SbF_5–FSO_3H samples were prepared in a drybox using weighed amounts of the constituents. When required, SO_2ClF was condensed into the nmr tubes on the vacuum line.

Acknowledgments. We thank the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research for generous financial assistance. We also thank Mr. J. I. A. Thompson for assistance in running nmr spectra. We are grateful to Dr. Commeyras and Professor Olah for making their manuscript available to us prior to publication.

Nuclear Magnetic Resonance Studies of Dimethylberyllium Adduct Species in Dimethyl Sulfide Solution

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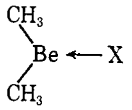
Abstract: Two equilibria are reported for dimethylberyllium in dimethyl sulfide: (A) $(CH_3)_2Be:S(CH_3)_2 + S(CH_3)_2 \rightleftharpoons (CH_3)_2Be:(S(CH_3)_2)_2$, and (B) $n(CH_3)_2Be:(S(CH_3)_2)_2 \rightleftharpoons ((CH_3)_2Be)_n:(S(CH_3)_2)_2 + (2n-2)S(CH_3)_2$, where n is as large as 9 in solution. Enthalpies for reactions A and B are found to be −3.23 and −9 kcal/mol, respectively. These data are compared with thermodynamic parameters for similar reactions. Methylberyllium chloride is shown to exist in dimethyl sulfide solution only as $(CH_3)BeCl:(S(CH_3)_2)_2$.

The reaction of Lewis bases with dimethylberyllium has been the subject of considerable interest. A tensimetric study of the reaction of solid dimethylberyllium with the bases trimethylamine, trimethylphosphine, trimethylarsine, dimethyl and diethyl ethers, and dimethyl sulfide has been reported.[1] In that investigation a measured quantity of an appropriate base was combined (in a bulb of known volume) with a quantitative sample of solid dimethylberyllium. The composition of the adduct was inferred from determination of the quantity of recoverable base at a given temperature. The bases trimethylamine,[2] trimethylphosphine, and dimethyl and diethyl ethers formed 1:1 (I) and 2:1 (II) adducts with dimethylberyllium, the 1:1 adducts being either monomeric or dimeric. At elevated temperatures the relatively weaker bases formed polymeric species (III) reminiscent of the structure of solid polymeric dimethylberyllium[3] with base molecules acting as chain ending groups. *There was no evidence for a reaction between dimethylberyllium and the bases dimethyl sulfide and trimethylarsine.*



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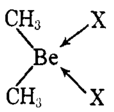

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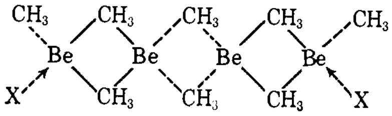

III

X = $P(CH_3)_3$, $O(CH_3)_2$, or $O(C_2H_5)_2$

The synthesis of beryllium alkyls by means of the Grignard reaction utilizing dimethyl sulfide as solvent[4] suggests that beryllium alkyls are soluble in this solvent. The Grignard method utilizing dimethyl sulfide as solvent in the synthesis of dimethylberyllium was performed successfully in this laboratory;[5] however, infrared analysis of the solid volatile product of this reaction indicated a complex with dimethyl sulfide. The infrared spectrum of this solid material matched the reported infrared spectrum of dimethylberyllium[6] only after about six sublimations indicating that dimethyl sulfide coordinates rather strongly to dimethylberyllium.

These preliminary observations suggest that dimethyl sulfide is able to rupture the electron-deficient bonds in solid polymeric dimethylberyllium resulting in the formation of adduct species. The nature of the adduct species present in dimethyl sulfide solution is an interesting question. Possible species include the 1:1 (I), 2:1 (II), and polymeric adduct (III) molecules. Proton magnetic resonance spectroscopy was invoked as the spectroscopic tool for analysis of these solutions, as each species is predicted to give rise to a different nmr resonance. Proton resonances of the methyl groups bonded to beryllium in II are expected at higher magnetic field than methyl groups bonded to beryllium in I. The species $(CH_3)_3B$ and $(CH_3)_3B:S(CH_3)_2$ exhibit proton resonance at 4.57 and 4.62 ppm relative to CH_2Cl_2 internal standard, respectively,[7] and bridging methyl groups involved in "electron-deficient" bonds are expected to resonate at lower field than methyl groups in terminal positions (bridging methyl groups in hexamethyldialuminum resonate at τ 9.93 while terminal methyl groups resonate at τ 10.50).[8]

