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#### Summary

The complexes ThBr<sub>4</sub>·xL (x = 2, L = CH<sub>3</sub>CON(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub> (dca), CH<sub>3</sub>CON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (dipa), C<sub>2</sub>H<sub>5</sub>CON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (dippa), (CH<sub>3</sub>)<sub>2</sub>CHCON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (dipiba), (CH<sub>3</sub>)<sub>3</sub>CCON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub> (dippva), (CH<sub>3</sub>)<sub>2</sub>CHCON(CH<sub>3</sub>)<sub>2</sub> (dmiba) and (CH<sub>3</sub>)<sub>3</sub>CCON(CH<sub>3</sub>)<sub>2</sub> (dmpva); x = 3, L = dca, C<sub>2</sub>H<sub>5</sub>CON(CH<sub>3</sub>)<sub>2</sub> (dmpa), C<sub>2</sub>H<sub>5</sub>CON(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (depa)), dipa, dippa, dipiba, dmiba and ThBr<sub>4</sub>·2dca·thf (thf = tetrahydrofuran) were prepared. The IR spectra of the complexes are reported and their stoichiometries are discussed in terms of steric crowding about the metal atom using a cone-packing model.

## 1. Introduction

Although several complexes of uranium tetrabromide with N,N-dialkyl carboxylic acid amides have been reported, complexes with thorium tetrabromide, ThBr<sub>4</sub>·xL, are known only for  $L \equiv CH_3CON(CH_3)_2$  (dma) with x = 2,4 [1] or x = 5 [2] and  $L \equiv (CH_3)_3CCON(CH_3)_2$  (dmpva) with x = 3 [3]. The analogous systems with thorium tetrachloride have been widely investigated, and in a recent paper [4] we reported a range of complexes of thorium and uranium tetrachlorides with a series of amides of increasing bulk. We have attempted to correlate the results in terms of a cone-angle approach to steric crowding [5], and this work is extended to the corresponding complexes of thorium tetrabromide in this paper.

#### 2. Experimental details

#### 2.1. Techniques and materials

The handling of air- and moisture-sensitive starting materials and products was carried out as described previously [6]. Solvents were dried as previously reported [7], and ThBr<sub>4</sub> [1] and the amides [7] were prepared using published methods.

## 2.2. Physical measurements

IR spectra were recorded as described previously [7].

# 2.3. Preparative methods

(a) ThBr<sub>4</sub>·3dmpa (dmpa  $\equiv C_2H_5CON(CH_3)_2$ ) was prepared by adding a large excess of dmpa (1.0 g (9.9 mmol)) to a filtered solution of ThBr<sub>4</sub> (0.6 g (1.08 mmol)) in tetrahydrofuran (thf) (10 cm<sup>3</sup>). A slightly yellow oily product separated immediately; this was ground under *n*-pentane, yielding the complex as a white solid which was washed three times with 3 cm<sup>3</sup> of *n*-pentane and was then recrystallized from a mixture of acetone and *n*-pentane. The colourless crystals were then vacuum dried for 8 h. The yield was about 60%. ThC<sub>15</sub>H<sub>33</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 27.1% Th, 21.1% C, 3.9% H, 4.9% N and 37.4% Br. The results of analysis were as follows: 26.9% Th, 20.6% C, 3.9% H, 4.4% N and 36.4% Br.

(b) TnBr<sub>4</sub>·3depa (depa =  $C_2H_5CON(C_2H_5)_2$ ) was prepared as in (a) except that after 30 min the product separated as a white solid which was washed twice with 3 cm<sup>3</sup> of thf, once with *n*-pentane and then vacuum dried for 8 h. The yield was about 80%. ThC<sub>21</sub>H<sub>45</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 24.7% Th, 26.8% C, 4.8% H, 4.5% N and 34.1% Br. The results of analysis were as follows: 24.6% Th, 26.6% C, 4.9% H, 4.5% N and 34.7% Br.

