439. *Structural Chemistry of the Alkoxides. Part VI.* Primary Alkoxides of Quadrivalent Cerium and Thorium.*

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Ceric alkoxides, $Ce(OR)_4$ where R = Me, Et, Pr^n, Bu^n, Bu^i, *n*-pentyl, or *neo*pentyl, have been prepared, by reactions involving $(C_5H_6N)_2CeCl_6$, ammonia, and the appropriate alcohol, and by alcohol interchange on $Ce(OPr^i)_4,Pr^iOH$. Only the *neo*pentyloxide was volatile. Molecular weights were determined in boiling benzene and in boiling toluene. Thorium alkoxides, $Th(OR)_4$ where R = Bu^n, *n*-pentyl and *neo*pentyl, were also prepared and their molecular weights determined ebullioscopically in benzene. The molecular complexities of normal alkoxides of Ti, Zr, Ce^{IV}, and Th are discussed from the theoretical viewpoint.

Earlier work on the alkoxides of Group IVA elements showed that for titanium,[1] zirconium,[1] hafnium,[2] and thorium [3] the volatility and molecular complexity of the metal alkoxide was chiefly determined by the radius of the metal atom and the degree of branching

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* Part V, *J.*, 1956, 1139.

[1] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025 (for earlier references).

[2] Bradley, Mehrotra, and Wardlaw, *J.*, 1953, 1634.

[3] Bradley, Saad, and Wardlaw, *J.*, 1954, 3488.

of the alkyl group. Since quadrivalent cerium may reasonably be regarded as a Group IVA element, the examination of ceric alkoxides was of special interest. In particular there was the possibility that ceric alkoxides might not exist as stable compounds, owing to the tendency of cerium to assume the tervalent state as revealed by the instability of all tetrahalides except the fluoride.

Although cerium tetrachloride is unstable, the dipyridinium cerium hexachloride $(C_5H_6N)_2CeCl_6$ is so stable that it may be dried at 120° *in vacuo.* Moreover, the complex chloride reacted exothermally with *n*-butyl alcohol and ammonia in benzene, and cerium tetra-*n*-butoxide was thus obtained :

$$(C_5H_6N)_2CeCl_6 + 4Bu^nOH + 6NH_3 \longrightarrow Ce(OBu^n)_4 + 2C_5H_5N + 6NH_4Cl$$

The tetramethoxide and the tetraethoxide were formed in analogous reactions but could not be isolated because they were insoluble. On the other hand, from the reaction involving *iso*propyl alcohol a soluble product $[Ce(OPr^i)_4]_3,C_5H_5N$ was isolated. Recrystallisation of this from pyridine afforded $Ce(OPr^i)_4,C_5H_5N$, and from *iso*propyl alcohol gave $Ce(OPr^i)_4,Pr^iOH$. This behaviour of cerium is analogous to that of zirconium [4] and differs from that of thorium.[5] The pure *iso*propoxide was used as starting material for the preparation, by alcohol interchange, of the primary alkoxides $Ce(OR)_4$, where R = Me, Et, Pr^n, Bu^n, Bu^i, *n*-pentyl, and *neo*pentyl. All of these compounds were bright yellow solids, extremely susceptible to hydrolysis. Only the *neo*pentyloxide could be volatilised (sublimes at 260°/0·05 mm.); the others decomposed, without melting, above 200° *in vacuo.* Molecular weights (see Table) were determined ebullioscopically in benzene and in toluene for all of these compounds, except the methoxide and the ethoxide which were insoluble. The most important feature of these results is the high degree of polymerisation of the non-volatile ceric alkoxides, and the lower molecular complexity of the volatile *neo*pentyloxide, in accord with the stereochemical theory [1,3] proposed to explain the properties of the Group IVA alkoxides. The results also show that chain length has little influence on the molecular complexity of the non-volatile compounds. On the other hand, increase in temperature lowers the molecular complexity from an average value of 4·22 in boiling benzene to 3·43 in boiling toluene. Before discussing these results in relation to the behaviour of the alkoxides of other Group IVA elements it is necessary to present some additional results on the primary alkoxides of thorium. In an earlier communication [5] it was shown that the methoxide and the ethoxide of thorium were insoluble non-volatile compounds. We have now found that the *n*-butyl, *n*-pentyl, and *neo*pentyl derivatives $Th(OR)_4$, are soluble in benzene and their molecular weights have been determined ebullioscopically (see Table). None of these thorium alkoxides could be volatilised *in vacuo* and their high molecular complexities are consistent with this. The remarkable steric effect of the *neo*pentyl group is again evident.

