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New tetranuclear copper(II) complexes obtained by using compartmental and *exo*-dentate ligands

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Abstract

The synthesis and crystal structures of two new tetranuclear complexes are described: $[\{L(\mu\text{-OH})Cu_2\}(\mu\text{-fum})\{Cu_2(\mu\text{-OH})L\}](ClO_4)_2$ (**1**) and $[\{L(\mu\text{-OH})Cu_2\}(\mu\text{-IN})_2\{Cu_2(\mu\text{-OH})L\}](ClO_4)_2 \cdot 2C_2H_5OH \cdot 0.5H_2O$ (**2**). The two complexes have been obtained through self-assembly processes involving a binuclear copper(II) complex, $[L(\mu\text{-OH})Cu_2](ClO_4)_2$ (L stands for a compartmental end-off ligand, 2,6-bis[*N*-2-pyridylethyl)formimidoyl]-phenolato), and *exo*-dentate ligands (the fumarate anion, fum^{2-}, and the isonicotinato anion, IN^-). The crystal structure of **1** consists of centrosymmetric tetranuclear cationic species, which result by connecting two binuclear units with one dicarboxylato linker. Each carboxylato group forms a third bridge between the copper(II) ions within the binuclear moiety (*syn–syn* bridging mode). The closest Cu···Cu distances in tetramer are 2.930(1) and 9.313(3) Å. Compound **2** contains cationic $[Cu_4]$ rectangles, with the short edges constructed from the preexisting μ-OH and μ-phenoxo groups [3.062(1) Å], and the long ones constructed from the isonicotinato linkers [9.352(1) Å]. In both compounds the copper(II) ions are pentacoordinated with a square-pyramidal stereochemistry.

Keywords: Tetranuclear copper(II) complexes; Schiff-bases; Molecular rectangles; Crystal structures

1. Introduction

The rational synthesis of multimetallic systems with pre-determined nuclearities and topologies of the metallic centers, as well as with tunable distances between metallic ions is an important goal in modern coordination chemistry. All these characteristics of the oligonuclear complexes are crucial for their magnetic or biomimetic properties. The larger the number of metallic centers the wider the variety of possible topologies. Taking the case of tetranuclear complexes, the metal ions can be displayed in several geometries: (a) linear; (b) tetrahedral; (c) square; (d) rectangular; (e) butterfly; (f) ‘U’-shaped; (g) heterocubane. Most of them may be illustrated in the coordination chemistry of copper(II) [1–7].

Recently, we have shown that a straightforward route leading to tretranuclear copper(II) complexes, with the metal ions located in the corners of a rectangle, consists in a self-assembly process involving binuclear copper(II) complexes and *exo*-dentate ligands [8,9]. As spacers we have used either *exo*-bidentate ligands (bis-(4-pyridyl) derivatives, 4,4′-bipyridyl-*N*,*N*′-dioxide), or *exo*-bis(bidentate) ligands (the dianion of the acetylenedicarboxylic acid). Following this approach we obtained a family of tetranuclear complexes with various distances between the metallic centers situated in the corners of a rectangle. Moreover, we have shown that these complexes can be obtained through a multicomponent self-assembly process, that is, the reaction between the ligands and the copper(II) salt.

In this paper, we report on two new such complexes, which have been synthesized by using an unsymmetrical

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spacer (the isonicotinato anion), and the dianion of the dicarboxylic acid.

2. Experimental

2.1. Synthesis

All solvents and chemicals were of analytical grade and have been used as received. 2,6-Diformyl-4-methylphenol was prepared according to Ref. [10]. The binuclear precursor $[L(\mu\text{-}OH)Cu_2](ClO_4)_2$ has been synthesized following the procedure reported in Ref. [11].

