

## Magnetic Superexchange Involving Tetrahedral Anions: One-Dimensional Antiferromagnetic Interactions via Sulfate Anions in $M(2,9\text{-di-CH}_3\text{-1,10-phenanthroline})\text{SO}_4$ ( $M = \text{Mn, Fe, Co, Ni, Cu}$ )

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The magnetic susceptibilities of powder samples of the polymeric compounds  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni, Cu}$ ;  $\text{dmp} = 2,9\text{-di-CH}_3\text{-1,10-phenanthroline}$ ) have now been studied at temperatures between 1.5 and 305 K. There is clear evidence of one-dimensional, antiferromagnetic interactions in the Mn, Fe, Co, and Ni compounds: from  $T \approx 300$  to 1.7 K, the magnetic moment *decreases steadily* from a value that is approximately the spin-only moment of the high-spin configuration to a value that is  $\sim 20\%$  of the spin-only moment, and the susceptibility-vs-temperature curve contains a *broad maximum at  $T \leq 30$  K*.  $\text{Cu}(\text{dmp})\text{SO}_4$ , however, exhibits almost perfect Curie-Weiss paramagnetism. These results when combined with the results of various spectroscopic studies lead to proposed molecular structures (chainlike polymers of *cis-MN}\_2\text{O}\_4* chromophores and *bridging-chelating sulfates*) and estimated energies of intrachain antiferromagnetic exchange ( $-0.5 \text{ K} \geq J/k_B \geq -10 \text{ K}$ ).

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### Introduction

The study of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni, and Cu}$ ; see Fig. 1 for a schematic of  $\text{dmp} = 2,9\text{-di-CH}_3\text{-1,10-phenanthroline}$ ) is a result of our interest in magnetic superexchange that occurs through highly symmetrical, diamagnetic anions like  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{ReO}_4^{1-}$  (1-9).

We are interested in learning not only how superexchange varies from one sort of polyatomic group to another, for instance, from  $\text{PO}_4^{3-}$  in  $\text{Fe}_2(\text{PO}_4)\text{Cl}$  to  $\text{MoO}_4^{2-}$  in  $\text{FeCl MoO}_4$  and  $\text{ReO}_4^{1-}$  in  $\text{Fe}(\text{ReO}_4)_2$ , but also how the superexchange occurring via one sort of polyatomic group varies as the

group is placed in different environments, for example, with the same metal in different valence states as in  $\text{Fe(III)ClMoO}_4$  compared to  $\text{LiFe(II)ClMoO}_4$ , or with the same metal in the same valence state but with or without the cooperation of hydrogen bonding as in  $M(2,2'\text{-bipyridine})(\text{H}_2\text{O})_2\text{SO}_4$  compared to  $M(\text{dmp})\text{SO}_4$  where  $M = \text{Fe, Ni, or Cu}$ , or among different metals with similar coordination as in  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni}$ ).

Plowman and co-workers began characterizing the  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Fe, Co, Ni, Cu, Zn}$ ) by far infrared and visible spectroscopy, X-ray powder diffraction, measurements of magnetic moments, and tests of solubility and conductivity—all at  $25^\circ\text{C}$  (10-14).

Researchers in our laboratory later used

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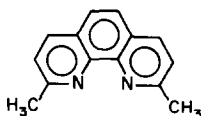


FIG. 1. Schematic of the  $\alpha$ -diimine ligand 2,9-dimethyl-1,10-phenanthroline (dmp).

Mössbauer spectroscopy and Faraday balance measurements to characterize Fe(dmp)SO<sub>4</sub> at temperatures from  $T \approx 300$  to 1.5 K and uncovered evidence of low-dimensional, antiferromagnetic interactions among 6-coordinate, high-spin Fe<sup>2+</sup> sites (15). The chemical shift  $\delta$  and the quadrupole splitting  $\Delta E_Q$  of Fe(dmp)SO<sub>4</sub> at  $T = 4.2$  K are 1.16 and 3.56 mm/sec, respectively. The magnetic moment decreases from  $\mu \approx 5.1 \beta$  at  $T \approx 300$  K to  $\mu \approx 0.90 \beta$  at  $T \approx 1.5$  K, and a broad maximum occurs in the corrected molar magnetic susceptibility  $\chi'_M$  at low temperatures ( $T \approx 11$  K).

Since then we have added the manganous complex to Plowman's original series and determined the magnetic behavior of four more  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ ) at temperatures from 305 to 1.7 K. From our results, we gain new insight as to the probable molecular structures of these complexes.

## Experimental

**Syntheses.** We synthesized Cu(dmp)SO<sub>4</sub> and Ni(dmp)SO<sub>4</sub> by the procedure that Plowman and co-workers used to obtain Cu(dmp)SO<sub>4</sub> (11). About 2.5 mmole of either CuSO<sub>4</sub> · 5H<sub>2</sub>O or NiSO<sub>4</sub> · 6H<sub>2</sub>O were dissolved with stirring in about 60 ml of pure methanol. We synthesized  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn}, \text{Co}, \text{Zn}$ ) by the method that Plowman and co-workers used to obtain Co(dmp)SO<sub>4</sub> (13). About 2.5 mmole of either MnSO<sub>4</sub> · H<sub>2</sub>O, CoSO<sub>4</sub> · 7H<sub>2</sub>O, or ZnSO<sub>4</sub> · 7H<sub>2</sub>O was dissolved with both stirring and heating ( $t \approx 70^\circ\text{C}$ ) in about 100 ml of a 50/50 (v/v) mixture of methanol

and water. The metal sulfate/methanol or metal sulfate/water-methanol solution was then heated and stirred while the dmp/methanol solution ( $\sim 2.6$  mmole of dmp in  $\sim 60$  ml of pure methanol) was added gradually. In each synthesis, a slight excess of the dmp ligand ( $\leq 5\%$  by stoichiometry) was added to ensure that all of the metal sulfate was complexed. The metal sulfate was used as supplied by the manufacturer; the dmp/methanol solution was filtered through glass wool. Less than 30 min after the dmp solution had been combined with the metal sulfate solution, the  $M(\text{dmp})\text{SO}_4$  product precipitated. The precipitate was collected on a sintered glass funnel by suction-filtration, washed with two 25-ml portions of pure methanol, and dried under vacuum ( $p \approx 15$  Torr) at room temperature ( $t \approx 23^\circ\text{C}$ ) for 15 to 20 hr. Each  $M(\text{dmp})\text{SO}_4$  complex was produced as a fine powder: Zn(dmp)SO<sub>4</sub> is chalk white; Cu(dmp)SO<sub>4</sub>, pale blue; Ni(dmp)SO<sub>4</sub>, pale green; Co(dmp)SO<sub>4</sub>, pink; Mn(dmp)SO<sub>4</sub>, cream white. The yields were  $>60\%$ .

**Far infrared spectroscopy.** The sample was prepared as a press-packed pellet of 2–3 mg of finely ground  $M(\text{dmp})\text{SO}_4$  mixed thoroughly into  $\sim 200$  mg of dried, finely ground KBr. Each spectrum was recorded at room temperature ( $t = 23^\circ\text{C}$ ) on a Perkin-Elmer Model 567 spectrophotometer purged with nitrogen gas. The calibrant was a polystyrene film (the calibration mark was the sharp peak at  $906.9 \text{ cm}^{-1}$ ).

**X-ray powder diffractometry.** The neat, finely ground sample of  $M(\text{dmp})\text{SO}_4$  was packed into a glass capillary, which was then mounted inside a Debye-Scherrer camera. The camera was attached to a Philips Electronics 12045P/3 X-ray generator. Nickel-filtered Cu- $K\alpha$  X-rays were used.

**Faraday balance measurements.** Our procedure for measuring magnetic susceptibilities at set temperatures by means of a Faraday balance has been described before (16). The calibrant was HgCo(NCS)<sub>4</sub> (17).

The correction for the diamagnetism of each  $M(\text{dmp})\text{SO}_4$  complex was calculated from Pascal's constants:  $-14$  for  $\text{Mn}^{2+}$ ,  $-12$  for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ ,  $-11$  for  $\text{Cu}^{2+}$ ,  $-40$  for  $\text{SO}_4^{2-}$ , and  $-152$  for dmp (the units for all of these constants are  $10^{-6}$  emu/mole) (18). We considered dmp to have the diamagnetism of 1,10-phenanthroline plus two carbon atoms and four hydrogen atoms.

*Electron paramagnetic resonance spectroscopy.* The EPR spectra of  $\text{Mn}(\text{dmp})\text{SO}_4$  and  $\text{Cu}(\text{dmp})\text{SO}_4$  at  $T \approx 296$  K and  $T \approx 77$  K were recorded at the X-band frequency on a Varian E-109 spectrometer. The field was calibrated from the NMR signal of the proton in water.

## Results

*Elemental analyses.* The results of the chemical analyses, which were performed by Galbraith Laboratories, Knoxville, Tennessee, are shown in Table I.

In view of the analyses, the Mn complex is best formulated as the monohydrate and the Ni complex as the hemihydrate (Table I).

Plowman and his co-workers point out that  $\text{Zn}(\text{dmp})\text{SO}_4$  "readily absorbs water from the atmosphere but this moisture is easily removed by heating at  $110^\circ\text{C}$ " (14). Such a mild condition for drying suggests that the water molecules in the hydrates of  $M(\text{dmp})\text{SO}_4$  (that is,  $M = \text{Mn}, \text{Ni}, \text{Zn}$ ) are

TABLE I  
CHEMICAL ANALYSES OF THE COMPOUNDS  
 $M(\text{dmp})\text{SO}_4$

Compound	Calculated %			Observed %		
	C	H	N	C	H	N
$\text{Mn}(\text{dmp})\text{SO}_4 \cdot \text{H}_2\text{O}$	44.57	3.74	7.43	44.56	3.70	7.55
$\text{Co}(\text{dmp})\text{SO}_4$	46.29	3.33	7.71	46.31	3.39	7.75
$\text{Ni}(\text{dmp})\text{SO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$	45.20	3.52	7.53	45.49	3.54	7.57
$\text{Cu}(\text{dmp})\text{SO}_4$	45.71	3.29	7.62	45.57	3.39	7.40

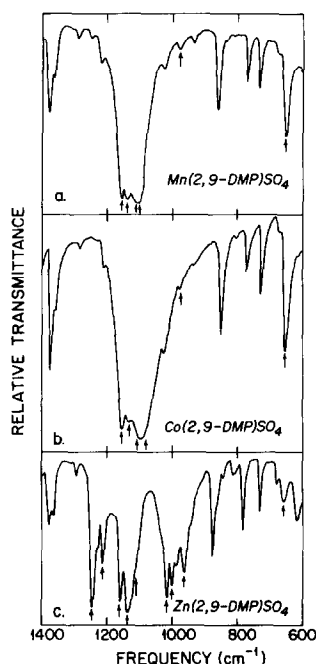


FIG. 2. Far infrared spectra of (a)  $\text{Mn}(\text{dmp})\text{SO}_4$ , (b)  $\text{Co}(\text{dmp})\text{SO}_4$ , and (c)  $\text{Zn}(\text{dmp})\text{SO}_4$  at  $T \approx 296$  K. Sulfate bands are marked by arrows ( $\uparrow$ ).

not coordinated to the metal  $M$  but are simply lattice water.

