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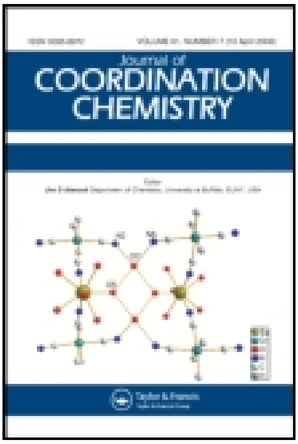

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis, crystal structure, and magnetic properties of a linear trinuclear Cu(II) complex

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Published online: 14 Jun 2011.

To cite this article: Qian Zhang , Fuping Huang , Hedong Bian & Qing Yu (2011) Synthesis, crystal structure, and magnetic properties of a linear trinuclear Cu(II) complex, Journal of Coordination Chemistry, 64:12, 2110-2116, DOI: 10.1080/00958972.2011.589900

To link to this article: http://dx.doi.org/10.1080/00958972.2011.589900

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Journal of Coordination Chemistry
Vol. 64, No. 12, 20 June 2011, 2110–2116

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Synthesis, crystal structure, and magnetic properties of a linear trinuclear Cu(II) complex

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(*Received 22 January 2011; in final form 22 April 2011*)

A new linear trinuclear Cu(II) complex, $[Cu_3(NTA)_2(4,4'\text{-bpt})_4(H_2O)_2] \cdot 10H_2O$ (H_3NTA = nitrilotriacetic acid, 4,4′-bpt = 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole) (**1**), was obtained from evaporation of an aqueous solution containing $Cu(NO_3)_2 \cdot 6H_2O$, 4,4′-bpt, nitrilotriacetic acid (H_3NTA), and NaOH. **1** was characterized using single-crystal X-ray diffraction, IR, and elemental analysis. In the trimer, the three linear copper ions are bridged by two NTA carboxylate groups in a *syn–anti* conformation and connected by 4,4′-bpt to produce a 1-D array. Temperature-dependent magnetic susceptibilities reveal the presence of weak antiferromagnetic exchange between metal centers.

Keywords: Linear trinuclear Cu(II) complex; Crystal structure; Magnetic studies

1. Introduction

The design and preparation of polynuclear complexes have received significant attention because of their various structural topologies and potential applications in catalysis, luminescence, gas adsorption, and magnetochemistry [1–7]. A series of trinuclear Cu(II) complexes has been reported, classified as (i) open triangular, (ii) closed triangular, and (iii) linear, according to the spatial arrangements of the metal centers [8–11]. Those with open triangle, having a non-linear angle, have generated great interest, mainly concerning their structural and redox properties in relation to their role in the active site of multicopper oxidases [12]. Those with closed triangle, in which the three Cu(II) ions are bridged together, are used to investigate intramolecular magnetic exchange and spin-frustration in a lattice containing three unpaired electrons [13, 14].

In the present case, we chose nitrilotriacetic acid (H_3NTA) and 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4′-bpt) as ligands, and a new trinuclear Cu(II) complex $[Cu_3(NTA)_2(4,4'\text{-bpt})_4(H_2O)_2] \cdot 10H_2O$ (**1**) with linear Cu_3 arrangement has been synthesized and structurally characterized. According to most of the previously reported linear Cu_3 entities, Cu(II) ions are in the same coordination environments: for example, $Cu(D_{3h})$–$Cu(D_{3h})$–$Cu(D_{3h})$ and $Cu(O_h)$–$Cu(O_h)$–$Cu(O_h)$ [9, 15–22]. However, in **1**, Cu(II)s have an interesting $Cu(D_{3h})$–$Cu(O_h)$–$Cu(D_{3h})$ coordination similar to that

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
DOI: 10.1080/00958972.2011.589900

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{36}H_{60}Cu_3N_{14}O_{26}$
Formula weight (M)	1295.63
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.5140(19)
b	11.414(2)
c	13.807(3)
α	68.07(3)
β	70.49(3)
γ	81.25(3)
Volume (Å^3), Z	1310.3(5), 1
Calculated density (g cm^{-3})	1.642
F(000)	669
θ range for data collection (°)	25.25
Reflections collected/unique	16195/5619 [R(int) = 0.0274]
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0390$, $\omega R_2 = 0.0866$
R indices (all data)	$R_1 = 0.0495$, $\omega R_2 = 0.0921$

reported by Kogane *et al*. [23–26]. Magnetic study revealed weak antiferromagnetic interaction within the trinuclear copper unit of **1**.