It was decided to record the variable-temperature pmr spectra of these solutions, since fast chemical ex-

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(1) G. E. Coates and N. D. Huck, *J. Chem. Soc.*, 4501 (1952).
(2) N. A. Bell and G. E. Coates, *Can. J. Chem.*, **44**, 744 (1966).
(3) A. Snow and R. Rundle, *Acta Crystallogr.*, **4**, 348 (1951).
(4) G. Bahr and K. H. Thiele, *Ber.*, **90**, 1578 (1957).
(5) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).
(6) J. Goubeau and K. Walter, *Z. Anorg. Allg. Chem.*, **58**, 322 (1963).
(7) T. D. Coyle and F. G. A. Stone, *J. Amer. Chem. Soc.*, **83**, 4138 (1961).
(8) K. C. Williams and T. L. Brown, *ibid.*, **88**, 5460 (1966).

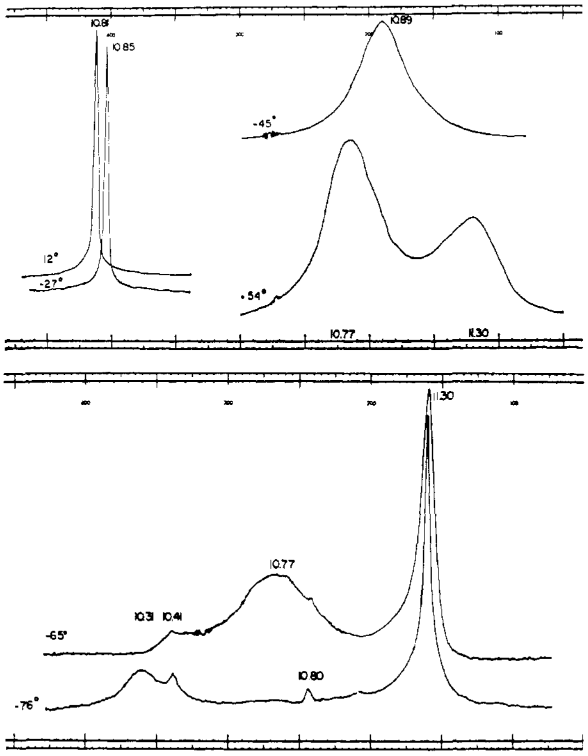

Figure 1. Representative proton magnetic resonance spectra of a solution of dimethylberyllium in dimethyl sulfide at different temperatures.

change between species at elevated temperatures is expected to result in an average signal. Nonequivalent bridging and terminal methyl environments in hexamethyldialuminum are not detected at temperatures higher than −40°.[8]

Variable-temperature magnetic resonance spectra of dimethyl sulfide solutions of CH_3BeCl species are expected to aid assignment of the variable-temperature spectra of dimethyl sulfide solutions of dimethylberyllium. The greater electronegativity of chlorine relative to a methyl group is expected to reduce diamagnetic shielding and correspondingly shift the resonance of the methyl group bonded to beryllium to lower field. Successive replacement of chlorine for methyl in the system, $(CH_3)_nMCl_{4-n}$, M = C, Si, Sn, n = 1–4, shifts the resonance of the CH_3M species to correspondingly lower fields[9] and ether solutions of CH_3BeX, X = Cl and Br, resonate at *lower* field than $(CH_3)_2Be$ species.[10]

Experimental Section

Because of the pyrophoric nature of organometallic beryllium compounds all sample preparations were performed in an inert atmosphere enclosure equipped with an atmosphere circulation system for removal of trace quantities of moisture and oxygen.[11]

Dimethylberyllium was prepared by the reaction of beryllium metal with dimethylmercury in a sealed tube at 120°.[12] The purity was checked by infrared[5] as well as nmr spectra.

Dimethyl sulfide solutions of dimethylberyllium were prepared by vapor transferring dimethyl sulfide onto dimethylberyllium in nmr tubes cooled with liquid nitrogen. The tubes were allowed to warm to room temperature accompanied with solution of the dimethylberyllium. The tubes were sealed under vacuum.

Methylberyllium chloride in dimethyl sulfide was prepared by the reaction of dimethylberyllium and beryllium chloride.[10]

$$(CH_3)_2Be + Cl_2Be = 2CH_3BeCl$$

Dimethyl sulfide was vapor transferred onto approximately a 4:1 molar ratio of dimethylberyllium and beryllium chloride in an nmr tube cooled with liquid nitrogen. The tube was allowed to warm to room temperature accompanied by solution of the reactants. The tube was degassed and sealed under vacuum.

