JOURNAL OF SOLID STATE CHEMISTRY 44, 141–149 (1982)

Low-Dimensionality Magnetic Interactions in the Linear-Chain Transition Metal Complexes $M(2,2'\text{-bipyridine})(H_2O)_2SO_4$ (M = Fe, Ni, and Cu)

CLAUDIO NICOLINI AND WILLIAM MICHAEL REIFF

Department of Chemistry, Northeastern University,
Boston, Massachusetts 02115

Received September 26, 1980; in final form January 30, 1981

The magnetic susceptibilities of polycrystalline samples of the chain compounds $M(2,2'$-bipyridine) $(H_2O)_2SO_4$ (M = Fe, Ni, and Cu) have been measured in the temperature range 1.7 to 300 K. The iron and nickel compounds exhibit broad maxima in χ'_M vs T at ~ 8 K. The experimental results can be interpreted in terms of antiferromagnetic linear-chain systems and provide information on the magnitude of the intrachain interactions. Zero-field Mössbauer spectra of a powder sample of *trans-μ*-sulfato-diaquo(2,2′-bipyridine)iron(II) over the preceding range were also determined. The chemical isomer shift value corresponds to 6-coordinate high-spin iron(II). Below 2.0 K the compound exhibits magnetic hyperfine splitting, suggesting long-range, three-dimensional ordering with a critical temperature of $T_N \lesssim 1.7$ K. By means of Oguchi's Green's function theory and the experimentally determined transition temperature T_N, an estimate of the ratio of the inter- to intrachain exchange interaction is obtained.

I. Introduction

The theoretical and experimental study of magnetic systems that exhibit exchange in one or two dimensions has recently been a very active research area (*1*). Our laboratory has been engaged in the last few years in a research program on the magnetic properties of certain materials with linear- and zig-zag-chain structures which may be expected to show interesting low-dimensional behavior. In some of these chains, the bridging between paramagnetic metallic centers involves high-symmetry tetrahedral anions, such as PO_4^{3-}, AsO_4^{-3}, and SO_4^{2-} (*2–4*). In addition to understanding the particular magnetic structure in question, the study of these compounds provides the opportunity to investigate superexchange effects as transmitted by different polyatomic bridging groups. As a part of this program, we now present the low-temperature magnetic properties of the linear-chain compounds *trans-μ*-sulfato-diaquo(2,2′-bipyridine)M(II); with M = Fe, Ni, and Cu. Single-crystal X-ray studies for the Ni and Cu polymeric systems have been reported (*5*). The metal is octahedrally coordinated by one molecule of 2,2′-bipyridine, two water molecules, and two SO_4^{-2} anions. The coordination octahedra are strongly distorted, while the sulfate anions have nearly regular geometry. The chain articulation occurs through the tetrahedral bidentate SO_4^{-2} bridging between $[M(2,2'\text{-bipyridine})(H_2O)_2]$ groups. Such chains are

0022-4596/82/110141–09$02.00/0

crosslinked to each other in a SO_4^{-2} --- H_2O hydrogen bonding network. The foregoing local coordination, chain articulation, and crosslinking are clearly illustrated in Ref. (5). In section III it is shown that the Fe and Ni systems exhibit one-dimensional antiferromagnetic behavior, due mainly to a superexchange mechanism via the one-dimensional pathway M–O–S–O–M. For Fe, 3D ordering at considerably lower temperatures is suggested.

II. Experimental

The Ni and Cu compounds were prepared as described previously (5). The new Fe compound was synthesized in an analogous manner but with a metal-to-ligand ratio of 1/1. After the solution is stirred at 65°C for 30 min, Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ precipitates as a red powder. All the compounds gave the required analysis (Table I). Cryogenic susceptibility measurements and zero-field Mössbauer spectroscopy measurements were determined as described previously (6). The X-ray powder pattern (Debye–Scherrer method) of the new iron compound was identical to those of the copper and nickel systems, indicating that these compounds constitute an isomorphous series.

