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The Magnetic Properties of a Series of Hydroxo-Bridged Complexes of 2,2′-Dipyridyl and Copper(II)

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The magnetic susceptibilities of the complexes [Cu(2,2′-dipy)(OH)]$_2$X$_{1,2}$·nH$_2$O where X = SO_4^{2-}, I^-, Br^-, and ClO_4^- and n = 5, 3, 4, and 0, respectively, have been measured in the temperature range 4.2–70°K. Electron paramagnetic resonance spectra of each complex demonstrate that the copper ions in the dimeric molecules are exchange coupled, and the magnetic susceptibility data are consistent with a triplet ground state in each case with values for the singlet–triplet splittings $2J_{I^-} > 150$; $100 > 2J_{ClO_4^-} > 50$; $80 > 2J_{Br^-} > 40$; and $50 > 2J_{SO_4^{2-}} > 40$ cm^{-1}.

Introduction

For several years, we have been investigating the magnetic properties of oxygen-bridged bimetallic copper complexes.[1] As a part of this continuing study, we have measured and interpreted the magnetic susceptibilities of the complexes [(dipy)Cu(OH)$_2$Cu(dipy)]X$_{1\text{ or }2}$·nH$_2$O where X = SO_4^{2-}, I^-, Br^-, and ClO_4^- and n = 5, 3, 4, and 0, respectively (dipy = 2,2′-dipyridyl).

These dimers were first reported by Harris, Sinn, Walker, and Woolliams[2] in a series of 2,2′-dipyridyl– and 1,10-phenanthroline–copper complexes. Recently the crystal structure and magnetic susceptibility data to 84°K have been reported for the complex with a sulfate anion by Casey, Hoskins, and Whillans.[3] They have shown this dimer to contain two copper-centered distorted square pyramids with a shared basal edge as is diagramatically shown in Figure 1. Their magnetic susceptibility data, some of which are included in Figure 2, showed an increase in the effective magnetic moment from 1.94 BM per copper atom at 298.5°K to 2.04 BM at 84°K. The reciprocal of the susceptibility followed the Curie–Weiss law with $\Theta = -11$°K. They interpreted the increase in magnetic moment to indicate that this complex has a triplet ground state with the singlet state of the dimer being appreciably higher in energy.

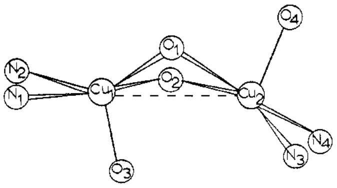

Figure 1.—The structure of [(dipy)Cu(OH)$_2$Cu(dipy)]SO$_4$·5H$_2$O. Cu(1)–O–Cu(2) angles 97°; bridging O–Cu–bridging O angles 83–84°; Cu–Cu distance 2.893 Å; Cu–bridging O distance 1.92–1.95 Å. O(3) is the oxygen atom of one of the water molecules. O(4) is from the sulfate anion. The nitrogens are from the two dipyridyl groups. Data are from ref 3.

Our magnetic susceptibility measurements for the four compounds at temperatures below 70°K tend to confirm the conclusions of Casey, *et al.*, with respect to the sulfate complex and to indicate that the other dimers also may be characterized by positive J values. The fitting of our data to the Van Vleck equation has allowed us to approximate the magnetic parameters of the four compounds.

