109. *Some Alkylberyllium Hydride Complexes, and the Infrared Absorption of Some Beryllium Hydrides and Deuterides.*

By N. A. Bell and G. E. Coates.

The salts $NaMe_2HBe$, $NaMe_2DBe$, $NaEt_2HBe$, and $NaEt_2DBe$ react with beryllium chloride to give mixed alkylberyllium hydrides from which co-ordination complexes can be obtained, *e.g.*, $(MeHBe,NMe_3)_2$, formulated with a BeH_2Be bridge, and an insoluble involatile apparently polymeric tetramethylethylenediamine complex. Ethylberyllium hydride has also been prepared from diethylberyllium and triethylstannane in diethyl ether; it yields a dimeric amine derivative, $(EtHBe,NMe_3)_2$.

Methylberyllium hydride disproportionates when heated, evolving dimethylberyllium and leaving a hydride-rich residue. The disproportionation of ethylberyllium hydride is catalysed by the salt $NaEt_2HBe$.

By comparison of the infrared spectra of $(MeHBe,NMe_3)_2$, $(EtHBe,NMe_3)_2$, and $(MeDBe,NMe_3)_2$, a strong absorption due to the BeH_2Be bridge has been identified at 1333—1344 cm.$^{-1}$ (in cyclohexane).

Sodium hydridodiethylberyllate,[1] prepared from sodium hydride and diethylberyllium in ether, reacts with beryllium chloride with precipitation of sodium chloride:

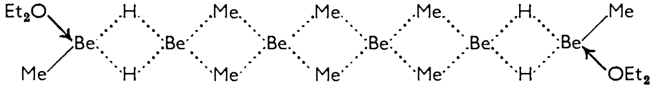
$$NaH + Et_2Be \longrightarrow NaEt_2HBe$$

$$2NaEt_2HBe + BeCl_2 \longrightarrow 2NaCl + \text{"}Et_4Be_3H_2\text{"}$$

We now describe some reactions of this solution and of similar solutions prepared from dimethylberyllium.

In contrast to $NaEt_2HBe$, which may readily be crystallized from diethyl ether (solubility about 30 g./l. at 20°), the analogous methyl compound is only sparingly soluble (about 1·6 g./l. at 20°) and may be crystallized only very slowly by the use of a Soxhlet extractor. For the preparation of many derivatives, isolation of the salt $NaMe_2HBe$ is fortunately not necessary. When a suspension of sodium hydride (in excess) in ethereal dimethylberyllium is boiled, the concentration of the latter gradually falls, as indicated by the amount of methane evolved when samples of supernatant liquid are hydrolysed. No further change appears to take place after about 48 hours, but addition of half a molecular proportion of ethereal beryllium chloride then causes all the beryllium together with hydrolysable methyl and hydrogen to reappear in solution in the molar ratio 3 : 4 : 2. Filtration from sodium chloride and excess of sodium hydride then yields a solution of "$Me_4Be_3H_2$." We have little evidence about the constitution of these solutions, but on the basis of their reaction with tertiary amines it is reasonable to believe that the main solute species are solvated dimethylberyllium and solvated methylberyllium hydride, though significant concentrations of trinuclear (*e.g.*, $Me_4Be_3H_2$) or more complex species could be present.

The colourless viscous oily residue obtained when solvent is pumped from ethereal "$Me_4Be_3H_2$" at room temperature has the approximate composition $Me_4Be_3H_2OEt_2$. Most of the ether is lost when this oily material is heated to about 50° under a vacuum. Since dimethylberyllium is an electron-deficient polymer,[2] insoluble or at least very sparingly soluble in solvents with which it does not react,[3] the viscous oil could be regarded as some kind of electron-deficient complex between dimethylberyllium and methylberyllium hydride such as (I) containing an element of the dimethylberyllium polymer chain. In this system many species are likely to be present in mobile equilibrium.



(I)

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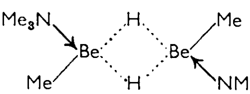
[1] G. E. Coates and G. F. Cox, *Chem. and Ind.*, 1962, 229.

[2] A. I. Snow and R. E. Rundle, *Acta Cryst.*, 1951, **4**, 348.

[3] G. E. Coates, F. Glockling, and N. D. Huck, *J.*, 1952, 4496.