III. Results and Discussion

The temperature dependence of the corrected molar susceptibility, χ'_M, its reciprocal, χ'^{-1}_M, and the magnetic moment, μ_{eff} of a powder sample (H_0 = 5.10 kG) for the range 1.5 to ~100 K are shown in Figs. 1, 2, and 3 for the Fe, Ni, and Cu compounds, respectively. The magnetic susceptibility is field independent for fields varying from 1.60 to 5.10 kG and indicates the absence of externally induced phase transitions (metamagnetism or spin-flop behavior) in this low-field range.

Mössbauer Spectra

Zero-field ^{57}Fe Mössbauer spectra for the Fe compound at 295, 4.25, and 1.70 K are shown in Fig. 4. The values of the Mössbauer spectral parameters measured at 295 and 4.25 K are given in Table II. The value of the isomer shift, δ, indicates 6-coordinate high-spin iron(II). This is in agreement with the magnetic susceptibility data to be discussed subsequently. At 295 K, the value of the isomer shift, δ, is in the range between all-oxygen- and all-nitrogen-donor ligands (7), reflecting the local coordination of Fe in Fe(2,2′-bipyridine)$(H_2O)_2SO_4$. The increase of δ as the temperature decreases can be ascribed to a second-order Doppler shift (8). At 1.70 K, incipient magnetic hyperfine splitting is observed in the Mössbauer spectrum (Fig. 4c). The relatively condensed polymeric structure of Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ and the magnetic susceptibility data to be considered below suggest that the hyperfine splitting is due to the onset of long-range (3D) magnetic order. Similar behavior of the zero-field Möss-

TABLE I

CHEMICAL ANALYSES OF THE COMPOUNDS M(2,2′-BIPYRIDINE)$(H_2O)SO_4$

	Calculated (%)			Observed (%)		
Compound	C	H	N	C	H	N
Fe(2,2′-bipyridine)$(H_2O)_2SO_4$	34.88	3.52	8.14	34.61	3.63	7.94
Ni(2,2′-bipyridine)$(H_2O)_2SO_4$	34.61	3.49	8.07	34.20	3.64	7.98
Cu(2,2′-bipyridine)$(H_2O)_2SO_4$	34.14	3.45	8.17	33.93	3.76	7.80

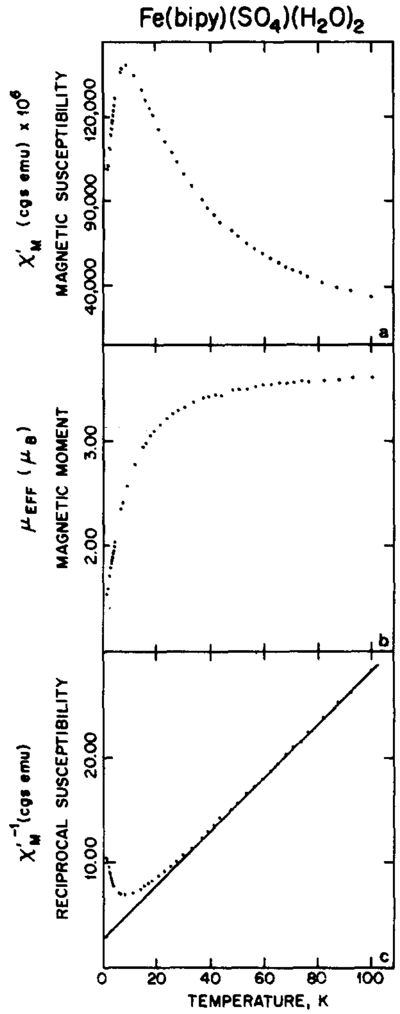


FIG. 1. (a) Molar magnetic susceptibility vs T (K) for Fe(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$, $H_0 = 5.10$ kG. (b) Magnetic moment vs T (K) for Fe(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$. (c) Reciprocal molar magnetic susceptibility for Fe(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$. Solid line is a least-squares computer fit for the Curie–Weiss Law given in the text.