Experimental Section

Preparation and Characterization of the Compounds.—The complexes were prepored using the general method of Harris, *et al.*[2,4]

Two preparations were made of [(dipy)Cu(OH)$_2$Cu(dipy)]I$_2$·3H$_2$O. In the first, 1.5 g of the sulfate dimer was dissolved in 100 ml of boiling water and added to 0.9 g of potassium iodide dissolved in 20 ml of hot water. The mixture was boiled with stirring and then cooled. The precipitate from the cooled mixture contained two distinct products, dark green-blue crystals and a fine, light green powder. The mother liquor was a blue-green solution. The precipitate was washed five times with 3-ml portions of water; the bright blue wash liquor showed no lessening of its color with successive washings. Because of the uncertainty of the nature of the product and because of the loss of product in washing, the mother liquor, wash liquor, and remaining product were combined with a solution containing an excess (about 1 g) of potassium iodide; the mixture was heated to boiling, and the precipitate was collected at once. It was washed with two 30-ml portions of water (the second being almost colorless), two 20-ml portions of ethanol, and two portions of ether. The product was air-dried and stored over P$_2$O$_5$ under vacuum; yield of green powder 1.20 g.

Because of the uncertainties of this preparation, the work was duplicated except that the green precipitate which formed upon mixing the hot solutions of sulfate dimer and potassium iodide was immediately collected and washed with water, ethanol, and ether before being air-dried and stored over P$_2$O$_5$ under vacuum, yield 0.70 g. Comparison of the analytical data shows that the product prepared on the second attempt is not as pure as the first product, probably because of the rapid precipitation associated with the formation of the second powder, which resulted in the "trapping" of impurities of the solid. This situation exists even though the second technique represents an exact duplication of the preparation reported by Harris, *et al.*, while the first preparation obviously included certain trial-and-error aspects. On the basis of the analytical results, the first product was used for all subsequent measurements.

To prepare [(dipy)Cu(OH)$_2$Cu(dipy)](ClO$_4$)$_2$·nH$_2$O, 2 g of the sulfate dimer in 50 ml of boiling water was added to 2 g of sodium perchlorate (G. Frederick Smith Chemical Co.) in 40 ml of hot water. A light blue powder precipitated immediately. It was digested with stirring and heating but without boiling and then cooled slowly. The powder was collected from an almost colorless mother liquor and washed with three 20-ml portions of water and then with dry ether. After air-drying, the product was stored over P$_2$O$_5$ under vacuum. The yield was 2 g.

The exact value of n, the number of waters of hydration, is un-

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[1] (a) W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, **2**, 629 (1963); (b) W. E. Hatfield, C. S. Fountain, and R. Whyman, *ibid.*, **5**, 1855 (1966); (c) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and R. Jones, *J. Amer. Chem. Soc.*, **92**, 4982 (1970); J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Commun.*, 1593 (1970).

[2] C. M. Harris, E. Sinn, W. R. Walker, and P. R. Woolliams, *Aust. J. Chem.*, **21**, 631 (1968).

[3] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

[4] F. M. Jaeger and J. A. Van Dijk, *Z. Anorg. Allg. Chem.*, **227**, 273 (1936).

TABLE I
ANALYTICAL DATA

Compound	% calcd C	H	N	X	% found C	H	N	X
$Cu(dipy)_2(OH)_2SO_4 \cdot 5H_2O$	36.4	4.3	8.5	...	36.5	4.0	8.3	...
$Cu(dipy)_2(OH)_2I_2 \cdot 3H_2O$	30.7	3.1	7.2	32.5[a]				
First preparation					30.8	3.0	7.2	32.8
Second preparation					30.6	2.6	7.1	
$Cu_2(dipy)_2(OH)_2Br_2 \cdot 4H_2O$	34.1	3.7	7.9	22.7[b]	34.0	3.6	7.9	22.9
$Cu_2(dipy)_2(OH)_2(ClO_4)_2 \cdot 0.5H_2O$	35.3	2.8	8.2	10.4[c]	35.1	2.8	8.3	10.4
$Cu_2(dipy)_2(OH)_2(ClO_4)_2$	35.7	2.7	8.3	10.6[c]	35.5	2.7	8.3	10.5

[a] Iodine. [b] Bromine. [c] Chlorine.

