t-Butoxyberyllium Halides and Related Compounds: the Series $X_2Be_3(OBu^t)_4$

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Two series of t-butoxyberyllium halides are described, *viz.*, $(XBeOBu^t,L)_2$ and $X_2Be_3(OBu^t)_4$ (X = Cl, Br, or I and L = Et_2O or tetrahydrofuran). The iodo-complex $(IBeOBu^t,OEt_2)_2$ dissociates extensively in benzene. The series $(XBeOBu^t,L)_2$ is formed from MeBeBr and acetone, from $LiOBu^t$ and BeX_2, or from $Be(OBu^t)_2$ and BeX_2. The series $X_2Be_3(OBu^t)_4$ is conveniently obtained from $Be(OBu^t)_2$ and BeX_2: the crystal structure of the chloride is known and those of the others are assumed to be similar. The halogen may be replaced by methyl or t-butyl, and reactions of $Me_2Be_3(OBu^t)_4$ with acids have given members of the series in which X = N_3, CN, NO_3, and with t-butylalcohol the known t-butoxide, $[Be(OBu^t)_2]_3$, is formed. Methanol and $Me_2Be_3(OBu^t)_4$ yield $[Be(OBu^t)_2]_3$ and polymeric $Be(OMe)_2$. With $LiSBu^t$, $Cl_2Be_3(OBu^t)_4$ yields $(Bu^tS)_2Be_3(OBu^t)_4$. The mixed alkoxy-amide, $(Me_2N)_2Be_3(OBu^t)_4$, and the methylamide, $Me_2Be_3(NMe_2)_4$, are described: the former yields a methiodide but the latter does not.

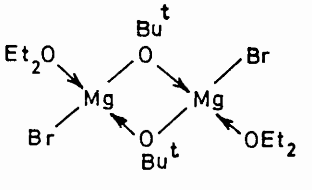
EQUIMOLAR mixtures of dimethyl- or diethyl-beryllium with beryllium chloride or bromide in diethyl ether react as alkylberyllium halides.[1] For example, methylberyllium hydride may conveniently be prepared by the reactions: [2]

$$Me_2Be + BeBr_2 \xrightarrow{Et_2O} 2MeBeBr$$

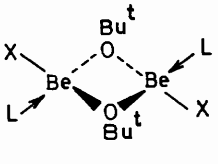
$$2MeBeBr + 2LiH \xrightarrow{Et_2O} (MeBeH,OEt_2)_2 + 2LiBr$$

That the equilibrium between R_2Be (R = Me or Ph) and BeX_2 (X = Cl or Br) in ether is predominantly if not entirely in favour of solvated RBeX has been confirmed by a detailed ^1H n.m.r. studies.[3]

The reaction product from methylmagnesium bromide and acetone in ether is the dimer (I).[4]



(I)



(II)

The *trans*-structure of (I) has been confirmed by an *X*-ray structure analysis.[5] Since this compound has several unusual structural features such as the Mg–O bonds in the Mg_2O_2 ring being significantly shorter than those outside the ring, and the planarity of the bonds formed by both alkoxy and ether oxygen atoms, we have studied some of the products from the reactions of alkylberyllium halides and acetone. The reaction between methylberyllium bromide and acetone in ether yields (II; L = Et_2O, X = Br) and the same product is formed from beryllium t-butoxide and beryllium bromide.

The *trans*-structure of (II; L = Et_2O and X = Br) has been confirmed by single-crystal *X*-ray analysis and has provided further examples of planar three-co-ordinate oxygen.[6]

With beryllium chloride in ether, beryllium t-butoxide yields (II; L = Et_2O, X = Cl) and it may be noted that attempts at the preparation of analogous chloromagnesium alkoxide–ether complexes failed. Insoluble products of no simple composition were generally obtained, though in one instance an ether-insoluble chloride, $Me_2CHC_2H_4Et_2COMgCl$, was prepared.[4] Even compound (I) loses ether readily at room temperature and several analogous magnesium compounds lose ether so readily that they can be kept only in an atmosphere of ether vapour. The t-butoxyberyllium chloride (II; L = Et_2O, X = Cl) has an ether dissociation pressure of 10·5 mmHg at 39·6° and 29 mmHg at 59·4°. It loses all of the ether when kept *in vacuo* for 24 h at room temperature (a different product is formed at elevated temperatures, see below), giving chloroberyllium t-butoxide which is tetrameric, $(ClBeOBu^t)_4$, in benzene. As alkoxy-groups normally form stronger bridges than bromide, and probably chloride too, this tetramer is likely to have a cubane-type structure analogous to that of $(MeZnOMe)_4$,[7] with oxygen rather than chlorine forming part of the cube. Unfortunately we were unable to obtain this compound other than in solution or in microcrystalline form. That chloroberyllium t-butoxide is tetrameric in contrast to the insoluble and doubtless polymeric halogenomagnesium alkoxides[4] (*e.g.* $BrMgOBu^t$), may be ascribed to the apparent co-ordination maximum of four for beryllium (except when the ligands are hydrogen [8]) in contrast to the higher co-ordination numbers attained by magnesium.

