SOME OXYGEN-DONOR COMPLEXES OF CYCLOPENTADIENYL THORIUM(IV) HALIDES*

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Summary

The complexes $[Th(cp)X_3L_y]$ (cp = $\eta^5 \cdot C_5H_5$; when y = 2, X = Br, L = thf and X = Cl, L = tppo; when y = 2.5, X = Cl, L = thf, dma and X = Cl, Br, L = dmpva; when y = 3.5, X = Br, L = dma), $[Th(cp)Br_3(tppo)_2(thf)]$, $[Th(cp)Cl_3(dma)_{1.5}(napy)]$ and $[ThBr_4(dmpva)_3]$ have been prepared. The attempted preparation of $[Th(cp)_2Cl_2L_y]$ (when y = 2, L = dma, tppo and when y = 1, L = thf, dmpva) resulted in disproportionation. The IR and ¹H NMR spectra of the complexes are discussed.

1. Introduction

The preparation of a series of oxygen-donor complexes of the cyclopentadienyl uranium(IV) halides $[U(cp)X_3L_2]$ (X = Cl, Br; L = MeCONMe₂ (dma), Me₃CCONMe₂(dmpva) and PPh₃O(tppo)) has been described in an earlier paper, in which it was shown that the replacement of a halogen atom in the complexes by a further cp group led to disproportionation to a mixture of compounds of the type $[U(cp_3)X]$ and $[U(cp)X_3L_y]$, together with the free ligand [1]. Compounds containing the Th(cp)Cl₃ entity have not previously been recorded, so it was of interest to examine Th(cp)Cl₃oxygen-donor ligand systems in order to ascertain whether the larger radius of the thorium(IV) ion (99 pm as compared with 93 pm for uranium(IV)) had any effect upon the stoichiometry of the complexes formed; such an effect has been found, for example, with the dma complexes of the tetrachlorides [2] [ThCl₄(dma)₄] and 2UCl₄·5dma.

2. Experimental

2.1. Materials

Thorium tetrachloride [3] and tetrabromide [3, 4], $[ThCl_4(dma)_4]$ [5], $[ThBr_4(dma)_5]$ [2], $[ThCl_4(dmpva)_2]$ [6], Tl(cp) [7] and 1,8-naphthyridine (napy) [8] were prepared by published methods; tppo (B.D.H.) was re-

^{*}Dedicated to Professor F. Fairbrother, founder editor of the journal (1959 · 1977).

crystallized twice from ethyl acetate. All the experimental work, including the drying of solvents and the handling of the air-sensitive and moisture-sensitive products, was carried out as described previously [6, 9, 10].

2.2. Physical measurements

¹H NMR and infrared spectra were obtained as described previously [10]. The ¹H NMR spectra were run in d⁶-acetone unless otherwise stated.

2.3. Preparative methods

(a) ThBr₄ (dmpva)₃ was prepared in the same way as ThCl₄ (dmpva)₂ [6] (yield, 58%). Analysis showed: Th, 25.1; C, 26.6; H, 4.8; N, 4.5; Br, 34.6%. ThC₂₁H₄₅N₃Br₄O₃ requires: Th, 24.7; C, 26.8; H, 4.8; N, 4.5; Br, 34.1%.

(b) $\text{Th}(\eta^5 - \text{C}_5 \text{H}_5)\text{Cl}_3(\text{thf})_{2.5}$ was prepared by adding Tl(cp) (0.7257 g, 2.698 mmol) to ThCl₄ (1.009 g, 2.698 mmol) dissolved in thf (60 cm³); after stirring overnight at room temperature, the colourless supernatant was evaporated *in vacuo* to 5 cm³, causing the colourless product to separate. The product was washed with thf (5 cm³) and vacuum dried (yield 58%). Analysis showed: Th, 40.6; C, 29.5; H, 3.9; Cl, 18.3%. ThC₁₅H₂₅Cl₃O_{2.5} requires: Th, 39.8; C, 30.8; H, 4.3; Cl, 18.3%.

