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Magnetic Superexchange Involving the Oxygen–Sulfur–Oxygen Pathway of the Sulfate Ion: A Mössbauer Spectroscopy and Magnetic Susceptibility Study of Fe(2,9-di-CH_3-phenanthroline) SO_4

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Zero-field Mössbauer spectra of powder samples of Fe(2,9-di-CH_3-phenanthroline) SO_4 over the range 1.7 to 300°K show a large (~ 3.6 mm/sec) temperature-independent quadrupole splitting corresponding to an orbital singlet ground term. The chemical isomer shift, $\delta_{\mathrm{FE-O}}$, is 1.16 mm/sec (source and absorber at 4.2°K) corresponding to six coordinate high-spin iron (II). Below 4.2°K, the compound exhibits magnetic hyperfine splitting suggesting slow relaxation and the possibility of long-range three-dimensional magnetic ordering with a critical temperature T_c such that $3.5°\mathrm{K} < T_c < 4.2°\mathrm{K}$ and an internal hyperfine field $H_n = 325$ kG at 1.69°K. High-field Mössbauer spectra at 300°K indicate that the principal component of the electric field gradient tensor is positive and axial. Similar spectra at 4.2°K show an absence of nuclear Zeeman splitting for applied fields up to 60 kG, and indicate that at 4.2°K the material is rapidly relaxing but with substantial magnetic polarization and a negative internal hyperfine field. The temperature dependence of the magnetic susceptibility confirms antiferromagnetic interactions with a broad maximum in χ'_M at ~ 11.8°K presumably due to low-dimensionality exchange interactions (possibly one) along M–O–S–O–M chains. Least-squares fits of χ'^{-1}_M versus T for $T > 50$°K indicate Curie–Weiss behavior with $C = 3.26$ emu/mole, $\theta = -21.95$°K, and $\mu_{\mathrm{eff}} = 5.11$.

Introduction

This article presents the low-temperature magnetic properties of Fe(2,9–di-CH_3-phenanthroline)SO_4, hereafter Fe(dmp)SO_4, as part of our general study of the transference of magnetic exchange effects via bridging tetrahedral xy_4^{m-} anions, e.g., SO_4^{2-}, ClO_4^-, BeF_4^{2-}, PO_4^{3-}. The preceding compound was first synthesized by Fox *et al.* (*1*) and in a latter study (*2*) the divalent Co, Ni, Cu, and Zn analogs were also reported. As these compounds are quite insoluble, they are obtained as polycrystalline powders, and thus no direct X-ray structure determination exists for any of them to date. However, previous powder X-ray and infrared studies appear to establish two types of M(II)(dmp)SO_4 systems for which the local environment is postulated to be as shown in Fig. 1a (isomorphous Fe, Co, Ni) and Fig. 1b (Cu, Zn) while a schematic of the ligand dmp is given in Fig. 1c. The structure proposed for the Cu and Zn complexes is probably strained as it contains both bidentate chelating as well as bridging SO_4^{2-} units. Spatial articulation of the structure unit of Fig. 1a in which each bridging SO_4^{2-} group is linked to four different metal atoms can lead to M–O–S–O–M chains that are further crosslinked by O–S–O–bridge units. Chains of this type have been found in an X-ray study (*3*) of Ni(2,2′-bipyridine)$SO_4 \cdot 2H_2O$ and the corresponding Cu(II) analog. Whether the system will then ultimately exhibit chain-like or primarily three-dimen-

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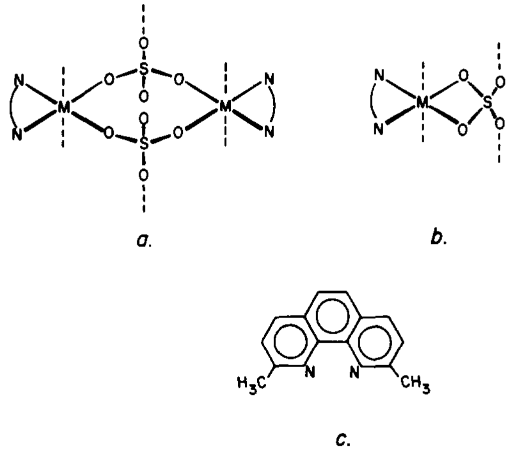