Exposure of (II; L = Et_2O, X = Br or I) to vacuum resulted in slow elimination of isobutene as well as ether, so we were unable to obtain the bromo- or iodo-analogues of $(ClBeOBu^t)_4$.

As expected, tetrahydrofuran displaces diethyl ether

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[1] H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, 1927, **49**, 2904.

[2] N. A. Bell and G. E. Coates, *J. Chem. Soc.* (*A*), 1966, 1069.

[3] J. R. Sanders, E. C. Ashby, and J. H. Carter, *J. Amer. Chem. Soc.*, 1968, **90**, 6385; *Chem. Comm.*, 1967, 997.

[4] G. E. Coates, J. A. Heslop, M. E. Redwood, and D. Ridley, *Chem. Soc.* (*A*), 1968, 1118.

[5] P. T. Moseley and H. M. M. Shearer, *Chem. Comm.*, 1968, 279.

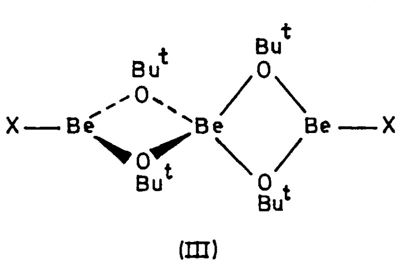
[6] H. M. M. Shearer and J. Twiss, personal communication.

[7] H. M. M. Shearer and C. B. Spencer, *Chem. Comm.*, 1966, 194.

[8] D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1971, **93**, 2322.

but not butoxy-groups from co-ordination positions about beryllium in (II; $L = Et_2O, X = Cl$ or Br) giving (II; $L = C_4H_8O$, $X = Cl$ or Br) rather than $ClBeOBu^t(thf)_2$.

When (II; $L = Et_2O$) is heated in benzene or toluene solution, disproportionation takes place and, on cooling, a complex $Cl_2Be_3(OBu^t)_4$ crystallizes. This has been shown [6] to have the structure (III; X = Cl).



(III)

The same complex, and its bromo- and iodo-analogues (X = Br or I), may more conveniently be obtained by crystallization of a mixture of beryllium halide and t-butoxide:

$$3BeX_2 + 2Be_3(OBu^t)_6 = 3X_2Be_3(OBu^t)_4$$

The structure (III) somewhat resembles that of the trimeric amino-compound [9] $Be_3(NMe_2)_6$, and it is very likely that beryllium di-t-butoxide has a similar structure. There appeared to be no reason why an extensive series of complexes (III) in which X is a one-electron ligand should not be capable of existence. One member of this series, in which X is not a halogen, has already been described, *viz.* $(PhC{\vdots}C)_2Be_3(OBu^t)_4$.[10]

Though the alkyl derivatives (III; X = Me or Bu^t) could be obtained, the methyl from dimethylberyllium and the appropriate amount of beryllium di-t-butoxide in ether, and the t-butyl from t-butyl-lithium and $Cl_2Be_3(OBu^t)_4$, we were unable to prepare the phenyl derivative $Ph_2Be_3(OBu^t)_4$ from Ph_2Be and $Be(OBu^t)_2$, or from Ph_2Be and Bu^tOH, or from $Cl_2Be_3(OBu^t)_4$ and phenyl-lithium. The methyl compound, $Me_2Be_3(OBu^t)_4$, may be recovered unchanged from solutions containing *NNN'N'*-tetramethylethylenediamine, so is unlikely to disproportionate significantly.

Reactions between dimethyltriberyllium tetra-t-butoxide (III; X = Me) and acids provide a convenient route to several derivatives, *viz.* $(N_3)_2Be_3(OBu^t)_4$, $(CN)_2Be_3(OBu^t)_4$, and $(NO_3)_2Be_3(OBu^t)_4$. Whereas the azido- and cyano-complexes are very likely to have structures analogous to (III), the nitrate group could act as a uni- or bi-dentate ligand. I.r. absorption of nitrato-complexes in the 1480—1530 cm^{-1} region has been shown to indicate unidentate co-ordination,[11] whereas absorption in the 1602—1640 cm^{-1} region is indicative of bidentate or bridging co-ordination.[12] Since dinitratotriberyllium tetra-t-butoxide absorbs at 1505 and 1515 cm^{-1}, we consider the nitrato-groups are bound to beryllium by one oxygen atom. This result is also to be expected from the considerable steric hindrance round chlorine demonstrated by the crystal-structure analysis of (III; X = Cl).[6] A high degree of covalent character in the bond to the nitrate group results in a shift to higher wave numbers, *e.g.* 1640 cm^{-1} in $MeNO_3$;[11] the Be–O bonds in the nitratoberyllium complex are likely to be highly polar as is consistent with the observed lower wave numbers.

