The complex $Pd(DMSO)_4^{2+}$ is the first example of DMSO exhibiting both sulfur and oxygen coordination sites in a complex; in fact, it is the first case to our knowledge where a neutral ligand exhibits well-defined mixed donor sites. Far-ir spectra suggest a *cis* arrangement of oxygen- and sulfur-bonded DMSO ligands. The complex $Pd(DMSO)_2Cl_2$ which exists as the *trans* isomer in the solid is found to convert to the *cis* isomer in acetonitrile solution.

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Contribution from the Research and Development Department, Ethyl Corporation,
Baton Rouge, Louisiana 70821

Amine Complexes of Beryllium Hydride[1]

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Several tertiary amine complexes of beryllium hydride have been synthesized by three different preparative routes. In the first, trimethylamine is allowed to react with the liquid adduct diethylberyllium–diethylaluminum hydride to produce the crystalline beryllium hydride–trimethylamine complex. The other two procedures involve direct reaction between the amine and polymeric beryllium hydride either by (1) heating the mixture in a sealed system or (2) ball-milling the reactants together. The complexes were characterized by chemical analysis, infrared and nmr spectra, and X-ray powder diffraction measurements. These data, along with molecular weight determinations, indicate that the fundamental unit in every case is the hydrogen-bridged BeH_2 dimer.

Introduction

Unlike the case of the group IIIa hydrides borane,[2] alane,[3] and gallane,[4] there have been no tertiary amine complexes reported for the simple hydrides of the group IIa metals. Because of its "electron-deficient" character, beryllium hydride is the one member of its group most likely to give stable complexes with donor molecules. Holley and Lemons[5] presented some evidence for the formation of beryllium hydride etherate, although the simple 1 : 1 adduct was not isolated. The existence of the trimethylamine complex was predicted by these authors, but a successful synthesis was never reported. The nearest approach was that of Bell and Coates[6] by their preparation of the trimethylamine complex of methylberyllium hydride, and since the hydrogen bridges in methylberyllium hydride were not cleaved by treatment with excess trimethylamine, one might conclude that it would be difficult to prepare the beryllium hydride adduct by direct combination of the amine with polymeric beryllium hydride.

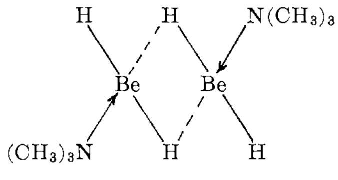
In this paper we report the synthesis and properties of a number of tertiary amine complexes of beryllium hydride. Three different methods of preparation are described, two of which involve a convenient, direct synthesis.

Results and Discussion

The trimethylamine complex of beryllium hydride (I) can be prepared by reaction of the diethylberyllium–diethylaluminum hydride adduct (II) with liquid trimethylamine

$$\underset{\text{II}}{(C_2H_5)_2Be\cdot 2(C_2H_5)_2AlH} + 3(CH_3)_3N \longrightarrow \underset{\text{I}}{(CH_3)_3N\cdot BeH_2} + 2(C_2H_5)_3Al\cdot N(CH_3)_3$$

When the excess trimethylamine is allowed to evaporate, I slowly precipitates from the liquid residue. It is recovered as colorless, needlelike crystals, which are sensitive to air and moisture. The complex is moderately soluble in trimethylamine and aromatic hydrocarbons. In diethyl ether it initially dissolves and then precipitates as an amine-deficient species by partial dissociation. Cryoscopic molecular weight measurements indicate that I is dimeric in benzene solution. The hydrogen-bridged structure



is proposed for the dimer. This structure is closely

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[1] This research was supported by the Advanced Research Projects Agency and the Air Force Rocket Propulsion Laboratory, Edwards, Calif. under Contracts AF04(611)-9376 and AF04(611)-9888.

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[5] C. E. Holley, Jr., and J. F. Lemons, "The Preparation of the Hydrides of Magnesium and Beryllium," Los Alamos Scientific Laboratory Report LA-1660, April 1, 1954.

