2′-bpy, 366-18-7; $[Pd(C_8H_{12}OCH_3)(bpy)]ClO_4$, 59301-93-8; Cl^-, 16887-00-6; Br^-, 24959-67-9.

Supplementary Material Available: Listings of specific kinetic data used to estimate kinetic constants reported in the paper (7 pages). Ordering information is given on any current masthead page.

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Relationship between the Singlet–Triplet Splitting and the Cu–O–Cu Bridge Angle in Hydroxo-Bridged Copper Dimers

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Received March 4, 1976 AIC60170U

Magnetic susceptibility and structural data for two additional di-μ-hydroxo-bridged copper(II) complexes are now available. The new data support the linear correlation between the singlet–triplet splitting, 2*J*, and the Cu–O–Cu bridge angle which has been observed. Magnetic susceptibility data for $[Cu(bpy)OH]_2(ClO_4)_2$ (bpy = 2,2′-bipyridine), for $[Cu(tmen)OH]_2(ClO_4)_2$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine), and for one complex for which there are no structural data, $[Cu(tmpd)OH]_2(ClO_4)_2$ (tmpd = *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine), yield 2*J* values of 93, −360, and 130 cm^{-1}, respectively. The complexes exhibit triplet-state EPR spectra, and the infrared spectra have been analyzed in terms of the coordination of the perchlorate ion.

Introduction

An extensive study of the structural and magnetic properties of di-μ-hydroxo-copper(II) dimers has yielded a linear correlative relationship between the Cu–O–Cu bridge angle and the exchange parameter 2*J*.[1-4] The latter is defined by the Hamiltonian

$$H = -2J\Sigma\vec{S}_1\cdot\vec{S}_2$$

The systems that have been investigated have the general formula $(CuLOH)_2^{2+}$, where L is the bidentate ligand 2,2′-bipyridine (bpy), 2-(2-dimethylaminoethyl)pyridine (dmaep), 2-(2-ethylaminoethyl)pyridine (eaep), *N,N,N′,N′*-tetraethylethylenediamine (teen), or *N,N,N′,N′*-tetramethylethylenediamine (tmen). The 2*J* values that have been observed in the series range from +172 to −509 cm^{-1}, and the Cu–O–Cu angles range from 95.6 to 104.1°. Since structural data for two additional members of the series, $[Cu(bpy)OH]_2(ClO_4)_2$[5] and $[Cu(tmen)OH]_2(ClO_4)_2$,[6] have become available recently, it was of interest to compare their exchange coupling constants with the angles at the bridging oxygen atoms. This comparison is reported here. In addition, the magnetic properties of di-μ-hydroxo-bis(*N,N,N′,N′*-tetramethyl-*o*-phenylenediamine)dicopper(II) perchlorate, $[Cu(tmpd)OH]_2(ClO_4)_2$, have been determined, and the properties of this compound are described herein.

Experimental Section

Di-μ-hydroxo-bis(*N,N,N′,N′*-tetramethyl-*o*-phenylenediamine)dicopper(II) perchlorate was prepared by adding *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine to a solution of hydrated copper(II) perchlorate dissolved in the minimum amount of water. The dark

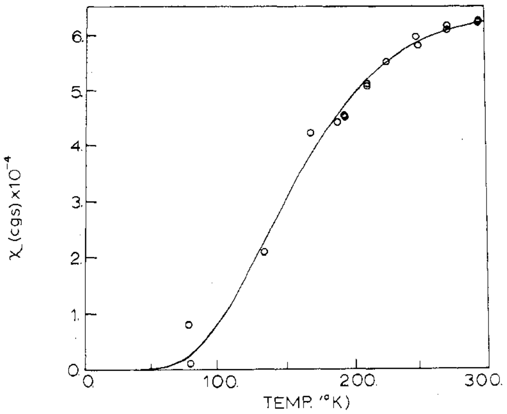

Figure 1. Magnetic susceptibility data (○) for $[Cu(tmen)OH]_2(ClO_4)_2$. Solid line was calculated from eq 1 with $g = 2.09$, $2J = -360$ cm^{-1}, and $N\alpha = 120 \times 10^{-6}$ cgsu.

blue complex was isolated by filtration, washed with diethyl ether, and air-dried. Anal. Calcd. for $Cu(C_{10}H_{16}N_2)(OH)(ClO_4)$: Cu, 18.46; C, 34.89; H, 4.98; N, 8.14. Found: Cu, 18.2; C, 34.70; H, 4.79; N, 7.99.