Neither ammonia nor dimethylamine react with dimethyltriberyllium tetra-t-butoxide, probably on account of steric hindrance to the access of the reagents to the terminal beryllium atoms. The stronger protic acids mentioned earlier (HN_3, HCN, and HNO_3) probably attack the somewhat negative methyl carbon bound to beryllium. It is of some interest that neither methanethiol nor 2-methylpropane-2-thiol react with $Me_2Be_3(OBu^t)_4$, but water, methanol, and t-butyl alcohol react rapidly. In the latter case beryllium t-butoxide is formed, but reaction with methanol results in disproportionation to insoluble polymeric beryllium methoxide and to the soluble t-butoxide:

$$Me_2Be_3(OBu^t)_4 + 2MeOH \longrightarrow [(MeO)_2Be_3(OBu^t)_4] \longrightarrow \frac{1}{x}[(MeO)_2Be]_x + \frac{2}{3}[Be(OBu^t)_2]_3$$

For this process to occur, it is necessary that the terminal BeOMe groups of two of the intermediate mixed alkoxides interact to form a $Be(OMe)_2Be$ bridge, for only in that event would Bu^tO–Be bonds be broken. The dimethyl compound does not react with the dichloride, since crystallization of an equimolar mixture gave $Cl_2Be_3(OBu^t)_4$ rather than $ClMeBe_3(Bu^tO)_4$. The chloride, however, is subject to anionic attack by some lithium compounds, *e.g.*

$$Cl_2Be_3(OBu^t)_4 + 2Bu^tSLi \longrightarrow (Bu^tS)_2Be_3(OBu^t)_4 + 2LiCl$$

This product, which is the first mixed beryllium alkyl sulphide alkyl oxide compound to be described, could have several different structures, but in view of the evident stability of the $Be_3(OBu^t)_4$ structural unit we think it likely that the t-butylthio-groups are terminal rather than bridging. In the case of bisdimethylaminoberyllium tetra-t-butoxide, prepared from the chloride and dimethylaminolithium or by redistribution of bisdimethylaminoberyllium and beryllium t-butoxide, reaction with methyl iodide yields a methiodide. Hence, either one or more of the dimethylamino-groups are terminal, or terminal dimethylamino-groups are present in any equilibrium which may exist in solution. The complex is not sufficiently soluble in benzene to afford a satisfactory ^1H n.m.r. spectrum. The sparing solubility in benzene not only of $(Me_2N)_2Be_3(OBu^t)_4$ but also of the analogous compounds $X_2Be_3(OBu^t)_4$ ($X = N_3$, NO_3, or SBu^t), itself argues in favour of the high degree of symmetry that would result from bridging t-butoxy and terminal X groups.

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[9] J. L. Atwood and G. D. Stucky, *Chem. Comm.*, 1967, 1169; *J. Amer. Chem. Soc.*, 1969, **91**, 4426.

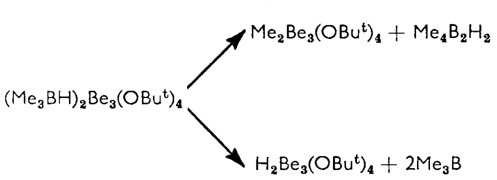
[10] G. E. Coates and B. R. Francis, *J. Chen. Soc.* (*A*), 1971, 160.

[11] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 1957, 4222.

[12] C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *J. Chem. Soc.* (*A*), 1967, 808.

An attempt at the preparation of $F_2Be_3(OBu^t)_4$ from $Me_2Be_3(OBu^t)_4$ and the boron trifluoride–ether complex resulted in an exothermic reaction, but we could not crystallize or purify the gelatinous product.

Efforts to prepare the hydride, $H_2Be_3(OBu^t)_4$ were also unsuccessful, though spectroscopic evidence was obtained for the presence of terminal Be–H bonds in one of the products. The bromide, $Br_2Be_3(OBu^t)_4$, did not react with lithium hydride either in diethyl ether or in boiling tetrahydrofuran during two days: only unchanged starting material was recovered. The reaction between $Cl_2Be_3(OBu^t)_4$ and sodium trimethylborohydride in benzene gave an immediate precipitate of salt. Presumably $(Me_3BH)_2Be_3(OBu^t)_4$ was also formed, perhaps only transiently, but this could eliminate di- or tri-methylborane:

