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Synthesis and Crystal Structure of a Rarely Seen Terephthalato-Bridged Dinuclear Copper(II) Complex $[Cu_2(CMP)_2(TPA)]\cdot[Cu_2(CMP)_2(MeOH)_2(TPA)]\cdot 2H_2O$

Shao-Song Qian,[1] Dong-Mei Xian,[2] Yue-Hu Chen,[1] Zhong-Lu You,[2] and Hai-Liang Zhu[1]
[1]*School of Life Sciences, Shandong University of Technology, ZiBo, P. R. China*
[2]*Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China*

A rarely seen terephthalato-bridged dinuclear copper(II) complex, $[Cu_2(CMP)_2(TPA)]\cdot[Cu_2(CMP)_2(MeOH)_2(TPA)]\cdot 2H_2O$ (CMP = 4-chloro-2-[(2-isopropylaminoethylimino)methyl]phenolate, TPA = terephthalate), has been prepared and characterized by elemental analysis, infrared spectrum, and single crystal X-ray determination. The complex crystallizes in the triclinic space group P–1, with $a = 9.741(1)$ Å, $b = 11.248(2)$ Å, $c = 17.659(2)$ Å, $\alpha = 95.915(2)°$, $\beta = 90.656(2)°$, $\gamma = 111.747(2)°$, $V = 1785.0(4)$ Å^3, $Z = 1$, GOOF = 1.033, $R_1 = 0.0432$, and $wR_2 = 0.1109$. The asymmetric unit of the complex contains two centrosymmetric terephthalato-bridged dinuclear copper(II) molecules and two water molecules of crystallization. The Cu atoms in one molecule are in square planar coordination, and in the other one are in square pyramidal coordination.

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Keywords copper complex, crystal structure, dinuclear complex, Schiff base, X-ray crystallography

INTRODUCTION

Polynuclear complexes have been widely investigated due to their versatile molecular structures and interesting functionalities.[1–3] The main strategy for designing polynuclear complexes is to use suitable bridging ligands such as azide, thiocyanate, cyanide, and so on.[4–7] Among polynuclear complexes, those containing Cu atoms usually possess interesting magnetic properties.[8–10] Multicarboxylate anions have also been extensively used to prepare polynuclear complexes. However, to the best of our knowledge, only seven Schiff base copper(II) complexes with multicarboxylate bridges have been reported.[11–17] As an extension of work on such complexes, in this study, a rarely seen terephthalato-bridged dinuclear copper(II) complex, $[Cu_2(CMP)_2(TPA)]\cdot[Cu_2(CMP)_2(MeOH)_2(TPA)]\cdot 2H_2O$ (CMP = 4-chloro-2-[(2-isopropylaminoethylimino)methyl]phenolate, TPA = terephthalate), has been successfully prepared and characterized.

EXPERIMENTAL

Materials and Measurements

5-Chlorosalicylaldehyde and *N*-isopropylethane-1,2-diamine were purchased from Lancaster (England). All other chemicals (reagent grade) were commercially available and used without further purification. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C elemental analyzer (Nanjing University, China). Infrared spectra were recorded on a Nicolet AVATAR 360 spectrophotometer (Liaoning Normal University, China) as KBr pellets.

Synthesis of HCMP

HCMP was prepared by condensation of equimolar quantities of 5-chlorosalicylaldehyde with *N*-isopropylethane-1,2-diamine in methanol at room temperature. Yield: 90%. Found: C, 59.7; H, 7.1; N, 11.7. Anal. Calcd. (%) for $C_{12}H_{17}ClN_2O$: C, 59.9; H, 7.1; N, 11.6.