ThBr<sub>4</sub>·3dipiba (dipiba =  $(CH_3)_2CHCON(i-C_3H_7)_2$ ) was prepared in the same way; it was finally washed three times with 5 cm<sup>3</sup> of *n*-pentane before vacuum drying. The yield was about 75%. ThC<sub>30</sub>H<sub>63</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 21.8% Th, 33.8% C, 5.9% H, 3.9% N and 30.0% Br. The results of analysis were as follows: 21.5% Th, 33.9% C, 6.2% H, 3.8% N and 29.5% Br.

(c) ThBr<sub>4</sub>·2dmiba (dmiba  $\equiv$  (CH<sub>3</sub>)<sub>2</sub>CHCON(CH<sub>3</sub>)<sub>2</sub>) was prepared in the same way as ThBr<sub>4</sub>·3dipiba; it was recrystallized by dissolution in 5 cm<sup>3</sup> of acetone, followed by the addition of *n*-pentane until the solution became cloudy. Acetone was then added dropwise until the solution cleared, and needles of the product separated on standing. The yield was about 68%. ThC<sub>12</sub>H<sub>26</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 29.7% Th, 18.4% C, 3.4% H, 3.6% N and 40.9% Br. The results of analysis were as follows: 29.7% Th, 18.4% C, 3.4% H, 3.5% N and 40.8% Br.

(d) ThBr<sub>4</sub>·3dmiba was prepared by adding a large excess of dmiba (0.5 g (4.3 mmol)) to a suspension of ThBr<sub>4</sub>·2dmiba (0.4 g (0.51 mmol)) in 3 cm<sup>3</sup> of thf. After standing overnight the mixture was vacuum evaporated to dryness, leaving an oily residue which yielded a white solid product when ground with toluene and then with *n*-pentane. This was washed three times with 3 cm<sup>3</sup> of *n*-pentane and vacuum dried for 8 h. The yield was about 75%. ThC<sub>18</sub>H<sub>39</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 25.9% Th, 24.1% C, 4.3% H, 4.7% N and 35.6% Br. The results of analysis were as follows: 25.5% Th, 24.0% C, 4.4% H, 4.3% N and 34.8% Br.

(e) ThBr<sub>4</sub>·2dmpva was prepared as in (a) except that the reaction mixture was vacuum evaporated to about 30% of the original volume at which point the product began to crystallize. After standing overnight, the crystals were washed twice with 3 cm<sup>3</sup> of *n*-pentane and vacuum dried for 8 h. The yield was about 60%. ThC<sub>14</sub>H<sub>30</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 28.6% Th, 20.7% C, 3.7% H, 3.5% N and 39.5% Br. The results of analysis were as follows: 29.1% Th, 20.8% C, 3.8% H, 3.4% N and 38.7% Br.

ThBr<sub>4</sub>·3dippa (dippa  $\equiv C_2H_5CON(i-C_3H_7)_2$ ) was prepared in the same way. The yield was 81%. ThC<sub>27</sub>H<sub>57</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 22.7% Th, 31.7% C, 5.6% H, 4.1% N and 31.3% Br. The results of analysis were as follows: 23.1% Th, 31.2% C, 5.5% H, 4.3% N and 30.9% Br.

ThBr<sub>4</sub>·3dca (dca = CH<sub>3</sub>CON(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>) was prepared in the same way as ThBr<sub>4</sub>·2dmpva, except that the crystals were washed twice with 3 cm<sup>3</sup> of *n*-hexane and then twice with 3 cm<sup>3</sup> of *n*-pentane before drying. The yield was about 45%. ThC<sub>42</sub>H<sub>75</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 19.0% Th, 41.3% C, 6.1% H, 3.4% N and 26.2% Br. The results of analysis were as follows: 19.1% Th, 41.3% C, 6.3% H, 3.3% N and 26.1% Br.