Reactions with Donor Molecules.—Addition of trimethylamine to ethereal " $Me_4Be_3H_2$ " yields a mixture of the dimethylberyllium complex [4] Me_2Be,NMe_3 and the trimethylamine complex (II) of methylberyllium hydride.[5] The complex (II), m. p. 73·0—73·2°, is dimeric in benzene, and is considerably less volatile than Me_2Be,NMe_3. Whereas the vapour pressure of Me_2Be,NMe_3 is 1·8 mm. at 30°, that of (II) is 1·8 mm. at 64° [$\log_{10} p(\text{mm.}) = 7{\cdot}483 - 2439/T$, for the liquid from 73 to 115°], and the two complexes may be separated by fractional condensation. The hydride (II) is formulated with a hydrogen rather than a methyl bridge, because the complex is not decomposed by excess of trimethylamine whereas the methyl bridges between beryllium atoms in the dimethylberyllium polymer are cleaved by trimethylamine.[4] Studies of reactions between dialkylaluminium hydrides and donor molecules have shown that the hydrogen bridges in these compounds are less readily cleaved than are the methyl bridges in trimethylaluminium.[6] From the vapour pressure equation, the latent heat of vaporization is 11·2 kcal. mole^{-1}; the extrapolated boiling point is 257° and the Trouton constant 21·1. The normal Trouton constant suggests that there is no change in the degree of association during the process of vaporization; thus, it is likely that the vapour, at least up to about 110°, consists mainly of dimer. An attempt to measure the molecular weight of (II) as vapour at higher temperatures (145—175°) was not entirely successful on account of some decomposition; however, the vapour appeared to be monomeric at 175° and to become more associated at lower temperatures.



(II)

Attempts to prepare monomeric complexes, L_2BeMeH, of methylberyllium hydride by the use of donor substances which readily form chelate complexes have not been successful. Addition of bipyridyl to ethereal " $Me_4Be_3H_2$ " results in an immediate yellow precipitate [7] of bipy $BeMe_2$, the solution becoming deep red. Though it is possible that the red colour was due to bipy BeMeH, the red soon turned to a dark brown and only tarry matter could be obtained on removal of solvent. Evidently the Be–H groups had reacted with the bipyridyl.

Reaction with *NNN'N'*-tetramethylethylenediamine results in the formation of the known chelate complex of dimethylberyllium [7] and the precipitation of a white, apparently amorphous, substance which is insoluble in ether, benzene, carbon disulphide, and carbon tetrachloride. Since the analysis of the insoluble product corresponds to the formula $[(MeBeH)_2Me_2NC_2H_4NMe_2]_n$, it appears that the hydrogen bridge is present, resulting in a polymeric constitution: $(\leftarrow Me_2N{\cdot}C_2H_4{\cdot}NMe_2 \rightarrow MeBeH_2BeMe \leftarrow)_n$. This involatile complex is not pyrophoric and does not fume in the air.

Reaction with 1,2-dimethoxyethane and subsequent evaporation of ether gives a mixture of solid and liquid products. When this is heated to about 50° in a vacuum, the 1,2-dimethoxyethane complex of dimethylberyllium [7] sublimes from the reaction vessel, leaving a very viscous oil which is insoluble in benzene. Since the analysis of the oil corresponds to the formula $[(MeBeH)_2MeOC_2H_4OMe]_n$ its constitution is probably similar to that of the tetramethylethylenediamine complex.

Reaction between diethylberyllium and triethylstannane in ether solution results in the formation of tetraethyltin and ethylberyllium hydride; hydrolysis of the involatile residue left after evaporation of the tetraethyltin yielded ethane and hydrogen in the ratio 1·016 : 1. The hydrogen–alkyl exchange which takes place when triethylstannane is heated with triethylaluminium (giving Et_2AlH) is inhibited by ether and by tertiary amines.[8] On the assumption that the exchange with triethylaluminium involves an electron-deficient intermediate, it is reasonable to expect that exchange should be inhibited by reagents

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[4] G. E. Coates and N. D. Huck, *J.*, 1952, 4501.

[5] N. A. Bell and G. E. Coates, *Proc. Chem. Soc.*, 1964, 59.

[6] E. G. Hoffmann and G. Schomburg, *Z. Elektrochem.*, 1957, **61**, 1101, 1110.

[7] G. E. Coates and S. I. E. Green, *J.*, 1962, 3340.

[8] W. P. Neumann and R. Sommer, *Angew. Chem.*, 1963, **75**, 788.

which remove the electron-deficient character of the alkylaluminium by forming co-ordination complexes. Since there is evidence that electron-deficient bridges persist in dimethylberyllium in the presence of ethers and trimethylphosphine,[4] it is not surprising that the tin hydride–alkylberyllium exchange reaction takes place in the presence of diethyl ether. Ethylberyllium hydride prepared by this method has been characterized by conversion into its trimethylamine complex, $(EtHBe,NMe_3)_2$, which is dimeric in benzene solution like its methyl analogue (II). Other complexes can readily be prepared by this method and will be described elsewhere.

