

75. *The Alkali-metal Zirconium Ennea-alkoxides, MZr<sub>2</sub>(OR)<sub>9</sub>.*

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Reactions of zirconium tetra-alkoxides, Zr(OR)<sub>4</sub>, where R = Et, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>, and Bu<sup>s</sup>, and the alkoxides M(OR), where M = Li, Na, K, Tl, Ca<sub>1/2</sub> and Et<sub>4</sub>N, were studied. With the alkali metals a series of stable double alkoxides with the general formula MZr<sub>2</sub>(OR)<sub>9</sub> were obtained, many of which sublimed or distilled unchanged under reduced pressure. They are soluble in typical organic solvents, and molecular weights were determined ebullioscopically in benzene and in their parent alcohols. Vapour pressures were determined in the pressure range 0.1–10.0 mm. The formation of the double ennea-alkoxides in solution was confirmed by titration of the single alkoxides. These new compounds appear to be examples of covalently bound alkali metals.

In recent researches on alkoxides of Group IV elements<sup>1</sup> it was noted that when alcoholic solutions of the alkoxides were titrated with alkali-metal alkoxides, with thymolphthalein as indicator, the reaction could be expressed by the equation  $MOR + 2Zr(OR)_4 \longrightarrow MZr_2(OR)_9$ . This was confirmed from analysis of the products. These new compounds, conveniently referred to as ennea-alkoxides (or 9-alkoxides), were obtained when M = Li, Na, K, Tl, Ca<sub>1/2</sub>, Et<sub>4</sub>N, and R = Et, Pr<sup>n</sup>, Pr<sup>i</sup>, Bu<sup>n</sup>, Bu<sup>s</sup>. The ease with which they hydrolysed decreased in the order MeO > EtO > Pr<sup>i</sup>O; consequently the *isopropoxides* were the most suitable for study. They were also the most readily obtained because the parent substance Zr(OPr<sup>i</sup>)<sub>4</sub>, Pr<sup>i</sup>OH can be prepared pure by crystallisation from *isopropyl* alcohol. The solvated double alkoxide LiZr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>, Pr<sup>i</sup>OH is made conveniently from the single alkoxides and undergoes alcohol interchange in benzene solution. As a preparative method, however, alcohol interchange has limitations. Starting with lithium zirconium *isopropoxide* we found that primary alcohols interchanged completely but the method failed with *tert.*-butyl and *tert.*-amyl alcohols. In the latter cases the reaction proceeded readily to the stage LiZr<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>(OR)<sub>5</sub> but not beyond. In attempting to isolate CoZr<sub>4</sub>(OPr<sup>i</sup>)<sub>18</sub> from cobaltous chloride and NaZr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub> in *isopropyl* alcohol a fine purple solid was obtained with the composition Na<sub>2</sub>[CoCl<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub>]. This is a new type of complex salt involving a Group VIII metal with co-ordinated alkoxide groups.

The molecular weights of several ennea-alkoxides were determined in boiling benzene

TABLE 1.

Compound	Mol. wt.	Mol. complexity	Compound	Mol. wt.	Mol. complexity
LiZr <sub>2</sub> (OEt) <sub>9</sub> .....	1240	2.1	NaZr <sub>2</sub> (OEt) <sub>9</sub> .....	710	1.2
LiZr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> .....	1230	1.7	NaZr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> .....	815	1.1
LiZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	1330	1.6	NaZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	858	1.0
LiZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	760	1.0	NaZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	761	1.0
LiZr <sub>2</sub> (OBu <sup>s</sup> ) <sub>9</sub> .....	847	1.0	KZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	890	1.0
LiZr <sub>2</sub> (OEt) <sub>4</sub> (OBu <sup>t</sup> ) <sub>5</sub> ...	737	1.0	KZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	760 *	1.0
LiZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> , Pr <sup>i</sup> OH ...	763	1.0	Et <sub>4</sub> NZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	1270	1.5

\* In *cyclohexane*.

and the results are given in Table 1. These figures show that most of the double alkoxides have the monomeric formula MZr<sub>2</sub>(OR)<sub>9</sub> in contrast to zirconium tetra-alkoxides which are associated. Alcohol interchange of the dimeric lithium zirconium enneaethoxide with *tert.*-butyl alcohol causes the molecular complexity to decrease until the monomeric LiZr<sub>2</sub>(OEt)<sub>4</sub>(OBu<sup>t</sup>)<sub>5</sub> is produced. In Table 2 the results are given of the molecular-weight determinations of some double alkoxides in boiling alcohols. All the compounds investigated were monomeric with the exception of tetraethylammonium zirconium ennea*isopropoxide*.

<sup>1</sup> Bradley and Wardlaw, *J.*, 1951, 280.

The fact that the ennea-*n*-butoxides tended to reflux rather than sublime led to attempts to measure b. p.s in a conventional semimicro-vacuum distillation apparatus. This proved unsatisfactory and a special apparatus was designed which allowed b. p.s to be measured at various pressures under total reflux. Rigid standardisation was necessary to ensure accuracy (cf. Bradley *et al.*<sup>2</sup>). The results are given in the form of plots of  $\log P$  against  $1/T$ , and straight lines of the familiar form  $\log P = a - b/T$  are obtained. These results are summarised in Table 3, where  $T_{5.0}$ ,  $L_v$ , and  $\Delta S_{5.0}$  are respectively the b. p. under 5.0 mm. pressure, the molar heat of vaporisation, and the entropy of vaporisation at 5.0 mm. pressure. The agreement between the duplicate sets of figures for lithium zirconium ennea*is*opropoxide and for zirconium tetra*is*opropoxide shows that the results are comparable both among themselves and to a less extent with those of Bradley,

TABLE 2.

