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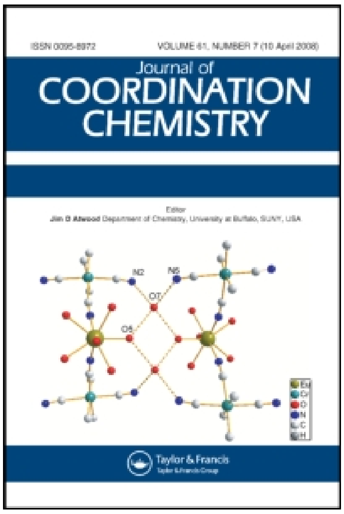

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Synthesis and structure of a one-dimensional copper(II) complex supported by 1,2-phenylenediacetate

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A Cu^{II} complex with 1,2-phenylenediacetate, $\{[Cu_2(PDA)_2(DMF)_2]\cdot 2H_2O\}_n$ ($H_2PDA = $ 1,2-phenylenediacetic acid), was synthesized and characterized by elemental analysis, IR, UV, EPR, TG and single-crystal X-ray diffraction. The complex crystallizes in triclinic system, space group $P\bar{1}$ with $a = 10.8156(3)$ Å, $b = 11.2137(3)$ Å, $c = 14.8172(1)$ Å, $\alpha = 72.0670(10)^\circ$, $\beta = 81.8790(10)^\circ$, $\gamma = 61.7230(10)^\circ$, $V = 1505.71(6)$ Å^3, $Z = 2$, and $R_1 = 0.0768$ for 4387 observed reflections. The complex has a 1D structure, in which two adjacent copper^{II} centers are linked by 1,2-phenylenediacetate ligands. The 1D structure are further aggregated via C–H$\cdots\pi$ interactions to a 2D sheet.

Keywords: Copper; 1,2-Phenylenediacetic acid; Synthesis and crystal structure

1. Introduction

The design and synthesis of metal–organic coordination polymers have rapidly developed in recent years due to their fascinating molecular topologies and crystal-packing motifs along with potential applications as functional materials [1]. A variety of coordination polymers have been prepared taking into account the coordination nature of the metal ion and the shape, functionality, flexibility, and symmetry of organic ligand [2]. Multi-carboxylate ligands have attracted much attention because of diversity of binding modes of the carboxylate group. A large number of metal coordination polymers have been isolated using multi-carboxylate ligands 1,2,4,5-benzenetetra-carboxylic acid (H_4btec) [3], 1,3,5-benzenetricarboxylic acid (H_3btc) [4], and 1,4-benzenedicarboxylic acid (p-H_2bdc) [5]. In this work, we present the synthesis and structural characterization of a one-dimensional (1D) coordination complex, $\{[Cu_2(PDA)_2(DMF)_2]\cdot 2H_2O\}_n$ ($H_2PDA = $ 1,2-phenylenediacetic acid, DMF = N,N'-dimethylformamide.

Compared with rigid 1,2-benzenedicarboxylate [6], 1,2-phenylenediacetate possesses two flexible terminal CH_2COO groups, which is expected to generate polymeric structures as helices, grids or cavities. Coordination polymers assembled with flexible 1,2-phenylenediacetate have not been studied. One probable reason is that the flexible

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terminal CH_2COO groups of PDA are not favorable for crystal growth. Thus, we explored the self-assembly of copper(II) with PDA to obtain a novel crystalline complex.

2. Experimental

2.1. *General produces*

All chemicals were of reagent grade and used without further purification. Elemental analysis was performed with a Vario EL *III* CHNOS Elemental Analyzer. The IR spectra of KBr pellets were recorded between 4000–400 cm^{-1} on a FTS-40 spectrophotometer. The UV-visible spectrum was recorded in water with a Perkin-Elmer Model L 19 spectrophotometer. The EPR spectrum was recorded on a FD-ESR-I spectrometer with the powdered sample at room temperature. The thermogravimetric analysis was performed in flowing N_2 on a Universal V2.4F TA instrument. Magnetic susceptibilities were measured with a MPMS-7 Superconducting Quantum Magnetometer in the temperature range of 5–300 K with a magnetic field of 0.1 T.

