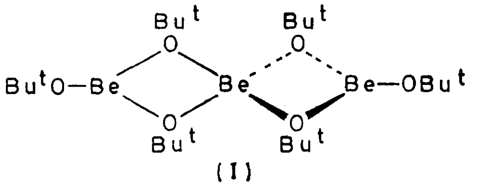
Some Sterically Hindered Beryllium Alkoxides and their Derivatives; Monomeric Beryllium 2,6-Di-t-butylphenoxide

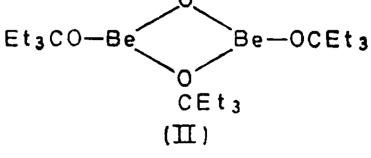
By **R. A. Andersen** and **G. E. Coates,*** Chemistry Department, University of Wyoming, Laramie, Wyoming 82070, U.S.A.

The alkoxides $[Be(OCMe_2Et)_2]_3$ and $[Be(OCMeEt_2)_2]_3$ are trimeric in benzene like the tertiary butoxide. The dimer $[Be(OCEt_3)_2]_2$ has been prepared by a new route. All these give rise to dimeric alkoxyberyllium chloride–tetrahydrofuran complexes, and one gives the complex $Cl_2Be_3(OCMe_2Et)_4$. Beryllium t-butoxide forms no adducts with ammonia, dimethylamine, tri- or tetra-methylethylenediamine, or pyridine, but 4-dimethylaminopyridine gives $Me_2NC_5H_4NBe(OBu^t)_2$. It forms a compound, $Me_3AlBe_3(OBu^t)_6$, on reaction with trimethylaluminium, but the structure of this is not known. Beryllium 2,6-di-t-butylphenoxide is monomeric in benzene, and is unique in this respect.

BERYLLIUM t-BUTOXIDE [1,2] is trimeric in solution in benzene, and on the basis of the observed 2 : 1 ratio of the ^1H n.m.r. resonances has been assigned the structure (I). The structure of a related compound, $Cl_2Be_3(OBu^t)_4$, in which the terminal butoxy-group in compound (I) is replaced by chlorine atoms, has been confirmed crystallographically.[3] Beryllium derivatives of less sterically hindered alcohols,[4] *e.g.* $Be(OMe)_2$ to $Be(OPr^i)_2$, have properties such as insolubility consistent with a polymeric constitution as would result from every beryllium atom having a co-ordination number of four. In the chlorobutoxide, $Cl_2Be_3(OBu^t)_4$, two of the three methyl groups belonging to each bridging t-butoxy are directed away from the central beryllium atom creating steric congestion about the terminal chlorine atoms, but minimizing hindrance about the one four-co-ordinate beryllium atom. We now find that either one or two of these methyl groups can be replaced by ethyl, still giving the trimers $[Be(OCEtMe_2)_2]_3$ and $[Be(OCEt_2Me)_2]_3$. Since $Be(OCEt_3)_2$, which we have prepared by a different route from that described earlier,[1] is a dimer in which the beryllium atoms can only be three-co-ordinate as in structure (II), it is evident that the presence of three ethyl groups attached to the carbon of the bridging alkoxy group is sufficient to prevent the beryllium being four-co-ordinate as the central atom in compound (I).

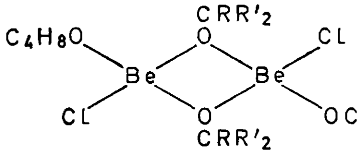


(I)



(II)

The alkoxyberyllium chloride–tetrahydrofuran complexes $RR'_2COBeCl,thf$ ($R = Et$, $R' = Me$; $R = Me$, $R' = Et$; and $R = R' = Et$) are all dimeric, like their t-butoxy analogue.[5] Only one bulky alkoxy group being bound to each metal atom, the normal four-co-ordination results, structure (III).



(III)

If the trimeric alkoxides $[Be(OCEtMe_2)_2]_3$ and $[Be(OCEt_2Me)_2]_3$ have structures similar to (I), then it should be possible to obtain the corresponding alkoxychlorides, analogous to $Cl_2Be_3(OBu^t)_4$. One of these, $Cl_2Be_3(OCMe_2Et)_4$, could be obtained without difficulty, but an attempt at the preparation of $Cl_2Be_3(OCMeEt_2)_4$ yielded a gelatinous, rather than a crystalline, product.