Compound	Mol. wt.	Mol. complexity	Compound	Mol. wt.	Mol. complexity
$LiZr_2(OEt)_9$ .....	605	1.0	$NaZr_2(OPr^i)_9$ .....	720	1.0
$LiZr_2(OPr^i)_9$ .....	703	1.0	$Et_4NZr_2(OPr^i)_9$ .....	540	0.65
$LiZr_2(OPr^i)_9, Pr^iOH$ ...	763	1.0			

TABLE 3.

Compound	<i>a</i>	<i>b</i>	$T_{5.0}$	$L_v$	$\Delta S_{5.0}$	Compound	<i>a</i>	<i>b</i>	$T_{5.0}$	$L_v$	$\Delta S_{5.0}$
$LiZr_2(OPr^n)_9$	14.4	7500	249°	34.3	65.7	$NaZr_2(OBu^n)_9$	13.0	6830	269	31.2	57.6
$LiZr_2(OPr^i)_9$	9.1	4150	219	19.0	38.6	$KZr_2(OBu^n)_9$	11.4	6060	292	27.7	49.0
"	9.1	4160	221	19.0	38.4	$Zr(OPr^i)_4$ ...	16.3	7390	202	33.8	71.2
$LiZr_2(OBu^n)_9$	13.4	7000	278	32.0	58.1	$Zr(OPr^i)_4^*$ ...	15.2	6895	204	31.5	66.0
$LiZr_2(OBu^s)_9$	14.2	6910	238	31.6	61.8	$Zr(OBu^t)_4^\dagger$	9.9	3330	89	15.2	42.0
$NaZr_2(OPr^i)_9$	9.9	4590	222	21.0	42.4						

\* Ref. 3.

† Ref. 2.

Mehrotra, Swanwick, and Wardlaw.<sup>3</sup> The volatility of the double alkoxides coupled with the general involatility of their products of hydrolysis was of practical importance when purifying the former. The stabilities of the ennea-alkoxides varied and were dependent both on the alkyl group and on the alkali metal concerned. Thus the ennea-*n*-butoxides of lithium, sodium, and potassium sublimed without change in the alkali metal : zirconium ratio; so also did the solvated lithium zirconium ennea*is*opropoxide and sodium zirconium ennea*is*opropoxide. With potassium zirconium ennea*is*opropoxide an initial ratio of 0.504 decreased to 0.485 on sublimation, whilst with lithium zirconium ennea-*sec.*-butoxide the Li : Zr ratio changed from 0.500 to 0.439 after one sublimation. On the other hand, the mixed ennea-alkoxide  $LiZr_2(OEt)_4(OBu^t)_5$  sublimed unchanged even under the drastic conditions of 200°/7.0 mm.

Most alkali zirconium double alkoxides are like the single alkoxides of aluminium and of zirconium and unlike those of the alkali metals in being soft solids which are very soluble in non-polar solvents. They differ similarly in melting and volatilising without decomposition when heated *in vacuo*, except for the salt  $[Et_4N][Zr_2(OPr^i)_9]$ . This compound is also exceptional in its osmotic properties, for whilst the lithium and the sodium zirconium ennea*is*opropoxides are both monomeric in boiling benzene or *isopropyl* alcohol the tetraethylammonium salt is associated (mol. complexity 1.5) in the first and dissociated (mol. complexity 0.65) in the second solvent. Moreover, the entropy of vaporisation ( $\Delta S_{5.0}$ ) for lithium zirconium ennea*is*opropoxide is even lower than that of zirconium *tert.*-butoxide,<sup>2</sup> so the former cannot dissociate on evaporation; this reinforces the conclusion that  $LiZr_2(OPr^i)_9$  is monomeric in the vapour phase. It is very probable, therefore, that the alkali zirconium alkoxides are covalent. Confirmation is provided by comparing the b. p.s at 15 mm. of  $LiZr_2(OPr^i)_9$  (extrapolated from Table 3) and of the hydrocarbon

<sup>2</sup> Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4202.

<sup>3</sup> Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

containing an equal number of carbon atoms,  $n\text{-C}_{27}\text{H}_{56}$  (interpolated from Karrer<sup>4</sup>). These are 248° and 276°, and the fact that the lithium compound boils at the lower temperature suggests that the screening effect of the *isopropoxide* groups is sufficiently complete to cause it to behave as a highly-branched hydrocarbon. The same must apply to  $\text{NaZr}_2(\text{OPr})_9$  and explains the similarity of its b. p. to that of the lithium analogue. As covalent compounds, the alkali zirconium alkoxides may be compared with the alkali ion complexes, their alkyls, and neutral covalent complexes. They obviously have little in common with the first group, most of which are salt solvates, or with the second, which are all polymerised with only the lithium derivatives volatile. They are, however, related to the third group more closely and it is of interest to reconsider the evidence for the covalent nature of the latter. In fact, it has depended mainly on the solubilities, often only slight, of the neutral alkali-metal complexes in non-polar solvents. Additional evidence was sometimes provided by an m. p. or the non-existence of corresponding compounds derived from isomers of the parent compound, but in no case did volatility unaccompanied by decomposition occur. It follows that the covalent character of the alkali zirconium alkoxides has been established with considerably greater certainty, since not only do they have very high solubilities in non-polar solvents and invariably melt if the pressure is high enough to prevent sublimation, but they can be distilled *in vacuo* without charring.

