Previously the spectra of $(CH_3)_3N{\cdot}B_3H_7$ in benzene and tetrahydrofuran were interpreted as an overlap of two octets (B_1 and $B_{2,3}$) with the chemical shift difference comparable to the $^{11}B-^{1}H$ coupling constant (about 35 Hz).[8b] The present study has shown that the B_1 resonance peaks for the other three amine adducts are structureless broad peaks. The same would be expected for the B_1 peak of the $(CH_3)_3N{\cdot}B_3H_7$ spectrum if the peak could be seen separated from the $B_{2,3}$ peak. It is therefore difficult to explain the enhanced sharpness of the fine structure peaks on the basis of the simple superposition of the two peaks. Assuming that B_1 and $B_{2,3}$ atoms are coupled to each other and are both coupled to seven hydrogens in the trimethylamine adduct as they are in the other adducts, the well-resolved perfectly symmetric resonance peak for $(CH_3)_3N{\cdot}B_3H_7$ in CH_2Cl_2 would be explained more appropriately as a case of "deceptive simplicity",[10] caused by the coincidence of the B_1 and $B_{2,3}$ chemical shifts. In benzene, diethyl ether and tetrahydrofuran, the chemical shifts of B_1 and $B_{2,3}$ are not equal but the difference is probably similar to the $^{11}B_1-^{11}B_{2,3}$ coupling constant (15–20 Hz) (Figure 4b). Therefore, the resulting spectrum is of complex second order and has a perturbed, dissymmetrical structure.

Experimental Section

Chemicals. Laboratory stock tetraborane(10), which had been prepared by the pyrolysis of diborane(6) in a hot–cold reactor, was purified by trap-to-trap fractionation in a vacuum line. The purified tetraborane(10) had a vapor pressure of 386 mmHg at 0 °C, and no impurity could be detected in the infrared spectrum of the sample. Dimethylamine was taken from a cylinder (Matheson Gas Products) and fractionated in the vacuum line. Monomethylamine and trimethylamine were prepared from their hydrochlorides by treating with concentrated sodium hydroxide solutions, drying the liberated amines with KOH pellets, and then fractionating them in the vacuum line. Ammonia (Matheson Gas Products) was stored over sodium metal. Diethyl ether and tetrahydrofuran were stored over $LiAlH_4$, and dichloromethane and benzene over molecular sieves. These reagents were distilled from the storage containers into the vacuum line as needed.

Amine–Triboranes(7). The method described earlier[2] for the preparation of ammonia–triborane(7) was followed closely for the preparations of the four amine–triboranes(7) described in this paper. The use of diethyl ether or dichloromethane as the solvent for the base-displacement reactions of tetrahydrofuran–triborane(7) with the amines gave results which were comparable to those when tetrahydrofuran was used as the solvent. The compounds are resistant toward complete hydrolysis in acid solutions. When treated with 6 N HCl for 2–3 days in sealed tubes at 95 °C, the monomethylamine and dimethylamine adducts yielded 104 and 85.7 mmol of hydrogen gas/g of the sample, respectively, whereas the calculated values based on the equation $\text{amine}{\cdot}B_3H_7 + H^+ + 9H_2O \rightarrow \text{amine}{\cdot}H^+ + 3B(OH)_3 + 8H_2$ are 113 and 94.6 mmol/g, respectively. Consequently the results of boron analysis on the sample solution after the hydrolyses were lower, but those of nitrogen analysis were consistent with the formulas. Anal. Calcd for $CH_3NH_2{\cdot}B_3H_7$: B, 46.0; N, 19.9. Found: B, 44.3; N, 19.9. Calcd for $(CH_3)_2NH{\cdot}B_3H_7$: B, 38.4; N, 16.6. Found: B, 38.1; N, 16.5. The sample solutions decolorized dilute solutions of iodine.

