Inorg. Chem. **1994,** *33,* 2085–2089

Synthesis, Crystal Structure, and Magnetic Properties of a Ferromagnetically Coupled Angular Trinuclear Copper(II) Complex $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$[†]

Shanmugam Meenakumari, Satish K. Tiwary, and Akhil R. Chakravarty*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received October 6, 1993[®]

The synthesis, X-ray crystal structure, and magnetic properties of an angular trinuclear copper(II) complex $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**), obtained from a reaction of $Cu_2(O_2CMe)_4(H_2O)_2$ with 2,2′-bipyridine (bpy) and NH_4PF_6 in ethanol, are reported. Complex **1** crystallizes in triclinic space group $P\bar{1}$ with $a = 11.529(1)$ Å, $b = 12.121(2)$ Å, $c = 17.153(2)$ Å, $\alpha = 82.01(1)°$, $\beta = 79.42(1)°$, $\gamma = 89.62(1)°$, and $Z = 2$. A total of 6928 data with $I > 2.5\sigma(I)$ were refined to $R = 0.0441$ and $R_w = 0.0557$. The structure consists of a trinuclear core bridged by four acetate ligands showing different bonding modes. The coordination geometry at each copper is distorted square-pyramidal with a $CuN_2O_2\cdots O$ chromophore. The Cu⋯Cu distances are 3.198(1) Å, 4.568(1) Å, and 6.277(1) Å. There are two monoatomic acetate bridges showing Cu–O–Cu angles of 93.1(1) and 97.5(1)°. Magnetic studies in the temperature range 39–297 K show the presence of a strong ferromagnetically coupled dicopper(II) unit ($2J = +158$ cm^{-1}) and an essentially isolated copper(II) center ($2J' = -0.4$ cm^{-1}) in **1**. The EPR spectra display an axial spectrum giving $g_\parallel = 2.28$ ($A_\parallel = 160 \times 10^{-4}$ cm^{-1}) and $g_\perp = 2.06$ ($A_\perp = 12 \times 10^{-4}$ cm^{-1}) for the normal copper and two intense isotropic signals with g values 2.70 and 1.74 for the strongly coupled copper pair. The structural features of **1** compare well with the first generation models for ascorbate oxidase.

Introduction

The chemistry of polynuclear copper(II) complexes has drawn considerable current interest following the discovery of multicopper active sites in several oxidases[1–4] and in the development of new inorganic materials showing molecular ferromagnetism.[5] The multicopper oxidases consist of three types of copper(II) active sites. The type 2 and type 3 centers together form a trinuclear moiety **I** (see Chart 1) which is believed to be the active site for the binding and multielectron reduction of dioxygen. While mono- and dinuclear model complexes for the type 1–type 3 sites have been extensively studied,[6] the chemistry of complexes modeling the angular trinuclear active sites of oxidases remains relatively unexplored[7] although several tricopper(II) complexes having either a $Cu_3(\mu\text{-}X)$ core (X = Cl, OH) or a nearly linear arrangement of three metal centers are reported.[8] The Cu⋯Cu separations in the trinuclear active site of the fully oxidized form of ascorbate oxidase (**I**) lie in the range 3.66–3.90 Å with an average distance of 3.74 Å.[4] It is thus of immense importance to synthesize low molecular weight trinuclear copper(II) complexes having an isosceles triangular arrangement of metal atoms.

Current efforts in this direction have led to the discovery[9–12] of complexes $[Cu_3(O_2CR)_4\{Et_2NC_2H_4O\}_2(H_2O)]$ (R = Ph, 2-MeC_6H_4), **II**, **III**, and $[Cu_3(\mu\text{-}Im)_3(Me_3tacn)_3]^{3+}$ as first-generation models for the active site of multicopper oxidases. While the Cu–Cu separations in the isosceles triangular dialkylamino species[9] are 3.03 and 5.0 Å, the Cu–Cu separations in the trinuclear unit of the hexanuclear complex are 3.11, 7.46, and 7.48 Å.[10] The hydroxo-bridged trinuclear complex has Cu⋯Cu separations of 3.62, 4.95, and 5.89 Å.[11] The imidazolate-bridged triazacyclononane (Me_3tacn) complex has an equilateral triangular arrangement of metal atoms giving a Cu⋯Cu distance of 5.92 Å.[12]

The present work stems from our study on the reactivity of copper(II) acetate monohydrate dimer with 2,2′-bipyridine (bpy). The reactions of bpy with $Cu_2(\mu\text{-}O_2CMe)_4(H_2O)_2$ are known[13,14] to form a variety of dimeric products. However, from the reaction we are able to isolate a novel trinuclear copper(II) complex. In

---

[†] Dedicated to Professor C. N. R. Rao on the occasion of his 60th birthday on June 30, 1994.

[®] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

(1) (a) Solomon, E. I. In *Copper Coordination Chemistry*: *Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; New York, Adenine: Guilderland, NY, 1983. (b) Reinhammar, B.; Malmström, B. G. In *Copper proteins*; Spiro, T. G., Ed.; Wiley Interscience: New York, 1981; Chapter 3. (c) Fee, J. A. *Struct. Bonding* (*Berlin*) **1975,** *23,* 1.

(2) *Metal clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988.

(3) (a) Malkin, R.; Malmström, B. G. *Adv. Enzymol.* **1970,** *33,* 177. (b) Spira-Solomon, D. J.; Allendorf, M. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1986,** *108,* 5318. (c) Cole, J. L.; Tan, G. O.; Yang, E. K.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1990,** *112,* 2243. (d) Cole, J. L.; Avigliano, L.; Morpugno, L.; Solomon, E. I. *J. Am. Chem. Soc.* **1991,** *113,* 9080.