2. Experimental

2.1. *Materials and synthesis*

All chemicals were commercial products without purification. The 4,4′-bpt was synthesized according to the literature [27, 28]. The title compound was prepared by adding $Cu(NO_3)_2 \cdot 6H_2O$ (0.3 mmol) to a mixture of H_3NTA (0.3 mmol), NaOH (1.2 mmol), and water (10 mL), stirring for 3 h at room temperature and then 4,4′-bpt (0.3 mmol) was added with stirring for another 3 h. The resulting light-green solution was filtered and well-shaped green crystals were obtained by slow evaporation of the solvent at room temperature. Yield: 65%. $C_{36}H_{60}Cu_3N_{14}O_{26}$ (1295.63): Calcd (%): C, 33.34; H, 4.63; N, 15.12. Found (%): C, 33.22; H, 4.51; N, 15.21.

2.2. *X-ray structure determinations*

The X-ray diffraction pattern of the complex was recorded at room temperature on a Bruker Smart CCD apparatus using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, successive Fourier difference syntheses, and refined by full-matrix least-squares based on F^2 [29]. Crystal data and details of the structure are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 2. Selected atomic distances (Å) and angles (°) for **1**.

Atomic distances (Å)			
Cu1–O5	1.981(2)	Cu2–N1	1.999(2)
Cu1–N7B	2.018(2)	Cu2–O6	2.016(2)
Cu1–O7	2.443(3)	Cu2–O3	2.023(2)
Cu2–N2	1.959(2)	Cu2–O2	2.070(2)
Bond angles (°)			
O7A–Cu1–O7	180.00	N2–Cu2–O3	96.94(10)
O5–Cu1–N7B	93.58(9)	N1–Cu2–O3	83.39(9)
O5–Cu1–O7	93.17(9)	O6–Cu2–O3	125.50(10)
N7B–Cu1–O7	87.81(10)	N2–Cu2–O2	101.45(10)
N2–Cu2–N1	175.93(9)	N1–Cu2–O2	82.21(9)
N2–Cu2–O6	93.37(9)	O6–Cu2–O2	120.41(10)
N1–Cu2–O6	83.18(9)	O3–Cu2–O2	109.58(11)

Symmetry codes: A $-x, -y, -z+1$; B $-x+1, -y+1, -z+1$.

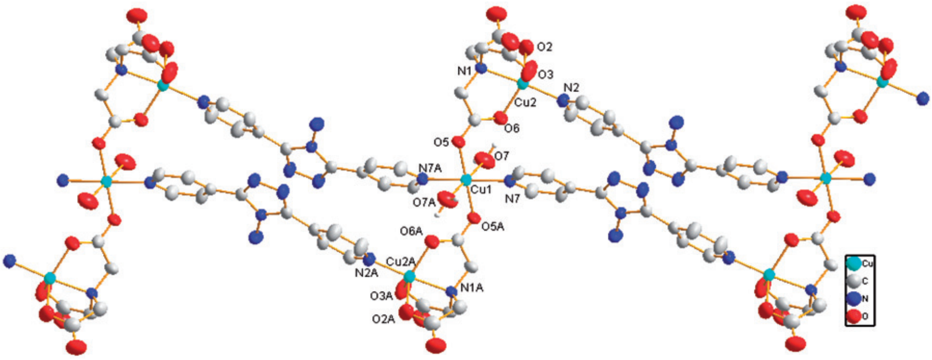

Figure 1. The coordination environments of Cu(II) ions.

