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A Novel Tetranuclear Copper(II) Complex with Alternating $\mu_{1,1}$-Azido and Phenoxo Bridges: Synthesis, Structure, and Magnetic Properties of $[Cu_4(\mu\text{-salen})_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$

Subratanath Koner,*,† Sandip Saha,† Ken-Ichi Okamoto,‡ and Jean-Pierre Tuchagues§

Department of Chemistry, Jadavpur University, Jadavpur, Calcutta 700 032, India, Department of Chemistry, Tsukuba University, Tsukuba, Ibaraki 305-8571, Japan, and Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 Route de Narbonne, 31077 Toulouse, Cedex, France

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A novel tetranuclear copper(II) complex containing alternating $\mu_{1,1}$-azido and monophenoxo bridges has been synthesized and characterized by spectroscopic methods, X-ray single-crystal analysis, and variable-temperature magnetic measurements. The magnetic behavior, investigated in the temperature range 2–300 K, indicates that the interactions between copper ions are antiferromagnetic in nature for both azido and phenoxo bridges. The temperature dependence of the magnetic susceptibility was fitted with $J_1 = -12.8$ cm^{-1}, $J_2 = -10$ cm^{-1}, $g = 2.171$, 2.1% paramagnetic component, and negligible temperature-independent paramagnetism (5×10^{-8}). At variance with the earlier reports of these types of complexes containing a $\mu_{1,1}$-azido group, the end-on double-azido-bridged copper(II) center in this complex shows an antiferromagnetic interaction.

Introduction

Investigations into the magnetic properties of molecule-based materials containing a polymetallic assembly have become a fascinating subject in the field of condensed matter physics and materials chemistry.[1] Polynuclear metal complexes have demonstrated many important properties such as catalysis,[2] clathration,[3] and molecular sieving,[4] besides their interesting magnetic properties.

Several strategies have been adopted to prepare polynuclear coordination complexes including the self-assembly or aggregation of metal centers and ligands,[5] connecting two or several metals with the help of bridging ligands, or direct incorporation of metal ions into designed polydentate ligands.[6] The second approach is advantageous over the first one as the course of reactions is easier to control in the second process. On the other hand, the use of different bridges and the control over the stereochemical character of the blocking ligands have afforded an impressive array of new architectures for polynuclear coordination complexes.[7] Pseudohalogens are versatile ligands for making such bridges.[8] Among them azide is the most efficient ligand with

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* To whom correspondence should be addressed. E-mail: skoner55@hotmail.com. Fax. +91-33-2414-6584.

† Jadavpur University.

‡ Tsukuba University.

§ Laboratoire de Chimie de Coordination du CNRS.

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regard to superexchange pathways between paramagnetic centers. The versatility and efficiency of azide lies in its functionality as a terminal monodentate or bridging bi-, tri-, and tetradentate ligand.[9] Besides, azide is also used as a ligand to study the interaction between small molecules and the metal center of metalloenzymes.[10] In many cases it has been observed that azide bridges metal centers in multicopper enzymes.[10c,11] In this context polynuclear copper(II) complexes have relevance in magneto−structural correlations, multielectron transfer, catalysis, and bioinorganic modeling. Although there are many examples of four $S = 1/2$ copper(II) spin systems, which exhibit a large diversity of structural types,[12] only a few of them are of linear type.[13]

In this paper we report the synthesis, characterization, and magnetic properties of a novel linear tetranuclear copper(II) complex. To our knowledge this is the first tetranuclear copper(II) complex having alternating azido and monophenoxo bridges.

Experimental Section

Materials. Salicyldehyde and ethylenediamine (Aldrich) were used as such. All other chemicals used here were of AR grade. SalenH_2 was prepared by following the standard procedure.[14]

Physical Measurements. The instruments used for IR and UV−VIS spectral measurement and CHN analyses were the same as reported earlier.[8b] The magnetic susceptibility of **1** was measured in the 1.96−300 K temperature range with a Quantum Design MPMS SQUID susceptometer under a 1 T magnetic field. Diamagnetic corrections were estimated from the Pascal constants.