*X-ray powder diffraction patterns and far infrared spectra.* Our results for the  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) are identical to the results reported by Plowman and co-workers (14). Both the X-ray powder diffraction patterns and the far infrared spectra indicate that there may be two distinct groups within the  $M(\text{dmp})\text{SO}_4$  series. Group A is comprised of the isomorphous Fe, Co, and Ni complexes while group B contains the isomorphous Cu and Zn complexes.

The X-ray powder diffraction pattern and the far infrared spectrum of  $\text{Mn}(\text{dmp})\text{SO}_4$ , our addition to Plowman's original series, show that this complex belongs in group A, along with the Fe, the Co, and the Ni complexes.

We present in Fig. 2 the far infrared spectra that we recorded from three of our

$M(\text{dmp})\text{SO}_4$  products ( $M = \text{Mn}, \text{Co}, \text{Zn}$ ). Comparing the far infrared spectrum of  $\text{Mn}(\text{dmp})\text{SO}_4$  to the spectra of  $\text{Fe}(\text{dmp})\text{SO}_4$ ,  $\text{Co}(\text{dmp})\text{SO}_4$ , and  $\text{Ni}(\text{dmp})\text{SO}_4$  enabled us to determine the bands due to  $\text{SO}_4^{2-}$  in  $\text{Mn}(\text{dmp})\text{SO}_4$ : 1158  $\text{cm}^{-1}$ , 1141, 1115, 1103 (all four are very strong), 980 (weak), and 652 (medium).

Plowman and coworkers (14) published the far infrared spectra of  $\text{Ni}(\text{dmp})\text{SO}_4$  and  $\text{Cu}(\text{dmp})\text{SO}_4$  along with a table of the far infrared bands assigned to the  $\text{SO}_4^{2-}$  group in the  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{and Zn}$ ). Those researchers identified the  $\text{SO}_4^{2-}$  bands by comparing the far infrared spectrum of each  $M(\text{dmp})\text{SO}_4$  complex to the spectrum of the corresponding halide  $M(\text{dmp})\text{X}_2$ .

It is important to recognize that the far infrared spectrum of each of our  $M(\text{dmp})\text{SO}_4$  preparations ( $M = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) is the duplicate of Plowman's spectrum for the complex.

Plowman's far infrared spectra were recorded from  $M(\text{dmp})\text{SO}_4/\text{Nujol}$  or  $M(\text{dmp})\text{SO}_4/\text{hexachlorobutadiene}$  mulls; our spectra were recorded from compressed  $M(\text{dmp})\text{SO}_4/\text{KBr}$  pellets. Reproducing his results through our slightly dif-

ferent procedure means that our method does not introduce ambiguities by displacing  $\text{SO}_4^{2-}$  bands or by adding bands.

Moreover, the spectra of our  $M(\text{dmp})\text{SO}_4$  products ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) are so similar both to each other and to Plowman's spectra of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Fe}, \text{Co}, \text{Ni}$ ) that we can almost rule out the possibility of  $\text{H}_2\text{O}$  molecules being bonded to the metal cations in our preparations of  $\text{Mn}(\text{dmp})\text{SO}_4$  and  $\text{Ni}(\text{dmp})\text{SO}_4$ . The  $\text{H}_2\text{O}$  molecules present in our preparations do not seem to interfere at all with the bonding between the metal cations and the sulfate ions.

*Magnetic Susceptibilities and Electron Paramagnetic Resonance Spectra.* The results of our magnetization studies using the Faraday balance on the  $M(\text{dmp})\text{SO}_4$  compounds ( $M = \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ ) at temperatures between 1.5 and 305 K and in an applied field of 5.1 kG are displayed in Figs. 3 through 6. The results for  $\text{Fe}(\text{dmp})\text{SO}_4$  have already been published (15).

Table II is a summary of the magnetic behavior of each paramagnetic  $M(\text{dmp})\text{SO}_4$  complex studied so far ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ). The magnetic moment at ambient temperature  $\mu_{300}$  reported in Table II, like the magnetic moments plotted in Figs. 3b,

TABLE II  
MAGNETIC CHARACTERISTICS FOR  $M(\text{dmp})\text{SO}_4$

$M$	$\mu_{\text{s.o.}}$ ( $\beta$ )	$\mu_{300}^a$ ( $\beta$ )	$\mu_{\text{eff}}^b$	$C$ ( $\frac{\text{emu} \cdot \text{K}}{\text{mole}}$ )	$\theta$ (K)	$T_{\text{low}}$ (K)	$T(\text{max-}\chi, 1\text{-D})$ (K)	$10^3 \times \text{max-}\chi$ ( $\frac{\text{emu}}{\text{mole}}$ )
Mn	5.92	5.72	5.78	4.18	-12.8	50	$3.2 \pm 0.5$	206.
Fe <sup>c</sup>	4.90	4.98	5.11	3.26	-22.0	55	$11.1 \pm 1.0$	79.1
Co	3.87	5.20	5.09	3.23	-44.8	60	$15.6 \pm 2.0$	55.2
Ni	2.83	3.04	3.39	1.44	-46.3	80	$25.2 \pm 5.0$	15.8
Cu	1.73	1.81	1.91	0.455	-0.838	~0	— <sup>d</sup>	— <sup>d</sup>

<sup>a</sup>  $\mu_{300} = 2.828\sqrt{\chi'_M \cdot T}$  where  $\chi'_M$  is the corrected molar magnetic susceptibility of the compound at  $T \approx 300$  K.

<sup>b</sup>  $\mu_{\text{eff}} = 2.828\sqrt{C}$  where  $C$  is obtained from a least-squares fit of the reciprocal form of the Curie-Weiss law to the results obtained at temperatures between 70 and 310 K.

<sup>c</sup> Reference (15).

<sup>d</sup> No broad maximum was observed in the  $\chi'_M$ -vs- $T$  curve for  $\text{Cu}(\text{dmp})\text{SO}_4$  at any temperature between 1.78 and 304 K.

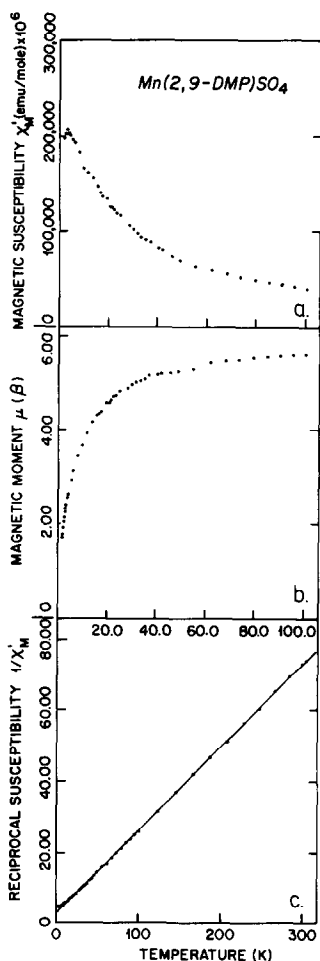


FIG. 3. Plots of (a)  $\chi'_M$  vs  $T$ , (b)  $\mu$  vs  $T$ , and (c)  $(\chi'_M)^{-1}$  vs  $T$  for  $\text{Mn}(\text{dmp})\text{SO}_4$  with  $H_0 = 5.1$  kG.

4b, 5b, and 6b, was calculated from the expression  $\mu(T) = 2.828\sqrt{\chi'_M \cdot T}$  where  $\chi'_M$  is the corrected molar magnetic susceptibility of the compound at a particular temperature. In contrast, the effective magnetic moment  $\mu_{\text{eff}}$  given in Table II was computed from the expression  $\mu_{\text{eff}} = 2.828\sqrt{C}$  where  $C$  is the Curie constant in the Curie-Weiss law  $\chi'_M = C/(T - \theta)$ . The Curie constant  $C$  and the paramagnetic Curie temperature  $\theta$  were obtained from a least-squares fit of the reciprocal form  $1/\chi'_M = (T - \theta)/C$  of the Curie-Weiss law to the corrected molar magnetic susceptibility-vs-temperature

$(\chi'_M$ -vs- $T)$  results. For greater reliability, the data for the fit were obtained from a large sample of each complex (ranging from  $\sim 11$  mg for the Mn complex to  $\sim 29$  mg for the Cu complex) at temperatures between 70 and 310 K, that is, over a temperature range for which there is little doubt that the magnetic behavior of each complex conforms to the Curie-Weiss law (see reciprocal susceptibility plots in Figs. 3c, 4c, 5c, and 6c).  $T_{\text{low}}$  in Table II is the lowest temperature to which this fit could be extended.

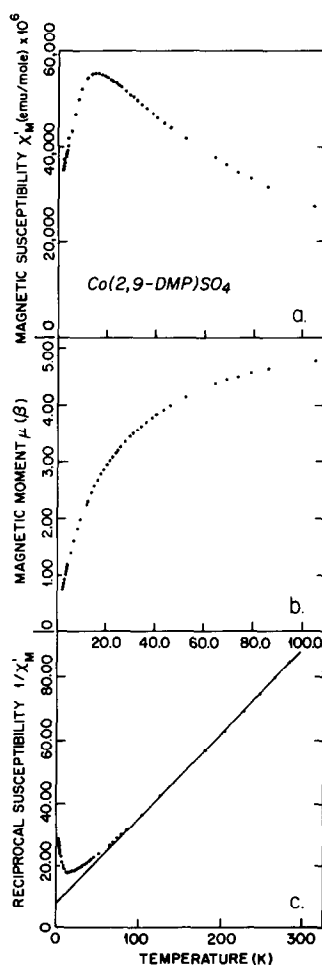


FIG. 4. Plots of (a)  $\chi'_M$  vs  $T$ , (b)  $\mu$  vs  $T$ , and (c)  $(\chi'_M)^{-1}$  vs  $T$  for  $\text{Co}(\text{dmp})\text{SO}_4$  with  $H_0 = 5.1$  kG.

