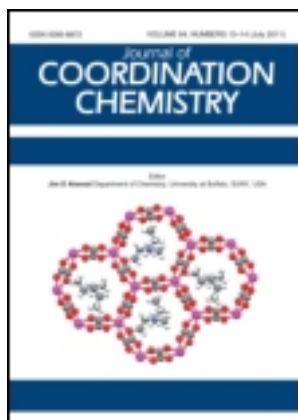


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Synthesis, structure, and magnetism of a new 2-D copper(II) complex based on two different dicarboxylates

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A new 2-D copper(II) complex, $[\text{Cu}_2\text{L}^1\text{L}^2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**) ($\text{H}_2\text{L}^1 = 2,4$ -dibenzoylisophthalic acid and $\text{H}_2\text{L}^2 = 2,5$ -dibenzoylterephthalic acid), has been synthesized by the reaction of copper(II) nitrate and two different dicarboxylates under hydrothermal conditions. This complex is characterized structurally by elemental analysis, IR spectra, thermogravimetric analysis, and X-ray diffraction. Complex **1** has a 2-D layer structure with $(4^4 \cdot 6^2)$ topology. The adjacent 2-D layers are further extended *via* O–H \cdots O hydrogen bonds into a 3-D supramolecular structure; **1** shows antiferromagnetic interactions.

Keywords: Copper(II); Complex; Dicarboxylate acid; Supramolecular; Antiferromagnetic

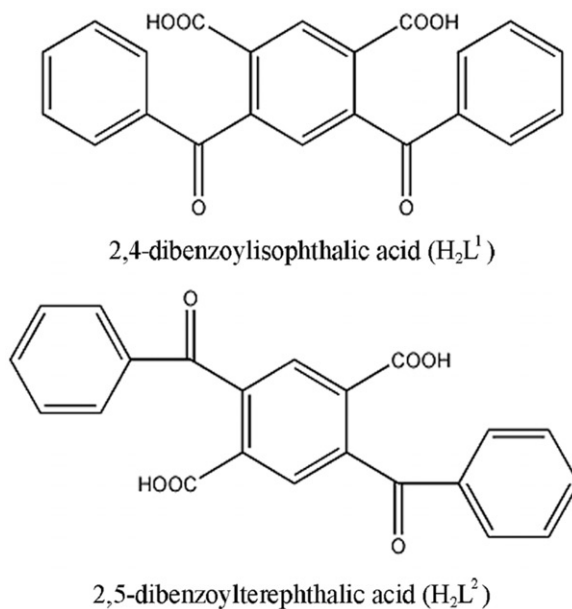
1. Introduction

Crystal engineering of solid-state metal coordination polymers has rapidly advanced because they have fascinating architectures and excellent physical and chemical properties, including magnetism, storage, nonlinear optics, and heterogeneous catalysis [1–4]. The strategies used for the architecture of functional systems depend on the nature of the interactional networks. One of the best strategies to construct 3-D supramolecular systems is to utilize noncovalent interactions (hydrogen bonds, $\pi \cdots \pi$, and C–H \cdots π) of the coordinated ligands [5].

Aromatic multicarboxylic acids are well-known versatile ligands which can chelate as well as bridge metal ions to build polynuclear and low-dimensional molecules [6]. Such ligands also form strong and directional hydrogen bonds [7, 8]. A large number of multicarboxylic acids, such as 1,*n*-benzenedicarboxylic acid ($n = 3$ and 4) [9, 10], 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid, are good choices for the construction of beautiful MOFs, owing to their versatile coordination modes [11–14]. However, far less effort has been expended on substituted aromatic dicarboxylic acids [15–18].

We chose two functionalized 2,4-dibenzoylisophthalic acids (H_2L^1) and 2,5-dibenzoylterephthalic acid (H_2L^2) (scheme 1) as ligands to construct new products. H_2L^1 and

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Scheme 1. The structures of H₂L¹ and H₂L².

