $2UCl_4 \cdot 7$dmppo was 82% and the results of analysis showed 26.5% U, 36.3% C, 4.5% H, 15.7% Cl and 11.3% P. $U_2C_{56}H_{77}Cl_8O_7P_7$ requires 26.0% U, 36.7% C, 4.2% H, 15.5% Cl and 11.8% P.

(5) The yield of $ThCl_4 \cdot 3$mdppo was 80% and the results of analysis showed 23.2% Th, 45.0% C, 3.7% H, 14.4% Cl and 8.6% P. $ThC_{39}H_{39}Cl_4O_3P_3$ requires 22.7% Th, 45.8% C, 3.8% H, 13.9% Cl and 9.1% P.

(b) $2UCl_4 \cdot 5$mdppo was obtained by dissolving $UCl_4 \cdot 3$mdppo (0.3 g) in methyl cyanide (15 cm^3), followed by addition of thf (15 cm^3) and a few drops of *n*-pentane. The green crystalline product which separated on standing for 3 days was washed with a 1:1 (by volume) mixture of thf and *n*-pentane (3×5 cm^3) and then vacuum dried (6 h). The yield was 30%. The results of analysis showed 25.8% U, 42.4% C, 3.7% H, 15.6% Cl and 8.6% P. $U_2C_{65}H_{65}Cl_8O_5P_5$ requires 25.9% U, 42.4% C, 3.5% H, 15.4% Cl and 8.4% P.

(c) $UCl_4 \cdot 2dmppo$ separated as a very pale green precipitate when the stoichiometric quantity of dmppo (0.42 g, 2.73 mmol) was added to a solution of UCl_4 (0.52 g, 1.37 mmol) in thf (30 cm^3). The mixture was stirred for 12 h and then the product was washed and dried as in (a). The yield was 76%. The results of analysis showed 34.6% U, 28.2% C, 3.3% H, 19.8% Cl and 9.2% P. $UC_{16}H_{22}Cl_4O_2P_2$ requires 34.6% U, 27:9% C, 3.2% H, 20.6% Cl and 9.0% P.

(d) $Th(NCS)_4 \cdot 4dmppo$ was prepared by treating $ThCl_4$ (0.48 g, 1.28 mmol), dissolved in thf (30 cm^3), with the stoichiometric amount of KNCS (0.50 g, 5.15 mmol). After stirring for 12 h, an excess of dmppo (1.36 g, 8.83 mmol) was added; the mixture was then stirred for 18 h, after which the supernatant was evaporated to dryness. The white residue was washed with a 1:2 (by volume) mixture of toluene and *n*-pentane (3 × 5 cm^3) and vacuum dried (8 h). The yield was 40%. The results of analysis showed 21.2% Th, 40.4% C, 4.2% H, 4.9% N, 11.6% P and 11.7% S. $ThC_{36}H_{44}N_4O_4P_4S_4$ requires 21.5% Th, 40.0% C, 4.1% H, 5.2% N, 11.5% P and 11.9% S.

The following were obtained in the same way.

(1) The yield of $U(NCS)_4 \cdot 4dmppo$ was about 50% and the results of analysis showed 21.2% U, 38.9% C, 3.8% H, 4.9% N, 11.1% P and 12.1% S. $UC_{36}H_{44}N_4O_4P_4S_4$ requires 21.9% U, 39.8% C, 4.1% H, 5.2% N, 11.4% P and 11.8% S.

(2) The yield of $Th(NCS)_4 \cdot 4mdppo$ was about 50% and the results of analysis showed 17.1% Th, 49.9% C, 3.9% H, 4.5% N, 8.9% P and 10.0% S. $ThC_{56}H_{52}N_4O_4P_4S_4$ requires 17.5% Th, 50.6% C, 3.9% H, 4.2% N, 9.3% P and 9.7% S.

(3) The yield of $U(NCS)_4 \cdot 4mdppo$ was about 50% and the results of analysis showed 17.3% U, 50.7% C, 3.9% H, 3.8% N, 9.4% P and 10.2% S. $UC_{56}H_{52}N_4O_4P_4S_4$ requires 17.8% U, 50.4% C, 3.7% H, 4.2% N, 9.3% P and 9.6% S.

