

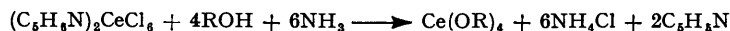
**671.** *Structural Chemistry of the Alkoxides. Part VII.<sup>1</sup> Secondary Alkoxides of Quadrivalent Cerium and Thorium.*

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Ceric secondary alkoxides,  $\text{Ce}(\text{O}\cdot\text{CHR}_2)_4$  where  $\text{R} = \text{Me}$  or  $\text{Et}$ , and  $\text{Ce}(\text{O}\cdot\text{CHMeR})_4$  where  $\text{R} = \text{Et}$ ,  $\text{Pr}^n$ , or  $\text{Pr}^i$ , have been prepared and their molecular weights determined ebullioscopically in benzene and in toluene. Ceric tetra*isopropoxide* sublimed at  $160\text{--}170^\circ/0.05$  mm. but the other derivatives were non-volatile. The non-volatile thorium secondary alkoxides  $\text{Th}(\text{O}\cdot\text{CHEtR})_4$ , where  $\text{R} = \text{Me}$  or  $\text{Et}$ , have also been prepared and their molecular weights determined ebullioscopically in benzene. The molecular weights and volatilities of the secondary alkoxides of Ti, Zr, Ce(IV), and Th are discussed from the theoretical viewpoint.

IN Part VI<sup>1</sup> we reported that the molecular complexities of thorium *n*-alkoxides were considerably greater than the complexities of the corresponding alkoxides of quadrivalent cerium, and suggested that (i) the pronounced ionic character of thorium alkoxides enhanced the polymerisation, or (ii), on a stereochemical basis, the atomic radius of thorium was greater than that of cerium although the literature suggests that their radii are equal. Moreover, it was clear from the anomalous behaviour of the *neopentyloxides* of cerium and thorium that stereochemical factors were operative. Consequently it seemed worthwhile to investigate fully the effect of chain branching on the properties of cerium alkoxides. In this communication we report the results obtained on some secondary alkoxides of cerium and thorium. The following derivatives were prepared:  $\text{Ce}(\text{O}\cdot\text{CHR}_2)_4$ , where  $\text{R} = \text{Me}$  and  $\text{Et}$ ;  $\text{Ce}(\text{O}\cdot\text{CHMeR})_4$ , where  $\text{R} = \text{Et}$ ,  $\text{Pr}^n$ , or  $\text{Pr}^i$ ; and  $\text{Th}(\text{O}\cdot\text{CHEtR})_4$ , where  $\text{R} = \text{Me}$  or  $\text{Et}$ .

Alcohol interchange from the *isopropoxides* was employed for the preparations. In addition, the cerium derivatives of pentan-3-ol and 3-methylbutan-2-ol were obtained from dipyridinium cerium hexachloride by the ammonia method:



The crystalline *isopropoxide*,  $\text{Ce}(\text{OPr}^i)_4\text{Pr}^i\text{OH}$ , also obtained from the pyridinium salt,<sup>1</sup> dissociated at  $100^\circ/0.05$  mm. and gave the tetra*isopropoxide* as a yellow glass, readily soluble in organic solvents. The tetra*isopropoxide* volatilised in a "molecular still" at  $160\text{--}170^\circ/0.05$  mm. and gave a yellow-green crystalline sublimate which slowly reverted to the original yellow colour when allowed to cool under nitrogen. None of the other secondary alkoxides of cerium could be sublimed under reduced pressure. The molecular weights of all the new cerium alkoxides were determined ebullioscopically in benzene and in toluene (see Table 1).

It is remarkable that there appears to be no systematic variation of molecular complexity with size or configuration of the secondary alkyl group in these compounds either in benzene or toluene. However, the average value in toluene ( $2.80 \pm 0.02$ ) is significantly lower than the average value in benzene ( $3.04 \pm 0.11$ ) and this is consistent

<sup>1</sup> Part VI, *J.*, 1956, 2260.

with the predicted decrease in molecular complexity with increase in boiling point of the solvent, owing to thermal dissociation.<sup>2</sup> This effect is much smaller in the secondary alkoxides than in the primary alkoxides of cerium (complexities: 4.22 in benzene and

TABLE 1.