(4) (a) Messerschmidt, A.; Rossi, A.; Ladenstein, R.; Huber, R.; Bolognesi, M.; Gatti, G.; Marchesini, A.; Petruzzelli, R.; Finazzi-Agro, A. *J. Mol. Biol.* **1989,** *206,* 513. (b) Messerschmidt, A.; Ladenstein, R.; Huber, R.; Bolognesi, M.; Avigliano, L.; Petruzzelli, R.; Rossi, A.; Finazzi-Agro, A. *J. Mol. Biol.* **1992,** *224,* 179.

(5) (a) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 834. (b) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series 198; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.

(6) Copper Coordination Chemistry: Bioinorganic Perspectives. In *J. Inorg. Biochem.* **1992,** *47,* and references therein.

(7) Fenton, D. E.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1993,** 1349.

(8) (a) Angaroni, M.; Ardizzoia, G. A.; Beringhelli, T.; Monica, G. L.; Gatteschi, D.; Masciocchi, N.; Moret, M. *J. Chem. Soc., Dalton Trans.* **1990,** 3305. (b) Bailey, N. A.; Fenton, D. E.; Moody, R.; Scrimshire, P. J.; Beloritzky, E.; Fries, P. H.; Latour, J.-M. *J. Chem. Soc., Dalton Trans.* **1988,** 2817 and references therein. (c) Agnus, Y.; Louis, R.; Metz, B.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Inorg. Chem.* **1991,** *30,* 3155. (d) Christodoulou, D.; George, C.; Keefer, L. K. *J. Chem. Soc., Chem. Commun.* **1993,** 937. (e) Chaudhuri, P.; Winter, M.; Della Vedova, B. P. C.; Bill, E.; Trautwein, A.; Gehring, S.; Fleischhauer, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991,** *30,* 2148. (f) van Koningsbruggen, P. J.; van Hal, J. W.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1993,** 2163.

(9) Gehring, S.; Fleischhauer, P.; Paulus, H.; Haase, W. *Inorg. Chem.* **1993,** *32,* 54.

(10) Karlin, K. D.; Gan, Q.-F.; Farooq, A.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1990,** *29,* 2549.

(11) Adams, H.; Bailey, N. A.; Dwyer, M. J. S.; Fenton, D. E.; Hellier, P. C.; Hempstead, P. D.; Latour, J. M. *J. Chem. Soc., Dalton Trans.* **1993,** 1207.

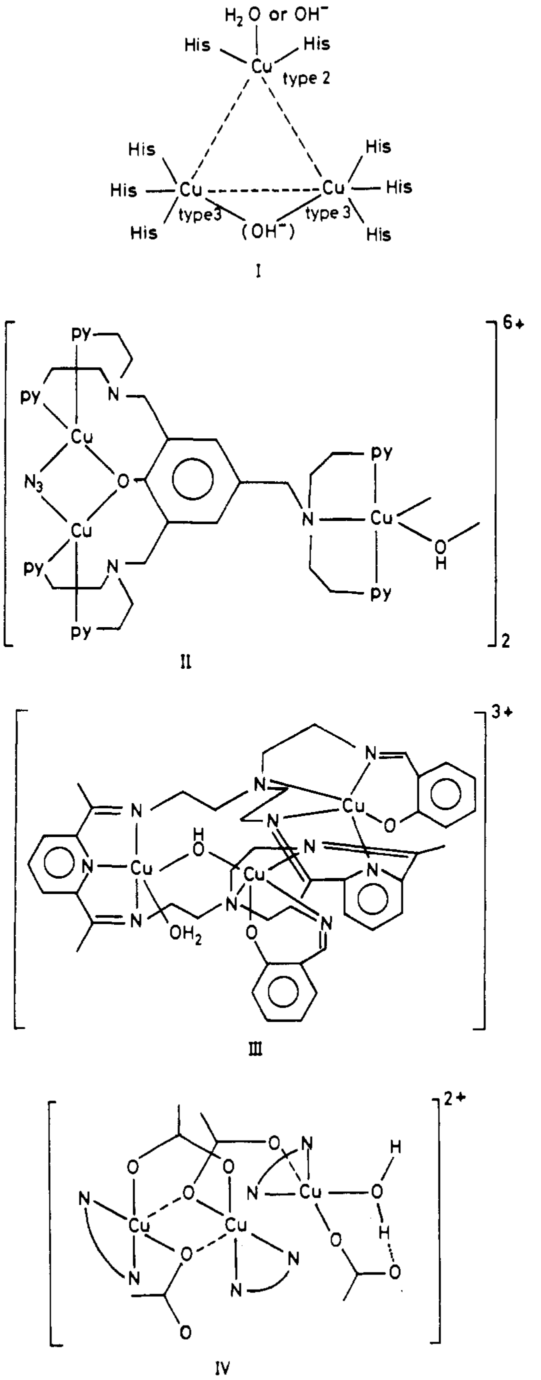
(12) Chaudhuri, P.; Karpenstein, I.; Winter, M.; Butzlaff, C.; Bill, E.; Trautwein, A. X.; Flörke, U.; Haupt, H.-J. *J. Chem. Soc., Chem. Commun.* **1992,** 321.

(13) Perlepes, S. P.; Libby, E.; Streib, W. E.; Folting, K.; Christou, G. *Polyhedron* **1992,** *11,* 923.

(14) Christou, G.; Perlepes, S. P.; Libby, E.; Folting, K.; Huffman, J. C.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990,** *29,* 3657.