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TABLE I

ANALYTICAL DATA FOR BERYLLIUM HYDRIDE–AMINE COMPLEXES

		Mol wt (as dimer)		Analyses, %						Chem shift,[a] ppm	
				Active H		Be		Amine			
Complex	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Free amine	Complex
$(CH_3)_3N\cdot BeH_2$	125–128	140	140	2.87	2.91	12.8	11.7			7.91	7.80
$(CH_3)_2NC_2H_5\cdot BeH_2$	53–57	168	162	2.40	2.82	10.7	13.0				
$(C_2H_5)_2NCH_3\cdot BeH_2$	39–41	196	176	2.05	2.11	9.2	10.2			7.91	7.78
$(C_2H_5)_3N\cdot BeH_2$	>43 dec			1.80	1.98	8.0	8.7	90.3	85.3		
$(CH_3)_2NCH_2C_6H_5\cdot BeH_2$	101–103			1.38	1.31						
$(CH_2)_4NCH_3\cdot BeH_2$	86–87	192	192	2.10	2.07	9.4	9.9	88.5	80.2	7.75	7.64
$(CH_2)_5NCH_3\cdot BeH_2$				1.80	1.98	8.0	9.1	90.2	90.4	7.88	7.77
$TMED\cdot 2BeH_2$						13.0	13.8				

[a] τ for the N-methyl protons.

related to that presented for the trimethylamine complexes of methylberyllium hydride[6] and phenylberyllium hydride.[7]

The infrared spectrum of I is characterized by a strong Be–N absorption[8] at 830 cm^{-1}, a BeH_2Be bridge stretching mode[9] at 1340 cm^{-1}, and two moderately strong absorptions at 1740 and 1780 cm^{-1} which may be due to terminal Be–H groups. Bell and Coates[9] reported that absorption due to terminal Be–H bonds should be located near 2100 cm^{-1}. Therefore, a shift from the 2100-cm^{-1} region to lower frequencies must be attributed to some mechanism such as partial, or loose, association of the terminal hydride groups. The absorptions at 1740 and 1780 cm^{-1} were not observed in the solution spectrum of methylberyllium hydride–trimethylamine,[9] the structure of which is formulated with terminal methyl groups, rather than hydride. The proton nuclear magnetic resonance spectrum of I shows a single sharp resonance for the methyl protons at τ 7.80. The hydride protons were not detected, evidently because of line broadening due to the nuclear quadrupole moment of beryllium and poor sensitivity caused by the limited solubility of the complex.

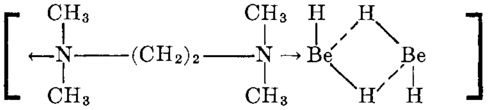
The low yield of I can be explained by its solubility in the coproduct triethylaluminum–trimethylamine, and probably for the same reason this route is unsatisfactory for the synthesis of higher amine complexes of beryllium hydride.

Alternate and more convenient preparative methods involve the reaction of the tertiary amine with polymeric beryllium hydride either by (1) heating the mixture at 120–180° for an extended period of time or (2) ball-milling the reactants together in a sealed vessel, according to the reaction

$$2[\mathrm{BeH_2}] + 2\mathrm{L} \rightarrow \underset{\mathrm{III}}{[\mathrm{L}\cdot\mathrm{BeH_2}]_2}$$

where L represents the tertiary amine ligand. With either method an excess of amine is used, from which III can be isolated by crystallization at low temperature. Yields in excess of 90% have been obtained in some instances. Tertiary amines used successfully in this direct synthesis include alkyl, alicyclic, aromatic, and bidentate types. Unsaturated heterocyclic amines, such as pyridine, are reduced by the hydride to mixtures of unidentified, highly colored products. Possibly as a result of low base strength or unfavorable steric effects, some simple tertiary amines are relatively unreactive toward beryllium hydride. The ball-milling technique is particularly useful in preparing complexes with these latter amines. For example, the triethylamine complex of beryllium hydride could be synthesized only by this method and in low yield. Physical properties and analytical data for several of the complexes prepared by these methods are given in Table I.

