trans-PdCl2(PMe3)(Ay), 57396-12-0; *trans*-PtCl2(PPhMe2)(Ay), 57396-13-1; *trans*-PtCl2(PMe3)(Ay), 57396-14-2; *trans*-PdCl2-(PPhMe2)(Sy), 57396-15-3; *cis*-PdCl2(PPhMe2)(Sy), 57456-88-9; *trans*-PdCl2(PMe3)(Sy), 57396-16-4; *cis*-PdCl2(PMe3)(Sy), 57456-89-0; *trans*-PtCl2(PPhMe2)(Sy), 57396-17-5; *cis*-PtCl2-(PPhMe2)(Sy), 57456-90-3; *trans*-PtBr2(PPhMe2)(Sy), 57396-18-6; *cis*-PtBr2(PPhMe2)(Sy), 57456-91-4; *trans*-PtI2(PPhMe2)(Sy), 57396-19-7; *cis*-PtI2(PPhMe2)(Sy), 57456-92-5; *trans*-PtCl2-(PMe3)(Sy), 57396-20-0; *trans*-PdCl2(PPhMe2)(Py), 57396-21-1; *trans*-PdCl2(PMe3)(Py), 57396-22-2; *trans*-PtCl2(PPhMe2)(Py), 57396-23-3; *trans*-PtBr2(PPhMe2)(Py), 57396-24-4; *trans*-PtI2-(PPhMe2)(Py), 57396-25-5; *trans*-PtCl2(PMe3)(Py), 57396-26-6; Ny, 25357-50-0; Ay, 24904-06-1; Sy, 5633-34-1; Py (charged form), 57395-87-6; di-μ-chloro-dichlorobis(dimethylphenylphosphine)di-platinum(II), 15699-79-3; di-μ-chloro-dichlorobis(dimethylphenyl-phosphine)dipalladium(II), 15699-80-6; Py (uncharged form), 57395-88-7.

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Magnetic Properties of α-Di-μ-hydroxo-bis[2-(2-dimethylaminoethyl)pyridinecopper(II)] Perchlorate, α-[Cu(DMAEP)OH]2(ClO4)2

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The magnetic susceptibility and electron paramagnetic resonance spectra of α-di-μ-hydroxo-bis[2-(2-dimethylamino-ethyl)pyridinecopper(II)] perchlorate are reported. The susceptibility data are characteristic of exchange-coupled copper(II) pairs with a small interpair interaction. The pairwise interaction results in a singlet ground state for the pair with a very low-lying triplet excited state. A crossover of the triplet and singlet energy levels is produced with an applied field of ~50 kG. The magnetic parameters derived are $J = -2.35 \pm 0.2$ cm^{-1}, $J' \simeq -0.1$ cm^{-1}, $g = 2.08 \pm 0.02$, and $D \approx 0.4$ cm^{-1}. The results are discussed in terms of the molecular structure of the complex and compared to structurally similar systems.

The preparation and characterization of a number of di-hydroxo-bridged copper(II) complexes which belong to the general class [Cu(L)OH]2X2·nH2O have been reported.[1-4] Here L has been a variety of chelating amines and X$^-$ has been several counterions such as ClO4$^-$, Br$^-$, $1/2$ SO4^{2-}, etc. The magnetic properties of this series are characteristic of exchange-coupled copper(II) ions. For these systems, the singlet–triplet (S–T) splitting energy, which results from the isotropic exchange interaction, ranges from large positive values (triplet ground states) to very large negative values (singlet ground states). Studies on this series have yielded much useful information in our continuing efforts to correlate the structural and magnetic properties of magnetically condensed systems. The structural properties vary only slightly throughout the series while the magnetic properties vary greatly. Our investigation of several members of the series has revealed[2-4] a striking correlation between the S–T splitting 2J and the Cu–O–Cu bridge angle ϕ.

Recently, Uhlig and co-workers reported[5] the preparation of complexes formed with copper(II) and N-substituted 2-(2-aminoethyl)pyridine which, on the basis of the spectral and high-temperature magnetic data, should belong to this series.

Of particular interest is the reaction of copper(II) perchlorate and 2-(2-dimethylaminoethyl)pyridine (DMAEP). Recent structural investigations[3,6] have revealed the existence of two forms of complex. The monoclinic β form does belong to the structural class and obeys the near-linear 2J vs. ϕ relationship. The triclinic α form, however, does not belong to this structural class since the copper(II) ions are bridged by the perchlorato anions as well as the hydroxo groups.