$[\{L(\mu\text{-}OH)Cu_2\}(\mu\text{-fum})\{Cu_2(\mu\text{-}OH)L\}](ClO_4)_2$ (**1**) and $[\{L(\mu\text{-}OH)Cu_2\}(\mu\text{-IN})_2\{Cu_2(\mu\text{-}OH)L\}](ClO_4)_2 \cdot 2C_2H_5OH \cdot 0.5H_2O$ (**2**) have been synthesized following the same general procedure: to the methanolic solution (20 ml) of the binuclear precursor $[L(\mu\text{-}OH)Cu_2](ClO_4)_2$ (0.22 mmol) has been added the ethanolic solution (10 ml) containing fumaric acid (0.22 mmol) and 0.22 mmol triethylamine for the compound **1,** or lithium izonicotinate (0.22 mmol) for the compound **2**. Green single-crystals of compounds **1** and **2** were obtained by the slow evaporation of the resulting solutions. IR data (KBr, cm^{-1}): **1**: 3426s, 2948w, 1679m, 1642s, 1610m, 1563s, 1447m, 1415m, 1342m, 1236w, 1118vs, 1088s, 980w, 889w, 769m, 649m, 933m. **2**: 3440s, 2964w, 2925w, 2860w, 1637s, 1602s, 1561s, 1479m, 1449m, 1411m, 1375s, 1337m, 1240m, 1094vs, 883w, 827w, 768m, 682m, 622m, 592w.

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities.

2.2. Physical measurements

The IR spectra (KBr pellets) were recorded with a BIO-RAD FTS 135 spectrophotometer. UV–Vis spectra (diffuse reflectance technique) were recorded with a UV4 (Unicam) spectrophotometer, using MgO as a standard.

2.3. X-ray crystallography

Experimental data for compounds 1 and 2 are given in Table 1. X-ray diffraction measurements for crystal **1** were performed at room temperature on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. The crystals **2** was measured at 182(2) K on a Bruker AXS SMART diffractometer (Mo Kα radiation monochromator). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97 crystallographic software package [12].

Table 1
Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Chemical formula	$C_{50}H_{50}Cl_2N_8O_{16}Cu_4$	$C_{62}H_{69}Cl_2N_{10}O_{18.50}Cu_4$
Molecular weight	1344.04	1575.33
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.149(2)	11.1804(5)
b (Å)	10.488(2)	14.4144(7)
c (Å)	12.692(3)	20.3197(10)
α (°)	92.20(3)	90.00
β (°)	104.61(3)	90.7910(10)
γ (°)	91.94(3)	90.00
V (Å^3)	1305.0(4)	3274.4(3)
D_{calc} ($Mg\,m^{-3}$)	1.710	1.598
Z	1	2
μ (mm^{-1})	1.790	1.443
$F(0\,0\,0)$	684	1618
θ Range (°)	1.66–29.00	1.73–26.99
R_1, wR_2 [$I > 2\sigma(I)$]	0.0196, 0.0338	0.0192, 0.0256
Goodness-of-fit on F^2	1.029	1.058
$\Delta\rho$, max, min (e Å^{-3})	0.926, −1.230	0.476, −0.249

3. Results and discussion

The synthetic approach towards tetranuclear complexes described in our previous papers seems to be general, at least when starting from binuclear copper(II) complexes with end-off compartmental ligands. Indeed, the reaction between the binuclear complex, $[L(\mu\text{-}OH)Cu_2](ClO_4)_2$, and the dianion of the fumaric acid leads to tetranuclear complexes with both short and long distances between the metallic centers (L = the compartmental end-off ligand, 2,6-bis[*N*-2-pyridylethyl)formimidoyl]-phenolato): $[\{L(\mu\text{-}OH)Cu_2\}(\mu\text{-fum})\{Cu_2(\mu\text{-}OH)L\}](ClO_4)_2$ (**1**). We also extended the self-assembly routine for an unsymmetrical linker, namely the isonicotinato anion. In this case (compound **2**) we obtained a new molecular rectangle, $[\{L(\mu\text{-}OH)Cu_2\}(\mu\text{-IN})_2\{Cu_2(\mu\text{-}OH)L\}]^{2+}$, with two types of copper(II) ions, which differ through their coordination environments.