3. Results and discussion

3.1. The complexes

The white thorium(IV) and green uranium(IV) tetrachloride complexes were prepared by reaction of the metal tetrachloride with the appropriate ligand in non-aqueous media. In the preparations using an excess of ligand, products of composition $ThCl_4 \cdot 5tmpo$, $UCl_4 \cdot 4tmpo$, $MCl_4 \cdot 3mdppo$ (M ≡ Th, U) and $2MCl_4 \cdot 7dmppo$ (M ≡ Th, U) were obtained, whereas with the stoichiometric quantity of dmppo the complex $UCl_4 \cdot 2dmppo$ was isolated. However, $ThCl_4 \cdot 2dmppo$ could not be obtained pure by this method. $UCl_4 \cdot 3mdppo$ yielded the complex $2UCl_4 \cdot 5mdppo$ on recrystallization, but $ThCl_4 \cdot 3mdppo$ did not degrade in this way.

In an attempt to ascertain the possible bonding arrangements in these complexes, the cone angle factor (CAF) approach to steric crowding [20] was applied to them. The calculated values of ΣCAF for 17 uranium(IV)

compounds of known structure average 0.80 ± 0.03 [20] and for values of ΣCAF less than 0.77, secondary crowding arising from bulky groups R in phosphine oxides PR_3O, such as $R \equiv C_6H_5$ or $(CH_3)_2N$, is necessary to achieve the formation of stable complexes. The average value of ΣCAF calculated for 20 thorium(IV) complexes of known structure is 0.80 ± 0.04 [21]. The average values of CAF for the oxygen atom of a phosphine oxide are 0.10 for thorium(IV) and 0.11 for uranium (IV), and the values for a terminal chlorine atom and the nitrogen atom of the NCS group are 0.14 and 0.11 respectively for both thorium(IV) and uranium(IV) [21].

The solid reflectance spectrum of the dmpo complex $2UCl_4 \cdot 7$dmppo includes bands at 1110, 1380 and 1560 nm, suggesting the presence of a seven-coordinate uranium(IV) centre as found for $[U(NCS)_4(dmiba)_3]$ (dmiba ≡ $Me_2CHCONMe_2$) in the spectrum of which these bands appear at 1130, 1390 and 1590 nm [22]. However, the spectrum of the complex in methyl cyanide solution exhibits both six- and seven-coordinate uranium(IV) features respectively at 1090, 1920 and 1950 nm and at 1125, 1350 and 1570 nm. This suggests that in the complexes $2MCl_4 \cdot 7$dmppo (M ≡ Th, U) there are two centres, the most likely forms being $[MCl(dmppo)_6]^{3+}$-$[MCl_5(dmppo)]^-2Cl^-$, for which the values of ΣCAF for the complex cation and anion would be 0.74 and 0.80 for M ≡ Th and 0.80 and 0.81 for M ≡ U. A less likely alternative for M ≡ Th only would be $[ThCl(dmppo)_7]^{3+}$-$[ThCl_6]^{2-}Cl^-$, for which ΣCAF would be 0.84 for both complex ions.

The solid reflectance spectrum of $2UCl_4 \cdot 5$mdppo shows six-coordinate (1100, 1895 and 1950 nm) and seven-coordinate uranium(IV) (1130, 1370 and 1660 nm) features, although its solution spectrum in methyl cyanide is predominantly that of six-coordinate uranium(IV). The reflectance spectrum suggests that the complex may be similar in structure to $2UCl_4 \cdot 5$depa (depa ≡ $EtCONEt_2$), $[UCl_3(depa)_4]^+[UCl_5(depa)]^-$ [23], but if so the values of ΣCAF for the cation and anion would be 0.86 and 0.81 respectively, whereas the corresponding values for $[UCl_2(mdppo)_5]^{2+}[UCl_6]^{2-}$ would be 0.83 and 0.84 respectively, which seems more likely.

For $UCl_4 \cdot 3$mdppo the solid reflectance spectrum shows a six-coordinate uranium(IV) feature at 1090 nm and seven-coordinate features at 1130, 1405, 1640 and 1670 nm, while in methyl cyanide solution additional six-coordinate features at 1930 and 1980 nm are prominent. Consequently the tris complexes $MCl_4 \cdot 3$mdppo (M ≡ Th, U) are unlikely to be either neutral species (ΣCAF = 0.86 (thorium) or ΣCAF = 0.89 (uranium)) or analogous to $UCl_4 \cdot 3$dmso (≡ $[UCl_2(dmso)_6]^{2+}[UCl_6]^{2-}$ [24]) (dmso ≡ dimethyl sulphoxide), with values of ΣCAF for the cation and anion of 0.88 and 0.84 (thorium) and 0.94 and 0.84 (uranium), but are more likely to be of the form $[MCl_2(mdppo)_5]^{2+}[MCl_5(mdppo)]^-Cl^-$, with ΣCAF = 0.78 and 0.80 (thorium), and ΣCAF = 0.83 and 0.81 (uranium).