An analytically pure sample of $[Cu(tmen)OH]_2(ClO_4)_2$ was provided by Professor S. F. Pavkovic. Additional samples were prepared by the above procedure for the synthesis of $[Cu(tmpd)OH]_2(ClO_4)_2$.

The magnetic susceptibility data as a function of temperature were collected as described previously.[7] The data were corrected for underlying diamagnetism[8] and temperature-independent paramagnetism (60×10^{-6} cgsu/mol of Cu).

Electron paramagnetic resonance (EPR) spectra were recorded on a JEOL ME 3X spectrometer at 77 K using a quartz liquid nitrogen insertion Dewar. Infrared spectra were recorded with a Digilab FTS-14 Fourier transform spectrometer using Nujol mulls.

Results

The magnetic susceptibility data for $[Cu(tmen)OH]_2(ClO_4)_2$ are shown as a function of temperature in Figure 1 along with the best fit line which was calculated from the Van Vleck equation[9] for exchange-coupled pairs of copper(II) ions (eq 1). In this expression $2J$ is the singlet–triplet splitting

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

or exchange parameter. The parameters which gave the best fit are $\langle g \rangle = 2.09 \pm 0.005$ and $2J = -360 \pm 10$ cm^{-1} and were obtained by minimizing the function

$$E = \Sigma[(\chi_{obsd} - \chi_{calcd})T]^2$$

using a Simplex routine.[10] The magnetic susceptibility data given in Figure 1 were calculated per copper, not per dimer.

The EPR spectrum of a powdered sample of $[Cu(tmen)OH]_2(ClO_4)_2$ at 296 K is, as expected, a typical triplet-state spectrum[11,12] for an exchange-coupled pair of copper(II) ions. The intensities of the lines in the spectrum decreased with decreasing temperature as expected for this singlet ground-state complex. Unfortunately the nature of the spectrum precludes an extraction of precise magnetic parameters. Efforts are under way to obtain a single crystal for a thorough EPR investigation; the results of that work will be reported later.

The magnetic susceptibility data for $[Cu(tmpd)OH]_2(ClO_4)_2$ are shown in Figure 2 as inverse susceptibility vs. temperature. To fit these data, the temperature term in eq 1 was replaced by $(T - \Theta)$ where the Θ parameter was added to account for interdimer (lattice) interactions which frequently arise in the case of ferromagnetically coupled copper(II) pairs.[13] The magnetic parameters which gave the best fit are $g = 2.05 \pm 0.005$, $2J = +130 \pm 5$ cm^{-1}, and $\Theta = 0.17 \pm 0.01$ K. The magnetic susceptibility data given in Figure 2 were calculated per copper, not per dimer.

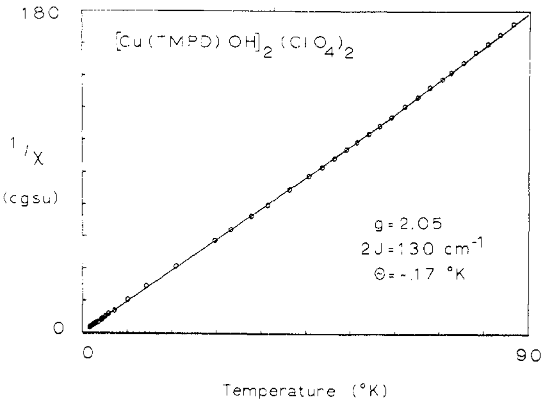

Figure 2. Inverse magnetic susceptibility data (○) for $[Cu(tmpd)OH]_2(ClO_4)_2$. Solid line was calculated from eq 1 with $g = 2.05$, $2J = +130$ cm^{-1}, $\Theta = 0.17$ K, and $N\alpha = 120 \times 10^{-6}$ cgsu.

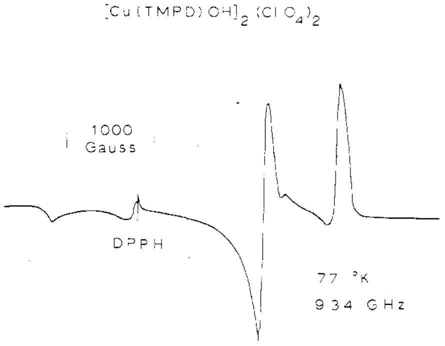

Figure 3. EPR spectrum of $[Cu(tmpd)OH]_2(ClO_4)_2$ at 77 K.