0020-1669/94/1333-2085$04.50/0

Chart 1



this report we present the synthesis, crystal structure, and magnetic properties of $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**). The cationic complex **IV** (see Chart 1) displays an angular arrangement of the copper(II) centers, four different bonding modes of the acetate ligands, and the presence of a strong ferromagnetically coupled pair of copper atoms along with a virtually isolated copper center. A preliminary report on **1** has been made.[15]

Experimental Section

Materials and Methods. All reagents and chemicals were purchased from commercial sources and used without further purification. The elemental analysis was done using a Heraeus CHN-O Rapid instrument. The electronic and EPR spectra were recorded on Hitachi U-3400 and Varian E-109 X-band spectrometers, respectively. Variable-temperature magnetic susceptibility data in the temperature range 39–297 K were obtained on polycrystalline samples from a Faraday type magnetometer equipped with a computer-controlled Cahn 2000 microbalance. $Hg[Co(NCS)_4]$ was used as a calibrant. Experimental susceptibility data were corrected for diamagnetic contributions.

Table 1. Crystallographic Data for $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**)

chem formula	$C_{38}H_{38}N_6O_9F_{12}P_2Cu_3$	fw	1203.3
a, Å	11.529(1)	space group	$P\bar{1}$ (No. 2)
b, Å	12.121(2)	*T*, °C	18
c, Å	17.153(2)	λ(Mo Kα), Å	0.7107
α, deg	82.01(1)	ρ_{calcd}, g cm^{-3}	1.71
β, deg	79.42(1)	μ(Mo Kα), cm^{-1}	15.3
γ, deg	89.62(1)	$R(F_o)^a$	0.0441
V, Å^3	2332.9(5)	$R_w(F_o)^a$	0.0557
Z	2		

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum|F_o|w^{1/2}$; $w = 1.0/[\sigma^2(F_o) + 0.003157(F_o)^2]$.

Preparation of $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (1). A 0.20-g amount (0.5 mmol) of copper(II) acetate monohydrate dimer was added to a magnetically stirred 10-mL ethanolic solution of 0.16 g (1.0 mmol) of 2,2′-bipyridine (bpy). The resulting mixture was heated to 50 °C for 5 min under stirring conditions, followed by cooling to ambient temperature. A 0.16-g amount (1.0 mmol) of NH_4PF_6 was added to the solution which was then filtered, and the filtrate was kept for 12 h at 25 °C. A sky-blue crystalline solid of composition $[Cu_2(O_2CMe)_3(bpy)_2](PF_6)$,[16] formed as a major product (~50% yield), was removed by filtration, and the filtrate was kept for slow evaporation. Dark-blue rectangular shaped crystalline blocks of **1** were obtained from the filtrate in ca. 10% yield. The crystalline mass was washed with a cold 1:1 $EtOH-H_2O$ mixture and was dried in vacuo over P_4O_{10}. Anal. Calcd for $C_{38}H_{38}N_6O_9P_2F_{12}Cu_3$: C, 37.90; H, 3.18; N, 6.98. Found: C, 37.28; H, 3.32; N, 6.46. Visible electronic spectral data in MeOH [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 633 (150).

X-ray Crystallographic Procedures. A dark-blue rectangular shaped crystal (0.4 × 0.4 × 0.2 mm) was mounted on a glass fiber. All geometric and intensity data were collected from this crystal using an automated Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The crystal orientation matrix and the unit-cell parameters were obtained from a least-squares fit to the goniometer settings of 25 reflections in the range $16 < 2\theta < 24°$. Data scans, which employed an $\omega-2\theta$ motion, were made for 8819 possible reflections in the range $4° \leq 2\theta \leq 50°$. The intensity data were corrected for Lorentz, polarization, and absorption[17] effects. The crystal showed no significant decay during the X-ray exposure time.

The structure was solved by the Patterson method which revealed the positions of the copper atoms in the crystallographic asymmetric unit. The remaining atoms were located in successive Fourier difference maps and refined by full-matrix least-squares techniques. All the hydrogen atoms were located from the Fourier difference maps and were used only for structure factor calculations in the final cycle of least-squares refinement of non-hydrogen atoms. All calculations were carried out using a VAX 88 computer and SHELX system of programs[18a] at the computer center of the Indian Institute of Science. Atomic scattering factors were taken from the ref 18b. Selected crystallographic data are presented in Table 1. The atomic coordinates with isotropic equivalent thermal parameters for the non-hydrogen atoms are given in Table 2. The final Fourier difference map showed a highest peak of 0.19 e/Å^3. The maximum shift/esd was 0.14 with an overall scale factor of 1.5.

Results

Synthesis. Copper(II) acetate monohydrate dimer forms diaxial adducts with a variety of unidentate ligands.[19-21] In these reactions the tetraacetato framework remains essentially unaltered

---

(15) Meenakumari, S.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 2749.

(16) The perchlorate salt of the cationic complex has been reported.[14]

(17) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(18) (a) Sheldrick, G. M. *SHELXS-86: A Computer program for Automatic Solution of Crystal Structures*; Universität Göttingen: Göttingen, FRG, 1986. Sheldrick, G. M. *SHELX-76: A program for Crystal Structure Determination*; Cambridge University Press: Cambridge, England, 1976. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(19) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45.