Synthesis of $[Cu_2(CMP)_2(TPA)]\cdot[Cu_2(CMP)_2(MeOH)_2(TPA)]\cdot 2H_2O$

Terephthalic acid (0.1 mmol, 16.6 mg) and LiOH (0.2 mmol, 4.8 mg) were mixed and stirred in distilled water (3 mL) for 30 min. In addition, the Schiff base ligand (0.2 mmol, 48.1 mg) and copper perchlorate (0.2 mmol, 75.0 mg) were mixed and stirred in methanol (15 mL) for 30 min. Then, two mixtures were combined together, and further stirred for 2 h at room temperature, and filtered. Upon keeping the filtrate in air for a few days, blue block-shaped crystals of the complex, suitable for X-ray crystal structure determination, were formed. The crystals were isolated by filtration, washed with methanol, and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield 37% on the basis of HCMP. Found: C, 48.5; H, 5.3; N, 6.7. Anal. Calcd. (%) for $C_{66}H_{84}Cl_4Cu_4N_8O_{16}$: C, 48.3; H, 5.2; N, 6.8.

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Address correspondence to Hai-Liang Zhu, School of Life Sciences, Shandong University of Technology, ZiBo 255049, P. R. China. E-mail: hailiang_zhu@163.com

TABLE 1
Crystallographic data and refinement parameters for the complex

Molecular formula	$C_{66}H_{84}Cl_4Cu_4N_8O_{16}$
Formula moiety	$C_{34}H_{44}Cl_2Cu_2N_4O_8 \cdot C_{32}H_{36}Cl_2Cu_2N_4O_6 \cdot 2H_2O$
Molecular weight	1641.4
Temperature (K)	298(2)
Crystal shape/color	Block/blue
Crystal dimensions (mm)	0.27 × 0.23 × 0.23
Crystal system	Triclinic
Space group	*P*–1
a (Å)	9.741(1)
b (Å)	11.248(2)
c (Å)	17.659(2)
α (°)	95.915(2)
β (°)	90.656(2)
γ (°)	111.747(2)
Volume (Å^3)	1785.0(4)
Z	1
d_{calc} (g cm^{-3})	1.527
Absorption coefficient (mm^{-1})	1.396
F(000)	848
θ range (°)	1.96/27.00
Range/indices (*h*, *k*, *l*)	–11/12, –13/14, –22/11
Absorption correction	Multi-scan
T_{min}	0.7043
T_{max}	0.4395
Reflections/parameters	7562/462
Independent reflections	6162
Restraints	6
Goodness of fit on F^2	1.033
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0432, 0.1109
R_1, wR_2 (all data)^a	0.0545, 0.1198

$^aR_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$, $w = [\sigma^2 Fo^2 + (0.0561(Fo^2 + 2Fc^2)/3)^2 + 2.1709(Fo^2 + 2Fc^2)/3]^{-1}$.

TABLE 2
Selected bond distances (Å) and angles (°) for the complex

Bond distances			
Cu1–O1	1.932(2)	Cu1–O2	1.9353(19)
Cu1–N1	1.944(2)	Cu1–N2	2.051(3)
Cu1–O4	2.315(2)		
Cu2–O5	1.912(2)	Cu2–O6	2.021(3)
Cu2–N3	1.943(2)	Cu2–N4	2.034(3)
Bond angles			
O1–Cu1–O2	91.7(1)	O1–Cu1–N1	92.4(1)
O2–Cu1–N1	171.3(1)	O1–Cu1–N2	176.5(1)
O2–Cu1–N2	91.7(1)	N1–Cu1–N2	84.4(1)
O5–Cu2–N3	91.9(1)	O5–Cu2–O6	88.4(1)
N3–Cu2–O6	177.6(1)	O5–Cu2–N4	166.2(1)
N3–Cu2–N4	84.2(1)	O6–Cu2–N4	96.0(1)
O1–Cu1–O4	93.7(1)	O2–Cu1–O4	87.6(1)
N1–Cu1–O4	99.8(1)	N2–Cu1–O4	85.6(1)

