Binuclear and Tetranuclear Copper(II) Complexes Bridged by Dimethylglyoxime

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Two novel copper(II) complexes, $[Cu_4(tacn)_2(Hdmg)_2(dmg)_2](ClO_4)_2$ (**1**) and $[Cu_2(dmg)(Hdmg)(H_2dmg)(H_2O)]ClO_4$ (**2**), bridged by dimethylglyoxime have been synthesized and characterized by single crystal X-ray diffraction method.

The dioxime ligands are known to coordinate as neutral dioximes and monoanionic dioximates via dissociation of one oxime proton. They can also act as bridging ligands via coordination of the imino nitrogen and the deprotonated oxygen. Recently researches are focused on the dimethylglyoxime used as bridging ligand.[1–6] A few reported complexes are mainly confined to heterotrinuclear complexes and centrosymmetrically coordinated homobinuclear complexes.[2,7–10] In order to make further investigation of crystal and molecular structures and throw light on the relationship between the structures and properties we prepared $[Cu_4(tacn)_2(Hdmg)_2(dmg)_2](ClO_4)_2$ (**1**) and $[Cu_2(dmg)(Hdmg)(H_2dmg)(H_2O)]ClO_4$ (**2**) (tacn = 1,4,7-triazacyclononane, H_2dmg = dimethylglyoxime).[11,12]

1 was prepared as follows: tacn (1.0 mmol) was added into an aqueous solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol) while stirring. After half an hour a mixture of H_2dmg (1.5 mmol) and several drops of triethyl ammine was added. The resulting brown solution was stirred for 12 h, then filtered. Dark green crystals were obtained after several days. **2** was prepared by refluxing water solution of equal amounts of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol), tris(hydroxymethyl)aminomethane (0.5 mmol) and tacn (1.0 mmol) for 2 h. Green crystals were obtained by evaporation of the filtrate.

Recently Burdinski et al. reported a series of trinuclear complexes: $[LM\{\mu\text{-}(dmg)_3M'\}ML](ClO_4)_2$, L = Me_3tacn.[2] M′ acts as a template center for the bicyclic ring. But in **1**, without template center, the coordinated nuclear numbers were enlarged which may offer a new kind of dioxime bridged complexes. **1** shows a 1D chain linked by intermolecular hydrogen bonds. The tetranuclear copper(II) complex may be described as two dimeric $[Cu_2(tacn)(Hdmg)(dmg)]^+$ units linked by relatively long out-of-plane oxime bonds through the Cu(2) and Cu(2A) atoms (Cu(2)–O(2A) = 2.256(9) Å; Cu(2A)–O(2) = 2.256(9) Å) to build a centrosymmetric tetrameric entity as depicted in Figure 1. The distances between Cu(1)···Cu(2A) and Cu(2)···Cu(2A) are 3.553 and 3.904 Å, respectively. In the dinuclear unit the coordination geometry around the two crystallographically independent copper atoms is distorted square pyramidal, CuN_3O_2 for Cu(1) and CuN_4O for Cu(2): three nitrogen atoms from the tacn and two oximate-oxygen atoms at Cu(1) and four oxime nitrogen atoms from dmg^{2-} chelating ligands and one oximate-oxygen atom at Cu(2). The three Cu(1)–N(tacn) bond distances are distributed into two groups, Cu(1)–N(2) = 2.243(9) Å, being longer than those of the others, Cu(1)–N(1) = 2.065(8) Å and Cu(1)–N(3) = 2.043(9) Å, caused by Jahn-Teller effect owing to the position of N(2) in the apex of the square pyramid. The two equatorial Cu(1)–O(oxime) bond distances are very similar. Cu(2)–N bond lengths lie in the range 1.945(7)–1.962(9) Å, which are common for in-plane Cu–N(oxime) distances.[10] The apex is occupied by an oximate oxygen atom at Cu(2) (2.256(8) Å for Cu(2)–O(2A)). Cu(1) and Cu(2) are linked by two in-plane oxime bonds with separation of 3.672(4) Å. To our knowledge, **1** is the first tetranuclear complex bridged by symmetrical out-of-plane oxime bonds. Maria et al. prepared $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, in which two equivalent halves are linked by an Rh–Rh bond and two Zn ions.[13] Resently Li et al. obtained $[Cu_4(dmg)_2(Hdmg)_2(H_2dmg)_2(H_2O)_3](ClO_4)_2{\cdot}3H_2O$, in which two dinuclear moieties are bridged by one oximate oxygen.[14] Further more, in **1** the oxime hydrogen atom forms hydrogen bond with the N_{tacn} in the neighbouring complex molecule to form one dimensional chain with N–O distance of 2.75(2) Å (as shown in Figure 2).