Displacement of Trimethylamine by Hydride Ion.—In the preparation of sodium hydridodialkylberyllates it is probable that hydride ion displaces co-ordinated ether (used as solvent).

$$H^- + R_2BeOEt_2 \longrightarrow \frac{1}{n}(R_2BeH)_n^{n-} + OEt_2$$

Hydride ion also displaces trimethylamine:

$$NaH + Et_2Be,NMe_3 \longrightarrow NaEt_2HBe + Me_3N$$

in a reaction very similar to the formation of sodium aluminium hydride from sodium hydride and trimethylamine–alane: [9]

$$NaH + H_3Al,NMe_3 \longrightarrow NaAlH_4 + Me_3N$$

Thermal Decomposition of Alkylberyllium Hydride–Dialkylberyllium Mixtures.—Attempts to prepare methylberyllium hydride by sublimation, under reduced pressure, of dimethylberyllium from the solid residue of approximate composition $Me_4Be_3H_2$ (from $2NaMe_2HBe + BeCl_2$) were not successful. At about 10^{-3} mm. pressure slow sublimation of dimethylberyllium was apparent from 60°, but we obtained no indication of any pause in the evolution of dimethylberyllium at a stage corresponding to a residue of methylberyllium hydride. In several experiments (detailed below), sublimation in the range 170—210° resulted in extensive disproportionation,

$$Me_nBe_{(n/2+m/2)}H_m \longrightarrow Me_{n-2}Be_{(n/2+m/2-1)}H_m + Me_2Be\uparrow$$

which continued until the hydride : methyl ratio in the residue was a little more than 10 : 1. We were unable to achieve a greater hydride : methyl ratio by reactions at higher temperatures on account of thermal decomposition of dimethylberyllium, shown by the formation of some methane.

Diethylberyllium separates more easily when the viscous residue, left after the evaporation of ether from solutions of approximate composition $Et_4Be_3H_2$, is heated. For example, a glassy residue evidently consisting mainly of ethylberyllium hydride was obtained after 8 hours' heating at 70—80°. The course of further reaction at higher temperatures is greatly affected by the composition of the diethylberyllium–ethylberyllium hydride solution.

If a solution of sodium hydridodiethylberyllate is prepared by stirring sodium hydride in excess with a boiling solution of diethylberyllium in ether, and, after determination of the $NaEt_2HBe$ content of the supernatant liquid (by hydrolysis of a small sample), exactly half a molecular proportion of beryllium chloride in ether is added without previous filtration from unreacted sodium hydride, then more sodium hydride dissolves and the filtrate contains a mixture of $NaEt_2HBe$ and $Et_4Be_3H_2$. In one preparation, described in the Experimental section, the residue after pyrolysis (finally 8 hr. at 180°) of such a solution contained 43% of sodium as well as 31% of beryllium, 8·7% of hydride hydrogen, and 2·6% of ethyl. Though some oxygen was probably present, as the analysis accounted for only 85% of the total weight, the composition of the residue roughly corresponded to a mixture of BeH_2 (5 mol.) + $Na_2Be_2H_6$ (3 mol.), or BeH_2 (8 mol.) + Na_2BeH_4 (3 mol.). We believe

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[9] J. K. Ruff and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 535.

the sodium was present as a complex sodium beryllium hydride rather than as free sodium hydride since reaction with cold water was very slow.

Further evidence for the existence of a sodium beryllium hydride, evidently insoluble in ether, was obtained from experiments in which solutions of $Et_4Be_3H_2$ in ether were boiled with an excess of sodium hydride for periods of up to several days. The hydrolysis of samples of solution showed that the ethyl : hydride ratio (in solution) was always at least 2 : 1, but since concentration of the filtered solution yielded $NaEt_2HBe$, showing that sodium had entered solution, it is evident that hydride must have left solution as some insoluble complex hydride. The formation of ether-insoluble lithium salts, $BeH_2\mathit{n}LiH$, has been reported in a preliminary communication.[10]

By a modification of the experimental procedure, the calculated amount of beryllium chloride was added to a solution of $NaEt_2HBe$ obtained by dissolving the washed crystalline salt in ether (and thus free from either diethylberyllium or unreacted sodium hydride). In one such experiment an amount of beryllium chloride was added which resulted in the presence of one atom of chloride in excess for every 870 atoms of beryllium. Pyrolysis (180°) of the filtrate after separation of sodium chloride yielded a product in which the H : Et ratio was only 2·55 : 1. A trace of chloride, but no sodium, was detected in this product.