We report here the magnetic properties of the α form of the DMAEP complex which indicate that the exchange interaction is greatly affected by this structural change. The magnetic properties of α-DMAEP are of special interest since an "S–T crossover" is produced by large applied magnetic fields, a phenomenon which has received very little attention in previous reports of exchange-coupled systems.

Experimental Section

Preparation. The addition of 2-(2-dimethylaminoethyl)pyridine to an equimolar quantity of copper(II) perchlorate hexahydrate in a minimum volume of an alcohol–ether solution yields a blue precipitate having the stoichiometry Cu(DMAEP)OHClO4. Magnetic measurements (vide supra) indicate that this precipitate is a mixture of the α and β forms of the complex. Crystal growth from an absolute
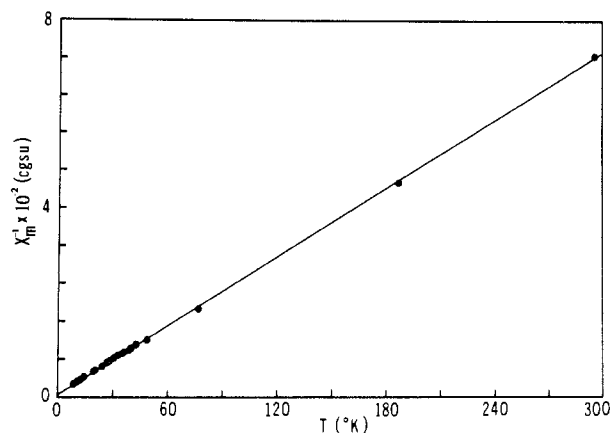
Figure 1. Temperature variation of the inverse susceptibility in the temperature range 9–300 K (●). The solid line shows the Curie–Weiss behavior in this temperature range.

ethanol–ether (7:3) solution enhances the formation of the needlelike monoclinic β form[3] while growth from a methanol–ether (7:3) solution favors the formation of the prismatic α form[6] of the complex.

Although very small single crystals of the α-DMAEP complex may be collected, the crystals tend to twin as crystal size increases. All crystals which were suitable for magnetic measurements were found to be severely twinned; however, the x-ray data clearly show the material to be the triclinic α form of the complex. Anal. Calcd for $CuClC_9H_{15}N_2O_5$: C, 32.64; H, 4.53; N, 8.58. Found: C, 32.79; H, 4.53; N, 8.44.

Bulk Susceptibility Measurements. Magnetic susceptibilities were measured on a powdered sample (prepared by grinding several crystals) in the temperature range 1.6–70 K and on a crystalline sample (weighing ~15 mg) in the temperature range 1.45–300 K. The susceptibility measurements for temperatures between 1.45 and 70 K were made with a PAR vibrating-sample magnetometer which was calibrated with a pure nickel sphere.[7] The magnetometer is equipped with a standard electromagnet which may be operated with magnetic fields of 0–16.3 kG and a Westinghouse superconducting solenoid which is capable of attaining field strengths of 50 kG. A complete data set was collected in the temperature range 1.45–50 K with an applied field of 30 kG. Some additional low-temperature data were collected with applied fields of 10, 15, and 50 kG. Susceptibility data in the temperature range 77–300 K were obtained by the Faraday method using a Cahn electrobalance equipped with a digital voltmeter. For the Faraday measurements, a $Hg[Co(SCN)_4]$ sample was used as the calibrant.[8] Temperature measurement was accomplished with a calibrated gallium–arsenide diode.[9]

EPR Measurements. EPR spectra were recorded with a Varian 4502 spectrometer which has been modified to operate at multiple microwave frequencies.[10] Spectra were recorded with X- and Q-band frequencies at temperatures in the 2–4.2 K range and at 77 K. The X-band spectra were obtained with a standard V4531 cavity and insertion dewars. The Q-band measurements were made with a cylindrical cavity which was immersed in the cryogen. In this arrangement, the magnetic field could be rotated 200° about the sample. A 100-kHz modulation frequency was used for all measurements. The magnetic field and microwave frequencies were measured with a Magnion 502 precision gaussmeter and a Hewlett-Packard 5245L frequency counter.

Results

The temperature variation of the inverse susceptibility of the complex in the temperature range 9–300 K is shown in Figure 1. The data obey a Curie–Weiss law having the form $\chi_m = C/(T - \theta)$ where $C = 0.406$ cgsu/deg and $\theta = 2$ K.