Table 2. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) with Their Estimated Standard Deviations for $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$

atom	*x*	*y*	*z*	U_{eq}[a]
Cu(1)	5104(0.3)	5732(0.3)	2339(0.2)	33(0.1)
Cu(2)	7227(0.3)	4032(0.3)	2077(0.2)	34(0.1)
Cu(3)	10167(0.3)	5310(0.3)	3197(0.2)	36(0.1)
P(1)	7301(1)	–943(1)	5115(1)	64(0.4)
P(2)	12202(1)	1289(1)	310(1)	65(1)
O(1)	5222(2)	5026(2)	3418(1)	44(1)
O(2)	6596(2)	3721(2)	3220(1)	42(1)
C(1)	5780(3)	4175(3)	3643(2)	35(1)
C(2)	5419(4)	3643(4)	4498(2)	52(2)
O(3)	5214(2)	4272(2)	1924(1)	36(1)
O(4)	3373(3)	4145(3)	2566(2)	69(1)
C(3)	4255(3)	3713(3)	2222(2)	40(1)
C(4)	4241(5)	2505(4)	2133(3)	72(2)
N(1)	7972(3)	4162(2)	928(2)	38(1)
C(11)	8061(4)	5090(3)	384(2)	49(1)
C(12)	8605(4)	5112(4)	–393(3)	61(2)
C(13)	9111(4)	4151(5)	–632(2)	67(2)
C(14)	9014(4)	3185(4)	–84(3)	59(2)
C(15)	8418(3)	3198(3)	687(2)	40(1)
N(2)	7639(3)	2429(2)	2037(2)	40(1)
C(21)	8211(3)	2229(3)	1307(2)	44(1)
C(22)	8550(4)	1156(4)	1174(3)	61(2)
C(23)	8275(5)	302(4)	1793(3)	72(2)
C(24)	7680(5)	517(3)	2520(4)	71(2)
C(25)	7378(4)	1582(3)	2626(3)	54(1)
N(3)	10047(3)	3654(2)	3323(2)	39(1)
C(31)	10574(4)	3019(3)	2787(3)	52(1)
C(32)	10461(4)	1872(4)	2927(3)	66(2)
C(33)	9807(5)	1382(4)	3662(4)	76(2)
C(34)	9276(4)	2020(3)	4186(3)	62(2)
C(35)	9390(3)	3183(3)	4015(2)	44(1)
N(4)	9072(3)	5056(2)	4261(2)	39(1)
C(41)	8845(3)	3957(3)	4549(2)	38(1)
C(42)	8134(4)	3640(4)	5304(2)	54(1)
C(43)	7655(3)	4455(4)	5736(2)	55(2)
C(44)	7885(3)	5564(4)	5432(3)	56(2)
C(45)	8603(3)	5832(3)	4703(2)	48(1)
N(5)	4849(3)	7232(2)	2700(2)	37(1)
C(51)	4984(4)	7495(3)	3410(2)	48(1)
C(52)	4808(5)	8547(4)	3607(3)	62(2)
C(53)	4500(5)	9366(3)	3031(3)	66(2)
C(54)	4389(4)	9114(3)	2303(2)	52(1)
C(55)	4554(3)	8029(3)	2145(2)	37(1)
N(6)	4652(2)	6566(2)	1354(2)	35(1)
C(61)	4434(3)	7645(3)	1386(2)	35(1)
C(62)	4123(4)	8325(3)	738(2)	47(1)
C(63)	4023(4)	7869(4)	60(2)	52(1)
C(64)	4257(4)	6762(4)	27(2)	51(1)
C(65)	4561(3)	6130(3)	694(2)	45(1)
O(5)	7105(2)	5662(2)	2037(1)	36(1)
O(6)	8824(2)	5426(2)	2386(2)	44(1)
C(5)	7998(3)	6041(3)	2253(2)	38(1)
C(6)	8014(4)	7247(3)	2338(4)	67(2)
O(7)	10298(2)	6888(2)	3249(2)	50(1)
O(8)	11904(4)	7392(3)	2361(3)	115(2)
C(7)	11043(4)	7607(3)	2846(3)	56(1)
C(8)	10853(5)	8791(4)	2995(4)	83(2)
O(9)	11549(2)	5362(2)	2328(2)	49(1)
F(1)	7052(7)	–8(7)	4447(5)	147(4)
F(2)	7480(7)	–1876(7)	5792(5)	138(4)
F(3)	7601(6)	–32(5)	5617(4)	113(3)
F(4)	6964(5)	–1874(5)	4611(3)	102(2)
F(5)	5942(6)	–883(6)	5487(4)	116(3)
F(6)	8605(7)	–976(7)	4725(5)	139(4)
F(7)	11348(6)	1964(6)	867(4)	122(3)
F(8)	12927(7)	2362(7)	–52(5)	146(4)
F(9)	13109(6)	993(6)	874(4)	125(3)
F(10)	11477(8)	194(8)	670(5)	172(5)
F(11)	12977(6)	589(6)	–288(4)	122(3)
F(12)	11318(7)	1498(7)	–274(5)	153(4)

[a] $U_{iso}(eq) = [\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j]/3$.