Infrared Spectra.—The $0 \longrightarrow 1$ vibrational transition of the ground state ($^2\Sigma^+$) of the BeH molecule, derived from band heads and band origins in emission electronic spectra,[11] is at 2058·6 cm.$^{-1}$, and at 2087·7 for the first excited $^2\Pi$-state. A *terminal* Be–H group could therefore be expected to cause absorption near 2100 cm.$^{-1}$, and a similar conclusion is reached by considering the changes with atomic number of the stretching frequencies of the hydrides of the other elements of the first short period. The position of the non-existent *Q* branch in the absorption spectrum of lithium hydride vapour [12] has been calculated (from data on the *P* and *R* branches) as 1406 cm.$^{-1}$. The vibrational modes, of mainly stretching character, of the *bridging* hydrogen atoms in a BeH_2Be group should cause absorption at frequencies well below 2100 cm.$^{-1}$, by analogy with the vibrational modes of the BH_2B groups in diborane and the various methyl- and ethyl-diboranes. Whereas terminal B–H bonds usually cause absorption in the 2200—2500 cm.$^{-1}$ region, the two modes due to the BH_2B bridge in diborane are at 1915 (ν_{13}, symmetrical out-of-phase) and 1606 cm.$^{-1}$ (ν_{17}, asymmetric in-phase); [13] for the numbering and description of these vibrations see ref. 13. The alkyldiboranes provide a closer analogy to the beryllium compounds formulated as (II) with BeH_2Be bridges. In the former the weak absorption corresponding to ν_{13} is observed at 1972 ($Me_4B_2H_2$), 1880 ($Me_3B_2H_3$), and 1852 cm.$^{-1}$ ($Et_4B_2H_2$), whereas the very strong absorption corresponding to ν_{17} is observed at 1605, 1605, and 1582 cm.$^{-1}$ in the three compounds, changing to 1186, 1183, and 1166 cm.$^{-1}$ on deuteration.[14]

The spectrum of (II) [Fig. (a)] contains a strong absorption at 1344 cm.$^{-1}$, shaded in the Figure, which is clearly due to one of the BeH_2Be stretching modes, since in the spectrum of the deutero-analogue, $(MeDBe{\cdot}NMe_3)_2$ [Fig. (b)] it moves to about 1020 cm.$^{-1}$ (also shaded) and evidently overlaps the absorption at 1007 cm.$^{-1}$ of (II) which is almost certainly due to $\nu_{asym}(NC_3)$ of the trimethylamine [see also Fig. (c)]. Absorption due to $\nu(BeH_2Be)$ is clearly evident at 1333 cm.$^{-1}$ in the spectrum of the ethyl derivative $(EtHBe,NMe_3)_2$ [Fig. (c)]. We do not know whether these absorptions correspond to ν_{13} or to ν_{17} of diborane. Other features of these spectra and of those of other organoberyllium compounds will be considered in another Paper.

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[10] E. Wiberg and R. Bauer, *Z. Naturforsch.*, 1951, **6**b, 171.

[11] G. Herzberg, " Molecular Spectra and Molecular Structure," Van Nostrand, Princeton, 1950, Vol. I, p. 508.

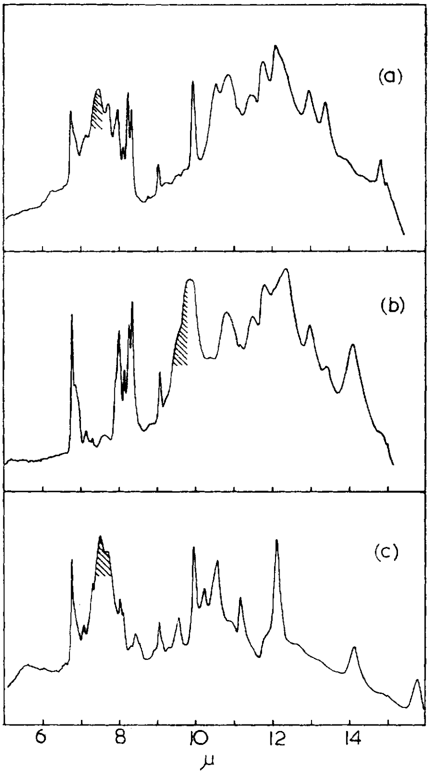
[12] T. C. James, W. G. Norris, and W. Klemperer, *J. Chem. Phys.*, 1960, **32**, 728.

[13] K. Nakamoto, " Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley, New York, 1963, p. 120; R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, 1945, *A*, **183**, 357.

[14] W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, 1961, **34**, 783.