FIG. 1a Schematic of the structure proposed for (Fe, Co, Ni)dmp SO_4. (b) Schematic of the structure proposed for (Cu, Zn)dmp SO_4. (c) Schematic of the ligand dmp.

sional network magnetic behavior will depend on the nature of the magnetic anisotropy and the relative strength of exchange interactions along the foregoing pathways. Some previously studied iron compounds in which chain (1D) as well as (3D) antiferromagnetic behaviour have been observed and which involve -O-S-O- superexchange pathways are $Fe(II)(N_2H_5)_2(SO_4)_2$ (*4, 5*) and $Fe(III)OHSO_4$ (*6*). However, for both of these compounds hydrogen bonding effects are likely to be involved in the exchange interactions, at least in the three-dimensional ordering at low temperatures. The present *M*(DMP)SO_4 compounds are anhydrous and involve a non-hydrogen-bonding organic ligand. They thus provide an opportunity for the study of magnetic exchange based exclusively on *M*-O-S-O-*M* pathways.

Experimental

The sample of Fe(dmp)SO_4 studied was prepared by the method of Fox *et al* (*1*) and gave the required analysis. Calculated: %C 46.69, %H 3.36, %N 7.78; observed: %C 45.87, %H 3.42, %N 7.97 (Galbraith Laboratories, Knoxville, Tenn.). Cryogenic susceptibility measurements and zero- and high-field Mössbauer measurements (longitudinal fields) at low temperatures were determined as described previously (*7*). Highfield Mösbauer spectra (transverse fields) at ambient temperature were determined using a Varian model 4004 electromagnet with cylindrical pole faces (4 in.) tapered to 1 in. such that a field of ~20 kG was obtained at maximum power (2 kW) for a 0.5-in. pole gap. Near infrared and visible electronic spectra were measured using a Cary 14 spectrometer with a standard reflectance attachment.

Results

Mössbauer and Optical Spectra

To our knowledge there have been no previous reports of Mössbauer spectra for Fe(dmp)SO_4. In favorable circumstances, the chemical isomer shift (δ) is diagnostic of spin and oxidation state and coordination number. For the present compound, δ clearly indicates six-coordinate, high-spin iron (II) in agreement with previous susceptibility (*1*) and infrared spectra (*2*) measurements at ambient temperature and consistent with the compound's stoichiometry and analysis. The near infrared visible spectrum was measured over the range 5000 to 30,000 cm^{-1}. The dry compound is pink as previously observed. In addition to high-energy charge transfer bands and low-energy ligand overtones, a very broad, weak transition centered at 9700 cm^{-1} is also seen and assigned to the $^5T \rightarrow {}^5E$ transition or a component thereof. This is consistent with the pseudooctahedral *cis*-FeN_2O_4 chromophore present in the complex (Fig. 1a).

The quadrupole doublet (Fig. 2a) observed at room temperature is essentially unchanged over the range 300 to 4.2°K (~3.5 mm/sec) and suggests ^5T splitting of

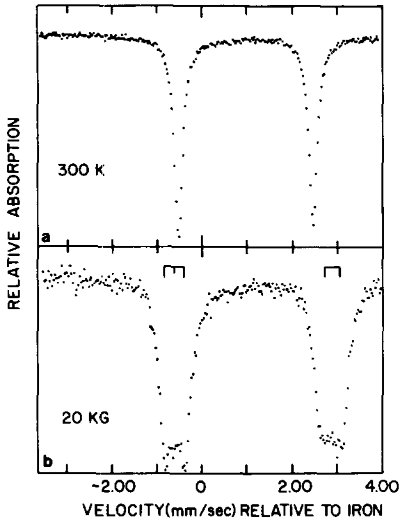


FIG. 2. Mössbauer spectra of Fe(dmp)SO_4 at (a) 300°K, $H_0 = 0$; and (b) 300°K, $H_0 = 20$ kG.

$\sim 1000\ \mathrm{cm}^{-1}$ or more. Its magnitude and temperature independence indicate an isolated orbital singlet (^5A or ^5B) ground term and a highly distorted local coordination environment. The local coordination proposed in Fig. 1a has at most C_{2v} symmetry and thus a ground orbital singlet is not unexpected. In subsequent discussion, the magnitude of the internal hyperfine field (H_n) will be seen related to the nature of the orbital ground state.