R in Ce(OR) <sub>4</sub>	Benzene		Toluene	
	M	Complexity	M	Complexity
Me <sub>2</sub> CH .....	1179	3.13	1045	2.78
MeEtCH .....	1293	2.99	1210	2.80
MePr <sup>n</sup> CH .....	1520	3.11	1363	2.79
MePr <sup>i</sup> CH .....	1464	3.00	1377	2.82
Et <sub>2</sub> CH .....	1420	2.90	1370	2.80

3.43 in toluene). We have already drawn attention to the striking behaviour of the *neopentyl*oxide group in the metal alkoxides and it is especially noteworthy that although cerium *neopentyl*oxide is less volatile than cerium *isopropyl*oxide yet it has the lower molecular complexity both in benzene and in toluene. Another interesting feature of Table 1 is that the complexities of the secondary alkoxides of cerium are significantly lower in both solvents than the complexities of the primary alkoxides. It is therefore evident that branching of the alkyl group leads to a decrease in molecular complexity in conformity with our stereochemical theory for the metal alkoxides. By the arguments advanced previously<sup>1</sup> it appears that in the secondary alkoxides of quadrivalent cerium the central atom is predominantly exhibiting the co-ordination number of six compared with the approximately equal degrees of 6- and 8-co-ordination suggested for the normal alkoxides. Moreover, the behaviour of the normal and secondary alkoxides in benzene and in toluene suggests that the intermolecular bonding in the 6-co-ordinate complexes is stronger than in the 8-co-ordinate complexes. Thus according to our structural models the proportions of 8-co-ordinate and 6-co-ordinate cerium are 46% and 54% respectively in boiling benzene, and 20% and 80% respectively in boiling toluene for the normal alkoxides. For the secondary alkoxides the cerium is predominantly 6-co-ordinate (~98%) in boiling benzene with only a small percentage in the 8-co-ordinate state, whilst in boiling toluene it appears that further dissociation of the trimeric molecules to the monomeric 4-co-ordinate state has only reduced the 6-co-ordinate cerium to 96% of the total. Although these calculations involve a gross simplification they undoubtedly illustrate the much greater dissociation of the 8-co-ordinate complexes compared with the 6-co-ordinate complexes over the same temperature range.

The preparation of some new alkoxides of thorium allows us to compare the molecular complexities (in boiling benzene) of a number of secondary alkoxides of titanium, zirconium, cerium, and thorium. Table 2 shows that the complexities of thorium secondary

TABLE 2.

R in M(OR) <sub>4</sub>	M =	Ti †	Zr †	Ce *	Th
Me <sub>2</sub> CH .....		1.4	3.0	3.1	3.8 ‡
MeEtCH .....		—	2.5	3.0	4.2 *
MePr <sup>n</sup> CH .....		1.0	2.0	3.1	—
MePr <sup>i</sup> CH .....		1.0	2.0	3.0	—
Et <sub>2</sub> CH .....		1.0	2.0	2.9	4.1 *

\* This research.

† Ref. 3.

‡ Ref. 4.

alkoxides are considerably greater than those of the corresponding cerium derivatives, which in turn are greater than those of zirconium secondary alkoxides. It is especially noteworthy that, although the complexities of cerium and thorium secondary alkoxides are lower than those of the normal alkoxides owing to the shielding effect of the branched alkoxide groups, yet the complexities of these secondary alkoxides do not depend on the size of the alkyl group. On the other hand, the corresponding zirconium secondary alkoxides show a marked dependence of complexity on the size of the alkyl group. This contrast in behaviour is probably due to the smaller shielding requirements of zirconium compared

<sup>1</sup> Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.<sup>2</sup> Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 5020.<sup>3</sup> Bradley, Saad, and Wardlaw, *J.*, 1954, 1091.