With an applied field of 10 kG the magnetic susceptibilities of the powdered sample increase with decreasing temperature and reach a maximum value at 3.9 K; however, the magnitudes of these susceptibilities are much smaller than would be expected for an exchange-coupled copper(II) dimer. This suggests that a substantial amount of diamagnetic impurity is present. In view of the analytical data, this effect could only

be produced by the presence of the β form of the complex which is diamagnetic at low temperatures.

The susceptibility data for the crystalline sample also maximize at 3.9 K and the magnitudes of the susceptibilities are in the expected range. The observed susceptibilities are highly field dependent in the low-temperature region. At temperatures near the maximum the apparent susceptibilities are significantly larger with an applied field of 30 kG than the corresponding values measured with an applied field of 10 kG. When a field strength of 50 kG is used, the data do not maximize but continue to increase until a saturation value is reached at ~1.45 K.

The EPR spectra of the crystalline sample reveal the crystal twinning as indicated by the x-ray films. There are several resonances which show angular dependence. The intrinsic line widths are large (~300G) and the resonances overlap resulting in a very broad uninterpretable spectrum for many orientations. At X-band frequencies, the resonances are found in the high-field region of the spectrum with the extreme absorption occurring at 7400 G. The Q-band spectra are very similar; only the resonances are found in the low-field region of the spectrum with the extreme absorption occurring at 7200 G. Complete characterization of the angular variation of the spectra is precluded by the crystal twinning even at the higher microwave frequency. The 77 K and the low-temperature measurements gave the same results.

Discussion

The Curie–Weiss plot for the susceptibility data above T_{max}, shown in Figure 1, yields a g value of 2.08 according to

$$g^2 = 3kC/N\beta^2 S(S + 1) \tag{1}$$

This value is taken to be an average value produced by the crystal twinning since no significant anisotropy was detected for different orientations of the applied field. The maximum in the susceptibility data at lower temperatures is characteristic of exchange-coupled dimeric systems; however, the field dependence of the data suggests that other interactions are important. The appropriate Hamiltonian is given by

$$H = gH_0S + D[S_x^2 - \tfrac{1}{3}S(S + 1)] + E(S_x^2 - S_y^2) - 2JS_1 \cdot S_2 \tag{2}$$

The symbols in (2) have their usual meanings. S_i ($i = 1, 2$) are the spin operators of ions 1 and 2 and S is the total spin operator, $S_1 + S_2$. For the present case $S_i = \tfrac{1}{2}$ so S can be 0 or 1. The isotropic exchange interaction results (for negative J) in a singlet ground state and a triplet excited state which is further split by the applied field H_0 and the zero-field terms D and E. By neglecting D and E, which are small compared to the remaining terms and assuming a Boltzmann distribution for the population of the singlet and triplet levels, the magnetization per mole of sample M_0 is given by (3).[11]

$$M_0 = \frac{N g\beta \sinh (g\beta H_0)}{\exp(-2J/kT) + 2 \cosh (g\beta H_0/kT) + 1} \tag{3}$$

The effect that the magnetic field has on the magnetization, which is calculated according to eq 3 for an appropriate set of parameters, is illustrated in Figure 2. As seen from the figure, when the Zeeman energy is larger than the isotropic exchange energy, the magnetization curve is similar to that of a noninteracting system, since a magnetic state lies lowest in energy. However, when $g\beta H_0$ is smaller than $2J$, the effects of the exchange interaction are apparent. Figure 2 also illustrates the effects of an interdimeric exchange interaction. Here the applied field has been replaced with an effective field H according to a Weiss molecular field model (4), where M

