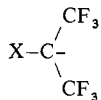
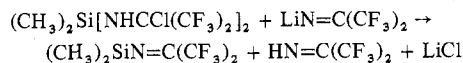


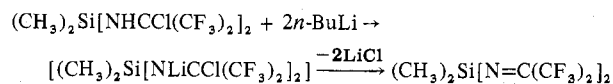
Previous work in this laboratory had shown that isopropyl halogens of the type



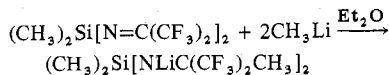
were susceptible to nucleophilic attack by $\text{LiN}=\text{C}(\text{CF}_3)_2$.¹¹ However, an effort to prevent intramolecular dehydrochlorination by replacing the chlorine of $(\text{CH}_3)_2\text{Si}[\text{NHCCl}(\text{CF}_3)_2]_2$ with the $(\text{CF}_3)_2\text{C}=\text{N}$ group resulted in regeneration of the original imine



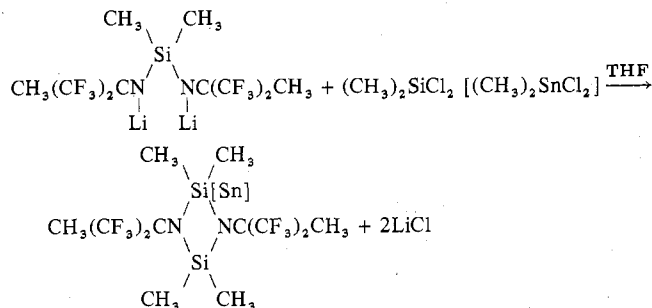
Since the NH of the silane was not sufficiently acidic to permit a direct reaction and the reaction was unaffected by a solvent, metalation of the silane at the nitrogen sites was undertaken. However, elimination of LiCl once again regenerated the original imine



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



This compound was isolated and characterized by ¹⁹F 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 $(\text{CH}_3)_2\text{Si}[\text{NHC}(\text{CF}_3)_2\text{CH}_3]_2$ 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 $\text{M}[\text{N}=\text{C}(\text{CF}_3)_2]_2$ 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. $(\text{CH}_3)_2\text{Si}[\text{NHCCl}(\text{CF}_3)_2]_2$, 57821-11-1; $(\text{CH}_3)_2\text{Si}[\text{N}(\text{Li}(\text{CF}_3)_2\text{CH}_3)]_2$, 57821-12-2; $\text{CH}_3(\text{CF}_3)_2\text{CNSi}(\text{CH}_3)_2\text{N}[\text{C}(\text{CF}_3)_2\text{CH}_3]_2$, 57821-13-3; $\text{CH}_3(\text{CF}_3)_2\text{CNSi}(\text{CH}_3)_2\text{N}[\text{C}(\text{CF}_3)_2\text{CH}_3]_2\text{Sn}(\text{CH}_3)_2$, 57821-14-4; $(\text{CH}_3)_2\text{Si}[\text{N}=\text{C}(\text{CF}_3)_2]_2$, 40168-55-6; $(\text{CH}_3)_2\text{SiCl}_2$, 75-78-5; $(\text{CH}_3)_2\text{Si}[\text{NHC}(\text{CF}_3)_2\text{CH}_3]_2$,

57821-15-5; $(\text{CH}_3)_2\text{SnCl}_2$, 753-73-1; HCl, 7647-01-0; CH_3Li , 917-54-4.

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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

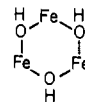
Raju Thundathil and Smith L. Holt*¹

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, $[\text{Fe}(\text{AA})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$, 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 $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ is a typical example, are thought to contain, as a basic unit, $(\text{FeOH})_3$ trimers,^{4,5} i.e.



Evidence cited for this conclusion includes magnetic⁴ and Mössbauer⁵ data.

Because of the biological relevance of Fe(III) polymers and the fact that the magnetic data for both the Fe_3O and the $(\text{FeOH})_3$ species do not extend below 80 K we have measured the magnetic susceptibilities of $[\text{Fe}(\text{proline})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$ and $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$.

Experimental Section

$[\text{Fe}(\text{proline})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$ and $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ 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.

