Inorg. Chem. **1994**, *33*, 2066–2068

Synthesis and Characterization of a New Copper(II) Dimer with Hydrogen-Bonded Bridges

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Received October 21, 1993

Introduction

There is continuing interest in the properties of binuclear copper(II) complexes, especially in understanding the factors that influence magnetic interactions between copper(II) centers. The magnetic properties of the multinuclear metal sites in metalloproteins such as the binuclear type 3 copper proteins[2–4] have stimulated activity in this area, and various types of binuclear copper(II) systems have been synthesized and studied extensively. Comparison of structural features and magnetic properties of hydroxo-bridged binuclear copper(II) complexes has revealed a linear relationship between the Cu–O–Cu bond angles, involving the hydroxo bridges, and the magnetic exchange coupling constant, J.[5–8] More recent work, however, demonstrated that the relationship is more complex in a number of other binuclear copper(II) systems, including those with hydrogen-bond bridges. Several other factors, including the nature of the bridging atoms or ligands and the dihedral angles between the planes containing the copper(II) ions, are clearly of importance.[9–12]

Binuclear copper(II) complexes resulting from cooperative hydrogen-bonding, in which the copper(II) centers are joined by two or more hydrogen bonds between the ligand units, have been found to exhibit antiferromagnetic coupling. The copper(II) centers in such complexes are separated by more than 4.5 Å, and the coupling is suggested to follow a superexchange mechanism. As very few examples are available for this type of binuclear copper(II) system,[13] no correlation between structural features and the magnitude of the magnetic exchange interaction has been observed so far. We have synthesized a new hydrogen-bonded copper(II) dimer by the condensation of the copper(II) complex of 2-aminoethanol (EtaH), $[Cu(EtaH)(Eta)]_2(ClO_4)_2$, the nitrate salt of which is also a hydrogen-bonded dimer,[13a] with formaldehyde and ammonia. In this paper we wish to report the synthesis and the structural and magnetic characterization of this new binuclear complex.

Table 1. Crystallographic Data for Complex **1**

formula	$C_{18}H_{42}Cl_2N_8O_{14}Cu_2$
fw	792.6
size, mm	0.34 × 0.46 × 0.58
temp, K	295
crystal system	monoclinic
space group	$P2_1/c$
a, Å	8.318(2)
b, Å	13.592(3)
c, Å	12.913(3)
β, deg	98.38(3)
U, Å^3	1444.3(6)
D_c, gcm^{-3}	1.822
Z	2
$F(000)$	820
μ, mm^{-1}	1.74
N	3317
$N_o(F > 6\sigma(F))$	2580
ranges of hkl	0 to 10, 0 to 17, −16 to +16
R^a	0.0415
$R_w{}^b$	0.0618

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Experimental Section

Synthesis of $[Cu(C_9H_{19}N_4O_2)]_2(ClO_4)_2\cdot 2H_2O$ (1). To an aqueous solution (20 cm^3) of 2-aminoethanol (0.610 g, 10 mmol) were added copper(II) perchlorate hexahydrate (1.85 g, 5 mmol), formaldehyde (4 cm^3, 37% w/v solution), and ammonia (8 cm^3, 30% w/v solution). The resultant dark blue solution (pH $\simeq$ 8.0) was stirred for 30 min at 60 °C and filtered. The dark blue filtrate was allowed to stand at room temperature for 3 days, after which well-formed purple-blue crystals of the product precipitated. The crystals were isolated by filtration, washed with cold water, and dried in air. Yield: 1.6 g (80%). Anal. Calcd for $[Cu(C_9H_{19}N_4O_2)]_2(ClO_4)_2\cdot 2H_2O$: C, 27.28; H, 5.34; N, 14.14; Cl, 8.94. Found: C, 27.35; H, 5.40; N, 14.27; Cl, 8.96.

Physical Methods. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic susceptibility measurements were performed by the Faraday method on equipment described elsewhere.[14] The molar susceptibility was corrected for ligand diamagnetism using Pascal's constants.