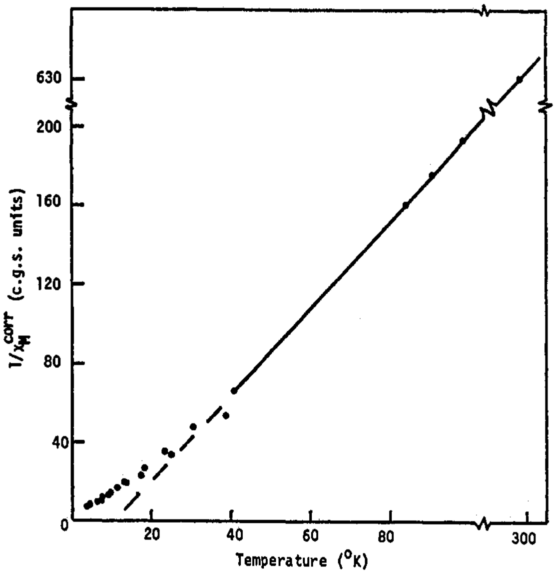

Figure 2.—The inverse of the magnetic susceptibility per copper atom of $[(dipy)Cu(OH)_2Cu(dipy)]SO_4 \cdot 5H_2O$ as a function of temperature. The solid and dashed line represents the Curie–Weiss behavior of the data at higher temperatures. (Data above 80°K are from ref 3.)

certain and seems to vary with storage conditions of the product. Harris, *et al.*, reported $n = 1$ for the compound when dried under vacuum over P_2O_5, mainly on the basis of weight loss at 120° (calcd for one water of hydration, 2.7; found, 2.2). Their analytical data are closer to those calculated for $n = {}^1/_2$. Analysis of our blue product at the time of preparation supports this latter value. After 2 months of storage over P_2O_5 under vacuum, our product had become purple; reanalysis indicated this to be the anhydrous complex. All analytical data are summarized in Table I. The purple product was used for all further measurements.

Magnetic Measurements.—Susceptibility data between 4.2 and 70°K were collected using a Foner-type vibrating sample magnetometer[5] manufactured by Princeton Applied Research, Inc. Measurements were made at field strengths of 10,000 and 2500 G. Temperatures were measured with a calibrated, precision germanium resistance thermometer. The data were corrected for the diamagnetism of the sample holder assembly, for the diamagnetism of the constituent atoms using Pascal's constants[6] (182, 200, 191, and 162 × 10^{-6} cgsu per copper for X = SO_4^{2-}, I^-, Br^-, and ClO_4^-, respectively), and for temperature-independent paramagnetism (60 × 10^{-6} cgsu per copper atom).

Epr measurements were made on powdered samples of the pure complexes in quartz tubes using a Varian E-3 spectrometer. Radiation used was 9.190 GHz (X band).

Results and Discussion

Casey, *et al.*, have shown[3] that in the sulfate dimer one copper ion is bonded to one of the waters of hydration while the other metal is bonded to one of the oxygens of the sulfate anion. Harris, *et al.*,[2] have argued on the basis of spectroscopic and conductivity measurements that in the iodide dimer the iodine atoms are coordinated to the copper atoms. This coordination is said to account for the green color of this complex. The color change associated with the dehydration of the perchlorate compound indicates a change in the coordination environment of at least one of the coppers, but it is impossible to evaluate this change from the information available.

Recently, the crystal structure of $[(dipy)Cu(OH)_2Cu(dipy)](NO_3)_2$ has been reported.[7] The structure of this complex is very similar to that of the sulfate dimer except that in this case the two copper–dipyridyl planes are parallel and are bridged across a center of symmetry. The fifth coordination position of each copper is occupied by an oxygen from one of the nitrate groups. Each dimeric unit is linked to two other molecules by an interaction between an oxygen of each nitrate group and the hydrogen of one of the hydroxo bridges of another molecule. Because of difficulties in preparative technique and because we have not yet measured the magnetic susceptibility of this complex, no further attempt will be made to relate this structure directly to our present work.

