506. *Structural Chemistry of the Alkoxides. Part IX.** tert.-*Alkoxides of Quadrivalent Cerium.*

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Ceric *tert.*-alkoxides $Ce(OR)_4$, where R = CMe_3, CMe_2Et, $CMeEt_2$, CEt_3, CMe_2Pr^n, CMe_2Pr^i, and $CMeEtPr^n$, have been prepared from $Ce(OPr^i)_4,Pr^iOH$ by alcohol interchange, and their molecular weights have been determined ebullioscopically in benzene and in toluene. The higher *tert.*-alkoxides are the first volatile liquid compounds of cerium(IV) to be reported and their boiling points under reduced pressure were determined. The results are discussed in terms of the stereochemical theory for the Group IVA metal alkoxides.

Recently we established that the molecular complexities of primary[1] and secondary[2] alkoxides of quadrivalent cerium were significantly lower than those of the corresponding derivatives of thorium. These results were surprising in view of the supposed equality in atomic radii of cerium and thorium and it was suggested that electronic factors rather than steric factors might be responsible for this contrast. We have now prepared a number

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* Part VIII, *J.*, 1956, 4439.

[1] Bradley, Chatterjee, and Wardlaw, *J.*, 1956, 2260.

[2] *Idem, J.*, 1956, 3469.

of *tert.*-alkoxides of cerium because it was expected that the higher *tert.*-alkoxides would be monomeric and less susceptible to electronic factors owing to the screening effect of the large *tert.*-alkoxide groups. Moreover, there was the added interest of determining whether stable monomeric compounds of quadrivalent cerium existed because the stability of the primary and secondary alkoxides might be ascribed to their complex nature.

Attempts to prepare *tert.*-alkoxides of cerium by the " ammonia method " on dipyridinium cerium hexachloride gave the monochloride tri-*tert.*-alkoxide complexes $CeCl(OR)_3,C_5H_5N$, where $R = CMe_3$ or CMe_2Et, and in this respect cerium resembles zirconium[3] which likewise gave the monochloride complex $ZrCl(OCMe_3)_3,2C_5H_5N$. The corresponding reaction for thorium has not yet been investigated but earlier work[4] on $(C_5H_6N)_2ThCl_6$ showed that some chlorine remained in the product when ethanol or propan-2-ol was used, in contrast to the behaviour of zirconium and cerium which gave tetra-alkoxides with primary and secondary alcohols. The new cerium tetra-*tert.*-alkoxides $Ce(OR)_4$, where $R = CMe_3$, CMe_2Et, $CMeEt_2$, CEt_3, CMe_2Pr^n, CMe_2Pr^i, and $CMeEtPr^n$, were prepared from cerium *iso*propoxide by alcohol interchange. All of these compounds are extremely sensitive to water but otherwise are stable. The *tert.*-butoxide and the *tert.*-amyloxide were deep yellow solids which sublimed unchanged in a " molecular still " whilst the higher *tert.*-alkoxides were bright yellow liquids which were distilled unchanged under reduced pressure. The boiling points and the molecular weights determined ebullioscopically in benzene and in toluene are recorded in Table 1 together with the molecular complexities. These are the first recorded examples of volatile liquid compounds of quadrivalent cerium and establish conclusively their stability. In fact our preliminary studies on tervalent cerium alkoxides show that the latter are relatively unstable since they are readily oxidised by traces of atmospheric oxygen to the ceric state. In view of the striking increase in stability from $CeCl_4$ to $[CeCl_6]^{2-}$ it seemed possible that the stability of the ceric primary[1] and secondary[2] alkoxides might be due to their complex nature. However, the data in Table 1 show that monomeric ceric alkoxides are also stable although it is possible that in these compounds stability is achieved by intramolecular covalency expansion, *viz.*, $^{-}Ce{=}O^{+}{-}R$. On the other hand this double bonding would lower the thermal stability in a *tert.*-alkoxide by promoting the release of a carbonium ion (cf. niobium alkoxides[5]), but in fact the ceric derivatives of 2-methylpentan-2-ol and 2 : 3-dimethylbutan-2-ol are more stable than the corresponding thorium derivatives[6] which decompose above 120° *in vacuo*.