The sign of the principal component of the electric field gradient tensor is *positive* in view of the high-field Mössbauer spectrum at ambient temperature (Fig. 2b). This spectrum shows that the transitions of the zero-field doublet have split to an apparent triplet at negative velocity relative to a broader doublet. This pattern is characteristic of a rapidly relaxing paramagnet ($H_n = 0$, $H_{\mathrm{eff}} = H_{\mathrm{appl}}$) with axial symmetry to the local coordination environment. The magnitude and sign of the quadrupole interaction can be rationalized in terms of a ground term based primarily on the real d_{xy} orbital. The problem of unequivocably relating this result to the details of the local coordination must, however, await single-crystal structure analysis. For the moment, one can speculate on a reasonable possibility: the axis of V_{zz} coincides with the local C_2 symmetry axis in which case $\eta \approx 0$ as observed. The positive sign must then correlate with higher metal d electron density in a plane normal to this axis.

High-field Mössbauer spectra up to a 60-kG applied field (Fig. 3a–e) at 4.2°K surprisingly exhibit only slight broadening of the transitions of the quadrupole doublet relative to zero field, and resolved nuclear

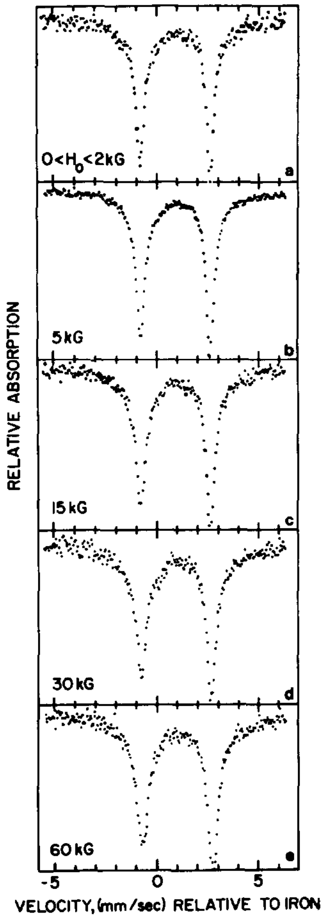


FIG. 3. Mössbauer spectra of Fe(dmp)SO_4 at (a) 4.2°K, $0 < H_0 < 2$ kG; (b) 4.2°K, $H_0 = 5$ kG; (c) 4.2°K, $H_0 = 15$ kG; (d) 4.2°K, $H_0 = 30$ kG; and (e) 4.2°K, $H_0 = 60$ kG.

Zeeman splitting is not observed. This behavior indicates that the material is rapidly relaxing at this temperature but with significant electron spin polarization and magnetization (proportional to the applied field) corresponding to a *negative internal hyperfine field* such as to essentially cancel the effect of the applied field. The preceding behavior is not common, and additional high-field Mössbauer spectra (to ~100 kG) at temperatures just above and below 4.2°K are the subject of future study.

Resolved magnetic hyperfine splitting is, however, observed in the temperature dependence of the zero-field spectra below 4.2°K (Figs. 4a–b, c; 5a, b; and 6). It is conceivable that this splitting is the result of slow paramagnetic relaxation owing to zero field ($D < 0$) and/or spin-orbit splitting of the single-ion spin quintet ground state to give a slowly relaxing ground Kramers spin–orbit doublet. However, slow relaxation is rare in the case of high-spin ferrous. The rather condensed nature of the compound, the relatively small temperature interval over which the splitting occurs, and finally susceptibility data to be considered