X-Ray Crystallography

Diffraction intensities for the complex were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer (Shandong University of Technology, China) with Mo*Kα* radiation (λ = 0.71073 Å). Collected data were reduced using SAINT,[18] and multiscan absorption corrections were performed using SADABS.[19] Structure of the complex was solved by direct method and refined against F^2 by full-matrix least-squares method using SHELXTL.[20] All of the non-hydrogen atoms were refined anisotropically. Water and amino H atoms in the complex were located in a difference Fourier map and refined isotropically, with O–H, N–H, and H···H distances restrained to 0.85(1), 0.90(1), and 1.37(2) Å, respectively. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

Crystal Structure Description of the Complex

The asymmetric unit of the compound contains two centrosymmetric terephthalato-bridged dinuclear copper(II)

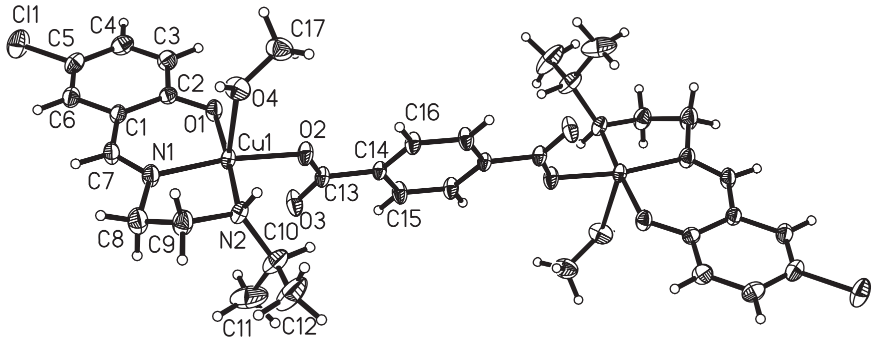

FIG. 1. The Cu1 complex molecule of the complex at 30% probability displacement. Unlabeled atoms are at the symmetry position 2 – *x*, – *y*, – *z*.

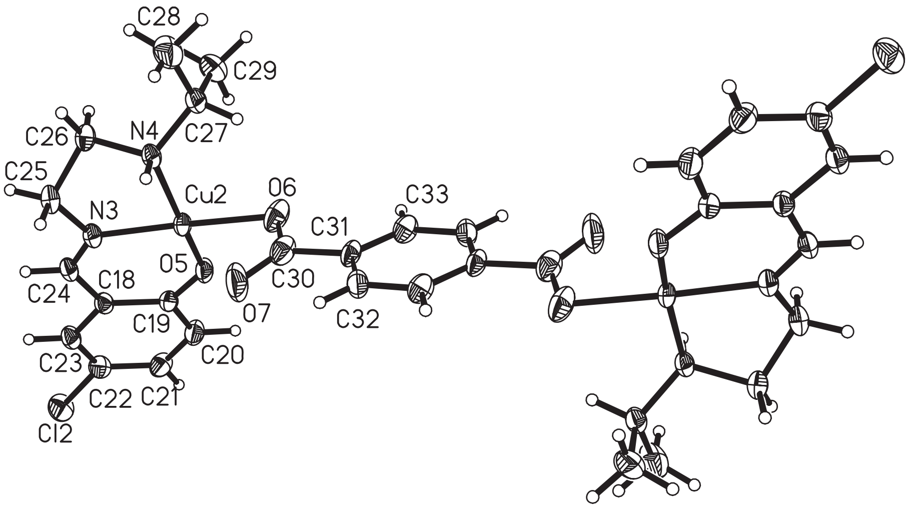

FIG. 2. The Cu2 complex molecule of the complex at 30% probability displacement. Unlabeled atoms are at the symmetry position 1 – *x*, 1 – *y*, 2 – *z*.