The IR spectrum of **1** shows the characteristic band of the azomethine group, ν(C=N), at 1643 cm^{-1}. The bands which are due to the carboxylato groups arising from the fumarato spacer, $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, are located at 1679 and 1447 cm^{-1}, respectively. The bands assigned to the uncoordinated perchlorate anions are located at 1118 and 633 cm^{-1}. For compound **2**, the IR spectrum presents also the absorption bands assigned to the imino group of the compartmental ligand, ν(C=N), at 1637 cm^{-1} and to the carboxylato group of the isonicotinate anion, $\nu_{as}(COO^-) = 1545$ cm^{-1} and $\nu_s(COO^-) = 1376$ cm^{-1}. The bands at 1094 and 622 cm^{-1} are due to the uncoordinated perchlorate ions.

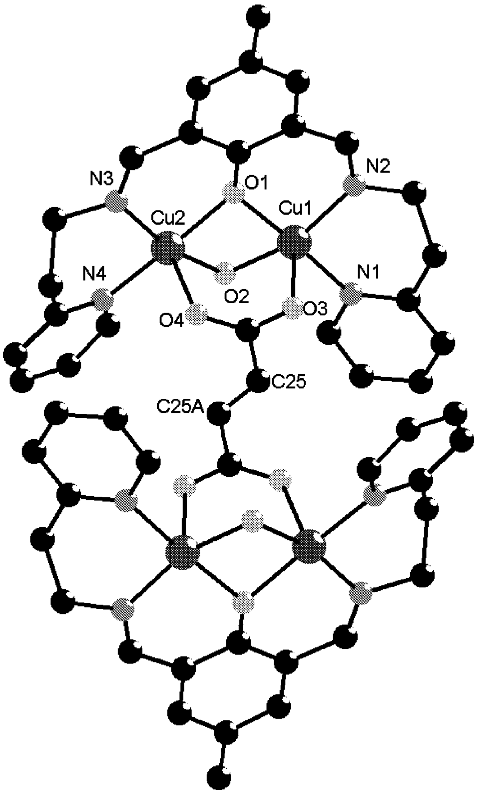

Fig. 1. Molecular structure of the tetranuclear entity in crystal **1**.

The diffuse reflectance spectra of the two compounds show in the visible domain a large band with maximum around 700 nm (complex **1**) and 800 nm (complex **2**), which is assigned to the d–d transitions. The shoulder at about 500 nm, the large unsymmetrical band with maximum at 400 nm (complex **1**), and the large unsymmetrical band with maximum at 420 nm (complex **2**) arise from intraligand (π–π*) and charge transfer transitions.