The sodium zirconium enneaoxide was very soluble in ethyl alcohol but addition of a trace of water converted it into a crystalline compound which was sparingly soluble even in hot alcohol and could be recrystallised from hot benzene or toluene. It was also formed by adding excess of sodium ethoxide to a solution of any hydrolysed zirconium ethoxide having an ethoxide : zirconium ratio within the range 2.0—3.9. A hydrolysed solution of zirconium *n*-propoxide gave a substance of very similar solubility and appearance when similarly treated, but hydrolysed zirconium *n*-butoxide or *isopropoxide* gave gums. Analysis showed the composition of the crystalline compounds to be  $\text{Na}_2\text{Zr}_3\text{O}(\text{OR})_{12}$  with  $\text{R} = \text{Et}$  or  $\text{Pr}^n$ . The composition of the ethoxide was unchanged by ten consecutive crystallisations from benzene and it appeared to be involatile. The methoxide was obtained as a microcrystalline powder by alcohol interchange of the ethoxide with methyl alcohol. It was practically insoluble in either boiling methyl alcohol or benzene and was reconverted into the ethoxide by alcohol interchange. These results throw further light on the discrepancies between the work of Meerwein and Bersin<sup>5</sup> and that of Bradley and Wardlaw<sup>1</sup> on the preparation and properties of zirconium ethoxide and the sodium zirconium ethoxide. Thus Meerwein and Bersin obtained compounds of the type  $\text{NaH}[\text{Zr}(\text{OR})_6]$ , where  $\text{R} = \text{Me}$  or  $\text{Et}$ , from reactions of alcoholic solutions of zirconium tetrachloride with sodium alkoxides. These compounds were sparingly soluble in alcohol but were crystallised from hot xylene. By treating the sodium zirconium alkoxide with the requisite amount of alcoholic hydrogen chloride, Meerwein and Bersin claimed to have obtained zirconium tetramethoxide and tetraethoxide as compounds soluble in benzene and which neutralised one equivalent of sodium methoxide when titrated with thymolphthalein as indicator. When Bradley and Wardlaw repeated this work they obtained a crystalline sodium zirconium ethoxide which was also insoluble in alcohol and soluble in hot benzene or xylene but their analytical data did not support the formula  $\text{NaH}[\text{Zr}(\text{OEt})_6]$  but were close to that for a hydrolysed product  $\text{Na}_4\text{Zr}_6(\text{OEt})_{21}(\text{OH})_7$ . Moreover, they found that pure zirconium tetraethoxide, prepared by another method, neutralised only half an equivalent of sodium ethoxide and that it was sparingly soluble in benzene or ethyl alcohol. Titration of zirconium tetraethoxide with sodium ethoxide has now confirmed Bradley and Wardlaw's results. When excess of sodium ethoxide was added to the tetraethoxide a small quantity of crystals was formed but with the composition  $\text{Na}_2\text{Zr}_3\text{O}(\text{OEt})_{12}$  which is close to that of Bradley and Wardlaw's product. On the other hand, the product isolated from the

<sup>4</sup> Karrer, "Organic Chemistry," New York, 1935, p. 30.

<sup>5</sup> Meerwein and Bersin, *Annalen*, 1929, 476, 113.

reaction in which zirconium tetraethoxide was just neutralised with sodium ethoxide was the sodium zirconium enneaethoxide which was quite soluble in alcohol. We must therefore conclude that the crystalline product obtained by Meerwein and Bersin was  $\text{Na}_2\text{Zr}_3\text{O}(\text{OEt})_{12}$  and not  $\text{NaH}[\text{Zr}(\text{OEt})_6]$  and that their zirconium tetraethoxide was a product of hydrolysis. This view is supported by Bradley and Wardlaw's observation that the reaction of zirconium tetrachloride with an alcohol is accompanied by a side-reaction which produces water and leads to formation of a hydrolysed zirconium alkoxide. Also, the properties of Meerwein and Bersin's zirconium "tetraethoxide" are consistent with those of a hydrolysis product. Thus their product was soluble in alcohol and benzene and was involatile whereas Bradley and Wardlaw found, and we have confirmed, that the tetraethoxide is very sparingly soluble and sublimes *in vacuo*, whilst hydrolysed products of zirconium ethoxide with ethoxide : zirconium ratios of 2.0—3.5 are highly soluble in cold alcohol.

#### EXPERIMENTAL

*Apparatus.*—Special precautions of the type already described<sup>2</sup> were taken to exclude moisture, and all-glass apparatus was used.

*Materials.*—The zirconium tetrachloride, zirconyl chloride hydrate, lithium, sodium, potassium, and calcium used were all of laboratory reagent grade.

*Analysis.*—Zirconium was determined gravimetrically as  $\text{ZrO}_2$ . Alkali metals were determined in the ammoniacal filtrate after removal of zirconium. The solution was evaporated to dryness with the aid of an infrared heater. For sodium or potassium the residue was transferred mechanically *via* glazed paper to a platinum dish to which were also added rinsings of the evaporating basin. The dried residue in the platinum dish was then gently heated to remove ammonium chloride and the final residue was dissolved in water and the chloride determined by Mohr's method. For lithium determinations the use of glazed paper was prevented by the deliquescent nature of the chloride, so the first residue was dissolved in water and thus transferred to the platinum dish. Calcium was determined after removal of zirconium by precipitation as the oxalate followed by titration with potassium permanganate.<sup>6</sup> Thallium was determined as iodide<sup>6</sup> after removal of zirconium. Methoxide, ethoxide, and *isopropoxide* were determined by Bradley, Halim, and Wardlaw's method.<sup>7</sup>

*Preparation of Zirconium Alkoxides.*—The tetra alkoxides were prepared either by alcohol interchange with the *isopropoxide isopropanolate*<sup>2,3</sup> or from the tetrachloride<sup>1</sup> or from pyridinium zirconium hexachloride.<sup>8</sup> In addition, it was found convenient to prepare zirconium *isopropoxide* by starting from zirconyl chloride. A solution of zirconyl chloride octahydrate (32 g.) in *isopropyl alcohol* (400 c.c.), benzene (80 c.c.), and hydrochloric acid (40 c.c., *d* 1.18) was azeotropically dehydrated, and the anhydrous solution was then treated with excess of ammonia. After separation of ammonium chloride the filtrate was evaporated to dryness under reduced pressure, and the residue recrystallised from *isopropyl alcohol*. The crystalline fraction (20 g. Found: Zr, 24.4;  $\text{Pr}^{\text{I}}\text{O}$ , 72.8%) was near in composition to the *isopropoxide isopropanolate* (Calc.: Zr, 23.5;  $\text{Pr}^{\text{I}}\text{O}$ , 76.2%), whilst the residue obtained from the mother liquor (9 g. Found: Zr, 38.8;  $\text{Pr}^{\text{I}}\text{O}$ , 48.9%;  $\text{Pr}^{\text{I}}\text{O}/\text{Zr}$ , 1.95) was substantially "zirconyl" *isopropoxide*. The crystalline fraction was further purified by distillation at 200°/0.5 mm. followed by three recrystallisations of the distillate from *isopropyl alcohol*. The final product (10 g.) was the *isopropoxide isopropanolate* [Found: Zr, 23.8;  $\text{Pr}^{\text{I}}\text{O}$ , 75.3. Calc. for  $\text{Zr}_2(\text{OPr}^{\text{I}})_8$ ,  $2\text{Pr}^{\text{I}}\text{OH}$ : Zr, 23.5;  $\text{Pr}^{\text{I}}\text{O}$ , 76.2%].