$$H = H_0 + \gamma M \tag{4}$$
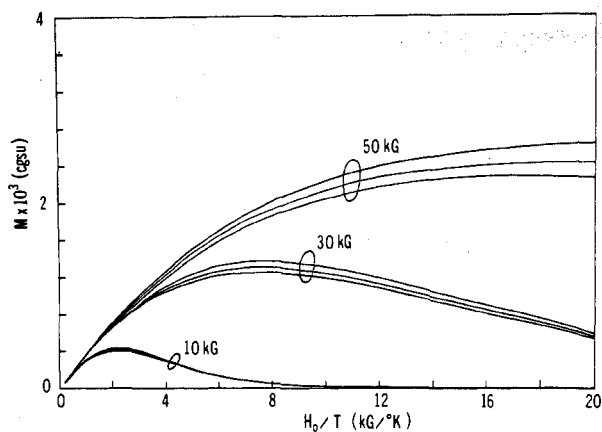
Figure 2. Magnetization of two exchange-coupled $S = \frac{1}{2}$ centers with an applied field of the same order of magnitude as the exchange coupling constant. The magnetic field dependence and the effects of a molecular field arising form interpair interactions are shown. All curves were generated with eq 3 where $g = 2.00$ and $J = -2.5$ cm^{-1}. The molecular fields were calculated according to eq 4. For each applied field, the upper, center, and lower curves correspond to $\gamma = 1$, 0, and -1, respectively.
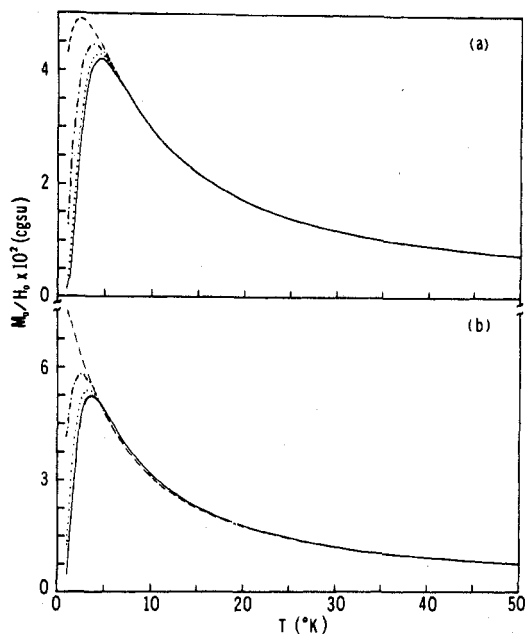

Figure 3. Comparison of the magnetic properties predicted by eq 3 and 5. The solid curves were generated with eq 5. The remaining curves were generated with eq 3 for $H_0 = 50$ kG (- - -), 35 kG (- · - ·), 20 kG (· · · ·). Note that both equations yield the same results for the parameters used with applied fields of 5 kG or less: (a) $J = 2.5$ cm^{-1}, $g = 2$, $\gamma = 0$; (b) $J = -2$ cm^{-1}, $g = 2$, $\gamma = 0$.

is the magnetization resulting from the effective field and the isotropic exchange interaction.[11] The curves shown in Figure 2 were generated by using the indicated values for γ and solving (4) by iteration until a self-consistent H is produced. It is interesting to note that when the susceptibilities maximize, the effect of H is largest near T_{max} and diminishes at lower temperatures; this result arises because H depends on M.

As the magnetic field and, hence, the Zeeman energies approach zero, eq 3 reduces to the well-known Bleaney–Bowers expression[12] for exchange-coupled $S = \frac{1}{2}$ systems (5), where

$$\chi_m = \frac{Ng^2\beta^2}{3kT}[1 + \frac{1}{3}\exp(-2J/kT)]^{-1} \tag{5}$$

$\chi_m = M_0/H_0$. The magnetic properties predicted by (3) and
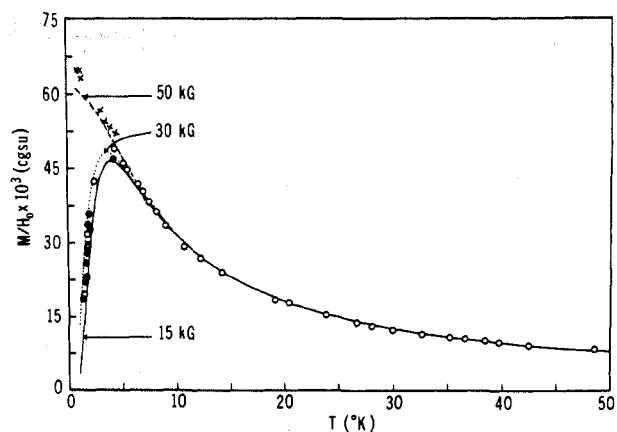
Figure 4. Temperature variation of the observed susceptibility (M/H_0) in the temperature range 1.45–48 K. The data collected for applied magnetic fields of 15 kG (●), 30 kG (○), and 50 kG (×) are shown. The solid curves were generated with eq 3 (see text).