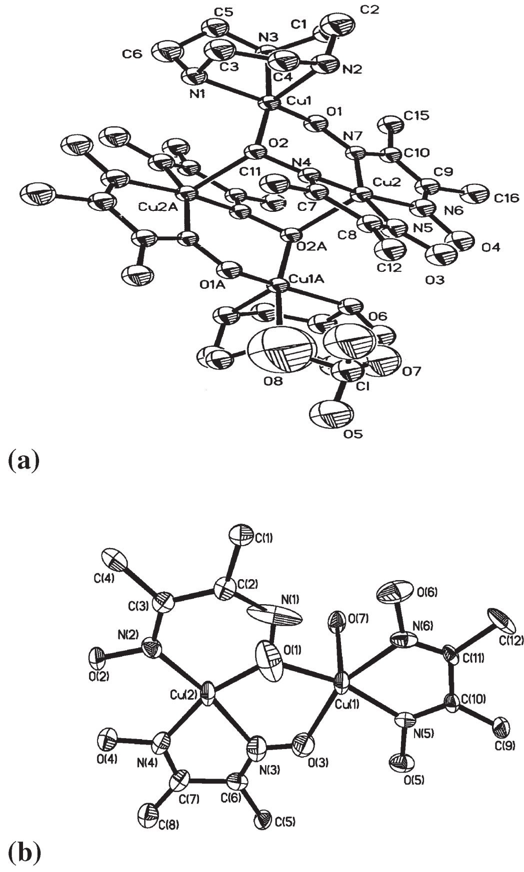

Figure 1. ORTEP drawing of $[Cu_4(tacn)_2(Hdmg)_2(dmg)_2](ClO_4)_2$ (**1**) (a) and ORTEP drawing of $[Cu_2(dmg)(Hdmg)_2(H_2O)]{\cdot}ClO_4$ (**2**) (b).

For published homobinuclear complexes,[9,10,15] the coordina-

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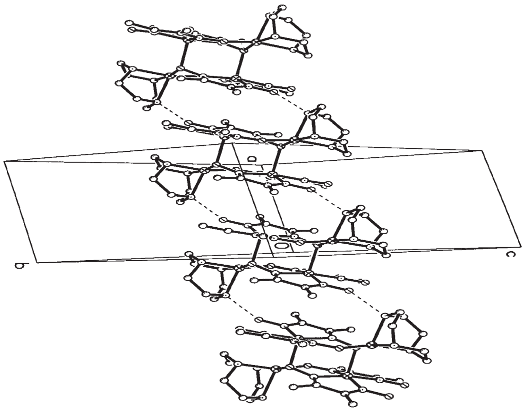

Figure 2. One-dimensional structure of $[Cu_4(tacn)_2(Hdmg)_2(dmg)_2](ClO_4)_2$ (**1**).

tion styles of two metal atoms are the same, but in **2** one copper atom is four-coordinated, the other is five-coordinated, which made it different from the ordinary binuclear complexes (as shown in Figure 1). Tris(hydroxymethyl)aminomethane is a mild ligand, and its bonds with copper were broken up due to the addition of H_2dmg. So the coordination style varied from the common conditions. The main difference lies in the coordination geometry of Cu(1) which is a distorted pyramid, CuN_2O_3, coordinated by two oximate nitrogen atoms, two oximate oxygen atoms and one water molecule. Cu(2) is in a distorted square planar with three oximate nitrogen atoms and one oximate oxygen atom. The Cu(1)$\cdots$Cu(2) separation is 3.346(5) Å. In the light of the reported dimethylglyoxime complexes,[16] it may be anticipated that the O(1) and O(3) are deprotonated. Two oxime protons are attached to O(5) and O(6). Actually the O(2)$\cdots$O(4) separation (2.44(9) Å) is consistent with the occurrence of a hydrogen bond which is similar to those published complexes. Thus the O(2) oxime proton would be attached to the O(4).

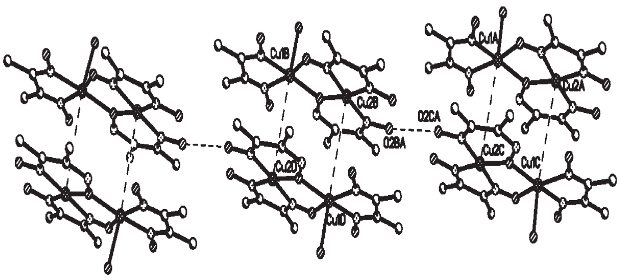

Figure 3. 1D chain of $[Cu_2(dmg)(Hdmg)_2(H_2O)]\cdot ClO_4$ (**2**).

Two $[Cu_2(dmg)(Hdmg)(H_2dmg)(H_2O)]\cdot ClO_4$ molecules are centrosymmetrically connected by weak co-ordinated bonds to form a dimer with Cu(1A)–Cu(2C) separation of 3.969(6) Å (as shown in Figure 3). The tetranuclear dimers are connected to each other via hydrogen bonds to form 1D chain (O(2BA)-H$\cdots$O(2CA) = 2.904 Å).

In summary, we have synthesized two new dimethylglyoximate complexes. **1** is the first tetranuclear copper(II) complexes with tacn and H_2dmg ligand. It breaks the familiar [LM{μ-(dmg)$_3$M′}ML]$(ClO_4)_2$ pattern, L = Me_3tacn.[2,7] The uncentrosymmetric coordination style in **2** is also infrequent.

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11 Crystal data for **1**. $C_{14}H_{28}ClCu_2N_7O_8$(588.99), monoclinic, $P2(1)/c$, $a = 8.0418(10)$ Å, $b = 19.126(2)$ Å, $c = 15.1010(10)$ Å, $\beta = 103.540(8)°$, $V = 2258.1(4)$ Å^3, $Z = 4$, 2806 uniq reflections measured, $R_1 = 0.0419$, wR2 = 0.1108.

12 Crystal data for **2**. $C_{12}H_{23}ClCu_2N_6O_{11}$(589.89), monoclinic, $P2(1)/n$, $a = 10.356(3)$ Å, $b = 20.938(7)$ Å, $c = 10.803(3)$ Å, $\beta = 111.775(6)°$, V = 2175.2(12) Å^3, $Z = 4$, 3575 uniq reflections measured, $R_1 = 0.0609$, wR2 = 0.1172.

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