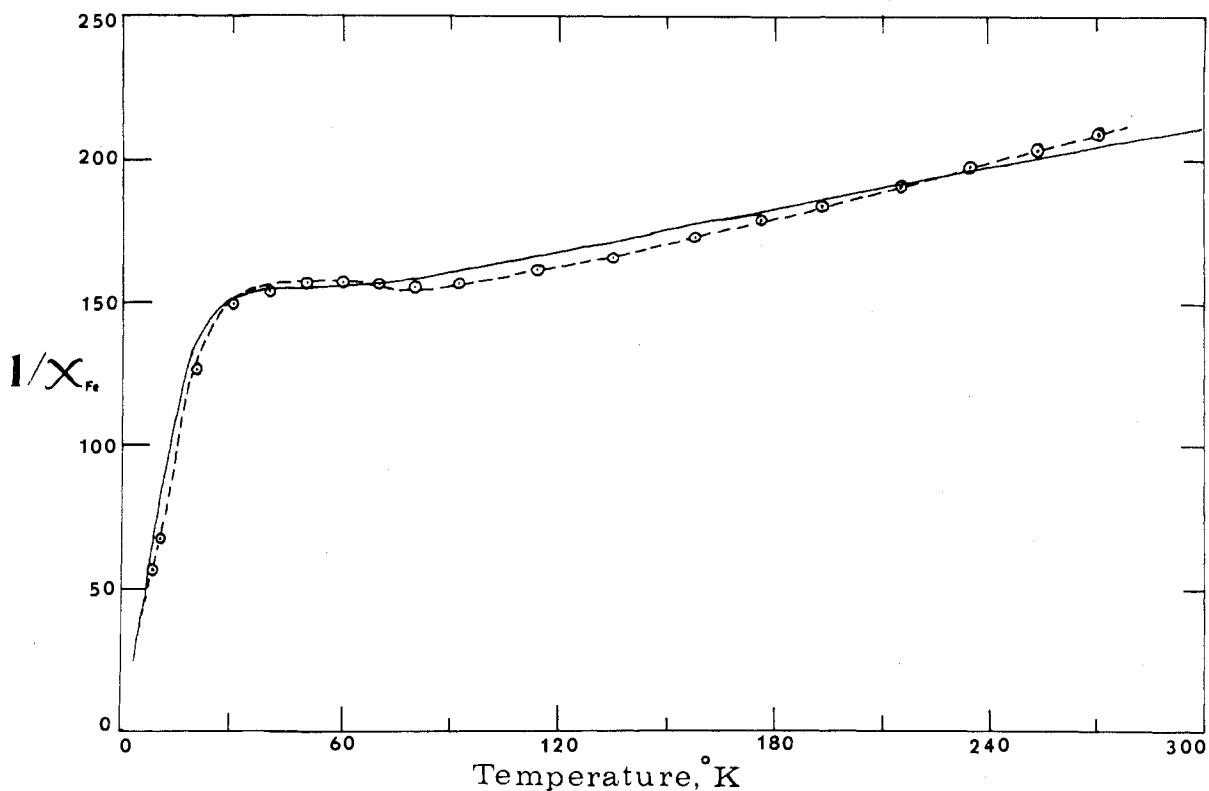


Figure 1. Experimental and calculated best fit values of $1/\chi_{Fe}$ vs. temperature for the iron(III)-proline complex and the isosceles triangular trimer (solid line). $J = -26.5$, $J_{13} = -24.0$.