Synthesis of [Cu_4(μ-salen)$_2$($\mu_{1,1}$-N_3)$_2$(N_3)$_2$], 1. To a 15 mL methanolic solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.5 g, 2 mmol) was added 0.28 g (1 mmol) of salen dissolved in 20 mL of acetone, and the resulting solution was stirred for ca. 10 min. To this a 20 mL methanolic or a 5 mL aqueous solution of NaN_3 (ca. 0.54 g, 8 mmol) was added slowly with stirring at room temperature, and stirring was continued for another 30 min. A small amount of green colored solid separated out during addition of the NaN_3 solution, but the precipitated green solid redissolved upon complete addition of NaN_3. The resulting dark solution thus produced was then kept undisturbed at room temperature. After about 2 days black block crystals appeared; they were collected by filtration, washed with methanol, and dried over $CaCl_2$ (yield: ca. 62%). A well-shaped crystal of this product was selected for X-ray single-crystal diffraction analysis. Anal. Calcd for $C_{16}H_{14}N_8O_2Cu_2$: C, 40.21; H, 2.96; N, 23.46. Found: C, 39.99; H, 3.15; N, 23.55. The IR spectrum shows two strong ν_{as}(azide) absorptions at 2062 and 2023 cm^{-1} indicating the presence of bridging azide in the complex.[15] The characteristic IR band for the azomethine group of salen appeared in the 1650−1600 cm^{-1} region, ca. 10 cm^{-1} lower than that of salenH_2. The electronic spectrum of complex **1** shows two peaks at ca. 564 and 356 nm for d−d transition and metal charge-transfer bands, respectively.

Table 1. Crystal Data and Structure Refinement for [Cu_4(μ-salen)$_2$($\mu_{1,1}$-N_3)$_2$(N_3)$_2$], **1**

empirical formula	$C_{16}H_{14}N_8O_2Cu_2$
fw	477.43
cryst system	monoclinic
space group	$P2_1/n$
a (Å)	10.240(6)
b (Å)	17.775(5)
c (Å)	9.689(4)
β (deg)	94.72(4)
V (Å^3)	1757(1)
Z	4
ρ_{calcd} (g cm^{-3})	1.804
μ (cm^{-1})	24.52
T (K)	296
R1[a]	0.049
R_w	0.153

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2\}^{1/2}$, $w = [\sigma_c^2(F_o^2) + (p(\mathrm{Max}(F_o^2, 0 + 2F_c^2)/3)^2]^{-1}$; $\sigma_c(F_o^2)$ = esd based on counting statistics; $p = 0.05$.

Caution! Azide derivatives are potentially explosive; only a small amount of material should be prepared, and it should be handled with proper care.

X-ray Crystallography. A black prismatic block crystal of **1** was selected for collecting X-ray data. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Over the course of data collection, the standards decreased by 1.5%. The structure was solved by direct methods (SIR 92)[16a] and difference Fourier techniques.[16] The structure was refined by full matrix least squares on F^2 using anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were included but not refined. Atomic scattering factors were taken form ref 17. All calculations were performed on a VAX computer using the teXsan[18] crystallographic software package of Molecular Structure Corp. The maximum and minimum peaks on the final difference Fourier map correspond to 1.25 and −1.25 e^-/Å^3, respectively. Crystallographic data for complex **1** are summarized in Table 1.

Result and Discussion

Synthesis of Complex 1. The X-ray structure analysis of [Cu(salen)] has established that the complex forms a dimer through an intermolecular semicoordinate bond via one of

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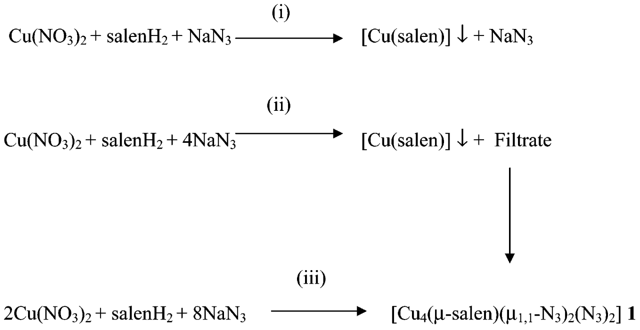
Scheme 1 [a]



[a] $Cu(NO_3)_2 \cdot H_2O$, salen, and NaN_3 are reacted as follows: (i) A 1:1:1 ratio in methanol or (ii) a 1:1:4 ratio in methanol is used, and the green product [Cu(salen)] is filtered off; complex **1** is obtained from the filtrate on slow evaporation (yield: ca. 20%). (iii) A 2:1:8 ratio in methanol is used, and complex **1** is obtained in ca.62% yield.