molecules (Figures 1 and 2), and two water molecules of crystallization. For the Cu1 molecule, each Cu atom is in a square pyramidal coordination, with the phenolic O, imino N, and amino N atoms of the Schiff base ligand, and with one terephthalate O atom defining the basal plane, and with one methanol O atom occupying the apical position. The distortion of the square pyramid can be observed from the coordinate bond angles among the apical and basal donor atoms, ranging from 85.6(1) to 99.8(1)°. The apical bond is much longer than the basal bonds. Cu1 atom deviates from the least-squares plane defined by the four basal donor atoms by 0.056(2) Å toward the apical donor atom. The intramolecular Cu···Cu separation is 11.0(2) Å. For the Cu2 molecule, each Cu atom is four-coordinated by the phenolic O, imino N, and amino N atoms of the Schiff base ligand, and by one terephthalate O atom, forming a square planar geometry. Cu2 atom deviates from the least-squares plane defined by the four donor atoms by 0.092(2) Å. The intramolecular Cu···Cu separation is 10.9(2) Å. Detailed comparison of the two molecules indicates that the coordinate bond lengths in Cu1 molecule are a little longer than those in Cu2 molecule. All the coordinate bond values are typical and comparable with those observed in other similar copper(II) complexes with Schiff bases.[11,16,17] In line with the amphimonodentate coordination mode of the carboxylate groups is the marked difference of 0.042(2) Å for O2-C13-O3 and 0.007(2) Å for O6-C30-O7 between the two C-O distances, implying a partial double bond character of C13-O3 and C30-O7 bonds. In the terephthalate groups, the dihedral angles between the benzene rings and the planes defined by the carboxylate groups are 3.6(3)° for Cu1 and 10.9(3)° for Cu2. The molecular packing structure of the complex is shown in Figure 3. The crystal of the complex is linked by intermolecular O–H···O and N–H···O hydrogen bonds.

IR Spectra

The characteristic feature of the infrared spectrum of the complex is the positions of ν_{as}(COO) and ν_{s}(COO) bands at 1593 and 1392 cm^{-1}, respectively. Their difference, $\Delta = 201$ cm^{-1}, is characteristic of the monodentate coordination mode of the terephthalate ligands.[21] The strong absorption band of the C=N bonds in the complex is at 1640 cm^{-1}. The O–H

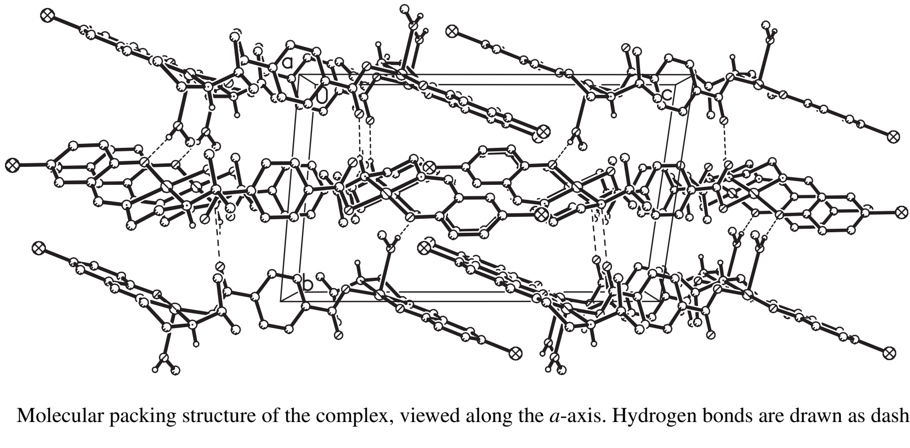

FIG. 3. Molecular packing structure of the complex, viewed along the *a*-axis. Hydrogen bonds are drawn as dashed lines.

and N–H vibrations are observed at 3436, 3331, and 3168 cm^{-1}. The weak bands located at the low numbers may be assigned to the ν(Cu–O) and ν(Cu–N).

CONCLUSIONS

A rarely seen terephthalato-bridged dinuclear copper(II) complex derived from 4-chloro-2-[(2-isopropylaminoethylimino)methyl]phenol and terephthalic acid was prepared and characterized. The single-crystal structure of the complex was determined. The synthesis of the complex indicates that the terephthalate anion is an interesting bridging group for the construction of polynuclear complexes. The present copper complex may possess interesting magnetic property, which deserves further investigation.

SUPPLEMENTARY MATERIALS

CCDC-867565 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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