X-ray Structure Determination. Cell constants were determined by least-squares fits to the setting parameters of 50 independent reflections. Data were measured on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.709\ 26$ Å; $\lambda(K\alpha_2) = 0.713\ 54$ Å] and a graphite monochromator. The data were corrected for Lorentz–polarization effects and absorption. The structure was solved by direct methods and refined by least-squares techniques with SHELXTL.[15] All hydrogen atoms were located in a Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically. The crystallographic data are listed in Table 1, and the non-hydrogen atom coordinates including the bridging hydrogen atom coordinates are listed in Table 2.

Results and Discussion

Synthesis. The template condensation of 2-aminoethanol, formaldehyde, and ammonia in the presence of copper(II) ion yielded the complex $[Cu(C_9H_{19}N_4O_2)]_2(ClO_4)_2\cdot 2H_2O$ (**1**). The complex crystallized from the reaction mixture, and the crystals were suitable for X-ray analysis. The crystal structure reveals the presence of the 1,3,5,7-tetraazabicyclo[3.3.1]nonane ring and hydrogen-bonded bridges, as will be described below. The product formation is quite expected, as similar reactions of a number of other copper(II) or nickel(II) complexes containing *cis*-disposed primary amines are known to form 1,3,5,7-tetraazabicyclo[3.3.1]-nonane ring-containing products.[16–20]

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	18978(1)	877(1)	1258(1)	26(1)
O(1)	20900(3)	1107(2)	633(2)	32(1)
O(2)	18922(3)	–573(2)	1166(2)	30(1)
N(1)	18603(3)	2337(2)	1245(2)	27(1)
N(4)	17174(3)	766(2)	2117(2)	26(1)
C(1)	21351(4)	2112(3)	830(3)	36(1)
C(2)	19851(4)	2743(3)	640(3)	36(1)
C(3)	18824(4)	2719(3)	2339(3)	33(1)
C(4)	16909(4)	2552(3)	725(3)	35(1)
C(5)	15967(5)	2689(3)	2342(3)	43(1)
C(6)	15655(4)	1156(3)	1469(3)	33(1)
C(7)	17515(4)	1352(3)	3106(3)	34(1)
C(8)	17049(5)	–290(2)	2365(3)	36(1)
C(9)	17394(4)	–903(2)	1442(3)	35(1)
N(2)	15698(4)	2211(2)	1326(3)	38(1)
N(3)	17538(4)	2401(2)	2918(2)	36(1)
Cl(1)	12471(1)	651(1)	3786(1)	39(1)
O(3)	13691(7)	80(3)	3496(5)	122(3)
O(4)	12871(9)	1612(3)	3777(5)	150(3)
O(5)	12073(7)	335(4)	4738(4)	118(2)
O(6)	11102(8)	487(6)	3035(5)	170(4)
O(1W)	2697(4)	9357(2)	726(2)	48(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

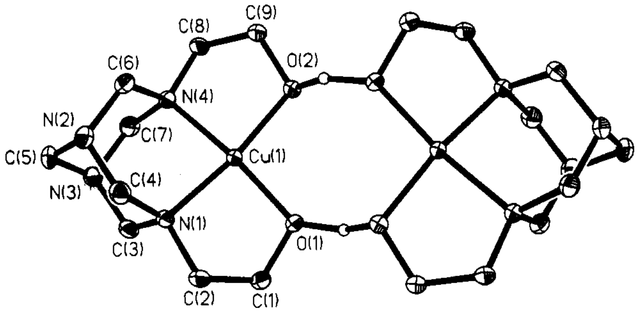

Figure 1. View of the cation in complex **1**, showing the hydrogen-bonded binuclear aggregation of the complex. The left-hand side of the complex is related to the right-hand side by a crystallographic inversion center. The hydrogen atom of the hydrogen bond is shown as an open circle, but all other hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**

	Bond Lengths		
Cu(1)–O(1)	1.919(3)	Cu(1)–O(2)	1.975(2)
Cu(1)–N(1)	2.008(3)	Cu(1)–N(4)	1.998(3)
	Bond Angles		
O(1)–Cu(1)–O(2)	98.7(1)	O(1)–Cu(1)–N(1)	88.5(1)
O(2)–Cu(1)–N(1)	169.5(1)	O(1)–Cu(1)–N(4)	170.2(1)
O(2)–Cu(1)–N(4)	86.8(1)	N(1)–Cu(1)–N(4)	87.2(1)

Description of the Structure of $[Cu(C_9H_{19}N_4O_2)]_2(ClO_4)_2 \cdot 2H_2O$ (1). The structure consists of $\{[Cu(C_9H_{19}N_4O_2)]_2\}^{2+}$ cations, perchlorate anions, and water molecules. A view of the cation with the atomic numbering scheme is shown in Figure 1. Selected bond distances and angles are listed in Table 3.

