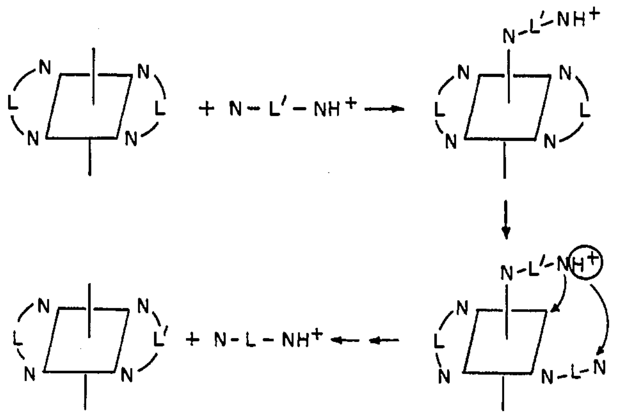
Scheme I



category IV reactions should have similar values for the rate constants, as is observed.

The rate constant calculated for reaction 1 in Table III lies well in the diffusion-controlled region and seems prohibitively high. It should be noted, however, that the value given in Table III is only about two or three times greater than the values for Cu(II)–en reactions given in Table II or reported by Kirschenbaum and Kustin[13] for 25°.

The high rate constants are the direct result of attributing "normal" relaxation times, such as those given in Table I, to paths involving a species (free en) which is present at very low concentration levels owing to its dibasic nature. A kinetically equivalent path involving the rapidly formed conjugate species of reaction 1 can also be written. The product of the concentrations of

$$\text{(hm)Cu(OH)}^+ + \text{Hen}^+ \underset{k_{-1'}}{\overset{k_{1'}}{\rightleftarrows}} \text{(hm)Cu(en)}^{2+} + \text{H}_2\text{O} \quad (1')$$

the species on the left-hand side of eq 1′ is greater than the corresponding product in eq 1; therefore, $k_{1'}$ will be smaller than k_1. The pK_a of (hm)Cu$(H_2O)_4{}^{2+}$ is about 7.0 (25°, μ = 0.1).[14,15] Assuming this value for 37° and using pK_{2a} equal to 9.7 for $^+$Hen, $k_{1'}$ is calculated to be 2×10^7 M^{-1} sec^{-1}. Reaction 1′ is essentially a category III reaction and is found here to have a rate constant which is consistent with other reactions of this category. Of particular significance is the similarity of the value deduced for $k_{1'}$ to the values found for other category III reactions involving $^+$Hen attack

$$\text{Cu(en)(hm)}^{2+} + {}^+\text{Hen} \longrightarrow \text{Cu(en)}_2{}^{2+} + {}^+\text{Hhm} \quad (1 \times 10^7\ M^{-1}\ \text{sec}^{-1})$$

and

$$\text{Cu(ser)}_2 + {}^+\text{Hen} \longrightarrow \text{Cu(en)(ser)} + \text{Hser}$$
$$(8 \times 10^6\ M^{-1}\ \text{sec}^{-1}, \text{ref } 5)$$

The rate constant for reaction 3 shows a "normal" value for water substitution to give a bis Cu(II) complex. However, this fact in itself does not necessarily rule out the existence of a parallel path analogous to (1′). The data only permit qualitative observations to be made regarding $k_{3'}$, however. Category III reactions involving $^+$Hhm attack have rate constants that are considerably smaller than are observed for $^+$Hen attack: for Cu(en)(hm)$^{2+}$ + $^+$Hhm → Cu(hm)$_2{}^{2+}$ + $^+$Hen, the rate constant is 3×10^3 M^{-1} sec^{-1} and for Cu(ser)$_2$ + $^+$Hhm → Cu(hm)(ser)$^+$ + Hser, a value of 1×10^5 M^{-1} sec^{-1} has been found.[5] Probably the low value of the former rate constant arises from interference between two bulky histamine molecules, and the latter is closer to being representative of reactions such as (3′).

$$\text{Cu(en)(OH)}^+ + {}^+\text{Hhm} \overset{k_{3'}}{\rightleftarrows} \text{Cu(en)(hm)}^{2+} + \text{H}_2\text{O} \quad (3')$$

Furthermore, Cu(en)$_{aq}{}^{2+}$ is a more stable complex than Cu(hm)$_{aq}{}^{2+}$. The higher Cu–N interaction should have the effect of lowering the acidity of Cu(en)$_{aq}{}^{2+}$ relative to Cu(hm)$_{aq}{}^{2+}$. This effect also would tend to reduce the rate of (3′) compared to (1′). Thus, while the alternate path (3′) cannot be definitely ruled out, it may contribute only a fraction of the overall rate which has been ascribed to (3).