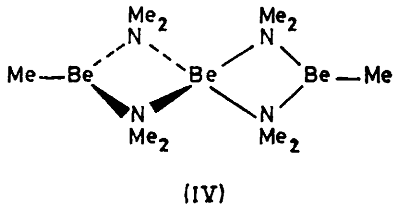


Crystallization from hexane after an hour had elapsed gave colourless prisms which melted over several degrees, 108—112°. Both methane and hydrogen were formed on hydrolysis, the ratio $(CH_4 + H_2) : Be$ being 1·3 : 1. The i.r. spectrum contained two sharp absorptions at 1947 (medium) and 2007 cm^{-1} (weak) indicative of terminal Be–H.[13] Reduction of the reaction time to ten minutes gave a product in which the ratio $(CH_4 + H_2) : Be$ was 1·45 : 1, whose melting range was 98—103°. The reaction of $Cl_2Be_3(OBu^t)_4$ with $NaEt_3BH$ was even less satisfactory.

Tetra-μ-dimethylamide-dimethyltriberyllium.—In view of the existence of the series $X_2Be_3(OBu^t)_4$ described above, it seems likely that similar series with other bridging groups (*e.g.* alkoxy- or dialkylamido-) should be capable of existence. One of these has now been prepared by the following reaction:

$$2Me_2Be + 2[(Me_2N)_2Be]_3 \longrightarrow 3Me_2Be_3(NMe_2)_4$$

We believe this complex has the structure (IV), but its ^1H n.m.r. spectrum is anomalous. Though the area ratio of the dimethylamino- to that of the methylberyllium-resonance (at τ 10·62) is 4 : 1, the dimethylamino-resonance is split into two at τ 7·81 and 7·90 in area ratio 5 : 1. We cannot explain this observation.



(IV)

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenk tube, vacuum-line, and glove-box techniques. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method [14] under standardized conditions. Alkoxy-groups were in some instances determined by isolation and weighing of the alcohol formed during the hydrolysis. Other components were determined by well established methods. ^1H N.m.r. spectra were recorded by use of a Varian HA 100 spectrometer, with benzene as solvent and internal reference unless otherwise stated. Many of the compounds described below decompose when heated without melting. In many such cases the main i.r. absorptions are quoted for characterization; these were recorded as Nujol mulls. Most of the compounds described below are sensitive to water and some to air, and to minimize the number of transfers from one apparatus to another, *e.g.* for weighing, yields were in general not recorded. Except when noted, yields were, apart from transfer losses, nearly quantitative.

t-Butoxyberyllium Halides

t-Butoxyberyllium Bromide–Diethyl Ether.—*A, From methylberyllium bromide and acetone.* Dimethylberyllium (0·30 g, 0·00697 mol) in ether (10 ml) was added to beryllium bromide (2·21 g, 0·00697 mol) in ether (30 ml). The solution was stirred 15 min after the addition was complete, then acetone (0·81 g, 0·0139 mol) in ether (5 ml) was added causing the mixture to boil. After 15 min ether was evaporated leaving a white residue which crystallized from benzene–ether (1 : 1) as colourless *prisms* whose i.r. spectrum was identical to that of the product obtained by method B, below.

B, From beryllium t-butoxide. Beryllium di-t-butoxide [15] (1·36 g, 0·0088 mol) in diethyl ether (15 ml) was added to the bisdiethyl ether complex of beryllium bromide (2·78 g, 0·0088 mol) in ether (40 ml). After 30 min the solvent was evaporated and the residue was crystallized from benzene–hexane [Found: Be, 3·9; Br, 33·85%; *M* (cryoscopically, 0·71 and 0·82% w/w in benzene), 449, 480. $C_{16}H_{38}Be_2Br_2O_4$ requires Be, 3·8; Br, 33·9%; *M*, 472]. The i.r. spectrum consisted of absorptions at 1388s, 1378m,sh, 1370s, 1330w, 1290w, 1243m, 1228w, 1188s, 1143s, 1082s, 1023s, 992s, 950s, 887s, 843w, 797s, 778s, 740s, 663m, 588s, 500m, and 460w cm^{-1}. When heated, it becomes yellow at 130°, brown at 230°, but does not melt. Its dissociation pressure is 7·5 mmHg at 36·5°.

t-Butoxyberyllium Bromide–Tetrahydrofuran.—This was obtained by crystallizing the diethyl ether complex from tetrahydrofuran at −20° [Found: Be, 3·91; Br, 33·8%; *M* (cryoscopically, 0·68 and 1·07% w/w in benzene), 438, 442. $C_{16}H_{34}Be_2Br_2O_4$ requires Be, 3·93; Br, 34·2%; *M*, 468].

t-Butoxyberyllium Chloride–Diethyl Ether.—Beryllium t-butoxide (1·90 g, 0·013 mol) in ether (15 ml) was added to the bisdiethyl ether complex of beryllium chloride (2·90 g, 0·013 mol) in ether (25 ml). Most of the product had precipitated when the addition was complete, but after filtration a small amount of material crystallized overnight and was shown by i.r. and m.p. to be identical to the

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[13] L. H. Shepherd, G. L. Ter Haar, and E. M. Marlett, *Inorg. Chem.*, 1969, **8**, 976; G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1969, 1008.