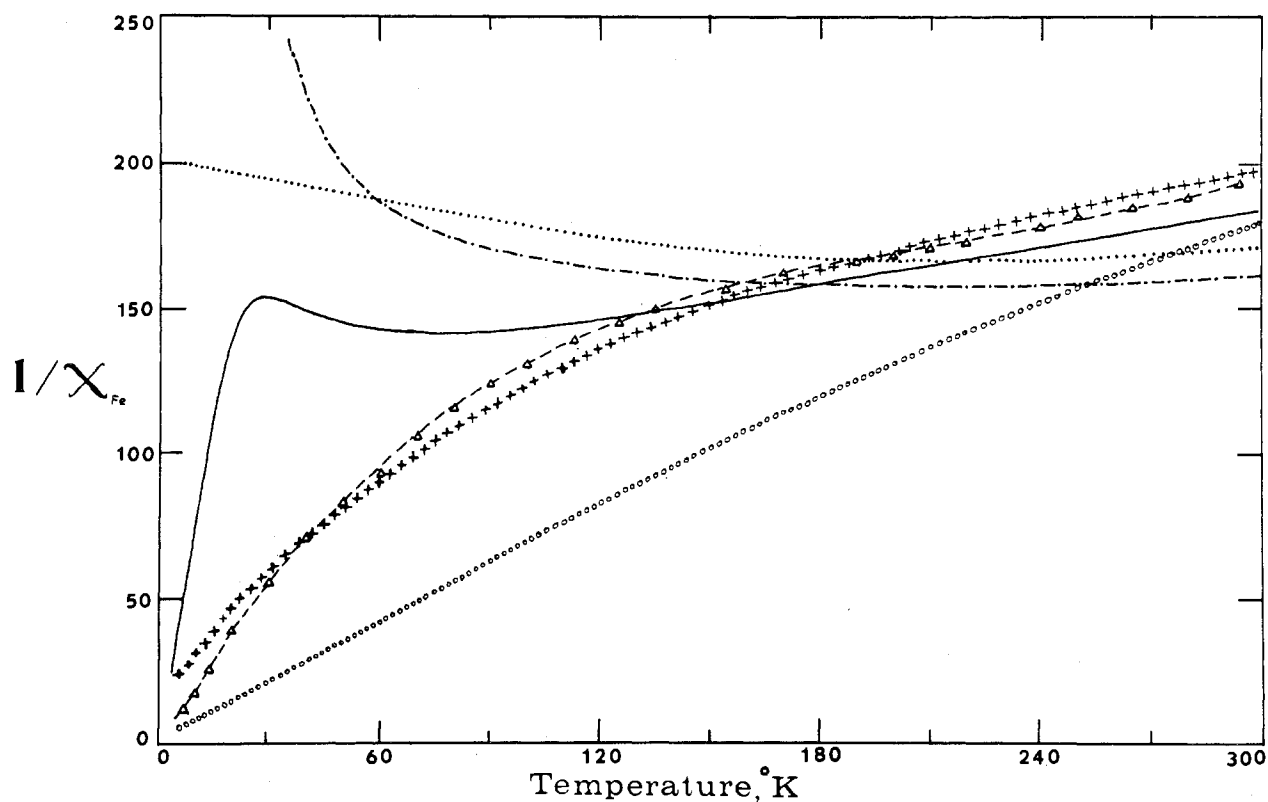


Figure 2. Experimental and calculated best fit values of $1/\chi_{Fe}$ vs. temperature for the iron(III)-hydroxysulfate complex and theoretical curves: \triangle , complex; $---$, dimer; $---$, equilateral triangular trimer; $+++$, isosceles triangular trimer; \cdots , Fisher infinite chain; \cdots , linear trimer. $J = -29.0$, $J_{13} = -19.0$

agreed, within experimental error, with those previously reported.^{3,4} No dependence of the susceptibility on field was noted through a range of 6000–20000 Oe.

The optical spectrum of $(C_9H_{19}NH_3)_2FeOH(SO_4)_2 \cdot C_2H_5OH \cdot H_2O$ was obtained in a Nujol mull using a Cary 14 RI recording spectrophotometer.

Results and Discussion

Figure 1 contains the experimental plot of $1/\chi_{\text{Fe}^{\text{cor}}}$ vs. T for $[\text{Fe}(\text{proline})\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$. The solid line accompanying the experimental data is the best fit theoretical curve for an isosceles triangular trimer of Fe(III) ions using the equation⁶

$$\chi = \frac{N\beta^2}{3kT} \mu_{\text{eff}}^2$$

where

$$\mu_{\text{eff}}^2 = \frac{g^2 \sum_{s, s^*} s'(s' + 1)(2s' + 1) \omega(s', s^*) \exp(-E(s', s^*)/kT)}{\sum_{s, s^*} (2s' + 1) \omega(s', s^*) \exp(-E(s', s^*)/kT)}$$

In this expression $E(s', s^*) = -J[s'(s' + 1) - s^*(s + 1) - s(s + 1)] - J_{13}[s^*(s^* + 1) - 2s(s + 1)]$ and $J = J_{12} = J_{23}$. The quantity s^* takes the values $s^* = (s_3 + s_1), (s_3 + s_1 - 1), \dots, |s_3 - s_1|$, and $s' = (s^* + s), (s^* + s + 1), \dots, |s^* - s|$. $\omega(s', s^*)$ indicates the permitted values of s, s^* , and s' . While the small inequality between J and J_{13} might lead one to apply the equation when $J = J_{13}$, i.e., an equilateral triangular trimer, initial attempts to apply such an equation required $J = -23.5$ to fit the data below 100 K while $J = -26.5$ was needed to obtain a comparable fit for data above 100 K. Based upon x-ray data, this result may reflect the actual case.⁷ (The structure of this compound is currently undergoing refinement and, while the refinement is far from complete, $R = 0.16$, the two independent Fe_3O clusters in the asymmetric unit show a common distortion away from equilateral geometry.)