(5) are compared in Figure 3. For the parameters given, the two equations give essentially the same results for $H_0 = 10$ kG, but when H_0 is increased, the susceptibility is markedly affected. Comparison of the a and b parts of Figure 3 illustrates the sensitivity of the observed properties with respect to the ratio $2J/H_0$. It is clear that the Zeeman interaction cannot be neglected in the characterization of complexes with small isotropic exchange energies.

We have used a nonlinear least-squares procedure to evaluate the magnetic parameters for the α-DMAEP complex. Least-squares fits to both (3) and (5) were determined. The isotropic exchange energy predicted from the 30-kG data set have similar magnitudes for both cases while the g values differ significantly. In the absence of an interdimer exchange parameter, J', the magnetization equation yields a g value of 2.00 while the Bleaney–Bowers expression results in $g = 1.92$ which is an unreasonable value for a copper(II) complex. In both cases the fits to the 30-kG data set, obtained in the $J' = 0$ limit, give reasonable fits in the low-temperature region but do not agree well with the high-temperature data; these latter data are predominant in the determination of g. By allowing some interdimer exchange the overall fit is improved in both cases but the Bleaney–Bowers expression fails to produce a reasonable g value. This is not unexpected in view of the plots shown in Figure 3. The least-squares routine minimizes the function

$$R = \Sigma(M_{obsd} - M_{calcd})^2 W/\Sigma M_{obsd}$$

as the criterion for the best fit. The data were weighted according to $W = 1/M_{obsd}$ in order to prevent overemphasis of the low-temperature data. The parameters derived from (3) which best fit all the data are $J = -2.35 \pm 0.2$ cm^{-1}, $g = 2.08 \pm 0.02$, and $\gamma = -1.0 \pm 0.4$ with R $= 2.6 \times 10^{-2}$. This g value agrees with the Curie–Weiss fit. The molecular field constant may be related to an interdimer exchange parameter J' according[11,13] to $Z'J' = \gamma Ng^2\beta^2k/2$, where Z' is the number of nearest-neighbor dimers. For the present case $J' \simeq 0.1$ cm^{-1} for $Z' = 4$. These parameters were used to generate the curves shown in Figure 4.

Although a thorough analysis of the angular variation of the zero-field splitting is precluded by the crystal twinning, it is possible to obtain approximate values for the zero-field parameters by application of the equations of Wasserman et al.[14] The observed transition fields are consistent with a value for D of $\sim$0.4 cm^{-1}. Although the rhombic splitting cannot be evaluated from these data, a value for E of $\simeq 10\% D$ is expected. The absorptions found in the X- and Q-band spectra
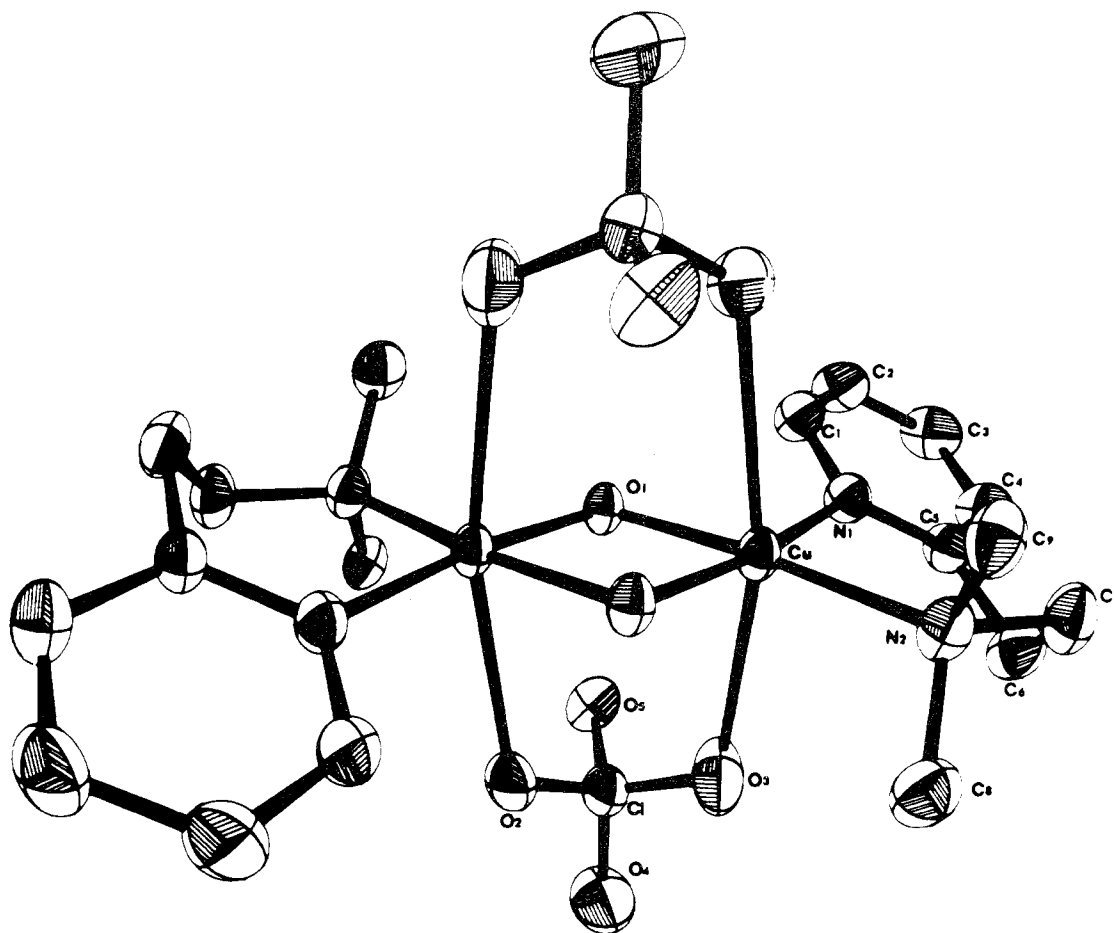
Figure 5. Molecular structure of α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$ (reproduced from ref 6).