3. Results and discussion

3.1. *Description of crystal structure*

The structure of **1**, established by X-ray analysis, reveals a 1-D system with a trinuclear Cu(II) (figure 1). In the trimer, the central copper, Cu1, is located on a crystallographic inversion center with a distorted octahedral coordination sphere (figure 2). The equatorial positions are occupied by O5 and O5A (symmetry codes: A $-x$, $-y$, $-z+1$) of the carboxylate of NTA and N7 and N7A of 4,4′-bpt, and two waters (O7, O7A) in axial positions. All the metal–ligand bonds are consistent with other Cu(II) systems, except for the Cu–O(water) bond distances which are relatively longer, that is 2.443 Å. However, compared to similar Cu analogs, the bonds in **1** are reasonable [9]. The coordination geometry around each Cu2 is a distorted trigonal bipyramid from O2, O3, and O6, Cu–O = 2.016(2)–2.070(2) Å, from NTA as the trigonal plane, and N1 from NTA and N2 from 4,4′-bpt, Cu–N = 1.959(2)–1.999(2) Å, as the apices. Cu1 is linked to Cu2 through NTA carboxylates in a *syn–anti* conformation, with a Cu1 ··· Cu2 separation of 5.237(1) Å. A linear Cu_3 unit based on $Cu(D_{3h})$–$Cu(O_h)$–$Cu(D_{3h})$

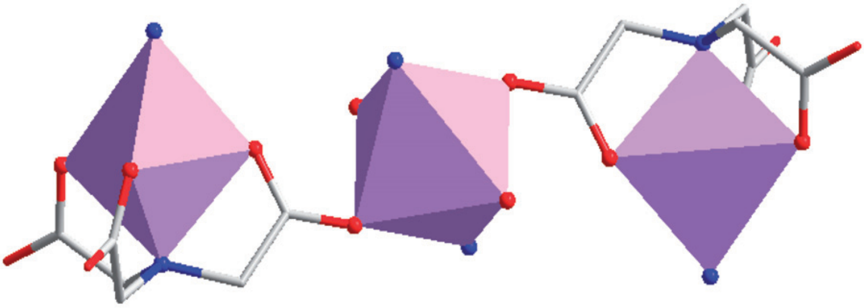

Figure 2. The Cu(D_{3h})–Cu(O_h)–Cu(D_{3h}) polyhedral mode of three Cu(II) ions.

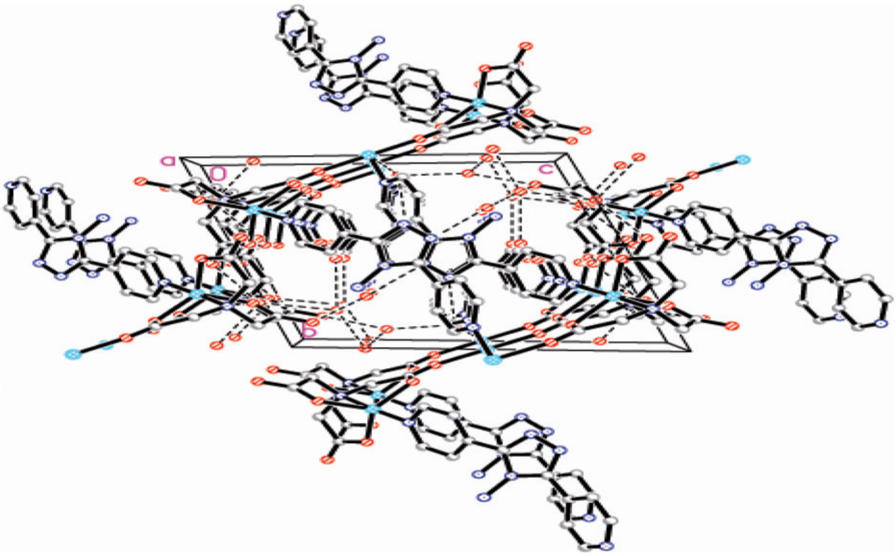

Figure 3. 3-D packing drawing of **1**.

arrangement has been built. Each 4,4′-bpt acts as a bismonodentate ligand linking two trimers, which extend to a 1-D chain. The complex was assembled to a 3-D supramolecular framework *via* intermolecular hydrogen bonding involving lattice water, the uncoordinated 4,4′-bpt nitrogens and uncoordinated carboxyl O atoms [30] (figure 3). Selected hydrogen-bond geometric parameters are listed in table 3.