The results in Table 1 show that the molecular complexity and volatility of ceric *tert.*-alkoxides are much more dependent on size and shape of the alkyl group than was found with the primary or secondary alkoxides, and this is consistent with the stereochemical theory already advanced to account for the physicochemical properties of Group IVA metal alkoxides. The lower complexities found in toluene confirm the depolymerising effect of the higher-boiling solvent as already noted for the primary and secondary

TABLE 1.

		In benzene		In toluene	
R in $Ce(OR)_4$	B. p./mm.	Mol. wt.	Complexity	Mol. wt.	Complexity
CMe_3	140—150°/0·1 *	1062	2·5	968	2·2
CMe_2Et	240°/0·1 *	1150	2·4	1050	2·2
$CMeEt_2$	140°/0·06	746·2	1·4	580·4	1·1
CMe_2Pr^n	146°/0·05	761·7	1·4	600	1·1
CMe_2Pr^i	132°/0·05	584	1·1	541·6	1·0
CEt_3	154°/0·05	650·3	1·1	604·7	1·0
$CMeEtPr^n$	150°/0·05	604·5	1·0	—	—

* Sublimation.

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[3] Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.
[4] Bradley, Saad, and Wardlaw, *J.*, 1954, 1091.
[5] Bradley, Chakravarti, and Wardlaw, *J.*, 1956, 2381.
[6] Bradley, Saad, and Wardlaw, *J.*, 1954, 3488.

alkoxides. A remarkable feature of the ebullioscopic measurements on metal alkoxides [1, 2, 5, 7] is the clear effect of temperature in dissociating the complex molecules in contrast to the absence of concentration effects within the range of concentrations studied. Unfortunately this prevents the calculation of dissociation constants or heats of dissociation for the complex alkoxides, and these would provide fundamentally sounder parameters for comparison than the molecular complexities.

The present results allow a very interesting comparison between tertiary alkoxides of titanium, zirconium, cerium(IV), and thorium. The boiling points (corrected to 0·1 mm.) and molecular complexities in benzene (in parentheses) are shown in Table 2 for a number of derivatives. These results reinforce the argument deduced from the behaviour of primary and secondary alkoxides that on the basis of stereochemical effects alone the atomic radii should be in the order Th > Ce > Zr > Ti. Thus the lower tertiary alkoxides of cerium are significantly less polymerised than the corresponding thorium derivatives. It is also clear that differences in ionic character of the metal–oxygen bonds cannot be very important because in the monomeric series of triethylcarbinol derivatives the boiling points are all within a few degrees of 160°. In fact the order of boiling points Zr > Ce > Th is exactly the reverse of that predicted from the order of ionic character Th > Ce > Zr required to explain the variation in molecular complexities of the lower tertiary alkoxides of these elements. On the other hand, the order of volatilities is not surprising in terms of the theory of the fundamental effect of mass on volatility [8] which suggests that in a series of compounds with similar molecular sizes and latent heats of vaporisation the heavier molecules may be the more volatile. Since we were dealing with essentially covalent compounds we have previously taken the covalent atomic radii given by Sidgwick [9] for comparative purposes (*i.e.*, $r_{Ce} = r_{Th} = 1·65$ Å). Similarly Moeller [10] gives values of $r_{Ce} = 1·646$ Å and $r_{Th} = 1·652$ Å. On the other hand Goldschmidt's [11] ionic radii for co-ordination number 6 are Ce^{4+} 1·02 Å, $Th^{4+} = 1·10$ Å, *i.e.*, in the order required from our studies on the alkoxides. Now according to Moeller [10] the covalent radii of these elements were deduced from interatomic distances in the metals and this should give comparable radii for metals of the same Group valency. However, although ceric cerium has a formal analogy to the Group IVA elements, yet in the cerous state it is also a member of the lanthanon series of tervalent metals. We suggest that the "covalent" radius of 1·65 Å assigned to cerium is not appropriate to this element in the quadricovalent state but suggest instead a value of 1·55—1·60 Å. This is supported by the fact that the value of 1·65 Å for cerium falls reasonably on a plot of covalent radius against atomic number from La = 1·69 Å to Sm = 1·64 Å, as expected for a tervalent metal and in contrast to the sudden reduction in radius from lutetium (1·56 Å) which is tervalent to hafnium (1·44 Å) which is quadrivalent. Moreover, europium (covalent radius 1·85 Å) is strikingly off this curve and has a value more appropriate to a bivalent metal (cf. Ba = 1·98 Å) and this accords with its well-known bivalency. Similarly the tervalent