Dimethyl sulfide was purchased from the Aldrich Chemical Co., Inc., and dried by heating to reflux over CaH_2 or $LiAlH_4$ followed by distillation.

The magnetic resonance spectra were recorded on a Varian Associates HA-100 nuclear magnetic resonance instrument. Proton chemical shifts were recorded relative to the solvent signal. The nmr probe for variable-temperature analysis was calibrated using the temperature-dependent resonance in CH_3OH. The spectrum at each temperature was recorded after equilibrium had been attained; this usually required 5 min for small (*i.e.*, 10°) changes in temperature.

Results

The room-temperature proton magnetic resonance of a solution of dimethylberyllium in dimethyl sulfide consisted of a single resonance (τ 10.81 at 12°). This resonance shifted to higher magnetic field upon cooling (Figure 1). At −45° this resonance is broadened significantly and appears at τ 10.89. This resonance is split into two new relatively broad signals, a low-field signal at τ 10.77 (environment A) and a high-field signal at τ 11.30 (environment B) at −54°. As the temperature is lowered further both signals become narrow and the area ratio, B/A, increases. At lower temperatures new low-field signals appear, one centered at τ 10.31, one at 10.41, and another at 10.80. As the temperature is lowered further the area of the τ 10.31 resonance increases relative to the new signals at τ 10.41 and 10.80. The temperature dependence of the chemical shift of the resonance present in the temperature range +40 to −45°, in Hz above the dimethyl sulfide resonance, is shown in Table I. At −54° and below the areas (normalized to one) of the signals at τ 10.77 and 11.30 are respectively −54°, 0.680 and 0.320; −65°, 0.585 and 0.415. The ratios of the combined areas of the signals at τ 10.31 and 10.41 to the area of the signal at τ 11.30 at each temperature are respectively −74°, 0.36 and 0.64; −80°, 0.43 and 0.57; −85°, 0.49 and 0.51; −87°, 0.50 and 0.50.

Table I. Thermodynamic Parameters for the Reaction $(CH_3)_2Be{:}S(CH_3)_2 + S(CH_3)_2 = (CH_3)_2Be{:}(S(CH_3)_2)_2$

Temp, °C	1/*T*	Chemical shift of av signal,[a]	*K*	Log *K*
12	0.0035	289	0.093	8.969–10
−27	0.00407	293	0.205	9.312–10
−47	0.00442	297	0.344	9.537–10
−54	0.00456		0.470	9.672–10
−65	0.0048		0.710	9.850–10

[a] In Hz above $(CH_3)_2S$ lock.

The variable-temperature proton magnetic resonance spectra of a sample containing beryllium chloride with excess dimethylberyllium in dimethyl sulfide are shown in Figure 2. The single resonance present at room temperature is broadened at −10°, and at −45° is split into two resonance signals, one centered at τ 10.89 and

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(9) M. P. Brown, *J. Phys. Chem.*, 64, 698 (1960).

(10) J. R. Sanders, Jr., E. C. Ashby, and J. H. Carter, II, *J. Amer. Chem. Soc.*, 90, 6385 (1968).

(11) T. L. Brown, D. W. Dickerhoff, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, 33, 491 (1961).

(12) H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, **49**, 2904 (1927).

one at 11.17. At −54° three resonance lines are present, a new low-field signal centered at τ 10.77, the signal at 11.17, and a new high-field signal at 11.30. At −76° three new resonance lines appear, at τ 10.31, 10.41, and 10.80 and the signal at 10.77 is no longer present.

These spectra were in all cases reversible with temperature. The changes that accompanied the cooling process matched in reverse the changes accompanying the warming process.

The values cited here, the dependence of the chemical shifts and relative resonance areas on temperature, are each representative of a number of determinations.

Discussion

The observed resonances at τ values greater than 10 are those expected for methyl groups bonded to electropositive metals. Ether solutions of methyllithium, dimethylmagnesium, and dimethylberyllium exhibit single resonances at τ 11.94,[13] 11.41,[13] and 11.16,[14] respectively. The decrease in the methyl-group chemical shift for these systems parallels the increase in electronegativity of the metals,[15] 0.98, 1.3, and 1.50, respectively. The resonance signals shown in Figures 1 and 2 range from τ 10.31 to 11.30 and are therefore attributed to *methyl*beryllium environments.

