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Synthesis and X-ray Structural Studies on a New Class of Pentanuclear Copper(II) Complexes Containing a $[Cu_5(\mu_3\text{-}OH)_2(\mu\text{-}O_2CMe)_6]^{2+}$ Core and Terminal Imidazole Ligands[†]

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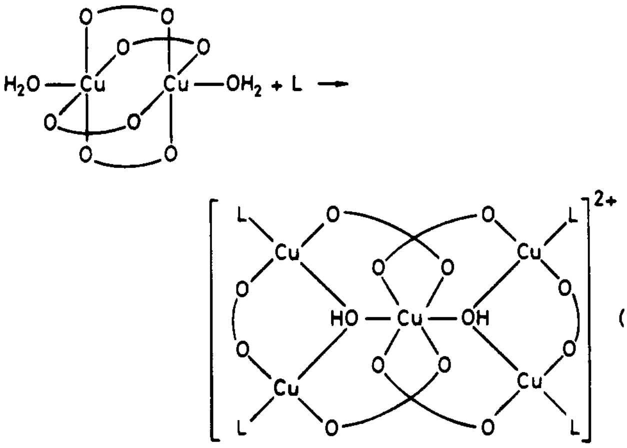
Introduction

Higher nuclearity copper(II) complexes are of considerable current interest[1−4] as models for the active sites of multicopper oxidases and as inorganic materials. In this paper we report the synthesis and X-ray structure of a new class of pentanuclear copper(II) complexes $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)](ClO_4)_2$ (**1**), $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)_4](ClO_4)_2$ (**2**), and $[Cu_5(OH)_2(O_2CMe)_6(1\text{-}Meim)_4](ClO_4)_2$ (**3**) [Him = imidazole; 1-Meim = 1-methylimidazole]. Complexes **1**−**3** are obtained from an unusual aggregation of the tetrakis(μ-acetato)dicopper(II) core of the copper(II) acetate hydrate dimer mediated by imidazole bases (L) (eq 1). Complexes **1**−**3** exhibit different coordination environments for the metal ions.



(1)

The pentanuclear unit in **1**−**3** is unique in showing the joining of two $Cu_3(\mu_3\text{-}OH)(\mu\text{-}O_2CMe)_3$ cores at a corner site, and hence the complexes show structural resemblance to the complexes belonging to the well-explored class of (μ_3-hydroxo)tricopper(II) systems.[5−10] Isolation of **1**−**3** is a significant development in the relatively unknown[11−14] chemistry of pentanuclear copper(II) complexes. A preliminary communication on **1** has been published.[15]

Experimental Section

Preparation of $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)](ClO_4)_2$ (1). An aqueous solution (10 mL) of copper(II) acetate hydrate dimer (200 mg, 0.5 mmol) was reacted with an ethanolic solution (5 mL) of imidazole (34 mg, 0.5 mmol) under stirring for 6 h at 25 °C. The reaction mixture was filtered, and the filtrate was treated with an aqueous solution (10 mL) of $NaClO_4$. Blue crystalline blocks of **1** were obtained in ~50% yield upon slow evaporation of the solvent at 25 °C after 15 days. The crystals were isolated, washed with an ice-cold water−ethanol mixture (1:1 v/v), and dried *in vacuo* over P_4O_{10}. Anal. Calcd for $C_{24}H_{38}N_8O_{23}Cl_2Cu_5$: C, 24.12; H, 3.21; N, 9.38. Found: C, 24.16; H, 3.25; N, 9.87. Visible spectral data, λ_{max} nm (ϵ, M^{-1} cm^{-1}), in H_2O: 683 (160). μ_{eff}/Cu, μ_B (*T*, K): 0.74 (80), 1.59 (291).