The interpretations of the reactions of Cu(II) are complicated by the as yet incompletely understood role of the dynamic Jahn–Teller effect and how it is influenced by coordinated ligands. With respect to this, the suggestion has been made[3] that the mechanisms of ligand substitution of Cu$_{aq}{}^{2+}$, Cu(gly)$^+$, and Cu(bipy)$^{2+}$ might all be different. The strong Lewis acid character of Cu(II) possibly adds a further complication by providing additional routes to complex formation *via* reaction of hydroxy complexes with protonated ligands. For metal ions with a strong Lewis acid character, such as Cu(II), reaction 1′ deserves consideration as a plausible alternate mechanism to the internal conjugate base mechanism which has been proposed[17] to account for simliar but slower effects in Ni(II) systems.

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The Magnetic Properties of the Complex Di-μ-hydroxo-bis[2-(2-ethylaminoethyl)pyridine]dicopper(II) Perchlorate

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In recent years much interest has been shown in the magnetic properties of oxygen-bridged, bimetallic copper(II) complexes.[2-6] Many of these complexes have been postulated to exhibit ferromagnetic interactions. Krahmer, *et al.*,[2] however, have shown that some of the 1:1 complexes with N-substituted 2-(2-

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[1] National Science Foundation Trainee, 1968–1971.

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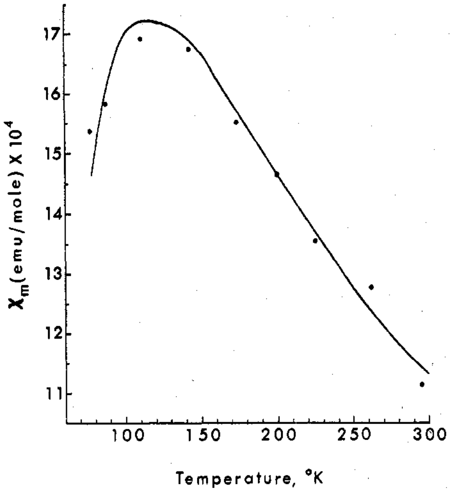

Figure 1.—The temperature variation of the magnetic susceptibility (●) and the calculated susceptibility for $g = 2.04$ and $2J = -130$ cm^{-1} (solid line) of $[Cu(EAEP)OH]_2(ClO_4)_2$ in the temperature range 60–300°K.

aminoethyl)pyridines (AEP) have relatively strong antiferromagnetic exchange and that others appear likely to display this effect as well. Thus, it becomes important to examine the properties, such as magnetic susceptibility and electron paramagnetic resonance spectra, of these substituted AEP complexes for more complete comparisons with the systems in which the ground state is thought to be a triplet and hopefully to gain a better insight into the influence which the bridging structure has upon the magnetic interactions. The results of our studies of the ethyl-substituted complex are reported in this note.

Experimental Section

Preparation.—The compound $[Cu(EAEP)OH]_2(ClO_4)_2$, where EAEP is 2-(2-ethylaminoethyl)pyridine, was prepared by the method of Krahmer, *et al.*,[2] with a slight modification. A stoichiometric quantity of EAEP was added to an ethanolic solution of copper(II) perchlorate. Upon standing, crystals of the desired di-μ-hydroxo complex were obtained. Satisfactory analyses were obtained for this compound.

Magnetic Measurements.—At multiple temperatures in the range 77–295°K, the magnetic susceptibility of powdered samples of the complex was measured using a Faraday balance.[7] Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[8] and the appropriate diamagnetic corrections for the substituent atoms were estimated from Pascal's constants.[9]

Epr Measurements.—The epr spectrum of a powdered sample of the complex was obtained at room temperature using a Varian Model 4502 X-band spectrometer operating at a microwave frequency of 9.51 GHz with a rectangular cavity and 100-kHz modulation. A cylindrical quartz sample tube was used.