In summary, it is obvious that the four complexes now under study and their nitrate analog do not have identical structures. However, the fact that the angles and bond lengths of the $[N_2Cu(OH)_2CuN_2]$ units of the sulfate and nitrate dimers are very similar (all angles agree within 1°, bond lengths within 0.02 Å) supports the validity of the structural generalizations made in our discussion of the mechanisms of magnetic coupling in a later section of this paper.

Magnetic susceptibility data for the four complexes studied are shown in Figures 2 and 3. At low temperatures, the magnetic susceptibilities were a function of the field strength used to make the measurements. To correct for this problem data were taken using a field of only 2500 G until the temperature was high enough so that there was no observable difference between the susceptibility measured at 2500 and 10,000 G or until the measured moment was too small for satisfactory significance. When one of these situations occurred, the field strength was increased to 10,000 G for all further measurements. For the bromide complex, two points at 4.27 and 2.93°K were measured using a field strength of 1000 G.

The $1/\chi_M^{cor}$ *vs.* T plot for the sulfate dimer is shown in Figure 2. At higher temperatures, the inverse of the susceptibility obeys the Curie–Weiss law with an intercept of the T axis at $T \simeq 11°$. At low temperatures, there is a clear deviation from Curie–Weiss

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[5] S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

[6] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

[7] R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, **74**, 3497 (1970).

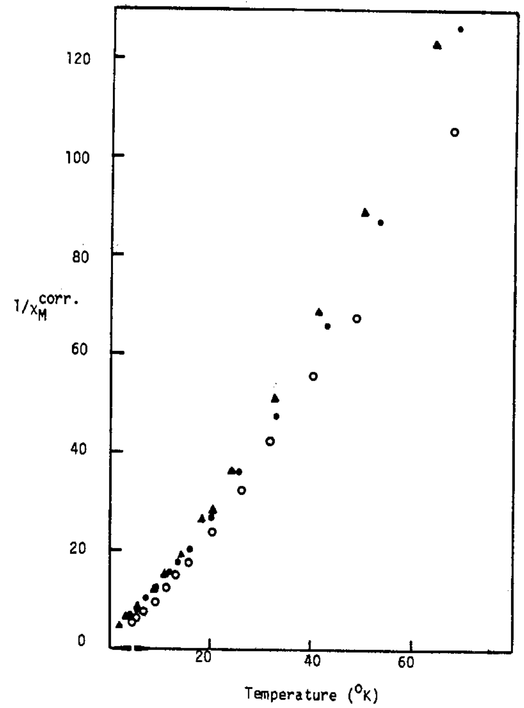

Figure 3.—The inverse of the magnetic susceptibility per copper atom of $[(\mathrm{dipy})\mathrm{Cu(OH)_2Cu}(\mathrm{dipy})]\mathrm{X_2}\cdot n\mathrm{H_2O}$ as a function of temperature: ●, $\mathrm{ClO_4^-}$; ○, $\mathrm{I^-}$; ▲, $\mathrm{Br^-}$.

behavior. The measured magnetic susceptibility of the complex is lower than that predicted by the Curie–Weiss law at temperatures below about 35°K. This behavior is in agreement with that predicted by the Van Vleck equation (eq 1) for exchange-coupled copper

$$\chi_M^{\mathrm{cor}} = \frac{g^2N\beta^2}{3kT}[1 + {}^1/_3\exp(-2J_{12}/kT)]^{-1} \qquad (1)$$

ions with a positive J_{12} value corresponding to a triplet ground state.