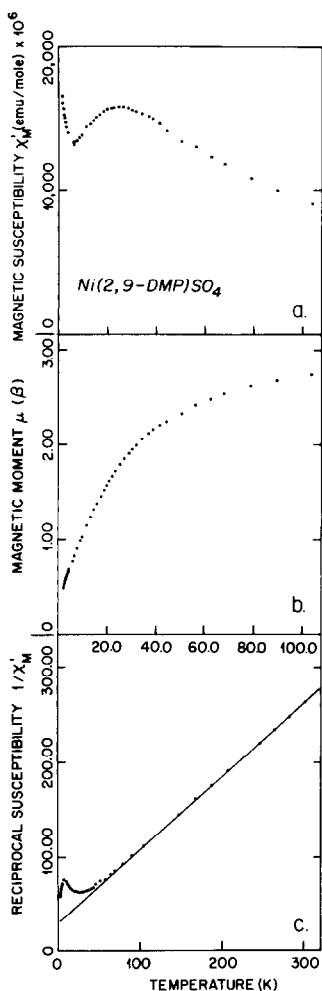


FIG. 5. Plots of (a)  $\chi'_M$  vs  $T$ , (b)  $\mu$  vs  $T$ , and (c)  $(\chi'_M)^{-1}$  vs  $T$  for  $\text{Ni}(\text{dmp})\text{SO}_4$  with  $H_0 = 5.1$  kG.

The magnitudes of the magnetic moments indicate that the  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) are high-spin complexes. It is also evident that there is a substantial orbital contribution to the magnetic moment of  $\text{Co}(\text{dmp})\text{SO}_4$  while there are smaller contributions in the cases of the Cu, the Ni, and the Fe complexes.

The magnetic susceptibilities of each  $M(\text{dmp})\text{SO}_4$  complex ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ) at temperatures between 2 and 300 K remain independent of the applied field  $H_0$

over the range  $1.7 \text{ kG} \leq H_0 \leq 5.1 \text{ kG}$  (the range that we customarily cover when we use the Faraday balance to measure magnetic susceptibilities). Stronger fields will be needed to induce transitions from one magnetic phase to another as in metamagnetism or spin-flop behavior.

The magnetic behavior of each  $M(\text{dmp})\text{SO}_4$  complex in group A ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) includes the three hallmarks of one-dimensional, antiferromagnetic interactions. First, the corrected molar mag-

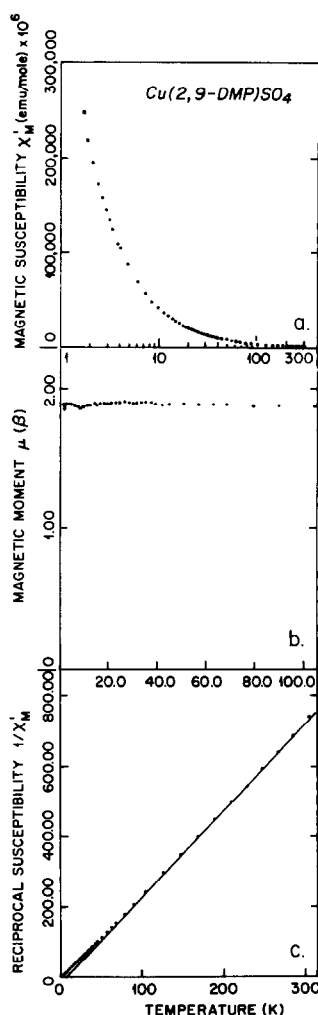


FIG. 6. Plots of (a)  $\chi'_M$  vs  $T$ , (b)  $\mu$  vs  $T$ , and (c)  $(\chi'_M)^{-1}$  vs  $T$  for  $\text{Cu}(\text{dmp})\text{SO}_4$  with  $H_0 = 5.1$  kG.

netic susceptibility-vs-temperature ( $\chi'_M$ -vs- $T$ ) curve for each complex passes through a broad maximum at low temperatures ( $T < 30$  K). Second, the magnetic moment  $\mu$  for each complex decreases steadily as the temperature is lowered, with the decrease being noticeable at temperatures well above  $T(\max-\chi, 1-D)$ , the absolute temperature at which the broad maximum in the  $\chi'_M$ -vs- $T$  curve occurs. Third, the paramagnetic Curie temperature  $\theta$  for each complex is negative.

The fact that  $T_{low}$ , the lowest temperature to which the least-squares fit of the reciprocal form of the Curie-Weiss law could be extended (Table II), is  $>3$  times  $T(\max-\chi, 1-D)$  for  $M(dmp)SO_4$  ( $M = Mn, Fe, Co, Ni$ ) indicates that the antiferromagnetic interactions in each of these complexes are rather strong.

One-dimensional, antiferromagnetic interactions are observed in all of the  $M(dmp)SO_4$  complexes in group A ( $M = Mn, Fe, Co, Ni$ ) but not in  $Cu(dmp)SO_4$ , the paramagnetic complex in group B ( $M = Cu, Zn$ ). The  $\chi'_M$ -vs- $T$  curve for  $Cu(dmp)SO_4$  does not pass through any maximum for temperatures between 1.78 and 305 K; the magnetic moment  $\mu$  for this complex at these temperatures remains nearly constant at a value slightly greater than the spin-only value  $\sqrt{3}$ , and the paramagnetic Curie temperature  $\theta$  is almost zero.  $Cu(dmp)SO_4$  exhibits nearly perfect Curie-Weiss paramagnetism.

Comparing Fig. 6 to Fig. 3, we infer that the magnetic interactions in  $Cu(dmp)SO_4$  are weaker than the interactions in  $Mn(dmp)SO_4$ . The electron paramagnetic resonance spectra of these complexes (Fig. 7) support this inference. Apparently dipolar interactions present in  $Mn(dmp)SO_4$  broaden the EPR transitions enough that they overlap each other and produce one wide, featureless absorption (at  $\bar{g} \approx 2.029 \pm 0.006$ ) with low  $S/N$  (Fig. 7a). Though recorded with about one-third of the gain

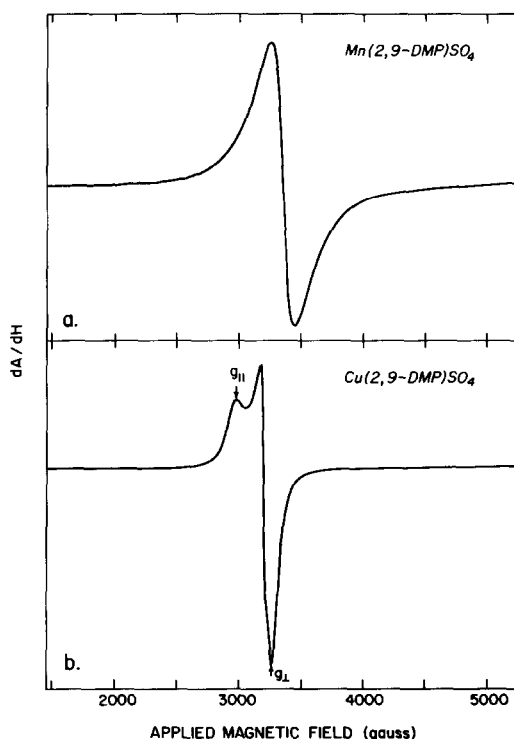


FIG. 7. X-band EPR spectra of (a)  $Mn(dmp)SO_4$  and (b)  $Cu(dmp)SO_4$  at  $T \approx 296$  K.

required for the spectrum of  $Mn(dmp)SO_4$ , the EPR spectrum of  $Cu(dmp)SO_4$  is more resolved (Fig. 7b). The two, readily distinguishable  $g$  values that we obtain for  $Cu(dmp)SO_4$  at  $T \approx 296$  K ( $g_{||} \approx 2.284 \pm 0.019$  and  $g_{\perp} \approx 2.082 \pm 0.016$ ) agree well with the values published before (19) and differ little from the  $g$  values recorded for the related sulfate complexes  $Cu(2,2'$ -bipyridine) $(H_2O)_2SO_4$  ( $g_{||} \approx 2.30$  and  $g_{\perp} \approx 2.07$ ) (20) and  $(N_2H_5)_2Cu(SO_4)_2$  ( $g_{||} \approx 2.33$  and  $g_{\perp} \approx 2.08$ ) (21).

## Discussion

**Proposed Molecular Structures.** By various spectroscopic methods, researchers have uncovered clues concerning the molecular structures of  $M(dmp)SO_4$  ( $M = Cu, Co, Fe$ ). The EPR spectrum of neat

$\text{Cu(dmp)SO}_4$  at  $T \approx 296$  K shows that this complex is a tetragonally elongated, pseudooctahedral  $\text{Cu}^{2+}$  complex (19, 22; 23, p. 912). The visible spectrum of  $\text{Co(dmp)SO}_4$  is consistent with an octahedral  $\text{Co}^{2+}$  complex like  $\text{Co(H}_2\text{O)}_6^{2+}$  (13). The isomer shift and the quadrupole splitting of the Mössbauer spectrum of  $\text{Fe(dmp)SO}_4$  at  $T \approx 296$  K indicate that the compound contains a high-spin, pseudooctahedral  $\text{Fe(II)N}_2\text{O}_4$  chromophore (15). It is quite likely that the metal sites in each member of the  $M(\text{dmp})\text{SO}_4$  series ( $M = \text{Mn, Fe, Co, Ni, Cu, Zn}$ ) are pseudooctahedral *cis*- $\text{MN}_2\text{O}_4$  chromophores and that each oxygen of every sulfate anion is consequently bonded to a metal  $M$ .

Among the techniques by which researchers try to distinguish a *chelating* sulfate from a *bridging* sulfate is far infrared spectroscopy. Evidence is accumulating (24) that at least one of the absorption bands in the spectrum of the chelating sulfate (but not the bridging sulfate) occurs at a frequency  $\tilde{\nu} > 1200$   $\text{cm}^{-1}$ .

Two of the bands attributed to the  $\text{SO}_4^{2-}$  ligand in either  $M(\text{dmp})\text{SO}_4$  complex in *group B* ( $M = \text{Cu or Zn}$ ) occur at frequencies  $> 1200$   $\text{cm}^{-1}$ . In contrast, every  $\text{SO}_4^{2-}$  band in the far infrared spectrum of each  $M(\text{dmp})\text{SO}_4$  complex in *group A* ( $M = \text{Mn, Fe, Co, Ni}$ ) occurs at a frequency  $\tilde{\nu} < 1200$   $\text{cm}^{-1}$ .