The mass spectra of the two adducts showed the highest *m*/*e* at 69 and 83 for $CH_3NH_2{\cdot}B_3H_7$ and $(CH_3)_2NH{\cdot}B_3H_7$, respectively. These values which are two units less than the molecular ion masses of the adducts are probably due to the facile loss of two hydrogen atoms from each molecule under the conditions employed in the instrument. Similar observations have been reported for other boron hydride compounds, e.g., B_4H_{10}, B_5H_{11}, and B_9H_{15}.[11] Infrared spectra (recorded on a Beckman IR-20 infrared spectrophotometer) are as follows. $CH_3NH_2{\cdot}B_3H_7$ (cm^{-1}) (liquid film): 3285 (s), 3255 (s), 3160 (sh), 3018 (ms), 2960 (ms), 2490 (vs), 2425 (vs), 2340 (sh), 2020 (w, br), 1563 (s), 1451 (s), 1430 (sh), 1304 (s), 1147 (s), 1127 (s), 1035 (sh), 978 (s, br), 920 (sh), 820 (w), 795 (w). $(CH_3)_2NH{\cdot}B_3H_7$ (cm^{-1}) (thin-layer solid): 3240 (vs), 3005 (m), 2960 (m), 2490 (s), 2455 (s), 2430 (s), 2360–2330 (br, sh), 2230 (m), 2060 (w), 2025 (w), 1460 (s), 1435 (sh), 1405 (m), 1305 (s), 1225 (w), 1145 (s), 1050 (w, br), 990 (s), 920 (s). The NMR spectra were recorded on a Varian XL-100-15 instrument equipped with a spin-decoupler unit (Gyrocode). The standard for boron chemical shifts, $BF_3{\cdot}O(C_2H_5)_2$, was used externally.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation through Grant No. GP-32079. A.R.D. is grateful to the University Research Committee of the University of Utah for the award of a University Graduate Research Fellowship, 1974–1975.

Registry No. $NH_3{\cdot}B_3H_7$, 57808-44-3; $CH_3NH_2{\cdot}B_3H_7$, 57808-46-5; $(CH_3)_2NH{\cdot}B_3H_7$, 57808-47-6; $(CH_3)_3N{\cdot}B_3H_7$, 57808-48-7; ^{11}B, 14798-13-1.

References and Notes

(1) See, for example, R. A. Geanangel and S. G. Shore, *Prep. Inorg. React.*, **3**, 130, 134 (1966).

(2) G. Kodama, R. W. Parry, and J. C. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).

(3) G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, **82**, 6250 (1960).

(4) L. J. Edwards, W. V. Hough, and M. D. Ford, *Proc. Int. Congr. Pure Appl. Chem.*, **16**, 475 (1958).

(5) G. Kodama and A. R. Dodds, Abstracts, 30th Northwest Regional Meeting of the American Chemical Society, Honolulu, Hawaii, June 1975, No. 169.

(6) E. Mayer, *Inorg. Chem.*, **11**, 866 (1972).

(7) (a) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, p 130; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds", W. A. Benjamin, New York, N.Y. 1969, p 61.

(8) (a) R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964); (b) M. A. Ring, E. F. Witucki, and R. C. Greenough, *ibid.*, **6**, 395 (1967).

(9) (a) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **86**, 1505 (1964); (b) D. F. Gaines and R. Schaeffer, *ibid.*, **85**, 3592 (1963); (c) H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

(10) See, for example, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Elmsford, N.Y., 1965, p 363.

(11) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, *Adv. Chem. Ser.*, **No. 32**, 127 (1961).

