ion in acidic solution causes the labilization of one arm of the tren ligand, generating $[Cr(trenH)F(H_2O)_2]^{3+}$ with a tridentate tren ligand. The photochemical reaction of $[Cr(tren)F_2]^+$ does not fit the pattern predicted by the currently available theoretical models of ligand field photochemistry of d^3 centers but is consistent with the semiempirical photolysis rules.

Registry No. $[Cr(tren)F_2]ClO_4$, 28650-58-0; $[Cr(tren)F(H_2O)](ClO_4)_2$, 73068-68-5; $[Cr(trenH)F(H_2O)_2]^{3+}$, 73017-55-7; $[Cr(tren)F_2]^+$, 46140-83-4; $[Cr(tren)F(H_2O)]^{2+}$, 73068-67-4.

Contribution from the Department of Chemistry, The University of North Carolina,
Chapel Hill, North Carolina 27514

Ferromagnetism in Copper(II) Oxydiacetate Hemihydrate

PETER J. CORVAN, WILLIAM E. ESTES, ROBERT R. WELLER, and WILLIAM E. HATFIELD*

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Magnetic susceptibility and isothermal magnetization studies on powdered samples of the layer compound copper(II) oxydiacetate hemihydrate have revealed that the substance undergoes a transition to a ferromagnetic state at 3.3 K. The copper(II) ions within a given layer are exchange coupled, and an exchange coupling constant $J = +4.66$ cm^{-1} resulted from a fit of a series expansion for a Heisenberg two-dimensional system to the magnetic susceptibility data. The out-of-plane anisotropy field was estimated to be 250 Oe, and the ratio of interplanar to intraplanar exchange was estimated to be 1.3×10^{-3}.

Introduction

Although ferromagnetic interactions leading to ferromagnetism are known in a limited number of ionic, insulating, layered solids[1] such as bis(benzylammonium) tetrachlorocuprate(II) and bis(methylammonium) tetrachlorochromate(II),[2] there are very few chelated coordination compounds which are ferromagnets. These include $K_2Cu(CO_3)_2$,[3] $Fe(detc)_2Cl_3$ ($detc^-$ = diethyldithiocarbamate),[4-6] and manganese(II) phthalocyanine.[7] The absence of ferromagnets in this wide range of compounds has stimulated much unpublished discussion and conjecture concerning the structural and electronic features which may be required for the realization of ferromagnetism in typical coordination compounds. As a starting point for subsequent discussions on this topic, we summarize here the guidelines which have been developed up to this time for the selection of good candidates for study. Structurally, the systems should be highly symmetrical so that superexchange pathways can be readily identified and controlled, and the bridging ligands should promote ferromagnetic interactions between neighboring paramagnetic ions. Toward this end, low-dimensional systems, especially layered structures, are good candidates, because the absence of tightly bonding networks between layers moderates the importance of superexchange interactions between the layers. Thus, if ferromagnetic interactions can be assured, then the problem is reduced to the determination of the factors which control the nature of the three-dimensional ordering. Furthermore, because of the more simple mathematical models, there exist a larger body of theoretical results for low-dimensional systems than for complex structures,[1] and, as a result, properties of these substances may be more easily systematized and understood. The metal ions should have a low total spin to eliminate complications from single ion anisotropy, and of course, systems containing such ions are more reflective of a quantum solid than those with ions having large, approaching classical, spins. These guidelines point to chelate compounds of low total spin metal ions in which the ligands are multidentate and capable of forming a polymeric two-dimensional layer. Fortunately, Whitlow and Davey[8] have provided us with structural data for such an example. We describe here the results of our measurements on copper(II) oxydiacetate hemihydrate which show that the compound is ferromagnetic and suggest that additional substances with this magnetic classification may be identified.

Experimental Section

Samples of copper(II) oxydiacetate were prepared by the procedure given by Whitlow and Davey.[8] Excess oxydiacetic acid (diglycolic acid, obtained from Aldrich Chemical Co.) was added to basic copper carbonate (Fishcer Scientific Co.), and the resultant royal blue compound was recrystallized from water to give rectangular platelets, which were twinned along the direction perpendicular to the plate. Analytical data for carbon and hydrogen obtained from Integral Microanalytical Laboratories, Inc., Raleigh, N.C., differed less than 0.3% from that calculated for $[Cu\{O(CH_2CO_2)_2\}]\cdot 0.5H_2O$.