If one considers eq 1, it is clear that $2J/kT$ becomes larger as the temperature is lowered so that the term $1/(3 \exp 2J/kT)$ approaches zero. Thus, as the temperature is lowered, the plot of $1/\chi_M^{\mathrm{cor}}$ *vs.* T should approach simple Curie law behavior. The curves for our data, especially for the perchlorate dimer, show a deviation from this Curie law limit. The measured susceptibilities are less than expected. There are several possible reasons for this deviation, including the following: field-dependent effects, error in temperature measurement, or a lattice-coupling mechanism with a small negative coupling constant (*i.e.*, an "antiferromagnetic" interaction). In spite of the fact that low-temperature measurements were made at a reduced field strength, near 4.2°K field effects are still expected to be present to some degree; and because of the limits of the magnetometer, it is unlikely that this problem can ever be fully eliminated.

Temperature measurement with the magnetometer is quite precise and reproducible. Unfortunately, there are problems in relating the measured temperature to the temperature of the sample. It is possible that under certain circumstances the sample is at a lower temperature than that measured because of the physical design of the equipment. Temperature measurements are normally made when the sample is at rest; susceptibility measurements are made with the sample vibrating. Careful observations of sample temperatures seem to indicate that the temperature is a fraction of a degree warmer when the system is vibrating than when it is at rest. This warming is probably caused by slight friction between the sample rod and the chamber wall. This small error would have little effect at higher temperatures, but near 4.2°K it could be significant enough to affect the data.

In spite of the above discussion, one must not overlook the possibility of simple chemical impurity of the sample as a source of this behavior, especially in the case of the perchlorate complex with its uncertain analysis.

The data were fitted to the Van Vleck equation by using a computer program in which the sums of the squares of the deviations weighted by the temperature were minimized. Although this weighting process does increase the significance of the fit, the Van Vleck equation is still not very sensitive to small changes in the value of J. For example, for the data for the iodide complex, the difference in the sums of the squares of the weighted deviations for $2J = 150\ \mathrm{cm^{-1}}$ and the best fit value of $2J = 485\ \mathrm{cm^{-1}}$ is 1 part in 500. Thus while it is legitimate to say that the $2J$ value for the iodide dimer is quite large, it is indeed questionable whether $2J$ is clearly $485\ \mathrm{cm^{-1}}$ rather than $150\ \mathrm{cm^{-1}}$. In spite of the lack of sensitivity of the fitting process, it was used to evaluate the data for the four complexes.

First, the data as measured and tabulated were fitted to eq 1. The best fits were obtained with $2J = 485$, 99, 77, and $47\ \mathrm{cm^{-1}}$ for the iodide, perchlorate, bromide, and sulfate complexes, respectively. In each case, $\langle g\rangle$ was taken to be 2.22.

Though the structural work reported by Casey, *et al.*, seems to eliminate the possibility of extensive, nondimeric interactions, weak lattice effects may still exist. To evaluate this possibility, the right-hand side of eq 1 was multiplied by $T/(T + \Theta)$ where Θ is a correction to the dimeric equation for lattice effects. This correction was evaluated by repeating the fitting process for each of the original data sets several times using values of Θ incremented by 0.5°K for each fit. Thus a best combination of $2J$, $\langle g\rangle$, and Θ could be derived. The calculated values were as follows for the iodide, perchlorate, bromide, and sulfate complexes, respectively: $2J = 485$, 93, 67, and $49\ \mathrm{cm^{-1}}$; $\langle g\rangle = 2.22$, 2.22, 2.22, and 2.20; $\Theta = -1.5$, -0.5, -1.0, and -1.0°K. The quality of the fitting process for these calculations was an improvement over the first calculation.

In summary, though the data admit many interpretations, certain generalizations are common to all of our evaluations of the data. The coupling constants may be arranged as follows: $2J_{\mathrm{I^-}} > 2J_{\mathrm{ClO_4^-}} > 2J_{\mathrm{Br^-}} > 2J_{\mathrm{SO_4^{2-}}} \simeq 45\ \mathrm{cm^{-1}}$. It is also reasonable to say that, within the limits of the above relationship, $2J_{\mathrm{I^-}} > 150$, $100 > 2J_{\mathrm{ClO_4^-}} > 50$, $80 > 2J_{\mathrm{Br^-}} > 40$, and $50 > 2J_{\mathrm{SO_4^{2-}}} > 40$, where all energies are in $\mathrm{cm^{-1}}$.