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Fluorinated Cyclic Compounds. A Cyclodisilazane and a 1,3-Diaza-2-stanna-4-silacyclobutane with Fluorinated Substituents on Nitrogen

Keith E. Peterman and Jean'ne M. Shreeve*

Received August 7, 1975 AIC505951

The existence of four-membered silicon–nitrogen rings (cyclodisilazanes) has been established for some time.[1] However, the analogous tin–nitrogen rings (cyclodistannazanes) have been synthesized only recently[2,3] and the mixed four-membered silicon–tin–nitrogen heterocycles are rarely evident in the literature.[3]

In general, the nitrogen substituents on these four-membered heterocycles are hydrogenated. The only examples of model compounds containing fluorinated substituents are cyclodisilazanes with pentafluorophenyl groups attached to the nitrogens.[4,5] Since the most frequently used methods for preparing totally hydrogenated cyclodisilazanes are not useful for synthesizing the fluorinated analogues, other approaches are required.

This work describes the chemistry involved in our efforts to synthesize four-membered silicon– or tin–nitrogen heterocycles which contain fluorinated nitrogen substituents. Generally, in order to obtain useful precursors, attempts were made to saturate the C=N bond of the hexafluoroisopropylidenimino group of $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ and $(CH_3)_2Sn[N{=}C(CF_3)_2]_2$,[6] via a one-step addition, by small polar molecules.[7] A dilithium salt, $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$, was obtained which proved to be an excellent precursor to some heterocycles.

Experimental Section

Materials. $(CH_3)_2SiCl_2$ (Matheson Coleman and Bell), $(CH_3)_2SnCl_2$ (PCR), HCl and HF (Matheson), and *n*-BuLi and CH_3Li (Alfa Inorganics) were used as received without further purification. Literature method preparations were used for $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ and $(CH_3)_2Sn[N{=}C(CF_3)_2]_2$,[6] $HN{=}C(CF_3)_2$,[8] and $LiN{=}C(CF_3)_2$.[9]

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Hydrogen fluoride was handled in a similar Monel vacuum apparatus. Products of lower volatility were weighed and handled via syringe. Volatile products were purified via trap-to-trap distillation and measured quantitatively by *PVT* techniques. The heterocycles were purified by sublimation and handled as solids.

Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. Gas-phase spectra were obtained at 10 Torr in a 50-mm Pyrex cell equipped with KBr windows. Nonvolatile liquids were prepared as smears by pressing the sample between two NaCl windows, and solid samples were prepared by grinding the sample with spectroquality KBr and forming into a pellet. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer by using Freon-11 (CCl_3F) as an internal standard. ^1H NMR spectra were obtained on a Varian EM-360 spectrometer by using $(CH_3)_4Si$ as an external standard. Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer at an ionization potential of 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany, and by Enviro Analytical Laboratory, Knoxville, Tenn.

Preparation of $(CH_3)_2Si[NHCCl(CF_3)_2]_2$. A weighed amount of $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ (5.8 mmol) was condensed at −183 °C into a round-bottom flask equipped with a side arm. A nitrogen atmosphere was introduced into the system and the vessel was immersed in an ice water bath. A cylinder of hydrogen chloride was attached to the side arm via Tygon tubing and the gas was slowly bubbled into the $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ through a tube immersed below the surface of the liquid. The reaction mixture was held at 0 °C and stirred while maintaining a relatively constant pressure above the surface of the liquid. The reaction is complete when the yellow color of the starting material completely disappears and a fine white precipitate begins to form. The pressure of the HCl gas being introduced also begins to rise rapidly upon completion of the reaction. The compound was isolated in 89% yield. Some hydrolysis of the Si—N bond occurs.

The infrared spectrum is as follows (cm^{-1}): 3410 (m), 2585 (vs), 1465 (m), 1420 (m), 1322 (ms), 1289 (s), 1210–1255 (vvs, br), 1187 (ms), 1166 (vs), 970 (s), 951 (ms), 866 (ms), 818 (m), 806 (m), 746 (m), 720 (ms). The ^{19}F NMR spectrum shows a single resonance at ϕ 77.5 and the ^1H NMR spectrum shows single resonances at δ 0.50 and 2.52. The highest *m/e* peak observed in the mass spectrum was M − H_2Cl_2.