Magnetic Measurements. Magnetic susceptibility and magnetization data were collected by using either a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) or a superconducting quantum interference device susceptometer, SQUID (Model A-401 SQUID sensor, and Model A-201 magnetometer electronics console: Superconducting Technology, Inc. (SCT), Mountain View, CA). The vibrating sample magnetometer was operated from zero field to 10 kOe. The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lusch Model 920 MCM rotating-coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li) over the field range 0.35–10 kOe and found to be linear to within better than 1% over the entire range. The field set accuracy is within ±0.3% at 300 G and better than 0.15% at 10 000 G. Fields below 0.35 kOe

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(1) de Jongh, L. J.; Miedema, A. R. *Adv. Phys.* **1974**, *23*, 1–260.
(2) Estes, W. E.; Losee, D. B.; Hatfield, W. E. *J. Chem. Phys.* **1980**, *72*, 630–8.
(3) Gregson, A. K.; Moxon, N. T., unpublished observations.
(4) Chapps, G. E.; McCann, S. W.; Wickman, H. H. *J. Chem. Phys.* **1974**, *60*, 990–7.
(5) DeFotis, G. C.; Palacio, F.; O'Connor, C. J.; Bhatia, S. N.; Carlin, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8314–5.
(6) Arai, N.; Sorai, M.; Suga, H.; Seki, S. *J. Phys. Chem. Solids* **1977**, 38.
(7) (a) Barraclough, C. G.; Martin, R. L.; Mitra, S.; Sherwood, R. C. *J. Chem. Phys.* **1970**, *53*, 1638–42. (b) Barraclough, C. G.; Gregson, A. L.; Mitra, S. *J. Chem. Phys.* **1974**, *60*, 962–8. (c) Miyoshi, H.; Ohya-Nishiguchi, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2724–8. (d) Miyoshi, H.; *J. Phys. Soc. Jpn.* **1974**, *37*, 50–6.
(8) Whitlow, S. H.; Davey, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1228–32.

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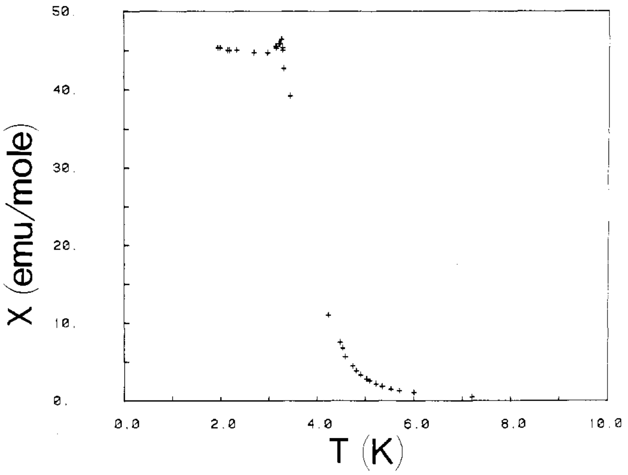

Figure 1. Magnetic susceptibility data collected by using the vibrating-sample magnetometer at 5 Oe on a powdered sample of copper(II) oxydiacetate hemihydrate.

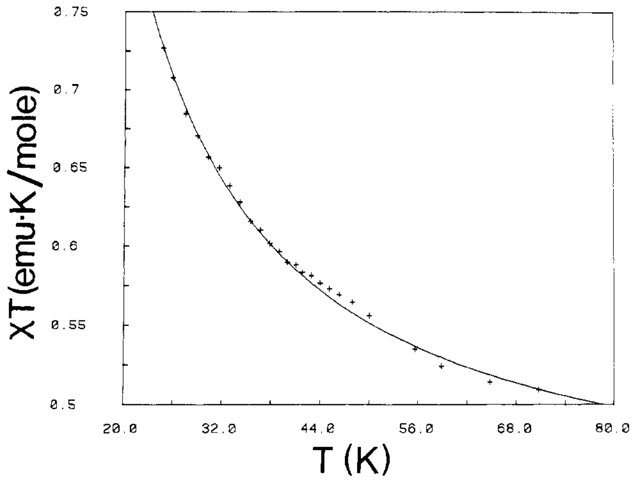

Figure 2. Fit of the Baker expansion for a two-dimensional Heisenberg system to the magnet susceptibility data collected at 10 kOe.