Solubility of the trialkylamine complexes of beryllium hydride increases with the increase in alkyl chain length; the product obtained with N,N-dimethyldodecylamine is soluble even in aliphatic hydrocarbons. Cryoscopic molecular weight data also indicate that the 1:1 complexes containing simple trialkylamines are dimeric, analogous to the hydrogen-bridged structure of I. On the other hand, tertiary diamines, such as N,N,N′,N′-tetramethylethylenediamine (TMED), give complexes which are insoluble in all common solvents. Furthermore, the beryllium content of the TMED adduct corresponds to a 1:2 mole ratio of amine to beryllium. This evidence clearly indicates that diamine complexes are not simple dimers analogous to III but, like the methylberyllium hydride–TMED adduct,[6] probably are linear coordination polymers, as shown by the structure



Even in this case one would conclude that the basic unit in these amine adducts is the hydrogen-bridged BeH_2 dimer. Attempts to purify these complexes by sublimation succeeded only with I, which can be sublimed at 90° in an evacuated, sealed system. With other trialkylamine complexes investigated, the amine is partially eliminated to give more highly associated, less volatile residues.

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(7) G. E. Coates and M. Tranah, *J. Chem. Soc., A*, 615 (1967).

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Table II
X-Ray Powder Diffraction Data

$(CH_3)_3N \cdot BeH_2$	$(CH_3)_2NC_2H_5 \cdot BeH_2$	$(C_2H_5)_2NCH_3 \cdot BeH_2$
6.91 vw	7.16 vw	6.86 vw
5.07 m	5.18 s	5.94 m
4.72 s	4.56 s	5.09 s
4.33 w	4.20 m	4.60 m
4.08 w	3.90 vw	4.25 w
3.77 vw	3.44 vw	3.99 w
3.60 vw	3.24 w	3.78 vw
3.47 vw	2.84 w	3.57 vw
3.06 vw	2.53 vw	3.39 vw
2.85 vw	2.47 vw	3.29 w
2.49 vw	2.41 vw	2.97 w
2.43 vw	2.26 vw	2.69 vw
		2.59 vw
		2.44 vw
		2.36 vw
		2.30 vw
		2.00 w

$(C_2H_5)_3N \cdot BeH_2$	$(CH_2)_4NCH_3 \cdot BeH_2$	$TMED \cdot (BeH_2)_2$
6.67 m	6.41 vw	7.97 vw
5.64 vw	5.83 m	5.18 s
5.34 w	5.28 vw	4.77 m
5.12 vw	4.87 s	4.13 w
4.85 s	4.55 m	3.97 w
4.19 vw	4.25 vw	3.80 m
3.87 vw	3.77 w	3.31 w
3.59 vw	3.43 vw	3.08 w
3.41 vw	3.25 vw	2.55 m
3.16 vw	3.10 vw	2.31 vw
2.79 vw	2.91 vw	2.14 vw
2.30 vw	2.71 w	2.01 vw
2.25 vw	2.21 vw	1.78 vw
2.14 vw	2.13 vw	

[a] Abbreviations: s, strong; m, medium; w, weak; v, very.

No single-crystal X-ray or other direct structural measurements were obtained for these complexes. All are highly crystalline, as evidenced by the X-ray powder diffraction data shown in Table II. The high *d* spacings are typical of crystalline organic compounds. The similarity in *d* spacings and relative intensities indicates a close relationship in type of unit cell and molecular symmetry.

Proton nuclear magnetic resonance spectra of complexes containing the N-methyl-substituted amines show, as expected, single methyl proton resonance signals shifted downfield relative to those observed for the free amine. This coordination chemical shift, which varies from 0.11 ppm in the case of trimethylamine to 0.18 ppm for N,N-dimethyldodecylamine, results from the reduction in the electron density on the methyl protons when the nitrogen atoms serve as donor ligands.

Attempts to extend the study to include phosphine and ether complexes were only partially successful. The trimethylphosphine adduct could not be prepared, but there is some evidence that a beryllium hydride tetrahydrofuranate was produced in low yield. A single attempt to prepare the N-methylpyrrolidine adduct of magnesium hydride by the ball-milling technique was unsuccessful.

Experimental Section

All experiments were carried out under a moisture-free nitrogen atmosphere.

The tertiary amines and other solvents were obtained from commercial sources. Prior to use they were dried over lithium aluminum hydride and distilled.