The complex temperature dependence of these spectra can be explained by either: (1) equilibrium between species, the relative amounts of which change with temperature; (2) rapid chemical exchange between two or more of these species at room temperature resulting in the detection of a single averaged signal, at lower temperatures chemical exchange being slow enough to allow detection of distinct chemical environments; or (3) a combination of factors 1 and 2.

The temperature dependence of the spectra shown in Figure 1 indicates that a combination of factors 1 and 2 is taking place. The signal present at −45° and above is an average, due to rapid exchange, of species A at τ 10.77 and species B at 11.30. Below −45° the exchange process is slowed and each distinct species is detected. The averaged signal moves to higher field indicating that this signal constitutes greater amounts of species B as the temperature is lowered. The chemical shift of the 40° signal at τ 10.78 is very close to the signal of species A at 10.77 indicating that at 40° the averaged signal is comprised almost entirely of species A. Below −45° the area of the signal at τ 11.30 (species B) increases relative to the signal at 10.77 (species A) as the temperature is lowered, analogous to the observation made for the averaged signal. The chemical shifts of species A and B below −45° are independent of temperature, indicating that these are distinct chemical species and are not themselves representative of an average of species whose abundances change with temperature.

At −65° and below new signals at τ 10.31, 10.41, and 10.80 appear and increase in intensity relative to the signal at τ 11.30 as the temperature is lowered. The chemical shift of these signals is temperature independent, indicating that these signals are due to distinct species and do not represent an average of species whose abundances change with temperature.

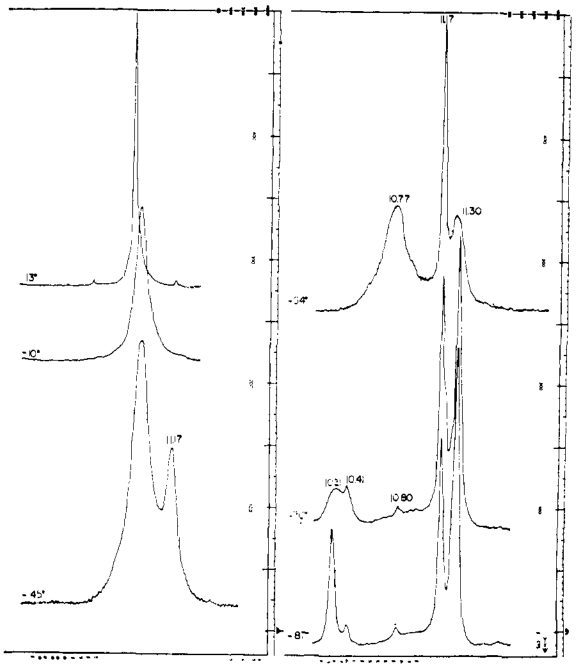


Figure 2. Representative proton magnetic resonance spectra of a solution of dimethylberyllium and methylberyllium chloride in dimethyl sulfide at different temperatures.

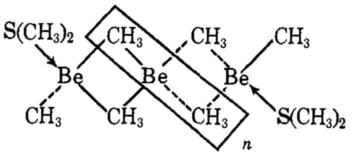
The temperature dependence of these spectra suggests the following equilibrium reactions

$$(CH_3)_2Be{:}S(CH_3)_2 + S(CH_3)_2 = (CH_3)_2Be{:}(S(CH_3)_2)_2 \quad (1a)$$

$$n(CH_3)_2Be{:}(S(CH_3)_2)_2 = ((CH_3)_2Be)_n{:}(S(CH_3)_2)_2 + (2n-2)S(CH_3)_2 \quad (1b)$$