were measured with a Hall probe (RFL, Inc., Model 505). Long-term stability at very low fields (10 Oe) was found to be excellent over the course of low field susceptibility runs. Magnetization data were always collected point by point with the magnet being placed in the regulated mode for the collection of each data point. The superconducting solenoid of the SQUID system was energized to the fields required for these experiments by supplying the desired current with a precision constant current source (Keithley Model 227, resolution better than 5 μA). The desired magnet flux was "trapped" in the sensor coils by heating a NbTi superconducting shield encasing the coils to the normal state while the magnet was energized and allowing the shield to cool back through the superconducting transition (SCT Susceptibility System Manual). The SQUID had been calibrated in electromagnetic units by the manufacturer by measuring the moment induced by a known current in a tiny precision wound coil. The magnetometers were initially calibrated against $HgCo(NCS)_4$,[9] and the calibrations were checked against a sample of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$.[10] The results using these two standards agreed to within 2%, and it is felt that this represents the upper limit to the uncertainty in the measurements of the magnetic susceptibility with the VSM since the field is known to a much higher degree of accuracy, and in the measurements with the SQUID susceptometer because of the much higher inherent sensitivity of the SQUID. Powdered samples of the calibrants and compounds used in this study were contained in precision milled Lucite sample holders. Approximately 150 mg of each were used. Diamagnetic corrections for the constituent atoms were made by using Pascal's constants, and a correction for temperature-independent paramagnetism was estimated from tabulated data.[11-13]

Temperature Measurement and Control. The temperature of the sample was measured by using a Ga/As diode[14] in conjunction with a constant current supply and a Dana Model 4700 4.5-place digital voltmeter.

A PAR cryogenic temperature controller along with the regulation of gas flow through the sample zone was used to vary the temperature in the VSM. When liquid helium was the cryogen, temperatures between 1.8 and 4.2 K were achieved by using standard pumping procedures along with the temperature controller, and temperatures between 4.2 and 90 K were obtained by using the proper combination of gas flow and heating. Temperature stability, using these methods, was routinely maintained to better than ±0.01 K. Comparable techniques were used with the SQUID system for temperatures greater than 4.2 K.

Electron Paramagnetic Resonance. EPR spectra were obtained from a Varian E-3 X-band spectrometer (~9.5 GHz). The magnetic field of the E-3 was calibrated by using an NMR gaussmeter (Magnion Model G-502) and a Hewlett-Packard precision frequency counter (Model 5340A). In addition, the klystron frequency was measured directly with the frequency counter. The free radical DPPH (g = 2.0036) was used as a field marker in all cases. Powder data were collected at room temperature or liquid-nitrogen temperature (77 K).

Results

Data collected with the vibrating-sample magnetometer at 5 Oe on a powdered sample in the temperature range 1.94–7.2 K are plotted in Figure 1, where a well-defined transition to the ferromagnetic state may be seen. The very large values of the susceptibility near the transition temperature and the abrupt rise in susceptibility as the temperature decreases are characteristics of the temperature dependence of the magnetic susceptibility of a ferromagnetic substance. The transition temperature of 3.3 K was determined from these data by taking the temperature at which the inflection occurred immediately below the rapid increase in susceptibility.