Preparation of $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)_4](ClO_4)_2$ (2). The complex was prepared in ~70% yield by following a procedure similar to that for **1** except for using a precursor:Him mole ratio of 1:2. Anal. Calcd for $C_{24}H_{44}N_8O_{26}Cl_2Cu_5$: C, 23.07; H, 3.55; N, 8.97. Found: C, 23.42; H, 3.17; N, 8.43. Visible spectral data, λ_{max}, nm (ϵ, M^{-1} cm^{-1}), in MeOH: 711 (270). μ_{eff}/Cu, μ_B (*T*, K): 1.40 (80), 1.82 (291).

Preparation of $[Cu_5(OH)_2(O_2CMe)_6(1\text{-}Meim)_4](ClO_4)_2$ (3). The preparative procedure for **3** was similar to that for **1** in methanol. Yield: ~50%. Anal. Calcd for $C_{28}H_{44}N_8O_{22}Cl_2Cu_5$: C, 27.27; H, 3.60; N, 9.09. Found: C, 27.97; H, 3.85; N, 9.82. Visible spectral data, λ_{max}, nm (ϵ, M^{-1} cm^{-1}), in MeOH: 718 (230). μ_{eff}/Cu, μ_B (*T*, K): 1.51 (80), 2.00 (291).

Caution! Perchlorate salts are potentially explosive and should be handled with care.

Complex **1** is soluble in water, complexes **2** and **3** are soluble in polar organic solvents, and the complexes are moderately stable in the solid state.

Measurements. The elemental analyses were 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. Magnetic susceptibility data at 80 and 291 K were obtained on polycrystalline samples from a Faraday type magnetometer equipped with Cahn 2000 microbalance. $Hg[Co(NCS)_4]$ was used as a calibrant.

X-ray Crystallographic Procedures. The crystal structures of **1**−**3** were obtained using general procedures reported[16,17] earlier. The intensity data collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα and Cu Kα radiations were corrected for Lorentz, polarization,

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[†] Dedicated to Professor A. Chakravorty with all best wishes and regards on the occasion of his 60th birthday.

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Table 1. Selected Crystallographic Data for **1**−**3**

	1	**2**	**3**
chem formula	$C_{24}H_{38}N_8$-$O_{23}Cl_2Cu_5$	$C_{24}H_{44}N_8$-$O_{26}Cl_2Cu_5$	$C_{28}H_{44}N_8$-$O_{22}Cl_2Cu_5$
fw	1195.2	1249.3	1233.4
a, Å	18.936(4)	11.761(4)	9.816(2)
b, Å	11.077(3)	11.542(1)	11.142(1)
c, Å	19.322(2)	16.662(5)	21.298(2)
β, deg	90.69(1)	102.72(2)	101.87(1)
V, Å^3	4052(2)	2206(1)	2280(1)
Z	4	2	2
space group	$I2/a$	$P2_1/n$	$P2_1/n$
T, °C	17	18	18
λ, Å	0.7107 (Mo Kα)	0.7107 (Mo Kα)	1.5418 (Cu Kα)
ϱ_{calcd}, g cm^{-3}	1.96	1.88	1.90
μ, cm^{-1}	28.2 (Mo Kα)	26.0 (Mo Kα)	33.9 (Cu Kα)
$R(F_o)^a$	0.0318	0.0564	0.0518
$R_w(F_o)^b$	0.0415	0.0620	0.0691

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum|F_o|w^{1/2}$; $w = K/[\sigma^2(F_o) + g(F_o)^2]$; g = 0.001 610 for **1**, 0.0 for **2**, and 0.004 507 for **3**.

and absorption effects[18] (transmission coefficients: 0.72−1.00 for **1**; 0.78−1.00 for **2**, and 0.73−0.94 for **3**). The structures were solved and refined by the SHELX program[19] using scattering factors taken from ref 20. All non-hydrogen atoms were refined anisotropically except the positionally disordered oxygen atoms of the perchlorate anion in **3**. The hydrogen atoms were used only for structure factor calculations using a fixed isotropic thermal parameter. The selected crystal data for **1**−**3** are summarized in Table 1.