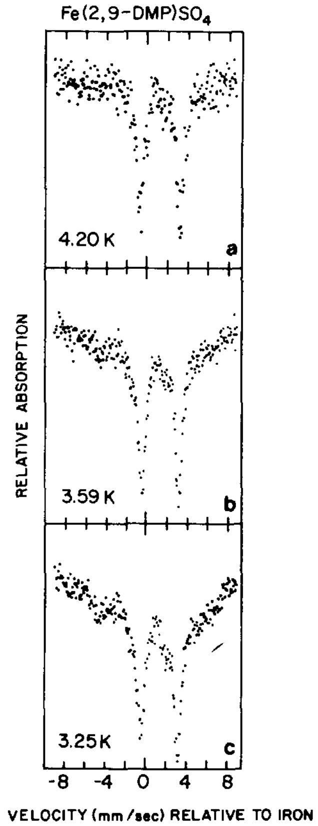


FIG. 4. Mössbauer spectra of Fe(dmp)SO_4 at; (a) $H_0 = 0$, $T = 4.2$°K; (b) $H_0 = 0$, $T = 3.59$°K; and (c) $H_0 = 0$, $T = 3.25$°K.

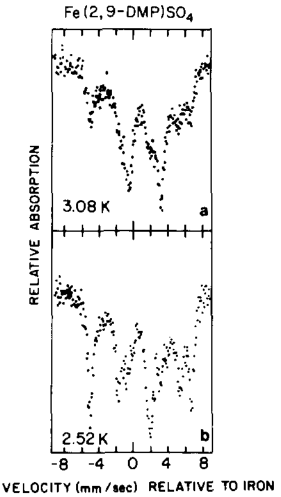


FIG. 5. Mössbauer spectra of Fe(dmp)SO_4 at; (a) $H_0 = 0$, $T = 3.08$°K; and (b) $H_0 = 0$, $T = 2.52$°K.

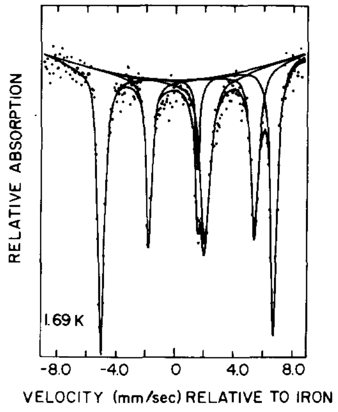


FIG. 6. Mössbauer spectrum of Fe(dmp)SO_4 at $H_0 = 0$, $T = 1.69$°K with least-squares Lorentzian fit.

subsequently suggest that the hyperfine splitting is the result of the onset of long-range (3D) magnetic order. However, slow single-ion or (as suggested by one of the referees of this work) entire chain spin orientation relaxation cannot be entirely ruled out as opposed to 3D ordering between 3 and 4°K. The latter is consistent with the observation that the overall magnetic splitting and hyperfine field are essentially unchanged below ~ 3.6°K.

The transitions of the quadrupole doublet of the paramagnetic phase have completely vanished at $T \sim 1.7$°K to give a spectrum in which the quadrupole interaction (shift of the inner four transitions relative to the outer two) is obvious (Fig. 6). The relation between the foregoing shift (S) and the quadrupole splitting (ΔE) is $S = -\Delta E(3\cos^2\theta - 1)$ (*8*) for the case of axial symmetry ($\eta = 0$) where θ is the polar angle of the internal hyperfine field (H_n) with respect to the principal axis of the electric field gradient tensor. Hence, for zero apparent shift, $\theta = \arccos(1/3)^{1/2}$ or $\sim 54°$. In the present case $S = +1.97$ mm/sec and the quadrupole splitting $\Delta E = +3.58$ mm/sec (at 4.2°K) leading to $\theta \sim 67°$. Thus, *assuming* that the principal axis of V_{zz} is, in fact, the C_2 axis depicted in Fig. 1a, the easy axis of magnetization is more or less along the direction of the M–O–S–O–M chains (dashed lines, Fig. 1a). The other angle describing the orientation of H_n with respect to V_{zz} is the azimuthal angle (ϕ) which is, however, indeterminant from the present powder sample Mössbauer spectra data.