Table I. Structural and Magnetic Data for Dimeric N-Substituted Aminoethylpyridine Complexes

Complex	Cu–N, A	Cu–O, A		Cu–Cu, A	Cu–O–Cu, deg	2J, cm⁻¹	∣D∣, cm⁻¹	g	Ref
		In plane	Out of plane						
α-DMAEP	2.017	1.947	2.782	2.938	98.4	−4.8	~0.4	2.08	6, this work
	2.056	1.936	2.716						
β-DMAEP	2.033	1.919	2.721	2.935	100.4	−201	0.43	2.03	3
	2.066	1.900							
EAEP[a]	1.981	1.895	2.562	2.917	98.8	−130	0.48	2.04	18, 19
	1.998	1.913	2.618		99.5				
	2.001	1.927							
	2.053	1.930							

[a] Noncentrosymmetric structure.

were assigned to the $\Delta M_s = \pm 1$ transitions of the triplet state. The possibility of "S–T" transitions is ruled out since the S–T separation is much larger than either microwave frequency. Also, the observed intensities are not consistent with the highly forbidden "S–T" transitions. The possibility that some of the observed transitions are due to some β-form impurity was eliminated by the low-temperature spectra. At 4.2 K the triplet-state population for α-DMAEP is 23% while for β-DMAEP the triplet state is infinitesimally populated.

This value for D is significantly larger than would be produced by dipolar interactions alone. A simple point-charge model based on the Cu–Cu separation predicts a dipolar energy of ~0.1 cm⁻¹. This suggests a substantial contribution to the zero-field splitting from the anisotropic exchange interaction. The anisotropic exchange contribution results from the spin–orbit interaction which mixes the ground- and excited-state wave functions and therefore affects the ground-state properties. The anisotropic exchange contribution is expected to be of the order $(\Delta g/g)^2(2J)$.[15] Assuming a typical g-factor anisotropy of 0.1, the observed anisotropic

exchange contribution is an order of magnitude larger[16,17] than is expected in view of the magnitude of the observed isotropic exchange, and it is much greater than that observed for β-DMAEP.[3]

The molecular structure[6] of α-[Cu(DMAEP)OH]$_2$(ClO$_4$)$_2$ may be described as two distorted octahedra sharing a common edge as seen in Figure 5. The in-plane structure is very similar to the other structurally characterized dimeric N-substituted aminoethylpyridine complexes β-DMAEP perchlorate and EAEP perchlorate[18] (EAEP is 2-(2-ethylaminoethyl)pyridine). A comparison of the structural and magnetic properties of these three complexes is given in Table I. The major structural difference between α-DMAEP and the other complexes is the bidentate perchlorate coordination which forms additional bridges between the copper ions. Although the nature of the copper–(perchlorate oxygen) bonds has been characterized[20] as semicoordination, the effect on the magnetic properties of this system is pronounced. According to the reported[2] $2J$ vs. ϕ relationship, an S–T splitting of −50 cm⁻¹ is predicted for α-DMAEP. The much smaller value implies