bauer spectra, but with a fully resolved magnetic hyperfine splitting, has been reported for the structurally related linear-chain antiferromagnets hydrazinium ferrous sulfate Fe(N$_2$H$_5$)$_2$(SO$_4$)$_2$ and Fe(2,9-di-CH$_3$-phenanthroline)SO$_4$. The transition to long-range magnetic order for these two systems occurs at ~6.3 and 3.5 K, respectively(*3*, *4*). In the present case fully resolved magnetic hyperfine splitting apparently occurs at temperatures below our experimental capability.

Magnetic Susceptibility

Least-squares computer fits of χ'^{-1}_M vs T show that the Fe and Ni compounds obey Curie–Weiss laws over the ranges 35 to 296 K and 25 to 296 K, respectively. The values of the Curie–Weiss parameters, μ_{eff}, paramagnetic Curie temperatures, θ, and Curie

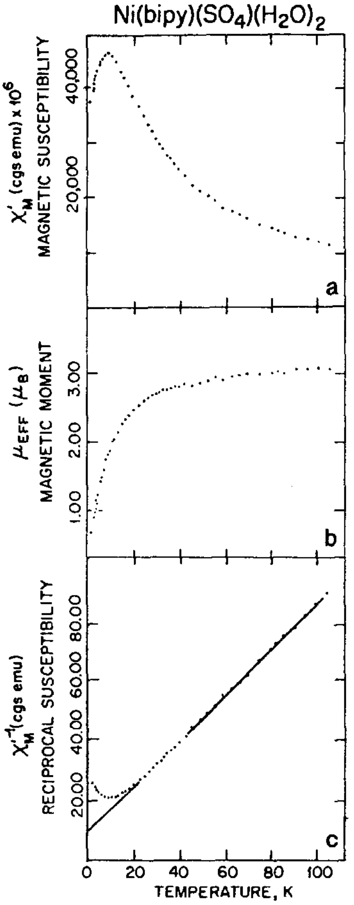


FIG. 2. (a) Molar magnetic susceptibility vs T (K) for Ni(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$, $H_0 = 5.10$ kG. (b) Magnetic moment vs T (K) for Ni(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$. (c) Reciprocal molar magnetic susceptibility for Ni(2,2′-bipyridine)(H$_2$O)$_2$SO$_4$. Solid line is a least-squares computer fit for the Curie–Weiss Law given in the text.

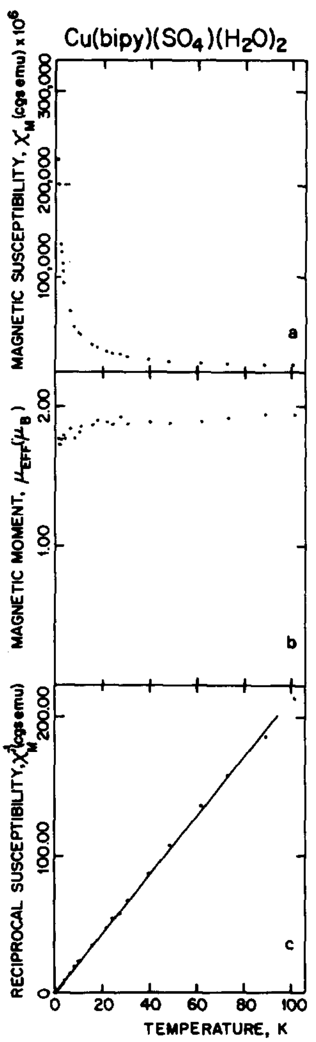


FIG. 3. (a) Molar magnetic susceptibility vs T (K) for Cu(2,2′-bipyridine)$(H_2O)_2SO_4$, $H_0 = 5.10$ kG. (b) Magnetic moment vs T (K) for Cu(2,2′-bipyridine)$(H_2O)_2SO_4$. (c) Reciprocal molar magnetic susceptibility for Cu(2,2′-bipyridine)$(H_2O)_2SO_4$.