Plowman and co-workers (14) concluded that the molecular structure of the  $M(\text{dmp})\text{SO}_4$  complexes in *group A* ( $M = \text{Fe, Co, Ni}$ ; we now add  $M = \text{Mn}$ ) is probably a polymeric network comprised of *cis*- $\text{MN}_2\text{O}_4$  chromophores and *bridging*  $\text{SO}_4^{2-}$  ligands.

But we find two objections to the structure that Plowman proposed for *group A*.

The first objection is steric hindrance. If there are just *bridging*  $\text{SO}_4^{2-}$  ligands and *cis*- $\text{MN}_2\text{O}_4$  chromophores in the molecular structure of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni}$ ), then no two oxygens of a  $\text{SO}_4^{2-}$  ligand

are bonded to the same metal  $M$ , and there must consequently be four different sulfates attached to each metal center. We have made many attempts to build such a structure from molecular models, and every attempt has demonstrated that the four sulfates crowd each other so much that the polymeric network cannot be extended beyond a single *cis*- $\text{MN}_2\text{O}_4$  center.

The second objection is the upper limit ( $T \approx 30$  K) of the temperatures at which the broad maximum in the  $\chi'_M$ -vs- $T$  curve occurs for each  $M(\text{dmp})\text{SO}_4$  complex in *group A* ( $M = \text{Mn, Fe, Co, Ni}$ ). If a polymeric network of *cis*- $\text{MN}_2\text{O}_4$  chromophores and bridging  $\text{SO}_4^{2-}$  ligands is possible for these complexes, then the effects of the resulting magnetic interactions are expected to appear at higher temperatures ( $T > 50$  K). For example, the molecular structures of  $\text{Fe(III)ClMoO}_4$  and  $\text{LiFe(II)ClMoO}_4$  are polymeric, layerlike networks; the interactions in either of these compounds cause a broad maximum at  $T > 70$  K (7, 8).

After many tries with molecular models, we are convinced that the most reasonable molecular structure for the  $M(\text{dmp})\text{SO}_4$  complexes in *group A* ( $M = \text{Mn, Fe, Co, Ni}$ ) is the *chainlike* polymer that Plowman and co-workers (14) proposed for the  $M(\text{dmp})\text{SO}_4$  complexes in *group B* ( $M = \text{Cu, Zn}$ ): a molecular structure comprised of *cis*- $\text{MN}_2\text{O}_4$  chromophores and *bridging-chelating*  $\text{SO}_4^{2-}$  ligands. We present a sketch of this chainlike polymer in the left half of Fig. 8. (The axis of the chain may be zig-zag. Strain in the model is relieved if the chain is allowed to contract like a stored accordion.)

This linear structure favors the one-dimensional, magnetic interactions seen in  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni}$ ), that is, interactions that produce a broad maximum in the  $\chi'_M$ -vs- $T$  curve at  $T < 30$  K. We suspect that the distances between metal sites  $M$  in this structure are too large (4.6–6.7 Å) for direct magnetic exchange to occur. The



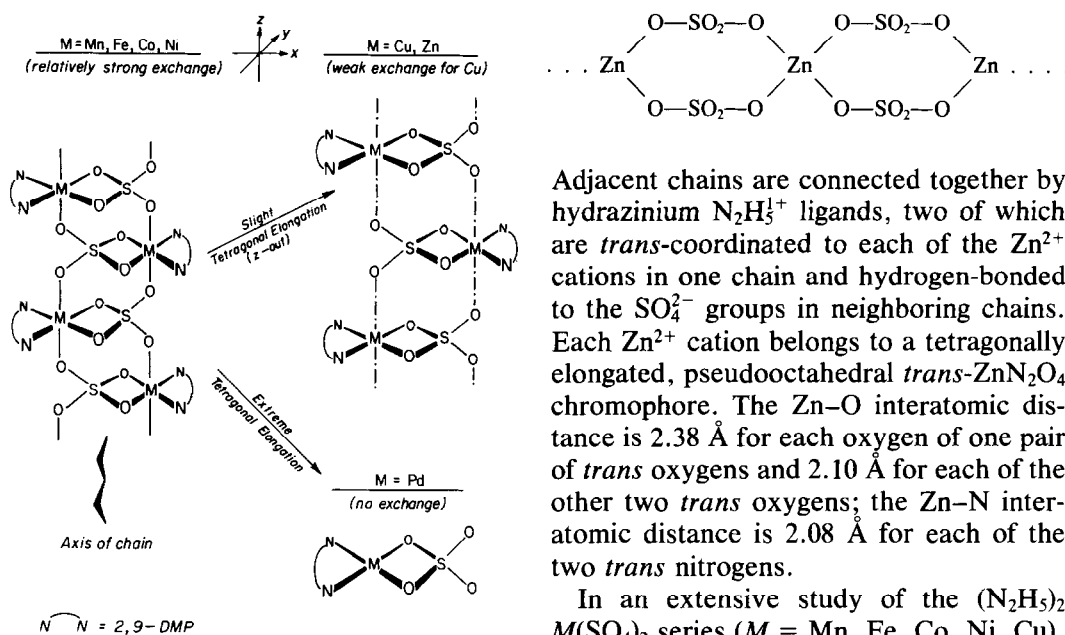


FIG. 8. Proposed molecular structures for  $M(\text{dmp})\text{SO}_4$ , where  $M = \text{Mn, Fe, Co, Ni, Cu, Zn, and Pd}$ .

one-dimensional, antiferromagnetic interactions occur instead by *superexchange* through the sulfate bridges ( $M\text{--O--S--O--M}$ ) that run approximately parallel to the axis of the chain.

Similar bridges are known to exist in the molecular structures of the chainlike complexes  $M(2,2'\text{-bipyridine})(\text{H}_2\text{O})_2\text{SO}_4$  ( $M = \text{Fe, Ni, Cu}$ ) (1, 20) and  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  ( $M = \text{Cr, Mn, Fe, Co, Ni, Cu, Zn}$ ) (21, 25, 26), and a broad maximum indicating one-dimensional antiferromagnetic interactions has been observed in the  $\chi'_M\text{--vs--}T$  curve of most of these complexes at  $T < 30\text{ K}$  (1, 27).

Prout and Powell (25) used X-ray crystallography to determine the molecular structure of the Zn member of the  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  series. The chainlike structure is comprised of  $\text{Zn}^{2+}$  cations, each cation joined to the next in the chain by two bridging  $\text{SO}_4^{2-}$  ligands:

Adjacent chains are connected together by hydrazinium  $\text{N}_2\text{H}_5^+$  ligands, two of which are *trans*-coordinated to each of the  $\text{Zn}^{2+}$  cations in one chain and hydrogen-bonded to the  $\text{SO}_4^{2-}$  groups in neighboring chains. Each  $\text{Zn}^{2+}$  cation belongs to a tetragonally elongated, pseudooctahedral *trans*- $\text{ZnN}_2\text{O}_4$  chromophore. The Zn–O interatomic distance is 2.38 Å for each oxygen of one pair of *trans* oxygens and 2.10 Å for each of the other two *trans* oxygens; the Zn–N interatomic distance is 2.08 Å for each of the two *trans* nitrogens.

In an extensive study of the  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  series ( $M = \text{Mn, Fe, Co, Ni, Cu}$ ), Nieuwpoort and Reedijk (21) designated the X-ray powder diffraction patterns of  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  ( $M = \text{Mn, Fe, Co, Ni, Zn}$ ) as type A and the “slightly different” pattern of  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$  as type A'. In still other studies, Prout and co-workers (25, 26) found that  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$  produces an X-ray powder diffraction pattern that is very similar to the pattern of  $(\text{N}_2\text{H}_5)_2\text{Cr}(\text{SO}_4)_2$  and that the electronic configuration of the latter complex is high-spin  $3d^4$ . Both of these  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  complexes ( $M = \text{Cr, Cu}$ ) are expected to undergo substantial tetragonal elongation because of the Jahn–Teller effect inherent to the  $t_{2g}^3e_g^1$  and the  $t_{2g}^6e_g^3$  configurations (23, p. 836; 23, p. 912). Concurring with earlier researchers (21, 26), we think that all of the members of the  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  series ( $M = \text{Cr, Mn, Fe, Co, Ni, Cu, Zn}$ ) have the same molecular structure and that  $(\text{N}_2\text{H}_5)_2\text{Cr}(\text{SO}_4)_2$  and  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$  differ only slightly from the other complexes in the series by having undergone a greater amount of tetragonal elongation.

Tedenac and co-workers (20) used X-ray crystallography to determine the molecular

structures of the  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  complexes ( $M = \text{Ni}, \text{Cu}$ ;  $\text{bipy} = 2,2'$ -bipyridine). The two, very similar, chainlike structures are comprised of  $M^{2+}$  cations, each cation joined to the next in the chain by *one bridging*  $\text{SO}_4^{2-}$  ligand:  $M-\text{O}-\text{SO}_2-\text{O}-M-\text{O}-\text{SO}_2-\text{O}-M$ . Adjacent chains are connected together by  $\text{H}_2\text{O}$  ligands, two of which are *cis*-coordinated to each of the  $M^{2+}$  cations in one chain and hydrogen-bonded to the  $\text{SO}_4^{2-}$  groups in neighboring chains. Because the two nitrogens from the 2,2'-bipyridine ligand must be *cis*-coordinated to the  $M^{2+}$  cation, the pseudo-octahedral  $M\text{N}_2\text{O}_4$  chromophore in  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  resembles the *cis*- $M\text{N}_2\text{O}_4$  chromophore in  $M(\text{dmp})\text{SO}_4$  more than the *trans*- $M\text{N}_2\text{O}_4$  chromophore in  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  does. The molecular structures of the two  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  complexes ( $\text{Ni}, \text{Cu}$ ) are different from each other in that  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  has clearly undergone the *tetragonal elongation expected* because of the Jahn–Teller effect (20). The  $\text{Cu}-\text{O}$  interatomic distance for each of the *trans*-coordinated  $\text{SO}_4^{2-}$  ligands is longer by  $\sim 0.44 \text{ \AA}$  or  $\sim 22\%$  than the two  $\text{Cu}-\text{O}$  distances for each of the *cis*-coordinated  $\text{H}_2\text{O}$  ligands or the two  $\text{Cu}-\text{N}$  distances. In the  $\text{Ni}$  complex, this difference in interatomic distances is only  $\sim 4\%$ .

The X-ray powder diffraction patterns of  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  ( $M = \text{Fe}, \text{Ni}, \text{Cu}$ ) show that the three complexes are isomorphous, and the Mössbauer spectrum of  $\text{Fe}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  at  $T \approx 296 \text{ K}$  reveals that this complex contains *cis*- $\text{FeN}_2\text{O}_4$  chromophores (1).  $\text{Fe}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  almost certainly has the same molecular structure as  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  ( $M = \text{Ni}, \text{Cu}$ ) (1, 20).