Since the crystal structure of $Cl_2Be_3(OBu^t)_4$ indicates considerable steric congestion about the terminal chlorine atoms, and since the terminal butoxy-groups in compound (I) would be at least as sterically hindered, we explored the extent to which beryllium t-butoxide forms adducts with Lewis acids and bases. No adducts were formed with ammonia, dimethylamine, tri- or tetramethylethylenediamine, nor with pyridine, presumably on account of the difficulty of access to the terminal three-co-ordinate beryllium atoms. Reaction with 4-dimethylaminopyridine results in destruction of the alkoxide bridges and formation of the monomeric adduct, $Me_2NC_5H_4NBe(OBu^t)_2$. So far this is the only known example of a complex of a monomeric beryllium alkoxide.

Beryllium t-butoxide is also depolymerized by reaction with certain alkoxide anions, forming compounds such as potassium tri-t-butoxyberyllate, $KBe(OBu^t)_3$, which will be described elsewhere.

Reaction of beryllium t-butoxide with trimethylaluminium gives the complex $Me_3AlBe_3(OBu^t)_6$ which is monomeric in benzene. The ^1H n.m.r. spectrum of $Me_3AlBe_3(OBu^t)_6$ in benzene solution consists only of two resonances CH_3–Al at τ 10·39 and $(CH_3)_3CO$– at 8·60. The melting point of this complex, 189—190°, is significantly higher than that of beryllium t-butoxide

---

[1] G. E. Coates and A. H. Fishwick, *J. Chem. Soc.* (*A*), 1968, 477.

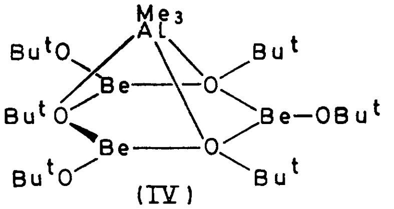
[2] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1968, 823.

[3] H. M. M. Schearer and J. Twiss, personal communication.

[4] M. Arora and R. C. Mehrotra, *Indian J. Chem.*, 1969, **7**, 399.

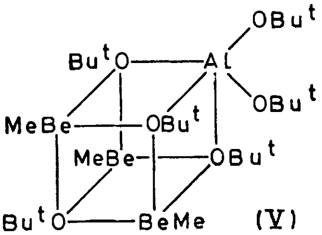
[5] R. A. Andersen, N. A. Bell, and G. E. Coates, *J.C.S. Dalton*, 1972, 577.

(112°). If the trimethylaluminium were bound to one of the terminal butoxy-groups of beryllium t-butoxide, a considerable reduction of symmetry would be expected, with consequently a lower melting point. Speculatively, a more symmetrical cyclic structure (IV) might be considered.



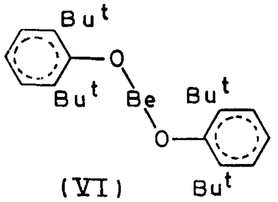
(IV)

Such a structure should give rise to two t-butoxy ^{1}H n.m.r. signals. However, even beryllium t-butoxide gives a single signal in benzene, though it gives the expected two in carbon tetrachloride (it is unwise to use this solvent for alkylaluminium compounds). Structure (IV) would not allow a second trimethylaluminium group to become bound in a similar way. Since methyl–aluminium and methyl–beryllium resonances occur in similar ranges, one cannot exclude the possibility that methyl-t-butoxy exchange took place, giving a product such as (V). An attempt to prepare $(Me_3Al)_2[Be(OBu^t)_2]_3$ was not successful.



(V)

With the object of preparing a monomeric beryllium alkoxide or aryloxide in which the metal has a co-ordination number of two, we allowed diethylberyllium to react with the highly hindered 2,6-di-t-butylphenol and obtained beryllium bis(2,6-di-t-butylphenoxide) (VI) as a colourless air-sensitive material which is



(VI)

monomeric in benzene. In structure (VI) it is probable that the two benzene rings are mutually perpendicular. This compound is probably the first example of a linear O–Be–O system.

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by the use of Schlenck tube, glove-box, and occasionally vacuum-line techniques. Melting points were taken in sealed tubes under argon. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method [6] under standardized conditions. Aluminium was determined gravimetrically as the 8-hydroxyquinoline complex. When feasible the alcohol produced during hydrolysis was isolated quantitatively and weighed. Many of the compounds described below are very sensitive to air and water, and to minimize the number of transfers from one vessel to another, *e.g.* for weighing, yields were in many instances not recorded. In general, yields appeared to be nearly quantitative apart from crystallization and transfer losses, but yields are given in cases when they were relatively low. Unless stated otherwise, ^{1}H n.m.r. spectra were recorded at 100 MHz, with benzene as solvent and reference.