Anal. Calcd for $C_8H_8Cl_2F_{12}N_2Si$: C, 20.92; H, 1.74; N, 6.10; F, 49.7; Cl, 15.47. Found: C, 21.09; H, 1.81; N, 6.19; F, 49.2; Cl, 15.63.

A similar reaction of HCl bubbled into a solution of $(CH_3)_2Sn[N{=}C(CF_3)_2]_2$ immediately gave a white precipitate with concomitant disappearance of the yellow liquid. The reaction was continued until the yellow liquid was consumed and the pressure of the system began to rise. Upon warming to ambient temperature the solid slowly liberated $HN{=}C(CF_3)_2$.

Preparation of $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$. Typically, a weighed amount of $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ (5.5 mmol) was condensed at −183 °C into a round-bottom flask equipped with a side arm and rubber septum. Nitrogen was introduced into the system and the vessel was immersed in a −50 °C slush bath. Methyllithium (11.0 mmol) in Et_2O was added slowly to the vessel via syringe through the side arm. The reaction mixture was stirred and allowed to warm slowly to ambient temperature over a 5-h period. A creamy white precipitate, $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$, appeared. After removing most of the solvent under dynamic vacuum, a sample of the solid was transferred to an NMR tube and dissolved in CF_3COOH. The ^{19}F NMR spectrum is a quartet at ϕ 74.9 ($J_{CH_3\text{–}CF_3}$ = 0.8 Hz) and the ^1H NMR spectrum is a septet at δ 0.84 and a singlet at δ 0.08.

Preparation of $CH_3(CF_3)_2C\overline{N\text{–}Si(CH_3)_2\text{–}N[C(CF_3)_2CH_3]\text{–}Si}(CH_3)_2$. Freshly distilled tetrahydrofuran (10 ml) was added to the dry lithium salt, $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$ (5.5 mmol). The mixture was stirred until all of the solid dissolved to give a brown solution. $(CH_3)_2SiCl_2$ (5.5 mmol) was condensed at −183 °C into the vessel and the reaction mixture was allowed to warm to ambient temperature. The mixture was stirred for 12 h after which the solvent was removed under dynamic vacuum. In an inert-atmosphere box, the solid was transferred to a sublimation apparatus. The product was isolated by sublimation (19% yield) under dynamic vacuum for 12 h onto a water-cooled cold finger. The yield could be increased by longer sublimation periods.

The infrared spectrum is as follows (cm^{-1}): 2982 (vw), 1470 (m), 1392 (m), 1292 (s), 1268 (s), 1165–1235 (vs), 1130 (vs), 1080 (s), 1034 (ms), 890 (s), 865 (s), 800 (ms), 700 (ms), 440 (m), 380 (m). The ^{19}F NMR spectrum is a multiplet at ϕ 75.9 and the ^1H NMR spectrum has poorly resolved peaks at δ 0.27 and 1.40. A molecular ion was observed in the mass spectrum.

Anal. Calcd for $C_{12}H_{18}F_{12}N_2Si_2$: C, 30.38; H, 3.80; N, 5.91; F, 48.10. Found: C, 30.33; H, 3.82; N, 5.64; F, 48.39; mp 82–84 °C.

Trace amounts of $(CH_3)_2Si[NHC(CF_3)_2CH_3]_2$ were isolated in a trap at −30 °C prior to transferring the solid to a sublimation apparatus. In methylene chloride, no evidence for the cyclodisilazane was observed although larger quantities of $(CH_3)_2Si[NH(CF_3)_2CH_3]_2$ were obtained.

The infrared spectrum of $(CH_3)_2Si[NH(CF_3)_2CH_3]_2$ is as follows (cm^{-1}): 3405 (m), 2965 (w), 1720 (w), 1480 (w), 1464 (m), 1430 (ms), 1392 (w), 1329 (w), 1288 (vs), 1265 (s), 1235 (vs), 1215 (vs), 1190 (vs), 1141 (ms), 1100 (s), 1080 (vs), 991 (ms), 858 (s), 801 (ms), 699 (s). The ^{19}F NMR spectrum is a single resonance at ϕ 79.8 and the ^1H NMR spectrum has single resonances at δ 0.12 and 1.43. A molecular ion was observed in the mass spectrum.