The positive value obtained for the exchange coupling constant J indicates a ferromagnetic exchange interaction with a triplet ground state and a singlet state 130 cm^{-1} higher in energy. Further evidence for the triplet state is provided by the EPR spectrum which is shown in Figure 3. The spectrum is qualitatively similar to that observed for other copper-pair triplet states with $|D| > h\nu$, e.g., β-$[Cu(dmaep)OH]_2(ClO_4)_2$ and $[Cu(eaep)OH]_2(ClO_4)_2$.[14] However, in this case it was not possible to analyze the spectrum in terms of the axial spin Hamiltonian using the equations of Wasserman, Snyder, and Yager;[15] no reasonable assignment of the transitions led to reasonable g values. This indicates that the distortion from axial symmetry is significant, a conclusion which is supported by the observed partial splitting of some of the EPR lines.

Discussion

An x-ray crystal structure of $[Cu(tmen)OH]_2(ClO_4)_2$[6] has been completed recently and it was found that the structural features of the compound are very similar to those of $[Cu(teen)OH]_2(ClO_4)_2$.[4] The most pertinent pieces of structural information for this study are the copper–copper separation of 2.966 Å and the copper–oxygen (bridge)–copper angle of 102.3 (4)°. Also, the perchlorate ions are not coordinated. These data along with the $2J$ value of -360 cm^{-1} determined here provide additional data to test the linear relationship between the singlet–triplet splitting and the Cu–O–Cu bridge angle.[1]

A second set of data pertaining to this problem have also become available recently. The structure of $[Cu(bpy)OH]_2(ClO_4)_2$[5] has been determined and briefly described. From the Cu–Cu separation of 2.87 Å and the Cu–O distance of 1.92 Å, a Cu–O–Cu angle of 96.73° may be calculated. On the other hand, if the O–O separation of 2.56 Å is used in conjunction with the Cu–O distance, an angle of 96.4° results.

Table I. Structural and Magnetic Properties of Di-μ-hydroxo-bridged Copper Compounds

Complex	R_{Cu-Cu}, Å	R_{Cu-O}, Å	$\phi_{Cu-O-Cu}$, deg	$2J$, cm^{-1}	g	Θ, K	Ref
$[Cu(bpy)OH]_2(NO_3)_2$	2.847	1.920–1.923	95.6 (1)	+172	2.10	−0.45	2, 17
$[Cu(bpy)OH]_2(ClO_4)_2$	2.870	1.92	96.6 (2)	+93	2.22	−0.5	5
$[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$	2.893	1.92–1.95	97.0 (2)	+49	2.20	0.10	16, 18–20
$[Cu(eaep)OH]_2(ClO_4)_2$	2.917	1.895–1.930	98.8–99.5 (3)	−130	2.04		14, 21, 22
β-$[Cu(dmaep)OH]_2(ClO_4)_2$	2.935	1.900–1.919	100.4 (1)	−200	2.03		3, 21
$[Cu(tmen)OH]_2(ClO_4)_2$	2.966	1.897–1.931	102.3 (4)	−360	2.09		6
$[Cu(teen)OH]_2(ClO_4)_2$	2.978	1.899–1.907	103.0 (3)	−410	2.05		2, 23
$[Cu(tmen)OH]_2Br_2$	3.000	1.902	104.1 (2)	−509	2.0		24–26

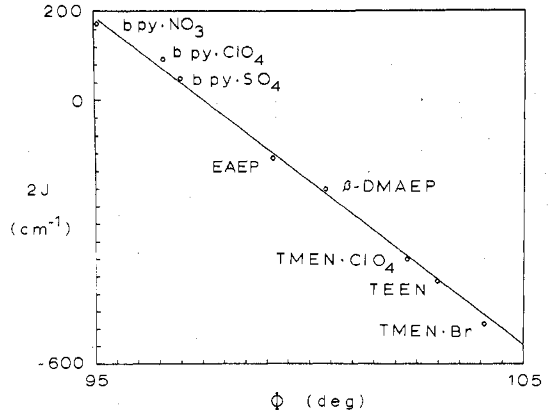

Figure 4. $2J$ vs. bridge angle (ϕ) for a series of hydroxo-bridged copper(II) dimers. Straight line was calculated from $2J = -74.53\phi + 7270$ cm^{-1}.

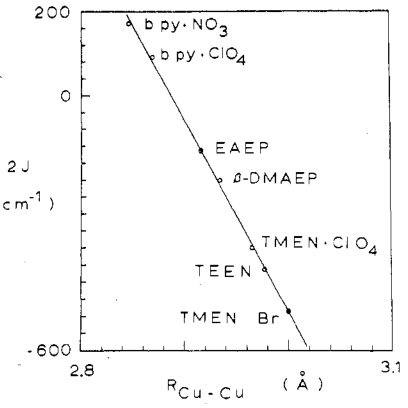

Figure 5. $2J$ vs. copper–copper separation (R_{Cu-Cu}) for a series of hydroxo-bridged copper(II) dimers. Straight line was calculated from $2J = -4508R_{Cu-Cu} + 13\,018$ cm^{-1}.