(c) $Th(\eta^5-C_5H_5)Br_3(thf)_2$ was prepared by the method described in (b) (yield, 62%). Analysis showed: Th, 33.9; C, 23.2; H, 3.2; Br, 34.7%. ThC₁₃-H₂₁Br₃O₂ requires; Th, 34.1; C, 22.9; H, 3.1; Br, 35.2%.

(d) Th $(\eta^5 \cdot C_5H_5)Cl_3(dma)_{2.5}$ was prepared by adding Tl(cp) (1.0146 g, 3.771 mmol) to a suspension of ThCl₄(dma)₄(2.7233 g, 3.771 mmol) in thf (50 cm³); after stirring overnight, the supernatant was evaporated to dryness *in vacuo*. The resulting oil yielded the product as a cream powder when triturated with n-pentane; this powder was then vacuum dried (yield, 65%). Analysis showed: Th, 36.2; C, 29.2; H, 4.5; N, 5.8; Cl, 17.1%. ThC₁₅H_{27.5}-N_{2.5}Cl₃O_{2.5} requires: Th, 37.4; C, 29.0; H, 4.4; N, 5.6; Cl, 17.2%.

(e) $\text{Th}(\eta^5 \cdot \text{C}_5\text{H}_5)\text{Br}_3(\text{dma})_{3.5}$ was prepared by the method described in (d); the product of vacuum evaporation was a white solid, which was washed with n-pentane (2 × 3 cm³) and vacuum dried (yield, 80%). Analysis showed: Th, 27.7; C, 27.2; H, 4.6; N, 6.1; Br, 28.2%. ThC₁₉H_{36.5}H_{3.5}Br₃O_{3.5} requires: Th, 27.6; C, 27.1; H, 4.3; N, 5.8; Br, 28.5%.

(f) Th(η^{5} -C₅H₅)Cl₃ (dmpva)_{2.5} was prepared by the method described in (d) (yield, 55%). Analysis showed: Th, 32.7; C, 36.9; H, 5.9; N, 4.2; Cl, 14.8%. ThC_{22.5}H_{42.5}N_{2.5}Cl₃O_{2.5} requires: Th, 32.0; C, 37.2; H, 5.9; N, 4.8; Cl, 14.7%.

(g) $Th(\eta^5-C_5H_5)Br_3(dmpva)_{2.5}$ was prepared by the method described in (d) (yield, 62%). Analysis showed: Th, 27.1; C, 30.6; H, 4.9; N, 4.25; Br, 28.4%. $ThC_{22.5}H_{42.5}N_{2.5}Br_3O_{2.5}$ requires: Th, 27.0; C, 31.4; H, 4.1; N, 4.9; Br, 27.9%.

(h) Th $(\eta^5$ -C₅H₅)Cl₃ (dma)_{1.5} (napy) was prepared by adding 1,8-naphthyridine (napy, 0.1986 g, 1.52 mmol) to a solution of Th $(\eta^5$ -C₅H₅)Cl₃-(dma)_{2.5} (0.6325 g, 1.01 mmol) in thf (40 cm³). The product precipitated as a white solid which was washed with thf $(4 \times 3 \text{ cm}^3)$ and vacuum dried (yield, 82%). The same product was obtained with a 3:1 molar ratio (napy: Th) of the reactants. Analysis showed: Th, 36.0; C, 34.3; H, 3.6; N, 6.7; Cl, 16.0%. ThC₁₉H_{24.5}N_{3.5}Cl₃O_{1.5} requires: Th, 34.9; C, 34.3; H, 3.7; N, 7.4; Cl, 16.0%.

