Dimeric Bis(nonafluoro-t-butoxy)beryllium and some of its Co-ordination Complexes

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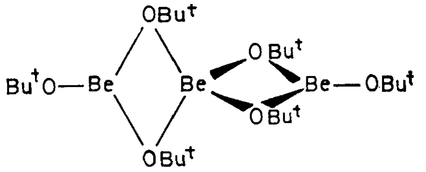
Bis(nonafluoro-t-butoxy)beryllium, $[\{[(CF_3)_3CO]_2Be\}_2]$, prepared from $(CF_3)_3COH$ and Et_2Be, is dimeric in C_6F_6 and is thermally stable well above its melting point. The abnormally weak bridge Be–O bond results in fission by diethyl ether yielding monomeric $[\{(CF_3)_3CO\}_2Be]\cdot OEt_2$. Complexes $[Be\{(CF_3)_3CO\}_2L_2]$ (L = ammonia or pyridine) are also described.

DIMETHOXYBERYLLIUM, $[Be(OMe)_2]$, is insolublein hydrocarbon solvents, non-volatile, and is doubtless polymeric, a constitution consistent with each beryllium atom being four-co-ordinate.[1] The simplest hydrocarbon-soluble alkoxide, di-t-butoxyberyllium, derived from the methoxide by replacement of each hydrogen atom with a methyl group, is trimeric in benzene and, beyond reasonable doubt, has structure (I) with one four-co-ordinate and two three-co-ordinate beryllium atoms.[2,3] Bis(trimethylsiloxy)beryllium, $[\{Be(OSiMe_3)_2\}_3]$, is also trimeric and is likely to have a structure similar to that of the t-butoxide.[4] Replacement of all three methyl groups in (I) with larger ethyl groups yielding $[\{Be(OCEt_3)_2\}_2]$ is necessary before the degree of association falls from three to two.[2,5] Only the very sterically hindered 2,6-di-t-butylphenol has so far afforded a monomeric phenoxide.[5] The beryllium atom is co-ordinatively unsaturated only when steric congestion about it prevents four-co-ordination.

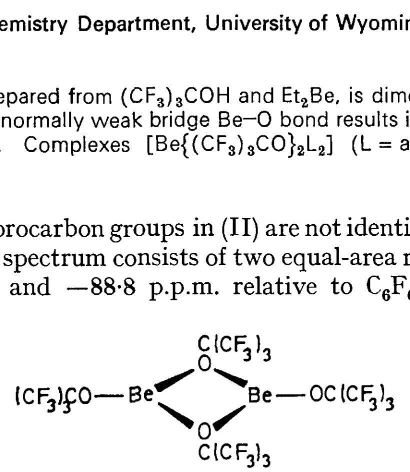


(I)

Replacement of methyl groups in (I) by trifluoromethyl groups should decrease the donor strength of the lone pairs of electrons on the oxygen atom at the same time increasing the overall size.

Addition of nonafluoro-t-butyl alcohol to diethylberyllium yields $[Be\{(CF_3)_3CO\}_2]$, which sublimes *in vacuo* at room temperature and is the most volatile alkoxide of beryllium known to date. In contrast, $[\{Be(OBu^t)_2\}_3]$, whose molecular weight is 465, sublimes *in vacuo* at *ca.* 100 °C and the monomeric phenoxide mentioned earlier ($M = 419$) sublimes *in vacuo* at 120—130 °C. The fluorocarbon alkoxide melts over the range 85—95 °C without decomposition and non-violently evolves a gas at *ca.* 130 °C, depositing a brown solid. It is insoluble in benzene and chlorobenzene, somewhat soluble in methylene chloride, though readily soluble in nitrobenzene (without apparent reaction) and hexafluorobenzene, being dimeric in the latter, (II).