Results

The temperature variation of the magnetic susceptibility of $[Cu(EAEP)OH]_2(ClO_4)_2$ is plotted in Figure 1. A distinct maximum in this plot is observed at about 120°K, and the data obey the Van Vleck equation[10]

$$\chi_M = \frac{g^2N\beta^2}{3kT}[1 + {}^1/_3 \exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

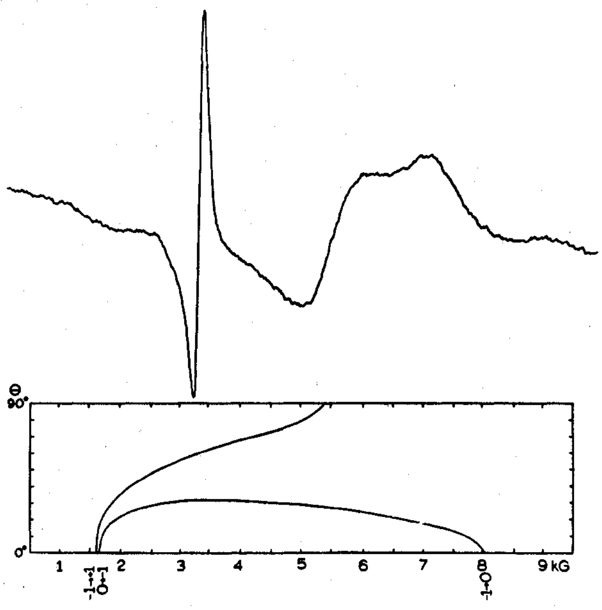

Figure 2.—The epr spectrum at room temperature of a powdered sample of $[Cu(EAEP)OH]_2(ClO_4)_2$ in the region 0–10,000 G, with a graph showing the angular dependence of the calculated resonance fields ($g_{||} = 2.12$, $g_\perp = 2.0$, $D = 0.48$ cm^{-1}, $E = 0.0$). At $\Theta = 0°$ the magnetic field is parallel with the z axis, and at $\Theta = 90°$ the magnetic field is in the xy plane. Transitions are labeled by quantum numbers which are exact for $\vec{H}||z$ and $E = 0$.

for magnetically coupled pairs of copper ions. The best least-squares fit of the data yields a singlet–triplet splitting $|2J|$ of 130 cm^{-1} and $g = 2.04$. In view of the broad maximum in the χ *vs.* T plot, the accuracy of the singlet–triplet splitting is probably no better than ±10% especially in view of the presence of the small amount of monomeric impurity, *vide post*.

The X-band epr spectrum of a powdered sample of $[Cu(EAEP)OH]_2(ClO_4)_2$, shown in Figure 2, can be interpreted using the effective spin Hamiltonian

$$\mathcal{H} = \beta\vec{H}\cdot g\cdot\vec{S} + D(S_z^2 - S(S+1)) \quad (2)$$

For $S = 1$ systems, resonant fields with the magnetic field parallel to the z axis, $H_{||}$, or in the xy plane, $H_\perp$, are given by[11]

$$\begin{aligned} (H_\perp)_1^2 &= (1/g_\perp\beta)^2[h\nu(h\nu - D)] \\ (H_\perp)_2^2 &= (1/g_\perp\beta)^2[h\nu(h\nu + D)] \\ (H_{||})_1 &= (1/g_{||}\beta)|h\nu - D| \\ (H_{||})_2 &= (1/g_{||}\beta)(h\nu + D) \end{aligned} \quad (3)$$

Features of the spectrum of a randomly oriented sample are expected to correlate with these resonance positions.[11] We assign $(H_{||})_1 = 1700$ G, $(H_\perp)_2 = 5400$ G, and $(H_{||})_2 = 8000$ G, and obtain $g_\perp = 2.0$, $g_{||} = 2.12$, and $|D| = 0.48$ cm^{-1}. Parameters were chosen so that $\langle g\rangle = 2.04$, as deduced from the magnetic susceptibility since it is expected that the analysis of both experiments should yield the same $\langle g\rangle$ value. Due to the broadness of the epr spectrum, the epr parameters are probably valid to only two significant figures. The feature observed at ~3300 G in the experimental spectrum is attributed to some monomeric impurity, the observation of which is relatively common. Also,

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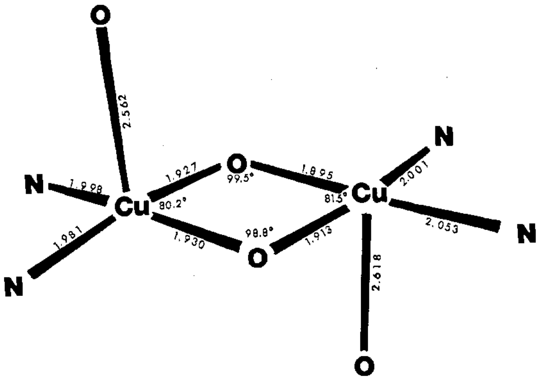

Figure 3.—A view of the coordination around the copper atoms in $[Cu(EAEP)OH]_2(ClO_4)_2$.