Results and Discussion

Copper(II) acetate hydrate dimer reacts smoothly with imidazole bases (L) to form a pentanuclear core (eq 2). The axial

$$5[Cu_2(O_2CMe)_4(H_2O)_2] + 8L + 4NaClO_4 \rightarrow 2[Cu_5(OH)_2(O_2CMe)_6L_4](ClO_4)_2 + 4MeCO_2H + 4NaO_2CMe + 6H_2O \quad (2)$$

sites at the copper centers of the pentanuclear core undergo further ligation with the aqua ligand in **1** and **2**. The complexes are 1:2 electrolytes and exhibit a visible band at ~700 nm. The molecular structures of **1**−**3** are obtained from single-crystal X-ray diffraction studies.

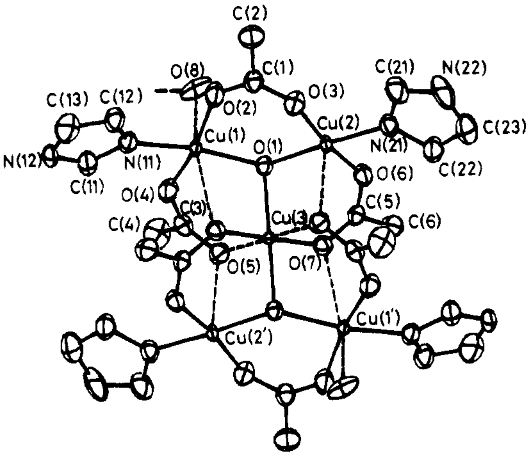

Figure 1. ORTEP view of the pentameric unit of the polymeric complex $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)](ClO_4)_2$ (**1**). The O(8) atom is on a crystallographic 2-fold axis.

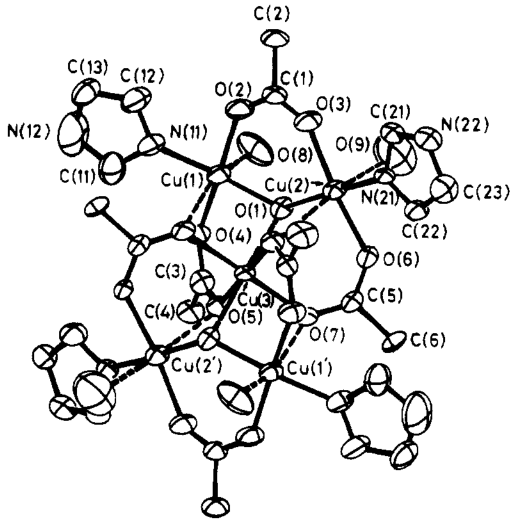

Figure 2. ORTEP view of the complex cation in $[Cu_5(OH)_2(O_2CMe)_6(Him)_4(H_2O)_4](ClO_4)_2$ (**2**).

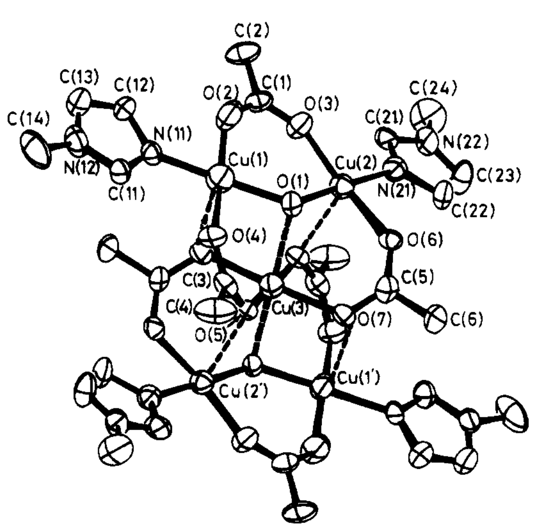

Figure 3. ORTEP view of the complex cation in $[Cu_5(OH)_2(O_2CMe)_6(1\text{-Meim})_4](ClO_4)_2$ (**3**).