Table 2
Selected bond distances (Å) and angles (°) for compounds **1** and **2**

1		**2**	
Bond lengths (Å)			
Cu(1)–O(2)	1.938(2)	Cu(1)–O(2)	1.9220(19)
Cu(1)–N(2)	1.961(3)	Cu(1)–N(1)	1.966(2)
Cu(1)–O(1)	1.987(2)	Cu(1)–O(1)	1.9938(16)
Cu(1)–N(1)	2.037(2)	Cu(1)–N(4)	2.027(2)
Cu(1)–O(3)	2.216(2)	Cu(1)–N(3)	2.303(2)
Cu(2)–O(2)	1.942(2)	Cu(2)–O(2)	1.9249(17)
Cu(2)–N(3)	1.973(2)	Cu(2)–N(2)	1.963(2)
Cu(2)–O(1)	1.979(2)	Cu (2)–O(1)	2.0044(17)
Cu(2)–N(4)	2.028(2)	Cu(2)–N(5)	2.039(2)
Cu(2)–O(4)	2.207(2)	Cu(2)–O(4)	2.2858(16)
Bond angles (°)			
O(2)–Cu(1)–N(2)	159.4(1)	O(2)–Cu(1)–N(1)	164.08(8)
O(2)–Cu(1)–O(1)	79.0(1)	O(2)–Cu(1)–O(1)	77.30(7)
N(2)–Cu(1)–O(1)	90.0(1)	N(1)–Cu(1)–O(1)	89.96(8)
O(2)–Cu(1)–N(1)	95.3(1)	O(2)–Cu(1)–N(4)	93.97(8)
N(2)–Cu(1)–N(1)	94.5(1)	N(1)–Cu(1)–N(4)	95.59(9)
O(1)–Cu(1)–N(1)	173.7(1)	O(1)–Cu(1)–N(4)	162.34(8)
O(2)–Cu(1)–O(3)	93.3(1)	O(2)–Cu(1)–N(3)	97.08(8)
N(2)–Cu(1)–O(3)	105.0(1)	N(1)–Cu(1)–N(3)	94.19(8)
O(1)–Cu(1)–O(3)	93.63(8)	O(1)–Cu(1)–N(3)	98.50(7)
N(1)–Cu(1)–O(3)	89.43(9)	N(4)–Cu(1)–N(3)	97.80(8)
O(2)–Cu(2)–N(3)	164.43(9)	O(2)–Cu(2)–N(2)	164.90(8)
O(2)–Cu(2)–O(1)	79.08(9)	O(2)–Cu(2)–O(1)	76.99(7)
N(3)–Cu(2)–O(1)	90.02(9)	N(2)–Cu(2)–O(1)	89.67(8)
O(2)–Cu(2)–N(4)	94.24(9)	O(2)–Cu(2)–N(5)	94.53(8)
N(3)–Cu(2)–N(4)	94.7(1)	N(2)–Cu(2)–N(5)	96.36(8)
O(1)–Cu(2)–N(4)	169.10(9)	O(1)–Cu(2)–N(5)	162.50(8)
O(2)–Cu(2)–O(4)	93.70(9)	O(2)–Cu(2)–O(4)	94.60(7)
N(3)–Cu(2)–O(4)	98.52(9)	N(2)–Cu(2)–O(4)	94.96(7)
O(1)–Cu(2)–O(4)	96.03(8)	O(1)–Cu(2)–O(4)	101.46(7)
N(4)–Cu(2)–O(4)	92.97(8)	N(5)–Cu(2)–O(4)	94.39(7)
Cu(2)–O(1)–Cu(1)	95.26(8)	Cu(1)–O(1)–Cu(2)	99.98(7)
Cu(1)–O(2)–Cu(2)	98.09(9)	Cu(1)–O(2)–Cu(2)	105.52(9)

The crystallographic study of **1** reveals the presence of centrosymmetric tetranuclear cationic species (Fig. 1) and uncoordinated perchlorate anions. One fumarate dianion links the two bimetallic moieties. Each carboxylato group forms a third bridge between the copper(II)

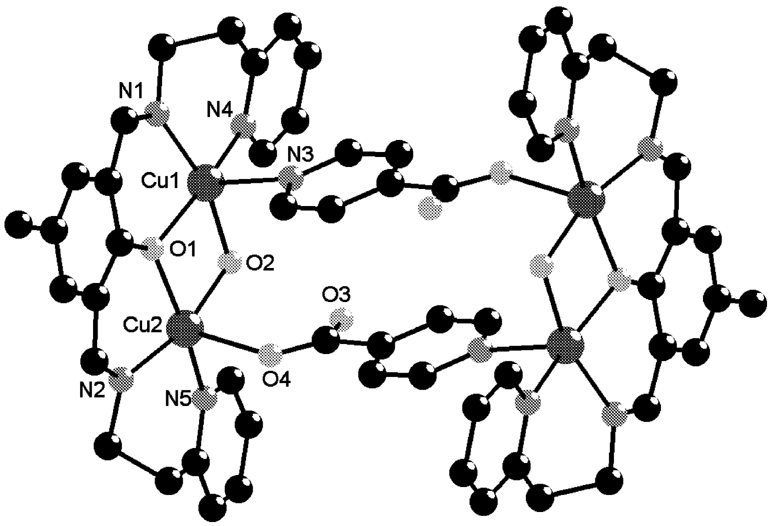

Fig. 2. Perspective view of the molecular rectangle in crystal **2**, along with the atom numbering scheme.