Curie–Weiss Parameters. Magnetic susceptibility data collected at 1 kOe in the temperature range 12 K (i.e., $\sim 4T_c$) to 75 K were found to fit the Curie–Weiss law

$$\chi = C/(T - \Theta)$$

(where $C = Ng^2\mu_B{}^2S(S+1)/3k$ and Θ is the Weiss constant) yielding the parameters g = 2.117 (30) and Θ = 8.57 (23) K. However, parameters obtained by fitting data from a wider range of temperatures or obtained at a higher external magnetic field were somewhat different from the magnetic parameters given here. The reasons for the discrepancies include uncertainties in the experimental measurements as well as the intrinsic field dependence of the magnetic susceptibility of magnetically condensed low-dimensional compounds. The value of these parameters may be supported by the fact that a positive Weiss constant, as expected for a ferromagnetic substance, does obtain for a realistic value of g for copper(II). In addition, this is the same g value obtained for the fit of the 10 kOe data to the Baker[15] expansion as described below.

Intralayer Exchange. The intralayer exchange constant was obtained from a 10-kOe data set obtained in the temperature range 25–75 K. This set was selected for the calculation because of the higher accuracy of magnetic susceptibility data collected at high applied field strengths. In addition, at 25

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(9) Brown, D. B.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

(10) McKim, F. R.; Wolf, W. P. *J. Sci. Instrum.* **1957**, *34*, 64.

(11) Figgis, B. N.; Lewis, J. In "Modern Coordination Chemistry"; Lewis, J., Wilkins, R. G., ed.; Interscience: New York, 1960; Chapter, 6, p 403.

(12) König, E. "Magnetic Properties of Transition Metal Compounds"; Springer-Verlag: West Berlin, 1966.

(13) Weller, R. R.; Hatfield, W. E., in press.

(14) Type TG-100 FPA (special), No. 4277, Lake Shore Cryotronics, Inc., Columbus, OH.

(15) Baker, G. A.; Gilbert, H. E.; Eve, J.; Rushbrooke, G. S. *Phys. Lett. A* **1967**, *25*, 207-9.

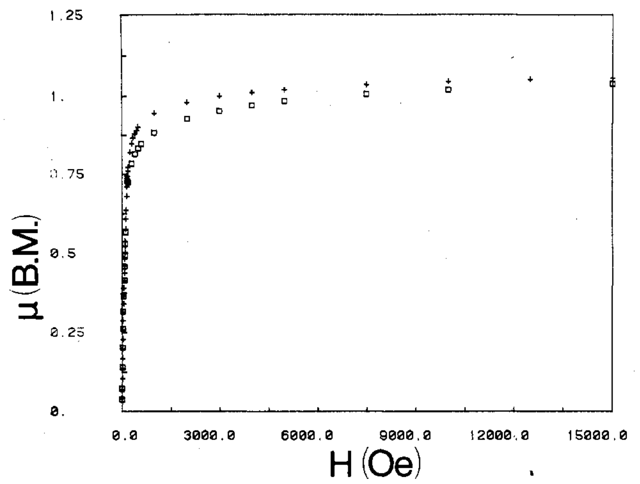

Figure 3. Isothermal magnetization data collected at 1.86 and 2.55 K by using the vibrating-sample magnetometer: (+) 1.86; (□) 2.55.

K and above, no field dependence of the magnetic susceptibility could be detected, although the magnetic susceptibility was field dependent below 25 K.

The 11-term quadratic layer series expansion for $S = {}^1/_2$ developed by Baker et al.,[15] eq 1, was fit to the data above 25

$$\frac{\chi(2D)_{H=0}kT}{Ng^2\mu_B{}^2} = 1 + \sum_{n\geq 1} \frac{\alpha^n}{2^n n!}(J/kT)^n \qquad (1)$$

K by using the Simplex nonlinear fitting routine with the criterion of best fit being the minimum value of the function $(1/n)\sum(\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2/\chi_i^{\text{obsd}}$. As shown in Figure 2, an excellent fit of the series expansion to the data was obtained with $J = +4.66$ cm^{-1} and $g = 2.12$. In the fitting process, the only adjustable parameters, J and g, were allowed to vary freely, and the best fit g value that was obtained agrees reasonably well with the observed average g value of 2.161 determined from EPR measurements.