ThBr<sub>4</sub>·3dipa (dipa  $\equiv$  CH<sub>3</sub>CON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>) was also prepared in the same way as ThBr<sub>4</sub>·2dmpva, except that crystallization required 3 days. The yield was about 55%. ThC<sub>24</sub>H<sub>51</sub>N<sub>3</sub>Br<sub>4</sub>O<sub>3</sub> requires 23.6% Th, 29.4% C, 5.2% H, 4.3% N and 32.6% Br. The results of analysis were as follows: 23.1% Th, 29.7% C, 5.5% H, 4.5% N and 31.8% Br.

(f) ThBr<sub>4</sub>·2dippva (dippva  $\equiv$  (CH<sub>3</sub>)<sub>3</sub>CCON(*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>) was prepared in the same way as ThBr<sub>4</sub>·3dmpa except that the supernatant from the reaction mixture was vacuum evaporated to dryness, leaving a honeycombed solid which was ground under *n*-pentane, washed three times with 3 cm<sup>3</sup> of *n*pentane and vacuum dried for 8 h. The yield was about 70%. ThC<sub>22</sub>H<sub>46</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 25.2% Th, 28.6% C, 5.0% H, 3.0% N and 34.7% Br. The results of analysis were as follows: 25.0% Th, 28.7% C, 5.1% H, 2.8% N and 34.1% Br.

(g) ThBr<sub>4</sub>·2dca·thf was prepared in the same way as ThBr<sub>4</sub>·3dca, but with the stoichiometric quantity of dca. The yield was about 65%. ThC<sub>32</sub>H<sub>58</sub>·N<sub>2</sub>Br<sub>4</sub>O<sub>3</sub> requires 21.7% Th, 35.9% C, 5.4% H, 2.6% N and 29.9% Br. The results of analysis were as follows: 22.0% Th, 36.5% C, 5.5% H, 2.7% N and 30.2% Br.

(h) ThBr<sub>4</sub>·2dca was prepared by adding a slight excess of dca (0.33 g (1.48 mmol)) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) to a suspension of ThBr<sub>4</sub> (0.4 g (0.72 mmol)) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>). After stirring overnight, *n*-pentane was added to the clear supernatant until crystallization started. The solution was left overnight, the supernatant was decanted and the crystalline product was washed twice with 3 cm<sup>3</sup> of *n*-pentane and then vacuum dried for 5 h. The yield was about 67%. ThC<sub>28</sub>H<sub>50</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 23.3% Th, 33.7% C, 5.0% H, 2.8% N and 32.1% Br. The results of analysis were as follows: 23.8% Th, 33.4% C, 5.3% H, 2.8% N and 32.4% Br.

ThBr<sub>4</sub>·2dippa was prepared in the same way. The yield was about 75%. ThC<sub>18</sub>H<sub>38</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 26.8% Th, 24.9% C, 4.4% H, 3.2% N and 37.0% Br. The results of analysis were as follows: 26.0% Th, 24.7% C, 4.5% H, 3.1% N and 36.5% Br.

ThBr<sub>4</sub>·2dipa was prepared in the same way. The yield was about 65%. ThC<sub>16</sub>H<sub>34</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 27.7% Th, 22.9% C, 4.1% H, 3.3% N and 38.2% Br. The results of analysis were as follows: 28.2% Th, 22.9% C, 4.3% H, 3.3% N and 38.0% Br.

(i) ThBr<sub>4</sub>·2dipiba was prepared by adding *n*-pentane to a solution of ThBr<sub>4</sub>·3dipiba (0.5 g (0.47 mmol)) in dichloromethane (10 cm<sup>3</sup>) until the

solution became cloudy. The solution was cleared by dropwise addition of dichloromethane, and the complex crystallized on standing overnight. The product was washed twice with 3 cm<sup>3</sup> of *n*-pentane and was then vacuum dried for 6 h. The yield was about 50%. ThC<sub>20</sub>H<sub>42</sub>N<sub>2</sub>Br<sub>4</sub>O<sub>2</sub> requires 26.0% Th, 26.8% C, 4.7% H, 3.1% N and 35.8% Br. The results of analysis were as follows: 26.0% Th, 26.5% C, 4.8% H, 3.0% N and 36.0% Br.