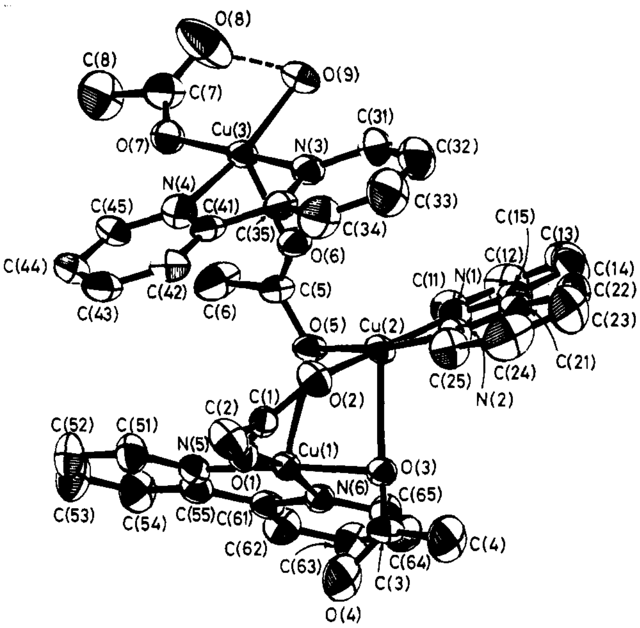


Figure 1. ORTEP view of the complex cation in $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**).

except for minor readjustments in the Cu–O–Cu and O–C–O angles due to variation in the Cu–Cu separations. Attempts to incorporate bidentate chelating ligand(s) in the axial and/or equatorial sites of the core, however, result in the transformations of the "paddle-wheel" structure.[13,14,22-24] We have investigated the reactivity of the core toward 2,2′-bipyridine (bpy) in ethanol. The reaction proceeds smoothly to form a dinuclear[16] and a trinuclear species. Although Christou and co-workers have reported a variety of dimeric products from similar reactions, the formation of a trinuclear species of formulation $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**) has not been observed earlier.[13,14]

X-ray Structure. An ORTEP[25] view of the cationic complex is shown in Figure 1. Selected bond distances and angles are given in Table 3. The structure consists of a trinuclear copper(II) core held by acetate bridges. The coordination geometry at the metal center is tetragonally elongated distorted square-pyramidal where the bpy ligands display a bidentate chelating mode of bonding in the 4 + 1 $CuN_2O_2\cdots O$ chromophore. The deviations of metal atoms from the square planes are as follows: 0.033(1) Å for Cu(1) from the O(1), O(3), N(5), N(6) plane; 0.019(1) Å for Cu(2) from the O(2), O(5), N(1), N(2) plane; 0.030(1) Å for Cu(3) from the O(7), O(9), N(3), N(4) plane. The dihedral angles (δ) between the planes made of Cu(1), O(1), O(3), N(5), N(6) (A); Cu(2), O(2), O(5), N(1), N(2) (B); and Cu(3), O(7), O(9), N(3), N(4) (C) are 150.3(1)° for A and B, 125.6(1)° for A and C, and 25.5(1)° for B and C.

---

(20) (a) Haanstra, W. G.; Driessen, W. L.; Reedijk, J.; Wood, J. S. *Acta Crystallogr.* **1992**, *C48*, 1405. (b) Uekusa, H.; Ohba, S.; Tokii, T.; Muto, Y.; Kato, M.; Husebye, S.; Steward, O. W.; Chang, S.-C.; Rose, J.-P.; Pletcher, J. P.; Suzuki, I. *Acta Crystallogr.* **1992**, *B48*, 650.

(21) Rao, V. M.; Sathyanarayana, D. N.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1983**, 2167 and references therein.

(22) (a) Butcher, R. J.; Overman, J. W.; Sinn, E. *J. Am. Chem. Soc.* **1980**, *102*, 3276. (b) Greenaway, A. M.; O'Connor, C. J.; Overman, J. W.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 1508. (c) Costes, J.-P.; Dahan, F.; Laurent, J.-P. *Inorg. Chem.* **1985**, *24*, 1018. (d) Chiari, B.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1988**, *27*, 3246.

(23) Some recent publications on the core transformations are as follows: (a) Meenakumari, S.; Tiwari, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2175. (b) Wang, S.; Smith, K. D. L.; Pang, Z.; Wagner, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1594. (c) Mori, W.; Suzuki, S.; Kakao, Y.; Nishimura, T.; Ichimura, A. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3189.

(24) (a) Holligan, B. M.; Jeffery, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 3337. (b) Jeffery, J. C.; Schatz, E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1921.

(25) Johnson, C. K. *ORTEP II*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 3. Selected Bond Lengths and Bond Angles for $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$