Magnetization Measurements. Isothermal magnetization measurements were made as a function of field at 1.86 and 2.55 K on the magnetically ordered phase of copper(II) oxydiacetate hemihydrate. In Figure 3 we have plotted the total magnetic moment (defined as $M = Ng\beta\langle S\rangle$) vs. applied field for the data taken from 0 to 15 000 kOe. Although only a limited number of data are plotted in Figure 3, the magnetization behavior was visually followed continuously as a function of field by means of the magnetometer output, and no unusual features were observed. It may be seen from the data in Figure 3 that the saturation moment is 1.05 as expected for a $S = {}^1/_2$ μ_B copper(II) system with $g = 2.12$. These data, which are characteristic of ferromagnetically ordered states, confirm the conclusion reached above, based on the temperature dependence of the magnetic susceptibility, that copper(II) oxydiacetate hemihydrate undergoes a phase transition to a ferromagnetic state at $T_c = 3.3$ K.

Electron Paramagnetic Resonance Spectrum. The EPR spectrum of copper(II) oxydiacetate hemihydrate was recorded at X-band at room temperature. The general features of the spectrum given in Figure 4 are similar to those frequently seen for copper(II) ions in 4 + 1 + 1 coordination environments. The values of $g_{\parallel} = 2.194$ and $g_{\perp} = 2.144$, obtained from the polycrystalline sample, are good approximations of the principal g values. In view of the low symmetry of the ligand environment about copper ion and the arrangement of these units in the crystal structure, a determination of the molecular principal g values would require an extensive study of single-crystal rotational data. Since these data are not necessary for the present study, we have not elected to pursue that problem. However, it is of interest to note that the g values do not differ very much from one another and that both are relatively large. This is very uncommon for copper(II) complexes and reflects the low symmetry of the coordination sphere.

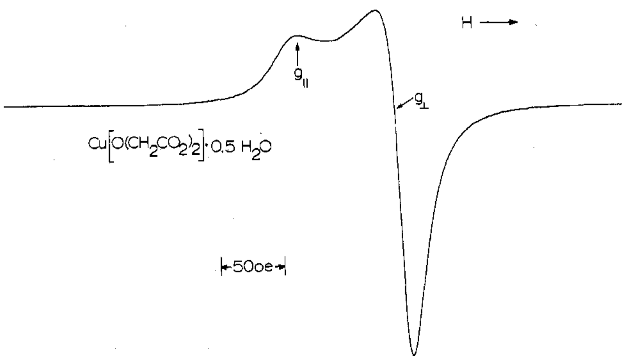

Figure 4. EPR spectrum of a powdered sample of copper(II) oxydiacetate hemihydrate at X-band, temperature = 298 K.

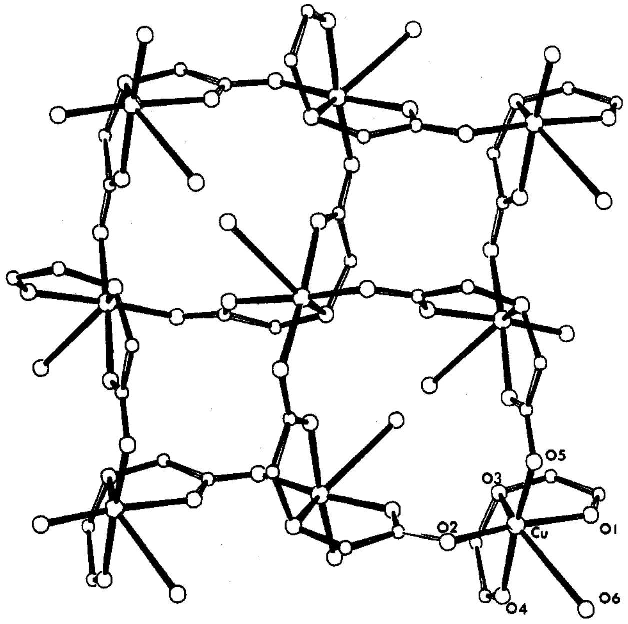

Figure 5. An ORTEP drawing of a projection of the layer structure on the *ac* plane. Note that this is a nine-formula unit segement of an infinite two-dimensional array.