TABLE 2.

R in $M(OR)_4$	Ti	Zr	Ce	Th
CMe_3	52 (1·0)	50 (1·0)	150 (2·4)	160 (3·4)
CMe_2Et	98 (1·0)	95 (1·0)	240 (2·3)	198 (2·8)
$CMeEt_2$	128 (1·0)	128 (1·0)	145 (1·4)	148 (1·8)
CMe_2Pr^n	144 (1·0)	137 (1·0)	152 (1·4)	Dec.* (2·6)
CMe_2Pr^i	153 (1·0)	133 (1·0)	138 (1·1)	Dec.* (2·3)
CEt_3	166 (1·0)	166 (1·0)	160 (1·1)	154 (1·0)
$CMeEtPr^n$	—	—	156 (1·0)	153 (1·7)

* Decomp. at 120°/0·1 mm.

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[7] Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.
[8] Bradley, *Nature*, 1954, **174**, 323.
[9] Sidgwick, "The Chemical Elements and Their Compounds," Oxford, 1950, Vol. I, p. xxix.
[10] Moeller, "Inorganic Chemistry," Wiley, New York, 1952, p. 135.
[11] Goldschmidt, *Ber.*, 1927, **60**, 1263.

ionic radii of Ce^{3+} (1·18 Å) and Eu^{3+} (1·13 Å) both fall on the smooth plot of $r_{M^{4+}}$ against atomic number for the lanthanons, whereas the value for Ce^{4+} is noticeably off it (see also Pr^{4+} 1·00 Å). We therefore conclude that the quadricovalent radius of cerium is less than that of thorium, in accordance with our deductions from the stereochemical behaviour of the tetra-alkoxides of the Group IVA elements.

EXPERIMENTAL

The experimental details of this work were similar to those previously described.[1, 2]

The Complex, $CeCl(OBu^t)_3,C_5H_5N$.—The complex chloride (4·5 g.) was suspended in *tert.*-butyl alcohol–benzene azeotrope (300 c.c.). Ammonia was passed into the suspension until it had cooled to room temperature. After the removal of excess of ammonia under reduced pressure and ammonium chloride by filtration, the filtrate was evaporated under reduced pressure to about half its original volume. The lemon-yellow crystalline *product* (12 g.) was filtered off and dried at 40°/0·1 mm. [Found: Ce, 29·7; Cl, 7·5. $CeCl(OC_4H_9)_3,C_5H_5N$ requires Ce, 29·6; Cl, 7·5%]. Even prolonged treatment of the foregoing product with ammonia and alcohol failed to replace the chlorine in the cerium complex.

The Complex, $CeCl(OCMe_2Et)_3,C_5H_5N$.—The complex cerium chloride (44 g.) was suspended in a mixture of *tert.*-amyl alcohol (100 c.c.) and benzene (350 c.c.), and ammonia was passed into it for long after the products had cooled to room temperature. From the filtered solution evaporated to half bulk was obtained a bright yellow crystalline *product* (15 g.) which was filtered off and dried at 40°/0·1 mm. [Found: Ce, 27·3; Cl, 6·9. $CeCl(OC_5H_{11})_3,C_5H_5N$ requires Ce, 27·2; Cl, 6·9%].