Infrared spectra were taken in toluene solution and in Nujol and Kel-F mulls with a Perkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer (benzene solutions with tetramethylsilane as internal standard). X-Ray powder diffraction data were obtained with a Philips Norelco X-ray unit, using an 11.14-cm diameter camera with Ni-filtered copper Kα radiation. Intensities were estimated visually.

Analysis for active hydride groups was made by hydrolysis using water (or dilute acid, if necessary) followed by mass spectrometric analysis of the gases evolved. Aliquots of the hydrolysis residue were analyzed for beryllium by precipitation with 8-hydroxyquinaldine[10] and for amine by acid–base titration. Melting points (sealed tube) are uncorrected.

Preparation of the Trimethylamine Complex.—Ether-free diethylberyllium was prepared by the Grignard procedure.[11] To 10.4 g (0.115 mol) of diethylaluminum hydride (95% purity) was added 3.85 g (0.057 mol) of diethylberyllium slowly with stirring at room temperature. There was a slight evolution of heat, resulting from formation of the $(C_2H_5)_2Be \cdot 2(C_2H_5)_2AlH$ adduct (II), a clear, colorless liquid. A portion (12.6 g) of II was added dropwise with stirring to excess (26 g) liquid trimethylamine, the temperature of which was maintained near 0°. The beryllium hydride–trimethylamine complex (I) precipitated slowly when the solution was concentrated by evaporation of the amine. The crystalline product was collected by filtration, washed with petroleum ether (bp 37–54°), and dried *in vacuo* at room temperature for 15 min. The yield of I was 1.33 g (36% of theory). It sublimed slowly at 90° under its own dissociation pressure in a closed system, which was evacuated to <0.1 mm and sealed. The complex condensed into long, white, hollow, needlelike crystals. Its density (by the sink–float method in benzene–heptane mixtures) was 0.83–0.84 g/cm^3.

Anal. Calcd for $(CH_3)_3N \cdot BeH_2$: active H, 2.87; Be, 12.8; amine, 84.3. Found: active H, 2.76; Be, 12.5; amine, 80.0.

An attempt to analyze the complex for C and H by combustion resulted in an explosion.

Preparation of Tertiary Amine Complexes. Method A.—Beryllium hydride used in these preparations was synthesized by pyrolysis of the di-*t*-butylberyllium etherate.[12] It was usually obtained as an impure gray amorphous solid.

In a typical preparation of a beryllium hydride–amine complex, about 2 g of beryllium hydride was placed in a 150-ml stainless steel pressure vessel and about 70 ml of amine was introduced. The vessel was sealed and heated to 160–170° (oil bath temperature) for several days. When cooled below the boiling point of the amine, the vessel was vented and the reaction mixture was filtered while still hot. The filtrate was transferred to a flask, sealed under nitrogen, and cooled to −10° overnight. The crystallized product was filtered off and washed with a small quantity of petroleum ether (bp 37–54°), and traces of solvent were removed under vacuum. Complexes were prepared by this method with the following amines (at the yields given): trimethylamine (93%), dimethylethylamine, methyldiethylamine (62%), N-methylpyrrolidine (93%), N-methylpiperidine, N,N-

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dimethyloctylamine, N,N-dimethyldodecylamine, N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine (40%), N,N,-N′,N′-tetramethylethylenediamine (93%), and triethylenediamine (used in benzene solution). Analytical data for several of these complexes are given in Table I.

Attempts to prepare the analogous triethylamine and N,N-dimethylaniline complexes were unsuccessful. With pyridine a dark green resinous solid was formed, which contained no active hydride groups.