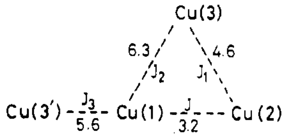
	Distances (Å)		
Cu(1)–Cu(2)	3.198(1)	Cu(2)–Cu(3)	4.568(1)
Cu(1)–Cu(3)	6.277(1)	Cu(1)–Cu(3′)	5.620(1)
Cu(1)–O(1)	1.956(2)	Cu(1)–O(3)	1.992(3)
Cu(1)–N(5)	2.004(3)	Cu(1)–N(6)	1.997(3)
Cu(1)–O(5)	2.273(2)	Cu(2)–O(2)	1.947(2)
Cu(2)–O(3)	2.394(2)	Cu(2)–N(1)	1.985(3)
Cu(2)–N(2)	2.005(3)	Cu(2)–O(5)	1.972(3)
Cu(3)–N(3)	1.992(3)	Cu(3)–N(4)	2.006(3)
Cu(3)–O(6)	2.255(3)	Cu(3)–O(7)	1.935(3)
Cu(3)–O(9)	1.967(3)	O(8)–O(9)	2.507(5)
O(4)–O(9′)	2.621(4)		
	Angles (deg)		
N(6)–Cu(1)–O(5)	104.2(1)	N(5)–Cu(1)–O(5)	102.3(1)
N(5)–Cu(1)–N(6)	81.0(1)	O(3)–Cu(1)–O(5)	82.3(1)
O(3)–Cu(1)–N(6)	94.3(1)	O(3)–Cu(1)–N(5)	174.1(1)
O(1)–Cu(1)–O(5)	87.1(1)	O(1)–Cu(1)–N(6)	167.7(1)
O(1)–Cu(1)–N(5)	92.0(1)	O(1)–Cu(1)–O(3)	92.0(1)
N(2)–Cu(2)–O(5)	170.3(1)	N(1)–Cu(2)–O(5)	92.4(1)
N(1)–Cu(2)–N(2)	81.7(1)	O(3)–Cu(2)–O(5)	79.6(1)
O(3)–Cu(2)–N(2)	108.8(1)	O(3)–Cu(2)–N(1)	98.7(1)
O(2)–Cu(2)–O(5)	94.3(1)	O(2)–Cu(2)–N(2)	91.3(1)
O(2)–Cu(2)–N(1)	172.6(1)	O(2)–Cu(2)–O(3)	85.6(1)
O(7)–Cu(3)–O(9)	92.4(1)	O(6)–Cu(3)–O(9)	95.3(1)
O(6)–Cu(3)–O(7)	97.1(1)	N(4)–Cu(3)–O(9)	164.2(1)
N(4)–Cu(3)–O(7)	91.8(1)	N(4)–Cu(3)–O(6)	99.2(1)
N(3)–Cu(3)–O(9)	92.5(1)	N(3)–Cu(3)–O(7)	171.1(1)
N(3)–Cu(3)–O(6)	89.8(1)	N(3)–Cu(3)–N(4)	81.5(1)
Cu(1)–O(1)–C(1)	130.2(2)	Cu(2)–O(2)–C(1)	130.3(2)
O(1)–C(1)–O(2)	126.4(3)	Cu(1)–O(3)–Cu(2)	93.1(1)
Cu(2)–O(3)–C(3)	133.7(2)	Cu(1)–O(3)–C(3)	108.3(2)
O(3)–C(3)–O(4)	122.0(4)	Cu(1)–O(5)–Cu(2)	97.5(1)
Cu(2)–O(5)–C(5)	109.3(2)	Cu(1)–O(5)–C(5)	139.0(2)
Cu(3)–O(6)–C(5)	137.1(3)	O(5)–C(5)–O(6)	120.8(3)
Cu(3)–O(7)–C(7)	129.9(3)	O(7)–C(7)–O(8)	124.3(4)
Cu(2)–N(1)–C(15)	114.7(2)	Cu(2)–N(1)–C(11)	126.6(3)
Cu(2)–N(2)–C(25)	127.2(3)	Cu(2)–N(2)–C(21)	113.5(2)
Cu(3)–N(3)–C(35)	114.6(2)	Cu(3)–N(3)–C(31)	125.2(3)
Cu(3)–N(4)–C(45)	127.1(3)	Cu(3)–N(4)–C(41)	113.5(2)
Cu(1)–N(5)–C(55)	114.4(2)	Cu(1)–N(5)–C(51)	126.1(2)
Cu(1)–N(6)–C(65)	125.3(2)	Cu(1)–N(6)–C(61)	115.0(2)

The Cu(1) and Cu(2) atoms are bridged by three acetate ligands displaying different bonding modes. The Cu(3) atom is linked with the Cu(1), Cu(2) pair by a bridging acetate ligand. The Cu(1)–Cu(2), Cu(1)–Cu(3), and Cu(2)–Cu(3) distances in the trinuclear core are 3.198(1), 6.277(1), and 4.568(1) Å, respectively. The terminal η^1-O_2CMe on Cu(3) is involved in strong intramolecular hydrogen bonding with the aqua ligand [O(8)···O(9) = 2.507(5) Å]. The trinuclear units form a 1D chain by intermolecular hydrogen bonds involving the aqua ligand on Cu(3) and the O(4) atom of a monoatomic bridging acetate ligand. The chains are well separated with PF_6 anions spaced between the chains. The O(4)···O(9′) and Cu(1)···Cu(3′) distances in the 1D chain are 2.621(4) and 5.620(1) Å, respectively.

The basal planes of the copper atoms show an average Cu–N,O distance of ~2.0 Å. The axial distances, however, lie between 2.255(3) and 2.394(2) Å. The considerably longer Cu(2)–O(3) bond length compared to the Cu(1)–O(5) and Cu(3)–O(6) distances could be related to the formation of the 1D chain involving the O(4) atom. As a consequence, the Cu(3)–O(9) distance in the basal plane of Cu(3) atom is found to be relatively longer compared to the Cu(3)–O(7), Cu(1)–O(1), and Cu(2)–O(2) distances. The aqua ligand on the Cu(3) atom imparts stability to the structure through its involvement in the inter- and intramolecular hydrogen bond formations. The monoatomic bridges are asymmetric[24] showing shorter Cu(1)–O(3) and Cu(2)–O(5) distances than the Cu(1)–O(5) and Cu(2)–O(3) bond lengths, thus causing a severe distortion in the square-pyramidal coordination geometries as evidenced from the deviation of the O–Cu–N, O angles from the ideal value of 90°.

The significant structural results can be summarized as follows: (i) an angular arrangement of the tricopper(II) core; (ii) three different Cu···Cu separations that are comparable to those observed[9-12] in the first-generation models of the active site of ascorbate oxidase; (iii) four different bonding modes of the acetate ligands; (iv) formation of a 1D chain by hydrogen-bonding linkage of the trinuclear units; (v) the smallest[14,22,26] monoatomic carboxylate bridge angle which is expected to promote strong ferromagnetic coupling between Cu(1) and Cu(2) atoms.