(i) Th $(\eta^5$ -C₅H₅)Cl₃ (tppo)₂ was prepared by adding an excess of tppo (0.8 g, 2.878 mmol) in thf (10 cm³) to a solution of Th $(\eta^5$ -C₅H₅)Cl₃ (thf)_{2.5} in thf (20 cm³); the white precipitate was washed with thf (4 × 3 cm³) and vacuum dried (yield, 85%). Analysis showed: Th, 24.1; C, 51.2; H, 3.7; Cl, 10.7%. ThC₄₁H₃₅Cl₃O₂P₂ requires: Th, 24.2; C, 51.3; H, 3.65; Cl, 11.1%.

(j) $Th(\eta^{5}-C_{5}H_{5})Br_{3}$ (tppo)₂ (thf) was prepared by the method described in (i) (yield, 83%). Analysis showed: Th, 19.8; C, 47.2; H, 3.8; Br, 20.3%. $ThC_{45}H_{43}Br_{3}O_{3}P_{2}$ requires: Th, 19.9; C, 46.4; H, 3.7; Br, 20.6%.

2.2. Analyses

The analyses were carried out as described previously [10, 11].

3. Results and discussion

3.1. Thorium(IV) complexes

All the complexes were white or cream solids, obtained by the reaction of thallium cyclopentadienide with thorium tetrachloride or tetrabromide (thf adducts) or with the appropriate oxygen-donor (dma, dmpva) complexes of the tetrahalides; the tppo and napy complexes precipitated on the addition of the ligand to solutions of the thf and dma complexes of Th(cp)Cl₃, respectively. Reaction of $(\eta$ -C₅H₅)ThCl₃L_x (x = 2, L = tppo; x = 2.5, L = thf, dmpva) with the stoichiometric quantity of Tl(C₅H₅) in thf followed by evaporation of the supernatant to dryness *in vacuo* yielded products of the approximate composition $(\eta$ -C₅H₅)₂ThCl₂L_y (y = 1, L = thf, dmpva; y = 2, L = tppo); the analogous reaction of ThCl₄ (dma)₄ with Tl(C₅H₅) (molar ratio Th:Tl(C₅H₅), 1:2) likewise yielded a product with a composition close to $(\eta$ -C₅H₅)₂ThCl₂ (dma)₂. However, it was not possible to prove that these were genuine compounds; it is probable that they are mixtures of disproportionation products, such as are found in the analogous uranium(IV) systems [1].

3.2. IR spectra

In the IR spectra of the complexes (Table 1), the shifts in ν (CO) (dma, dmpva) and ν (PO) (tppo) in the complexes containing these ligands were similar to, although somewhat smaller than, those observed in the spectra of the corresponding uranium(IV) complexes [1]. In the IR spectra of the thf complexes, very strong features appear at around 1000 and 840 cm⁻¹; these can be assigned to the asymmetric and symmetric C-O-C stretching vibrations of coordinated thf. Relative to the spectrum of free thf, these features are shifted to lower frequencies by approximately 70 cm⁻¹; it

TABLE 1

The	infrared	spectra	of	the	complexes	(cm^{-1}))
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Complex	Ligand vibrations	ν (Th–Cl)	ν (Th-C ₅ H ₅)
$ThBr_4(dmpva)_3$	$\nu(CO), 1575vs; \Delta\nu(CO), 57$		
$Th(cp)Cl_3(thf)_{2.5}$	$\nu_{as}(COC), 1000vs; \Delta \nu_{as}(COC), 65$ $\nu_{s}(COC), 845vs; \Delta \nu(COC), 64$	270s ^a (?)	252s ^a
$Th(cp)Br_3(thf)_2$	$\nu_{as}(COC), 995vs; \Delta \nu_{as}(COC), 70$ $\nu_{s}(COC), 840vs; \Delta \nu_{s}(COC), 69$		264vs
$\nu(CO), 1600vs; \Delta\nu(CO), 47$		234s	
$Th(cp)Br_3(dma)_{3,5}$	$\nu(CO), 1600vs; \Delta\nu(CO), 47$		246m
$Th(cp)Cl_3(dmpva)_{2,5}$	$\nu(CO), 1575vs; \Delta\nu(CO), 57$	231s	
$Th(cp)Br_3(dmpva)_{2.5}^{b}$	ν (CO), 1630m; 1575vs $\Delta \nu$ (CO), 0, 57		246s
$Th(cp)Cl_3(dma)_{1,5}(napy)$	$\nu(CO), 1615vs; \Delta\nu(CO), 32$	251s	230s
$Th(cp)Cl_3(tppo)_2$	$\nu(PO), 1080s; \Delta\nu(PO), 110$	261s	234s ^a
$Th(cp)Br_3(tppo)_2(thf)$	ν (PO), 1080s; $\Delta \nu$ (PO), 110 ν_{as} (COC), 1000s ^a		243m