$$n = 2, 3, 4, \ldots$$

where equilibrium 1a applies at temperatures higher than −65° while 1b applies at temperatures lower then −65°. The resonance at τ 10.77 is assigned to the 1:1 adduct species, $(CH_3)_2Be{:}S(CH_3)_2$, while the signal at τ 11.30 is assigned to the 2:1 adduct species, $(CH_3)_2Be{:}(S(CH_3)_2)_2$. The upfield shift is expected since the diamagnetic shielding of two coordinated dimethyl sulfide molecules is expected to be greater than one. In comparison, the *methyl*beryllium chemical shift in $(CH_3)_2Be{:}N(CH_3)_3$ at τ 11.19 increases to 11.52 in $(CH_3)_2Be{:}(N(CH_3)_2CH_2)_2$.[14] The *methyl*beryllium resonance of each sulfide adduct occurs at lower field than the corresponding amine adduct which is consistent with the known relative base strengths of the sulfide and amine molecules.[1,16,17] The *methyl*boron proton chemical shifts in $(CH_3)_3B{:}S(CH_3)_2$ and in $(CH_3)_3B{:}N(CH_3)_3$ are at 4.62 and 5.65 ppm relative to CH_2Cl_2 internal standard, respectively.[7] Reaction 1b applies at temperatures lower than −65°. The new resonances which appear in this temperature range are assigned to the polymeric species



$n = 0, 1, 2, 3, \ldots$

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[13] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, **86**, 2135 (1964).

[14] N. A. Bell, G. E. Coates, and J. W. Emsley, *J. Chem. Soc.*, *A*, 49 (1966).

[15] A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

[16] R. S. Drago, *Chem. Brit.*, **3**, 516 (1967).

[17] N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 316 (1942).

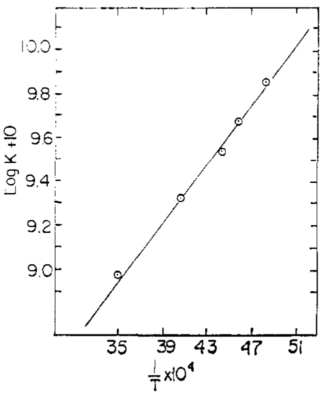

Figure 3. Plot of log *K vs.* $1/T$ for equilibrium reaction: $(CH_3)_2Be{:}S(CH_3)_2 + S(CH_3)_2 = (CH_3)_2Be{:}(S(CH_3)_2)_2$.

This species is expected to exhibit three distinct methylberyllium environments. These are terminal methyl and two types of bridging methyl groups; methyl groups which are at the ends of the polymer chain and thus are affected by the coordinated dimethyl sulfide groups and methyl groups which are incorporated in the interior of the polymer structure (for $n > 1$) and thus are not affected by the coordinated dimethyl sulfide groups. The terminal methyl environment is assigned to the low intensity signal at τ 10.80, the bridging methyl groups at the ends of the polymer to the low-intensity signal at τ 10.41, and the bridging methyl groups which are incorporated in the interior of the polymer to the signal at τ 10.31. Both bridging methyl environments are expected to show resonance at significantly lower field than the terminal methyl groups, since the bridging methyl groups are engaged in electron-deficient bonding and are consequently deshielded with respect to groups bonded by normal electron-pair bonds in terminal positions. The terminal methyl environment in the polymer at τ 10.80 is expected to be very similar to the methylberyllium environment in $(CH_3)_2Be{:}S(CH_3)_2$ which resonates at τ 10.77. The relative positions of the two bridging methyl environments are predicted by the distances of each of these from the coordinated base molecules at the end of the polymer chain. The bridging methyl groups at the ends of the polymer chain are nearer the coordinated base molecules and therefore resonate at higher field (0.1 ppm) than the bridging methyl groups which are incorporated in the interior of the polymer structure. The area ratios of these signals are temperature sensitive. At −65°, only the signals at τ 10.41 and 10.80 of approximate area ratio 2:1, respectively, are present. These resonances are consistent with a trimer ($n = 1$ in the formula). Such a polymer contains only end-bridging methyl groups and terminal methyl groups. At −75° the signal at τ 10.31 is present along with the signals at τ 10.41 and 10.80, indicating that species with $n > 1$ are being formed. As the temperature is lowered further this signal increases in intensity. At −81° this signal is roughly four times the area of the signal at τ 10.41 and eight times the area of the signal at τ 10.80 indicating that at this low temperature a polymer with n equal to nine is formed.

The fact that polymer signals at τ 10.41 and 10.80 and the signal due to the 1:1 adduct at τ 10.77 are present in the −65° spectrum indicates that at this intermediate temperature both equilibria apply simultaneously.