The epr spectra of the four complexes are of great interest, for they are very similar to the spectrum for the copper(II) cyanoacetate system which has been characterized by Wasson, Shyr, and Trapp[8] using a relatively large zero-field splitting parameter of $D = 0.39\ \mathrm{cm^{-1}}$. Unfortunately our spectra are not as well defined as those reported by Wasson, *et al.*, but we have been able to use their approach to interpret our data

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(8) J. R. Wasson, C. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

and approximate zero-field splitting parameters of each of our dipyridyl complexes.

The spectra for the iodide, perchlorate, and sulfate complexes contain the same basic features, a relatively sharp peak at about 3000 G and a much broader one near 5000 G. The spectra of the sulfate and perchlorate complexes are shown in Figure 4. The spectrum of the bromide compound is of much poorer quality and will not be presented here. We can offer no explanation for this difficulty.

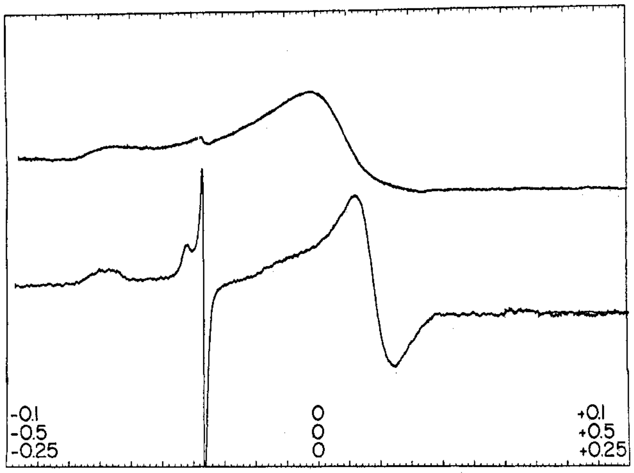

Figure 4.—The X-band epr spectra of powdered samples of [(dipy)Cu(OH)$_2$Cu(dipy)]$^{2+}$ salts at room temperature. The upper trace is the spectrum of the perchlorate salt and the bottom trace is the spectrum of the sulfate salt. The range is 0–10,000 G.

To aid in matching the three similar spectra to the copper(II) cyanoacetate model, two basic assumptions were made. First, it was assumed that the zero-field splitting parameter E is so small as to be considered equal to zero. Of course, it is obvious from the known[3] structure of the sulfate complex that the copper ions are not located on sites of axial symmetry, but our work[1c] with bis(pyridine *N*-oxide)copper(II) nitrate and the present model system[8] seems to indicate that this assumption is acceptable within the limits of our approximation. Second, we assumed that the band at about 3000 G resulted from the simple paramagnetism of monomeric impurity present in our samples. Unfortunately, we are unable to offer conclusive evidence to support this assumption, but band-shape and temperature-dependence studies do not conflict with this assignment. In the copper(II) cyanoacetate system, Wasson, *et al.*, were able to support a similar assignment of a similar band on the basis of the temperature dependence of the peak intensities. Having made these two assumptions the spectra may be interpreted using the analysis of Wasserman, Synder, and Yager[9] as adapted by Wasson, *et al.*[8]

