

A Magnetic Susceptibility and Mössbauer Spectroscopy Study of Bis(thiosemicarbazide)iron(II) Sulfate. A Case of Zero Field Splitting

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The magnetic susceptibility of a polycrystalline powder sample of bis(thiosemicarbazide)iron(II) sulfate, a sulfato bridged polymer, has been determined over the range 100 K to 2 K using vibrating sample magnetometry. The susceptibility behavior is interpreted in terms of zero field splitting ($|D| \sim 5 \text{ cm}^{-1}$) of the spin quintet ground state and an absence of exchange interaction.

Introduction

The sulfate bridged polymer $\text{Fe(II)(tsc)}_2\text{SO}_4$, where tsc is thiosemicarbazide (Fig. 1), is unusual among ferrous complexes in that it exhibits one of the largest quadrupole splittings [1] thus far observed for six coordinate, high-spin iron II. The compound has been the subject of a zero field Mössbauer [1] study as well as a high field investigation [2]. The

latter study indicated a positive quadrupole splitting consistent with a 5B ground term based on the dxy orbital.

The single crystal X-ray structural determination [3] shows that this sulfato bridged polymer consists of alternating $\text{FeS}_2\text{N}_2\text{O}_2$ octahedra of different spatial orientations in a monoclinic unit cell, space group $I_{21/a}$. As can be seen from the structure (Fig. 1), the $\text{FeN}_2\text{S}_2\text{O}_2$ chromophores alternate between the *cis* and *trans* forms as one proceeds along the polymer chain. In $\text{Fe(tsc)}_2\text{SO}_4$, two distorted and crystallographically different ferrous sites are present. However, Mössbauer spectroscopy does not distinguish them [1, 2].

The polymeric structure of $\text{Fe(tsc)}_2\text{SO}_4$ suggests the possibility of a magnetic exchange interaction along the sulfate bridged chains. Recently there have been susceptibility studies of other ferrous-sulfate polymers [4–6] along with correlations with structural results. These include metal hydrazinium sulfate and $\text{M}(2,2'\text{-bipyridine})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ chains. These polymers quite often undergo a transition to an antiferromagnetic phase at low temperatures.

It is the purpose of this article to report the low temperature magnetic susceptibility data and Mössbauer spectra to aid in further elucidating the nature of the magnetic interactions of such sulfato bridged transition metal ion polymers.

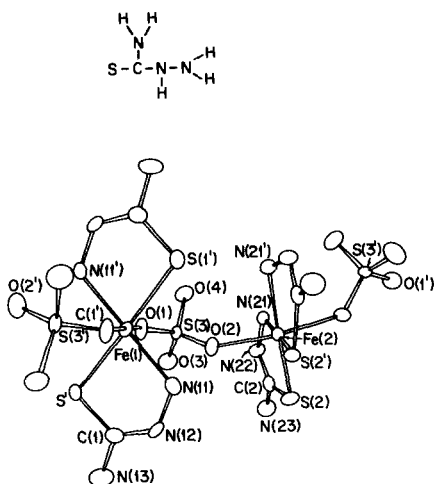


Fig. 1. a) Schematic of the thiosemicarbazide ligand. b) Polymer chain structure of bis(thiosemicarbazide)iron(II), reference 3. Note the alternating *cis* and *trans* $\text{FeN}_2\text{S}_2\text{O}_2$ coordination polyhedra and the *single* sulfate bridges.

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Experimental

Synthesis

This compound was prepared by the method of Campbell [2]. The quantity 2.78 grams of ferrous sulfate-heptahydrate was dissolved in hot distilled water and added to a warm aqueous solution of 2.20 grams of thiosemicarbazide. Both solutions were filtered prior to the mixing. A green solution resulted immediately and small needle-like crystals appeared on cooling. The crystals were collected, washed with distilled water, methanol, and anhydrous ether. Their identity and purity were confirmed using Mössbauer spectroscopy at ambient and 77 K. An excess of

thiosemicarbazide was used because it was found that otherwise uncomplexed FeSO_4 would crystallize along with the desired polymer product.

Magnetic susceptibility measurements and isothermal magnetization field sweeps were determined using a Princeton Applied Research Co. FM-1 vibrating sample magnetometer in conjunction with a Walker 9" electromagnet (applied fields varying from 0 to 14 kG), a Walker field sweep unit, a F. W. Bell model 610 Hall probe Gaussmeter and a Janis Super-Vari-Temp. cryostat. The sample was suspended in a static atmosphere (10 torr) of dry helium gas that had been previously deoxygenated by passing it over hot copper metal filings. Temperature measurement and control were achieved using a combination of calibrated gallium arsenide and uncalibrated silicon diodes. These were driven by a Lakeshore Cryotronics Co. model CCS-10B current source and a Lakeshore model DTC-500 set point controller respectively. Temperatures below 4.2 K were determined using a calibrated diode and helium vapor pressure measurements while the rate of helium pumping was controlled via an LJ Engineering Co. model 329 vacuum regulator valve.

