Trimethylamine complexes of diethylberyllium

Dimethylberyllium and trimethylamine form a volatile complex, $(CH_3)_2Be\cdot N(CH_3)_3$, which is monomeric in the vapor phase[1]. The compound may be dimeric in the liquid or solid state (m.p. 36°) but its insolubility in benzene has prevented molecular weight measurements in solution. At temperatures below 10° the unusual compound $[(CH_3)_2Be]_2[N(CH_3)_3]_3$ is stable[1]. Even at −30° $[(CH_3)_2Be]_2[N(CH_3)_3]_3$ persists in the presence of free trimethylamine. There is no indication that dimethylberyllium bis(trimethylamine) forms.

A bis(trimethylamine) adduct of diethylberyllium has been characterized recently in this laboratory as well as a mono(trimethylamine) adduct. The questions why a bis-amine complex forms with diethylberyllium and not dimethylberyllium and what factors permit the formation of a bis(trimethylphosphine)[1] adduct of dimethylberyllium remain to be answered. Explanations based on beryllium ligand electronegativity seem inadequate (the Hammett σ constants[2,3] for the *p*-methyl- and *p*-ethylbenzoic acids of −0.171 and −0.151 respectively do not appear to provide enough difference for the observed results). Consideration of steric factors point to the inverse of the observed results wherein the larger groups attached to beryllium favor the formation of bis-addition compounds. It is possible that polymerization of $R_2Be\cdot N(CH_3)_3$ molecules by way of alkyl bridges can compete with dative bonding between $R_2Be\cdot N(CH_3)_3$ monomers and trimethylamine in achieving a tetracoordinate state for beryllium. The tendency for alkyl bridging may be enhanced when R is methyl and diminished when R is a larger alkyl group. Diethylberyllium mono(trimethylamine) is somewhat associated in freezing cyclohexane solution and diisopropylberyllium mono(trimethylamine) is monomeric in freezing benzene solution[4].

Diethylberyllium bis(trimethylamine), in a closed system under vacuum, begins to lose trimethylamine at approximately −35°. The vapor pressure of amine is 1.1 mm at −33° and 11.0 mm at −15.5°, the melting point of the compound (range −15.5° to −14.0°). The low vapor pressure of trimethylamine over $(C_2H_5)_2Be\cdot 2N(CH_3)_3$ above −35° shows the existence of an equilibrium between $(C_2H_5)_2Be\cdot 2N(CH_3)_3$ and $(C_2H_5)_2Be\cdot N(CH_3)_3 + N(CH_3)_3$. Amine can be pumped from the system readily at room temperature, shifting the equilibrium and leaving the stable mono(trimethylamine) complex of diethylberyllium.

Diethylberyllium bis(trimethylamine) was prepared by treating $(C_2H_5)_2Be\cdot N(CH_3)_3$ with either an equimolar portion or an excess of trimethylamine. When an excess of amine is used prolonged pumping on the sample in high vacuum at −65° removes a portion of the amine leaving a residue having the composition $(C_2H_5)_2Be\cdot 2N(CH_3)_3$. Confirmation of the chemical determination of the composition of the bis(trimethylamine) adduct was sought unsuccessfully with nuclear magnetic resonance spectrometry. Mixtures of $(C_2H_5)_2Be\cdot N(CH_3)_3$ and $N(CH_3)_3$ representing a variety of stoichiometries were examined at room temperature and below. In every case a single $N–CH_3$ band was observed instead of 2 or more bands representing each of the species present in solution. Such an effect is to be expected at room temperature where an exchange of trimethylamine molecules among species is probably rapid[5,6,7]. If the exchange rate were slowed to the extent that a $N–CH_3$ peak could be observed for each species present, the composition of each could be determined by comparing the relative intensities of the bands. A cyclopentane solution containing $(C_2H_5)_2Be\cdot$

$N(CH_3)_3$ and $N(CH_3)_3$ in a 1 to 2 molar ratio was examined from —90° to room temperature. No splitting of the $N–CH_3$ band occurred. Since the existence of $(C_2H_5)_2Be·N(CH_3)_3$ is unambiguous, the lack of splitting cannot be attributed to magnetic equivalence of the $N–CH_3$ groups, and is explainable in terms of the rapid exchange of trimethylamine molecules even at very low temperatures.