The  $\chi'_M$ -vs- $T$  curves for two ( $M = \text{Fe}, \text{Ni}$ ) of the three  $M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  complexes studied so far at low temperatures and four ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) of the five  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  complexes studied contain a broad maximum at temperatures  $4 \text{ K} < T < 16 \text{ K}$  (1, 27). But the broad maximum for  $(\text{N}_2\text{H}_5)_2$

$\text{Cu}(\text{SO}_4)_2$  occurs at  $T \approx 2 \text{ K}$  (27) while the maximum for  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  does not appear at any temperature from 300 to as low as 1.7 K (1).

Tetragonal elongation makes intrachain magnetic interactions in  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$  weaker than the interactions in  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ) but not so weak as the interactions in  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$ . While there is just *one*  $\text{SO}_4^{2-}$  bridge linking each pair of  $\text{Cu}^{2+}$  cations in the chains of  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$ , there are *two*  $\text{SO}_4^{2-}$  bridges joining each pair of  $\text{Cu}^{2+}$  cations in the chains of  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$ ; tetragonal elongation stretches and weakens one *but not both* of these bridges.

$\text{Cu}(\text{dmp})\text{SO}_4$ , a  $\text{Cu}^{2+}$  complex like  $(\text{N}_2\text{H}_5)_2\text{Cu}(\text{SO}_4)_2$  and  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$ , is subject to the Jahn–Teller effect. The EPR spectrum of  $\text{Cu}(\text{dmp})\text{SO}_4$  (Fig. 7b) reveals that this complex, like the other  $\text{Cu}^{2+}$  complexes just cited, is tetragonally elongated (22). The strong resemblance between the  $\chi'_M$ -vs- $T$  curve (Fig. 6a) of  $\text{Cu}(\text{dmp})\text{SO}_4$  and the  $\chi'_M$ -vs- $T$  curve for  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  (1) suggests that the one-dimensional magnetic interactions in  $\text{Cu}(\text{dmp})\text{SO}_4$  are as weak as the interactions in  $\text{Cu}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$ . We think that all of the members of the  $M(\text{dmp})\text{SO}_4$  series ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ ) have essentially the same molecular structure and that tetragonal elongation of the *cis*- $\text{CuN}_2\text{O}_4$  chromophore makes the magnetic interactions in  $\text{Cu}(\text{dmp})\text{SO}_4$  weaker than the interactions in the other paramagnetic  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ ). We present in the upper right corner of Fig. 8 a sketch of the stretched and weakened chainlike polymer of  $\text{Cu}(\text{dmp})\text{SO}_4$ .

Extreme tetragonal elongation of each *cis*- $M\text{N}_2\text{O}_4$  chromophore in the  $M(\text{dmp})\text{SO}_4$  chain produces a lattice of monomeric, square-planar *cis*- $M\text{N}_2\text{O}_2$  complexes. A square-planar monomer (depicted in the lower right corner of Fig. 8) is just the molecular structure expected for a  $\text{Pd}^{2+}$  com-

plex (23, p. 1030) like Pd(dmp)SO<sub>4</sub>. It is no surprise that the far infrared spectra of Pd(dmp)SO<sub>4</sub> and Cu(dmp)SO<sub>4</sub> are very similar (28).

After reviewing the results accumulated so far through spectroscopic studies and magnetic studies of the *M*(dmp)SO<sub>4</sub> series, we strongly suspect that the X-ray powder diffraction pattern and the far infrared spectrum of Cu(dmp)SO<sub>4</sub> are different from the patterns and the spectra of *M*(dmp)SO<sub>4</sub> (*M* = Mn, Fe, Co, Ni) not because of different fundamental molecular structures but because of different packing arrangements within the lattices of the compounds.

*Intrachain exchange energies* (27, 29). The Heisenberg model is often an adequate description of magnetic interactions in Cu<sup>2+</sup> compounds. Bonner and Fisher (30) developed a theoretical model for *chainlike* compounds that exhibit the magnetic behavior of a Heisenberg system with spin  $S = \frac{1}{2}$ . In this model, the relation between the intrachain exchange energy  $J/k_B$  and the temperature  $T(\text{max-}\chi, 1\text{-D})$  at which the broad maximum in the  $\chi'_M$ -vs- $T$  curve appears is given by the following equation.

$$|J|/k_B = T(\text{max-}\chi, 1\text{-D})/1.282 \quad (1)$$

The  $\chi'_M$ -vs- $T$  curve for Cu(dmp)SO<sub>4</sub> does not contain at any temperature between 1.78 and 305 K and for any applied field between 1.7 and 5.1 kG the broad maximum characteristic of low-dimensional, antiferromagnetic interactions (Fig. 6a). If we assume that for Cu(dmp)SO<sub>4</sub> the temperature  $T(\text{max-}\chi, 1\text{-D}) < 1.8$  K, then by the preceding equation  $|J|/k_B < 1.4$  K; and if the interactions are antiferromagnetic, we need to consider only the negative values of  $J/k_B$ :  $0 > J/k_B > -1.4$  K. The intrachain exchange in Cu(dmp)SO<sub>4</sub> is about as strong as the exchange in Cu(bipy)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> for which  $J/k_B \approx -1$  K (1). Reedijk and co-workers (27) detected a "broad" maximum in the  $\chi'_M$ -vs- $T$  curve of (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub> at  $T \approx 2.1$  K; Klaaijzen and co-workers (31) found such a

maximum in the magnetic specific heat-vs-temperature ( $C_{\text{mag}}$ -vs- $T$ ) curve of this complex at  $T \approx 1.95$  K. These researchers consequently estimated that the exchange energy in this compound is  $\sim -1.9$  K. We list the estimated intrachain magnetic exchange energies for Cu(dmp)SO<sub>4</sub>, Cu(bipy)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub>, and (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub> in Table III.

The  $\chi'_M$ -vs- $T$  curve for Ni(dmp)SO<sub>4</sub> includes a broad maximum at  $T = 25.2 \pm 5.0$  K (Fig. 5a). The Heisenberg model often fits the magnetic behavior of Ni<sup>2+</sup> complexes also. Utilizing an interpolation scheme, Weng (32) built a set of theoretical models to describe the antiferromagnetic Heisenberg exchange in chainlike or linear complexes with spin  $S = \frac{1}{2}, 1, \frac{3}{2}, 2,$  or  $\frac{5}{2}$ . In Weng's model for spin  $S = 1$ , the intrachain exchange energy  $J/k_B$  and the temperature  $T(\text{max-}\chi, 1\text{-D})$  where the broad maximum appears are related by the following equation.

$$|J|/k_B = T(\text{max-}\chi, 1\text{-D})/2.7 \quad (2)$$

Inserting  $T(\text{max-}\chi, 1\text{-D}) = 25.2 \pm 5.0$  K into this equation, we compute  $|J|/k_B = 9.3 \pm 1.9$  K; to indicate that the magnetic interactions are antiferromagnetic, we add a negative sign to the estimated energy:  $J/k_B = -9.3 \pm 1.9$  K. The intrachain magnetic exchange in Ni(dmp)SO<sub>4</sub> is much stronger than the exchange in either Ni(bipy)(H<sub>2</sub>O)<sub>2</sub>SO<sub>4</sub> (1) or (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Ni(SO<sub>4</sub>)<sub>2</sub> (27) where  $J/k_B \approx -3$  K (Table III).

We neglect the influence of single-ion zero-field splitting on the magnetic susceptibility of Ni(dmp)SO<sub>4</sub> despite the fact that in Ni<sup>2+</sup> complexes this splitting can be significant (33, pp. 65, 205). Examining how the magnetic specific heat of Ni(dmp)SO<sub>4</sub> varies with temperature will reveal the strength of the zero-field splitting, but this study must be completed in another laboratory, one equipped with the needed instruments. The magnetic moment  $\mu$  of Ni(dmp)SO<sub>4</sub> decreases gradually but stead-

TABLE III  
INTRACHAIN MAGNETIC EXCHANGE ENERGIES  $J/k_B$  FOR  $M(\text{dmp})\text{SO}_4$  AND RELATED METAL SULFATE COMPLEXES

$M$	$M(\text{dmp})\text{SO}_4$				
	$J/k_B$ from $T(\text{max-}\chi, 1\text{-D})$ (K)	$J/k_B$ from reduced-spin plot (K)	Estimated $J/k_B$ (K)	$(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2^a$ Estimated $J/k_B$ (K)	$M(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4^b$ Estimated $J/k_B$ (K)
Mn	$-0.36 \pm 0.06^c$	$-0.86 \pm 0.02$	$\sim -0.6$	-0.55	Not studied
Fe	$-1.5 \pm 0.1$	$-2.2 \pm 0.7$	$\sim -2.$	-2.5	-1.0
Co	$-3.3 \pm 0.4^d$	$-5.9 \pm 0.2$	$\sim -5.$	-7. <sup>e</sup>	Not studied
Ni	$-9.3 \pm 1.9$	$-11.5 \pm 0.4$	$\sim -10.$	-3.3	-3.1
Cu	$\sim 1$	$\sim 0$	$\sim -0.5$	-1.9	$\sim -1$

<sup>a</sup> Reference (27).

<sup>b</sup> Reference (1).

<sup>c</sup>  $J/k_B$  computed from  $\bar{g}$  and  $\text{max-}\chi$  is  $-0.733 \pm 0.021$  K.

<sup>d</sup>  $J/k_B$  computed by either Heisenberg model ( $S = \frac{3}{2}$ ) or Ising model ( $S = \frac{3}{2}$ ).

<sup>e</sup>  $J/k_B$  obtained by models with  $S = \frac{1}{2}$ ; see Ref. (27).

ily from  $3.04 \beta$  at  $T \approx 302$  K to  $0.50 \beta$  at  $T \approx 1.86$  K, and this gradual, steady decrease evident at  $T \gg T(\text{max-}\chi, 1\text{-D})$  leads us to conclude for now that the zero-field splitting in this compound is small compared to the antiferromagnetic interactions.