*Sodium Zirconium Enneamethoxide.*—Sublimed (360°/0.005 mm.) zirconium tetramethoxide (4.8 g.) was treated with a solution of sodium (0.255 g.) in methyl alcohol (50 c.c.). The solution was evaporated under reduced pressure, and the residue heated at 290°/0.02 gave a white sublimate [Found: Na, 5.04; Zr, 38.4.  $\text{NaZr}_2(\text{OMe})_9$  requires Na, 4.75; Zr, 37.6%]. Although this sublimate was not the pure *enneamethoxide* it is noteworthy that it was more volatile than zirconium tetramethoxide.

*Lithium Zirconium Enneaethoxide.*—To a solution of lithium (0.144 g.) in ethyl alcohol

<sup>6</sup> Scott and Furman, "Standard Methods of Chemical Analysis," New York, 1939, Vol. 1, pp. 211, 942.

<sup>7</sup> Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

<sup>8</sup> Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032.

(65 c.c.) was added zirconium tetraethoxide (11 g.), and the solution boiled for  $\frac{1}{2}$  hr. Evaporation failed to induce crystallisation and the residue finally obtained was distilled ( $260^{\circ}/0.2$  mm.) and gave a glassy distillate (7 g.) (Found: Li, 1.30; Zr, 31.5; EtO, 65.4%; Li/Zr, 0.54). Recrystallisation from benzene gave a microcrystalline *product* [Found: Li, 1.43; Zr, 30.5; EtO, 68.3.  $\text{LiZr}_2(\text{OEt})_9$  requires Li, 1.17; Zr, 30.7; EtO, 68.2%].

*Sodium Zirconium Enneaethoxide.*—Zirconium tetraethoxide (22.6 g.) was treated with the requisite quantity of boiling alcoholic 0.517N-sodium ethoxide (80.5 c.c.). The cooled solution was filtered to remove a small quantity of crystals and the filtrate was evaporated to dryness and the residue distilled at  $230^{\circ}/0.1$  mm. The soft crystalline sublimate (18.3 g.) melted in a sealed tube under nitrogen over a range of  $165\text{--}305^{\circ}$ . A sample was heated under nitrogen until a clear melt was obtained, and then allowed to cool slowly and crystallise. Then it was reheated until about two-thirds was molten whereupon the liquid was decanted off the crystals and both were allowed to cool. Analysis showed that both fractions were the *enneaethoxide* (Found, for lower-melting fraction: Na, 3.73; Zr, 29.9; EtO, 64.8. Found, for higher-melting fraction: Na, 3.85; Zr, 30.0; EtO, 64.6.  $\text{NaZr}_2(\text{OEt})_9$  requires Na, 3.76; Zr, 29.9; EtO, 66.4%). The product readily dissolved in ethyl alcohol or benzene but the solutions were very easily hydrolysed.

*Calcium Zirconium Octadecaethoxide.*—Zirconium tetraethoxide (30 g.) was dissolved in ethyl alcohol (150 c.c.), and the solution refluxed with calcium (1.11 g.) for 12 hr. The cooled solution gave a white crystalline product (30 g.) [Found: Ca, 3.15; Zr, 29.1; EtO, 66.2.  $\text{CaZr}_4(\text{OEt})_{18}$  requires Ca, 3.30; Zr, 30.0; EtO, 66.7%]. The *compound* could be crystallised from hot benzene and was distilled at  $280^{\circ}$  *in vacuo*.

*Lithium Zirconium Ennea-n-propoxide.*—(a) Lithium (0.371 g.) was dissolved in a solution of zirconium *n*-propoxide (35 g.) in *n*-propanol (120 c.c.). Crystallisation could not be induced so the solution was evaporated to dryness and the residue on distillation ( $226^{\circ}/0.3$  mm.) gave a glassy distillate (34 g.) [Found: Li, 0.94; Zr, 25.5.  $\text{LiZr}_2(\text{OPr})_9$  requires Li, 0.96; Zr, 25.3%]. (b) Lithium zirconium *enneaisopropoxide* (10 g.) was caused to react with *n*-propyl alcohol (20 c.c.) in benzene (50 c.c.) and the liberated *isopropyl* alcohol was removed by azeotropic distillation. The solution was then evaporated to dryness, and the residue distilled ( $250^{\circ}/0.5$  mm.) to give a glassy solid (Found: Li, 0.98; Zr, 25.7%). The *lithium zirconium ennea-n-propoxide* gave the following vapour pressures:  $211^{\circ}/0.41$  mm.;  $216^{\circ}/0.55$ ;  $226^{\circ}/0.90$ ;  $235^{\circ}/2.0$ ;  $240^{\circ}/3.0$ ;  $244^{\circ}/4.0$ ;  $250^{\circ}/5.0$ ;  $263^{\circ}/9.3$ . The distillate was analysed (Found: Li, 0.98; Zr, 25.7%).