The geometry about each copper center is distorted square-planar, with the coordinating atoms being the 1- and 7-nitrogen atoms and the ethoxy and 2-hydroxyethyl oxygen atoms of the ligand, 1-ethoxy-7-(2-hydroxyethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane. The copper–oxygen and copper–nitrogen distances (Table 3) are normal and comparable to those of the parent complex $[Cu(EtaH)(Eta)]_2(NO_3)_2$.[13a] A principal difference between the geometries in these two complexes, however, is that in $[Cu(EtaH)(Eta)]_2(NO_3)_2$ the copper and the four ligating atoms are nearly coplanar but in **1** they are severely distorted from coplanarity. The distortion observed in **1** may be attributed to the strain caused by the rigid bicyclononane ring. Consequently, atoms O(1) and N(4) lie 0.138 and 0.148 Å, respectively, above the least-squares plane through the four ligating atoms, while O(2) and N(1) lie 0.138 and 0.147 Å, respectively, below it; the copper atom is approximately in this plane. Alternatively, the dihedral angle τ between the Cu(1)O(1)O(2) and Cu(1)N(1)N(4) planes is 11.5°; this dihedral angle would be 0° in a perfectly square-planar system and 90° in an ideally tetrahedral complex. The distortion is also reflected by *cis*-ligation angles in the range 86.8(1)–98.7(1)° and *trans*-ligation angles of 169.5(1) and 170.2(1)°. The (1-ethoxy-7-(2-hydroxyethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane)copper(II) units are associated into hydrogen-bonded dimers as a result of pairwise hydrogen-bonding between the ethanoxy oxygen atoms and the 2-hydroxyethyl groups of adjacent copper(II) units. The oxygen–oxygen distance of 2.459 Å is comparable to that of 2.452 Å in $[Cu(EtaH)(Eta)]_2(NO_3)_2$.[13a] However, the copper–copper distance of 4.555 Å is considerably shorter than the value of 4.941 Å in the parent complex and, in fact, is the shortest Cu···Cu separation observed in all hydrogen-bonded copper(II) dimers studied so far.[13]

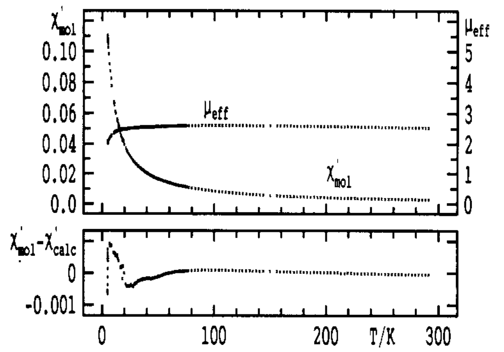

Figure 2. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for complex **1**. The lower curve shows the fit of the susceptibility data to the values calculated using the parameters $g = 2.107$ and $2J = -4.09$ cm^{-1}.

Spectral and Magnetic Properties. The electronic absorption spectrum of **1** in acetonitrile reveals a band at 583 nm ($\epsilon = 276$ dm^3 mol^{-1} cm^{-1}) corresponding to the d–d transition. The occurrence of the d–d transition at such a low wavelength for this CuN_2O_2 complex may be attributed to the extraordinarily strong ligand field exerted by the squeezing effect of the bicyclononane ligand.[20]

The magnetic susceptibility and effective magnetic moment of the complex in the temperature range 4–295 K are shown in Figure 2. Above approximately 60 K, the effective magnetic moment is roughly constant at 2.6 μ_B but declines slowly between 60 and 15 K and more rapidly at temperatures below 15 K. No maximum in the susceptibility is observed above 4.5 K.