The  $\chi'_M$ -vs- $T$  curve for  $\text{Co}(\text{dmp})\text{SO}_4$  contains a broad maximum at  $T = 15.6 \pm 2.0$  K (Fig. 4a). In Weng's model (32) for a linear antiferromagnetic Heisenberg system with spin  $S = \frac{3}{2}$ , the exchange energy  $J/k_B$  and the temperature  $T(\text{max-}\chi, 1\text{-D})$  are related by the following equation.

$$|J|/k_B = T(\text{max-}\chi, 1\text{-D})/4.75 \quad (3)$$

Substituting  $T(\text{max-}\chi, 1\text{-D}) = 15.6 \pm 2.0$  K into this equation, we calculate  $|J|/k_B = 3.28 \pm 0.42$  K, and because the interactions are antiferromagnetic, we make this number negative:  $J/k_B = -3.28 \pm 0.42$  K. The magnetic exchange in many  $\text{Co}^{2+}$  compounds, however, is too anisotropic to be represented by a Heisenberg model. Researchers then resort to an Ising model (27). The following equation relating  $J/k_B$  to  $T(\text{max-}\chi_{\parallel}, 1\text{-D})$  is taken from the theoretical model that Suzuki and co-workers (34) de-

veloped for a linear antiferromagnetic Ising system with spin  $S = \frac{3}{2}$ .

$$|J|/k_B = T(\text{max-}\chi_{\parallel}, 1\text{-D})/4.70 \quad (4)$$

With  $T(\text{max-}\chi, 1\text{-D}) = 15.6 \pm 2.0$  K and this equation, we obtain  $J/k_B = -3.32 \pm 0.43$  K as an estimate of the exchange energy in the case where  $\text{Co}(\text{dmp})\text{SO}_4$  is considered to be an antiferromagnetic Ising system.

We must recognize (27) that while the equation for a Heisenberg system gives  $|J|/k_B$  as a function of  $T(\text{max-}\chi_{\text{avg}}, 1\text{-D})$ , the equation for an Ising system makes  $|J|/k_B$  a function of  $T(\text{max-}\chi_{\parallel}, 1\text{-D})$ . The  $\chi'_M$ -vs- $T$  curve from a powder sample is actually an average of both  $\chi_{\parallel}$ , the magnetic susceptibility that is parallel to the direction of spin alignment, and  $\chi_{\perp}$ , the susceptibility that is perpendicular to this direction.

$$\chi_{\text{avg}} = \frac{1}{3}\chi_{\parallel} + \frac{2}{3}\chi_{\perp} \quad (5)$$

For our estimate, we ignore the contribution of  $\chi_{\perp}$  to  $\chi_{\text{avg}}$ , and we use  $T(\text{max-}\chi_{\text{avg}}, 1\text{-D}) = 15.6 \pm 2.0$  K instead of  $T(\text{max-}\chi_{\parallel}, 1\text{-D})$ . The antiferromagnetic exchange energy to be calculated from  $T(\text{max-}\chi_{\parallel}, 1\text{-D})$  and Suzuki's equation for an Ising system is

probably even stronger than our estimate (that is, even  $< -3.3$  K) because for a chainlike antiferromagnet  $T(\max-\chi_{\parallel}, 1-D)$  is typically greater than  $T(\max-\chi_{\perp}, 1-D)$  (35). In Table III we present the intrachain exchange energy calculated (roughly) by the Ising model and the intrachain exchange energy calculated by the Heisenberg model: by either model,  $J/k_B = -3.3 \pm 0.4$  K for  $\text{Co}(\text{dmp})\text{SO}_4$ .

We emphasize that in both estimates, we used equations taken from models designed for systems with spin  $S = \frac{3}{2}$ . Some  $\text{Co}^{2+}$  compounds, however, exhibit at low temperatures an effective spin or pseudospin  $S' = \frac{1}{2}$  (33, p. 69) rather than the value  $S = \frac{3}{2}$  expected for a high-spin  $3d^7$  configuration. Studies of the magnetic specific heat of  $(\text{N}_2\text{H}_5)_2\text{Co}(\text{SO}_4)_2$ , for example, showed that this complex at  $T < 50$  K does indeed have an effective spin  $S' = \frac{1}{2}$  (27, 31). Lacking such information for  $\text{Co}(\text{dmp})\text{SO}_4$ , we choose to employ just the mathematical models available for spin  $S = \frac{3}{2}$ .

High-spin  $\text{Fe}^{2+}$  complexes like  $\text{Fe}(\text{dmp})\text{SO}_4$  often exhibit a magnetic behavior that is best represented by a model intermediate between the Heisenberg model and the Ising model. Not having such a model, we will follow the strategy of Witteveen and Reedijk (27). We will apply to our data first the equation derived from a Heisenberg model and then the equation derived from an Ising model; finally, we will take the mean of the two exchange energies as our estimate for  $\text{Fe}(\text{dmp})\text{SO}_4$ . In Weng's model (32) for an antiferromagnetic Heisenberg system with spin  $S = 2$ ,  $J/k_B$  and  $T(\max-\chi, 1-D)$  are related by the following equation

$$|J|/k_B = T(\max-\chi, 1-D)/6.9 \quad (6)$$

With  $T(\max-\chi, 1-D) = 11.1 \pm 1.0$  K and this equation, we obtain  $J/k_B = -1.6 \pm 0.2$  K for  $\text{Fe}(\text{dmp})\text{SO}_4$  considered as a Heisenberg antiferromagnet. Witteveen and Reedijk (27) derived an equation relating  $J/k_B$  to

$T(\max-\chi_{\parallel}, 1-D)$  for an antiferromagnetic Ising system with  $S = 2$ .

$$|J|/k_B = T(\max-\chi_{\parallel}, 1-D)/7.5 \quad (7)$$

With  $T(\max-\chi_{\text{avg}}, 1-D) = 11.1 \pm 1.0$  K and this equation, we obtain  $J/k_B = -1.5 \pm 0.1$  K for  $\text{Fe}(\text{dmp})\text{SO}_4$  considered as an Ising antiferromagnet. This approximation contains the error that we tolerated in applying the Ising model to the data for  $\text{Co}(\text{dmp})\text{SO}_4$ : that is, we are using  $T(\max-\chi_{\text{avg}}, 1-D)$  recorded from a powder sample rather than  $T(\max-\chi_{\parallel}, 1-D)$  to be gained from a suitable single crystal. The mean of our two estimates for  $\text{Fe}(\text{dmp})\text{SO}_4$  is  $J/k_B = -1.5 \pm 0.1$  K. The intrachain antiferromagnetic exchange in  $\text{Fe}(\text{dmp})\text{SO}_4$  is about as strong as the exchange in  $\text{Fe}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$  where  $J/k_B \approx -1$  K (1) but weaker than the exchange in  $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$  where  $J/k_B \approx -2.5$  K (27) (Table III).

We apply just the Heisenberg model to our results for  $\text{Mn}(\text{dmp})\text{SO}_4$  because the magnetic interactions in high-spin  $\text{Mn}^{2+}$  compounds are usually isotropic. We can benefit from two separate models for an antiferromagnetic Heisenberg chain with spin  $S = \frac{5}{2}$ . In one model, developed by Friedberg and co-workers (36) through a scaling method, the intrachain exchange energy  $J/k_B$  and the temperature  $T(\max-\chi, 1-D)$  are related by the following equation.

$$|J|/k_B = T(\max-\chi, 1-D)/8.2 \quad (8)$$

With  $T(\max-\chi, 1-D) = 3.25 \pm 0.50$  K (Fig. 3a) and this equation, we obtain  $J/k_B = -0.40 \pm 0.06$  K. Like the mathematical models cited before in this section, Friedberg's model includes another equation, which relates the exchange energy  $J/k_B$  to  $\max-\chi$ , the highest value that the corrected molar magnetic susceptibility  $\chi'_M$  reaches along the broad maximum in the  $\chi'_M$ -vs- $T$  curve.

$$|J|/k_B = [0.1004 N g^2 \beta^2] / [(\max-\chi) k_B] \quad (9)$$

In this equation,  $N$  is Avogadro's number;

$g$  is the spectroscopic splitting factor;  $\beta$  is the Bohr magneton; and  $k_B$  is Boltzmann's constant. Inserting into Eq. (9)  $\bar{g} = 2.029 \pm 0.006$  from the EPR spectrum of  $\text{Mn}(\text{dmp})\text{SO}_4$  at  $T \approx 296$  K and  $\text{max-}\chi = 0.206 \pm 0.005$  emu/mole from our measurements with the Faraday balance, we find  $J/k_B = -0.754 \pm 0.005$  K. Weng (32) with his interpolation scheme developed a slightly different model with another pair of equations.

$$|J|/k_B = T(\text{max-}\chi, 1-D)/9.8 \quad (10)$$

$$|J|/k_B = [0.0949 N g^2 \beta^2] / [(\text{max-}\chi) k_B] \quad (11)$$

By these two equations, we calculate  $J/k_B = -0.33 \pm 0.05$  K and  $J/k_B = -0.712 \pm 0.004$  K respectively. As the results obtained by Weng's equations are close to the results obtained by Friedberg's equations, we present in Table III the mean ( $J/k_B = -0.36 \pm 0.06$  K) of the two values computed from  $T(\text{max-}\chi, 1-D)$  and the mean ( $J/k_B = -0.733 \pm 0.021$  K) of the two values computed from  $\bar{g}$  and  $\text{max-}\chi$ .

Another way to estimate the energy of intrachain magnetic exchange in a one-dimensional molecular structure is the "reduced-spin" model that Emori and co-workers applied to a group of chainlike complexes  $[\text{Cat}]_2\text{MnF}_5$  ( $\text{Cat} = \text{Li}, \text{Na}, \text{NH}_4$ ) (37). The conventional exchange energy  $J/k_B$  is calculated from the "reduced-spin" exchange energy  $J_{rs}/k_B$  by the following equation.

$$J/k_B = \{3/[4S(S+1)]\} \{J_{rs}/k_B\} \quad (12)$$

The "reduced-spin" exchange energy  $J_{rs}/k_B$  can be obtained through the use of the following equation.

$$\chi'_M = [N g^2 \beta^2 S(S+1) / (3k_B T)] \exp(J_{rs}/k_B T) \quad (13)$$

The quantities  $N$ ,  $g$ ,  $\beta$ , and  $k_B$  in this equation are defined as they were for Eq. (9) above; the quantity  $S$  is the total amount of spin angular momentum due to the un-

paired electrons at each metal center. If the "reduced-spin" model fits the  $\chi'_M$ -vs- $T$  results, a plot of each ordinate  $y = \ln[(3k_B T \chi'_M)/(N \beta^2)]$  against the corresponding abscissa  $x = 1/T$  will produce a straight line with slope  $m = J_{rs}/k_B$ .

The "reduced-spin" plots for  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn}, \text{Co}, \text{Ni}$ ) are shown in Fig. 9. The fits for these complexes are satisfactory, although deviations occur at  $T > 200$  K. The conventional intrachain exchange energies  $J/k_B$  obtained from the "reduced-spin" model compare favorably with the energies computed by the other models (Table III).