Bis-1,1-*dimethylpropoxyberyllium*, $[Be(OCEtMe_2)_2]_3$.—n-Butyl-lithium (27·5 ml of a 3·20M benzene solution, 0·088 mol) was added to 1,1-dimethylpropanol (8·8 g, 0·088 mol) in diethyl ether (100 ml) at −78°. The mixture was warmed to room temperature and stirred for 30 min. The resulting solution of 1,1-dimethylpropoxylithium was added to beryllium chloride (10·0 g of the bis-diethyl ether complex, 0·044 mol) in ether (100 ml), giving an immediate white precipitate. After the addition, the suspension was stirred for 1 h, lithium chloride was then removed by filtration and solvents were evaporated from the filtrate leaving the white solid alkoxide. The latter had m.p. 48—50° after sublimation at 100—105° (bath temperature) and 10^{-3} mmHg (yield, 5·7 g, 63%) [Found: Be, 4·9%; *M* (cryoscopic, 0·70 and 1·53 wt. % in benzene), 554 and 531. $C_{30}H_{66}O_6Be_3$ requires Be, 4·9%; *M*, 549].

Bis-1-*ethyl*-1-*methylpropoxyberyllium*, $[Be(OCEt_2Me)_2]_3$.—This was similarly prepared from 1-ethyl-1-methylpropanol (12·75 g, 0·125 mol), but in this case removal of solvents after separation of lithium chloride left a rather viscous liquid residue which was distilled, b.p. 120—125° ($<10^{-3}$ mmHg, bath temperature 160—175°). The distillate slowly crystallized at room temperature (argon atmosphere) giving the *alkoxide*, m.p. 38—40° (9·2 g, 70%) [Found: Be, 4·4%; *M* (cryoscopic, 0·87 and 1·29 wt. % in benzene), 614 and 602. $C_{36}H_{78}O_6Be_3$ requires Be, 4·3%; *M*, 633]. The ^{1}H n.m.r. spectrum consisted of a complex multiplet due to $O-CH_2-CH_3$ centred at τ 8·03, two singlets due to $-OCH_3$ centred at τ 8·55, and a multiplet due to $-OCH_2CH_3$ centred at τ 8·91 in area ratio 4 : 3 : 6.

Bis-1,2-*diethylpropoxyberyllium*, $[Be(OCEt_3)_2]_2$.—Similarly prepared from lithium 1,1-diethylpropoxide and beryllium chloride, this was sublimed at 60—70° (bath temperature) and 10^{-3} mmHg, and had a m.p. and i.r. spectrum identical to that of the alkoxide prepared from diethylberyllium and pentan-3-one.[1]

Alkoxyberyllium Chloride–Tetrahydrofuran Complexes.—(a) ($Me_2EtCOBeCl$,thf). The alkoxide $[Be(OCEtMe_2)_2]_3$ (0·87 g) in ether (15 ml) was added to the calculated amount of beryllium chloride bis-diethyl ether complex (1·08 g) in ether (15 ml). The mixture was stirred for 15 min, when evaporation of the ether left a sticky residue. This was dissolved in tetrahydrofuran (3 ml), the solvent evaporated, and the white solid residue crystallized from benzene–hexane (5 : 1) as colourless *rectangles*, m.p. 149—150° [Found: Be, 4·5; Cl, 17·7%, *M* (cryoscopic, 0·67 and 1·00 wt. % in benzene), 370 and 377. $C_{18}H_{38}Be_2Cl_2O_4$ requires Be, 4·4; Cl, 17·5%; *M*, 407]. The complex was sparingly soluble in benzene. (b) $(Et_2MeCOBeCl,thf)_2$. Similarly prepared, this crystallized from benzene as colourless

---

[6] D. A. Everest, 'The Chemistry of Beryllium,' Elsevier, 1964, p. 120.

needles, m.p. 126—128° [Found: Be, 4·2; Cl, 16·6%, *M* (cryoscopic, 0·56 and 0·83 wt. % in benzene), 409 and 409. $C_{20}H_{42}Be_2Cl_2O_4$ requires Be, 4·15; Cl, 16·35%; *M*, 435]. (c) $(Et_3COBeCl,thf)_2$. Similarly prepared, this crystallized from benzene–hexane (5 : 1) as colourless *rectangles*, m.p. 63—64° [Found: Be, 4·0; Cl, 15·3%, *M* (cryoscopic, 0·58 and 0·86 wt. % in benzene), 465 and 445. $C_{22}H_{46}Be_2Cl_2O_4$ requires Be, 3·9; Cl, 15·4%; *M*, 463]. The complex is rather sparingly soluble in benzene.