The spectra of the tetramethylethylenediamine complexes of dimethylberyllium and of methylberyllium hydride (as Nujol mulls) are very similar, but that of the hydride complex contains a very strong absorption at 1331 cm.$^{-1}$, and a weak one at 1754, absent from that of the dimethylberyllium complex.

The presence of binuclear anions $[Et_4Be_2H_2]^{2-}$ in sodium hydridodiethylberyllate has now been confirmed by an *X*-ray diffraction analysis by Dr. H. M. M. Shearer and Mr. G. W. Adamson of this department. The salt crystallizes from ether with one molecule of ether of crystallization, which is associated with the sodium ions, and the ether dissociation pressure is so high (17 mm. at 20°) that all the ether is lost during the normal process of drying at low pressure. A comparison of the spectra of $NaMe_2HBe$ and $NaMe_2DBe$ (both as Nujol mulls), which may reasonably be assumed also to contain BeH_2-(or D_2)Be bridges, indicates that absorptions due to BeH_2Be bridges are at 1328 and 1165 cm.$^{-1}$, those due to BeD_2Be being at 917 and 869 cm.$^{-1}$: $NaMe_2HBe$, *1328s*, 1255ms, 1189s, *1165s*, 1138vs, 1086sh, 1018vs, 789vs, 754m, 612vw; $NaMe_2DBe$, 1261m, 1199ms, 1144s, 1075sh, 1015vs, *917vs*, *869vs*, 797vs, 777s, 595vw. The absorption at 1328 cm.$^{-1}$ in the spectrum of $NaMe_2HBe$ is somewhat obscured by the Nujol, but it is significant that it contains no pronounced features between 800 and 1000 cm.$^{-1}$, so the very strong absorptions at 869 and 917 cm.$^{-1}$ in the spectrum of the deutero-compound must be due to a BeD mode. The ratios ν_H/ν_D are 1·45 and 1·34, and though the former is unexpectedly large the significance of this is doubtful on account of the difficulty in measuring the absorption at 1328 cm.$^{-1}$. The spectra of $NaEt_2HBe$ and $NaEt_2DBe$ are more complicated, as expected, but a comparison of the two shows ν(BeH) at 1294s and 1065vs cm.$^{-1}$ and ν(BeD) at 951s and 835vs cm.$^{-1}$, ν_H/ν_D being 1·36 and 1·28. The remaining absorptions are very similar for the two compounds, except for a band of medium intensity at 912 cm.$^{-1}$ in the spectrum of the hydrogen compound,



Infrared spectra in cyclohexane.
(a) $(MeHBe,NMe_3)_2$;
(b) $(MeDBe,NMe_3)_2$;
(c) $(EtHBe,NMe_3)_2$.

The spectrum of (II) as saturated vapour, using a 10-cm. heated gas cell, has also been recorded and is very similar to the spectrum of a solution in cyclohexane. In the vapour ν(BeH_2Be) is at 1342 cm.$^{-1}$, very close to the frequency recorded for a solution in cyclohexane. At 50° (vapour pressure *ca.* 0·9 mm.) there was no appreciable absorption between 1500 and 2500 cm.$^{-1}$, but at 65° and particularly at 80° a sharp absorption at 2141 cm.$^{-1}$ appeared. We believe this absorption at 2141 cm.$^{-1}$ is due to terminal ν(Be–H) in monomeric $MeHBe,NMe_3$, since vapour density measurements indicated extensive dissociation with increasing temperature (145—175°). Between 65 and 80° the amount of monomer in saturated vapour could begin to be significant. Unfortunately, we could not study the unsaturated vapour at higher temperatures on account of defects in the heated gas cell.

EXPERIMENTAL

Compounds were generally decomposed for analysis by cautious addition of 2-methoxyethanol, sometimes with cooling, followed by degassed water and finally dilute sulphuric acid. Hydrogen and methane were collected by a Töpler pump. If both gases were present, the mixture was burnt with an excess of dry oxygen and combustion products measured. Other gases were collected in cold traps, identified by their infrared spectra, and measured in the usual way. Gas volumes expressed as c.c. refer to volumes reduced to s.t.p. Solids were always transferred from one vessel to another in a glove-box equipped with a circulatory nitrogen-purifying system. Specimens for infrared examination were also prepared, *e.g.*, as Nujol mulls, in a glove-box. Infrared spectra were recorded using Grubb–Parsons GS2A and Spectromaster prism-grating spectrometers.