The fluorocarbon groups in (II) are not identical and its ^{19}F n.m.r. spectrum consists of two equal-area resonances at −92·2 and −88·8 p.p.m. relative to C_6F_6 at room temperature. Substitution of the methyl groups in (I) by either an ethyl group or a trifluoromethyl group results in a decrease in degree of association by one unit. The dimeric constitution of (II) is most reasonably ascribed to the increase in steric congestion about the central beryllium atom in a hypothetical trimer, CF_3 being larger than CH_3. Further, *X*-ray crystallographic analysis of $[Be_2Cl_2(OBu^t)_4]$, formally derived from (I) by substitution of two terminal Bu^tO groups by Cl atoms, shows that four of the twelve methyl groups on the quaternary carbon atoms are orientated towards the central beryllium atom while the remaining eight are rotated away from the central metal atom, so as to minimize steric hindrance about the central four-co-ordinate beryllium atom, and this conformation is also likely in (I) as well as in other crystalline linear trimers.[6]



(II)

Reaction of $(CF_3)_3CONa$ with beryllium chloride in diethyl ether gives the distillable liquid, $[Be\{(CF_3)_3CO\}_2]\cdot OEt_2$, which is monomeric in benzene solution and is only the second example of a three-co-ordinate monomeric beryllium alkoxide complex, the 4-dimethylaminopyridine complex of beryllium t-butoxide being the other.[5] The co-ordinative unsaturation in this instance is doubtless due to steric hindrance which would result in a high dissociation pressure of a hypothetical 1 : 2 diethyl ether complex and also diethyl ether is a weaker base than ammonia and pyridine, which form 1 : 2 complexes $[Be\{(CF_3)_3CO\}_2L_2]$ (L = NH_3 or pyridine). These are the only 1 : 2 complexes of a beryllium alkoxide to have been described. The ^{19}F n.m.r. spectrum of the diethyl ether complex consists of a single resonance at −88·7 p.p.m. with respect to C_6F_6, and the 1 : 2 amine complexes, $[Be\{(CF_3)_3CO\}_2L_2]$, also have single resonances at −88·7 (L = NH_3) and −91·0 p.p.m. (L = pyridine).

The cleavage of the bridge Be–O bond in the dimer (II)

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

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

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

[4] R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1974, 1729.

[5] R. A. Andersen and G. E. Coates, *J.C.S. Dalton*, 1972, 2153.

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

by diethyl ether is noteworthy since neither pyridine nor quinuclidine (1-azabicyclo[2.2.2]octane)[5] react with the hydrogen analogue (I). The evidently weak basicity of lone pairs on the bridging oxygens in (II) is to be expected from the strong inductive effect of the fluorine atoms, and is in marked contrast to the strong basicity of the oxygen atoms in the numerous tetrameric alkylberyllium alkoxides, $[(RBeOR')_4]$, in which both lone pairs of each oxygen are used to form oxygen bridges.[2]

EXPERIMENTAL

All manipulations were carried out with careful exclusion of air and moisture by use of Schlenk tube, glove-box, and vacuum-line techniques. M.p.s were taken in sealed tubes under argon. Compounds were analysed by cautious hydrolysis followed by volumetric determination of beryllium by the fluoride method[7] under standardized conditions and the alcohol was isolated quantitatively and weighed. Ammonia was determined by the Kjeldahl method. The ^1H n.m.r. spectra were recorded at 100 MHz in benzene as solvent and internal reference and expressed in τ values using τ 2·73 for benzene, and ^{19}F n.m.r. spectra were recorded at 94·1 MHz in C_6F_6 as solvent and internal reference.

Bis(nonafluoro-t-butoxy)beryllium.—Perfluoro-t-butyl alcohol (6·1 g, 0·026 mol) in hexane (5 ml) was added to diethylberyllium (0·86 g, 0·013 mol) in hexane (5 ml) at −78 °C. After warming to room temperature the jelly-like suspension was stirred for 30 min. Hexane was removed *in vacuo* and the white solid residue was sublimed at 25—30 °C, 10^{-2} mmHg (yield 4·0 g, 65%). When heated it shrank at *ca.* 50 °C, turned to a jelly at *ca.* 70 °C, and finally melted (85—92 °C) [Found: hydrolysable perfluoro-t-butoxy, 98·4; Be, 1·9%; *M* (cryoscopically, in C_6F_6 1·39 and 1·00 w/w % using C_6F_5Br as a reference solute), 977 and 967 respectively. $C_{16}Be_2F_{36}O_4$ requires perfluoro-t-butoxy, 98·1; Be, 1·9%; *M*, 958].