Discussion

The crystal and molecular structure of copper(II) oxydiacetate hemihydrate has been determined by Whitlow and Davey,[8] and an ORTEP[16] drawing which shows a view along the *b* axis is given in Figure 5. It may be seen that the copper ion is coordinated by two carboxyl oxygens (Cu–O bond distance of 1.95 Å) and the ether oxygen (Cu–O bond distance of 2.49 Å) of a given oxydiacetate ligand. The coordination sphere of the copper(II) ion is completed by bonding to carboxyl oxygens (Cu–O bond distances of 1.94–1.95 Å) from separate adjacent moieties, and 50% of the time a water occupies the sixth coordination position (Cu–O bond distance of 2.73 Å). The two-dimensional polymeric array arises from the bidentate bonding of the carboxyl groups to two copper(II) ions. There are no chemical bonds between atoms in adjacent layers, and, as a result, these layers are held together only by van der Waal's forces. A projection onto the *ab* plane of nine formula units in adjacent planes which illustrates the sepa-

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(16) Johnson, C. K. ORNL Report No. 5138: Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(17) Estes, E. D.; Hodgson, D. J., unpublished results.

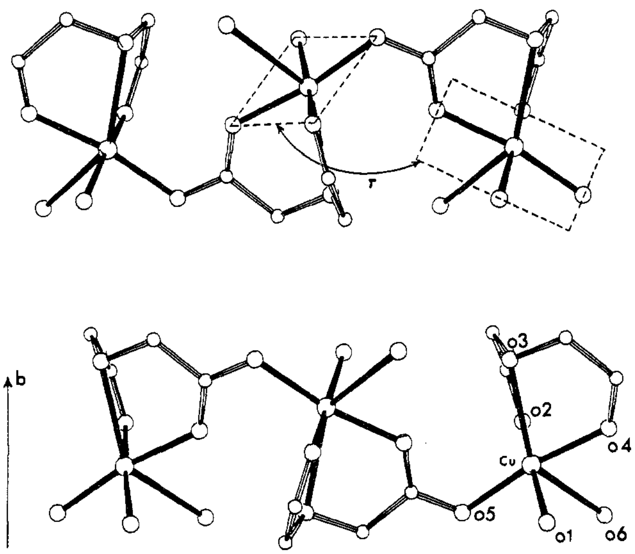

Figure 6. A projection onto the *ab* plane of nine formula units which illustrates the separation between the layers and the relative orientations of the carboxylate coordination planes to the bridging carboxylate group.

ration between the layers is shown in Figure 6.

In a given layer the superexchange network linking adjacent copper ions is of the type shown in Figure 6, where only the carboxylate bridge is important in transmitting spin–spin interactions. The magnetic susceptibility data show that these interactions are ferromagnetic in nature with an exchange constant $J = +4.66$ cm^{-1} resulting from a fit of the Baker expansion for a quadratic Heisenberg spin system to the magnetic susceptibility data.

There are potentially two superexchange pathways connecting the largely metal-based unpaired electrons which are in σ^* ($d_{x^2-y^2}$) orbitals on copper. One of these involves the orthogonal σ orbitals of the $-CO_2^-$ group, while the second pathway involves the π-electron system of the carboxylate. Although the structural data emphasize the low symmetry of the superexchange pathways, which could suggest antiferromagnetic interactions since the orbitals in the pathways are not orthogonal, it is known that the carbonate ion transmits ferromagnetic interactions in $Na_2Cu(CO_3)_2$,[18] and the $-CO_2^-$ pathways are comparable in some respects in $Na_2Cu(CO_3)_2$ and the present compound. The intralayer exchange-coupling constant J is $+4.1 \pm 0.7$ in $Na_2Cu(CO_3)_2$,[18] a value which is comparable to the exchange-coupling constant found here.