$(H_\perp)_1$ is not observed if D is greater than $h\nu$. A graph illustrating the angular dependence of the calculated resonance positions is included in Figure 2. All transitions predicted with the fitted parameters are included.[12] The very broad magnetic field range spanned by this spectrum is characteristic of dimeric copper complexes with large zero-field splittings. These include copper(II) acetate monohydrate,[13,14] copper propionate monohydrate,[15] and several copper benzoates.[16]

Discussion

A complete X-ray structural determination (R factor on F = 0.042)[17] has shown that $[Cu(EAEP)OH]_2(ClO_4)_2$ is dimeric consisting of two copper-centered, distorted square pyramids with a shared basal plane edge as represented in Figure 3. The basal plane is made up of two cis hydroxo bridges and the two nitrogen atoms of the EAEP ligand with the fifth coordination site occupied by a perchlorate oxygen at a distance of about 2.6 Å. The angles of the two Cu–O–Cu bridges are approximately 98.8 and 99.5°. The copper and oxygen atoms are approximately coplanar with a Cu–Cu distance of 2.92 Å.

The copper(II) environment found here is similar to those found in di-μ-hydroxo-bis(N,N,N',N'-tetramethylethylenediamine)dicopper(II) bromide (hereafter the ligand is abbreviated as tmen)[18] and di-μ-hydroxo-bis(bipyridyl)dicopper(II) sulfate pentahydrate.[4] The main differences among these complexes are found in the geometric arrangement at the bridging oxygen atoms. In these three complexes, the Cu–O–Cu bridge angles are 97 (bipyridyl), 99 (EAEP), and 104° (tmen). Another structural difference is in the angle between the two basal planes. In both the EAEP and the tmen complexes, the planes are nearly coplanar while in the bipyridyl complex the dihedral angle between the planes is 7.9°. The copper–copper internuclear separations are 2.89 (bipyridyl), 2.92 (EAEP), and 3.00 Å (tmen).

Magnetically, great differences are found among these complexes. An antiferromagnetic interaction giving a singlet–triplet energy separation of 130 cm^{-1} is found in the EAEP complex, whereas the tmen[19] complex has been reported to have $2J = -509$ cm^{-1}. Even more striking is the fact that the data for the bipyridyl complex have been interpreted to indicate a ferromagnetic interaction resulting a triplet ground state with a singlet state about 48 cm^{-1} above it.[5] Since the gross structural features of these three complexes are not radically different, it appears that the magnetic properties may be quite sensitive to minor bridge angle changes. It is postulated that, since the bridge bonding arrangement consists of hybrid oxygen orbitals, the M–O–M angle reflects the amount of s orbital character and that when this contribution is small, the exchange interaction is ferromagnetic. As the amount of s character increases, the interaction ultimately becomes antiferromagnetic. It is further suggested that the magnitude of the interaction, whether ferromagnetic or antiferromagnetic, is a function of the electron density at the bridging oxygen. McWhinnie[20] has shown in his investigation of the alkoxo-bridged complexes of the general formula $[(2\text{-}NH_2py)_2Cu(OR)]_2(NO_3)_2$, where R = H, methyl, or ethyl, that the room-temperature magnetic moments are 1.49, 0.95, and 0.70 BM, respectively. As more electron density is available to the oxygen bridge, the pathway for the antiferromagnetic interaction is enhanced. Similar results obtain in systems in which the hydroxo bridge is hydrogen bonded, thus also altering the oxygen electron density.[21] It seems possible that hydrogen bonding can account, in part, for the difference in magnitude of the interaction between the EAEP and the tmen complexes; it is probable that the hydrogen bonding to a bromide anion found in the tmen complex is stronger than any such bonding to perchlorate which could exist in the EAEP complex.

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Reactions of Carboxamido Complexes with Halogens and Mercuric Chloride

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Transition metal–alkyl bonds may be cleaved by halogens, *e.g.*

$$C_5H_5Fe(CO)_2R + X_2 \longrightarrow C_5H_5Fe(CO)_2X + XR \quad (1)$$

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