Anal. Calcd for $C_{10}H_{14}F_{12}N_2Si$: C, 28.70; H, 3.35; N, 6.70; F, 54.55. Found: C, 28.47; H, 3.12; N, 6.47; F, 54.42.

Preparation of $CH_3(CF_3)_2C\overline{N\text{–}Si(CH_3)_2\text{–}N[C(CF_3)_2CH_3]\text{–}Sn}(CH_3)_2$. Using an analogous method, a solution of $(CH_3)_2SnCl_2$ (6.8 mmol) in tetrahydrofuran was allowed to drip slowly into a solution of $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$ (6.8 mmol) in tetrahydrofuran at 0 °C. After the reaction mixture was warmed to ambient temperature and was stirred for 14 h, the solvent was removed under dynamic vacuum. In an inert-atmosphere box, the solid was transferred to a sublimation apparatus. The product was isolated by sublimation (21% yield) under dynamic vacuum for 12 h onto a water-cooled cold finger.

The infrared spectrum is as follows (cm^{-1}): 2960 (vw), 1470 (m), 1390 (m), 1290 (s), 1260 (s), 1160–1225 (vs), 1118 (s), 1078 (s), 1030 (m), 1016 (m), 862 (ms), 835 (m), 770 (ms), 698 (m), 540 (m), 410 (w), 380 (w). The ^{19}F NMR spectrum is a single resonance at ϕ 78.3 and the ^1H NMR spectrum has peaks at δ 0.05, 0.38, and 1.24. A molecular ion was observed in the mass spectrum.

Anal. Calcd for $C_{12}H_{18}F_{12}N_2SiSn$: C, 25.50; H, 3.18; N, 4.95; F, 40.37; Sn, 21.02. Found: C, 25.48; H, 3.18; N, 4.75; F, 40.66; Sn, 20.77; mp 112–115 °C.

Discussion

The polar addition of HCl to $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ proceeds readily at 0 °C to produce $(CH_3)_2Si[NHCCl(CF_3)_2]_2$ accompanied by minimal cleavage of the Si—N bond. A similar reaction with HF at 25° showed no evidence of addition to the C=N bond of $(CH_3)_2Si[N{=}C(CF_3)_2]_2$ although small amounts of $(CH_3)_2SiF_2$ and $HN{=}C(CF_3)_2$ were produced upon cleavage of the Si—N bond. Hydrogen chloride reacts with $(CH_3)_2Sn[N{=}C(CF_3)_2]_2$ at 0 °C to produce a white solid; however, upon warming to ambient temperature, $HN{=}C(CF_3)_2$ is liberated

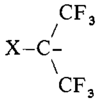
$$(CH_3)_2Sn[N{=}C(CF_3)_2]_2 + 2HCl \rightarrow (CH_3)_2SnCl_2 + 2HN{=}C(CF_3)_2$$

Similar cleavage of Sn—N bonds by protic compounds had been established earlier.[10]

Unsuccessful attempts to react the potentially useful heterocyclic precursor, $(CH_3)_2Si[NHCCl(CF_3)_2]_2$, with species containing labile halogens showed that the hydrogen bonded to nitrogen was not sufficiently acidic to permit a direct reaction. Use of weakly basic or polar solvents, such as tetrahydrofuran and methylene chloride, did not enhance the reaction. The presence of more basic solvents, such as pyridine, caused intramolecular dehydrochlorination to occur

$$(CH_3)_2Si[NHCCl(CF_3)_2]_2 \xrightarrow{py} (CH_3)_2Si[N{=}C(CF_3)_2]_2 + pyH^+Cl^-$$