While the pentanuclear complexes **2** and **3** are discrete in nature, complex **1** is polymeric with the aqua oxygen atom O(8), lying on a crystallographic 2-fold axis, bridging the pentanuclear units. The ORTEP[21] views showing 50% probability thermal ellipsoids of the cationic complexes in **1**−**3** are shown in Figures 1−3. Selected bond distances and angles are given in Table 2. The structures consist of a pentanuclear copper(II) core held by two hydroxo and six acetate ligands. The imidazole ligands occupy the terminal sites of the core. The coordination geometry of the central copper atom, positioned at the inversion center, is tetragonally elongated octahedral (4 + 2) showing a CuO_6 chromophore. While one of the axial sites of Cu(1) and Cu(2) is vacant in **3**, an aqua ligation on one copper in **1** and two coppers in **2** besides the weak axial coordination of the $MeCO_2^-$ ligand are observed in the asymmetric unit of the unit cell. In these pentanuclear cores, the edge copper atoms Cu(1) and Cu(2) show weak axial coordinations involving the oxygen atoms O(5′) and O(7′) of the bridging acetate ligands bonded to the central copper atoms. The coordination geometries for Cu(1) and Cu(2) atoms are essentially 4 + 2 and 4 + 1 for **1**, 4 + 2 and 4 + 2 for **2**, and 4 + 1 and 4 + 1 for **3** (Table 2). The copper atoms in the core are coplanar and form two triangles

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Table 2. Selected Distances (Å) and Angles (deg) for **1**−**3**