## 3. Results and discussion

# 3.1. Preparation and steric crowding effects

The complexes were prepared by treating thorium tetrabromide with an excess of the ligand in thf or  $(ThBr_4 \cdot 2dca, ThBr_4 \cdot 2dipa and ThBr_4 \cdot 2dippa)$  in dichloromethane using only a slight excess of the ligand. ThBr\_4 \cdot 2dipiba was obtained by recrystallizing the tris complex from dichloromethane. The attempted preparation of ThBr\_4 \cdot 2dca and ThBr\_4 \cdot 2dippa by this route was unsuccessful.

Most of the complexes are only slightly soluble in dichloromethane, but are more soluble in thf and in acetone;  $ThBr_4 \cdot 3dipa$ ,  $ThBr_4 \cdot 3dippa$  and  $ThBr_4 \cdot 3dipiba$  are more soluble in dichloromethane than any of the other complexes. The bis complexes  $ThBr_4 \cdot 2L$ , with  $L \equiv dca$ , dipa, dippa, dippva and dipiba, are very hygroscopic.

Accurate values of the Th-Br bond length are not available, and in calculating the total cone angle factors  $\Sigma CAF$  [5] this bond length was estimated from the available data for Th-Cl and U-Br bond lengths, from which the cone angle factor (CAF) and fan angle (FA) for bromine were found to be approximately 0.138 and 43.6° respectively. The "undercrowded" [5] complexes ThCl<sub>4</sub>·2L ( $L \equiv dmpa$  [8], depa [8], dmiba [8], dipa [4] and dippa [4]) could not be isolated ( $\Sigma CAF = 0.72$ ), whereas the analogous complexes ThBr<sub>4</sub>· 2L ( $L \equiv dca$ , dipa, dippa, dipiba, dippva, dmiba and dmpva) ( $\Sigma CAF = 0.76$ ) were obtained in this work. However, with dmpa and depa only the tris complexes  $ThBr_4$ ·3L ( $\Sigma CAF = 0.86$ ) could be obtained, a difference which may be due to smaller secondary steric effects with these two ligands compared with the bulkier ligands dca, dipa, dippa, dipiba, dippva, dmiba and dmpva which would be expected to yield tris complexes that were either unstable with respect to loss of the amide ligand or to ionization as  $[ThBr_3L_3]^+Br^-$ . However, in the latter case the complex cations would be undercrowded ( $\Sigma CAF = 0.72$ ), although they might be stabilized by the large secondary crowding effects of the bulky ligands.

## 3.2. IR spectra

The spectra are summarized in Table 1. The shifts in  $\nu_{CO}$  on coordination of the amide ligands are larger for the tris complexes ThBr<sub>4</sub>·3L (L = dca, dipa, dippa and dmiba) than those in the spectra of the corresponding bis complexes. This may be due to a less crowded situation around the thorium atom in the tris complexes which would support the ionic formulation