*Lithium Zirconium Ennea-n-butoxide.*—Zirconium *n*-butoxide (32 g.) in *n*-butyl alcohol (100 c.c.) was boiled with lithium (0.290 g.) until all was dissolved. After evaporation to dryness the residue was distilled ( $221\text{--}235^{\circ}/0.3$  mm.) giving a colourless glass [Found: Li, 0.82; Zr, 21.7.  $\text{LiZr}_2(\text{OBu})_9$  requires Li, 0.82; Zr, 21.5%]. The following vapour pressures were obtained:  $230^{\circ}/0.32$  mm.;  $237^{\circ}/0.46$ ;  $240^{\circ}/0.65$ ;  $246^{\circ}/0.80$ ;  $250^{\circ}/1.1$ ;  $256^{\circ}/1.5$ ;  $262^{\circ}/2.1$ ;  $268^{\circ}/3.3$ ;  $274^{\circ}/4.3$ . The distillate was analysed (Found: Li, 0.82; Zr, 21.8%).

*Sodium Zirconium Ennea-n-butoxide.*—(a) Sodium (1.08 g.) was dissolved in *n*-butyl alcohol (100 c.c.) containing zirconium tetrabutoxide (34 g.). After evaporation of the solution to dryness the residue was distilled ( $218\text{--}225^{\circ}/0.37$  mm.) giving a white partially crystalline *product* (31 g.) which was very soluble in *n*-butyl alcohol and in benzene [Found: Na, 2.85; Zr, 21.3.  $\text{NaZr}_2(\text{OBu})_9$  requires Na, 2.64; Zr, 21.1%].

(b) Sodium zirconium *enneaisopropoxide* (10 g.) was caused to react with *n*-butyl alcohol (20 c.c.) in benzene (100 c.c.) and the liberated *isopropyl* alcohol was removed by azeotropic distillation. The solution was evaporated to dryness, and the residue distilled (Found: Zr, 21.2%). The following vapour pressures were obtained:  $220^{\circ}/0.29$  mm.;  $229^{\circ}/0.50$ ;  $232^{\circ}/0.59$ ;  $238^{\circ}/0.9$ ;  $256^{\circ}/2.6$ ;  $263^{\circ}/3.5$ ;  $242^{\circ}/1.2$ ;  $248^{\circ}/1.6$ ;  $252^{\circ}/2.0$ . The distillate was analysed (Found: Na, 2.85; Zr, 21.3%).

*Potassium Zirconium Ennea-n-butoxide.*—Potassium (2.65 g.) was dissolved in a solution of zirconium tetrabutoxide (26 g.) in butyl alcohol (80 c.c.) under nitrogen and the solution was evaporated to dryness. Distillation of the residue gave a pale yellow distillate (24 g.) (Found: K, 7.60; Zr, 19.5%) to which more zirconium butoxide (9.6 g.) was added and the mixture was distilled *in vacuo* to give a colourless distillate [Found: K, 4.44; Zr, 20.8.  $\text{KZr}_2(\text{OBu})_9$  requires K, 4.45; Zr, 20.7%]. The following vapour pressures were determined:  $238^{\circ}/0.38$  mm.;  $242^{\circ}/0.48$ ;  $250^{\circ}/0.66$ ;  $252^{\circ}/0.80$ ;  $256^{\circ}/0.92$ ;  $258^{\circ}/1.1$ ;  $262^{\circ}/1.4$ . The distillate was analysed (Found: K, 4.44; Zr, 20.8%).

*Lithium Zirconium Enneaisopropoxide isopropanolate*.—(a) Zirconium isopropoxide isopropanolate (127 g.) was refluxed in isopropyl alcohol (500 c.c.) with lithium (1.53 g.) until all was dissolved. The residue obtained after evaporation of the solvent was distilled ( $193^\circ/1.0$  mm.) and crystallised from isopropyl alcohol (300 g.). The compound (120 g.) was very soluble in benzene, light petroleum, ether, or acetone and it melted at  $206^\circ$  [Found: Li, 0.90; Zr, 23.4;  $\text{Pr}^{\text{I}}\text{O}$ , 76.4; active H, 0.134.  $\text{LiZr}_2(\text{OPr}^{\text{I}})_9, \text{Pr}^{\text{I}}\text{OH}$  requires Li, 0.89; Zr, 23.35;  $\text{Pr}^{\text{I}}\text{O}$ , 75.6; active H, 0.129%]. The compound sublimed at  $160^\circ/0.2$  mm. (Found: Li, 0.95; Zr, 24.7;  $\text{Pr}^{\text{I}}\text{O}$ , 75.8%).

(b) Lithium zirconium enneaethoxide (10 g.) was caused to react with isopropyl alcohol (200 c.c.) until no more ethyl alcohol was liberated. The enneaaisopropoxide isopropanolate (9 g., m. p.  $204\text{--}206^\circ$ ) was obtained after twice recrystallising it from isopropyl alcohol.

*Lithium Zirconium Enneaisopropoxide*.—The foregoing product (19.5 g.) was heated at  $200^\circ$  under nitrogen at 10 mm. pressure and the pressure was gradually reduced to 2 mm., causing effervescence and melting. When effervescence ceased the mobile liquid was distilled and gave a colourless distillate which set to a hard solid [Found: Li, 0.965; Zr, 25.4.  $\text{LiZr}_2(\text{OPr}^{\text{I}})_9$  requires Li, 0.96; Zr, 25.3%]. The following vapour pressures were obtained: (a)  $207^\circ/3.0$  mm.;  $210^\circ/3.5$ ;  $214^\circ/4.0$ ;  $220^\circ/5.0$ ;  $224^\circ/6.0$ ;  $228^\circ/7.0$ ;  $235^\circ/9.0$ . (b)  $208^\circ/2.8$ ;  $217^\circ/4.1$ ;  $223^\circ/5.7$ ;  $230^\circ/7.2$ ;  $238^\circ/9.8$ ;  $232^\circ/7.5$ ;  $228^\circ/5.9$ ;  $221^\circ/5.1$ . The distillates were analysed [Found: Li, (a) 0.96, (b) 0.98; Zr, (a) 25.4, (b) 25.4%].