The equilibrium constant at each temperature in the range +40 to −65° for equilibrium 1a was extracted from these nmr data. The beryllium species involved in reaction 1a contain equal numbers of methylberyllium groups. In the slow exchange region (−50 to −65°) this constant was calculated from the relative areas of each species. In the rapid exchange region (+40 to −45°) the relative concentrations of each species were calculated from a knowledge of the chemical shift of the 1:1 and 2:1 adduct species (under conditions of slow exchange) and the chemical shift of the averaged signal at each temperature of interest with the aid of the equations[18]

$$\delta_{av} = N_a\delta_a + N_b\delta_b$$

$$N_a + N_b = 1$$

where δ_{av} = the position in Hz above $(CH_3)_2S$ protons of the averaged signal; N_a and N_b are the mole fractions of 1:1 and 2:1 adduct species, respectively; δ_a and δ_b are the chemical shifts of the 1:1 and 2:1 adduct species. The equilibrium constant obtained in this manner is of the form

$$K = [(CH_3)_2Be{:}(S(CH_3)_2)_2]/[(CH_3)_2Be{:}S(CH_3)_2]$$

and does not contain a term representing the concentration of free uncomplexed base. Since this species is the solvent and is present in large excess, changes in the concentration of base are expected to be small and this term, therefore, is not needed. The pertinent thermodynamic parameters are listed in Table I. An extension of the Gibbs-Helmholtz relation allows the heat of reaction to be extracted from a plot of log *K vs.* $1/T$. The entropy change at a given temperature is calculated from the equilibrium constant at that temperature and the heat of reaction. The plot of log *K vs.* $1/T$ is shown in Figure 3. The linear dependence is verification of an equilibrium process. The heat of reaction is −3.2 kcal/mol, and the entropy change at −47° is −16 eu.

The magnitude and sign of the enthalpy and entropy are in excellent agreement with reaction 1a. This reaction is associative in nature, consistent with the negative entropy. This reaction also involves the formation of Be–S bonds and is, therefore, expected to be exothermic, in agreement with the negative enthalpy. In addition, the enthalpy for this reaction is expected to be significantly smaller than the −8 kcal/mol[19] for the reaction $(CH_3)_3Ga + S(CH_3)_2 = (CH_3)_3Ga{:}S(CH_3)_2$, a result predicted from both steric and inductive arguments.[20] The inductive effect of a coordinated dimethyl sulfide group in $(CH_3)_2Be{:}S(CH_3)_2$ is expected to make beryllium a weaker acid than gallium in $(CH_3)_3Ga$. The larger size of a dimethyl sulfide group relative to a methyl group will sterically inhibit adduct formation. The similar entropies, −16 eu for reaction 1a and −19 eu for formation of $(CH_3)_3Ga{:}S(CH_3)_2$,[19] are further verification. Trimethylgallium is an excellent molecule with which to make comparison since trimethylgallium and dimethylberyllium are acids of comparable strength. This is indicated from the fact that the enthalpy for for-

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(18) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 282.

(19) G. E. Coates, *J Chem. Soc.*, 2003 (1951).

(20) H. C. Brown, *ibid.*, 1248 (1956).

mation of a mole of the trimethylamine adduct from dimethylberyllium[1] and trimethylgallium[21] is −21 kcal/mol in each case.

Evidence for formation of polymeric species was observed at lower temperatures. This is undoubtedly due to the fact that dimethyl sulfide is a relatively weak base[16] and that polymerization is, under conditions of low temperature, able to successfully compete with adduct formation as a mode of coordinative saturation. This system thus dramatizes the strength and thermodynamic stability of the bridging, electron-deficient bonds in the long-chain polymers. The equilibrium reactions for the stepwise formation of polymer molecules with increasing chain length are indicated below

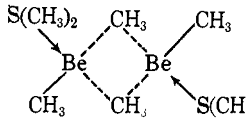
$$\underset{\mathrm{II}}{2((\mathrm{CH_3})_2\mathrm{Be{:}(S(CH_3)_2)_2}} = \underset{\mathrm{III}}{(\mathrm{CH_3})_4\mathrm{Be_2{:}(S(CH_3)_2)_2}} + 2\mathrm{S(CH_3)_2}$$

$$\mathrm{II} + \mathrm{III} = \underset{\mathrm{IV}}{(\mathrm{CH_3})_6\mathrm{Be_3{:}(S(CH_3)_2)_2}} + 2\mathrm{S(CH_3)_2}$$

$$\mathrm{II} + \mathrm{IV} = \underset{\mathrm{V}}{(\mathrm{CH_3})_8\mathrm{Be_4{:}(S(CH_3)_2)_2}} + 2\mathrm{S(CH_3)_2}$$

The structures of III, IV, and V correspond to the polymeric species formula with $n = 0$, 1, and 2, respectively.