For the purposes of this study the rounded mean of 96.6° will be used. The $2J$ value of +93 cm^{-1} for $[Cu(bpy)OH]_2(ClO_4)_2$ was reported several years ago by Barnes, Hodgson, and Hatfield.[16]

The new magnetic and structural data for the compounds $[Cu(tmen)OH]_2(ClO_4)_2$ and $[Cu(bpy)OH]_2(ClO_4)_2$ are included in the plot of bridge angle vs. $2J$ shown in Figure 4. These data are also listed in Table I with the available structural and magnetic data for di-μ-hydroxo-bridged copper(II) complexes.[1-6,14,16-26] These new data points are fitted very closely by the best least-squares line which has been given previously.[1] Addition of these new data to the data set yields slightly modified parameters with the best least-squares fit yielding

$$2J = -74.53\phi + 7270 \text{ cm}^{-1}$$

and a linear correlation coefficient, R, of −0.9986.

As shown in Figure 5, there is also a good correlation between the exchange parameter and the copper–copper distance. This is to be expected since the Cu_2O_2 system is very nearly planar in all compounds but one, that being $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$,[18] and the Cu–O bond distances are all comparable, being 1.92 ± 0.03 Å. The small variances in the copper–oxygen bond distances may be seen in the data in Table I.

Since $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$ contains a nonplanar Cu_2O_2 network, the data for this compound were not included in the fitting process from which the equation for the best least-squares line was found to be

$$2J = -4508R_{Cu-Cu} + 13\,018 \text{ cm}^{-1}$$

with an R coefficient of −0.9994.

Using the linear correlation between $2J$ and the Cu–O–Cu angle, the $2J$ value of +130 cm^{-1} for $[Cu(tmpd)OH]_2(ClO_4)_2$ leads to a prediction for the Cu–O–Cu angle of 96.2°, while the correlation between $2J$ and the copper–copper separation predicts a Cu–Cu distance of 2.86 Å. It must be recognized that these predictions are dependent upon the bonding of the perchlorate ion, since ClO_4^- exhibits several bonding arrangements in its compounds. In $[Cu(teen)OH]_2(ClO_4)_2$,[4] the perchlorate ion is not bonded to copper; in β-$[Cu(dmaep)OH]_2(ClO_4)_2$,[3] it is bonded to copper as a unidentate ligand; but in α-$[Cu(dmaep)OH]_2(ClO_4)_2$,[27] the perchlorate ion bridges the two copper ions. The magnetic and structural correlation does not hold for α-$[Cu(dmaep)OH]_2(ClO_4)_2$, and it is thought that the additional bridges either provide an additional pathway for superexchange or that the coordination has a pronounced effect on the electronic structure of the interacting system.[28] On the basis of the observed Cu–O–Cu angle, the exchange interaction in α-$[Cu(dmaep)OH]_2(ClO_4)_2$ was predicted to be about −50 cm^{-1}, while the experimentally determined value of $2J$ is −4.8 cm^{-1}.[28] The predictions given here for $[Cu(tmpd)OH]_2(ClO_4)_2$ are made with the assumption that the perchlorate ion is not acting as a bridging ligand.

With an aim toward determining the bonding mode of the perchlorate ions in $[Cu(tmpd)OH]_2(ClO_4)_2$, the infrared spectrum was recorded in the region 500–1200 cm^{-1}. There are several spectral features in this region which are diagnostic of perchlorate bonding.[29] Nonbonded perchlorate ions exhibit bands near 600 and 1100 cm^{-1} which arise from antisymmetric angle deformations (ν_4 in T_d) and antisymmetric bond stretching motions (ν_3 in T_d), respectively.[30] Upon coordination these bands broaden and in the limit of strong bonding split into one or more components depending upon the local symmetry of the perchlorate ion. The appearance of a band near 650 cm^{-1} has been considered to be a very sensitive test for perchlorate coordination.[29]

In the ir spectrum of $[Cu(tmpd)OH]_2(ClO_4)_2$ there is a strong band near 1100 cm^{-1} which shows a distinct splitting with components at 1070 and 1110 cm^{-1}. However, there is no band in the 650–660-cm^{-1} region. Although the band at 1100 cm^{-1} is split, it is not particularly broadened compared with the comparable band in compounds with coordinated perchlorate ions, and it resembles the spectral band[29] in $[Cu(teen)OH]_2(ClO_4)_2$, a compound with noncoordinated perchlorate. There is also a strong band centered at 615 cm^{-1}

which is attributable to antisymmetric angle deformations. The band is significantly split, an observation contrary to that observed for the noncoordinated example; the splitting is less than that observed for unidentate or bidentate coordination. Thus, unfortunately, the infrared data do not rule out bidentate perchlorate bonding, but the nature of the spectral features does seem to discount the possibility. The crystal structure of this complex is currently under investigation in our laboratories.