Bis(nonafluoro-t-butoxy)beryllium–Diethyl Ether Complex.—Sodium perfluoro-t-butoxide[8] (10·3 g, 0·040 mol) in diethyl ether (10 ml) was added to beryllium dichloride–bis(diethyl ether) complex (4·5 g, 0·020 mol) in diethyl ether (25 ml). After being stirred (15 min) the suspension was filtered, the diethyl ether was removed *in vacuo*, and the resulting liquid was distilled at 43—48 °C, 10^{-3} mmHg (bath temperature 85 °C) [Found: hydrolysable perfluoro-t-butoxy, 84·8; Be, 1·6%; *M* (cryoscopically, in benzene 2·32 and 1·67 w/w %), 537 and 533. $C_{12}H_{10}BeF_{18}O_3$ requires hydrolysable perfluoro-t-butoxy, 85·0; Be, 1·6%; *M*, 533]. The ^1H n.m.r. spectrum consists of a quartet centred at τ 6·36 (J = 7 Hz) due to $CH_3C\mathit{H}_2OBe$ and a triplet centred at τ 8·99 (J = 7 Hz) due to $C\mathit{H}_3CH_2OBe$ in an area ratio of 2 : 3. The complex was also prepared, as shown by its ^1H n.m.r. spectrum, by dissolving $[\{(CF_3)_3CO\}_2Be]$ in diethyl ether.

Bis(nonafluoro-t-butoxy)beryllium–Bis(ammonia) Complex.—Excess of ammonia was condensed onto the diethyl ether complex (1·0 g, 0·0018 mol) dissolved in hexane (5 ml) at liquid-nitrogen temperature. After the mixture had been warmed to room temperature with stirring (20 min), the volatile materials were removed *in vacuo* and the white residue was crystallised from hexane–benzene (2 : 1) to give white *needles* in 68% yield (0·61 g). When heated it shrank at *ca.* 90 °C and melted at 94—96 °C [Found: hydrolysable perfluoro-t-butoxy, 94·2; Be, 1·8; ammonia, 6·5%; *M* (cryoscopically, 2·13 and 1·53 w/w % in benzene), 515 and 534. $C_8H_6BeF_{18}N_2O_2$ requires hydrolysable perfluoro-t-butoxy, 93·5; Be, 1·7; ammonia, 6·6%; *M*, 513]. The i.r. spectrum recorded as a Nujol mull contained absorptions at 3400m, 3320w, and 1615w cm^{-1}.

Bis(nonafluoro-t-butoxy)beryllium–Bis(pyridine) Complex.—Pyridine (1 ml, an excess) was added to the diethyl ether complex (0·95 g, 0·0017 mol) in hexane (5 ml). The white suspension was stirred for 15 min, the volatile matter was evaporated, and the resulting white residue was crystallised from hexane–benzene (3 : 1) as *plates* in 85% yield (0·92 g), m.p. 128 °C [Found: hydrolysable perfluoro-t-butoxy, 74·0; Be, 1·4%; *M* (cryoscopically, 2·60 and 1·88 w/w % in benzene), 603 and 627. $C_{18}H_{10}BeF_{18}N_2O_2$ requires hydrolysable perfluoro-t-butoxy, 73·8; Be, 1·4%; *M*, 637].

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

[8] R. E. A. Dear, W. B. Fox, R. J. Fredreichs, E. E. Gilbert, and D. K. Huggins, *Inorg. Chem.*, 1970, **9**, 2590.