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2.2. *Synthesis of* $\{[Cu_2(PDA)_2(DMF)_2]\cdot 2H_2O\}_n$

A mixture of $CuCl_2\cdot 2H_2O$ (0.25 g, 1.47 mmol), 1,2-phenylenediacetic acid (0.21 g, 1.08 mmol), DMF (5 mL) and H_2O (10 mL) was stirred for 30 min, and then the solution was allowed to stand at room temperature for 10 days, resulting in blue crystals. Anal. Calcd for $C_{26}H_{34}Cu_2N_2O_{12}$: C, 45.09; H, 4.87; N, 4.11%. Found: C, 45.02; H, 4.94; N, 4.04%. IR (KBr pellet, cm^{-1}): 3446 (s), 1657 (s), 1618 (s), 1443 (s), 1406 (s), 1319 (w), 1105 (s), 1059 (w), 752 (s), 737 (s), 677 (s), 646 (w). UV-vis(aqueous solution): 800 nm.

2.3. *X-ray crystallography*

X-ray intensities from a single crystal of the complex were collected with a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL-97 [7]. All nonhydrogen atoms were refined anisotropically. Crystallographic data are summarized in table 1, selected bond lengths and angles are listed in table 2.

3. Results and discussion

Blue crystals of the title complex were synthesized in high yield (71%) by reacting $CuCl_2\cdot 2H_2O$ with 1,2-phenylenediacetic acid in a mixed solution of DMF and H_2O at room temperature. The elemental analyses match the formula of the complex. The IR spectrum shows strong absorption bands between 1350 and 1550 cm^{-1} that are diagnostic of coordinated carboxylate groups [8]. The absence of a strong carboxyl

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Table 1. Crystallographic parameters of the compound.

Molecule formula	$C_{26}H_{34}Cu_2N_2O_{12}$
Molecule weight	693.63
Crystal size (mm^3)	0.31 × 0.22 × 0.15
Crystal color	Blue
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.8156(3)
b (Å)	11.2137(3)
c (Å)	14.81720(10)
V (Å^3)	1505.71(6)
Z	2
D_c (g cm^{-3})	1.53
F (000)	716
Goodness-of-fit on F^2	1.246
Absorption coefficient (mm^{-1})	1.476
Max. shift (Δ/σ) in final cycle	0.001
Largest diff. peak and hole (e Å^{-3})	1.863/−0.865
Data/restraints/parameters	5255/0/366
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0768$, $wR_2 = 0.1486$
R indices (all data)	$R_1 = 0.0832$, $wR_2 = 0.1756$

$^aR_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w\ (F_o{}^2)^2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Cu(2)–O(2)#1	1.965(9)	Cu(2)–O(1)#3	1.969(10)
Cu(2)–O(8)#2	1.968(9)	Cu(2)–O(10)	2.153(10)
O(6)#1–Cu(1)–O(4)	88.8(4)	O(9)–Cu(2)–O(2)#1	88.3(4)
O(6)#1–Cu(1)–O(3)#1	89.0(4)	O(9)–Cu(2)–O(8)#2	167.6(4)
O(4)–Cu(1)–O(3)#1	168.1(4)	O(2)#1–Cu(2)–O(8)#2	89.2(4)
O(6)#1–Cu(1)–O(5)	168.6(4)	O(9)–Cu(2)–O(1)#3	90.5(4)
O(4)–Cu(1)–O(5)	89.4(4)	O(2)#1–Cu(2)–O(1)#3	167.8(4)
O(3)#1–Cu(1)–O(5)	90.5(4)	O(8)#2–Cu(2)–O(1)#3	89.4(4)
O(6)#1–Cu(1)–O(7)	99.3(4)	O(9)–Cu(2)–O(10)	94.0(4)
O(4)–Cu(1)–O(7)	97.7(4)	O(2)#1–Cu(2)–O(10)	98.4(4)
O(3)#1–Cu(1)–O(7)	94.1(4)	O(8)#2–Cu(2)–O(10)	98.4(4)
O(5)–Cu(1)–O(7)	92.1(4)	O(1)#3–Cu(2)–O(10)	93.8(4)

Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+1, -z$; #2: $-x, -y, -z+1$; #3: $x, y-1, z+1$.

absorption band around 1700 cm^{-1} for COOH indicates complete deprotonation of H_2PDA. The complex is soluble in water. Its electronic spectrum measured in aqueous solution shows a broad absorption centered at 800 nm, which may be ascribed to the d–d transition in the five-coordinate Cu^{II} center with square-pyramidal geometry [9]. The structural information is consistent with the results of the X-ray analysis.