TABLE II

MÖSSBAUER SPECTRUM PARAMETERS OF Fe(2,2′-BIPYRIDINE)$(H_2O)_2SO_4$

T (K)	δ^a (mm $\sec^{-1}$)	ΔE_Q (mm $\sec^{-1}$)	Γ_1 (mm $\sec^{-1}$)	Γ_2 (mm $\sec^{-1}$)
295	1.10	1.51	0.27	0.26
4.2	1.24	2.27	0.33	0.33

[a] Relative to Fe metal.

constants, C, are listed in Table III. There is deviation from Curie–Weiss behavior for all 10 fields below 30 K (Fe) and 24 K (Ni). Figures 1a and 2a show the temperature dependence of χ'_M of a powder sample (H_0 = 5.10 kG) of Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ and Ni(2,2′-bipyridine)$(H_2O)_2SO_4$, respectively. A broad maximum in χ'_M is observed for the Fe compound at $T_{\max} = 7.3$ K. The maximum in χ'_M for the Ni complex occurs at $T_{\max} = 8.3$ K. The steady decrease of the magnetic moment with decreasing temperatures (Figs. 1b and 2b) and the negative paramagnetic Curie temperatures (Table III) observed for these systems indicate a dominant AF interaction. Moreover, as

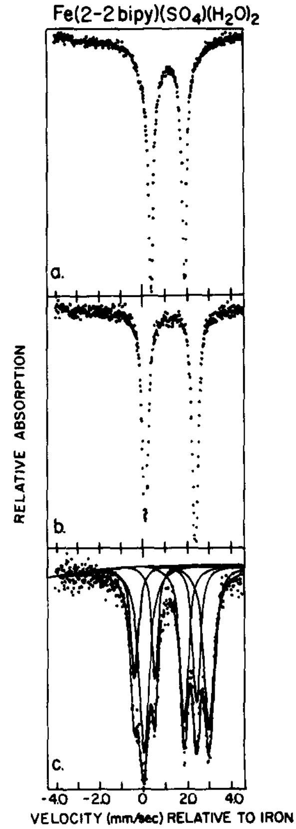


FIG. 4. Zero-field Mössbauer spectra for Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ (a) T = 295 K, (b) T = 4.5 K, and (c) T = 1.70 K (with least-squares Lorentzian fits).

TABLE III

MAGNETIC PARAMETERS

Compound	$\mu_{eff}{}^a$	Θ^a (K)	C^a (emu mole^{-1})	$\chi_{max} \times 10^3$ (emu mole^{-1})	T_{max} (K)
Fe(2,2'-bipyridine)$(H_2O)_2SO_4$	5.30	−8.10	3.52	14.20	7.3
Ni(2,2'-bipyridine)$(H_2O)_2SO_4$	3.20	−15.51	1.29	46.77	8.3
Cu(2,2'-bipyridine)$(H_2O)_2SO_4$	2.07	−22.7	0.54	Not observed	—

[a] Values obtained from least-squares computer fits of $\chi_M'^{-1}$ vs T to the expression $\chi_M'^{-1} = (T - \theta)/C$.

mentioned before, the 3D magnetic ordering for the Fe compound occurs at very low temperatures as suggested by its zero-field Mössbauer spectrum at ~1.70 K. On the basis of the crystal structure, it is plausible to interpret the magnetic properties of the Fe and Ni systems in terms of an AF interaction, with the broad maximum in χ_M' due to one-dimensional (intrachain) superexchange along a single M–O–S–O–M pathway between metal atoms. Linear-chain antiferromagnetism has also been observed in the compounds $M(N_2H_5)_2(SO_4)_2$ with M = Mn, Fe, Co, Ni, and Cu (*9*) and Fe(2,9-di-CH_3-phenanthroline)SO_4 (*4*). The intrachain interaction is again due to a superexchange mechanism via the M–O–S–O–M pathway, and comparisons of the present results with those for the preceding compounds are made subsequently.