the phenoxo oxygen atoms of salen.[19] In the dimer copper(II) has a tetragonally elongated square-pyramidal configuration with donor atoms $N_2O_2(O')$. We synthesized the azido derivative of [Cu(salen)] in anticipation that azide would complete the coordination of copper(II) to six, yielding a polynuclear copper(II) compound by connecting the [Cu(salen)] dimers. Complex **1** could not be obtained in a straightforward preparation procedure (Scheme 1): Reaction of $Cu(NO_3)_2$, salen, and NaN_3 in 1:1:1 molar ratio in methanol afforded no azide derivative; instead a pure [Cu(salen)] complex was obtained in this process (Scheme 1i). But reaction of the copper(II), salen, and azide in 1:1:4 ratio at first yielded a green precipitate; it was filtered off, and the filtrate was allowed to evaporate slowly. The black block crystals of the title complex were separated from this filtrate after about 2 days (Scheme 1ii). The presence of two ν_{as}(azide) IR absorptions in the 2000−2100 cm^{-1} region clearly evidenced the presence of bridging azido groups in the black crystal, while elemental analyses indicate that the empirical composition of the crystal is $Cu_2(salen)(N_3)_2$. Later, the exact chemical composition of the crystals was found as $Cu_4(salen)_2(N_3)_4$ from X-ray analysis (see below). The yield of the desired complex prepared in this process was very low (ca. 20%). Finally, we prepared the title complex in a higher yield by reacting copper(II), salen, and azide in 2:1:8 molar ratio (Experimental Section and Scheme 1iii). Spectroscopic and analytical data showed that the intermediate green precipitate in procedure ii was [Cu(salen)].

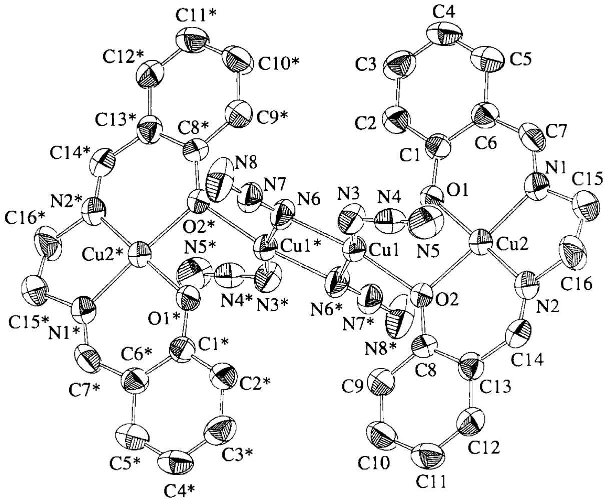


Figure 1. ORTEP[31] diagram of complex **1** with the atom numbering scheme.

Table 2. Selected Bond Lengths and Angles for Complex **1**

	Bond Lengths (Å)		
Cu(1)−O(2)	2.027(4)	Cu(1)−N(3)	1.940(5)
Cu(1)−N(6)	2.000(5)	Cu(1)−N(6)*	1.979(5)
Cu (2)−O(1)	1. 892(4)	Cu(2)−O(2)	1.930(4)
Cu(2)−N(1)	1.922(5)	O(2)−C(8)	1.329(6)
O(1)−C(1)	1.307(6)	N(1)−C(15)	1.452(8)
N(1)−C(7)	1.272(7)	N(2)−C(16)	1.475(8)
N(2)−C(14)	1.254(7)	N(4)−N(5)	1.128(7)
N(3)−N(4)	1.195(7)	N(7)−N(8)	1.143(7)
N(6)−N(7)	1.205(7)	C(1)−C(6)	1.429(8)
	Bond Angles (deg)		
O(2)−Cu(1)−N(3)	93.8(2)	O(2)−Cu(1)−N(6)	170.7(2)
O(2)−Cu(1)−N(6)*	96.2(2)	N(3)−Cu(1)−N(6)	92.2(2)
N(3)−Cu(1)−N(6)*	165.6(2)	N(6)−Cu(1)−N(6)*	76.7(2)
O(1)−Cu(2)−O(2)	84.5(2)	O(1)−Cu(2)−N(1)	95.2(2)
O(1)−Cu(2)−N(2)	175.8(2)	O(2)−Cu(2)−N(1)	174.9(2)
O(2)−Cu(2)−N(2)	94.2(2)	N(1)−Cu(2)−N(2)	85.7(2)
Cu(2)−O(1)−C(1)	126.7(4)	Cu(1)−O(2)−Cu(2)	103.2(2)
Cu(1)−O(2)−C(8)	129.2(4)	Cu(2)−O(2)−C(8)	126.0(3)
Cu(2)−N(1)−C(7)	125.1(4)	Cu(2)−N(1)−C(15)	112.6(4)
C(7)−N(1)−C(15)	122.2(5)	Cu(2)−N(2)−C(14)	125.8(4)
Cu(2)−N(2)−C(16)	112.0(4)	C(14)−N(2)−C(16)	122.0(5)
Cu(1)−N(3)N(4)	121.6(4)	N(3)−N(4)−N(5)	178.0(7)
Cu(1)−N(6)−Cu(1)*	103.3(2)	Cu(1)−N(6)−N(7)	124.1(4)
Cu(1)−N(6)*−N(7)*	126.3(4)	N(6)−N(7)−N(8)	177.5(7)