3.2. *IR spectra*

IR spectra of **1** show broad absorptions at 3500–3200 cm^{-1}, characteristic of N–H and O–H in 4,4′-bpt, H_3NTA, and water. Strong absorptions around 1620–1590 cm^{-1} of **1** are characteristic for asymmetric and symmetric vibrations of the carboxylate of

Table 3. Selected hydrogen-bond geometric parameters (Å) for **1**.

D–H···*A*	*D*–*H*	*H*···*A*	*D*···*A*	*D*–H···*A*
N3–H3*C*···O13	0.85	2.25	3.027(4)	150
N3–H3*D*···O9#2	0.80	2.20	2.997(5)	172
O7–H7*A*···N5#1	0.83	2.14	2.951(4)	166
O7–H7*B*···O6#3	0.81	2.57	3.085(3)	122
O7–H7*B*···O13	0.81	2.22	2.887(4)	140
O8–H8*A*···O3#4	0.83	2.40	3.076(5)	140
O8–H8*B*···O4#5	0.82	2.16	2.956(5)	165
O9–H9*B*···O11#6	0.84	2.00	2.812(5)	163
O10–H10*A*···O11	0.85	1.91	2.743(4)	169
O10–H10*B*···O9#7	0.85	1.99	2.800(6)	158
O11–H11A···O2	0.81	1.98	2.783(4)	170
O11–H11B···O4#6	0.82	1.97	2.788(4)	177
O12–H12B···O1#6	0.82	2.24	2.857(5)	132
O13–H13A···O10#3	*0.85*	1.83	2.666(5)	167
O13–H13B···O1#6	0.84	1.96	2.777(4)	164

Symmetry codes: #1 $-x+1, -y+1, -z+1$; #2 $x+1, y, z$; #3 $x, y+1, z$; #4 $-x, -y+1, -z+1$; #5 $x, y, z+1$; #6 $-x+1, -y+1, -z$; #7 $x+1, y-1, z$.

NTA^{3-} trianion; these bands are proximate to those of reported Cu(II) complexes [9, 19]. The main bands in the complex are in agreement with a reported Cu(II) complex containing NTA^{3-} [19].

3.3. *Magnetic properties*

The temperature dependence of the magnetic susceptibilities was measured from 300 to 2 K in an applied field of 1000 Oe. Figure 4 shows the magnetic behavior of **1** in the form of $\chi_M T$ *versus* T and χ_M *versus* T plots. The value of $\chi_M T$ at room temperature ($1.11\ \mathrm{cm^3\,mol^{-1}\,K}$) is close to the spin-only value of $1.13\ \mathrm{cm^3\,mol^{-1}\,K}$ ($g=2.0$) expected for three spin-isolated Cu(II) ions ($S=1/2$). On cooling, $\chi_M T$ smoothly decreases from 1.11 to $1.10\ \mathrm{cm^3\,mol^{-1}\,K}$ between 300 and 25 K and then decreases more steeply to $0.72\ \mathrm{cm^3\,mol^{-1}\,K}$ at 2 K, suggesting weak antiferromagnetic interactions between spin centers of Cu(II) [22, 31, 32]. For a linear trinuclear compound, the magnetic susceptibility can be calculated using the Hamiltonian $H=-2J\ (S_1{\cdot}S_2+S_2{\cdot}S_3)-2J_{13}S_1{\cdot}S_3$ with $S_1=S_2=S_3=1/2$, where J and J_{13} represent the exchange constants between neighboring coppers bridged by carboxylates and between the terminal coppers, respectively. In the absence of a clearly defined exchange pathway between terminal metal ions, J_{13} was taken as zero. In order to evaluate the exchange interaction between neighboring Cu(II)s, the variable-temperature susceptibility data were analyzed using equations (1) and (2) [30, 33] derived from the Heisenberg isotropic spin Hamiltonian. In the equation, $\chi=J/k$, J is the intratrimer coupling constant between Cu(II) ions. N, β, zJ', and k are Avogadro's number, the Bohr magneton, intertrimer interaction, and Boltzmann's constants, respectively. A best fit, which affords the solid line in figure 3, was obtained with values of $g=1.99$, $J=-0.69\ \mathrm{cm^{-1}}$, and $zJ'=-0.02\ \mathrm{cm^{-1}}$. The negative J demonstrates a very weak antiferromagnetic coupling between Cu(II) ions through *syn–anti* carboxylate bridges [34]. In general, polynuclear Cu(II) complexes bridged by carboxylate groups have various coordination