*Sodium Zirconium Enneaisopropoxide*.—Zirconium isopropoxide isopropanolate (104 g.) and sodium (3.04 g.) were dissolved in boiling isopropyl alcohol (400 c.c.) and the solution evaporated to dryness. The residue was distilled at  $260^\circ/1$  mm. and gave a hard solid distillate (92 g., m. p.  $168\text{--}180^\circ$  sealed tube) [Found: Na, 3.05; Zr, 24.9.  $\text{NaZr}_2(\text{OPr}^{\text{I}})_9$  requires Na, 3.12; Zr, 24.7%]. A sample (1.853 g.) was sublimed, giving a residue (0.287 g.;  $\text{Pr}^{\text{I}}\text{O}$ , 44%) and a sublimate (1.543 g. Found: Na, 3.07; Zr, 24.9;  $\text{Pr}^{\text{I}}\text{O}$ , 73.1%). The following vapour pressures were obtained:  $196^\circ/1.5$  mm.;  $202^\circ/2.0$ ;  $210^\circ/3.0$ ;  $215^\circ/4.0$ ;  $220^\circ/4.6$ ;  $228^\circ/6.0$ .

*Potassium Zirconium Enneaisopropoxide*.—Zirconium isopropoxide isopropanolate (19.76 g.) in benzene (30 c.c.) was titrated with isopropanolic potassium isopropoxide (136.1 c.c., 0.198N), thymolphthalein being used as indicator. The end-point corresponded to  $\text{K/Zr} = 0.528$ . After removal of solvent the residue was sublimed at  $200^\circ/0.2$  mm. [Found: K, 5.20; Zr, 24.1;  $\text{Pr}^{\text{I}}\text{O}$ , 72.9.  $\text{KZr}_2(\text{OPr}^{\text{I}})_9$  requires K, 5.19; Zr, 24.2;  $\text{Pr}^{\text{I}}\text{O}$ , 70.6%]. The compound was resublimed without change in composition and it was very soluble in ether, isopropyl alcohol, benzene, carbon tetrachloride, or light petroleum and it could not be crystallised from any of these solvents.

*Thallium Zirconium Enneaisopropoxide*.—Thallium (7 g.) was caused to react with vapour from boiling ethyl alcohol (100 c.c.) in a stream of oxygen (cf. Sidgwick and Sutton<sup>9</sup>) and the alcoholic solution of thallous ethoxide was interchanged with isopropyl alcohol (300 c.c.) and the ethyl alcohol removed by fractional distillation. To the resulting solution, zirconium isopropoxide isopropanolate (24 g.) was added and the solution was then concentrated to about 50 c.c. and allowed to cool. Large plate-like crystals which were deposited were filtered off and dried at  $20^\circ/0.5$  mm. [Found: Tl, 20.8; Zr, 19.9.  $\text{TlZr}_2(\text{OPr}^{\text{I}})_9$  requires Tl, 22.2; Zr, 19.9%]. The compound was sublimed at  $220^\circ/0.5$  mm. and gave needle crystals which contained thallium and zirconium.

*Tetraethylammonium Zirconium Enneaisopropoxide*.—Tetraethylammonium iodide (100 g.) in water was added to a boiling aqueous solution (3 l.) of lead chloride (72 g.). Lead iodide was filtered off, the filtrate evaporated to dryness, and the residue extracted with alcohol (500 c.c.). The alcoholic extract was concentrated until the tetraethylammonium chloride crystallised. The latter was dried at  $100^\circ/0.1$  mm., dissolved in isopropyl alcohol (65.5 c.c.), and then treated with the requisite amount of isopropanolic sodium isopropoxide (200 c.c., 0.090N). The filtered solution was standardised acidimetrically and the requisite amount (190 c.c.) was treated with a solution of zirconium isopropoxide isopropanolate (9.3 g.) in benzene (20 c.c.). Evaporation of solvent left a brown gum [Found: Zr, 20.0.  $(\text{Et}_4\text{N})\text{Zr}_2(\text{OPr}^{\text{I}})_9$  requires Zr, 21.6%]. The compound, heated at  $180^\circ/0.1$  mm., suddenly effervesced and the pressure rose to 10 mm. before reverting to 1.0 mm. A colourless liquid distilled over at  $194^\circ/1.0$  mm. and was evidently zirconium tetraaisopropoxide since it crystallised from isopropyl alcohol in characteristic fashion. Further evidence for the dissociation of the tetraethylammonium enneaaisopropoxide was afforded by an alkaline condensate collected in the cold trap. In another preparation the

<sup>9</sup> Sidgwick and Sutton, *J.*, 1930, 1461.

*tetraethylammonium* compound tended to crystallise from solution on standing. The crystals were dried at  $100^{\circ}/0.5$  mm. [Found: Zr, 21.5; Pr<sup>i</sup>O, 60.2.  $(Et_4N)Zr_2(OPr^i)_6$  requires Zr, 21.6; Pr<sup>i</sup>O, 63.0%].

*Lithium Zirconium Ennea-sec.-butoxide*.—Lithium zirconium ennea-isopropoxide isopropanolate (20 g.) was caused to react with *sec.*-butyl alcohol (40 c.c.) in benzene (100 c.c.) and the liberated isopropyl alcohol was removed by fractional distillation. The resulting solution was evaporated to dryness and the residue was distilled at  $200$ — $210^{\circ}/0.2$  mm., giving a colourless solid distillate [Found: Li, 0.75; Zr, 22.3.  $LiZr_2(OBu^s)_6$  requires Li, 0.82; Zr, 21.5%]. The following vapour pressures were obtained:  $217^{\circ}/1.3$  mm.;  $224^{\circ}/2.0$ ;  $230^{\circ}/3.1$ ;  $233^{\circ}/3.5$ ;  $236^{\circ}/4.5$ ;  $238^{\circ}/5.0$ ;  $241^{\circ}/6.0$ ;  $248^{\circ}/8.4$ . The distillate was analysed (Found: Li, 0.63; Zr, 22.4%).