Magnetic Results

The magnetic susceptibility, moment and reciprocal susceptibility data are plotted against temperature in Fig. 2a, b, c. As seen from the plots there is nothing unusual in the higher temperature region ($T > 20$ K) data and the compound behaves as expected for a quintet spin state. The magnetic data were least squares fit to a Curie-Weiss law with $C = 3.64$ emu/mol, $\theta = -5.39$ K, and $\mu_{\text{eff}} = 5.40$ B.M. As the temperature approaches 15 °K the moment drops off significantly, from 4.48 to 2.63 B.M. This decrease is characteristic of zero field splitting, a single ion phenomenon.

Zero field splitting is not uncommon for high spin ferrous ions in distorted octahedral ligand fields. The spin-orbit coupling has the effect of partially lifting spin degeneracy of the M_s levels. The magnitude of D , the axial zero field splitting parameter, may be found by computer fitting the molar susceptibility as a function of the temperature to the function [7]:

$$\chi_m = \frac{2N\beta^2 g^2}{3kT} \left(\frac{X}{A} \right) + \frac{4N\beta^2 g^2}{9D} \left(\frac{Y}{A} \right)$$

- g = spectroscopic splitting factor
- β = Bohr magneton (ergs/Gauss)
- k = Boltzman's constant (ergs/Gauss)
- T = temperature (°K)
- $A = 1 - 2e^{-x} + 2e^{-4x}$
- $X = e^{-x} + 4e^{-4x}$
- $Y = 9 - 7e^{-x} - 2e^{-4x}$

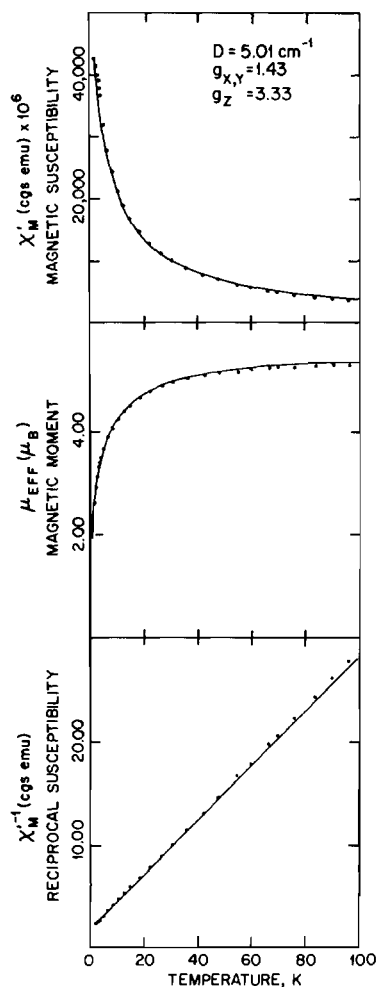


Fig. 2. a) χ'_m vs. T. b) μ vs. T. c) χ_m^{-1} vs. T. Note, the solid line in each figure corresponds to a least squares computer fit for the function described in the text, reference 7, for the parameters given in the figure.

where $x = D/kT$. The foregoing expression considers spin-only behavior. Sufficient information is not available from the powder susceptibility data to ascertain the sign of D . The temperature dependence of the magnetic anisotropy (principal moments) can lead to the determination of the sign of the splitting. However, this is not always possible from the analysis of the average powder moment [8, 9].

The results of the non-linear least squares fits of the magnetic data along with the experimental and theoretical moments are listed in Table I. The solid lines in Fig. 2a, b, c, represent the theoretical results of the fits. There is excellent agreement between the experimental and theoretical results for a powder averaged moment. Also, there is no evidence of polycrystal field orientation phenomena [10, 11]. The large value of D (5.00 cm^{-1}) is consistent with a significant decrease in the magnetic moment below

TABLE I. Table of Selected Calculated and Observed Moments of $\text{Fe}(\text{tsc})_2\text{SO}_4$ with $D = 5.00 \text{ cm}^{-1}$, $g_{\parallel} = 1.43$, $g_{\perp} = 3.33$.

T(K)	$\mu_{\text{calc}}(\text{B.M.})^{\text{a}}$	$\mu_{\text{exp}}(\text{B.M.})$	T(K)	$\mu_{\text{calc}}(\text{B.M.})^{\text{a}}$	$\mu_{\text{exp}}(\text{B.M.})$
2.0	2.63	2.61	18.5	4.65	4.64
2.6	2.93	2.92	22.3	4.78	4.77
3.1	3.13	3.13	26.6	4.88	4.87
3.5	3.29	3.33	30.6	4.96	4.91
3.8	3.36	3.40	36.0	5.03	5.02
4.2	3.46	3.51	42.2	5.10	5.08
5.3	3.66	3.67	47.7	5.14	5.13
6.8	3.86	3.89	54.8	5.19	5.13
8.5	4.03	4.06	60.0	5.21	5.19
10.6	4.22	4.24	66.4	5.24	5.20
12.8	4.37	4.39	69.8	5.25	5.24
15.0	4.50	4.48	76.1	5.27	5.25

^aNon-linear least squares fit.

the normal spin-only, $\sqrt{24}$ B.M. It is important to note that characteristic of antiferromagnetic interactions are not observed in the molar susceptibility data. The sign of D , not determinable at this point, will be discussed in the Mössbauer results that follow, but it should be noted that the respective magnitudes of g_{\perp} and g_{\parallel} are consistent with a positive zero field splitting [9]. When $D > 0$, g_{\perp} is usually greater than g_{\parallel} although this condition does not always hold [12]. The single ion anisotropy of the compound, as reflected by the magnitude of the g values, is normal for a ferrous ion which still has unquenched orbital angular momentum.