^a Tentative assignment.

^bSpectra as solid (mull) and in CH₂Cl₂ solution.

vs = very strong; s = strong; m = medium.

therefore appears that all the thf is bonded to the metal atom. This is consistent with the observation that none of the thf could be removed from $Th(cp)Cl_3(thf)_{2.5}$ by washing the solid with n-pentane or by heating it at 70 °C and 10^{-3} Torr.

In the spectra of the complexes the characteristic cp vibrations appeared as strong features in the ranges $1012 \cdot 1031 \text{ cm}^{-1}$ and $780 \cdot 798 \text{ cm}^{-1}$; strong features in the range $252 \cdot 261 \text{ cm}^{-1}$ were assigned to $\nu(\text{Th-Cl})$, except for $\text{Th}(\text{cp})\text{Cl}_3\text{L}_{2.5}$ (L = dma, dmpva) in the spectra of which this feature was not resolved from $\nu(\text{Th-C}_5\text{H}_5)$. The broad strong bands at 234 cm^{-1} (dma) and 231 cm^{-1} (dmpva) presumably include $\nu(\text{Th-Cl})$. Higher frequency features in the range $230 \cdot 264 \text{ cm}^{-1}$ were assigned to $\nu(\text{Th-C}_5\text{H}_5)$, but the assignments to $\nu(\text{Th-C}_5\text{H}_5)$ and to $\nu(\text{Th-Cl})$ should be regarded as tentative.

In the IR spectrum of $Th(cp)Cl_3$ (dma)_{1.5} (napy) the skeletal modes of napy are shifted to higher frequency on complexation, from 403, 600, 760, 1026, 1045, 1128 and 1556 cm⁻¹ to 423, 630, 803, 1035, 1056, 1145 and 1580 cm⁻¹, respectively.

3.3. ¹H NMR spectra

All resonances are reported as τ values (TMS = 10 τ). In the spectra of the thf complexes a sharp singlet at 3.55 τ (Th(cp)Cl₃ (thf)_{2.5}) or 3.50 τ (Th(cp)Br₃(thf)₂) is due to the cyclopentadienyl ring protons, indicating that the ring is η^5 -bonded to the metal atom in both complexes. The resonances at 6.32 and 8.16 τ (chloride) or 6.39 and 8.21 τ (bromide) are assigned to thf molecules bonded to the thorium atom; the integrals of these

resonances $(C_5H_5:C_4H_8O)$ are in the ratio 1:4 (chloride) and 5:16 (bromide), in agreement with the analytical stoichiometry.

In the spectra of the dma complexes, the sharp singlet due to the cp ring protons is at 3.65 τ (chloride) and 3.49 τ (bromide). A doublet at 6.8 τ (both complexes) is due to the non-equivalence of the two N-CH₃ groups which results from restricted rotation about the C-N bond; the resonances at 7.65 τ (chloride) and 7.69 τ (bromide) are assigned to the C-CH₃ protons of dma. Th(cp)Br₃ (dma)_{3.5} decomposes with the liberation of dma in toluene, benzene and pyridine, as shown by the appearance of free ligand vibrations in the infrared spectrum and confirmed by the ¹H NMR spectrum in d⁶-benzene. The latter exhibits three resonances at 7.31, 7.81 and 8.28 τ (1:1:1) which are due to the methyl protons of the ligand and a sharp singlet at 2.82 τ which is due to the cp ring protons; the integrals of these resonances (C₅H₅:dma) are in the ratio 1:3. Similar dissociation behaviour has been reported for solutions of complexes of uranium tetrabromide with lactams and with N, N-diphenylformamide [12].