	$Ce(OR)_4$ in benzene		$Ce(OR)_4$ in toluene		$Th(OR)_4$ in benzene	
R	*M*	Mol. complexity	*M*	Mol. complexity	*M*	Mol. complexity
Pr^n	1620	4·30	1295	3·44	—	—
Bu^n	1820	4·20	1504	3·48	3370	6·44
Bu^i	1810	4·20	1470	3·40	—	—
n-Pentyl	2050	4·20	1660	3·40	3595	6·20
*neo*Pentyl	1236	2·53	1200	2·45	2325	4·01

The molecular complexities (in boiling benzene) of the tetra-*n*-alkoxides of titanium, zirconium, cerium, and thorium are now known, *viz.*, Ti < 3·0, Zr 3·4, Ce 4·2, Th 6·3. In terms of our stereochemical theory for metal alkoxides these values imply the order of atomic radii, Th > Ce > Zr > Ti. Recorded values [6] are Ti 1·36, Zr 1·48, Ce 1·65, Th 1·65 Å. The properties of cerium *n*-alkoxides are thus extremely interesting. On the one hand they resemble the zirconium derivatives more than the thorium derivatives in molecular complexity, but on the other their lack of volatility places them close to

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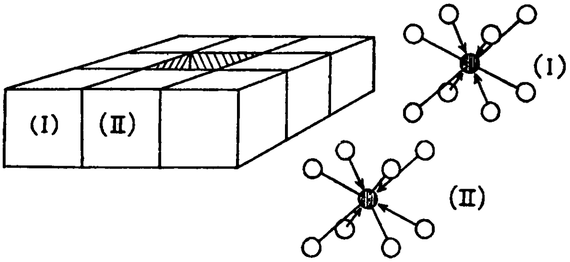
[4] Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.

[5] Bradley, Saad, and Wardlaw, *J.*, 1954, 1091.

[6] Sidgwick, " The Chemical Elements and their Compounds," Oxford, 1950, Vol. I., p. xxix.

the thorium compounds. Again, cerium forms the compounds $Ce(OPr^i)_4,C_5H_5N$ and $Ce(OPr^i)_4,Pr^iOH$ analogously to zirconium whilst thorium tetra*iso*propoxide does not take up an addendum. If the values recorded for the atomic radii are assumed to be correct it appears that the differences between the alkoxides of cerium and thorium must be caused by electronic factors. This is qualitatively confirmed by the fact that thorium alkoxides are alkaline to phenolphthalein or thymolphthalein whereas cerium alkoxides are feebly acidic. It is also in accord with the preparation of chloride-free cerium alkoxides from pyridinium cerium hexachloride (analogously to zirconium[4]) in contrast to the behaviour of pyridinium thorium hexachloride.[5] It may well be that the ionic character of thorium *n*-alkoxides is responsible for the higher molecular complexities of these compounds compared with the cerium derivatives.

Structure of $M_8(OR)_{32}$.



● M. ○ O *in* OR.

With regard to the structural aspects of the Group IVA alkoxides we have already pointed out [1, 7] that the smallest polymer available to a tetra-alkoxide in which the metal is 6-co-ordinate is the trimer $[M(OR)_4]_3$. This appears to be true for titanium *n*-alkoxides which approach the limiting trimeric state at high concentrations in benzene, the maximum covalency of titanium being six. Zirconium, cerium, and thorium form tetra-acetylacetone compounds in which the metal is presumably 8-co-ordinate, hence it is not surprising that their *n*-alkoxides have molecular complexities exceeding three. The smallest possible polymer unit for a tetra-alkoxide of a metal exhibiting the co-ordination number 8 is an octamer. The framework of this structure consisting of eight cubes arranged in a flat ring is shown in the Figure. Hence, the molecular complexities of normal alkoxides of zirconium, cerium, and thorium should be within the range 3—8 depending on the proportion of 6-co-ordination to 8-co-ordination exhibited by the metal. For example, in a system containing only trimers and octamers with the number of 6-co-ordinate metal atoms equalling the number of 8-co-ordinate the average complexity would be 4·36 (cf. Ce 4·23). Similarly for thorium *n*-alkoxides (complexity 6·3) it appears that approximately 20% of the thorium is 6-co-ordinate and the remainder 8-co-ordinate, whilst for zirconium *n*-alkoxides (complexity 3·4) it appears that over 80% of the zirconium is 6-co-ordinate. The comparative behaviour of cerium alkoxides in benzene and in toluene shows that these proportions of 6-co-ordination to 8-co-ordination for the metal are strongly temperature-dependent.