*Lithium Zirconium Tetraethoxide Penta-tert.-butoxide*.—Lithium zirconium enneaethoxide (21.4 g.) was caused to react with *tert.*-butyl alcohol (34 c.c.) in benzene (300 c.c.) and the liberated alcohol removed by azeotropic fractional distillation. Evaporation of the solvent gave a solid (28.2 g.) [Found: Zr, 23.8; EtO, 24.5.  $LiZr_2(OEt)_4(OBu^t)_6$  requires Zr, 24.8; EtO, 24.5%]. The compound was sublimed at  $140^{\circ}/0.2$  mm. (Found: Zr, 24.7; EtO, 24.9%) and distilled at  $168$ — $173^{\circ}/0.3$ — $0.5$  mm. (Found: Li, 0.95; Zr, 24.9; EtO, 24.7%). The compound was very soluble in benzene but was crystallised from *tert.*-butyl alcohol and the crystals of *solvate* were dried at  $20^{\circ}/0.2$  mm. [Found: Zr, 23.3; EtO, 22.9.  $LiZr_2(OEt)_4(OBu^t)_6 \cdot Bu^tOH$  requires Zr, 22.5; EtO, 22.3%].

*Lithium Zirconium Tetraisopropoxide Penta-tert.-butoxide*.—Lithium zirconium ennea-isopropoxide isopropanolate (20 g.) was caused to interchange with *tert.*-butyl alcohol in the foregoing manner and the solid *product* finally obtained was dried at  $80^{\circ}/0.5$  mm. [Found: Zr, 22.6; Pr<sup>i</sup>O, 29.8.  $LiZr_2(OPr^i)_4(OBu^t)_6$  requires Zr, 23.1; Pr<sup>i</sup>O, 29.9%].

*Lithium Zirconium Tetraisopropoxide Penta-tert.-amyloxide*.—Treatment of lithium zirconium 9-isopropoxide isopropanolate (20 g.) with *tert.*-amyl alcohol followed by removal of isopropyl alcohol and excess of *tert.*-amyl alcohol left a brown liquid [Found: Zr, 20.6; Pr<sup>i</sup>O, 26.8.  $LiZr_2(OPr^i)_4(OCMe_2Et)_6$  requires Zr, 21.2; Pr<sup>i</sup>O, 26.1%].

*Disodium Trizirconium Oxydodecaethoxide*.—(a) Zirconyl chloride octahydrate (100 g.), dissolved in ethyl alcohol (500 c.c.), was azeotropically dehydrated, benzene (80 c.c.) being used to form the tertiary azeotrope. More benzene (500 c.c.) was then added, and the solution treated with excess of ammonia. After separation of the ammonium chloride the filtrate was treated with a solution of sodium (7 g.) in alcohol (300 c.c.) and then fractionated to remove benzene, whereupon a white solid was precipitated. This was filtered off and twice recrystallised from toluene, giving large dense plates (44 g.) [Found: Na, 5.25; Zr, 31.3; EtO, 61.6.  $Na_2Zr_3O(OEt)_{12}$  requires Na, 5.25; Zr, 31.2; EtO, 61.7%]. The compound was non-volatile up to  $240^{\circ}/0.5$  mm. A sample (5 g.) was recrystallised ten times from toluene (500 c.c.) and gave large plates (3.5 g.) (Found: Na, 5.24; Zr, 31.5; EtO, 61.3%). (b) Zirconium oxide ethoxide (2.8 g.; EtO/Zr, 2.62) was treated with excess of alcoholic sodium ethoxide, and the solution concentrated to 40 c.c. The crystals produced were recrystallised from toluene and gave dense needles (1 g.) (Found: Na, 5.1; Zr, 31.7; EtO, 60.4%). (c) Zirconium oxide ethoxide (8 g.; EtO/Zr, 2.94) was likewise treated with excess of alcoholic sodium ethoxide and gave a precipitate (7 g.) which was recrystallised from toluene (400 g.), giving a crystalline product (5 g.) which was dried at  $100^{\circ}/0.5$  mm. (Found: Zr, 31.3; EtO, 61.1%). The sodium zirconium oxydodecaethoxide was similarly obtained by starting with zirconium oxide ethoxides having ratios of EtO/Zr = 3.47 or 3.90.

*Disodium Trizirconium Oxydodeca-n-propoxide*.—Zirconium tetra-*n*-propoxide (10 g.) in *n*-propyl alcohol (200 c.c.) was treated with excess of propanolic sodium *n*-propoxide (40 c.c., *n*) and a white precipitate (4 g.) slowly appeared; this was separated and dried at  $100^{\circ}/0.5$  mm. (Found: Na, 5.02; Zr, 26.0%). The substance recrystallised from boiling benzene (1.5% solution) in large dense plates [Found: Na, 4.34; Zr, 26.4.  $Na_2Zr_3O(OPr^n)_{12}$  requires Na, 4.40; Zr, 26.2%].

*Disodium Dichlorodiisopropoxycobaltate*.—(a) Cobaltous chloride hexahydrate (14 g.) was dehydrated over a small flame, and the anhydrous salt dissolved in isopropyl alcohol. This solution, added to a solution of sodium (2.3 g.) in isopropyl alcohol (200 g.), caused immediate precipitation of a deep purple solid. After being refluxed for 10 min. the solid was filtered off and dried at  $100^{\circ}/0.5$  mm. [Found: Na, 15.9; Co, 19.5; Cl, 24.5.  $Na_2[CoCl_2(OPr^i)_2]$  requires Na, 15.6; Co, 20.1; Cl, 24.1%]. (b) Sodium zirconium ennea-isopropoxide (5.8 g.) was refluxed

for 10 min. with a solution of cobaltous chloride in *isopropyl alcohol* (31.7 c.c., 0.249N). The purple precipitate (1 g.) was dried at 100°/0.5 mm. (Found: Na, 14.9; Zr, 5.3; Co, 13.5; Cl, 23.5%). This substance was evidently Na<sub>2</sub>[CoCl<sub>2</sub>(OPr<sup>i</sup>)<sub>2</sub>] contaminated with some zirconium *isopropoxide*. Evaporation of the foregoing filtrate gave a purple solid which was extracted

TABLE 4.