Sodium Deuterodimethylberyllate.—Sodium deuteride (Metal Hydrides Inc.) (0·139 g., 0·00556 mole) was stirred overnight with boiling ether (60 c.c.) to which dimethylberyllium (7·0 c.c. of a 0·929M-solution in ether) had been added. Next morning the mixture was transferred to a double Schlenk tube,[15] repeatedly extracted with boiling ether, and the colourless small *needles* were separated by filtration without being removed from the Schlenk tube and dried at low pressure, m. p. 196° (Found: hydrolysable-methyl, 46·9; -deuteride, 3·1. C_2H_6BeDNa requires hydrolysable-methyl, 46·9; -deuteride, 3·1%). *Sodium hydridodimethylberyllate,* m. p. 195—196°, was similarly prepared, though larger quantities were more conveniently purified by the use of a Soxhlet extractor (Found: by hydrolysis, hydrolysable-methyl, 47·8, 46·8; -hydride, 1·59, 1·62; Be, 15·1, 14·6. C_2H_7BeNa requires hydrolysable-methyl, 47·5; -hydride, 1·60; Be, 14·3%).

Sodium Deuterodiethylberyllate.—Sodium deuteride (0·2655 g., 0·0106 mole) was stirred overnight with boiling ether (60 c.c.) to which diethylberyllium (7·0 c.c. of 1·50M-solution in ether) had been added. Next morning there was little solid residue. The mixture was transferred to a double Schlenk tube, filtered, concentrated to about 10 c.c., and cooled to 0°. The colourless *needles* were separated by filtration and solvent was removed under reduced pressure, m. p. 200—201° (Found: hydrolysable-ethyl, 63·1; -deuteride, 2·19. $C_4H_{10}BeDNa$ requires hydrolysable-ethyl, 63·0; -deuteride, 2·17%). Sodium hydridodiethylberyllate, m. p. 198°, has been described.[1]

The Methylberyllium Hydride, "$Me_4Be_3H_2$," and its Thermal Decomposition.—A suspension of sodium hydridodimethylberyllate together with a little sodium hydride was prepared by boiling a stirred suspension of sodium hydride (1·00 g., 0·0417 mole, washed with pentane) with dimethylberyllium (20 c.c. of a 1·76M-solution in ether, 0·0352 mole) for 48 hr. Beryllium chloride (1·50 g., 0·0187 mole) in ether (50 c.c.) was added to the boiling reaction mixture, which was boiled under reflux overnight. Next morning the mixture was allowed to cool to room temperature and the solid matter, mainly sodium chloride, was seen to settle more readily than before the addition of beryllium chloride. A sample (0·70 c.c.) of the clear supernatant liquid yielded, after hydrolysis (all gas volumes refer to s.t.p.) methane (5·80 c.c.), hydrogen (2·99 c.c.), and beryllium oxide (0·0050 g.). Chloride ion could not be detected. The ratio $CH_3 : Be : H$ was therefore 3·89 : 3 : 2·00.

The reaction mixture was filtered and ether distilled out until the volume of the residue was about 30 c.c.; no beryllium could be detected in the distillate. Volatile matter was removed from the residual solution at low pressure; the condensate (about 30 c.c.) consisted of ether

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[15] E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

with about 0·00024 mole of dimethylberyllium, measured by hydrolysis and also identified by the formation of a small amount of the characteristic yellow bipyridyl complex.[7] The residue (1·3 g.) was a colourless viscous oil, most of which (1·1 g.) was heated under a vacuum. At 51° the oil bubbled and frothed, evolving diethyl ether (153·3 c.c. of gas, 0·00684 mole) leaving a white residue (0·85 g.) of amorphous appearance; thus the viscous oil contained " $Me_4Be_3H_2$ " and diethyl ether in approximately equal molar ratio.

The solid residue was transferred to a sublimation apparatus and heated at 120° with continuous pumping for 10 days, although very slow sublimation had started at 60°. The sublimate (0·355 g.) was dimethylberyllium, and the residue (0·226 g.) was a mixed methylberyllium hydride (hydride : methyl ratio, by hydrolysis, 2·16 : 1).

In another preparation of the colourless viscous oil, heating was at 51° under vacuum to remove ether, and then at 170—180° for 3 days. Hydrolysis of the residue gave hydride : methyl ratios of 10·30 and 10·25 : 1. An attempt to raise the hydride : methyl ratio by heating at 160° for 1 day followed by 3 hr. at 190° resulted in the evolution of methane (1·57 c.c.) and hydrogen (0·70 c.c.), from a preparation containing 0·054 g.-atom of beryllium. In another preparation, heating at 200—210° for 8 hr. yielded a residue with a hydride : methyl ratio of 10·4 : 1.