X-ray Structure of [$Cu_4(\mu$-salen$)_2(\mu_{1,1}$-$N_3)_2(N_3)_2$], 1. The structure determination revealed that the copper atoms are bridged alternately by end-on azido and salen ligands in the prepared tetrameric copper(II) complex **1**. A perspective view with atom numbering scheme of the title complex is shown in Figure 1, and selected bond distances and angles of complex **1** are gathered in Table 2. Cu(2) is coordinated to two phenolato oxygen and two imine nitrogen atoms. Cu(1) is coordinated to three nitrogen atoms, one terminal azido and two end-on azido's [N(6) and its neighboring symmetry-related counterpart N(6*)]. The fourth coordination site of Cu(1) is occupied by the phenolato oxygen bridging Cu(1) and Cu(2). The other half of the molecule is related by a center of inversion to the first half described above (Figure 1). The coordination environment of Cu(2) is best described as a rhombically distorted square plane whereas that of Cu(1) is a tetrahedrally distorted square plane. While Cu−N bond distances around Cu(2) are very close to each other, Cu−O distances show significant differences [Cu(2)−O(1) = 1.892(4) Å, Cu(2)−O(2) = 1.930(4)Å] attributable to the Cu(1)−O(2)−Cu(2) bridge. The Cu(2)−O−Cu(1) and Cu(1)−N(6)−Cu(1)* angles are 103.2(2) and 103.3(2)°, respectively. The Cu(2)−Cu(1) and Cu(1)−Cu(1)* distances in complex **1** are 3.102(2) and 3.120(3) Å, respectively. Other distances and angles fall within the range of the corresponding reported data.[8b,d,19,20] Although metal−phenoxo−metal bridges have been reported for macrocyclic[21] and compartmental ligands[22] and some Schiff bases,[23] to our knowledge

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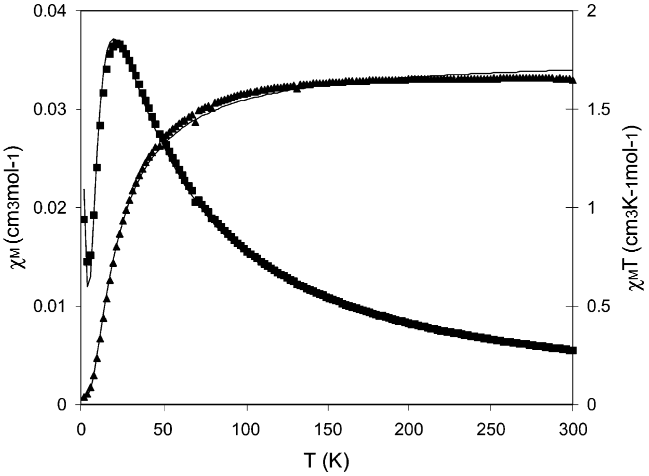
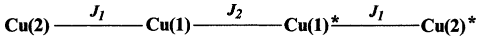


Figure 2. χ_M vs T (■) and χ_MT product vs T (▲) under an applied magnetic field of 1.0 T for [Cu$_4$(μ-salen)$_2$($\mu_{1,1}$-N$_3$)$_2$(N$_3$)$_2$], **1**. Solid lines represent the best fit of the data with the symmetry model described in the text.

Chart 1



this is the first complex where salen acts as a bridging ligand through its phenoxo groups.

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility, χ_M, for complex **1** in the temperature range 1.96−300 K is shown in Figure 2. The 5.50×10^{-3} cm^3 mol^{-1} value at 300 K is slightly higher than the value expected for four magnetically uncoupled copper(II) ions ($\chi_M = 5.01 \times 10^{-3}$ cm^3 mol^{-1}, $g = 2.00$). Upon cooling, χ_M increases, reaching a 3.66×10^{-2} cm^3 mol^{-1} maximum around 22 K, and then rapidly decreases with temperature, indicating a bulk antiferromagnetic behavior.