with cerium and thorium and this is in line with the fact that for titanium, which has a smaller atomic radius than zirconium, all of the secondary alkoxides except the *isopropoxide* are monomeric. The differences in molecular complexities of the Group IVA secondary alkoxides are also reflected in the volatilities of these compounds. Thus all of the titanium and zirconium secondary alkoxides may be distilled under reduced pressure, the titanium compounds being the more volatile. However, with cerium and thorium only the *isopropoxides* could be volatilised and it is significant that cerium *isopropoxide*, which has the same molecular complexity as zirconium *isopropoxide*, can be sublimed in the molecular still at a temperature near to the boiling point (at 0.1 mm.) of the zirconium derivative. The lack of volatility of the higher secondary alkoxides of cerium is evidently due to the increase in latent heat of sublimation which results from the increase in size of the trimeric molecules from the *isopropoxide* to the derivative of pentan-3-ol. This view is supported by the behaviour of the corresponding zirconium compounds. For example, the complexities of the compounds  $Zr(O\cdot CHMe_2)_4$ ,  $Zr(O\cdot CHMeEt)_4$ , and  $Zr(O\cdot CHEt_2)_4$  are 3.0, 2.5, and 2.0 respectively, while the boiling points (at 0.1 mm.) are 160°, 164°, and 181° respectively. This shows that the tendency towards increased volatility caused by the lowering of the molecular complexity is not quite sufficient to counterbalance the opposing effect due to increase in the size of the alkyl groups. In the case of cerium or thorium secondary alkoxides the effect of increased size of the alkyl groups is unopposed since there is no change in molecular complexity.

It is clear from the data in Table 2 that the order of molecular complexities of these compounds is always  $Th > Ce > Zr > Ti$ . If stereochemical factors are primarily responsible for this behaviour then it follows that the order of atomic radii should be  $Th > Ce > Zr > Ti$  and this agrees with our conclusion from the study of the normal alkoxides.<sup>1</sup> However, we have also pointed out that the ionic character of thorium alkoxides may be another factor to consider in this comparison because electrostatic attraction involving  $Th \overset{\delta+}{-} OR \overset{\delta-}{-}$  dipoles might cause enhanced molecular association. Alternatively it is possible that intermolecular bonding of the type  $\begin{matrix} M \\ \diagup \\ R > O \end{matrix} \longrightarrow M$  is stronger in thorium alkoxides than in the cerium alkoxides and this point will be further considered when dealing with the tertiary alkoxides. The molecular weight of cerium *isopropoxide* was also determined in boiling *isopropyl alcohol* and showed that the compound was dimeric and thus resembled zirconium *isopropoxide*.<sup>5</sup> The *isopropoxides* of zirconium and cerium give derivatives of the type  $M(OPr^i)_4$ ,  $Pr^iOH$  and  $M(OPr^i)_4 \cdot C_5H_5N$ , and it seems reasonable to suppose that in these compounds the metals are 6-co-ordinated, as depicted in the dimeric structure proposed earlier for the zirconium compound.<sup>5</sup> On the other hand, thorium *isopropoxide*, which does not form complexes of the above type, gave a molecular complexity of 1.8 in boiling *isopropyl alcohol*<sup>4</sup> and this low result may well be due to ionic dissociation, as indicated by the alkaline reaction of the solution.

## EXPERIMENTAL

The experimental details were similar to those previously described.<sup>1</sup>

*Preparation of Alkoxides of Cerium and Thorium.*—Typical results are presented in Table 3.

TABLE 3.