X-ray single-crystal diffraction analysis reveals that the complex contains two crystallographically independent Cu^{II} centers, Cu1 and Cu2. A locally expanded unit is shown in figure 1, showing the coordination environments of metal atoms and PDA ligands. Each Cu^{II} is bound to four carboxylate groups from four PDA ligands and one O donor from DMF, giving a square pyramidal coordination geometry. Four carboxyl oxygens are in the equatorial plane of the square pyramid with mean deviation of 0.0039 Å for Cu1 and 0.0016 Å for Cu2. The Cu1 atom is raised above the equatorial plane by 0.199 Å towards the apical oxygen (O7) with the Cu–O7 distance of 2.147(10) Å, while Cu2 atom is raised above the equatorial plane by 0.2104 Å towards the apical oxygen (O10) with the Cu–O10 distance of 2.153(10) Å. As shown in figure 1, in each Cu^{II} center there exists a centrosymmetric dimeric unit, with the Cu1–Cu1A separation of 2.629(3) Å and Cu2–Cu2A 2.645(3) Å. The distances are similar to those found in other Cu carboxylate dimers [10].

The two PDA ligands display the same coordination mode (scheme 1); two oxygen atoms of each carboxylate are bound to two metal centers in a *syn–syn* fashion. As shown in figure 2, the dimeric Cu1–Cu1A and Cu2–Cu2A units are bridged by two PDA ligands through their CH_2COO groups to form a 1D belt-like structure. There exist two types of weak interaction ($C–H \cdots \pi$ and $C–H \cdots O$) in the molecular structures of the title complex. Adjacent belts are aggregated via $C–H \cdots \pi$ interactions to form a two-dimensional (2D) sheet (figure 3). The 2D sheets are further stabilized by $C–H \cdots O$ interactions. The $H6 \cdots C_g^i$ separation (C_g is the centroid of C14–C18 benzene ring; symmetric code: (i) $1-x, -y, -z$) and the $C6–H6 \cdots C_g^i$ angle are 2.643 Å and 150.1°, respectively. The $C \cdots O$ contacts and the $C–H \cdots O$ angles are in the range of 3.38(2)–3.54(2) Å and 153.3–159.8°, respectively.

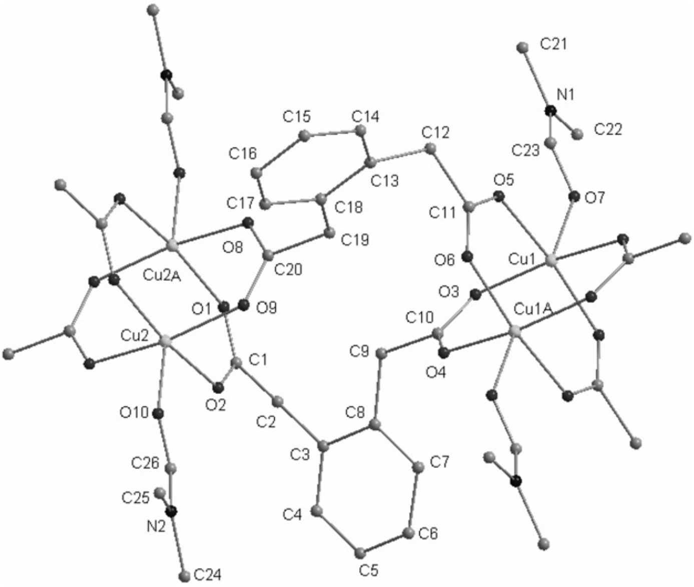
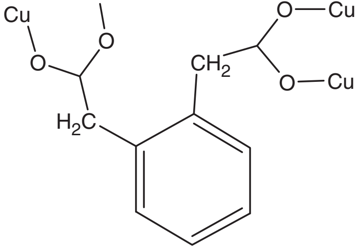


Figure 1. A locally expanded unit in the complex, displaying the coordination environment of copper.