H₂L² ligands, as derivatives of 1,*n*-benzenedicarboxylic acid (*n* = 3 and 4), are rarely reported in the field of coordination polymers [19–24]. H₂L¹ and H₂L² may provide supramolecular recognition sites for hydrogen bonds due to the existence of ketonic oxygen. Herein, we report a new 2-D complex [Cu₂L¹L²(H₂O)₂]·3H₂O (**1**); intermolecular O–H···O hydrogen bonds join the 2-D coordination sheets into a 3-D supramolecular network. Coordination polymers constructed by two different dicarboxylates are rarely reported [25, 26]. Moreover, magnetic study of **1** exhibits strong antiferromagnetic interactions between the two Cu(II) ions.

2. Experimental

2.1. Materials and instrumentation

The chemicals were purchased from commercial sources and used without purification. The ligands H₂L¹ and H₂L² were synthesized according to the literature method [27]. FT-IR spectra were measured in KBr pellets from 4000 to 400 cm⁻¹ on a Mattson Alpha-Centauri spectrometer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer Thermal Analyzer under N₂ with a heating rate of 10°C min⁻¹. Magnetic susceptibility measurements were carried out on polycrystalline samples on a Quantum Design MPMS-XL5 SQUID magnetometer from 2 to 300 K with an applied field of 1000 Oe. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms.

Table 1. Crystal data and structure refinement for **1**^{a,b}.

Formula	C ₄₄ H ₃₄ Cu ₂ O ₁₇
Formula weight	961.82
Crystal system	Monoclinic
Space group	<i>P2/c</i>
Unit cell dimensions (Å, °)	
<i>a</i>	10.796(5)
<i>b</i>	10.684(5)
<i>c</i>	18.639(10)
α	90
β	98.187(9)
γ	90
Volume (Å ³), <i>Z</i>	2128.0(18), 2
μ (mm ⁻¹)	1.075
Calculated density (g cm ⁻³)	1.498
2 θ range for data collection (°)	2.20–25.02
<i>F</i> (000)	980.0
Reflections collected/unique	13351/3729
<i>R</i> _{int}	0.0737
Goodness of fit on <i>F</i> ²	1.077
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0616, 0.1318
<i>R</i> ₁ , <i>wR</i> ₂ ^b (all data)	0.0885, 0.1494

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|}; \quad ^b wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}.$$

2.2. Syntheses of [Cu₂L¹L²(H₂O)₂] · 3H₂O (**1**)

A mixture of Cu(NO₃)₂ · 3H₂O (24.2 mg, 0.1 mmol), H₂L¹ (37.4 mg, 0.1 mmol), H₂L² (37.4 mg, 0.1 mmol), and H₂O (15 mL) was stirred for 30 min, and the pH of the solution was adjusted to 5.5 with 1 mol L⁻¹ NaOH. After stirring for another 30 min, the mixture was placed in a Teflon-lined stainless-steel vessel and heated at 150 °C for 4 days. Then the reaction system was cooled to room temperature during 50 h, and blue block crystals were obtained in 64% yield based on Cu(NO₃)₂ · 3H₂O. Elemental analysis (%) Calcd for C₄₄H₃₄Cu₂O₁₇ (961.82): C, 54.94; H, 3.56. Found (%): C, 55.12; H, 3.77. IR (KBr, cm⁻¹): 1673 (s), 1602 (m), 1485 (w), 1409 (m), 1344 (s), 1253 (s), 1072 (w), 927 (m), 794 (s), 695 (w).

2.3. X-ray crystallography

Single-crystal X-ray diffraction data for **1** were recorded at 293(2) K on an Oxford Diffraction Gemini R Ultra diffractometer using the ω -scan technique with Mo-K α radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the multiscan technique. All structures were solved by the Direct Method of SHELXS-97 and refined by full-matrix least-squares using SHELXL-97. Non-hydrogen atoms were refined with anisotropic temperature parameters and hydrogens of the ligands were refined as rigid groups. Hydrogens associated with water, O2W, were not located from the difference Fourier maps. For **1**, the restraint SIMU has been applied to *U*_{ij} values for C9, C10, C18, C19, C20, C21, C22, C23, O2W, and O3W atoms. In addition, ISOR restraint is adapted to restrain the anisotropic displacement parameters (ADPs) of O6 and O1W, respectively. Crystal data and structure refinement parameters for **1** are summarized in table 1. Selected bond distances and angles are listed in table 2.