We must note that a spin-only model like

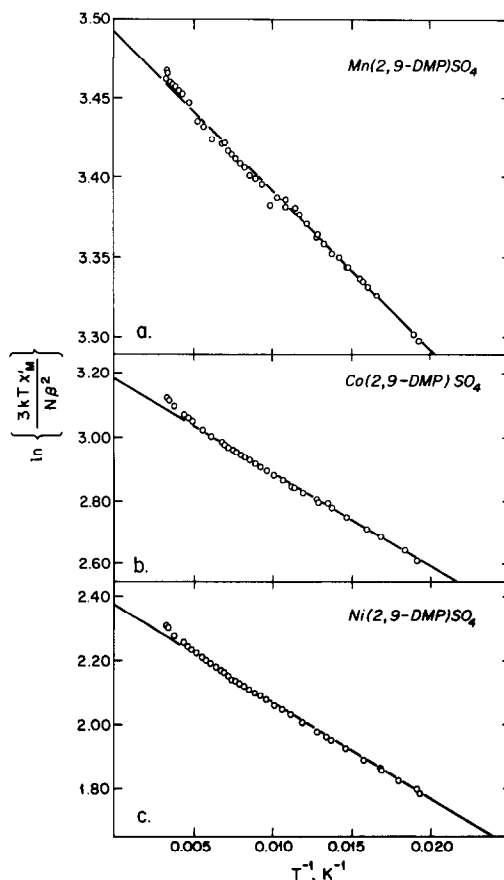


FIG. 9. Reduced-spin plots for (a)  $\text{Mn}(\text{dmp})\text{SO}_4$ , (b)  $\text{Co}(\text{dmp})\text{SO}_4$ , and (c)  $\text{Ni}(\text{dmp})\text{SO}_4$  at  $50 \text{ K} < T < 305 \text{ K}$  and for  $H_0 = 5.1 \text{ kG}$ .

the "reduced-spin" model neglects the orbital contribution to the magnetic behavior of a complex. A spin-only model works well for  $\text{Mn(dmp)SO}_4$  because the  ${}^6A$  ground state of a high-spin  $\text{Mn}^{2+}$  complex lacks an orbital contribution ( $\vec{L} = 0$ ; see Table II). A spin-only model works for high-spin  $\text{Ni}^{2+}$  complexes like  $\text{Ni(dmp)SO}_4$  because of their  ${}^3A$  ground state. But we did not anticipate the success of the "reduced-spin" plot for  $\text{Co(dmp)SO}_4$ . The  ${}^4T$  ground state of high-spin  $\text{Co}^{2+}$  is nominally octahedral symmetry is expected to have an orbital contribution, and the high values of the magnetic moment for  $\text{Co(dmp)SO}_4$  (Table II) do indicate that the orbital contribution is significant (spin-only moment  $\approx 3.87 \beta$ ) at the temperatures considered in the "reduced-spin" plot ( $50 \text{ K} < T < 305 \text{ K}$ ).

The "reduced-spin" plots for  $\text{Fe(dmp)SO}_4$  with a  ${}^5A$  or  ${}^5B$  ground state (15) and for  $\text{Cu(dmp)SO}_4$  with a  ${}^2E$  or more likely a  ${}^2A$  ground state are for some reason very poor. We can consequently take just slight comfort from the fact that for  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Fe}, \text{Cu}$ ) the exchange energy  $J/k_B$  obtained through the "reduced-spin" model does not differ much from our other estimates (Table III).

*Interchain exchange and three-dimensional (3-D) Antiferromagnet ordering in  $\text{Fe(dmp)SO}_4$ .* The linear structure presented in the left half of Fig. 8 provides paths for not only intrachain exchange but also *interchain* interactions and 3-D, long-range, antiferromagnetic ordering. Previous studies involving Faraday balance measurements and Mössbauer spectroscopy demonstrated that  $\text{Fe(dmp)SO}_4$  orders antiferromagnetically at  $T_{\text{Néel}} \approx 3.8 \text{ K}$  (15). Ordering can occur *along* the chain by the bridging portion of each sulfate and *across* the chain through the chelating portion. Magnetic ordering or just interactions may occur *between* chains if the almost planar dmp ligands on adjacent chains interleave and overlap one another enough for the  $\pi$

systems to couple. Such overlapping (by  $\sim 20\%$ ) was discovered in the chainlike molecular structure of  $\alpha\text{-Co(bipy)Cl}_2$ , a compound that orders ferromagnetically (rather than antiferromagnetically) at  $T_{\text{Curie}} \approx 4 \text{ K}$  (38).

We can use the results for  $\text{Fe(dmp)SO}_4$  to estimate the strength of the *interchain* exchange  $J_{\text{inter}}/k_B$  in the  $M(\text{dmp})\text{SO}_4$  complexes. Oguchi (39) applied Green's function theory to antiferromagnetic behavior (both interactions and ordering) and developed a mathematical model that gives the interchain exchange energy  $J_{\text{inter}}/k_B$  as a function of the Néel temperature  $T_{\text{Néel}}$  and the intrachain exchange energy  $J_{\text{intra}}/k_B$  (our  $J/k_B$  above). The results of the calculations involving Oguchi's formulae are expressed as a ratio of the energy of interchain exchange to the energy of intrachain exchange:  $|J_{\text{inter}}/J_{\text{intra}}|$ . Substituting  $|J_{\text{intra}}/k_B| = 1.54 \text{ K}$  and  $T_{\text{Néel}} = 3.85 \text{ K}$  into Oguchi's formulae, we find  $|J_{\text{inter}}/J_{\text{intra}}| = 0.04$  for  $\text{Fe(dmp)SO}_4$ . In Table IV we give this ratio for  $\text{Fe(dmp)SO}_4$  as well as the ratios obtained in the same way for  $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$  and  $\text{Fe(bipy)}(\text{H}_2\text{O})_2\text{SO}_4$ . These results indicate that the magnetic interactions in  $\text{Fe(dmp)SO}_4$  are *as one-dimensional as* the interactions in the two known chainlike complexes  $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$  and  $\text{Fe(bipy)}(\text{H}_2\text{O})_2\text{SO}_4$ . Furthermore, the fact that these three ratios are so similar suggest that there may be *interchain* exchange occurring via coupling of the  $\pi$  systems on the dmp ligands of adjacent chains in  $\text{Fe(dmp)SO}_4$ , an exchange that is about as strong as the *interchain* exchange occurring via hydrogen bonding in  $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$  and  $\text{Fe(bipy)}(\text{H}_2\text{O})_2\text{SO}_4$ .

*Additional comments on the magnetic exchange in  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Fe}, \text{Ni}$ ).* The increase in the  $\chi'_M$ -vs- $T$  curve (Fig. 5a) for  $\text{Ni(dmp)SO}_4$  at  $T < 10 \text{ K}$ , that is, at temperatures *well below*  $T(\text{max-}\chi, 1\text{-D})$ , has also been observed for  $\text{Fe(dmp)SO}_4$  (15) and for each of the following *chainlike* polymeric

TABLE IV  
COMPARISON OF INTERCHAIN AND INTRACHAIN ANTIFERROMAGNETIC EXCHANGE ENERGIES FOR  
THREE FERROUS SULFATE COMPLEXES

Compound	$T(\max-\chi, 1-D)^a$ (K)	$J_{\text{intra}}/k_B^b$ (K)	$T_{\text{Néel}}^c$ (K)	$ J_{\text{inter}}/J_{\text{intra}} $ (K)
$(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$	15.3	-2.13	6.60 <sup>d</sup>	0.06
$\text{Fe}(\text{dmp})\text{SO}_4$	11.1	-1.54	3.85	0.04
$\text{Fe}(\text{bipy})(\text{H}_2\text{O})_2\text{SO}_4$	7.3	-1.02	1.70	0.02

<sup>a</sup>  $T(\max-\chi, 1-D)$  was taken from  $\chi'_M$ -vs- $T$  curve recorded through either vibrating sample magnetometry or Faraday balance measurements; see references (27, 15, 1).

<sup>b</sup>  $J_{\text{intra}}/k_B$  was computed from  $T(\max-\chi, 1-D)$  alone.

<sup>c</sup>  $T_{\text{Néel}}$  was determined through Mössbauer spectroscopy; see references (4, 15, 1).

<sup>d</sup>  $T_{\text{Néel}}$  determined through specific-heat studies is 6.0 K (31).

compounds:  $\text{Fe}(5\text{-CH}_3\text{-phenanthroline})\text{Cl}_2$  (40),  $\text{Fe}(\text{bipy})(\text{NCS})_2$  (41),  $\text{Mn}(\text{bipy})(\text{NCS})_2$  (42), and  $\text{Li}_2\text{MnF}_5$  (37). We found no evidence of a paramagnetic contaminant. Instead we suspect that the second increase is due to canted antiferromagnetism (33, p. 184) occurring before the onset of long-range, 3-D, antiferromagnetic order.

The magnetic susceptibility of a substance exhibiting canted antiferromagnetism resembles the magnetic susceptibility of a compound displaying ordered ferromagnetism. The susceptibility in either case depends inversely on the applied field  $H_0$  because  $H_0$  perturbs the internally generated magnetic field (35, 40, 42). An inverse dependence of the corrected molar magnetic susceptibility  $\chi'_M$  on the applied field  $H_0$  has been recorded for  $\text{Mn}(\text{bipy})(\text{NCS})_2$  at temperatures  $T < 10$  K, in just the region where  $\chi'_M$  increases again after it has passed through the broad maximum at  $T(\max-\chi, 1-D) \approx 20$  K (42). The inverse dependence for  $\text{Mn}(\text{bipy})(\text{NCS})_2$  is obvious at  $T < 5$  K and for  $H_0 > 10$  kG.

$\text{Li}_2\text{MnF}_5$  and  $(\text{NH}_4)_2\text{MnF}_5$  are isomorphous (37). The  $\chi'_M$ -vs- $T$  curve for  $\text{Li}_2\text{MnF}_5$  increases again at  $T \ll T(\max-\chi, 1-D) \approx 30$  K. The  $\chi'_M$ -vs- $T$  curve for  $(\text{NH}_4)_2\text{MnF}_5$  increases again at  $T \ll T(\max-\chi, 1-D) \approx 58$  K, but for this compound, the second increase

leads to a well-defined, sharper, second maximum at  $T \approx 6$  K. This second, sharper maximum is "attributable to a three-dimensional long-range ordering" (37).