# TABLE 1

# The IR spectra of the complexes

Complex		$\nu_{\rm CO}^{a}$ (cm <sup>-1</sup> )	$\Delta \nu_{\rm CO}$ (cm <sup>-1</sup> )
ThBr <sub>4</sub> •2dca	Nujol mull	1561(s)	66
	CH <sub>2</sub> Cl <sub>2</sub> solution	1560(s)	67
	thf solution	1541(s), 1633(w)	86, (—6)
ThBr4·2dca·thf	Nujol mull <sup>b</sup>	1552(s)	75
	CH <sub>2</sub> Cl <sub>2</sub> solution	1544(s,b)	83
	thf solution	1540(s,b), 1632(w)	87, (—5)
ThBr <sub>4</sub> ·3dca	Nujol mull	1546(s)	81
	CH <sub>2</sub> Cl <sub>2</sub> solution	1552(s), 1622(vw)	75, 5
	thf solution	1547(s), 1630(m)	80, (—3)
ThBr4•3dmpa	Nujol mull	1594(s,b)	51
	CH <sub>2</sub> Cl <sub>2</sub> solution	1589(s)	56
	thf solution	1585(s), 1646(w,sh)	60, (—1)
ThBr4•3depa	Nujol mull	1569(s,b)	69
	CH <sub>2</sub> Cl <sub>2</sub> solution	1570(s)	68
	thf solution	1569(s), 1638(w)	69, 0
ThBr4•2dipa	Nujol mull	1577(s)	56
	CH <sub>2</sub> Cl <sub>2</sub> solution	1573(s)	60
	thf solution	1557(s), 1637(w)	76, (4)
ThBr4•3dipa	Nujol mull	1555(s)	78
	CH <sub>2</sub> Cl <sub>2</sub> solution	1554(s)	79
	thf solution	1540(s,b), 1633(w)	93,0
ThBr₄•2dippa	Nujol mull	1555(s,b)	79
	CH <sub>2</sub> Cl <sub>2</sub> solution	1559(s,b)	75
	thf solution	1541(s,b), 1629(m)	93,5
ThBr4•3dippa	Nujol mull	1550(s)	84
	CH <sub>2</sub> Cl <sub>2</sub> solution	1548(s), 1627(vw,sh)	86,7
	thf solution	1540(s), 1635(m)	94,(—1)
ThBr4•2dipiba	Nujol mull	1536(s)	95
	CH <sub>2</sub> Cl <sub>2</sub> solution	1541(s)	90
	thf solution	1537(m), 1633(s)	94, (—2)
ThBr <sub>4</sub> •3dipiba	Nujol mull	1527(s)	104
	CH <sub>2</sub> Cl <sub>2</sub> solution	1531(s), 1620(w)	100,11
	thf solution	1534(m), 1628(s)	97,3
ThBr <sub>4</sub> •2dippva	Nujol mull	1540(s)	90
	CH <sub>2</sub> Cl <sub>2</sub> solution	1531(s), 1612(vw,sh)	99,18
	thf solution	1530(m), 1623(s)	100,7

(continued)

Complex		$\frac{\nu_{\rm CO}}{(\rm cm^{-1}})$	$\Delta \nu_{\rm CO} \ ({\rm cm}^{-1})$
ThBr <sub>4</sub> •2dmiba	Nujol mull	1600(s)	32
	$CH_2Cl_2$ solution	1593(s)	39
	thf solution	1582(s), 1640(w)	50, (-8)
ThBr <sub>4</sub> •3dmiba	Nujol mull	1580(s,b)	52
	$CH_2Cl_2$ solution	1587(s), 1630(vw,sh)	45,2
	thf solution	1580(s), 1640(m)	52, (-8)
ThBr4•2dmpva	Nujol mull	1587(s)	43
	$CH_2Cl_2$ solution	1573(s)	57
	thf solution	1561(s), 1628(w)	69, 2

#### TABLE 1 (continued)

<sup>a</sup>s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder.

<sup>b</sup>An additional feature appears in the spectrum at 972 cm<sup>-1</sup> compared with the spectrum of ThBr<sub>4</sub>·2dca; this is presumably  $\nu_{COC}$  of the thf molecule.

 $[ThBr_3L_3]^+Br^-$  mentioned above, for if the tris complexes were neutral species one would expect the shifts in  $\nu_{CO}$  to be smaller than those for the bis complexes. The spectra of all the complexes in thf solution show that free ligand is present, presumably because of partial replacement of the ligand by the smaller thf molecule. In the cases of the complexes ThBr<sub>4</sub>·3L (L = dca, dipiba, dippa and dmiba) and ThBr<sub>4</sub>·2dippva free ligand was also observed in the dichloromethane solution spectra, consistent with the ease of degradation of the tris complexes to ThBr<sub>4</sub>·2L and with extreme secondary crowding by the dippva molecule.

# Acknowledgments

We wish to thank Mr. M. A. Hart for the microanalyses (thorium, carbon, hydrogen, nitrogen and bromine). One of us (A.G.M.A.-D.) is indebted to the Government of Iraq for the award of a scholarship.

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