Magnetic Properties. Variable-temperature magnetic susceptibility data were obtained on powdered samples in the temperature range 39–297 K. The data are typical of a ferromagnetically coupled system with an effective magnetic moment (μ_{eff}) per copper increasing from 2.02 at 297 K to 2.2 μ_B at 39.5 K. The spin system in **1** can be modeled as



in which J, J_1, J_2, and J_3 are the exchange coupling constants for the pairs of atoms Cu(1), Cu(2); Cu(2), Cu(3); Cu(1), Cu(3); and Cu(1), Cu(3′), respectively. The interunit coupling is expected to be negligible in absence of any covalent linkage between Cu(1) and Cu(3′). Hence the J_3 value is assumed to be zero and the magnetic interaction in the discrete trinuclear core has been considered for the fitting of the susceptibility data. Within the core the order of the Cu···Cu separations [Cu(1)–Cu(2) = 3.2 Å < Cu(2)–Cu(3) = 4.6 Å < Cu(1)–Cu(3) = 6.3 Å] and the bridging environments at the metal sites suggest that the exchange coupling between Cu(1) and Cu(2) should be much stronger than the same in the other two pairs. The magnetic interactions in the pairs Cu(1), Cu(3) and Cu(2), Cu(3) are through the same bridging acetate. As the O(6) atom of the acetate is located at the elongated axial site of Cu(3), the trinuclear core may be assumed to have an isosceles triangular arrangement of spins with $J_1 = J_2 = J'$.

For interpreting the magnetic behavior of **1** we have used Kambe's approach[27] for three paramagnetic centers. The Heisenberg Hamiltonian for such a system is derived as $\hat{H} = -2J(\hat{S}_1\hat{S}_2) - 2J'(\hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3)$. The resulting spin quantum numbers for the trimer can be written as $S^* = S_1 + S_3$ and $S^T = S_1 + S_2 + S_3 = {}^3/_2$. The energy levels for the spin states $|S^T,S^*\rangle$ have the energies $E(S^T,S^*)$ as $E({}^3/_2,1) = -J/2 - J'$, $E({}^1/_2,1) = -J/2 - 2J'$, and $E({}^1/_2,0) = 3J/2$. Putting these values in the Van Vleck equation,

$$\chi_M = \frac{\chi_0\sum_S[S(S+1)(2S+1)O(S)\exp(-W(S)/kT)]}{\sum_S(2S+1)O(S)\exp(-W(S)/kT)} \tag{1}$$

with $O(S)$ as the degeneracy of the state,[28] $\chi_0 = Ng^2\beta^2/3kT$, and S as the effective spin value, yields the following expression for molar susceptibility of the complex:

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\left(\frac{F_1}{F_2}\right) + N_\alpha \tag{2}$$

where

---

(26) (a) Hämäläinen, R.; Ahlgrén, M.; Turpeinen, U. *Acta Crystallogr.* **1982**, *B38*, 1577. (b) Chiari, B.; Helms, J. H.; Piovesana, O.; Tarantelli, T.; Zanazzi, P. F. *Inorg. Chem.* **1986**, *25*, 2408.

(27) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48.

(28) $O(S)$ is the degeneracy of the spin state which can be calculated from the expression $O(S) = W(S) - W(S+1)$, where $W(S)$ is the coefficient of S in the expansion $(X^S + X^{S-1} + ... + X^{-S+1} + X^{-S})^n$. $O(S)$ has a value of unity in the present case.

$$F_1 = 10\exp(J'/kT) + \exp(-2J'/kT) + \exp(-2J/kT) \quad (3)$$

$$F_2 = 2\exp(J'/kT) + \exp(-2J'/kT) + \exp(-2J/kT) \quad (4)$$

The best fit of the susceptibility data, shown in Figure 2, is obtained with $J = 79$ cm^{-1}, $J' = -0.2$ cm^{-1}, $g = 2.19$, and a TIP value of 60×10^{-6} cm^3 mol^{-1}/copper atom. The agreement factor, $R = \sum_n(|\chi_{exp} - \chi_{calc}|/\chi_{exp})/n$, was 9.55×10^{-3}.

It is apparent from the coupling constant values that the magnetic interaction between Cu(1) and Cu(2) atoms is much stronger than the same in the other two pairs. The complex seems to behave magnetically as an equimolar mixture of a strong ferromagnetically coupled dimeric [Cu(1),Cu(2)] and a monomeric [Cu(3)] species. This is again evidenced from a reasonably good fit of the susceptibility data obtained by assuming such a mixture giving $J = 77$ cm^{-1}, $\Theta = -2$ K, $g_1 = 2.22$, $g_2 = 2.13$, and $R = 9.71 \times 10^{-3}$ using eq 5 in which the Bleaney–Bowers and the Curie–Weiss terms for spin = $^1/_2$ systems are for the coupled dimer Cu(1), Cu(2) and for the isolated Cu(3) center.

$$\chi_M = (2N\beta^2 g_1^{\,2}/kT)[3 + \exp(-2J/kT)]^{-1} + N\beta^2 g_2^{\,2}/4K(T - \Theta) + N_\alpha \quad (5)$$

The EPR spectrum of the complex, recorded in the X-band frequency in frozen methanol, exhibits well-resolved resonances that correspond to $\Delta M_S = \pm 1$ giving $g_\parallel$ and $g_\perp$ values of 2.28 and 2.06, respectively ($A_\parallel = 160 \times 10^{-4}$ cm^{-1}; $A_\perp = 12 \times 10^{-4}$ cm^{-1}).[15] The high $A_\parallel$ value in **1** compares well with those observed for the type 2 center of laccase.[1,29] The EPR spectrum also displays two additional isotropic signals near 2390 and 2730 G with g-values of 2.70 and 1.74, respectively ($g_i = 2.22$). The significantly high intensity and large separation of the isotropic signals indicate the presence of a strongly coupled dimeric unit in the trinuclear complex **1**.