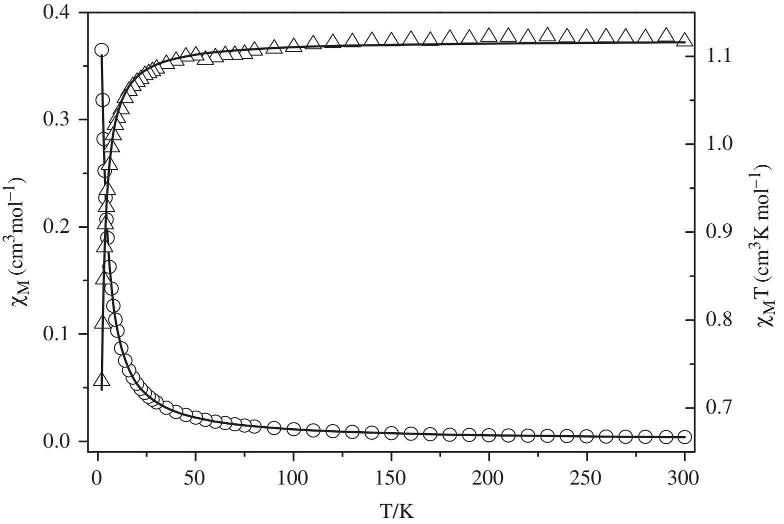

Figure 4. Plots of the χ_M (○) and $\chi_M T$ (△) *vs.* T for the complex. Solid line shows the best fit of the data.

modes, the most common being the so-called *syn–syn*, *syn–anti*, and *anti–anti* modes. The *syn–anti* mode in linear Cu_3 entities usually transmits weak antiferromagnetic interaction [35–38]. The exchange ($J = -0.69\,\mathrm{cm}^{-1}$) is comparable to those reported for other linear Cu_3 complexes bridged by carboxylates [9, 15–22], even though there are different coordination geometries in Cu(D_{3h})–Cu(O_h)–Cu(D_{3h}). The different coordination environments may lead to the local isotropy of Cu(II).

$$\chi_{tri} = \frac{Ng^2\beta^2}{4kT} \times \frac{1 + e^{2J/kT} + 10e^{3J/kT}}{1 + e^{2J/kT} + 2e^{3J/kT}}, \tag{1}$$

$$\chi_M = \frac{\chi_{tri}}{1 - (2zJ'/Ng^2\beta^2)\chi_{tri}}. \tag{2}$$

4. Conclusion

We have presented the synthesis and crystal structure of a linear trinuclear Cu(II) complex using H_3NTA and 4,4′-bpt as mixed ligands, giving Cu(D_{3h})–Cu(O_h)–Cu(D_{3h}) coordinated arrangement in the trimer. Most previously reported linear Cu_3 entities, Cu(II) ions have the same coordination environment: for example, D_{3h}–D_{3h}–D_{3h} and O_h–O_h–O_h. We anticipated interesting magneto-structural correlation in Cu_3 entities in **1**, having an interesting D_{3h}–O_h–D_{3h} coordinated arrangement. Unfortunately, the magnetic study revealed the occurrence of normal weak antiferromagnetic interactions within the trimer through *syn–anti* carboxylate bridges. The different coordination environments may attribute to the local isotropy of Cu(II) ions.

Supplementary material

CCDC 796699 contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21061002), Guangxi Natural Science Foundation of China.

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