The second increase in the  $\chi'_M$ -vs- $T$  curve for  $\text{Fe}(\text{dmp})\text{SO}_4$  occurs at the temperature where hyperfine splitting due to 3-D, antiferromagnetic ordering is registered in the Mössbauer spectrum of the compound ( $T_{\text{Néel}} \approx 3.8$  K). If the ratio  $|J_{\text{inter}}/J_{\text{intra}}|$  for  $\text{Fe}(\text{dmp})\text{SO}_4$  and the ratio for  $\text{Ni}(\text{dmp})\text{SO}_4$  are approximately equal, then  $T_{\text{Néel}}$  for  $\text{Ni}(\text{dmp})\text{SO}_4$  lies between  $T \approx 4$  K and  $T \approx 13$  K, that is, at just the temperatures where the second increase in  $\chi'_M$  for this compound is observed.

Additional studies using Mössbauer spectroscopy on  $\text{Fe}(\text{dmp})\text{SO}_4$  at  $T < 8$  K and  $H_0 > 60$  kG and vibrating sample magnetometry on  $\text{Ni}(\text{dmp})\text{SO}_4$  at  $T < 100$  K and  $H_0 > 7$  kG are planned in an effort to define the nature of the second increase in the corrected molar magnetic susceptibility  $\chi'_M$  of each compound at  $T < T(\max-\chi, 1-D)$ .

## Conclusions

Superexchange via bridging, polyatomic, diamagnetic anions like  $\text{SO}_4^{2-}$  can be remarkably strong:  $|J|/k_B > 1$  K (Table III).

The results of measuring the specific



heats of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Fe, Co, Ni}$ ) at  $T < 80$  K will corroborate our observations of strong, one-dimensional, antiferromagnetic interactions occurring by superexchange through the  $\text{SO}_4^{2-}$  ligands. In addition, studies of the specific heats may uncover 3-D, long-range, antiferromagnetic ordering in  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Fe, Co, Ni}$ ) at temperatures below  $T(\text{max-}\chi, 1\text{-D})$ . Measurements of the magnetic susceptibilities and the specific heats of  $(\text{N}_2\text{H}_5)_2M(\text{SO}_4)_2$  ( $M = \text{Mn, Fe, Co, Ni, Cu}$ ) proved to be quite complementary (27, 31).

It is encouraging to recall that 3-D, long-range, antiferromagnetic ordering was detected in  $(\text{N}_2\text{H}_5)_2\text{Fe}(\text{SO}_4)_2$  at  $T \approx 6.0$  K through studies of specific heats (31) and at  $T \approx 6.6$  K through Mössbauer spectroscopy (4). We believe that 3-D, long-range, antiferromagnetic ordering causes the hyperfine splitting seen in the Mössbauer spectrum of  $\text{Fe}(\text{dmp})\text{SO}_4$  at  $T \approx 3.8$  K.

Measuring the specific heats will reveal the strength of zero-field splitting in  $\text{Ni}(\text{dmp})\text{SO}_4$  and will determine whether the effective spin of  $\text{Co}^{2+}$  in  $\text{Co}(\text{dmp})\text{SO}_4$  is  $\frac{3}{2}$  or  $\frac{1}{2}$  and may help explain the increase in the corrected molar magnetic susceptibility  $\chi'_M$  of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Fe, Ni}$ ) at temperatures below  $T(\text{max-}\chi, 1\text{-D})$ .

Future research must include additional attempts to learn the details of the crystal and the molecular structures of the  $M(\text{dmp})\text{SO}_4$  complexes. The results obtained so far indicate that the  $M(\text{dmp})\text{SO}_4$  complexes ( $M = \text{Mn, Fe, Co, Ni, Cu}$ ) may have the molecular structure that Plowman and coworkers proposed for  $\text{Cu}(\text{dmp})\text{SO}_4$  and  $\text{Zn}(\text{dmp})\text{SO}_4$ : a chainlike polymer in which each sulfate bridges two metal cations and chelates a third (Fig. 8). As X-ray crystallographic analyses of single crystals will show definitively whether or not all of the  $M(\text{dmp})\text{SO}_4$  complexes have this structure, we are continuing our efforts to obtain suitable crystals of  $M(\text{dmp})\text{SO}_4$  ( $M = \text{Mn, Co, Ni, Cu, Zn}$ ).

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## References

1. C. NICOLINI AND W. M. REIFF, *J. Solid State Chem.* **44**, 141 (1982).
2. G. A. EISMAN AND W. M. REIFF, *Inorg. Chim. Acta* **50**, 239 (1981).
3. W. M. REIFF, H. WONG, R. B. FRANKEL, AND S. FONER, *Inorg. Chem.* **16**, 1036 (1977).
4. C. CHENG, H. WONG, AND W. M. REIFF, *Inorg. Chem.* **16**, 819 (1977).
5. C. NICOLINI AND W. M. REIFF, *J. Phys. (Paris)* **41**, C1:287 (1980).
6. C. NICOLINI, G. A. EISMAN, W. M. REIFF, AND E. KOSTINER, *J. Magn. Magn. Mater.* **15-18**, 1049 (1980).
7. C. C. TORARDI, J. C. CALABRESE, K. LÁZÁR, AND W. M. REIFF, *J. Solid State Chem.* **51**, 376 (1984).
8. C. C. TORARDI, K. LÁZÁR, AND W. M. REIFF, "Abstracts, 186th National Meeting of the American Chemical Society, Washington, D.C., August, 1983," No. INOR 175.
9. C. C. TORARDI, J. C. CALABRESE, K. LÁZÁR, AND W. M. REIFF, "Abstracts, 187th National Meeting of the American Chemical Society, St. Louis, Missouri, March, 1984." No. INOR 155.
10. D. B. FOX, J. R. HALL, AND R. A. PLOWMAN, *Aust. J. Chem.* **15**, 235 (1962).
11. J. R. HALL, N. K. MARCHANT, AND R. A. PLOWMAN, *Aust. J. Chem.* **15**, 480 (1962).
12. J. R. HALL, N. K. MARCHANT, AND R. A. PLOWMAN, *Aust. J. Chem.* **16**, 34 (1963).
13. D. B. FOX, J. R. HALL, AND R. A. PLOWMAN, *Aust. J. Chem.* **18**, 691 (1965).
14. J. R. HALL, C. H. L. KENNARD, AND R. A. PLOWMAN, *J. Inorg. Nucl. Chem.* **28**, 467 (1966); see also H. S. PRESTON, C. H. L. KENNARD, AND R. A. PLOWMAN, *J. Inorg. Nucl. Chem.* **30**, 1463 (1968).
15. W. M. REIFF AND B. W. DOCKUM, *J. Solid State Chem.* **31**, 407 (1980); see also E. KÖNIG, G. RITTER, AND K. MADEJA, *J. Inorg. Nucl. Chem.* **43**, 2273 (1981).
16. C. CHENG AND W. M. REIFF, *Inorg. Chem.* **16**, 2097 (1977).

17. J.-C. G. BUNZLI, *Inorg. Chim. Acta* **36**, L413 (1979).
18. L. N. MULAY, "Techniques of Chemistry," Vol. 1, "Physical Methods of Chemistry," Part IV, "Determination of Mass, Transport, and Electrical-Magnetic Properties" (A. Weissberger and B. W. Rossiter, Eds.), Chap. VII. Wiley-Interscience, New York (1972).
19. P. THOMAS, D. REHOREK, AND H. SPINDLER, *Z. Anorg. Allg. Chem.* **397**, 138 (1973).
20. J. C. TEDENAC, N. D. PHUNG, C. AVINENS, AND M. MAURIN, *J. Inorg. Nucl. Chem.* **38**, 85 (1976).
21. A. NIEUWPOORT AND J. REEDIJK, *Inorg. Chim. Acta* **7**, 323 (1973).
22. B. J. HATHAWAY AND D. E. BILLING, *Coord. Chem. Rev.* **5**, 143 (1970).
23. F. A. COTTON AND G. WILKINSON, "Advanced Inorganic Chemistry," 3rd ed., Wiley-Interscience, New York (1972).
24. K. NAKAMOTO, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., p. 241, Wiley-Interscience, New York (1978).
25. C. K. PROUT AND H. M. POWELL, *J. Chem. Soc.*, 4177 (1961).
26. D. W. HAND AND C. K. PROUT, *J. Chem. Soc. A*, 168 (1966).
27. H. T. WITTEVEEN AND J. REEDIJK, *J. Solid State Chem.* **10**, 151 (1974).
28. R. A. PLOWMAN AND L. F. POWER, *Aust. J. Chem.* **24**, 309 (1971).
29. L. J. DE JONGH AND A. R. MIEDEMA, *Advan. Phys.* **23**, 1 (1974).
30. J. C. BONNER AND M. E. FISHER, *Phys. Rev. A* **135**, 640 (1964).
31. F. W. KLAAIJSEN, H. DEN ADEL, Z. DOKOUPIL, AND W. J. HUISKAMP, *Physica B (Amsterdam)*, **79**, 113 (1975).
32. C.-Y. WENG, "Finite Exchange-Coupled Magnetic Systems," Ph.D. dissertation, Carnegie-Mellon University, Pittsburgh, Pa. (1968).
33. R. L. CARLIN AND A. J. VAN DUYNVELDT, "Inorganic Chemistry Concepts," Vol. 2, "Magnetic Properties of Transition Metal Compounds," Springer-Verlag, New York (1977).
34. M. SUZUKI, B. TSUJIYAMA, AND S. KATSURA, *J. Math. Phys.* **8**, 124 (1967).
35. R. L. CARLIN, *Acc. Chem. Res.* **9**, 67 (1976).
36. G. R. WAGNER AND S. A. FRIEDBERG, *Phys. Lett.* **9**, 11 (1964); T. SMITH AND S. A. FRIEDBERG, *Phys. Rev.* **176**, 660 (1968).
37. S. EMORI, M. INOUE, M. KISHITA, AND M. KUBO, *Inorg. Chem.* **8**, 1385 (1969).
38. W. M. REIFF, H. WONG, G. A. EISMAN, W. RODE, AND B. FOXMAN, "Abstracts, 179th National Meeting of the American Chemical Society, Houston, Texas, March, 1980," No. INOR 22; see also G. A. EISMAN, Ph.D. Dissertation, Northeastern University, Boston, Mass. (1980).
39. T. OGUCHI, *Phys. Rev. A* **133**, 1098 (1964).
40. F. F. CHARRON JR., G. A. EISMAN, H. WONG, AND W. M. REIFF, *Inorg. Chim. Acta*, **68**, 233 (1983).
41. B. W. DOCKUM AND W. M. REIFF, *Inorg. Chem.* **21**, 391 (1982).
42. B. W. DOCKUM, G. A. EISMAN, E. H. WITTEN, AND W. M. REIFF, *Inorg. Chem.* **22**, 150 (1983).