The equilibrium constant for the stepwise formation of polymeric species is of the form $K = (\text{polymer})/(\mathrm{II})^n$, where the degree of association in the polymer is n. It is assumed that the heats of reaction in each step are similar and that the average heat per reaction can be extracted from the cumulative equilibrium constant expression. The concentration of polymer is related to the area of the τ 10.31 and 10.41 signals while the concentration of the 2:1 monomeric adduct is proportional to the area of the τ 11.30 resonance. The equilibrium constant was evaluated at −87, −85, −80, and −74° from the relative areas of these signals. The pertinent data are shown in Table II. The plot of log K *vs.* $1/T$ is shown in Figure 4. The linearity of this plot indicates that the enthalpy of each reaction (−9 kcal/mol from the slope of this plot) for the stepwise formation of polymer is constant within experimental error. This enthalpy relates the energy required to break two Be–S bonds and form two electron-deficient Be–C–Be bonds from two normal, electron-pair Be–C bonds. Assuming the average strength of a Be–S bond to be 3.2 kcal (from equilibrium 1a) the heat of formation of two electron-deficient bonds from four normal bonds is −15.4 kcal (2 × (−3.2) − 9 = −15.4). This compares to −21 kcal[22] for the reaction 2 Al(CH$_3$)$_3$ = Al$_2$(CH$_3$)$_6$ in similar solvents. The inductive and steric effects of a dimethyl sulfide group relative to a methyl group in the case of the reaction

$2(\mathrm{CH_3})_2\mathrm{Be{:}S(CH_3)_2} =$ 

are expected to make (CH$_3$)$_2$Be:S(CH$_3$)$_2$ a weaker acid than monomeric trimethylaluminum which is reflected in the relative polymerization energies, −21 compared to −15.4 kcal.

Table II. Thermodynamic Parameters for the Polymerization Reaction

Temp, °C	$1/T$	K	Log K
−87	0.00538	1.00	10.00–10
−85	0.00530	0.96	9.98–10
−80	0.00518	0.76	9.88–10
−74	0.00503	0.56	9.75–10

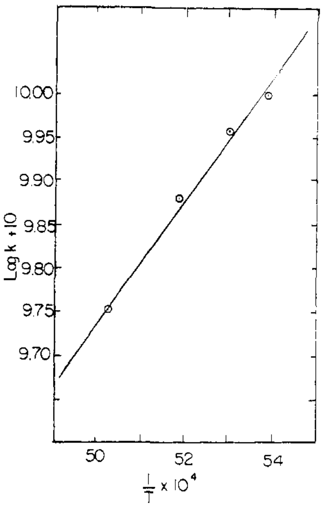


Figure 4. Plot of log K *vs.* $1/T$ for the polymerization reaction.

The *alternative* explanation for these data, the possibility that the 1:1 adduct, (CH$_3$)$_2$Be:(CH$_3$)$_2$, exists as a dimer rather than a monomer, is excluded by these data. This explanation demands that there be rapid intramolecular exchange between bridging and terminal methyl groups of this dimeric 1:1 adduct at all temperatures in order to give rise to the resonance at τ 10.77. The presence of resonances at τ 10.41, 10.77, and 10.80 in the spectrum at −65° demands that there be *rapid* intramolecular exchange in this dimer but *slow* intramolecular exchange in the longer chained polymers which give rise to the resonances at τ 10.41 and 10.80, a very unlikely result. Intramolecular exchange of bridging and terminal methyl groups of hexamethyldialuminum is slow enough to allow the detection of nonequivalent methyl environments at temperatures lower than −40°,[8] and the species (CH$_3$)$_2$Be:N(CH$_3$)$_3$[1] and dimethylberyllium in diethyl ether[10] are monomeric.

(CH$_3$)$_2$Be + BeCl$_2$ in (CH$_3$)$_2$S. At −45° the single resonance which is present in the room-temperature spectrum is split into two signals at τ 10.89 and 11.17 (Figure 2). The low-field resonance is assigned, by analogy with the −45° spectrum of dimethylberyllium in dimethyl sulfide (Figure 1), to the averaged signal representing the 1:1 and 2:1 adducts of dimethylberyllium. The new methylberyllium resonance at τ 11.17 is therefore assigned to a methylberyllium chloride species. As the temperature is lowered further, the resonance at τ 10.89 is split into two new signals, one at τ 10.77 which has been assigned to $(\mathit{CH}_3)_2\mathrm{Be{:}S(CH_3)_2}$ and one at τ 11.30 which has been assigned to $(\mathit{CH}_3)_2\mathrm{Be{:}(S(CH_3)_2)_2}$. The other changes that accompany further cooling are completely analogous to changes that occur in the variable temperature spectra of di-

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[21] G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1960, p 149.