The magnitude of the internal hyperfine field can be determined from the ground state ($I = 1/2$) Zeeman splitting. For the least-squares Lorentzian fit (Fig. 6) of the spectrum at 1.69°K this corresponds to either $\Delta_{2\text{-}4}$ (3.84 mm/sec) or $\Delta_{3\text{-}5}$ (3.89 mm/sec) divided by 0.1188 mm/sec/Tesla (*9*) or $\langle H_n \rangle = 325$ kG, a value probably close to the limiting low-temperature saturation value. For high-spin iron(II) $\langle S \rangle = 2$ and thus, the expected contribution to H_n from the Fermi contact interaction (H_F) is ~ 440 kG (*8*). The residual opposing orbital contribution to H_n, i.e. H_L, is expected to be relatively small in view of the near spin-only moment and orbital singlet ground term (see susceptibility results) of the complex. On the other hand, the dipolar contribution (H_D) to H_n is probably not negligible, in view of the large electric field gradient (i.e., $|H_\text{D}| = \mu_\beta V_{zz/e}$) (*8*) and is also usually of opposite sign to H_F. Hence, the observed value of $H_n = 325$ kG is not unreasonable for the expected Fermi contribution reduced somewhat by both opposing dipolar and to a lesser extent orbital contributions. Further reduction of H_F is probably also occurring through covalency–delocalization effects (decreased $\langle r^{-3} \rangle_{3d}$) involving the dmp ligand.

With increasing temperature the hyperfine splitting collapses to near zero at 4.2°K, and the spectra suggest a critical ordering temperature between 3.5 and 4.2°K. However, the quadrupole doublet of the paramagnetic phase appears to persist to well below this temperature range to at least 2.0°K, suggesting superparamagnetic behavior. The rapid precipitation that accompanies the formation of the compound could result in the formation of the small domain clusters required for this type of magnetic behavior. In any event, the exchange interactions appear to be antiferromagnetic as indicated by susceptibility data to be discussed now.

Magnetic Susceptibility

The temperature dependence of the corrected molar susceptibility and magnetic moment of a powder sample for an applied field of 5.1 kG are shown in Fig. 7 for the range 1.5 to ~ 100°K with some sample moment data given in Table I. The magnetic susceptibility has the same form for fields of 1.6 to 5.1 kG indicating the absence of externally induced (low field) phase transitions, e.g., spin-flop or metamagnetic behavior in

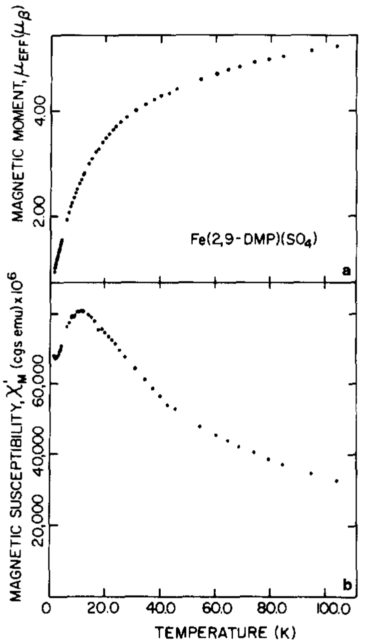


FIG. 7. (a) μ versus T for Fe(dmp)SO$_4$, $H_0 = 5.1$ kG (b) χ'_M versus T for Fe(dmp)SO$_4$, $H_0 = 5.1$ kG.

this range. To our knowledge, the sole previous magnetic measurement for this system is a report (*1*) of the ambient temperature moment (5.13 μ_β) with which our value ($\mu_{\text{eff}} = 5.11$) agrees quite well. These values are close to the spin-only value for high-spin ferrous, i.e., $(24)^{1/2}$ for $S = 2$, $g = 2$, and suggest little orbital contribution to the moment. This is consistent with the large single-ion distortion reflected in the quadrupole splitting corresponding to an isolated orbital singlet ground term. Least-squares computer fits of χ'^{-1}_M vs T over the range 50 to 303°K show the compound to obey a Curie–Weiss law in this range with the following parameters: $\mu_{\text{eff}} = 5.11$, paramagnetic Curie temperature $\theta = -21.95$°K, and Curie constant $C = 3.26$ emu/mole. At lower temperatures there is deviation from Curie–Weiss behavior for all (10) fields. The moment begins to drop (see table I) significantly below the spin-only value at temperatures