Intra- and Interchain Interactions

The exchange interaction in a magnetic system is usually expressed by a parameter called the exchange constant, J (cm^{-1}), which is often written as J/k (K).

The effective spin Hamiltonian

$$H = -2J\sum_{ij}[aS_i^zS_j^z + b(S_i^xS_j^x + S_i^yS_j^y)] \quad (1)$$

has been widely used in the interpretation of experimental results of magnetic systems (*1*). In this expression, J is the exchange constant between nearest neighbors and has a negative sign for AF coupling; S^x, S^y, and S^z are the components of spin S, and the ratio a/b is an anisotropy parameter. The Ising model, which is obtained by setting $b = 0$, describes the case of extreme anisotropic spin coupling (*1*). The anisotropic coupling obtained when $a = 0$ is called the XY model. If $a = b$, there is complete rotational symmetry in spin space and we obtain the Heisenberg model. Most real systems fall somewhere in between, though in general, ions with isotropic g values usually provide Heisenberg systems, while highly anisotropic g values often imply Ising behavior. Only a few XY magnetic systems have been discovered so far (*1*).

Many Ni^{2+} compounds have been successfully described by the Heisenberg model. On the basis of the spin Hamiltonian (*1*), Weng (*10*) has obtained the theoretical susceptibility as a function of temperature for AF Heisenberg chains with $S = 1$. For this susceptibility calculation the relations

$$kT_{max}(\chi)/|J| = 2.7, \quad (2)$$

$$J\chi_{max}/Ng^2\beta^2 = 0.0872 \quad (3)$$

hold, where T_{max} is the temperature corresponding to χ_{max}, N = Avogadro's number, and β = Bohr magneton. From the experimentally determined values of χ_{max} and T_{max} for the Ni(2,2'-bipyridine)$(H_2O)_2SO_4$ chain (Table III), we calculate, using (2), $J/k = -3.1$ K. This value is comparable with those obtained for the structurally related chain $Ni(N_2H_5)_2(SO_4)_2$ ($J/k \approx 3.3$ K) (*9*). In this analysis an error of ±0.5 K in the estimate of T_{max} (χ) for our data results in a variation of $|J/k|$ from 3.3 to 2.9 K.

At this point we mention that single-ion zero-field splitting effects can be large for Ni^{2+} and in some cases are comparable to the exchange interaction involved (*1*). Probably, the best method for evaluating this complication is a determination of the temperature dependence of the magnetic heat capacity. Unfortunately, facilities to carry out this experiment are not available to us. However, the temperature variation and large decrease in the absolute value of the magnetic moment for the Ni^{2+} and Fe^{2+} complexes strongly suggest that the exchange interaction dominates over the zero-field splitting effects. In the absence of magnetic heat capacity data, we do not consider zero-field effects any further herein.

An analogous calculation of J/k can be performed for the Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ chain within the Heisenberg model, although it must be stated that it is usually not possible to describe the magnetic properties of Fe^{2+} compounds by either the pure Heisenberg or Ising models. In Fe^{2+} compounds, the crystalline field anisotropy and the magnetic exchange interaction can be of the same order of magnitude, thus precluding the interpretation of the data in terms of these two simplified and extreme situations. In any event, we give the calculations for each case as a rough estimate. The relations derived by Reedijk and Witteveen using Weng's type of calculation are