Scheme 1. The coordination mode of carboxylate groups in the complex.

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The EPR spectrum of the powdered sample of the complex measured at room temperature exhibits features typical for dimeric carboxylato copper(II) complexes [11], with absorptions at low and high field ($H_{z1} \approx 350$ and $H_{z2} \approx 6000$ G, respectively) and line $H\perp_2 \approx 4800$ G. The EPR spectrum was interpreted by using the effective spin Hamiltonian [12] for a randomly oriented triplet state $S = 1$. The calculated spin Hamiltonian parameters are $g_\perp = 2.142$, $g_\parallel = 2.423$ and $D = 0.371\,\mathrm{cm}^{-1}$. The magnetic susceptibility of the complex was measured in the temperature range of 5–300 K. At 300 K the observed value of $\chi_m T$ is $1.01\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$. On lowering the temperature, the $\chi_m T$ value continuously decreases until it reaches a value of $0.0169\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ at 5 K. This trend indicates an antiferromagnetic exchange between the two copper(II) atoms in the dimeric units [13].

The thermal behavior of the complex was studied from room temperature to 600°C. The TGA curve indicates four steps of weight-loss. The first begins at 140°C and ends at about 180°C, corresponding to the removal of crystalline water with observed weight loss of 5.11%, in agreement with the calculated 5.19%. The second step occurs between 180° and 250°C, corresponding to removal of DMF with 20.8% weight loss (Calcd 21.05%). The last two steps (250°–450°C) should correspond to loss of

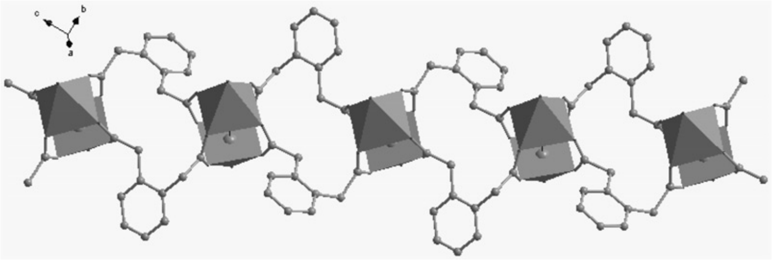

Figure 2. One-dimensional structure in the complex (all N and C atoms of DMF molecules are omitted for clarity).

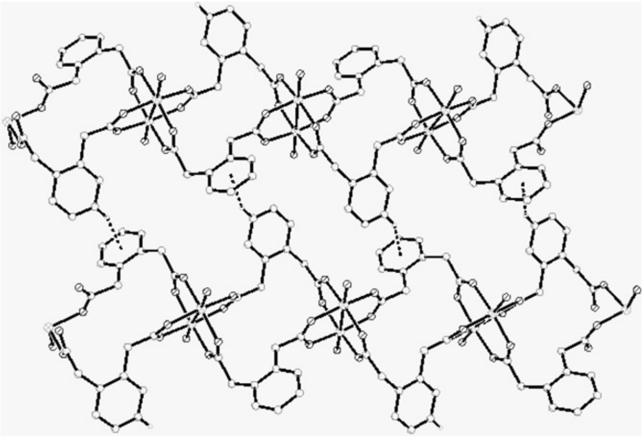

Figure 3. Two-dimensional supramolecular sheet formed by C–H···π interactions in the complex (all N and C atoms of DMF molecules are omitted for clarity).

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PDA (Calcd 55.36%). However, the observed weight loss (46.7%) is lower than the predicted value. This is due to the retention of some carbonaceous residue in the final solid phase (black in color).

In conclusion, we synthesized a new 1D polymer supported by 1,2-phenylenediacetate. Although various metal complexes have been studied by selecting multi-carboxylate ligands, metal coordination polymers assembled by flexible carboxylate-containing ligands are not common. Therefore, it will be of interest to select flexible ligands (such as 1,2-phenylenediacetate) to assemble novel structures. The work is ongoing in our laboratory.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-289353. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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