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

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

precipitate. Reverse addition yielded an identical product, m.p. 85—86° [Found: Be, 4·6; Cl, 18·2%; *M* (cryoscopically, 0·68 and 1·01% w/w in benzene), 350 and 345. $C_{16}H_{38}Be_2Cl_2O_4$ requires Be, 4·7; Cl, 18·5%; *M*, 382].

The same product was obtained when beryllium chloride (0·0234 mol) and lithium t-butoxide (0·0234 mol) were mixed in ether (150 ml). After removal of the lithium chloride which precipitated immediately, concentration of the filtrate gave the *diethyl ether complex* [Found: Be, 4·7; Cl, 18·3; ether, 38·4%; *M* (cryoscopically, 0·74 and 1·11% w/w in benzene), 372 and 377. $C_{16}H_{38}Be_2Cl_2O_4$ requires Be, 4·7; Cl, 18·5; ether, 38·8%; *M*, 382].

t-Butoxyberyllium Chloride–Tetrahydrofuran.—This was obtained by displacement of diethyl ether from the preceding complex, and was recrystallized as colourless *needles* from 5 : 1 benzene–tetrahydrofuran, m.p. 175—177° (decomp.) [Found: Be, 4·7; Cl, 18·4%; *M* (cryoscopically, 0·64 and 0·95% w/w in benzene), 380 and 383. $C_{16}H_{34}Be_2Cl_2O_4$ requires Be, 4·75; Cl, 18·75%; *M*, 189·5].

t-Butoxyberyllium Chloride.—The diethyl ether complex (0·430 g) was weighed into a vessel connected to a vacuum line and over 24 h diethyl ether (50·0 ml reduced to s.t.p., 99% of theoretical) was collected. The residue was soluble both in ether and in benzene. It became yellow at 130° and progressively darkened at higher temperatures [Found: Be, 7·7; Cl, 30·4%; *M* (cryoscopically, 1·45 and 2·14% w/w in benzene), 466 and 468. $C_{16}H_{36}Be_4Cl_4O_4$ requires Be, 7·6; Cl, 30·2%; *M*, 470]. The ^1H n.m.r. spectrum consisted of a singlet due to Bu^tO at τ 8·16. The i.r. spectrum consisted of absorptions at 1397s, 1258s, 1145m, 1037w, 918w, 830s, 780s,sh, 765s, 735w,sh, 667s,sh, 660s, and 443m cm^{-1}. It dissolved neither in cold water nor in cold 2N-sulphuric acid.

t-Butoxyberyllium Iodide–Diethyl Ether.—Iodine (1·52 g, 0·012 g atom) in ether (40 ml) was added to diethylberyllium (6·0 ml of 1·0M solution in ether). After 10 min, t-butyl alcohol (0·45 g, 0·006 mol) in ether (10 ml) was added, gas evolution being observed. Solvent was then evaporated until crystallization took place. The *ether complex* darkened from 160° and did not melt [Found: Be, 3·1; I, 42·5; ether, 28·9%; *M* (cryoscopically, 0·77, 1·16, and 1·59% w/w in benzene), 358, 390, and 393. $C_{16}H_{38}Be_2I_2O_4$ requires Be, 3·2; I, 44·9; ether, 26·8%; *M*, 586]. The ether complex evidently dissociates extensively in solution. The i.r. spectrum contained absorptions at 1385s, 1360s, 1330w, 1282vw, 1245m, 1230w, 1185m, 1140m, 1082w, 1073w, 1010s, 985w, 943s, 881s, 828w, 796w, 772s, 741s, 650w, 572s, 483s, and 448w cm^{-1}.

The Series $X_2Be_3(OBu^t)_4$.—*The chloride.* Beryllium chloride bisdiethyl ether complex (2·54 g, 0·011 mol) in ether (25 ml) was added to beryllium di-t-butoxide (3·50 g, 0·023 mol) in ether (15 ml). The product began to crystallize when about three quarters of the beryllium chloride had been added. After the mixture had been stirred for 15 min the solvent was removed and the residue was recrystallized, in nearly quantitative yield, from benzene–hexane. The product became yellow at 330° and brown at 400°: it did not melt [Found: Be, 6·7; Cl, 18·1%; *M* (cryoscopically, 0·51 and 0·75% w/w in benzene), 409 and 373. $C_{16}H_{36}Be_3Cl_2O_4$ requires Be, 6·9; Cl, 18·2%; *M*, 390]. The i.r. spectrum consisted of absorptions at 1390s, 1253s, 1235m, 1183m, 1036s,sh, 990s, 960m,sh, 937m,sh, 855m,sh, 830s, 778w, 606s, 518s, 460w, and 420w cm^{-1}. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·16.