	1	**2**	**3**
	Distances		
Cu(1)−Cu(2)	3.577(1)	3.525(2)	3.503(1)
Cu(1)−Cu(3)	3.178(1)	3.196(1)	3.183(1)
Cu(2)−Cu(3)	3.042(1)	3.163(1)	3.071(1)
Cu(1)−O(1)	1.978(2)	1.919(4)	1.927(4)
Cu(2)−O(1)	1.970(2)	1.928(3)	1.911(4)
Cu(3)−O(1)	2.016(2)	2.295(4)	2.282(4)
Cu(1)−O(2)	1.956(2)	1.940(5)	1.926(4)
Cu(1)−O(4)	1.963(2)	1.968(3)	1.959(4)
Cu(1)−N(11)	1.991(3)	1.980(6)	1.988(5)
Cu(2)−O(3)	1.928(2)	1.955(5)	1.950(4)
Cu(2)−O(6)	1.959(2)	1.958(3)	1.974(5)
Cu(2)−N(21)	1.978(3)	1.969(5)	1.972(5)
Cu(3)−O(5)	2.261(2)	2.003(3)	2.016(4)
Cu(3)−O(7)	1.982(2)	2.006(3)	1.992(3)
Cu(1)−O(8)	2.425(2)	2.665(8)	
Cu(2)−O(9)		2.509(12)	
Cu(1)−O(7′)	2.641(2)	2.685(4)	2.566(4)
Cu(2)−O(5′)	2.521(2)	2.629(4)	2.498(4)
	Angles		
Cu(1)−O(1)−Cu(2)	129.9(1)	132.8(2)	131.7(2)
Cu(1)−O(1)−Cu(3)	105.4(1)	98.3(2)	97.9(2)
Cu(2)−O(1)−Cu(3)	99.5(1)	96.6(2)	93.8(2)
O(1)−Cu(1)−O(2)	93.8(1)	93.5(2)	94.0(2)
O(1)−Cu(1)−O(4)	92.8(1)	91.2(2)	90.3(2)
O(1)−Cu(1)−N(11)	166.9(1)	173.3(2)	175.3(2)
O(1)−Cu(1)−O(8)	89.7(1)	93.6(2)	
O(2)−Cu(1)−O(4)	167.5(1)	171.4(2)	172.0(2)
O(2)−Cu(1)−N(11)	87.4(2)	88.6(2)	88.0(2)
O(2)−Cu(1)−O(8)	87.0(1)	93.2(2)	
O(4)−Cu(1)−N(11)	88.6(1)	87.5(2)	87.3(2)
O(4)−Cu(1)−O(8)	82.4(1)	79.2(2)	
N(11)−Cu(1)−O(8)	103.3(1)	92.6(2)	
O(7′)−Cu(1)−O(1)	72.4(1)	80.5(1)	80.9(2)
O(7′)−Cu(1)−O(2)	107.0(1)	104.7(2)	102.9(2)
O(7′)−Cu(1)−O(4)	85.2(1)	83.2(2)	84.4(2)
O(7′)−Cu(1)−N(11)	94.8(1)	92.8(2)	102.9(2)
O(7′)−Cu(1)−O(8)	157.7(1)	161.4(2)	
O(1)−Cu(2)−O(3)	94.5(1)	93.5(2)	94.3(2)
O(1)−Cu(2)−O(6)	90.0(1)	91.1(2)	90.0(2)
O(1)−Cu(2)−N(21)	177.0(1)	175.2(2)	177.8(2)
O(1)−Cu(2)−O(9)		95.9(3)	
O(3)−Cu(2)−O(6)	170.7(1)	172.8(2)	173.6(2)
O(3)−Cu(2)−O(9)		86.2(3)	
O(3)−Cu(2)−N(21)	86.8(1)	87.9(2)	87.9(2)
O(6)−Cu(2)−N(21)	89.1(1)	88.0(2)	87.8(2)
O(6)−Cu(2)−O(9)		87.8(3)	
N(21)−Cu(2)−O(9)		88.8(3)	
O(5′)−Cu(2)−O(1)	83.8(1)	81.5(1)	85.6(1)
O(5′)−Cu(2)−O(3)	96.6(1)	99.7(2)	96.2(1)
O(5′)−Cu(2)−O(6)	91.9(1)	86.5(1)	88.8(2)
O(5′)−Cu(2)−N(21)	93.4(1)	93.7(2)	94.0(2)
O(5′)−Cu(2)−O(9)		173.7(2)	
O(1)−Cu(3)−O(5)	90.2(1)	89.1(1)	89.3(2)
O(1)−Cu(3)−O(7)	91.9(1)	90.6(1)	92.8(1)
O(5)−Cu(3)−O(7)	84.3(1)	94.7(1)	91.4(1)
Cu(1)−O(8)−Cu(1″)	136.9(1)		
Cu(1)−O(2)−C(1)	135.6(3)	135.8(4)	135.0(4)
Cu(1)−O(4)−C(3)	137.0(2)	135.9(4)	134.6(4)
O(2)−C(1)−O(3)	126.2(4)	126.9(6)	125.9(5)
Cu(2)−O(3)−C(1)	133.9(2)	135.1(5)	135.8(4)
Cu(2)−O(6)−C(5)	131.7(2)	134.0(4)	130.9(3)
O(4)−C(3)−O(5)	125.3(4)	125.6(6)	127.1(5)
Cu(3)−O(5)−C(3)	121.6(2)	125.6(4)	125.8(4)
Cu(3)−O(7)−C(5)	126.9(2)	126.5(3)	125.6(4)
O(6)−C(5)−O(7)	124.7(3)	126.7(5)	127.0(5)
Cu(1)−O(7′)−Cu(3)	85.6(1)	84.6(1)	87.6(1)
Cu(2)−O(5′)−Cu(3)	78.8(1)	85.0(1)	85.0(1)

with a common vertex which is the position of the central copper atom. Three copper atoms and the μ_3-OH form a trigonal pyramid in which the oxygen atom is displaced from the tricopper(II) plane by 0.532(2) Å in **1**, 0.619(5) Å in **2**, and 0.669(4) Å in **3**. Within the Cu_3OH unit, the Cu−O distances are essentially same for **1** but they differ for **2** and **3**. The axial elongation for Cu(3) is along O(1) for **2** and **3**, while it is along O(5) for **1**.