Method B.—To a 1-l. stainless steel jar mill containing 350 cm^3 of 0.5-in. steel balls were added about 2 g of beryllium hydride and 70–100 ml of amine. The jar was sealed and rotated at room temperature for periods of 1–3 days. The reaction mixture was decanted and the mill contents rinsed with fresh amine. After filtration the filtrate was allowed to stand overnight at −10°. The crystalline product was recovered, washed with petroleum ether, and vacuum dried. Complexes containing the following amines were prepared by this method (at the yields given): triethylamine (16%), N-methylpyrrolidine (93%), methyldiethylamine (93%), and N-methylmorpholine (60%).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA

Preparation and Properties of Pentafluorosulfanyldichloramine, SF_5NCl_2[1]

BY ALAN F. CLIFFORD AND GERALD R. ZEILENGA

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The reaction of NSF_3 and ClF yields pentafluorosulfanyldichloramine, SF_5NCl_2. The compound is a light yellow liquid with a boiling point of 64° and a melting point of −120°. It is sensitive to mechanical shock and is thermally unstable at 80°. Hydrolysis and the reaction of SF_5NCl_2 with mercury were slow.

Introduction

The addition of HF to the triple bond in NSF_3 to form SF_5NH_2 has been reported.[2] The preparation of perfluoroalkyldichloramines by the addition of ClF to perfluoronitriles was also reported recently.[3] In an analogous manner, ClF reacted with NSF_3 yielding the new compound pentafluorosulfanyldichloramine, SF_5NCl_2.

Experimental Section

Apparatus.—Reactions were carried out in Hoke stainless steel cylinders. An all-glass high-vacuum system was used for handling the materials. Stopcocks and joints were lubricated with Kel-F No. 90 grease. The mercury in the manometers was covered with Halocarbon oil to reduce attack by ClF on the mercury.

Materials.—Chlorine (Matheson), chlorine trifluoride (Matheson), sulfur tetrafluoride (Matheson), silver(I) fluoride (Harshaw), and silver(II) fluoride (Harshaw) were used without purification.

Chlorine monofluoride was prepared by the reaction of ClF_3 with a slight excess of Cl_2. The reaction mixture was heated to 400° and then quenched in water. The products were passed through a −119° trap (ethyl bromide slush). The ClF passed through and was stored in stainless steel cylinders until used.

Fluoroformyliminosulfur difluoride, prepared by the reaction of silicon tetraisocyanate and sulfur tetrafluoride at 120°,[4] was fluorinated with AgF_2 to give thiazyl trifluoride, NSF_3.[5]

Reaction of Thiazyl Trifluoride with Chlorine Monofluoride.—In a typical reaction 7 mmol of NSF_3 and 28 mmol of ClF were condensed into a 75-ml stainless steel cylinder and held at −78° (Dry Ice–trichloroethylene). The reaction was complete after 2 hr. The products were passed through −95° (toluene slush), −131° (*n*-pentane slush), and −196° (liquid nitrogen) traps. The SF_5NCl_2 collected at −95°, the −131° trap collected Cl_2, and SF_6 and unreacted ClF collected at −196°. Some noncondensable material passed through to the pump.

With a ratio of ClF to NSF_3 of greater than 4:1, pure liquid SF_5NCl_2 was collected at −95°. A typical yield was 1.48 g of SF_5NCl_2 (2.2 mmol) based on NSF_3.

With a 2:1 ratio of ClF to NSF_3, impurities were present in the SF_5NCl_2 fraction, and SF_5Cl was obtained instead of SF_6. Some unreacted NSF_3 was also recovered under these conditions.

Properties of Pentafluorosulfanyldichloramine, SF_5NCl_2.—The product is a light yellow liquid with a melting point of −119 to −121° and an extrapolated boiling point of 64°. The material could be handled in a vacuum line without decomposition but was unstable at 80° giving SF_5Cl, N_2, and Cl_2. On one occasion a sample exploded when subjected to mechanical shock. The compound reacted slowly with mercury producing NSF_3.

The molecular weight was determined by vapor density measurements to be 211.2. The theoretical value for SF_5NCl_2 is 212.

Anal. Calcd for SF_5NCl_2: Cl, 33.2; S, 13.8. Found: Cl, 33.5; S, 15.1.

Vapor pressures were determined using a mercury manometer in a vacuum system. The data are presented in Table I.

Results and Discussion

The reaction of NSF_3 and ClF at −78° gave 25–32% yields of the new compound SF_5NCl_2. With an excess of ClF, the products Cl_2 and N_2 were also obtained. It is postulated that there were two reactions occurring.

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[1] Taken in part from the thesis submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy by G. R. Zeilenga.

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