Addition of beryllium di-t-butoxide to the same molar proportion of beryllium chloride yielded the same product. Dichlorotriberyllium tetra-t-butoxide was first prepared by boiling a solution of $(Bu^tOBeCl,OEt_2)_2$ in toluene, but the methods described above are better.

The Bromide, $Br_2Be_3(OBu^t)_4$.—This was similarly prepared, adding the di-butoxide (0·96 g, 0·006 mol) in ether (20 ml) to beryllium bromide bisdiethyl ether (0·98 g, 0·003 mol) in ether (40 ml). The *bromide* was crystallized ftom benzene–hexane. It became yellow at 180°, brown at 230° and did not melt [Found: Be, 5·6; Br, 33·3%; *M* (cryoscopically, 0·36 and 0·54% w/w in benzene), 477 and 495. $C_{16}H_{36}Be_3Br_2O_4$ requires Be, 5·5; Br, 32·8%; *M*, 479]. The i.r. spectrum was as follows: 1384m, 1360s, 1248m, 1230w,sh, 1178m, 1027w, 990s, 968m,sh, 916m, 905w, 847w,sh, 822s, 770w, 710w, and 598m cm^{-1}. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·59.

The Iodide, $I_2Be_3(OBu^t)_4$.—Iodine (1·52 g, 0·012 g atom) in ether (40 ml) was added to diethylberyllium (3·0 ml of a 1·0M solution in ether). After 10 min solvent was removed and the residue ($BeI_2,2Et_2O$) held *in vacuo* for 1 h after which it was dissolved in benzene (5 ml). Beryllium di-t-butoxide (0·93 g, 0·006 mol) in benzene (10 ml) was added to the beryllium iodide solution. After 15 min the benzene was evaporated and the residue was recrystallized from benzene–hexane. It became yellow at 155°, brown at 280°, black at 360° and did not melt [Found: Be, 4·8; I, 43·2%; *M* (cryoscopically, 0·48 and 0·72% w/w in benzene), 578 and 569. $C_{16}H_{36}Be_3I_2O_4$ requires Be, 4·7; I, 44·4%; *M*, 573]. The i.r. spectrum was as follows: 1385m, 1370m, 1247m, 1233m,sh, 1176m, 1140w, 1042w,sh, 1024w,sh, 990s, 946w,sh, 910w, 893m, 843w,sh, 828w,sh, 805m, 769w, 710w, 593m, and 510m cm^{-1}. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·58.

Dimethyltriberyllium Tetra-t-butoxide, $Me_2Be_3(OBu^t)_4$.—(Preparation by Dr. B. R. FRANCIS.) t-Butyl alcohol (1·60 ml, 0·017 mol) in benzene (5 ml) was slowly added to a stirred suspension of dimethylberyllium (0·496 g, 0·0127 mol) in benzene (10 ml). The mixture became warm and gas was evolved. Evaporation of solvent left a white residue which was recrystallized from hexane as colourless *plates*, m.p. 188° [Found: Be, 7·7; hydrolysable methyl, 8·65%; *M* (cryoscopically, 0·33 and 0·50% w/w in benzene), 358 and 320. $C_{18}H_{42}Be_3O_4$ requires Be, 7·7; hydrolysable methyl, 8·6%; *M*, 349]. It is only sparingly soluble in benzene and in hexane. The ^1H n.m.r. spectrum consists of a singlet at τ 8·60 (*Bu*^{t}O) and one at τ 10·41 (CH_3–Be) in area ratio 6 : 1.

Reaction of Dimethyltriberyllium Tetra-t-butoxide with t-Butyl Alcohol.—The alcohol (0·63 g, 0·00854 mol) in ether (10 ml) was added to $Me_2Be_3(OBu^t)_4$ (1·49 g, 0·00427 mol) in ether (30 ml). The ether boiled during the addition, and after 15 min, with stirring, evaporation of ether left a residue which crystallized from hexane (−5°) as colourless prisms, m.p. 109—110°, whose i.r. spectrum was identical to that of beryllium t-butoxide, $[Be(OBu^t)_2]_3$, (lit.,[15,16] m.p. 112°).