$$KT_{max}(\chi)/|J| = 6.9, \tag{4}$$

$$|J|\chi_{max}/Ng^2\beta^2 = 0.0937. \tag{5}$$

From the experimental value of T_{max} (Table III) and using (4) we calculate $J/k = -1.13$ for Fe(2,2′-bipyridine)$(H_2O)_2SO_4$. Because g is not known for this compound and because g is usually anisotropic for Fe^{2+} complexes, we have not used Eq. (5) to calculate J/k. The value of J/k obtained for the Fe chain is similar to that obtained for $Fe(N_2H_5)_2(SO_4)_2$ ($J/k = -2.2$ K) (*9*) using the same Heisenberg-type calculation. Witteveen and Reedijk also calculated an estimate of J/k using the Ising model owing to the probable magnetic anisotropy of this iron compound. In their work the parallel susceptibility, $\chi_{\parallel}$, of linear AF chains with $S = 2$ is calculated by computer methods. From the numerical results obtained for $S = 2$, the theoretical curve in which $|J|\chi_{\parallel}/Ng^2\beta^2$ is given as a function of $kT/|J|$ is composed. For this general curve within the assumptions involved,

$$kT_{max}(\chi)/|J| = 7.5, \tag{6}$$

and

$$|J|\chi_{max}/Ng^2\beta^2 = 0.1009. \tag{7}$$

From (6), using other powder data, Witteveen and Reedjik calculated the value $J/k = -2.04$ K for the linear-chain $Fe(N_2H_5)_2(SO_4)$ within the Ising model. Similarly, we calculate for the Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ chain, $J/k = -0.97$ K. Nevertheless, as the authors point out, a calculation of J/k using Eq. (6) introduces an error because the powder-susceptibility curve is made up of $\chi_{\parallel}$ and $\chi_{\perp}$. Regrettably, for an Ising chain system, a theoretical result of $\chi_{\perp}$ is only known for spin $S = \frac{1}{2}$.

Another method for evaluating J/k is from application of the "reduced spin model" (*11*). In this method, based on the Ising model, the magnetic susceptibility is expressed as

$$\chi_M' = \frac{Ng^2\beta^2S(S+1)}{3kT}\exp(J'/kT), \tag{8}$$

where J' represents the exchange energy for a system composed of spins capable of orienting only parallel or antiparallel. J' is related to the true intrachain exchange constant J by

$$J/k = \frac{3/4\, J'/k}{S(S + 1)}\,.$$

Figure 5 shows a plot of $\log(3k\chi'_M T/N\beta^2)$ vs $1/T$ ($T > 40$ K) for the Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ chain. From the slope, $J'/2.30$, and intercept, $\log[g^2S(S + 1)]$, of the straight line of best fit, the values of the intrachain constant (J/k) and effective magnetic moment (μ_{eff}) can be calculated. They are 0.96 K and 5.30, respectively. The value of J/k is quite close to that obtained from the Heisenberg and Ising methods described above, indicating that the reduced spin method is a reasonable approximation for the present one-dimensional AF linear chains and that $J/k \sim 1$ K. The μ_{eff} value obtained by the reduced spin method is identical to the value obtained from the Curie–Weiss fit of the susceptibility data.

Although it has been demonstrated theoretically that in an Ising or Heisenberg chain with nearest-neighbor interaction only, no long-range order (spontaneous magnetization) can occur for $T > 0$ (*12*), compounds having low-dimensional magnetic properties practically always undergo a transition to long-range (3D) order. This is due to the relatively weak interchain interaction (J_{inter}) that becomes more important as the temperature decreases.

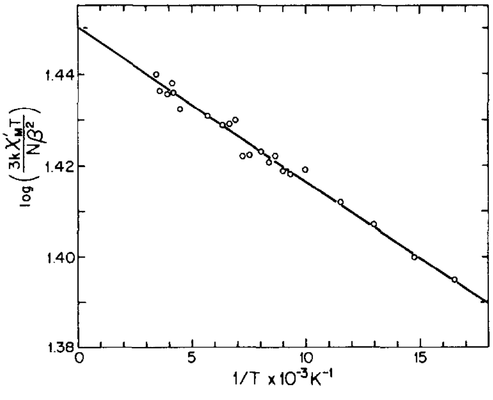


FIG. 5. Plot of susceptibility data at 40 K < $T \leq$ 300 K using the "reduced spin model" for Fe(2,2′-bipyridine)$(H_2O)_2SO_4$.