R	ROH taken (c.c.)	Starting material (g.)	C <sub>5</sub> H <sub>6</sub> (c.c.)	New alkoxide (g.)	Metal (%)	
					Found	Calc.
MeEtCH .....	40	4.14 <sup>a</sup>	200	4.0	32.4 <sup>d</sup>	32.4
„ .....	20.5	4.32	80	4.84	44.3 <sup>c</sup>	44.3
MePr <sup>i</sup> CH .....	15.4	5.26 <sup>a</sup>	100	5.73	28.6 <sup>d</sup>	28.7
MePr <sup>i</sup> CH .....	38.5	21.2 <sup>b</sup>	150	5.8	28.8 <sup>d</sup>	28.7
„ .....	14.8	6.47 <sup>a</sup>	110	2.6* + 4.2†	28.7 <sup>d</sup>	28.7
Et <sub>2</sub> CH .....	21.0	7.68 <sup>a</sup>	200	8.49	28.8 <sup>d</sup>	28.7
„ .....	10.9	4.57 <sup>c</sup>	75	5.01	40.3 <sup>e</sup>	40.0
„ .....	35	19.5 <sup>b</sup>	150	9.85	28.8 <sup>d</sup>	28.7

<sup>a</sup> Ce(OPr<sup>i</sup>)<sub>4</sub>, Pr<sup>i</sup>OH; <sup>b</sup> (C<sub>5</sub>H<sub>6</sub>N)<sub>3</sub>CeCl<sub>3</sub>; <sup>c</sup> Th(OPr<sup>i</sup>)<sub>4</sub>; <sup>d</sup> Ce; <sup>e</sup> Th.

\* 1st crop.

† 2nd crop.

<sup>5</sup> Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

*Molecular-weight Determinations.*—Determinations by the method involving the use of the apparatus constant (found with azobenzene) were checked by "internal calibration" with fluorene.<sup>1</sup> The results obtained by the two methods differed by less than 1%. Typical results

TABLE 4.

Alkoxide	Range in <i>m</i> (g.)	Wt. of benzene (g.)	$\Delta T/m$ (°C./g.)	Mol. wt.	
				Found	Calc.
Ce(OPr <sup>i</sup> ) <sub>4</sub> .....	0.0233—0.1985	15.10	0.1645	1180	376.1
Ce(OPr <sup>i</sup> ) <sub>4</sub> , PrOH .....	0.0171—0.2652	12.50 *	0.1415	850	436.1
Ce(O·CHMeEt) <sub>4</sub> .....	0.0322—0.2568	15.30	0.1480	1295	432.1
Ce(O·CHEt <sub>2</sub> ) <sub>4</sub> .....	0.0593—0.3002	15.76	0.1310	1420	488.1
Ce(O·CHMePr <sup>n</sup> ) <sub>4</sub> .....	0.0217—0.2600	14.63	0.1320	1520	488.1
Ce(O·CHMePr <sup>i</sup> ) <sub>4</sub> .....	0.0440—0.1936	16.91	0.1185	1465	488.1
Th(O·CHMeEt) <sub>4</sub> .....	0.0582—0.2502	14.48	0.0920	2200	524.1
Th(O·CHEt <sub>2</sub> ) <sub>4</sub> .....	0.0479—0.2259	14.48	0.0875	2330	580.1

\* In boiling *isopropyl alcohol*.

TABLE 5.

R in Ce(OR) <sub>4</sub>	Alkoxide		Fluorene		Mol. wt.	
	Range in <i>m</i> (g.)	$\Delta T/m$ (mm./g.) *	Range in <i>m</i> (g.)	$\Delta T/m$ (mm./g.) *	Found	Calc.
Me <sub>2</sub> CH .....	0.0370—0.1750	112	0.0062—0.0213	712	1055	376.1
MeEtCH .....	0.0310—0.1692	100	0.0048—0.0365	728	1210	432.1
Et <sub>2</sub> CH .....	0.0554—0.2380	100	0.0038—0.0255	825	1370	488.1
MePr <sup>n</sup> CH .....	0.0136—0.1062	75	0.0062—0.0432	615.5	1365	488.1
MePr <sup>i</sup> CH .....	0.0332—0.1400	64.5	0.0130—0.0318	534	1375	488.1

\*  $\Delta T$  in mm. of water pressure.

for the first method (in benzene or *isopropyl alcohol*) are given in Table 4 and for the internal calibration method (in toluene) in Table 5.

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