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Angular trinuclear copper(II) complexes of N_4O-donor ligand: Syntheses, crystal structures and magnetic properties

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ABSTRACT

Two trinuclear copper(II) complexes of a Schiff-base type N_4O-donor ligand (LH) derived from 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione and 1,3-diaminopropan-2-ol are reported. Complex $[Cu_3L_2(ClO_4)_4]$ (**1**) has an angular C_2-symmetric trinuclear core as revealed from single-crystal X-ray diffraction studies. The terminal coppers are in square-pyramidal geometry with an N_3O_2 coordination environment while the central one is in octahedral geometry with an N_2O_4 donor environment. Complex $[Cu_3L_2(ClO_4)(N_3)(H_2O)](ClO_4)_2 \cdot H_2O$ (**2**) has an unsymmetrical trinuclear core with an intramolecular hydrogen bonding interaction between the water and azide anion coordinated to Cu(1) and Cu(3) center, respectively. All the copper centers in **2** are in square-pyramidal geometry. The average Cu···Cu distance between closest metal ions in both the complexes is 3.897 Å. The coordination environment of coppers in **1** approximately mimics that of multicopper oxidases in the oxidized form and the environment in **2** mimics that of the azide derivative of ascorbate oxidase. Both **1** and **2** exhibit doublet spin ground state due to strong antiferromagnetic coupling operating through the alkoxo-bridged oxygen atoms between the copper centers.

1. Introduction

Polynuclear metal complexes have generated a lot of interest in bioinorganic chemistry to investigate the structure and magnetic properties of polynuclear active sites in metalloproteins. Trinuclear complexes are of particular interest in connection with the activation and multielectron reduction of dioxygen to water in multicopper oxidases, such as ascorbate oxidase and laccase [1–10]. The active site of multicopper oxidases has an angular trinuclear copper unit consisting of a mononuclear type-2 and a strongly antiferromagnetically coupled dinuclear type-3 centers. The trinuclear unit is about 12 Å apart from the type-1 blue copper center in ascorbate oxidase [11]. In the active site, the normal type-2 copper center is coordinated by two histidines and an aqua ligand, whereas each copper in the type-3 dinuclear unit is coordinated by three histidines and one bridging hydroxide in its oxidized form. The crystal structure shows that the oxidized form of the active site of ascorbate oxidase consists of an angular trinuclear copper(II) moiety with approximate C_2 symmetry and average Cu···Cu distance of 3.74 Å [12]. In the crystal structure of the azide derivative of ascorbate oxidase, it has been shown that there is a structural change at the trinuclear copper site. Two azide ions bind terminally to one of the copper of the type-3 unit by replacing the bridging hydroxide ligand with an increase of average Cu···Cu distance [13].

A large number of trinuclear copper(II) complexes have been reported in the literature having either a linear geometry of the metal ions [14–19] or $Cu_3(\mu_3\text{–}X)$ unit (X = Cl, OH/OR) [20–27]. In addition, angular trinuclear copper clusters consisting of triangular arrays of copper ions are also reported [28–41]. In spite of the presence of a large number of trinuclear copper(II) complexes exhibiting varying structural and magnetic properties, report on C_2-symmetric angular trinuclear copper(II) model complex is rare [42]. We have initiated a project on design and synthesis of angular tricopper core using a combination of amine based diketone ligand and 1,3-diaminopropan-2-ol that can give rise to an approximate ligand environment as found in multicopper oxidases (Chart 1). We report herein, the synthesis, molecular structures and magnetic properties of a C_2-symmetric angular trinuclear copper(II) complex $[Cu_3L_2(ClO_4)_4]$ (**1**) and an unsymmetrical angular trinuclear copper(II) complex $[Cu_3L_2(ClO_4)(N_3)(H_2O)](ClO_4)_2 \cdot H_2O$ (**2**) as models for the active site of ascorbate oxidase. Complexes **1** and **2** exhibit doublet spin ground state due to antiferromagnetic coupling between the copper(II) centers in the trinuclear core.