Previous work in this laboratory had shown that isopropyl halogens of the type



$$X{-}C(CF_3)_2{-}$$

were susceptible to nucleophilic attack by $LiN{=}C(CF_3)_2$.[11] However, an effort to prevent intramolecular dehydrochlorination by replacing the chlorine of $(CH_3)_2Si[NHCCl(CF_3)_2]_2$ with the $(CF_3)_2C{=}N{-}$ group resulted in regeneration of the original imine

$$(CH_3)_2Si[NHCCl(CF_3)_2]_2 + LiN{=}C(CF_3)_2 \rightarrow (CH_3)_2SiN{=}C(CF_3)_2 + HN{=}C(CF_3)_2 + LiCl$$

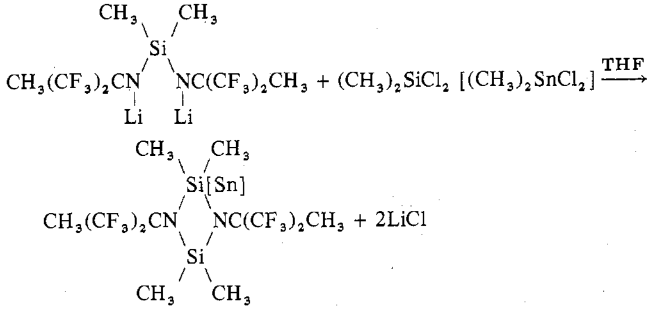
Since the NH of the silane was not sufficiently acidic to permit a direct reaction and the reaction was unaffected by a solvent, metalation of the silane at the nitrogen sites was undertaken. However, elimination of LiCl once again regenerated the original imine

$$(CH_3)_2Si[NHCCl(CF_3)_2]_2 + 2n\text{-BuLi} \rightarrow [(CH_3)_2Si[NLiCCl(CF_3)_2]_2] \xrightarrow{-2LiCl} (CH_3)_2Si[N{=}C(CF_3)_2]_2$$

Finally, a dilithium salt was obtained by the polar addition of methyllithium across the C=N bond

$$(CH_3)_2Si[N{=}C(CF_3)_2]_2 + 2CH_3Li \xrightarrow{Et_2O} (CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$$

This compound was isolated and characterized by ^{19}F and ^1H NMR and is found to be a very useful precursor to inorganic heterocycles containing fluorinated nitrogen substituents. The dilithium salt is completely soluble in THF but only slightly soluble in methylene chloride. In THF, a cyclodisilazane is formed by the direct reaction of the dilithium salt with dimethyldichlorosilane or the 1,3-diaza-2-stanna-4-silacyclobutane forms with dimethyldichlorostannane



However, in methylene chloride, no evidence for the formation of the disilazane is observed although significant quantities of $(CH_3)_2Si[NHC(CF_3)_2CH_3]_2$ are obtained.

The results of this work suggest that a wide variety of cyclic derivatives containing totally and partially fluorinated nitrogen substituents may be synthesized by utilizing the technique of adding polar RLi or R_fLi molecules across the C=N bond of molecules of the type $M[N{=}C(CF_3)_2]_2$ in order to obtain the precursors.

Acknowledgment. Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Mr. Stanley Morse for mass spectra and Mr. Craig Burton for ^1H NMR spectra.

Registry No. $(CH_3)_2Si[NHCCl(CF_3)_2]_2$, 57821-11-1; $(CH_3)_2Si[NLiC(CF_3)_2CH_3]_2$, 57821-12-2; $CH_3(CF_3)_2CNSi(CH_3)_2N[C(CF_3)_2CH_3]Si(CH_3)_2$, 57821-13-3; $CH_3(CF_3)_2CNSi(CH_3)_2N[C(CF_3)_2CH_3]Sn(CH_3)_2$, 57821-14-4; $(CH_3)_2Si[N{=}C(CF_3)_2]_2$, 40168-55-6; $(CH_3)_2SiCl_2$, 75-78-5; $(CH_3)_2Si[NHC(CF_3)_2CH_3]_2$, 57821-15-5; $(CH_3)_2SnCl_2$, 753-73-1; HCl, 7647-01-0; CH_3Li, 917-54-4.