Diethylberyllium mono(trimethylamine) appears to be stable in vacuum up to its boiling point of 65–66°/10^{-3} mm where it loses a small amount of amine during distillation.

Experimental

Diethylberyllium was prepared from the reaction of ethylmagnesium bromide and beryllium chloride in ether solution[8]. The product was freed of residual ether by first heating it at 50° over beryllium chloride in a nitrogen atmosphere and then distilling it in vacuum, b.p. 56–57°/10^{-3} mm. (Found: C, 71.6; H, 15.0; Be, 13.1. $C_4H_{10}Be$ calcd.: C, 72.0; H, 15.1; Be, 13.4%.)*

Diethylberyllium mono(trimethylamine) was prepared by the reaction of equimolar amounts of trimethylamine (Matheson Co.; dried over P_4H_{10} and distilled before use) and diethylberyllium on the vacuum line. The compound boils at 65–66°/10^{-3} mm. (Found: Be, 7.5; N, 11.1. $C_7H_{19}BeN$ calcd.: Be, 7.2; N, 11.1%.) A cryoscopic molecular weight determination was conducted in cyclohexane: Found, 170 at molal concentration 0.16. Calcd. for $(C_2H_5)_2Be·N(CH_3)_3$, 126.

Diethylberyllium mono(trimethylamine) (3.157 g, 0.025 mole) was treated with trimethylamine (0.0370 mole) in a vacuum line at —78°. The reaction mixture was evacuated at —65° for 4.5 h through a —196° trap. The amine was estimated in calibrated volume. Found: 0.0117 mole. Thus the residue contained 0.025 mole of $(C_2H_5)_2Be·N(CH_3)_3$ in combination with 0.0253 mole of $N(CH_3)_3$. The vapor pressure of the residue, measured in a small section of the vacuum line, was 1.1 mm at —33.0°, 6.8 mm at —22.6°, 11.0 mm at —15.5°, and 20.5 mm at —7.6°.

In a similar experiment conducted at —70° for 6 h a mixture of $(C_2H_5)_2Be·N(CH_3)_3$ (0.2470 g, 1.95 mmole) and trimethylamine (5.88 mmole) yielded 4.0 mmole of amine in the —196° trap. The residue contained 1.95 mmole of $(C_2H_5)_2Be·N(CH_3)_3$ in combination with 1.88 mmole of $N(CH_3)_3$.

A Varian Associates A-60 nuclear magnetic resonance spectrometer was used to record the spectra of neat liquids and cyclopentane solutions of mixtures of $(C_2H_5)_2Be·N(CH_3)_3$ and $N(CH_3)_3$. Low temperature experiments were conducted with the aid of a Varian Associates V-6040 Variable Temperature Controller.

Acknowledgements

The financial support by the Office of Naval Research is gratefully acknowledged. The author wishes to express appreciation for the helpful discussions of the work with Dr. CHARLES P. HABER of this laboratory.

U.S. Naval Ordnance Laboratory,
Corona, California (U.S.A.)

FRANCES M. PETERS

---

* Elemental analyses were conducted by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

1 G. E. Coates and N. D. Huck, *J. Chem. Soc.*, (1952) 4501.
2 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill, New York, 1st ed., 1940, p. 188.
3 J. W. Baker, J. F. J. Dippy and J. E. Page, *J. Chem. Soc.*, (1937) 1774.
4 G. E. Coates and F. Glockling, *J. Chem. Soc.*, (1953) 22.
5 T. Mole, *Chem. Ind. (London)*, (1964) 281.
6 J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, pp. 61–64.
7 N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, 82 (1960) 248.
8 H. Gilman and F. Schulze, *J. Chem. Soc.*, (1927) 2663.

Received May 25th, 1964