2. Experimental

2.1. Chemicals

Commercial grade chemicals were used for the synthetic purposes and solvents were distilled and dried before use. Although no problems were encountered during the synthesis of

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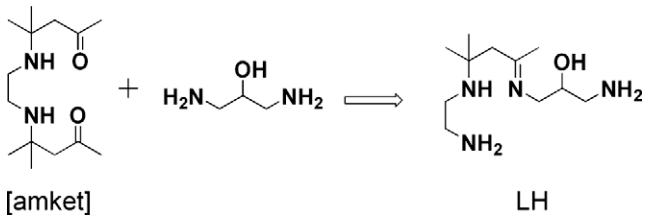

Chart 1.

the ligand and the complex, perchlorate salts are potentially explosive and should be handled with care [43]. The dihydroperchlorate of 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione, $[amketH_2](ClO_4)_2$ was synthesized by the reaction of ethane1,2-diamine dihydroperchlorate with acetone according to a literature procedure [44].

2.2. Syntheses

2.2.1. Complex $[Cu_3L_2(ClO_4)_4]$ (**1**)

To a mixture of $[amketH_2](ClO_4)_2$ (0.45 g, 1 mmol) and 1,3-diaminopropan-2-ol (0.27 g, 3 mmol) in methanol (15 mL) was added a methanolic solution (10 mL) of $CuCl_2 \cdot 2H_2O$ (0.26 g, 1.5 mmol) and $NaClO_4 \cdot H_2O$ (0.42 g, 3 mmol). The blue solution was stirred at room temperature for 36 h. The solution was then filtered and the filtrate was kept for slow evaporation of solvent to get blue crystalline compound. Yield: 0.24 g (46%). *Anal.* Calc. for $C_{22}H_{50}Cl_4Cu_3N_8O_{18}$: C, 25.23; H, 4.81; N, 11.15. Found: C, 25.0; H, 4.8; N, 11.1%. IR (KBr, cm^{-1}): 3433–3234 (s), 2972–2881 (w), 1666 (s), 1591(m), 1460(w), 1373(m), 1143–1090(vs), 625(s). ESI-MS (positive ion mode, methanol): m/z = 948.62 (10%, $[L_2Cu_3(ClO_4)_3]^+$), 846.63 (12%, $[L_2Cu_3(ClO_4)_2]^+$), 553.33 (10%, $[(HL)Cu_2(ClO_4)_2]^+$), 491.31 (10%, $[(HL)Cu(ClO_4)_2]^+$), 455.31 (20%, $[(HL)Cu_2(ClO_4)]^+$), 355.31 (20%, $[LCu_2]^+$) and 292.33 (100%, $[CuL]^+$). UV–Vis in acetonitrile (λ, nm; ε, $M^{-1}\,cm^{-1}$): 568(280), 335(sh), 258(sh), 230(22 000).

2.2.2. Complex $[Cu_3L_2(ClO_4)(N_3)(H_2O)](ClO_4)_2$ (**2**)

Complex **1** (0.26 g, 0.25 mmol) was treated with sodium azide (0.016 g, 0.25 mmol) in a solvent mixture of methanol (10 mL) and acetonitrile (10 mL). The solution was stirred at room temperature for 10 h to isolate a deep blue microcrystalline solid. X-ray quality single crystals were obtained by slow evaporation of the filtrate. Yield: 0.22 g (86%). *Anal.* Calc. for $C_{22}H_{52}Cl_3Cu_3N_{11}O_{15}$: C, 26.22; H, 5.20; N, 15.29. Found: C, 26.5; H, 5.2; N, 15.3%. IR (KBr, cm^{-1}): 3460–3230(s), 2978–2887(m), 2039(vs), 1668(s), 1583(s), 1373 (s), 1110–1058(vs), 625(s). ESI-MS (positive ion mode, acetonitrile): m/z = 1008.24 (5%, $[L_2Cu_3(N_3)(ClO_4)_3(H_2O)]^+$), 453.68 (15%, $[(HL)Cu(N_3)(ClO_4)(H_2O)+H]^+$), 392.11 (32%, $[(HL)Cu(ClO_4)]^+$) and 292.15 (100%, $[LCu]^+$). UV–Vis in acetonitrile (λ, nm; ε, $M^{-1}\,cm^{-1}$): 586(300), 333(sh), 260(sh), 230(20 000).