In the particular case of the Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ chain and in the absence of specific heat measurements, an upper bound to the transition temperature to long-range order (T_N) is taken as 1.70 K from the magnetic hyperfine splitting of its Mössbauer spectrum at that temperature. An estimate of the ratio of the intrachain exchange constant, J_{intra}, to the interchain interaction, J_{inter}, can be given by means of a theory developed by Oguchi for antiferromagnetic Heisenberg linear chains on the basis of double-time temperature-dependent Green's function theory (*13*). Using the experimentally determined $T_N \simeq 1.70$ K and the intrachain interaction constant $J/k = -1.13$, the ratio $|J_{\text{inter}}/J_{\text{intra}}| \simeq 1 \times 10^{-2}$ is obtained for the Fe system. This estimated value is fairly close to the $|J_{\text{inter}}/J_{\text{intra}}|$ value found for the structurally related AF $Fe(N_2H_5)_2(SO_4)_2$ ($|J_{\text{inter}}/J_{\text{intra}}| = 3 \times 10^{-2}$ (*9*). For this compound, the one- and three-dimensional magnetic interactions are observed in the temperature dependence of the heat capacity (*14*). A broad maximum in Cp vs T is observed at 12.3 K and is associated with the intrachain interactions, while a λ anomaly corresponding to long-range (interchain) magnetic ordering is observed at 6.9 K. Moreover, the stronger interchain (3D) magnetic interactions are clearly seen in the magnetic hyperfine splitting of the Mössbauer spectrum of this complex with $T_N \simeq 6.3$ K (*3*). The smaller $|J_{\text{inter}}/J_{\text{intra}}|$ ratio calculated for the Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ chain is clearly consistent with our Mössbauer spectroscopy data for this system, i.e., incipient hyperfine splitting of its Mössbauer spectrum at lower temperatures.

The Cu(2,2′-bipyridine)$(H_2O)_2SO_4$ chain does not show the broad maximum in χ'_M vs T as observed for the Ni and Fe chains and μ is close to the spin-only value at all temperatures. Clearly, the exchange interac-

TABLE IV

COMPARISON OF THE VALUES OF J/k, $|J_{\text{inter}}/J_{\text{intra}}|$, AND $T_{\max}$ FOR M(2,2′-BIPYRIDINE)$(H_2O)_2SO_4$[a] COMPOUNDS AND THEIR $M(N_2H_5)_2SO_4$ ANALOGS[b,c]

Compound	$T_{\max}$ (χ) (K)	J/k from $T_{\max}$ (χ) (K)	$T_{\max}$ (Cp) (K)	J/k from $T_{\max}$ (Cp) (K)	$\lvert J_{\text{inter}}/J_{\text{intra}}\rvert$
Fe(2,2′-bipyridine)$(H_2O)_2SO_4$	7.3	−1.0	—	—	1×10^{-2}
$Fe(N_2H_5)_2(SO_4)_2$	15.3	−2.2	11.7	2.9	3×10^{-2}
Ni(2,2′-bipyridine)$(H_2O)_2SO_4$	8.3	−3.1	—	—	—
$Ni(N_2H_5)_2(SO_4)_2$	8.7	−3.2	3.7	−2.0	$<1 \times 10^{-2}$
Cu(2,2′-bipyridine)$(H_2O)_2SO_4$	Not observed	—	—	—	—
$Cu(N_2H_5)_2(SO_4)_2$	2.1	−1.65	−1.95	−1.9	$<1.5 \times 10^{-1}$

[a] This work.

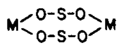
[b] Reference (*9*).