In Figure 2 we have experimental $1/\chi_{\text{Fe}^{\text{cor}}}$ vs. T data for $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$. In this figure we have also compared our data with equations for an $S = 5/2$ dimer,⁸ a linear chain,⁶ an equilateral triangular trimer, an isosceles triangular trimer, and an infinite linear chain.⁹ As may be seen from the figure the experimental data are most nearly fit by the equation for an isosceles trimer with $J = -29.0$ and $J_{13} = -19.0$. These values differ somewhat from those values reported by Catrall et al., but, considering the different temperature ranges over which the fit was made and that different measurement techniques were utilized, this disagreement is not extreme.

In an effort to provide a better picture of the trimeric unit in $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ we have carried out a preliminary x-ray investigation. The material readily forms blocky crystals with well-developed faces. Precession and Weissenberg photographs indicate a tetragonal cell with the long distance in excess of 40 Å. In addition, the photographs resemble those of large proteins and indicate only short-range order. This suggests the possibility of a molecule considerably more complex than merely a simple $(\text{FeOH})_3$ -containing species.

Some information as to the basic geometry around the Fe(III) can be obtained from the absorption spectrum of the solid, Figure 3. This spectrum shows two maxima. One maximum, the weaker of the two, occurs at 12800 cm^{-1} while the more intense maximum is observed at 23200 cm^{-1} . This spectrum is similar, though not identical, to the spectrum obtained for the iron-proline complex³ suggesting that the iron atom in $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ is in an octahedral environment. With the complete χ vs. T data for these two compounds it is in order to determine the compatibility of our results with those of ferritin and the iron core polymer of Spiro and Saltman.¹⁰ Schoffa¹¹ and Blaise et al.¹²

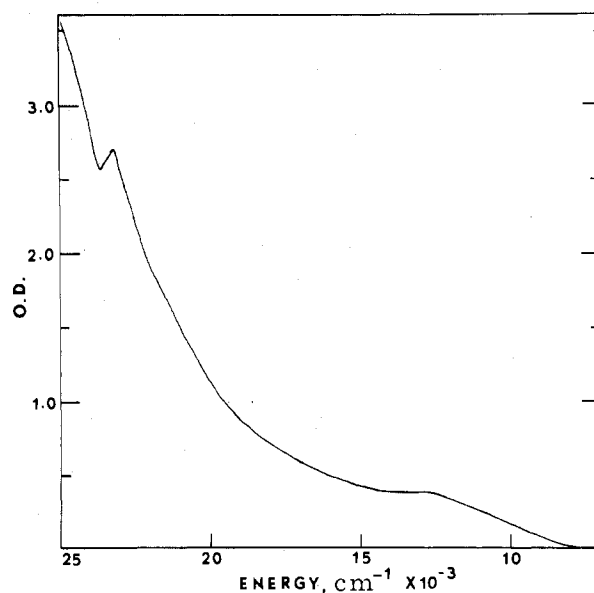


Figure 3. Absorption spectrum of the iron(III)-hydroxysulfate complex.

have investigated the χ vs. T behavior for ferritin down to 4.2 K. Schoffa has fit his data to the theoretical result expected for the $S = 3/2$ dimer. Blaise et al. have reproduced Schoffa's results and have also demonstrated that the magnetic susceptibility of ferritin is strongly field dependent at low temperatures. In both cases as well as in the synthetic iron core polymer of Spiro and Saltman the susceptibility behavior is in opposition to what is observed for the iron trimers in that the susceptibility increases with temperature to some temperature and then decreases rapidly. This decrease occurs at 8 K for the synthetic iron core polymer and ~ 20 K for ferritin. Thus, while the optical spectra and Mössbauer parameters would support a trimeric model^{2,3} as a subunit in ferritin, the detailed magnetic behavior does not.

Acknowledgment. S.L.H. wishes to express his appreciation to Professor Paul Hagenmuller for the use of his facilities and to the Fulbright-Hays Commission for a fellowship. This work was supported in part by a grant from the National Institutes of Health (HL-14590). We also wish to thank Professor Barry Garrett of the Department of Chemistry at Florida State University for his assistance in the theoretical calculations.

Registry No. $[\text{Fe}(\text{proline})_2\text{H}_2\text{O}]_3\text{O}(\text{ClO}_4)_7$, 54816-03-4; $(\text{C}_9\text{H}_{19}\text{NH}_3)_2\text{FeOH}(\text{SO}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$, 36569-13-8.

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