EXPERIMENTAL

The experimental technique followed was similar to that already described [1, 3, 4, 5] for the preparation of other metal alkoxides which are readily hydrolysed.

Cerium was determined by precipitation as ceric hydroxide followed by ignition to CeO_2. In the determinations of methoxide, ethoxide, and *iso*propoxide allowance was made for the liberation of iodine caused by the reduction of cerium from Ce^{IV} to Ce^{III}.

The starting material was pure ceric ammonium sulphate prepared from cerium dioxide containing less than 0·1% of other lanthanons.

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[7] Bradley, Wardlaw, and Whitley, *J.*, 1955, 726.

Dipyridinium Cerium Hexachloride.—Previous methods [8,9] for preparing this compound were unsatisfactory and the following method is the result of considerable research. Ceric hydroxide was precipitated by the addition of excess of aqueous sodium hydroxide (containing some bromine) to a solution of ceric ammonium sulphate (50 g.). After repeated washing, first with water, then with absolute alcohol, the ceric hydroxide was suspended in absolute alcohol (500 c.c.), and anhydrous hydrogen chloride was passed in. The solution was cooled during the absorption of hydrogen chloride (about 20 hr. required) and finally filtered. Pyridine (" AnalaR "; 14 c.c.) was added to the deep red filtrate, and the solution treated with more hydrogen chloride. The bright yellow complex chloride then crystallised and was filtered off and dried at 120°/0·1 mm. for 3 hr. (yield 31·7 g.) [Found: Ce, 27·3; Cl, 41·4. Calc. for $(C_5H_6N)_2CeCl_6$: Ce, 27·3; Cl, 41·5%].

Formation of Ceric Alkoxides from the Complex Chloride.—(a) *Methoxide.* Ammonia, passed into the red solution of the complex chloride (11 g.) in methyl alcohol (47 g.) and benzene (43 g.), caused an exothermic reaction and precipitation of a yellow solid. The filtrate contained no cerium but the residue (MeO : Ce = 3·3) evidently contained precipitated $Ce(OMe)_4$.

(b) *Ethoxide.* A similar reaction occurred between the complex chloride (6·1 g.), ethyl alcohol (39 g.), benzene (94 g.), and ammonia. The yellow precipitate (7·1 g.; EtO : Ce = 3·8) contained precipitated $Ce(OEt)_4$.

(c) iso*Propoxide.* The reaction involving the complex chloride (18·3 g.), *iso*propyl alcohol (41·5 g.), and ammonia in benzene (167·5 g.) produced a voluminous white precipitate. After removal of excess of ammonia the *product* was filtered off. A yellow solid (10 g.) was obtained by evaporation of the filtrate {Found: Ce, 35·0; Pr^iO, 58·1. $[Ce(OPr^i)_4]_3,C_5H_5N$ requires Ce, 34·8; Pr^iO, 58·6%}. This material (4 g.) was crystallised from pyridine (10 c.c.), and the crystalline *product* (3·5 g.) was dried at 0·1 mm. and room temperature [Found: Ce, 30·8; Pr^iO, 51·6. $Ce(OPr^i)_4,C_5H_5N$ requires Ce, 30·8; Pr^iO 51·9%]. Another sample of the original product was recrystallised four times from *iso*propyl alcohol, and the final *product* dried at room temperature under reduced pressure [Found: Ce, 32·2; Pr^iO, 67·5. $Ce(OPr^i)_4,Pr^iOH$ requires Ce, 32·1; Pr^iO, 67·6%].

(d) n-*Butoxide.* From the reaction involving the complex chloride (28·9 g.), *n*-butyl alcohol (136 g.), and ammonia in benzene (180 g.), a yellow solid *alkoxide* (7·2 g.) was finally obtained after removal of ammonium chloride and evaporation to dryness [Found: Ce, 32·3. $Ce(OBu^n)_4$ requires Ce, 32·4%].

Ceric Alkoxides prepared by Alcohol-interchange.—(a) *Methoxide.* Addition of methyl alcohol (130 g.) to a solution of ceric *iso*propoxide, $Ce(OPr^i)_4,Pr^iOH$ (4·8 g.) in benzene (50 g.) caused immediate precipitation of a yellow powder. After refluxing for 3 hr. the supernatant liquor was removed by decantation, more methyl alcohol (120 g.) added to the residue, and the previous treatment repeated. Yellow crystals (3·1 g.) were obtained after drying at 0·1 mm. and room temperature [Found: Ce, 53·1; MeO, 45·9. $Ce(OMe)_4$ requires Ce, 53·0; MeO, 47·0%]. The *tetramethoxide* was insoluble in boiling methyl alcohol, benzene, or pyridine.