ions within the binuclear moiety (*syn–syn* bridging mode). The copper ions are pentacoordinated with a square-pyramidal geometry, in which the apical positions are occupied by the oxygen atoms arising from the carboxylato bridge [Cu(1)–O(3) = 2.216(2); Cu(2)–O(4) = 2.207(2) Å]. The basal plane is formed by two nitrogen atoms arising from the Schiff-base ligand and two oxygen atoms (one from the phenolato endogenous

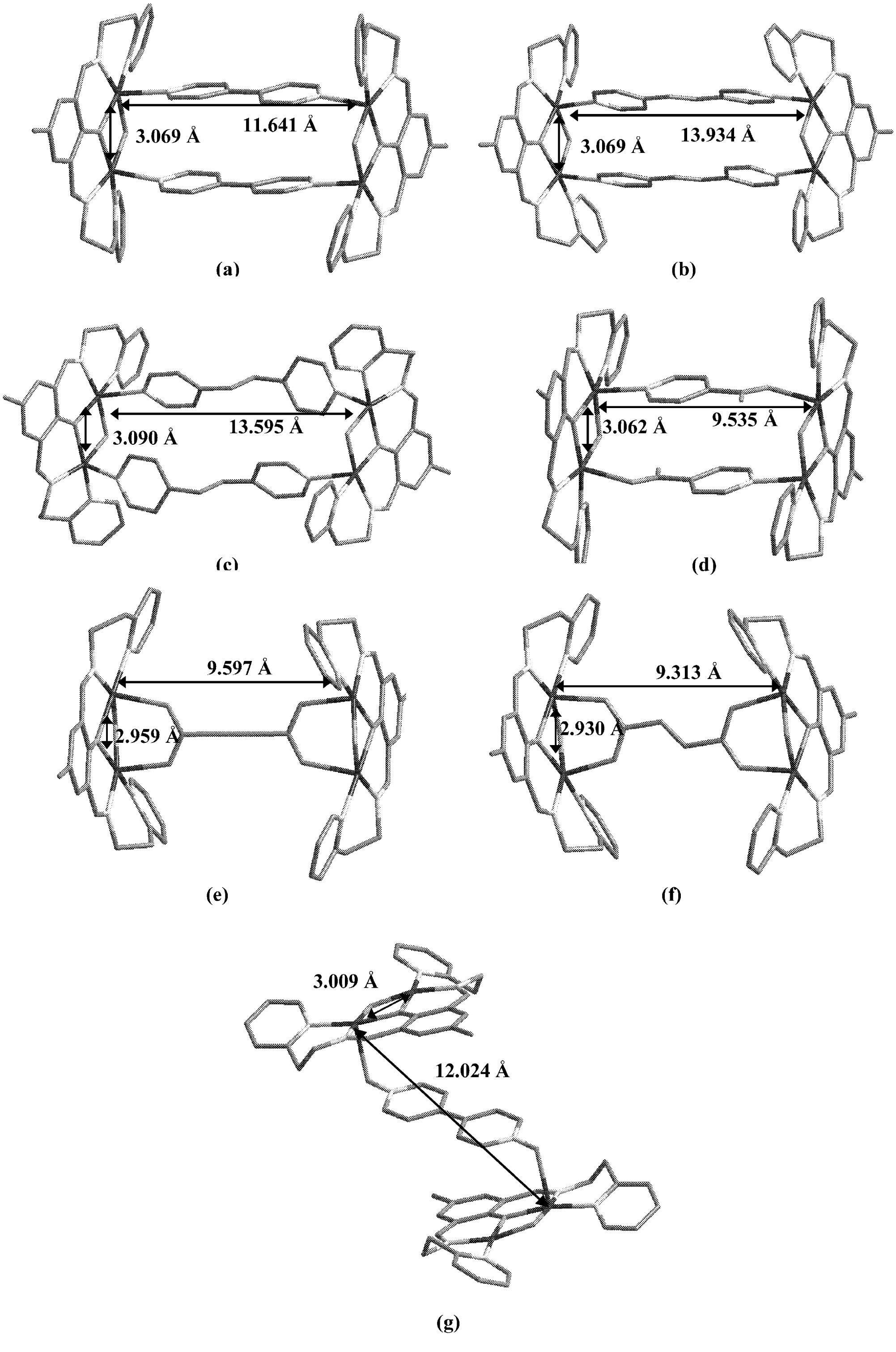

Fig. 3. Tetranuclear complexes obtained by self-assembly processes involving binuclear complexes and *exo*-dentate ligands: (a) 4,4′-bipyridine [8]; (b) bis(4-pyridyl)ethylene [8]; (c) bis(4-pyridyl)ethane [9]; (d) the isonicotinato ion (this work); (e) the dianion of the acetylenedicarboxylic acid [9]; (f) the dianion of the fumaric acid (this work); (g) 4,4′-bipyridyl-*N*,*N*′-dioxide [9]. The pictures have been generated from single crystal X-ray data.

bridge, and the other one from the hydroxo bridge). The values of the two Cu–O–Cu angles are: Cu(1)–O(1)–Cu(2) = 95.26(8)° and Cu(1)–O(2)–Cu(2) = 98.09(9)°. The distance between the triply bridged copper atoms is Cu(1)–Cu(2) = 2.930(1) Å. The distance between the double bonded carbon atoms in the fumarato ligand is 1.304(5) Å. The copper atoms describe a parallelogram with the sides 2.930(1) × 9.313(3) Å and Cu–Cu–Cu angle 83.61(3)°. Selected bond distances and angles are given in Table 2.