Trimethylamine–Methylberyllium Hydride.—Sodium hydride (1·6 g., 0·0667 mole) was stirred for 2 days in boiling ether (100 c.c.) to which dimethylberyllium (60 c.c. of a 0·929M-solution in ether) had been added. After addition of beryllium chloride (2·2 g., 0·0275 mole) in ether (60 c.c.), the mixture was boiled under reflux overnight and filtered. Trimethylamine (2·63 g.) was condensed on a part (80 c.c.) of the filtrate which had been cooled in liquid nitrogen. After the mixture had warmed to room temperature ether and excess of amine were removed at reduced pressure. The residual colourless crystalline mass was allowed to evaporate, the vapours being pumped through a trap at 0°, in which the *complex* $(Me_3N,BeMeH)_2$, m. p. 73·0—73·2° condensed as colourless prisms (Found: hydrolysable-methyl, 17·5, 17·7; -hydride, 1·20, 1·20; Me_3N, 70·5; Be, 10·8%; *M*, cryoscopically, 0·4 wt. % in benzene, 166. $C_8H_{26}Be_2N_2$ requires hydrolysable-methyl, 17·8; -hydride, 1·20; Me_3N, 70·3; Be, 10·7%; *M*, 168). A second trap (−196°) contained trimethylamine–dimethylberyllium,[4] m. p. 36°.

Trimethylamine–Methylberyllium Deuteride.—Sodium deuteride (0·53 g., 0·021 mole) was stirred for 2 days with boiling ether (200 c.c.) to which dimethylberyllium (8·0 c.c. of a 2·42M-solution in ether) had been added. After addition of beryllium chloride (0·65 g., 0·0081 mole) the mixture was boiled under reflux for 1 hr. and filtered. Trimethylamine (2·9 g., 0·049 mole) was condensed on to the filtrate which had been cooled in liquid nitrogen, and, after the mixture had warmed to room temperature, ether and excess of amine were removed under reduced pressure. The colourless crystalline *complex*, m. p. 75—76°, was separated from Me_2Be,NMe_3 in exactly the same way as the analogous hydride complex (Found: hydrolysable-methyl, 17·6; -deuteride, 2·35. $C_4H_{12}BeDN$ requires hydrolysable-methyl, 17·6; -deuteride, 2·35%).

Tetramethylethylenediamine Complex.—The ditertiary amine in excess was condensed on an ethereal solution of " $Me_4Be_3H_2$," prepared as described earlier and contained in one limb of a double Schlenk tube. As the mixture was allowed to warm to room temperature a white precipitate was formed; this was collected on the sintered disc separating the two limbs, and twice washed with ether condensed from the filtrate. The filtrate was evaporated, and the residue, when sublimed, yielded colourless prisms of the tetramethylethylenediamine complex of dimethylberyllium,[7] m. p. 81°. The apparently amorphous precipitated *complex* was hydrolysed by 2-methoxyethanol, followed by 2N-sulphuric acid (Found: hydrolysable-methyl, 17·9; -hydride, 1·20; diamine, 69·4; Be, 11·0. $C_4H_{12}BeN$ requires hydrolysable-methyl, 18·05; -hydride, 1·21; diamine, 69·9; Be, 10·85%. The ratio Be : H : Me was 1 : 1·01 : 0·97).

1,2-*Dimethoxyethane Complex.*—Addition of 1,2-dimethoxyethane in excess to ethereal " $Me_4Be_3H_2$," followed by removal of ethers, yielded a semi-solid mass. At 48—50° in a vacuum, the 1,2-dimethoxyethane complex of dimethylberyllium,[7] m. p. 101°, sublimed from the reaction mixture, leaving a very viscous oil (Found: hydrolysable-methyl, 21·6, 21·5; -hydride, 1·38, 1·37; Be, 13·1, 13·2. C_3H_9BeO requires hydrolysable-methyl, 21·4; -hydride, 1·44; Be, 12·9%).

Trimethylamine–Ethylberyllium Hydride, $(Me_3N,BeEtH)_2$.—Triethylstannane (5·2 g., 0·0252 mole) was added to diethylberyllium (0·0251 mole, 16·0 c.c. of a 1·57M-solution in ether). The mixture was heated at 40° for 2 hr. and then at 75° for 2 hr. after which most of the ether had evaporated. After the vessel had cooled to room temperature the pressure was reduced to about 10^{-3} mm. overnight, any volatile matter being collected. Next morning the temperature was raised to 35° for 2 hr., and at this stage the vessel contained a viscous glassy residue (which became a white solid after prolonged pumping) of ethylberyllium hydride. Ether (20 c.c) was condensed on this residue, which dissolved forming a clear colourless solution Hydrolysis of a sample (2 c.c.) yielded hydrogen (31·0 c.c.) and ethane (31·5 c.c.). Tetraethyltin (4·05 g., 71%) was collected from the volatile products of the reaction, and its infrared spectrum showed that only a trace of triethylstannane was present.