The dmpva system appears to be somewhat more complicated than the dma system; the ¹H NMR spectrum of the free ligand at room temperature consists of a singlet at 6.97 τ which is due to the N–CH₃ protons and which indicates free rotation about the C–N bond, and a singlet at 8.75 τ which is due to the C–CH₃ protons, with the integrals in the ratio 2:3. At -90 °C two sharp signals appear at 6.78 and 7.15 τ (1:1) indicating the nonequivalence of the two N-CH₃ groups, the C-CH₃ signal remaining unchanged. The corresponding spectrum of $Th(cp)Cl_3(dmpva)_{25}$ at room temperature consists of N–CH₃ and C–CH₃ resonances at 6.72 and 8.58 τ , respectively, and a sharp singlet at 3.66 τ which is due to the cp ring protons (integrals, C_5H_5 : dmpva = 1:7.5, in agreement with the stoichiometry). The spectrum remains unchanged down to -65 °C, but below this temperature the spectrum indicates both free and bound ligand and at -90 °C sharp resonances appear at 6.77 and 7.14 τ ; these are due to the two nonequivalent N-CH₃ groups of the free dmpva, with the C-CH₃ of the free ligand at 8.76 τ . The proton integration gave a ratio of non-bonded: bonded dmpva of 1:4; the ratio of bonded dmpva: C_5H_5 protons was 6:1. Thus in d^6 -acetone there appears to be an equilibrium of the form

$$2Th(cp)Cl_3(dmpva)_{2,5} \rightleftharpoons 2Th(cp)ThCl_3(dmpva)_2 + dmpva$$

with an exchange of free and bonded ligand which is fast on the NMR time scale at room temperature. The IR spectrum indicates that all the dmpva is bonded in the solid compound, in contrast to the IR spectrum of Th(cp)-Br₃ (dmpva) _{2.5}, which clearly shows the presence of both bonded and nonbonded dmpva in the solid and in solution in dichloromethane. The ¹H NMR spectrum of the bromide at room temperature is very similar to that of the chloride (N-CH₃ protons at 6.72τ , C-CH₃ at 8.58τ and C₅H₅ ring protons at 3.50τ ; integral, C₅H₅:dmpva = 1:7.5); evidence for the free ligand appeared only below -65 °C. At -90 °C resonances due to the free ligand protons appeared at 6.82 and 7.18τ (non-equivalent N-CH₃ groups) and 8.79 τ (C-CH₃ protons); the proton integration again gave a ratio of non-bonded:bonded dmpva of 1:4. On warming to room temperature the spectrum reverted to that described above. Presumably the solid complex contains Th(cp)Br₃ (dmpva)₂ associated with an average of 0.5 mol of dmpva in the lattice.

 $Th(cp)Cl_3(tppo)_2$ is insoluble in acetone or thf but soluble in dichloromethane and methyl cyanide, so that the ¹H NMR spectra were recorded using solutions in CD_2Cl_2 and CD_3CN . The spectrum consists of a multiplet at 2.4 τ which is due to the C₆H₅ ring protons of tppo and a singlet at 3.92 τ which is due to the C_5H_5 ring protons, but the proton integration gave a ratio $(C_5H_5:C_6H_5$ protons) of 2:15 and not 1:6 as expected from the analytical stoichiometry. This suggests that $Th(cp)Cl_3(tppo)_{25}$ is present in the solution, a result which is inexplicable. The corresponding bromide crystallizes as Th(cp)Br₃(tppo)₂(thf); in its IR spectrum ν (P-O) is split, possibly because of the presence of non-equivalent tppo molecules in the crystal, and there is a weak feature at 1192 cm^{-1} which may be due to nonbonded tppo. In its ¹H NMR spectrum in CD_2Cl_2 , the resonances at 6.20 and 7.88 τ (1:1 ratio) are assigned to coordinated thf (the ratio of total tppo:thf protons is 30:8) and the sharp singlet at 3.50τ to the cp ring protons. Two broad resonances at 1.85 and 2.30 τ are attributed to bonded and nonbonded tppo (3:1 ratio) but all attempts to remove free tppo from the solid compound by washing it with thf were unsuccessful; presumably the nonbonded tppo is held quite strongly in the lattice. These results suggest that the formula of the compound should be written as $[Th(cp)Br_3(tppo)]_{1,5}$. $(thf)]_{2}$ ·(tppo).