Discussion

Complex **1** has a unique trinuclear core in which a dicopper(II) unit held by two monoatomic and one three-atom bridging acetate ligands exhibits an unusually large positive J value. A comparison of the magnetostructural data of **1** with those of bis(μ-hydroxo)dicopper(II)[30] and (μ-hydroxo/alkoxo)(μ-carboxylato)dicopper(II)[23a,31,32] complexes reveals that the small monoatomic bridge angles, viz. Cu(1)–O(3)–Cu(2) and Cu(1)–O(5)–Cu(2) in **1**, should promote a ferromagnetic interaction between Cu(1) and Cu(2). Earlier theoretical studies[33] followed by empirical magnetostructural correlations[30] made on several di-μ-hydroxo complexes predict a positive J value for a Cu–OH–Cu angle of <98°. It has recently been observed[23a] that substitution of a hydroxo by a three-atom bridging carboxylato ligand significantly alters the singlet–triplet separation ($2J$).

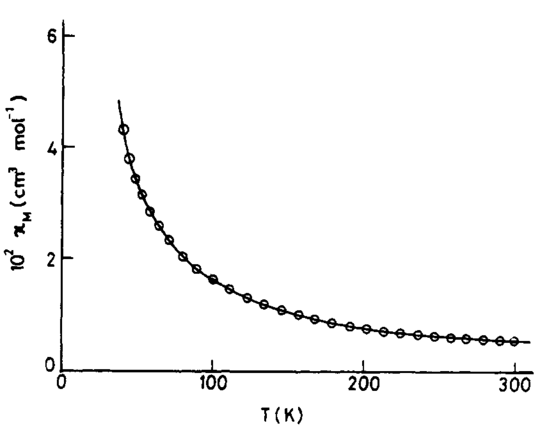
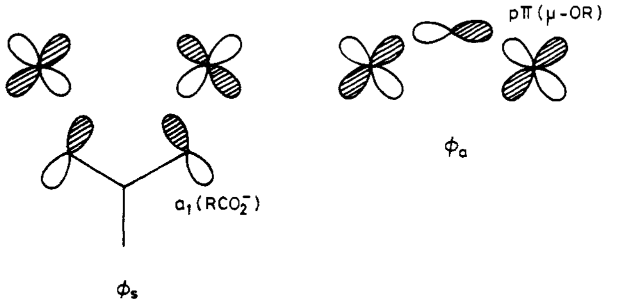


Figure 2. Molar susceptibilities vs temperature plot for $[Cu_3(O_2CMe)_4(bpy)_3(H_2O)](PF_6)_2$ (**1**). The circles are the experimental points, and the solid line is the least-squares fit of the experimental data using the expression given in eq 1 of the text.

In the bis(μ-hydroxo)dicopper(II) core, the magnitude of antiferromagnetic interactions is proportional to the energy separation between two highest d-like MO's, viz., symmetric (ϕ_s)- and antisymmetric (ϕ_a) combinations of magnetic orbitals, irrespective of their energy order.[33] Nishida[31] and Reed[34] have indicated that in a (μ-alkoxo)(μ-carboxylato)dicopper(II) core, the interactions of RO⁻ and RCO_2^- with the magnetic orbitals of the metal are "countercomplementary". While the ϕ_s orbital is destabilized by the a_1 orbital of the acetate, the oxygen pπ orbital of the alkoxo bridge destabilizes the ϕ_a orbital. The extent of destabilization is similar in both cases, and a net reduction of the magnitude of antiferromagnetic interaction is observed in these asymmetrically dibridged complexes. The countercomplementary nature of the overlap has also been envisaged[14] by Christou and co-workers in explaining the weak ferromagnetic behavior ($J = 3.6$ cm^{-1}) of a tribridged dicopper(II) complex $[Cu_2(O_2CMe)_3(bpy)_2](ClO_4)$ having one monoatomic and two three-atom bridging acetate ligands.



We rationalize the large positive J value in **1** by proposing the countercomplementary interactions to be operative in which the strong ferromagnetic interactions between Cu(1) and Cu(2) atoms mediated by two monoatomic bridges override the effect of antiferromagnetic interactions through the three-atom bridging acetate ligand.

Acknowledgment. We thank Dr. S. Vasudevan for his valuable help in the magnetochemical studies and the Department of Science and Technology, Government of India, for financial support.

Supplementary Material Available: A packing diagram of the 1D chains and full lists of crystallographic data, hydrogen atom coordinates, anisotropic thermal parameters, bond lengths and angles, details on least-squares planes and dihedral angles, and variable-temperature magnetic susceptibility data (24 pages). Ordering information is given on any current masthead page.

---

(29) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1.

(30) (a) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173. (b) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105. (c) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

(31) Nishida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633.

(32) (a) Fallon, G. D.; Murray, K. S.; Mazurek, W.; O'Connor, M. J. *Inorg. Chim. Acta* **1985**, *96*, L53. (b) Mazurek, W.; Kennedy, B. J.; Murray, K. S.; O'Connor, M. J.; Rodgers, J. R.; Snow, M. R.; Wedd, A. G.; Zwack, P. R. *Inorg. Chem.* **1985**, *24*, 3258.

(33) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(34) McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.