Mössbauer Spectroscopy Results

The zero field Mössbauer spectrum of $\text{Fe}(\text{tsc})_2\text{SO}_4$ at 1.89 K is shown in Fig. 3. The narrow linewidth

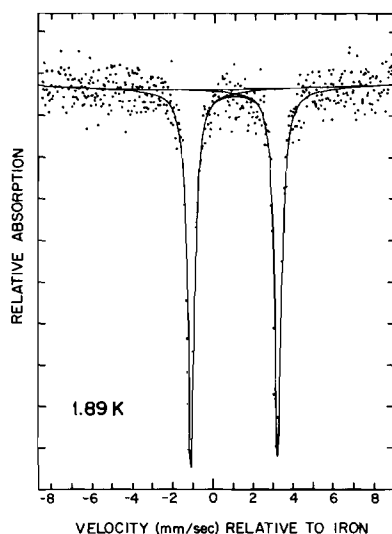


Fig. 3. Zero field Mössbauer spectrum of $\text{Fe}(\text{tsc})_2\text{SO}_4$ at 1.89 K.

doublet with a quadrupole splitting of 4.33 mm/sec and an isomer shift of 1.05 mm/sec is in agreement with previous results at 4.2 K [1]. The isomer shift and quadrupole splitting values as a function of temperature are presented in Table II. The splitting is

Table II. Mössbauer Spectra Parameters of $\text{Fe}(\text{tsc})_2\text{SO}_4$.

T(K)	I.S. (mm/sec) ^a	ΔE_{q} (mm/sec)	Γ_1^{b}	Γ_2^{b}
77.00	1.03	4.37	0.317	0.302
4.36	1.06	4.33	0.459	0.434
1.89	1.05	4.33	0.423	0.432

^aRelative to natural iron metal. ^bFull width at half maximum (mm/sec).

independent of temperature and is indicative of a separation of the ^5B and ^5E states of approximately 1000 cm^{-1} . The linewidths (Table II) are also independent of temperature which is consistent with the absence of slow paramagnetic relaxation. This implies a non-magnetic, singlet ground state ($M_s = 0$) and therefore that D is probably *positive*. The absence of magnetic hyperfine splitting in the zero field Mössbauer spectrum at 1.89 K also suggests that any extended, cooperative three dimensional magnetic ordering—exchange effects are very weak and that the material clearly behaves as a simple, rapidly relaxing paramagnet at these temperatures.

If the single electron spin—orbital coupling constant (ζ) and the separation of the ^5B and ^5E states are known, the zero field splitting constant may be approximated. The absence of a temperature dependence of the quadrupole splitting in the Mössbauer spectra is indicative of a large separation ranging from 500 – 1000 cm^{-1} . If ζ is taken to be 280 cm^{-1} , a range of D values can be estimated using the following relationship [13]

$$D = \frac{\xi^2}{16} \left[\frac{1}{E(^5E) - E(^5B)} \right]$$

D is then found to be in the range $10 > D > 5 \text{ cm}^{-1}$, consistent with the value obtained from the present susceptibility data.

Conclusions

While the magnetic susceptibility data in the temperature range 1.7 to 100 K suggest significant (5.00 cm^{-1}) zero field splitting and the Mössbauer spectroscopy results imply $D > 0$, the magnetic data for this sulfate bridged system do not indicate significant exchange interactions. One and three dimensional antiferromagnetic interactions ($J < 0$) though absent in the present study have been observed in similar sulfate bridged chains. The magnetic susceptibility data [6] of ferrous hydrazinium sulfate ($\text{Fe}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$) exhibit a broad maximum at approximately 15 K corresponding to intrachain antiferromagnetism. Three dimensional order was observed in the magnetic heat capacity [14] and Mössbauer spectroscopy data [15] for this complex at 6.05 K. Similarly, $\text{Fe}(2,2'\text{-bipyridine})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ exhibits chain antiferromagnetism in the low temperature molar susceptibility data [16]. In both structures, hydrogen bonding is present and is postulated to be responsible for the interchain magnetic interactions. In the single crystal structure determination [3] of $\text{Fe}(\text{tsc})_2\text{SO}_4$ neither the details of the interchain separations nor the occurrence of hydrogen bonding were considered in detail. To fully characterize the presence or absence of extended (three dimensional) magnetic interactions, such information must be available; until then, direct comparisons to like systems cannot be made. However, the absence of one dimensional antiferromagnetic exchange for the present system may be related to

the presence of *single* sulfato bridges between metal atoms as opposed to two found in the $\text{M}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2$ systems.

Acknowledgements

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