Table 2. Bond lengths (Å) and angles (°) for **1**^a.

Cu(1)–O(1)#1	1.960(3)	Cu(1)–O(2)	1.968(3)
Cu(1)–O(3)#1	1.960(3)	Cu(1)–O(4)	1.954(3)
Cu(1)–O(1W)	2.129(4)	O(4)–Cu(1)–O(1)#1	88.54(15)
O(4)–Cu(1)–O(3)#1	168.07(14)	O(1)#1–Cu(1)–O(3)#1	88.78(18)
O(4)–Cu(1)–O(2)	88.23(15)	O(1)#1–Cu(1)–O(2)	167.89(16)
O(3)#1–Cu(1)–O(2)	91.99(15)	O(4)–Cu(1)–O(1W)	93.22(17)
O(1)#1–Cu(1)–O(1W)	101.81(18)	O(3)#1–Cu(1)–O(1W)	98.71(17)
O(2)–Cu(1)–O(1W)	90.02(18)	–	–

^aSymmetry code for **1**: #1 1–x, 1–y, –z.

3. Results and discussion

3.1. Description of the structures

[Cu₂L¹L²(H₂O)₂]·3H₂O (**1**). Single-crystal X-ray structural analysis indicates that **1** crystallizes in the monoclinic space group *P2/c* and shows a 2-D coordination network. The asymmetric unit of **1** contains one Cu(II), half one L¹ anion, half one L² anion, a coordinated water, and one and a half solvent waters. As illustrated in figure 1, Cu(II) is surrounded by two carboxylate oxygens of two L¹ anions, two carboxylate oxygens of two L² anions (Cu–O 1.953(4)–1.970(4) Å), and one oxygen from coordinated water (Cu–O 2.128(5) Å) in square-pyramidal coordination spheres, with the O1W occupying apical positions. L¹ anion and L² anion act as a tetradentate ligand (chart S1). Two neighboring Cu1 and Cu1#1 ions are joined through four bidentate bridging carboxylates of two L¹ anions and two L² anions with Cu···Cu separation of 2.6499(16) Å. As a result, two Cu(II) ions (Cu1 and Cu1#1), two L1 anions, two L2 anions, and two coordinated waters constitute a paddle-wheel secondary building unit. As shown in figure 2, the paddle-wheel building units connect L¹ and L² anions giving a 2-D layer structure of a 4⁴·6² network.

Classical O–H···O intermolecular hydrogen bonds are observed among the benzoyl oxygen and coordinated water (O1W···O6, 2.795 Å, table S1). The intermolecular hydrogen bonds further link adjacent 2-D layers to generate a 3-D supramolecular framework (figure 3).

3.2. Thermal analyses

The thermal stability of **1** was carried out from room temperature to 900°C under nitrogen (figure S1). The TGA curve of **1** suggests weight loss of 10.27% from 60°C to 160°C, corresponding to the loss of two lattice waters and three coordinated waters (Calcd 9.35%). The residual framework decomposes at 300°C and does not stop until heating at 410°C.

3.3. Magnetism

The temperature dependence of the magnetic susceptibility from 2 to 300 K for **1** was measured at an applied field of 1000 Oe and the $\chi_M T$ versus *T* plot and χ_M versus *T* plot are shown in figure 4 (χ_M is the molar magnetic susceptibility per Cu(II)). At 300 K, the value of $\chi_M T$ is 0.4294 cm³ mol^{−1} K, which is below the spin-only value for two