The angle between the planes which are defined by the carboxylate oxygen atoms coordinated to copper ions in adjacent formula units, which is designated τ in Figure 6, was calculated by using a computer program[17] and found to be 119.8°. This angle may understood in terms of the sp^2 hybridization of the exocyclic carboxylate oxygen atom. In high-symmetry cases, orthogonal orbital pathway may accompany this kind of geometry, and it is likely that the dominant terms in the exchange intergral, the positive ones, are a result of this geometry, since the observed intralayer coupling constant is positive and the intralayer exchange is ferromagnetic in nature.

There is an additional reasonably short oxygen to next neighbor copper ion separation, that being the O1 (see Figure 5) Cu distance of 2.95 Å. In view of the distance, it is unlikely that this pathway is important in the exchange processes.

The Hamiltonian for the two-dimensional system is given by[19]

$$\mathcal{H} = -2J\sum_{i,j}(\hat{S}_i^z\hat{S}_j^z + \xi\hat{S}_i^x\hat{S}_j^x + \eta\hat{S}_i^y\hat{S}_j^y) - 2J'\sum_{k,l}\mathbf{S}_k\cdot\mathbf{S}_l$$

where $0 < \xi, \eta < 1$, the S_i^z ($q = x, y, z$) are the components of the spin operators along the Cartesian coordinates, J and J' are the intra- and interlayer exchange constants, and ξ and η are constants which account for anisotropy in the intralayer exchange. The Heisenberg case arises when $\xi = \eta = 1$. When z is taken as the easy axis of magnetization then the exchange anisotropy is Ising-like when $\xi = \eta < 1$ and is XY-like when $\xi = 1$ and $\eta < 1$.

The effective intralayer exchange field may be calculated from the equation[20]

$$H_{ex} = 2ZJS/g\mu_B$$

where Z is the number of nearest neighbors in the layer. Using the magnetic parameters determined in this study, we find the intraplanar exchange field, $H_{ex} = 1.89 \times 10^5$ Oe. With data from a powdered sample, it is not possible to determine the in-plane anisotropy. Assuming axial symmetry, we may estimate the out-of-plane anisotropy from the magnetization data. By plotting the ratios of small differences $\Delta M/\Delta H$ vs. field,[21] this was determined to be about 250 Oe. For comparison, we note that the out-of-plane anisotropy field of 1140 Oe was determined by measurements on a single crystal of the ferromagnetic layer compound bis(benzylammonium) tetrachlorocuprate(II),[2] which has an ordering temperature of 8.0 ± 0.5 K and an exchange coupling constant of 24.6 cm^{-1}. An out-of-plane anisotropy field (which is largely the interlayer exchange field) of 5400 Oe was estimated for $Na_2Cu(CO_3)_2$ from powder susceptibility data.[18] This much greater value of H_{AF} in $Na_2Cu(CO_3)_2$ reflects the short interlayer copper–copper separation of 5.64 (2) Å[22] and accounts for the much larger ratio of J'/J observed in $Na_2Cu(CO_3)_2$ than in copper oxydiacetate hemihydrate, where we have found that $J_{inter}/J_{intra} \approx 1.3 \times 10^{-3}$.

In conclusion, we note that in recent years a great deal of progress has been made in the experimentally controlled design and synthesis of materials with desired physical properties. If one important outstanding problem were solved, it appears that it would be possible to produce insulating ferromagnets following the set of guidelines set out in the Introduction. This problem concerns the ultimate nature in the three-dimensional ordering of layered compounds which exhibit ferromagnetic intralayer exchange. The determination of the structural and electronic factors which control the ordering (ferromagnetic or antiferromagnetic) of these layers will continue to be the focus of systematic research.

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Registry No. Copper(II) oxydiacetate hemihydrate, 56977-72-1.

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[18] Gregson, A. K.; Healy, P. C. *Inorg. Chem.* **1978**, *17*, 2969–70.

[19] Oguchi, T. *J. Phys. Soc. Jpn.* **1971**, *31*, 1021 and references therein.

[20] Smart, J. S. "Effective Field Theories of Magnetism"; W. B. Saunders Co.: Philadelphia, 1966; Chapter 3.

[21] Losee, D. B.; Hatfield, W. E. *Phys. Rev. B* **1974**, *10*, 1122–6.

[22] Healy, P. C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1913–7.