2.3. Physical methods

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN series. Solution electronic spectra were measured on an Agilent 8453 diode array spectrophotometer. Electro-spray mass spectra were recorded with a Waters QTOF Micro YA263. Magnetic susceptibilities of the polycrystalline samples were recorded on a SQUID magnetometer (MPMS, Quantum Design) in the temperature range 2–290 K with an applied field of 1 *T*. Diamagnetic contributions were estimated for each compound by using Pascal's constants. The programme julX written by E. Bill was used for the simulation and analysis of magnetic susceptibility data calculating through full-matrix diagonalization of the Spin-Hamiltonian [45]. Conductivity measurements were carried out at room temperature on a Systronics Conductivity Meter 306.

2.3.1. X-ray crystallographic data collection and refinement of the structures

Crystallographic data for **1** and **2** are summarized in Table 1. Diffraction data for **1** were collected at room temperature on a Nonius DIP-1030H system (Mo Kα radiation, λ = 0.71073 Å). Cell refinement, indexing and scaling of the data set were carried out using packages Denzo and Scalepack [46]. Diffraction data for **2** were collected at room temperature on a Bruker Smart APEX II (Mo Kα radiation, λ = 0.71073 Å). Cell refinement, indexing and scaling of the data set were carried out using the APEX2 v2.1-0 software [47]. The structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections [48]. A residual in the ΔFourier map of **2** was interpreted as a lattice water molecule. All the calculations were performed using the WinGX System, Ver 1.70.01 [49].

3. Results and discussion

3.1. Syntheses

Complex **1** is synthesized by reacting $[amketH_2](ClO_4)_2$ [44] with 1,3-diaminoprapan-2-ol, $CuCl_2 \cdot 2H_2O$ and $NaClO_4 \cdot H_2O$ in methanol at room temperature where the ligand (LH) is formed *in situ* during the reaction (Scheme 1). In this reaction, amket backbone gets modified after the condensation with 1,3-diaminopropan-2-ol. The ligand is formed by copper(II)-mediated template reaction since the free ligand is not isolated in the absence of copper(II) ions. Complex **2** is prepared by reacting **1** with sodium azide in a solvent mixture of methanol and acetonitrile (1:1) at room temperature in high yield.

Complexes **1** and **2** are characterized by different analytical and spectroscopic techniques. In the IR spectra of **1** and **2** (see Section 2) there are strong and broad perchlorate stretching bands in the region 1140–1060 cm^{-1}. In addition complex **2** shows very strong

Table 1
Crystallographic data for complexes **1** and **2**.

	1	**2**
Empirical formula	$C_{22}H_{50}Cl_4Cu_3N_8O_{18}$	$C_{22}H_{54}Cl_3Cu_3N_{11}O_{16}$
Formula weight	1047.12	1025.73
Crystal system	monoclinic	triclinic
Space group	*C*2/c	$P\bar{1}$
a (Å)	23.538(4)	8.711(3)
b (Å)	10.294(3)	13.319(4)
c (Å)	17.205(4)	18.256(4)
α (°)		79.82(2)
β (°)	108.93(3)	80.096(19)
γ (°)		78.69(2)
V (Å^3)	3943.2(16)	2023.5(10)
Z	4	2
D_{calc} (Mg/m^3)	1.764	1.683
μ (Mo Kα) (mm^{-1})	1.956	1.838
F(0 0 0)	2148	1058
θ Range data collection (°)	2.36–29.45	1.58–24.00
Reflections unique	3773	6303
Data ($I > 2\sigma(I)$])	1933	3964
Parameters	264	508
Goodness-of-fit (GOF) on F^2	0.822	1.029
R_1 [$I > 2\sigma(I)$]	0.0450	0.0606
wR_2	0.1058	0.1370
Residuals (e Å^{-3})	0.554, −0.409	0.737, −0.506