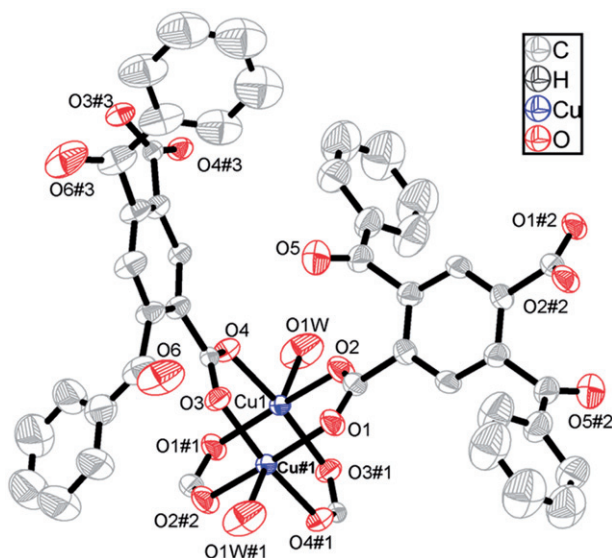


Figure 1. ORTEP diagram showing the coordination environments for Cu in **1** at 30% probability. All hydrogens and waters are omitted for clarity. Symmetry code: #1 = $1-x, 1-y, -z$; #2 = $-x, 1-y, -z$; #3 = $1-x, y, 0.5-z$.

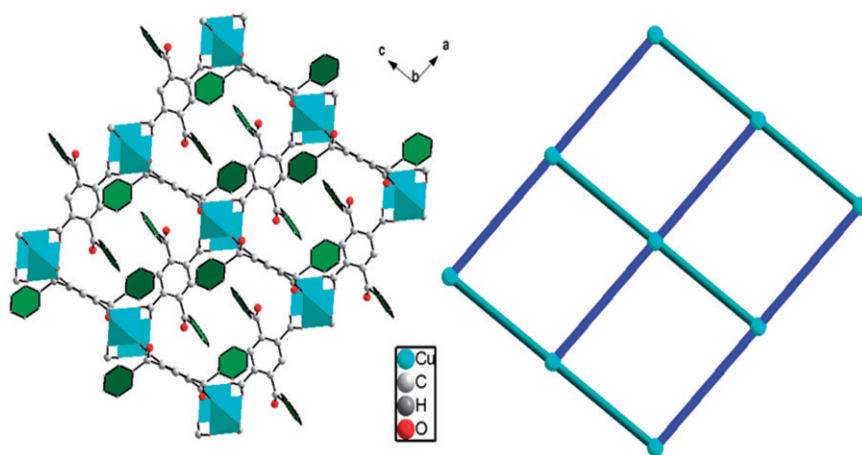


Figure 2. View of the 2-D sheet structure and $4^4 \cdot 6^2$ topology of **1**.

non-interacting Cu(II) ions ($0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at RT). Upon lowering the temperature, the $\chi_M T$ decreases rapidly from room temperature to $0.0180 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 30 K and gradually approaches $0.0113 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K, indicating strong antiferromagnetic interactions between Cu(II) ions. The χ_M curve further confirms the facts mentioned above.

Carboxylato bridges in *syn-syn* conformation can mediate very strong antiferromagnetic interactions in dinuclear copper(II) complexes [28]. Based on the structure of **1**, we attempt to interpret the magnetic behavior of **1** by fitting the magnetic data using