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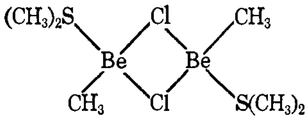
methyl sulfide solutions of dimethylberyllium (Figure 1). The methylberyllium chloride species resonates at slightly lower field (13 Hz) than $(CH_3)_2Be:(S(CH_3)_2)_2$ and is therefore assigned to $CH_3BeCl:(S(CH_3)_2)_2$. The greater electronegativity of chlorine relative to a methyl group is expected to reduce diamagnetic shielding and thus shift the resonance of the methyl group bonded to beryllium to lower field.[9] This argument predicts that proton resonance of the methyl groups bonded to beryllium in the monomeric 1:1 adduct, $CH_3BeCl:S(CH_3)_2$, or dimeric 1:1 adduct



would resonate at lower field than $(CH_3)_2Be:S(CH_3)_2$ at τ 10.77. The methylberyllium chloride species present in ethereal solution is monomeric.[10] The relatively high Be^9 resonance signal (4.24 ppm below aqueous beryllium nitrate) is further indication of a four-coordinate adduct species.[23]

In summary, this investigation has characterized the reaction between dimethylberyllium and dimethyl sulfide. Preliminary observations have indicated that dimethyl sulfide coordinates rather strongly to dimethylberyllium, contrary to earlier results.[1] Variable-temperature proton magnetic resonance analysis of dimethyl sulfide solutions of dimethylberyllium has provided *direct*, spectroscopic evidence of species present in solution. The species observed are analogous to those suggested for the reaction of dimethylberyllium with trimethylphosphine and diethyl and dimethyl ethers.[1] Thermodynamic data for equilibria between these species have been extracted from the nmr spectral data and interpreted successfully in terms of thermodynamic parameters for similar reactions.

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(23) R. A. Kovar and G. L. Morgan, submitted for publication.

Observations on the Rare Earths. LXXXII.[1] Nuclear Magnetic Resonance and Calorimetric Studies of Complexes of the Tripositive Ions with Substituted Pyridine Molecules

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Abstract: Direct calorimetric measurements indicate that the ions Pr^{3+} and Nd^{3+} react exothermally with substituted pyridine molecules in anhydrous acetonitrile with enthalpy changes < -3 kcal mol^{-1} for the formation of 1:1 complexes and still less for the formation of higher order species. At ligand to metal ion mole ratios above six, the 3:1 complexes appear to be the most stable ones. Substitution of nitrate for perchlorate ion or of Nd^{3+} for Pr^{3+} ion does not affect the measured enthalpy change. Large isotropic shifts of resonances of the ligand protons are observed upon coordination to these paramagnetic cations. These shifts can be resolved qualitatively into contact and pseudocontact shifts of nearly equal magnitude but opposite sign. The contact shift at the *ortho* position of the pyridine ring is *ca.* -1000 cps from the diamagnetic value. In spite of the weakness of the covalent interaction, large contact shifts result, in part as a consequence of the large J values of the cations.

The use of nuclear magnetic resonance spectroscopy (nmr) to indicate the nature of bonding in paramagnetic complexes of metal ions is complicated by the difficulty in distinguishing between contact and pseudocontact shifts. The contact shift can yield information relating to the extent of covalent bonding and to the mechanisms of σ- and π-electron density delocalization in the paramagnetic species.[3] The pseudocontact shift can provide information relating to the geometrical configuration of ligands about a metal ion in solution[4] and to metal ion–solvent molecule interactions.[5] The contact and pseudocontact shifts often appear simultaneously in the spectrum of a complex, thus making the absolute interpretation of the isotropic nuclear shift difficult. With a d-transition metal complex, a reasonable assumption as to geometry in solution can lead to at least a qualitative estimate of the magnitude of the pseudocontact shift. Subtraction of the pseudocontact contribution from the total isotropic nuclear shift then usually leaves a large contact contribution which is useful in estimating the relative amounts of σ and π bonding in the species.

Estimating the size of the pseudocontact shift in the spectrum of a paramagnetic lanthanide complex in-

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