By employing an unsymmetrical linker (the isonicotinato ion, IN^-) we obtained a molecular rectangle with the short edges constructed from the preexisting μ-OH and μ-phenoxo groups, and the long ones constructed from IN^- ions (Fig. 2). Selected bond distances and angles are collected in Table 2. The copper(II) ions within the short edge have a square pyramidal stereochemistry, but different coordination environments. The basal plane is the same for both copper(II) ions: two nitrogen atoms from the Schiff-base, and the two oxygen atoms arising from the preexisting bridges in the binuclear moieties. The apical position for one copper atom is occupied by the nitrogen atom arising from the pyridyl group of the isonicotinato bridge [Cu(1)–N(3) = 2.303(2) Å], while for the other one is occupied by the oxygen atom from the unidentate carboxylato group of the IN^- linker [Cu(2)–(O4) = 2.286(2) Å]. The values of the two Cu–O–Cu angles [Cu(1)–O(1)–Cu(2) = 99.98(7)°; Cu(1)–O(2)–Cu(1) = 105.52(8)°] are higher than those found in compound **1**. Consequently, the Cu(1)–Cu(2) separation [3.062(1) Å] is slightly longer than in **1**. The dimensions of the rectangle are: 3.062(1) × 9.535(1) Å. This is the smallest rectangle obtained following this synthetic approach [8,9].

The reaction between binuclear complexes with compartmental end-off ligands and various *exo*-dentate ligands (including unsymmetrical spacers) represents a straightforward synthetic route towards tetranuclear copper(II) complexes. The distances between the metallic centers can be tuned by using appropriate spacers. Fig. 3 illustrates all the tetranuclear complexes we have synthesized, along with the distances between the metallic centers.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 199 989 and 199 990 Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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