Dichlorotriberylliumtetra-1,1-*dimethylpropoxide*, $Cl_2Be_3(OCMe_2Et)_4$.—Bis-1,1-dimethylpropoxyberyllium (1·82 g) in ether (10 ml) was added to beryllium chloride diethyl ether complex (1·12 g) in ether 30 ml. The mixture was stirred for 15 min, then removal of ether left a white solid which crystallized from hexane as large hexagonal *plates*, m.p. 85—86° [Found: Be, 6·1; Cl, 15·7%, *M* (cryoscopic, 0·96 and 1·28 wt. % in benzene), 414 and 423. $C_{20}H_{44}Be_3Cl_2O_4$ requires Be, 6·05; Cl, 15·9%; *M*, 446].

Adducts of Beryllium t-*Butoxide*.—Attempts to prepare these were made by addition of the base to a solution of the alkoxide in hexane. In the cases of ammonia, dimethylamine, *NNN′*-trimethylethylenediamine, *NNN′N′*-tetramethylethylenediamine, and pyridine, evaporation of volatile material yielded unchanged beryllium t-butoxide, identified by m.p. and i.r. spectrum.[1,2]

4-*Dimethylaminopyridine Beryllium* t-*Butoxide*, $Me_2NC_5H_4NBe(OBu^t)_2$.—The pyridine (0·40 g) in benzene (10 ml) was added to beryllium t-butoxide (0·50 g) in benzene (5 ml). The mixture was stirred for 15 min and heated to boiling. Solvent was removed by evaporation after the mixture had cooled, and the residual white *adduct* crystallized from benzene–hexane, m.p. 157—158° [Found: Be, 3·2; $C_7H_{10}N_2$, 45·0%; *M* (cryoscopic, 0·82 and 1·22 wt. % in benzene), 240 and 282. $C_{15}H_{28}BeN_2O_2$ requires Be, 3·25; $C_7H_{10}N_2$, 44·1%; *M*, 277]. The ^1H n.m.r. spectrum is anomalous, consisting of singlets at τ 7·74 and 8·23 and a triplet centred at τ 8·48 (*J* 1), in area ratio 1 : 1 : 2.

Trimethylaluminium–Triberyllium–Hexa-t-*butoxide*, $Me_3Al[Be(OBu^t)_2]_3$.—Beryllium t-butoxide (1·38 g) in hexane (15 ml) was added to trimethylaluminium (0·64 g, an excess), resulting in the immediate formation of a white precipitate and a temperature rise to about 50°. After solvent was evaporated, the *adduct* was crystallized from benzene–hexane (−78°), m.p. 189—190° [Found: Al, 4·9; Be, 4·9; hydrolysable methyl, 10·3%; *M* (cryoscopic, 0·42 and 0·62 wt. % in benzene), 506 and 516. $C_{27}H_{63}AlBe_3O_6$ requires Al, 5·0; Be, 5·0; Hydrolysable methyl, 10·8%; *M*, 537].

Beryllium 2,6-*Di-t-butylphenoxide*.—2,6-Di-t-butylphenol (7·92 g, 0·0384 mol) dissolved in ether (20 ml) was added to diethylberyllium diethyl ether complex (2·21 g, 0·0192 mol) in ether (20 ml) at −78°. As the resulting mixture warmed to room temperature, gas evolution was seen at *ca.* 0°. After 15 min stirring at room temperature, ether was evaporated leaving a liquid which slowly solidified when kept *in vacuo*. The product crystallized from benzene–hexane (1 : 1) as colourless *needles*, m.p. 174—175° (decomp.). It sublimed at 120—130°, 10^{-2} mmHg [Found: Be, 2·1; 2,6-di-t-butylphenol, 97·3%; *M* (cryoscopic, 1·66 and 2·23 wt. % in benzene), 423 and 433. $C_{28}H_{42}BeO_2$ requires Be, 2·15; 2,6-di-t-butylphenol, 97·9%; *M*, 419]. The compound oxidizes very easily with the development of a red colour, and its molecular weight was determined using carefully degassed benzene.

The authors thank the National Science Foundation for support of this work and the Dyestuffs Division of I.C.I. Ltd. for a gift of 4-dimethylaminopyridine.

[2/639 *Received*, 20*th March*, 1972]