Half of the tetranuclear complex **1** being symmetry related to the other half, three coupling constants are required to explain its magnetic properties. However, as magnetic interactions through next nearest neighbors are expected to be at least 1 order of magnitude below those between nearest neighbors, to avoid overparametrization two coupling constants, J_1 between Cu(1) and Cu(2) and symmetry-related Cu(1)* and Cu(2)* and J_2 between Cu(1) and Cu(1)* are considered (Chart 1).

The spin Hamiltonian $\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - 2J_2\hat{S}_2\hat{S}_3$ appropriate for this type of tetranuclear copper(II) system has been used to derive the susceptibility expression. To calculate the energy levels and magnetic properties, diagonalization of the full matrix has been carried out.[24] Least-squares fittings were accomplished with an adapted version of the function-minimization program MINUIT.[25] The best fit of the magnetic data was obtained with the following set of parameters $J_1 = -12.8$ cm^{-1}, $J_2 = -10$ cm^{-1}, $g = 2.171$, 2.1% paramagnetic component, and negligible temperature-independent paramagnetism (5×10^{-8}). To check the quality of fitting of J_1 and J_2 the reliability parameter FCN is calculated using MINUIT.[25] Figure 3 shows the contour plot for J_1 and J_2. The minimum FCN value (corresponding to the best fit) is 0.1; it is in the middle of the 1.0 contour. There is no secondary minimum in this plot.

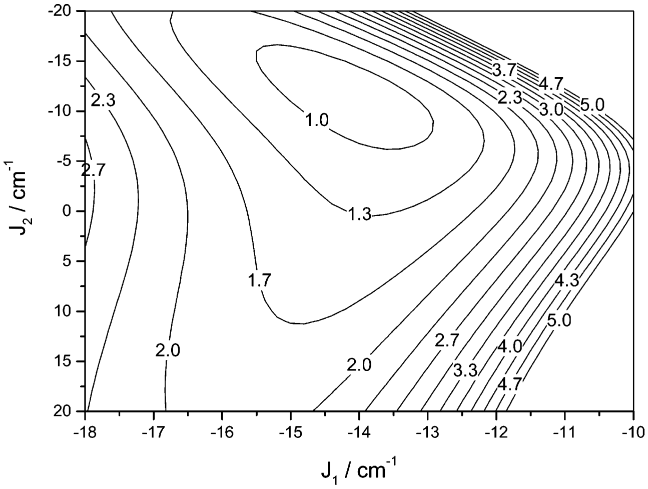


Figure 3. Contour plot of J_1 and J_2. The numerical figures mentioned on the curves are the values of the reliability parameter FCN.

Density functional calculations (DFT)[26] show that the nature of coupling between two copper ions with an end-on azido bridge depends on two parameters: (a) the Cu−N(azido)−Cu angle; (b) the Cu−N(azido) bond distance.[27] If the Cu−N(azido)−Cu angle is in the 96−104° range, the interaction is ferromagnetic; otherwise it is antiferromagnetic. This is almost in line with Thompson's prediction on the basis of extrapolation of magneto−structural correlations for $\mu_{1,1}$-azido complexes.[28] All end-on azido-bridged copper(II) polynuclear complexes reported so far exhibit a ferromagnetic interaction irrespective of their nuclearity.[8b,20,27,29] In the present complex the Cu−N(azido)−Cu angles (103.3°) are very close to the cutoff angle for a ferromagnetic coupling. The Cu−N(azido) bond distance is marginally lower than the critical distance (2.05 Å) for ferro- to antiferromagnetic crossover. This is thus the first complex where such bridging mode yields an antiferromagnetic interaction between copper(II) centers. It is noteworthy that the Cu−Cu magnetic interactions of phenoxo-bridged complexes are usually antiferromagnetic in nature.[30] As a result,

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complex **1** shows a global antiferromagnetic behavior (Figure 2).

It is interesting to note that at variance with all examples reported so far this study shows that the magnetic interaction between end-on double-azido-bridged copper(II) centers is antiferromagnetic, which is rather unusual, even though the Cu−N(azido)−Cu angles and the Cu−N(azido) distances in this complex were within the limit for which the coupling should have been ferromagnetic as predicted theoretically.[27]

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Supporting Information Available: Tables, figures, and CIF files presenting complete information for the X-ray data collection and refinement of the structure, final values of all refined atomic coordinates, all anisotropic thermal parameters, bond lengths and angles, torsion angles, packing diagrams, and magnetic susceptibility data for the complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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