The temperature dependence of the magnetic susceptibility was approximated by the expression

$$\chi_{mol,exp} \simeq \chi_{mol,calc} = -\frac{N}{H}\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T$$

by minimization of the function

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$$\sum_T \frac{[\chi'_{\mathrm{mol,exp}}(T) - \chi'_{\mathrm{mol,calc}}(T)]^2}{\sigma^2(\chi') + \left(\dfrac{\partial\chi}{\partial T}\right)^2 \sigma^2(T)}$$

within the framework of regression analysis. The term C/T accounts for the presence of small quantities of (presumably monomeric) paramagnetic impurities, while K accounts for temperature-independent paramagnetism (TIP) and for any minor deviations in the corrections for the diamagnetism of the atoms. The energies E_i of the various components of the ground-state manifold were obtained using the Hamiltonian operator

$$H = -2J(\hat{S}_1\cdot\hat{S}_2) + g_1\beta\hat{S}_1\cdot\hat{H} + g_2\beta\hat{S}_2\cdot\hat{H}$$

where we have assumed that the g values for the two copper atoms are identical; *i.e.*, we have set $g_1 = g_2$. Since we have two $S = {}^1/_2$ centers in the complexes, the Heisenberg term $-2J(\hat{S}_1\cdot\hat{S}_2)$ in the Hamiltonian gives rise to states with $S = 0$ (singlet) and 1 (triplet) with energies of 0 and $-2J$, respectively. For the hydrogen-bonded complex **1**, the fitting leads to a value of $2J = -4.09$ cm^{-1} with $g = 2.107$, and a value for C equivalent to the presence of 0.8% monomeric Cu(II) impurity. This observed $2J$ value of approximately -4 cm^{-1} for **1** is very much smaller (in magnitude) than those of -56 to -94 cm^{-1} reported for apparently analogous binuclear hydrogen-bonded copper(II) complexes.[13]

As was noted above, the principal difference between the structure of **1** and those of the earlier complexes is the distortion from planarity at the copper centers. Sinn and co-workers[21] have noted that such distortions, defined in the present complex by the dihedral angle τ between the CuO_2 and the CuN_2 planes, can lead to a significant diminution in the magnitude of the value of the triplet energy in copper(II) dimers, and we have rationalized this effect elsewhere.[22] The present result, therefore, demonstrates that these concepts, originally postulated for tightly bound dimeric systems, are equally applicable to the more weakly bound hydrogen-bonded binuclear complexes. If other distorted systems become available, we shall be able to investigate the possible existence of a quantitative correlation between τ and J.

Acknowledgment. This work was supported by the National Science Foundation through Grant No. CHE-9007607 (to D.J.H.) and by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant No. CRG 910277 (to D.J.H. and J.G.).

Supplementary Material Available: Hydrogen atom parameters (Table S1), anisotropic thermal parameters (Table S2), and complete bond distances and angles (Tables S3 and S4) (4 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure amplitudes are available from D.J.H. on request.

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Additions and Corrections

1993, Volume 32

Pierre Braunstein,* Daniele Cauzzi, David Kelly, Maurizio Lanfranchi, and Antonio Tiripicchio: Reactivity of the Cyanometalate $Na[Cp'Mn(CO)_2CN]$ with Titanium, Zirconium, and Hafnium Halides. Crystal and Molecular Structure of the μ-Cyano μ-Oxo Tetranuclear Complex $[Cp_2Zr\{(\mu\text{-}NC)MnCp'(CO)_2\}]_2(\mu\text{-}O)$ (Cp = η-C_5H_5; Cp′ = η-MeC_5H_4).

Page 3375. For $Cp_2Ti[(\mu\text{-}NC)MnCp'(CO)_2]_2$ (**1**), the second ^{1}H NMR (C_7D_8) assignment should read δ 4.34 (m, 8 H, $2C_5H_4CH_3$). For $Cp_2Hf[(\mu\text{-}NC)MnCp'(CO)_2]_2$ (**3**), the intensities of the IR absorptions should read as follows: IR (C_7H_8) ν(CN) 2020 s, 1995 m cm^{-1}; IR (Nujol) ν(CN) 2037 m, 2019 m, 2008 m, 1991 s cm^{-1}.

Page 3376. For $Cp_2Ti[(\mu\text{-}NC)MnCp'(CO)_2]Cl$ (**8**), the IR (Nujol) values should read as follows: ν(CN) 1995 s cm^{-1}; ν(CO) 1910 m, 1860 s cm^{-1}.