(b) *Ethoxide.* Ceric *iso*propoxide (3·1 g.) in benzene (20 c.c.) was converted into the *ethoxide* by successive treatments with ethyl alcohol (300 c.c.; 100 c.c.) as in the foregoing experiment. The yellow insoluble product (2·1 g.) was dried as above [Found: Ce, 43·9; EtO, 56·0. $Ce(OEt)_4$ requires Ce, 43·8; EtO, 56·2%].

(c) *Higher alkoxides.* These were prepared by azeotropic distillation of ceric *iso*propoxide and the appropriate alcohol in benzene. The new *alkoxides* were obtained by evaporating the solution remaining after the removal of the benzene–*iso*propyl alcohol azeotrope (see Table).

R	ROH taken (c.c.)	$Ce(OPr^i)_4$, Pr^iOH taken (g.)	C_6H_6 (c.c.)	Yield of $Ce(OR)_4$ (g.)	Ce (%)	
					Found	Reqd.
Pr^n	16·5	2·84	100	2·46	37·2	37·2
Bu^i	10·0	4·2	50	3·8	32·45	32·4
Bu^n	40	4·14	200	3·9	32·4	32·4
*neo*Pentyl ...	7·1	4·8	150	2·0 * + 2·5 †	28·8 ‡	28·7
n-Pentyl	9·4	4·2	100	2·3 *	28·9	28·7

* 1st crop of crystals. † 2nd crop of crystals.
‡ Analysis of sublimate (260°/0·05 mm.).

Preparation of Thorium Alkoxides.—The new *alkoxides* (see Table, p. 2264) were obtained by alcohol interchange on thorium tetra*iso*propoxide.[5]

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[8] Köppel, *Z. anorg. Chem.*, 1898, **18**, 305.

[9] Grant and James, *J. Amer. Chem. Soc.*, 1915, **37**, 2652.

R	ROH taken (c.c.)	$Th(OPr^i)_4$ taken (g.)	C_6H_6 (c.c.)	Yield of $Th(OR)_4$ (g.)	Th (%)	
					Found	Reqd.
Bu^n	40	3·0	200	3·2	44·3	44·3
*neo*Pentyl	7·8	3·2	100	3·5	40·2	40·0
n-Pentyl	25	3·5	200	3·8	40·15	40·0

Molecular-weight Determinations.—These were made in the modified Menzies–Wright ebulliometer described previously[10] with the technique[11] involving "internal calibration" to check the results obtained by the normal method.[1] Some typical results are tabulated.

Alkoxide	Range of *m* (g.)	Solvent (g.)	$\Delta T/m$	*M*	
				Found	Calc.
$Ce(OPr^n)_4$	0·0415—0·4122	16·0 [a]	0·114° *	1620	376·1
,,	0·0552—0·2588	15·59 [b]	93·3 †	1295	,,
$Ce(OBu^n)_4$	0·0528—0·1286	15·84 [a]	0·102 *	1820	432·1
,,	0·0402—0·1014	15·23 [b]	82·3 †	1504	,,
$Ce(OBu^i)_4$	0·0164—0·1248	13·64 [a]	0·119 *	1810	,,
,,	0·0451—0·1592	15·68 [b]	81·8 †	1470	,,
$Ce(OAm^n)_4$	0·0526—0·2934	16·30 [a]	0·088 *	2050	488·1
,,	0·0381—0·2152	16·21 [b]	69·8 †	1660	,,
$Ce(OCH_2Bu^t)_4$	0·0170—0·1679	17·08 [a]	0·139 *	1236	,,
,,	0·0198—0·1749	14·37 [b]	109·1 †	1200	—
$Th(OBu^n)_4$	0·0841—0·2780	13·23 [a]	0·0614 *	3370	524·1
$Th(OC_5H_{11}\text{-}n)_4$	0·0812—0·2271	15·72 [a]	0·0822 *	3595	580·1
$Th(OCH_2Bu^t)_4$	0·0402—0·1734	16·72 [a]	0·0678 *	2325	,,

[a] Benzene. [b] Toluene.

* ΔT in °c. † ΔT in mm. of water-pressure difference in the water-thermometer.

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[10] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.

[11] Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.