The solution of ethylberyllium hydride was cooled (liquid N_2), and trimethylamine (500 c.c., an excess) was condensed on it. After ether and excess of amine had been evaporated, the crystalline residue of *trimethylamine–ethylberyllium hydride* was purified by sublimation at 40—45° *ca.*, 10^{-2} mm. The product condensed as colourless prisms, m. p. 90—91°, which fume in the air and react vigorously with water (Found: hydrolysable-hydride, 1·00; -ethyl, 29·0; Be, 9·3%; *M*, cryoscopically, 0·36, 0·55, 0·78 wt.-% benzene solution, 193, 200, 202. $C_{10}H_{30}Be_2N_2$ requires hydrolysable-hydride, 1·03; -ethyl, 29·6; Be, 9·2%; *M*, 196).

Trimethylamine–Diethylberyllium.—This was prepared by addition of excess of the amine to diethylberyllium in ether followed by evaporation of ether and excess of amine and by distillation at room temperature (*ca* 10^{-2} mm.); it fumes strongly in the air and is vigorously hydrolysed by water. It is liquid at −40° (Found: hydrolysable ethyl, 45·5, 45·1; Be, 7·25, 7·23; Me_3N, 45·8. $C_7H_{19}BeN$ requires hydrolysable ethyl, 45·6; Be, 7·1; Me_3N, 46·5%).

Displacement of Trimethylamine by Hydride Ion.—Trimethylamine–diethylberyllium (1·6 g., 0·013 mole) and sodium hydride (2·0 g., 0·083 mole) were stirred overnight in boiling ether (100 c.c.) during which time trimethylamine (0·28 g., 0·0047 mole) was evolved and was absorbed in hydrochloric acid and characterized as hydrochloride. The mixture was transferred to a double Schlenk tube, repeatedly extracted with boiling ether, and the sodium hydridodiethylberyllate separated by filtration, dried at low pressure, and identified by m. p. and infrared spectrum.

The Thermal Decomposition of a Mixture of $NaEt_2HBe$ *and* $Et_4Be_3H_2$.—A suspension of sodium hydride (2·0 g., 0·083 mole) in diethyl ether (100 c.c.), to which diethylberyllium (0·06 mole, 40 c.c. of a 1·5M-solution in ether) had been added, was boiled with reflux for 24 hr. with continuous stirring. Beryllium chloride (2·40 g., 0·030 mole) in ether (50 c.c.) was then added and boiling continued for a further 1 hr. The mixture was filtered, and two samples (3·0 c.c.) of filtrate yielded 23·2 and 23·1 c.c. of hydrogen, and 46·6 and 46·5 c.c. of ethane after hydrolysis.

Solvent was evaporated from part (30 c.c.) of the same filtrate, and the oily residue was heated at 60—70°/$\sim 10^{-3}$ mm. for 24 hr., then at 120° for a further 24 hr., and finally at 180° for 8 hr. During this period diethylberyllium (0·0107 mole, measured by hydrolysis) and ether were condensed at −78°, ethylene (14 c.c.) was condensed at −196°, and no gas that could not be condensed at −196° was produced during the reaction since any such gas would have been collected in a Töpler pump.

Hydrolysis of the residue yielded hydrogen (242 c.c., 0·0108 mole) and ethane (1·80 c.c., $8{\cdot}03 \times 10^{-5}$ mole, identified by infrared spectrum). No ether was detected. The residue contained 0·00550 g.-atom of beryllium.

Evaporation of ether from a further sample of the same solution of $Et_4Be_3H_2$, followed by pyrolysis under the same conditions as those described above, yielded an involatile residue which contained sodium (Found: Na, 43; Be, 30·9; hydrolysable-hydride, 8·72; -ethyl, 2·6. Calc. for a mixture of $3Na_2Be_2H_6 + 5BeH_2$: Na, 52; Be, 37·3; H, 10·6%). This product evolved hydrogen slowly at 280°, and gas evolution appeared complete after 7—8 min. at 300°. It neither caught fire nor fumed in the air, and reacted only slowly with cold water. No absorption in the 3 μ region was apparent in the infrared spectrum of a sample examined as a mull in perfluoromethyldecalin. The infrared spectrum (Nujol) differed from those of beryllium hydride containing less sodium in having absorptions at 1760 and 1629 cm.$^{-1}$ instead of a relatively broad and strong absorption centred on 1754 cm.$^{-1}$. The product did not dissolve when stirred with diethylberyllium in ether for 2 hr. at room temperature or during 4 hr. at 90° after removal of much of the solvent by distillation.

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