References and Notes

(1) W. Fink, *Angew. Chem.*, **78**, 803 (1966); *Angew. Chem., Int. Ed., Engl.*, **5**, 760 (1966).
(2) D. Hanssgen and I. Pohl, *Angew. Chem.*, **86**, 676 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 607 (1974).
(3) M. Veith, *Angew. Chem., Int. Ed. Engl.*, **14**, 263 (1975).
(4) I. Haiduc and H. Gilman, *J. Organomet. Chem.*, **18**, P5 (1969).
(5) I. Haiduc and H. Gilman, *Synth. Inorg. Met.-Org. Chem.*, **1**, 75 (1971).
(6) M. F. Lappert and D. E. Palmer, *J. Chem. Soc., Dalton Trans.*, 157 (1973).
(7) K. E. Peterman and J. M. Shreeve, *Inorg. Chem.*, **13**, 2705 (1974).
(8) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).
(9) R. F. Swindell, D. P. Babb, T. J. Ouellette, and J. M. Shreeve, *Inorg. Chem.*, **11**, 242 (1972).
(10) M. F. Lappert, J. McMeeking, and D. E. Palmer, *J. Chem. Soc., Dalton Trans.*, 151 (1973).
(11) K. E. Peterman and J. M. Shreeve, *J. Fluorine Chem.*, **6**, 83 (1975).

Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071, and the Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, Talence, France

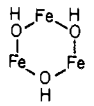
Magnetic Properties of Two Polymeric Iron(III) Compounds

Raju Thundathil and Smith L. Holt*[1]

Received October 14, 1975 AIC50744F

Recently the magnetic behavior, between 80 and 300 K, of two polymeric Fe(III) species has been reported.[2-4] The first of these materials, $[Fe(AA)_2H_2O]_3O(ClO_4)_7$, where AA is a simple amino acid such as alanine, glycine, proline, valine, leucine, or isoleucine, has been shown to possess the iron acetate structure.[3] Compounds of this class have structures which consist of a central oxygen atom bound to three iron atoms which are, in turn, bonded to an oxygen of the carboxyl group of each of four amino acid residues. The sixth coordination site is occupied by a water molecule. The possible utility of these compounds as a model for the iron storage protein, ferritin, has been pointed out.[2,3]

The second class of compounds, of which $(C_9H_{19}NH_3)_2FeOH(SO_4)_2{\cdot}C_2H_5OH{\cdot}H_2O$ is a typical example, are thought to contain, as a basic unit, $(FeOH)_3$ trimers,[4,5] i.e.



Evidence cited for this conclusion includes magnetic[4] and Mössbauer[5] data.

Because of the biological relevance of Fe(III) polymers and the fact that the magnetic data for both the Fe_3O and the $(FeOH)_3$ species do not extend below 80 K we have measured the magnetic susceptibilities of $[Fe(proline)_2H_2O]_3O(ClO_4)_7$ and $(C_9H_{19}NH_3)_2FeOH(SO_4)_2{\cdot}C_2H_5OH{\cdot}H_2O$.

Experimental Section

$[Fe(proline)H_2O]_3O(ClO_4)_7$ and $(C_9H_{19}NH_3)_2FeOH(SO_4)_2{\cdot}C_2H_5OH{\cdot}H_2O$ were prepared as previously described.[3,4] Measurements below 80 K were made using a PAR vibrating-sample magnetometer, while those measurements above 80 K were obtained utilizing the Faraday method with the samples sealed in gold tubing. Preparation of the proline compound for magnetic measurements was done in a drybox because of the hygroscopic nature of the material. The room-temperature magnetic susceptibilities of the two compounds

---

* To whom correspondence should be addressed at the University of Wyoming.