With Methanol.—Methanol (0·28 g, 0·0087 mol) in ether (5 ml) was added to $Me_2Be_3(OBu^t)_4$ (1·52 g, $0{\cdot}0043_5$ mol) in ether (30 ml) resulting in boiling and the immediate formation of a white precipitate. The suspension was stirred 15 min and solvent was then evaporated. After benzene (25 ml) had been added, the suspension was filtered. The residue was identified as beryllium meth-

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

oxide, $[Be(OMe)_2]_x$, by its i.r. spectrum.[15] Removal of benzene from the filtrate left a white residue which crystallized from hexane (−5°) as colourless prisms, m.p. 115—116°, whose i.r. spectrum was identical to that of beryllium t-butoxide.[15]

Di-t-butyltriberyllium Tetra-t-butoxide, $Bu^t_2Be_3(OBu^t)_4$.—t-Butyl-lithium (4·6 ml of a 2·26M solution in pentane) was added to dichlorotriberyllium tetra-t-butoxide (2·0 g, 0·005 mol) in benzene (40 ml). Lithium chloride began to precipitate only about 15 min, at room temperature, after the addition had been completed. After 1·5 h, the precipitated lithium chloride was separated and the solvent removed from the filtrate, leaving a pale yellow oil. This solidified on addition of a little hexane. The product was then dissolved in hexane (3 ml), and crystallized at −78°, m.p. 98—99° [Found: Be, 6·2; hydrolysable butyl, 24·6%; *M* (cryoscopically, 1·24 and 1·82% w/w in benzene), 384 and 394. $C_{24}H_{54}Be_3O_4$ requires Be, 6·2; hydrolysable butyl, 26·4%; *M*, 433]. This compound is very soluble both in benzene and in hexane and the yield was not quantitative. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·52 due to Bu^t–O and one at τ 8·62 due to Bu^t–Be in area ratio 2 : 1.

Reactions between $Bu^t_2Be(thf)$ (3 mol) and t-butyl alcohol (4 mol), $Bu^t_2Be(thf)$ (1 mol) and $Be(OBu^t)_2$ (2 mol reckoned as monomer), Bu^t_2Be,OEt_2 (1 mol) and $Be(OBu^t)_2$ (2 mol) all yielded beryllium di-t-butoxide as the only product that could be isolated by crystallization.

Diazidotriberyllium Tetra-t-butoxide, $(N_3)_2Be_3(OBu^t)_4$.—Hydrogen azide in excess (*ca.* 2 ml in 10 ml ether) was added to dimethyltriberyllium tetra-t-butoxide (0·48 g, 0·0014 mol) in ether (20 ml). Gas was slowly evolved during the addition and a gelatinous precipitate formed. After the addition was complete the mixture was stirred 15 min and solvent was then removed by evaporation. The white residue was crystallized from benzene as colourless *plates*, which became brown at 270° and did not melt (Found: Be, 6·4; N_3, 19·8%. $C_{16}H_{36}Be_3N_6O_4$ requires Be, 6·7; N_3, 20·8%). The azido-complex is not sufficiently soluble in benzene to allow its molecular weight to be measured. Its i.r. spectrum was as follows: 2200s, 2103s, 1388m, 1375m, 1247m, 1230w, 1193m, 1028w, 968s, 807s, 781s, 750s, 693w, 625w, 535w, and 467w cm^{-1}.

Dicyanotriberyllium Tetra-t-butoxide, $(CN)_2Be_3(OBu^t)_4$.—Hydrogen cyanide in excess was condensed on a solution of dimethyltriberyllium tetra-t-butoxide (0·47 g) in benzene (10 ml) which had been frozen at −196°. The mixture was allowed to warm to room temperature and stirred for 15 min. Evaporation of solvent and excess hydrogen cyanide left a white residue which crystallized from benzene–hexane (2 : 1) as colourless *prisms* [Found: Be, 7·2%; *M* (cryoscopically, 0·28 and 0·42% w/w in benzene), 306 and 324. $C_{18}H_{36}Be_3N_2O_4$ requires Be, 7·3%; *M*, 371]. The cyanide neither melted nor darkened when heated to 400°. Its i.r. spectrum was as follows: 2195w, 1385m, 1372m, 1245m, 1225m, 1193m, 1024w, 967s, 906w, 805s, 790s,sh, 762s, 698m, and 625m cm^{-1}. The ^1H n.m.r. spectrum consisted of a singlet at τ 8·43.

Dinitratotriberyllium Tetra-t-butoxide, $(NO_3)_2Be_3(OBu^t)_4$.—Anhydrous nitric acid (*ca.* 0·3 g) in light petroleum (10 ml) was added to dimethyltriberyllium tetra-t-butoxide (1 g) in tetrahydrofuran (30 ml) at −78°. The mixture was allowed to warm to room temperature and stirring was was continued for 30 min. Evaporation of volatile material left a yellow residue which crystallized from hexane–tetrahydrofuran (3 : 1) as colourless *needles*, which became yellow at 150° and did not melt (Found: Be, 6·0; t-butoxy, 64·8%. $C_{16}H_{36}Be_3N_2O_{10}$ requires Be, 6·1; t-butoxy, 65·9%). The i.r. spectrum was as follows: 1515m, 1505w,sh, 1385s, 1375s,sh, 1345w,sh, 1321m, 1245m, 1230w,sh, 1190m, 1013s, 960s, 913w, 874m, 818w, 798m, 760s, 708w, 670m, 575s, and 472w. It is only sparingly soluble in benzene.