[c] Reference (*14*).

tions are much weaker. This also appears to be the case in the hydrazinium sulfate series $M(N_2H_5)_2(SO_4)_2$ (M = Fe, Ni, and Cu) (*9*). The exchange interaction is again weaker for the Cu chain as compared with the Fe and Ni compounds, although a maximum in χ vs T is barely observed at $T_{\max} \approx$ 2.1 K and at $T \sim$ 1.95 K from specific heat measurements (*14*). This is believed to be due to the 1D antiferromagnetic interactions. From the latter results, J/k for $Cu(N_2H_5)_2SO_4$ has been estimated to be approximately −1.99 K. By comparison with the results for $Cu(N_2H_5)_2(SO_4)_2$ we may assume J/k is approximately −1 or less for the Cu(2,2′-bipyridine)$(H_2O)_2SO_4$ complex. There is no evidence of 3D ordering for either Cu(2,2′-bipyridine)$(H_2O)_2SO_4$ or $Cu(N_2H_5)_2(SO_4)_2$.

We conclude this work by briefly comparing the (values) of J/k presented here for the M(2,2′-bipyridine)$(H_2O)_2SO_4$ linear-chain complexes with those found for the hydrazinium sulfate systems in terms of their known structure. Table IV shows the J/k values for the two series of linear-chain systems.

It can be seen that the low-dimensional interchain magnetic interactions are generally stronger for the $M(N_2H_5)_2(SO_4)_2$ series. $T_{\max}$ for these compounds occurs at higher temperatures than for the M(2,2′-bipyridine)$(H_2O)_2SO_4$ complexes. This observation can be rationalized in terms of the number of M–O–S–O–M pathways present in each series. In the $M(N_2H_5)_2(SO_4)$ series, there are two such



pathways. This apparently leads to stronger 1D antiferromagnetic interactions than for the M(2,2′-bipyridine)$(H_2O)_2SO_4$ chains in which there is only one for a sulfato bridge between adjacent metal ions of the chain.

A high-field Mössbauer spectroscopy study of the nature of the electric field gradient tensor and magnetic exchange of Fe(2,2′-bipyridine)$(H_2O)_2SO_4$ is now in progress.

Acknowledgments

The authors are pleased to acknowledge the support of the National Science Foundation, Division of Materials Solid State Chemistry Program, Grant DMR 8016441.

References

1. L. J. DE JONGH AND A. R. MIEDEMA, "Experiments on Simple Magnetic Model Systems," Taylor & Francis, London (1974).

2. C. NICOLINI, G. EISMAN, W. M. REIFF, AND E.

KOSTINER, *J. Magn. Magn. Mater.* **15–18,** 1049 (1980).

3a. C. CHENG, H. WONG, AND W. M. REIFF, *Inorg. Chem.* **16,** 819 (1977).

3b. W. M. REIFF, H. WONG, R. B. FRANKEL, AND S. FONER, *Inorg. Chem.* **16,** 1036 (1977).

4. W. M. REIFF AND B. W. DOCKUM, *J. Solid State Chem.* **31,** 407 (1980).

5. J. C. TEDENAC, N. D. PHONG, C. AVIENS, AND M. MAURIN, *J. Inorg. Nucl. Chem.* **38,** 85 (1976).

6. C. CHENG AND W. M. REIFF. *Inorg. Chem.* **16,** 2097 (1977).

7. R. INGALLS, *Phys. Rev.* **113,** A787 (1964).

8. Y. HAZONY, *J. Chem. Phys.* **45,** 2664 (1966).

9. H. T. WITEVEEN AND J. REEDIJK, *J. Solid State Chem.* **10,** 151 (1974).

10. C. WENG, Ph.D thesis, Carnegie–Mellon University (1968).

11. S. EMORI, M. INOUE, M. KISHITA, AND M. KUBA, *Inorg. Chem.* **8,** 1835 (1969).

12. L. D. LANDAU AND E. M. LIFSCHITZ, "Statistical Physics," p. 482, Oxford Univ. Press, London/New York. (1958).

13. T. OGUCHI, *Phys. Rev.* **133,** A1098 (1964).

14. F. W. KLAAIJSEN, H. DEN ADEL, Z. DOKOUPIL, AND W. J. HUISKAMP, *Physica B* **79,** 113 (1975).