The solid reflectance and solution spectra of $UCl_4 \cdot 4$tmpo show the presence of a six-coordinate uranium(IV) centre, but no evidence for other coordination number sites could be obtained. It is possible that the structures of the tmpo complexes may be related to that of $UCl_4 \cdot 6$tmpo

($\equiv [UCl(tmpo)_6]^{3+}3Cl^-$ [10]), with $ThCl_4 \cdot 5tmpo$ probably of the form $[ThCl_2(tmpo)_5]^{2+}2Cl^-$ ($\Sigma CAF = 0.78$), and $UCl_4 \cdot 4tmpo$ possibly of the form $[UCl_2(tmpo)_4]^{2+}2Cl^-$ ($\Sigma CAF = 0.72$), but these are only speculations and crystal structure determinations are required to confirm or disprove all the above-suggested structures.

The corresponding *N*-thiocyanates $M(NCS)_4 \cdot 4L$ prepared from the tetrachloride and the stoichiometric quantity of KNCS in thf, together with an excess of the ligand, are probably neutral complexes for M ≡ Th ($\Sigma CAF = 0.84$) but, although this seems rather unlikely for the uranium analogues ($\Sigma CAF = 0.88$), their solid reflectance and solution (in thf) spectra are consistent with the presence of eight-coordinate uranium(IV), being almost identical with the spectrum of $U(NCS)_4 \cdot 4dmpa$ (dmpa ≡ $EtCONMe_2$) [22], so that an ionic species of the form $[U(NCS)_3L_4]^+NCS^-$ ($\Sigma CAF = 0.77$) seems to be ruled out.

3.2. IR spectra

In the IR spectra of the complexes (Table 1), the shifts in ν_{PO} for the dmppo and mdppo complexes are intermediate between those observed [2, 3, 9] for the known tmpo and tppo complexes except for $UCl_4 \cdot 2dmppo$, for which the shift is comparable with that reported [3] for $UCl_4 \cdot 2tppo$. In the spectra of the *N*-thiocyanate complexes, ν_{CN} appears at 2015 - 2080 cm^{-1}, which is consistent with nitrogen bonding of the thiocyanate group [25] and the relatively high intensity of this feature also suggests nitrogen-bonded thiocyanate [26, 27]. The C—S mode in the IR spectra of nitrogen-bonded thiocyanates usually appears at 760 - 880 cm^{-1}, compared with 700 cm^{-1} for sulphur-bonded thiocyanate [28, 29], but this feature could not be identified in the spectra owing to interference from modes arising

TABLE 1

The IR spectra of the complexes

Complex	ν_{PO} (cm^{-1})	$\Delta\nu_{PO}$ (cm^{-1})	ν_{M-Cl} (cm^{-1})	ν_{CN} (cm^{-1})
$ThCl_4 \cdot 5tmpo$	1105	58 [a]	250	—
$UCl_4 \cdot 4tmpo$	1070	93 [b]	252	—
$2ThCl_4 \cdot 7dmppo$	1090	85	260	—
$2UCl_4 \cdot 7dmppo$	1088	87	255	—
$UCl_4 \cdot 2dmppo$	1045	130	260	—
$ThCl_4 \cdot 3mdppo$	1080	90	248	—
$UCl_4 \cdot 3mdppo$	1080	90	255	—
$2UCl_4 \cdot 5mdppo$	1070	100	255	—
$Th(NCS)_4 \cdot 4dmppo$	1065	110	—	2020
$U(NCS)_4 \cdot 4dmppo$	1070	105	—	2015
$Th(NCS)_4 \cdot 4mdppo$	1070	100	—	2040
$U(NCS)_4 \cdot 4mdppo$	1080	90	—	2080, 2040

[a] $\Delta\nu_{PO}$ = 88 and 101 cm^{-1} for $ThCl_4 \cdot 6tmpo$ [2].
[b] $\Delta\nu_{PO}$ = 101 cm^{-1} for $UCl_4 \cdot 6tmpo$ [2].

from the organic ligands. Solution IR spectra showed that all the neutral ligand molecules were bonded to the metal atom.

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