Zr(OR) <sub>4</sub>		M(OR)				M/Zr
R	Wt. taken (g.)	M	Normality	Req. (c.c.)	Calc. (c.c.)	
Et	0.929 *	Na	0.111	14.99	15.40	0.487
"	0.518 *	"	"	8.04	8.59	0.468
"	4.165	"	0.558	14.05	13.74	0.511
Pr <sup>n</sup>	2.829	Na	0.901	5.05	4.79	0.527
Bu <sup>n</sup>	6.218	Na	1.085	7.74	7.47	0.518
"	2.938	"	"	3.65	3.53	0.517
Pr <sup>i</sup> †	5.739	Na	0.0868	88.2	85.3	0.517
"	4.415	"	"	67.0	65.7	0.511
"	0.648	(NEt <sub>4</sub> )	0.088	10.15	9.50	0.534
"	2.645	"	"	41.3	38.8	0.532

\* Ref. 1.

† Zr(OPr<sup>i</sup>)<sub>4</sub>, Pr<sup>i</sup>OH taken.

with benzene and left a purple residue but gave a practically colourless extract which was evaporated to dryness. The residue was recrystallised from *isopropyl alcohol* and the crystalline zirconium *isopropoxide isopropanolate* was dried at 20°/0.5 mm. [Found: Zr, 24.2; Pr<sup>i</sup>O, 75.5. Calc. for Zr(OPr<sup>i</sup>)<sub>4</sub>, Pr<sup>i</sup>OH: Zr, 23.5; Pr<sup>i</sup>O, 76.2%].

*Titrations.*—The appropriate alcohol was used as solvent in all cases except that zirconium *isopropoxide* required the addition of some benzene to enhance its solubility. The alkali alkoxide solutions were prepared by dissolving in the alcohol a suitable weight of the metal, cut and weighed under benzene, under a guard tube filled with silica gel and pellets of potassium hydroxide. The titration assembly, consisting of a burette fitted into a titration flask with a grooved rubber bung, was similarly guarded. Solid indicator was used. The alkali alkoxide solutions were standardised against hydrochloric acid, potassium hydrogen phthalate, or benzoic acid. The results are presented in Table 4.

*Molecular-weight Determinations.*—Ebullioscopic measurements were made in a suitably

TABLE 5.

Compound	Range of <i>m</i> (g.)	Solvent	<i>T/m</i>	<i>M</i>	
				Found	Calc.
LiZr <sub>2</sub> (OEt) <sub>9</sub> .....	0.4786—2.963	EtOH	0.0603°	605	595
NaZr <sub>2</sub> (OEt) <sub>9</sub> .....	0.1326—1.658	C <sub>6</sub> H <sub>6</sub>	0.0631	1240	"
LiZr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> .....	0.2419—1.101	"	0.0955	820	611
LiZr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> .....	0.2980—1.521	"	0.0638	1230	721
NaZr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> .....	0.3244—1.991	"	0.0963	815	737
".....	0.3328—1.023	"	0.0971	808	"
LiZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	0.2532—0.955	"	0.0589	1330	847
NaZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	0.3349—2.119	"	0.0915	858	863
KZr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> .....	0.2151—2.623	"	0.0827	952	879
".....	0.2291—2.482	"	0.0886	886	"
Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>6</sub> , 2Pr <sup>i</sup> OH.....	0.4162—2.032	Pr <sup>i</sup> OH	0.0611	773	775
LiZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> , Pr <sup>i</sup> OH.....	0.3665—2.434	"	0.0620	763	780
LiZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> , Pr <sup>i</sup> OH.....	0.3172—1.136	C <sub>6</sub> H <sub>6</sub>	0.0883	763	"
LiZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	0.3864—1.204	"	0.1033	760	721
NaZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	0.1258—1.432	Pr <sup>i</sup> OH	0.0701	681	737
".....	0.0692—0.9237	"	0.0679	703	"
".....	0.2009—1.261	C <sub>6</sub> H <sub>6</sub>	0.1066	725	"
NaZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> *.....	0.3227—1.940	Pr <sup>i</sup> OH	0.0663	720	"
".....	0.2337—1.859	C <sub>6</sub> H <sub>6</sub>	0.1007	767	"
(Et <sub>4</sub> N) <sup>+</sup> Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	0.5978—1.211	"	0.057	1380	844
".....	0.2400—1.745	Pr <sup>i</sup> OH	0.0874	541	"
KZr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .....	1.041—1.814	C <sub>6</sub> H <sub>12</sub> †	0.079	904	879
LiZr <sub>2</sub> (OBu <sup>t</sup> ) <sub>9</sub> .....	0.6088—1.884	C <sub>6</sub> H <sub>6</sub>	0.0927	847	847
LiZr <sub>2</sub> (OEt) <sub>4</sub> (OBu <sup>t</sup> ) <sub>5</sub> .....	0.3362—1.427	"	0.1069	737	735

\* Compound which had been stored for 3 months.

† *cycloHexane*, 43.4 c.c., *d* 0.776 g./c.c.; apparatus constant 28.6°/100 g. of solvent/mole of solute.



adapted Menzies-Wright apparatus using a differential water-thermometer.<sup>2</sup> The same amount of solvent (40.0 c.c.), measured directly from a burette into the ebulliometer, was taken in each determination. The apparatus was calibrated for each solvent by using vacuum-distilled azobenzene. The following constants were obtained: Benzene, 31.4°, 31.4°; ethanol, 14.6°, 14.6°; *isopropyl* alcohol, 18.9°, 19.0°. The results are given in Table 5.

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