Note Added in Proof. Complete structural details for $[Cu(bipy)OH]_2(ClO_4)_2$ are now available [M. Toofan, A. Boushehri, and M. Haque, *J. Chem. Soc., Dalton Trans.*, 217 (1976)]. The refined structural results reveal that the Cu–O–Cu angle, ϕ, is 96.94°, and that the perchlorate ion is coordinated in the bidentate manner described for α-$[Cu(dmaep)OH]_2(ClO_4)_2$. The new value for ϕ gives a $2J$ prediction of $+45\ cm^{-1}$. The more positive experimental value of $+93\ cm^{-1}$ deviates from the linear relationship in the same manner that has been noted for α-$[Cu(dmaep)OH]_2(ClO_4)_2$, that is, $2J$ was predicted to be $-50\ cm^{-1}$ while the experimental value was found to be $-4.8\ cm^{-1}$.

Acknowledgment. We wish to thank Professor Stephen F. Pavkovic for making his structural data for $[Cu(tmen)OH]_2(ClO_4)_2$ available to us prior to publication and for permission to use those data in this paper. The research was supported by the National Science Foundation through Grant No. MPS74-11495 and by the Materials Research Center of the University of North Carolina under Grant DMR72-03024 from the National Science Foundation.

Registry No. $[Cu(tmen)OH]_2(ClO_4)_2$, 14266-63-8; $[Cu(tmpd)OH]_2(ClO_4)_2$, 59532-73-9.

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Chelation in Organoaluminum–Nitrogen Chemistry[1]

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Received January 15, 1976 AIC60044Q

The various factors affecting the formation and stability of neutral, chelated four-coordinate organoaluminum–nitrogen compounds have been investigated. A variety of new compounds have been prepared and fully characterized. Cryoscopic molecular weight data suggest the predominant species to be the chelated monomer for the compounds $(CH_3)_2Al(C_2H_5)NC_2H_4N(C_2H_5)_2$, $(C_2H_5)_2Al(CH_3)NC_2H_4N(CH_3)_2$, $(C_6H_5)_2Al(C_2H_5)NC_2H_4N(CH_3)_2$, $Cl_2Al(C_2H_5)NC_2H_4N(CH_3)_2$, and $(CH_3)_2AlSC_2H_4N(CH_3)_2$. At lowered temperatures, NMR studies and additional molecular weight data suggest that an equilibrium exists between the monomeric chelate and a dimer. Other compounds such as $(CH_3)_2Al(CH_3)NC_2H_4N(CH_3)_2$, $(CH_3)_2Al(CH_3)NC_3H_6N(CH_3)_2$, and $(C_2H_5)_2Al(CH_3)NC_3H_6N(CH_3)_2$ show a significant concentration of the dimeric species at room temperature. The dimer molecule can exist in cis and trans conformations relative to the nitrogen of the four-membered ring. In all cases observed, the cis isomer is preferred. An unusual observation is that $[(CH_3)_2AlN(CH_3)C_2H_4N(CH_3)_2]_2$ is present as only the cis isomer at low temperature. Many factors are shown to affect the position of the monomer–dimer equilibrium. These include steric effects of groups bound to aluminum, steric effects of groups bound to potentially bridging and terminal nitrogens of the ligand, ligand base strength, and chelate ring size. There is also evidence that the mechanism of formation may affect chelation and association.

Introduction

The reaction of an organoaluminum compound with a Lewis base containing an acidic hydrogen such as $N(CH_3)_2H$ results in the formation of a derivative of the aluminum compound such as $[(CH_3)_2AlN(CH_3)_2]_2$ and an alkane. Many of these aluminum derivatives have been found to be associated by bridging through the base group. The degree of association is variable and often not readily predictable. Several factors including electronic effects, steric effects, thermodynamic effects, and the mechanism of formation are considered to play important roles in determining the extent of these associations.[2-4] Compounds of this type which have bidentate ligands also have an unpredictable degree of association. Chelated monomers have been observed in the case of $(CH_3)_2Al$-