The Hamiltonian for the triplet state of dimeric copper complexes is shown in eq 2.[9] This Hamiltonian

$$\mathcal{H} = \beta HgS + DS_z^2 + E(S_x^2 - S_y^2) - (2/3)D \quad (2)$$

leads one to expect an epr spectrum to contain seven bands, one isotropic $\Delta M_s = \pm 2$ transition and six $\Delta M_s = \pm 1$ transitions.[9] If $E = 0$, then the resonance fields are

$$\begin{aligned} H_{x_1}^2 = H_{y_1}^2 = H_{\perp_1}^2 &= (g_e/g_\perp)^2[H_0(H_0 - D')] \\ H_{x_2}^2 = H_{y_2}^2 = H_{\perp_2}^2 &= (g_e/g_\perp)^2[H_0(H_0 + D')] \\ H_{z_1}^2 &= (g_e/g_z)^2(H_0 - D')^2 \qquad (3) \\ H_{z_2}^2 &= (g_e/g_z)^2(H_0 + D')^2 \end{aligned}$$

where $H_0 = h\nu/g_e\beta$, $D' = D/g_e\beta$, and $g_e = g$ value of free electron. If $D > h\nu$, as is likely in the present case, the low-field perpendicular line, $H_{\perp_1}$, will not be observed; so that only four transitions are expected, a high-field perpendicular line, high- and low-field parallel lines, and a $\Delta M_s = \pm 2$ transition. (The notation used to designate various transitions is traditional but not absolutely accurate, for some mixing of states does occur at low fields.)

To make matters more difficult, the $\Delta M_s = \pm 2$ transition is forbidden and thus of very low intensity if it can be observed at all. Also, with these samples, we have found it nearly impossible to observe with our E-3 spectrometer any peaks at field strengths near or below 1000 G; thus it is unlikely that we will be able to identify the low-field parallel transition which often lies below 1000 G.

With the aid of the copper(II) cyanoacetate analysis and the above approximations, our experimental spectra may be interpreted as follows. The major broad line near 5000 G is assigned to the high-field perpendicular transition. Any high-field shoulder on this peak results from the high-field parallel transition. Any bands below the 3000-G impurity peak result from either the $\Delta M_s = \pm 2$ or the low-field parallel transition. The application of these assignments to the observed spectra is summarized in Table II.

TABLE II

OBSERVED EPR TRANSITIONS FOR [(dipy)Cu(OH)$_2$Cu(dipy)]X AND CALCULATED ZERO-FIELD SPLITTING PARAMETERS

X	H_{z_1} or $\Delta M_s = \pm 2^a$	$H_{\perp_2}{}^a$	$H_{z_2}{}^a$	$\lvert D\rvert^b$ $g_\perp = 2.05$	$\lvert D\rvert^b$ $g_\perp = 2.10$
I_2	. . .	4800^d	5900^c	0.382	0.416
$(ClO_4)_2$	1800^c	5900^d	. . .	0.734	0.785
SO_4	1700	5975^d	. . .	0.761	0.813

[a] All field positions in gauss, corrected to 9.190 GHz. All spectra measured with samples at 77°K. [b] Energy in reciprocal centimeters. [c] Data ±150 G. [d] Data ±25 G.

The range of experimentally observed values for $g_\perp$ in copper complexes is quite small; the parameter rarely exceeds a value of 2.10. In order to approximate the value of $|D|$, we have assumed $g_\perp$ to equal 2.05 and 2.10 and then have used these values of $g_\perp$ with the known value of $H_{\perp_2}$ to calculate $|D|$. These calculated values are also shown in Table II. It may be observed that the ordering of the three complexes on the basis of J values has been retained in an inverted form for the value of $|D|$.

The mechanism of the magnetic coupling is best discussed in terms of structural information. Thus, the sulfate complex is of first interest. Using the terminology suggested by Goodenough,[10] the magnetic coupling in this compound may be of two types, direct cation–cation interactions and 90° cation–anion–cation interactions.

The copper–copper separations found for the sulfate[3]

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[9] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

[10] J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience, New York, N. Y., 1963.