that the exchange interaction is greatly affected by the perchlorate coordination. The observed effect could be produced in the following two ways. The additional coordination certainly acts as a perturbation on the electronic structure of the complex and could alter the electron density available to the hydroxo oxygen atoms and hence affect this superexchange mechanism. Alternatively, the perchlorate bridges could be integrally involved in the exchange interaction and provide an additional superexchange pathway. Although the former possibility could produce the observed effect, the analysis of the zero-field interaction lends some credence to the latter. Since the observed zero-field parameter has an unusually large contribution from the anisotropic exchange interaction, the possibility of a significant involvement of the perchlorate bridges in a superexchange mechanism cannot be excluded.

Registry No. α-[Cu(DMAEP)OH]₂(ClO₄)₂, 42476-26-6.

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Organomercury Compounds Containing Three-Coordinate Mercury. Synthesis and Spectroscopic Studies of Cationic Complexes of Methylmercury(II) with Neutral Donor Ligands

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Synthetic and spectroscopic studies of cationic complexes of methylmercury(II), [MeHgL][NO₃], are reported. The complexes [MeHgL][NO₃] (L = pyridine; 2-methyl-, 3-methyl-, 4-methyl-, 2-benzyl-, 2,4-dimethyl-, and 2,6-dimethylpyridine; 2,2'-bipyridyl; 3,3'-dimethyl-, 4,4'-dimethyl-, 5,5'-dimethyl-, and 6,6'-dimethyl-2,2'-bipyridyl; 1,10-phenanthroline; 2,9-dimethyl-, 4,7-dimethyl-, and 5,6-dimethyl-1,10-phenanthroline) are obtained from addition reactions in acetone. A complex of composition MeHgNO₃·¹/₂L is also formed by 3,3'-dimethyl-2,2'-bipyridyl. Infrared evidence for coordination of ligands in the solid complexes is presented. Proton magnetic resonance spectra indicate that the complexes of 2,2'-bipyridyls (except for those of 3,3'-dimethyl-2,2'-bipyridyl) and 1,10-phenanthrolines have three-coordinate mercury in solution. A linear correlation is observed between $J(^1H–^{199}Hg)$ and protonation constants of the ligands, with separate relationships for complexes of unidentate ligands, bidentate 2,2'-bipyridyls, and 1,10-phenanthrolines. Aspects of bonding in three-coordinate complexes are deduced from ^1H and ^{13}C NMR of the complexes and an x-ray structural determination of [MeHg(2,2'-bpy)][NO₃]. Bonding between mercury and carbon in the three-coordinate complexes is considered to be similar to that in the linear sp-hybridized complexes of pyridine ligands. Comparison of structural data for the 2,2'-bipyridyl and some amino acid complexes of methylmercury suggests that a similar sp hybridization bonding model is applicable for the latter complexes.

A major feature of bonding in organomercury chemistry is the strong tendency for linear two-coordination for mercury.[1,2] Consequently, spectroscopic studies of bonding in organomercury chemistry have been restricted almost entirely to linear two-coordinate geometry in R₂Hg, RHgX, and [RHgL][X] (L = unidentate ligand). However, recent structural studies indicate that even the simplest organomercury cation, MeHg⁺, may achieve effective coordination numbers of 3 and 4 for mercury in the amino acid complexes MeHg⁺–NH₂CH(CO₂⁻)CMe₂SHgMe[3] and MeHg⁺–NH₂CH(CO₂⁻)CH₂CH₂SMe,[4] respectively. For the amine-bonded methylmercury groups the mercury–carboxylate

oxygen contacts are only ca. 0.2 Å less than the sum of van der Waals radii and thus may be ionic interactions resulting from the zwitterionic nature of the complexes.[4] In view of the importance of these complexes in the biological chemistry of methylmercury pollutants an understanding of the bonding of mercury in methylmercury compounds with coordination number greater than 2 is desirable. NMR spectroscopy is particularly useful for bonding studies of methylmercury compounds[5,6] but may not be applicable for a study of methylmercury with coordination number of mercury greater than 2 in the above amino acid complexes because Rabenstein et al. have concluded from ^1H NMR studies that similar amino