TABLE I

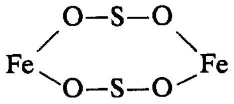
SAMPLE MAGNETIC DATA

T (°K)	$\mu(\mu_\beta)$
1.52	0.89
1.80	0.97
2.04	1.03
2.26	1.09
2.50	1.15
2.75	1.20
3.01	1.26
3.25	1.31
3.50	1.37
3.76	1.43
4.00	1.48
4.20	1.53
5.97	1.89
6.80	2.03
7.34	2.12
7.87	2.20
8.60	2.32
9.19	2.40
9.70	2.47
10.39	2.56
11.10	2.65
11.81	2.73
12.18	2.77
13.91	2.94
14.97	3.03
16.32	3.08
17.50	3.12
18.84	3.34
20.03	3.43
21.21	3.49
22.49	3.57
23.59	3.64
25.18	3.71
27.46	3.81
30.91	3.94
34.44	4.06
37.48	4.15
40.14	4.21
42.96	4.26
45.63	4.34
54.39	4.51
60.33	4.62
64.55	4.69
68.56	4.73
73.90	4.82
79.27	4.87
84.38	4.93
94.46	5.03
103.77	5.11

well above the three-dimensional ordering temperature (~3.5°K) suggested by the zero-field Mössbauer spectra. This and the negative θ value suggest dominant antiferromagnetic interactions. A broad maximum in χ'_M versus T is observed at ~11.7°K while at lower temperatures χ'_M appears to start increasing again. The latter rise in χ'_M is probably due to trace (nonordering) paramagnetic impurities, e.g., ferric species. The steady decrease of μ with T is indicative of strong pairwise magnetic interactions while the broad maximum in χ'_M at lower temperatures is a hallmark of low, presumably one- or possibly two-dimensional magnetic behavior, antiferromagnetic spin correlation along M–O–S–O–M chains.

Discussion

In some respects, the low-temperature magnetic and Mössbauer spectroscopy behavior of Fe(dmp)SO_4 are similar to those of the previously studied linear chain antiferromagnet ferrous hydrazinium sulfate, $Fe(N_2H_5)_2(SO_3)_2$, whose structure is known and a comparison of them is useful. This compound exhibits a broad maximum in χ'_M at ~15.9°K which is associated with 1D intra chain antiferromagnetic interactions. This maximum is broad such that a distinct, sharp lower temperature (3D) maximum in χ'_M is not observed (*5*). Extended three-dimensional magnetic ordering and interchain interactions are, however, clearly seen (*10, 11*) in terms of magnetic hyperfine splitting of the Mössbauer spectra which indicate $T_{\text{Néel}}$ ~6.3°K. The observation of *distinct one- and three-dimensional* magnetic interactions is seen (*12*) in the temperature dependence of the heat capacity of $Fe(N_2H_5)_2(SO_4)_2$. A broad maximum in C_p versus T is observed at 12.3°K and is associated with the intrachain antiferromagnetism while a sharp λ anomaly corresponding to three-dimensional (interchain) magnetic order is observed at 5.9°K. Thus, on the basis of C_p versus T, the separation of the 1D and 3D effects is ~6.4°K. The combined Mössbauer and susceptibility results of the present investigation indicate a comparable separation (~8.2°K, i.e., 11.7–3.5°K) and comparable magnetic exchange effects in Fe (dmp)SO_4. In the absence of more detailed structural and heat capacity data, we summarize for the present as follows: (a) the broad maximum in χ'_M for Fe(dmp)SO_4 is probably the result of 1D chain antiferromagnetism along M–O–S–O–M pathways analogous to $Fe(N_2H_5)_2(SO_4)_2$; (b) the ultimate 3D ordering is the result of further O–S–O crosslinking while in $Fe(N_2H_5)_2(SO_4)_2$ it is more likely due to interchain hydrogen bonding (*5, 13*).



We conclude this work by indicating that the magnetic properties of the entire series M(dmp)SO_4 (M = Mn, Co, Ni, Cu) are presently under study. The magnetic behavior will be further clarified when the single-crystal X-ray structure of a member of each of the isomorphous sets (Co, Fe, Ni) (Cu, Zn) has been determined along with low-temperature heat capacity measurements. As mentioned earlier, our attempts to produce suitable single crystals of Fe(dmp)SO_4 have so far failed. In these attempts, gelatinous (perhaps hydroxyferric) species resulted. We are now focusing on the more oxidatively stable Zn and NI systems.

Acknowledgments

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