(2.89 Å) and nitrate[5] (2.85 Å) complexes are small enough to require that we consider the possibility of magnetic interactions directly between the cations. Goodenough[10] and Martin[11] have subdivided this type of interaction into three categories: (1) overlap of two half-filled orbitals, (2) overlap of a half-filled and a full orbital, and (3) overlap of a half-filled and an empty orbital. Obviously the third category does not apply to the present d^9–d^9 systems. The first mechanism makes a negative (antiferromagnetic) contribution to J, for the Pauli principle limits a given orbital to one electron of each spin. The second mechanism provides the following pathway for magnetic interaction: an electron may be transferred from the full orbital on atom A to the half-full one on atom B and back again. For this transfer to take place, the spin of the transferred electron must be antiparallel to the spin of the electron in the half-filled orbital. If a second orbital on A is half-filled, Hund's rule favors the transfer of the electron in the filled orbital whose spin is also antiparallel to the unpaired electron in this half-filled orbital. Thus an interaction is favored in which the spin of the transferred electron is antiparallel to the spins of the unpaired electrons on both A and B so that the latter spins must be parallel. This mechanism will make a positive contribution to J. Structural considerations eliminate the possibility of two half-filled orbitals overlapping in the present complexes so that the only contribution from a cation–cation interaction to the final value of J must be positive.

The mechanisms contributing to magnetic coupling through a 90° cation–anion–cation pathway have been discussed in detail elsewhere[10,11] and will be mentioned here only briefly. The two unpaired electrons in the dipyridyl complexes will be located in the $d_{x^2-y^2}$ orbitals of the copper ions. These electrons may be antiferromagnetically coupled through oxygen s orbitals and ferromagnetically coupled through two p orbitals. The latter mechanism is expected to be stronger than the former because of the greater radial extension of the p orbitals.

Since all the major pathways available for magnetic coupling make positive contributions to J, the sign of experimentally measured data is reasonable. The preceding discussion of mechanisms offers no explanation for the different J values determined for the four complexes under study. The assumption used in the above model that the unpaired electrons existed in "pure" $d_{x^2-y^2}$ orbitals is of course naive. The spatial distribution of the unpaired electron spin around the copper ions is very much a function of the environment of the ions. As the spin density changes slightly with changes in anion, changes in the magnitude of the coupling would be expected. We have been able to suggest general mechanisms to explain the sign of J, but much more complete characterization of the complexes is needed before changes in the magnitude of J within this series of compounds can be fully understood. Presumably electronic effects arising from changes in the coordinated counterion(s) and water molecules contribute to the trend, but we do not choose to speculate in the absence of structural data.

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[11] R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968.

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The Isomers of the Bis(diethylenetriamine)cobalt(III) Ion and a New Source of Optical Activity

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The three geometric isomers of the $[Co(dien)_2]^{3+}$ ion s-cis, u-cis, and trans have been separated by various methods, and the u-cis and trans isomers have been resolved into optical isomers through diastereoisomer formation. The configurations have been unequivocally assigned to these geometric forms from the different racemization behavior of the u-cis and trans optical isomers. Factors determining relative isomer stabilities are discussed, and infrared and pmr criteria for assigning isomer configurations are examined.

Introduction

The problem of the existence of the three geometric isomers which are possible for a complex $[M(dien)_2]^{3+}$ (where dien designates the tridentate ligand diethylenetriamine)[1] has remained ever since the cobalt(III) complex ion of this formulation was first isolated as the iodide $[Co(dien)_2]I_3$ by Mann in 1934.[2] The corresponding chromium(III) complex $[Cr(dien)_2]I_3$ has also been prepared[3] and again isomers have not been isolated. This paper describes the isolation and characterization of all the geometric and optical isomers which

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[1] Abbreviations used: en, ethylenediamine; *N*-Meen, *N*-methylethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine; tetraen, tetraethylenepentamine; penten, pentaethylenehexamine (double branched chain isomer); sarc, sarcosinato; tart, tartrate; mal, malonato.

[2] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[3] V. O. Kling and H. L. Schlafer, *Z. Anorg. Allg. Chem.*, **313**, 187 (1961).