Cerium Tetra-tert.-*butoxide.*—The benzene–*tert.*-butyl alcohol azeotrope (400 c.c.) and the recrystallised complex *iso*propoxide (6·15 g.) were refluxed for about 12 hr. The distillate was then collected first very slowly and then rather rapidly, until 50 c.c. of the liquid remained. To this were added another (450 c.c.) of *tert.*-butyl alcohol–benzene azeotrope. The azeotropic distillation was repeated and most of the solvent was distilled off; on cooling, yellow needles (5·8 g.) separated and were dried at 70°/0·1 mm. [Found: Ce, 32·4. $Ce(OC_4H_9)_4$ requires Ce, 32·4%].

The Higher Alkoxides.—The tetra-*tert.*-amyloxide and all other higher alkoxides were prepared by alcohol interchange involving ceric *iso*propoxide and the alcohol in benzene. Some typical results are in Table 3.

TABLE 3.

R	ROH taken (g.)	$Ce(OPr^i)_4,Pr^iOH$ taken (g.)	C_6H_6 (c.c.)	Yield of $Ce(OR)_4$ (g.)	Ce (%)	
					Found	Reqd.
CMe_2Et	13·5	3·7	100	3·1 [a]	28·8	28·7
$CMeEt_2$	50	8·5	200	8·2 [b]	25·7	25·7
CMe_2Pr^n	27·7	4·8	120	4·5 [b]	25·6	25·7
CMe_2Pr^i	24	7	150	4·8 [b]	25·7	25·7
CEt_3	30·1	20	150	24 [b]	23·3	23·3
$CMeEtPr^n$ ...	48·4	5·1	110	6·2 [b]	23·4	23·3

[a] Yellow solid. [b] Mobile liquid.

TABLE 4.

R in $Ce(OR)_4$	Range of *m*(g.)	Wt. of C_6H_6 (g.)	$\Delta T/m$ (°c/g.)	Mol. wt.	
				Found	Calc.
CMe_3	0·0376—0·2484	16·06	0·1765	1041	432·1
CMe_2Et	0·0247—0·2592	16·34	0·1570	1150	488·1
$CMeEt_2$	0·0586—0·1718	15·03	0·3360	584	544·1
CMe_2Pr^n	0·0252—0·3760	14·54	0·2710	749	544·1
CMe_2Pr^i	0·0249—0·3542	15·24	0·2542	761·7	544·1
CEt_3	0·0404—0·3077	15·93	0·2838	650·3	600·1
$CMeEtPr^n$	0·1502—0·2405	16·26	0·2982	604·5	600·1

Molecular-weight Determinations.—All determinations involving the use of the apparatus constant (found with azobenzene) were checked by the internal calibration technique using fluorene.[1, 2] Typical results for the first method (in benzene) are given in Table 4 and for the internal calibration method (in toluene) in Table 5.

TABLE 5.

R in Ce(OR)$_4$	Alkoxide Range of *m*(g.)	Alkoxide $\Delta T/m$ (mm./g.) *	Fluorene Range of *m*(g.)	Fluorene $\Delta T/M$ (mm./g.) *	Mol. wt. Found	Mol. wt. Calc.
CMe$_3$	0·0211—0·1360	130	0·0080—0·0516	749	958	432·1
CMe$_2$Et	0·0251—0·1452	117·4	0·0068—0·0459	742	1050	488·1
CMeEt$_2$	0·0298—0·1390	232·5	0·0150—0·0378	739	541·6	544·1
CMe$_2$Pr^n	0·0114—0·1130	210	0·0265—0·0540	757·1	600	544·1
CMe$_2$Pr^i	0·0097—0·0935	200	0·0034—0·0314	679	564·2	544·1
CEt$_3$	0·0295—0·1377	244	0·0079—0·0453	882·1	601	600·1

* ΔT in terms of mm. of water pressure.

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