The significant structural features in the $Cu_3(\mu_3\text{-OH})$ unit of **1**−**3** are the large variations in the Cu−Cu and Cu−OH distances and in the Cu−OH−Cu angles. The Cu(1)−Cu(2) distances in **1**−**3** are considerably longer than the Cu(1)−Cu(3) and Cu(2)−Cu(3) separations. The Cu(1)−Cu(3) and Cu(2)−Cu(3) distances are also significantly different from each other in **1** and **3** but marginally different in **2**. The Cu−OH−Cu angle involving the outer metal atoms of the pentameric core is ~130°, while those around the central copper atom are ~100°.

The pentanuclear units in **1** are symmetrically linked by weak covalent attachment of aqua ligands to form a 1-D chain. The interunit Cu(1)···Cu(1″) separation is 4.507(1) Å. The core is also found to be hydrogen-bonded with the anion involving O(8) and N(12) atoms of the complex cation and O(11) and O(13) atoms of the perchlorate anion. A similar kind of hydrogen-bonding network has been observed in **2** involving the O(1), O(8), and O(9) atoms of the complex cation and the O(11) and O(13) atoms of the perchlorate anion giving an O···O distance of ~3 Å. The core in **2** forms a 1-D chain by intermolecular hydrogen bonds involving the aqua ligand on Cu(2) and O(12) of the perchlorate anion from the other crystallographic asymmetric unit [O(9)···O(12), 2.879(12) Å]. The hydroxide ligand of **3** undergoes a hydrogen-bonding interaction with the perchlorate oxygen showing a distance of ~2.9 Å.

A frozen aqueous solution of **1** shows an axial spectrum giving $g_\parallel = 2.2$ and $g_\perp = 2.1$. A methanol glass of **2** displays well-resolved axial signals giving $g_\parallel = 2.33$ ($A_\parallel = 63 \times 10^{-4}$ cm^{-1}) and $g_\perp = 2.03$. A similar type of axial spectrum but with a larger $A_\parallel$ value is observed for an acetonitrile glass of **3** ($g_\parallel = 2.29$, $A_\parallel = 170 \times 10^{-4}$ cm^{-1}, $g_\perp = 2.07$). The μ_{eff} values for **1**−**3** decrease on lowering the temperature. This suggests an overall antiferromagnetic behavior of the pentanuclear core.

The chemistry of pentanuclear copper(II) complexes has been limited[11−14] to only a few species. In $[Cu_3\{Cu(cdta)\}_2(NO_3)_2]\cdot 15H_2O$, the coordination geometries of the metal centers are known[11] to be square-pyramidal (4 + 1), square-planar, and tetragonally elongated octahedral (4 + 2) (H_4cdta, *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetic acid) giving a Cu−Cu distance of 5.23 Å. The complex $[Cu_5(OH)_2(L^1)_2(NO_3)_4]\cdot 2.5H_2O$,[12] where H_2L^1 is 3,6-bis[(4-methylpiperazino)methyl]pyrocatechol, has two (μ_2-hydroxo)dicopper(II) units linked to the central copper atom. In this molecule the five copper atoms are arranged in a rectangular-based pyramid form with a copper at the apex of the pyramid. The Cu−Cu separations vary from 3.3 to 5.7 Å. The Cu−Cu distances in another pentacopper(II) complex $[Cu_5A_4](ClO_4)_2\cdot 5H_2O$[13] are 3.2 and 4.6 Å ($H_2A$, 3-amino-*N*-hydroxypropanamide). This complex, however, lacks any structural resemblance to **1**−**3**. A recent addition to this pentacopper(II) chemistry is a series of copper(II) metallacrowns reported[14] by Gibney et al. The Cu···Cu distances in these complexes range from 3.26 to 4.65 Å. In conclusion, complexes **1**−**3** with a novel pentanuclear core present a new structural motif in copper(II) chemistry.

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Supporting Information Available: Full lists of crystal data, positional parameters, anisotropic thermal parameters, and bond distances and angles for **1**−**3** (31 pages). Ordering information is given on any current masthead page.

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