In the ¹H NMR spectrum of Th(cp)Cl₃(dma)_{1.5}(napy) the three resonances at 0.40, 1.42 and 2.15τ (1:1:1 ratio) are due to H(2,7), H(3,6) and H(4,5) of the napy, respectively, while the doublet at 6.80 τ and the singlet at 7.62 τ are assigned to the N-CH₃ and C-CH₃ protons, respectively, of dma; a sharp singlet at 3.88 τ is due to the cp protons. The spectrum also showed the presence of non-bonded thf of unknown provenance.

3.4. Mass spectra

The molecular ion of highest mass in the spectrum of Th(cp)Cl₃-(dma)_{2.5} is $[Th(cp)Cl_3]_2^*$ (*m/e*, 807) which undergoes asymmetric cleavage to $[Th(cp)Cl_4]^*$ (*m/e*, 439) and, by subsequent loss of chloride, forms the ions $[Th(cp)Cl_x]^*$ (x = 3,2,0); this behaviour may indicate that the parent complex is a dimer involving both bridging and terminal chlorine atoms. In the mass spectrum of Th(cp)Cl₃ (tppo)₂ the parent ion appears to be $[Th(cp)_3 Cl]^*$ (*m/e*, 397.5) which does not appear to lose a cp ring or a chlorine atom. Similar behaviour has been reported for $[U(cp)_3 Cl]$ [13].

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References

- 1 K. W. Bagnall, J. Edwards and A. C. Tempest, J. Chem. Soc., Dalton Trans., (1978) 295.
- 2 K. W. Bagnall, D. Brown, F. Lux and G. Wirth, Z. Naturforsch., Teil B, 24 (1969) 214.
- 3 K. W. Bagnall, D. Brown, P. J. Jones and J. G. H. du Preez, J. Chem. Soc. A, (1966) 737.
- 4 G. W. A. Fowles and F. H. Pollard, J. Chem. Soc., (1953) 4128.
- 5 K. W. Bagnall, D. Brown, P. J. Jones and P. S. Robinson, J. Chem. Soc., (1964) 2531.
- 6 K. W. Bagnall, J. G. H. du Preez, J. Bajorek, L. Bonner, H. Cooper and G. Segal, J. Chem. Soc., Dalton Trans., (1973) 2682.
- 7 E. O. Fischer, Angew. Chem., 69 (1957) 207.
- 8 W. W. Paudler and T. J. Kress, J. Org. Chem., 32 (1967) 832.
- 9 K. W. Bagnall and J. Edwards, J. Organomet. Chem., 80 (1974) C14.
- 10 K. W. Bagnall, J. G. H. du Preez, J. Edwards and R. F. Warren, J. Chem. Soc., Dalton Trans., (1975) 140.
- 11 P. J. Alvey, K. W. Bagnall, D. Brown and J. Edwards, J. Chem. Soc., Dalton Trans., (1973) 2308.
- 12 J. G. H. du Preez, M. L. Gibson and C. P. J. van Vuuren, J. S. Afr. Chem. Inst., 24 (1971) 135.
- 13 M. L. Anderson and L. R. Crisler, J. Organomet. Chem., 17 (1969) 345.