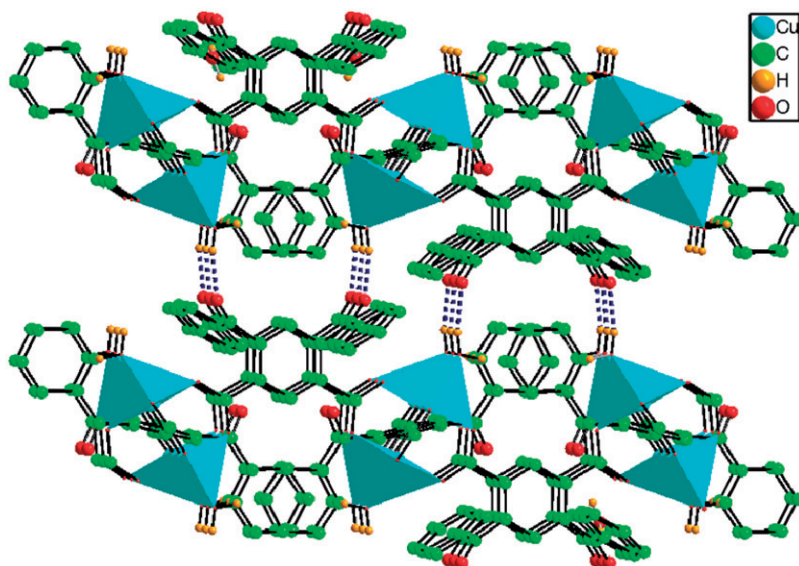


Figure 3. The 3-D supramolecular structure via O–H···O interactions of **1**.

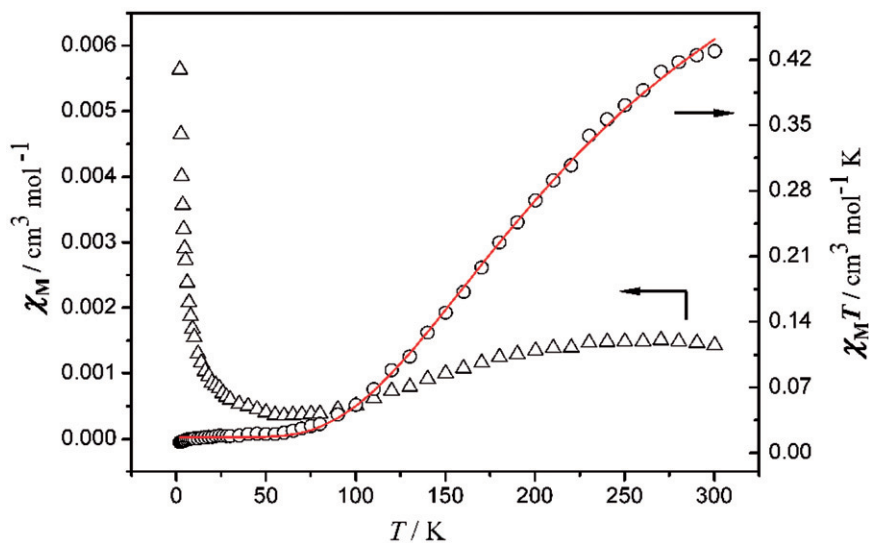


Figure 4. Plot of $\chi_M T$ vs. T for the polycrystalline samples (o) and plot of χ_M vs. T for **1** (Δ). The red solid line is theoretical fit based on the equation.

the Bleaney–Bowers equation derived from the isotropic spin Heisenberg Hamiltonian $H = -JS_1S_2$ with local spin $S = 1/2$, and modified to include the fraction ρ of monomeric Cu(II) impurities [29]:

$$\chi_M = (1 - \rho) \times \frac{2Ng^2\beta^2}{kT} \times \frac{e^{2J/kT}}{1 + 3e^{2J/kT}} + \frac{Ng^2\beta^2}{2kT} \rho$$

in which N , g , β , and K have their usual meanings [30]. The best least-squares fitting parameters give $g = 2.0082$, $J = -157.45 \text{ cm}^{-1}$, $\rho = 2.01\%$ with the agreement factor $R = \Sigma[(\chi_{MT})_{\text{obsd}} - (\chi_{MT})_{\text{calcd}}]^2 / \Sigma[(\chi_{MT})_{\text{obsd}}]^2 = 1 \times 10^{-5}$. The larger J value indicates the existence of a strong antiferromagnetic interaction, which is common for Cu(II) paddle-wheel complexes with a square-pyramidal coordination geometry [31, 32].

4. Conclusion

We have constructed a 2-D Cu(II) complex with the two different dicarboxylates; such complexes comprising mixed carboxylate ligands are uncommon. The overall magnetic behavior is antiferromagnetic among Cu(II) ions. We are currently continuing this work with other metal ions.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center; CCDC number is 783322 for **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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