Di-(t-butylthio)triberyllium Tetra-t-butoxide, $(Bu^tS)_2Be_3(OBu^t)_4$.—n-Butyl-lithium (2·48 ml of a 3·38M solution in benzene, 0·0084 mol) was added to t-butanethiol in excess dissolved in ether (15 ml) at −78°. The mixture was then allowed to warm to room temperature and stirred 15 min. Volatile material was then removed by evaporation and the residual powder was exposed to vacuum for 30 min. It was dissolved in tetrahydrofuran (10 ml) and to this solution was added dichlorotriberyllium tetra-t-butoxide (1·64 g, 0·0042 mol) in tetrahydrofuran (10 ml). The clear solution was stirred 1 h after which evaporation of tetrahydrofuran left a white solid. Benzene (20 ml) was added and the resulting suspension stirred 15 min. After filtration from lithium chloride, evaporation of benzene left a white residue which crystallized from hexane–tetrahydrofuran (4 : 3) as pale yellow prisms; it shrank at 70°, became brown at 280°, and did not melt (Found: Be, 5·5; t-butylthio, 34·6%. $C_{24}H_{54}Be_3O_4S_2$ requires Be, 5·4; t-butylthio, 35·8%). The i.r. spectrum was as follows: 1385m, 1375m, 1245m, 1230m, 1197m, 1021s, 966s, 917w, 880m, 852w, 800s, 770s, 705w, 676m, 598s, and 483m cm^{-1}. It is only sparingly soluble in benzene. Dimethyltriberyllium tetra-t-butoxide did not react with t-butanethiol in benzene.

Bisdimethylaminotriberyllium Tetra-t-butoxide, $(Me_2N)_2Be_3(OBu^t)_4$.—n-Butyl-lithium (2·5 ml of a 3·38M solution in benzene) was added to dimethylamine in excess dissolved in ether (15 ml) at −78°. The resulting suspension was allowed to warm to room temperature and stirred 15 min. After removal of volatile matter the residue was exposed to vacuum for 30 min. The residue was then suspended in ether (20 ml) and to it was added dichlorotriberyllium tetra-t-butoxide (1·64 g, 0·0042 mol) dissolved in ether (50 ml). The mixture was stirred 2 h after the addition was complete. After the ether had been evaporated, benzene (30 ml) was added, the suspension stirred 15 min and filtered from lithium chloride. Evaporation of benzene from the filtrate left a white residue which was insoluble in hexane, and sparingly soluble in benzene: it was purified by sublimation (70—80°, 10^{-3} mmHg), m.p. 93—94° (Found: Be, 6·5; dimethylamino, 22·0. $C_{20}H_{48}Be_3N_2O_4$ requires Be, 6·6; dimethylamino, 21·6%). This compound was not formed from dimethylamine and dimethyltriberyllium tetra-t-butoxide, since no reaction took place (in benzene solution).

Dimethylaminotriberyllium Tetra-t-butoxide Trimethylammonium Iodide, $[Me_2NBe_3(Bu^tO)_4NMe_3]I$.—Methyl iodide (0·59 g, 0·00418 mol) in hexane (5 ml) was added to bisdimethylaminotriberyllium tetra-t-butoxide (0·85 g, 0·00209 mol) in hexane (10 ml). A white precipitate began to appear when the addition had been completed, and the suspension was stirred 3 h. Evaporation of the hexane left a white powder which was insoluble in hexane, benzene, and tetrahydrofuran. The *methiodide* was washed with hexane (3 × 5 ml) and dried *in vacuo*. It became red-brown at 180° and did not melt (Found: Be, 5·1; I, 24·4%. $C_{21}H_{51}Be_3IN_2O_4$ requires Be, 4·9; I, 23·15%).

Tetra-μ-dimethylamide-dimethyltriberyllium, $Me_2Be_3(NMe_2)_4$.—Bisdimethylaminoberyllium (the sublimed trimeric form,[17] 1·49 g) dissolved in ether (15 ml) was added to dimethylberyllium (0·33 g) in ether (10 ml). After the mixture had been stirred 15 min, evaporation of ether left a white residue which crystallized from hexane (+5°) as colourless *prisms*, m.p. 38—39° [Found: Be, 11·6; hydrolysable methyl, 12·9%; *M* (cryoscopically, 0·73 and 1·07% w/w in benzene), 227 and 213. $C_{10}H_{30}Be_3N_4$ requires Be, 11·6; hydrolysable methyl, 12·9%; *M*, 233]. Addition of methyl iodide to a solution of this compound in benzene yielded no precipitate after 1 h at room temperature.

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