

1D Chain Crystal Structure of Copper(II) Oxalate Containing a 4,4'-Bipyridine and 1,10-Phenanthroline Ligands: $[\text{Cu}_2(\text{ox})(4,4'\text{-bpy})(\text{phen})_2](\text{NO}_3)_2$

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Recently much attention has been paid to design and synthesis of metal-organic hybrid materials with fascinating network topologies¹⁻³ and potential applications as functional materials.⁴⁻⁶ The most commonly used strategy for designing such materials relies on the utilization of multidentate N- or O-donor ligands which have the capacity to bridge between metal centers to form polymeric structures. For example, 4,4'-bipyridine (4,4'-bpy) is an excellent ligand and a number of one-, two- and three-dimensional infinite metal-4,4'-bpy frameworks have been generated.⁷⁻¹⁰ Multi-carboxylates as important flexible spacer ligands have also been used to form metal-organic frameworks (MOF), due to their conformational and coordination versatility.¹¹⁻¹³

We have been pursuing synthetic strategies for the preparation of non-interpenetrating open frameworks with variable cavities or channels, in which rod-like rigid spacers such as 4,4'-bpy and related species are chosen as building blocks.¹⁴⁻¹⁶ One of our research interests has focused on a systematic study of the discrete polynuclear transition metal(II) compounds with aliphatic dicarboxylates. Although many interesting examples of the metal-carboxylate complexes have been reported,¹⁷⁻¹⁹ the development of synthetic routes to systems containing the dicarboxylate is still required for the rational design and synthesis.

In this context, we have successfully prepared the title compound of **1** by employing the oxalic acid, 4,4'-bpy, 1,10-phen, and copper(II) salt, respectively. The title compound consists of a 1D zig-zag chain structure, in which the corner units $[\text{Cu}(\text{phen})]^{2+}$ are interconnected alternately by bridging 4,4'-bpy and oxalate anion. Although the copper(II) oxalates with 1,10-phen or 4,4'-bpy such as $[\text{Cu}_2(\text{ox})(\text{phen})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ ²⁰ (ox = oxalate) and $[\text{Cu}(\text{ox})(4,4'\text{-bpy})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ ²¹ have been isolated, such a 1D zig-zag chain structure of **1** has never been reported in the literature. To the best of our knowledge, the title compound is the first example of copper(II) oxalate with mixed-ligand of 1,10-phen and 4,4'-bpy. In this work, we report the synthesis, thermal property, and crystal structure of the title compound, $[\text{Cu}_2(\text{ox})(4,4'\text{-bpy})(\text{phen})_2](\text{NO}_3)_2$ (**1**).

Experimental Section

All chemicals are commercially available and were used as received without further purification. Elemental analyses (C, H, N) were performed on a Carlo Erba EA-1106 Elemental Analyzer. Infrared spectra were recorded in the range from

4000 to 400 cm^{-1} on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu DTG-60 instrument with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$.

Preparation of $[\text{Cu}_2(\text{ox})(4,4'\text{-bpy})(\text{phen})_2](\text{NO}_3)_2$ (1**).** A methanolic solution (8 mL) of 1,10-phenanthroline (1 mmol, 0.180 g) was allowed to react with aqueous solution (5 mL) of Cu $(\text{NO}_3)_2\cdot 5/2\text{H}_2\text{O}$ (1 mmol, 0.233 g) and stirred for 20 min. Then an aqueous solution (5 mL) of oxalic acid (1 mmol, 0.127 g) and NaOH (2 mmol, 0.08 g) was poured slowly. To the mixture a methanolic solution (5 mL) of 4,4'-bipyridine (0.5 mmol, 0.078 g) was added and refluxed for 2 h. It was allowed to cool and the filtrate was kept at ambient temperature. A mixture of green blocks of **1** as a minor phase and blue blocks of $[\text{Cu}(\text{ox})(\text{phen})(\text{H}_2\text{O})]\cdot \text{H}_2\text{O}$ ²² (**2**) constituting the major product were obtained after a few days. Each complex was separated mechanically and suitable for X-ray determination. Attempts to prepare **1** as a monophasic material were unsuccessful. Yield of **1** was 20% (0.086 g) based on Cu. Anal. Calcd. for $\text{C}_{36}\text{H}_{24}\text{N}_8\text{O}_{10}\text{Cu}_2$: C, 50.53; H, 2.83; N, 13.09. Found: C, 50.54; H, 3.01; N, 13.67%. IR (KBr pellet, cm^{-1}): 3190(w), 3060(w), 1609(w), 1587(w), 1523(m), 1429(m), 1383(s), 1310(s), 851(m), 721(m).

X-ray structure determination. Single crystals of **1** were obtained by the method described in the above procedures. Structural measurement for the complex was performed on a Bruker SMART CCD²³ diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). A multi-scan absorption correction was applied using the SADABS program.²⁴ The structures were solved by direct method and refined on F^2 by full-matrix least-squares procedures using the SHELXS 97 and SHELXL 97 programs,²⁵ respectively. All non-hydrogen atoms were refined using anisotropic thermal parameters. CH Hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. The O atoms of the nitrate anion is both disordered over two positions with site-occupancy factors from refinement of 0.54(2) and 0.46(2) (for the O atoms). Images were created with the ORTEP²⁶ or DIAMOND program.²⁷ The crystallographic data for complex **1** are listed in Table 1.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 748368(**1**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-003; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Table 1. Crystal data and structure refinement for the complex of **1**

Complex	1
Empirical formula	C ₃₆ H ₂₄ Cu ₂ N ₈ O ₁₀
Formula weight	855.72
T (K)	173(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
<i>a</i> (Å)	23.144(2)
<i>b</i> (Å)	10.6601(7)
<i>c</i> (Å)	13.4363(9)
β (°)	93.1230(10)
<i>V</i> (Å ³)	3310.0(4)
<i>Z</i>	4
μ (mm ⁻¹)	1.362
<i>F</i> (000)	1736
θ (°)	1.76 to 27.00
Absorption correction	multi-scan $T_{\min} = 0.843$, $T_{\max} = 0.870$
Limiting indices	$-29 \leq h \leq 22$, $-13 \leq k \leq 10$, $-15 \leq l < 17$
Reflections collected	9967
Independent reflections	3604 [R(int) = 0.0475]
Observed reflections [$I \geq 2\sigma(I)$]	2751
Goodness-of-fit on F^2	1.065
R_1 [$I \geq 2\sigma(I)$]	0.0403
wR_2 [$I \geq 2\sigma(I)$]	0.0925
R_1	0.0592
wR_2	0.1061
Largest peak and hole (e Å ⁻³)	0.343 and -0.431

Table 2. Selected bond lengths (Å) and angles (°) for the complex of **1**

Cu-O1	1.989(2)	Cu-O2	1.969(2)
Cu-N1	2.000(3)	Cu-N2	1.997(3)
Cu-N3	2.236(3)	O1-C18	1.255(3)
O2-C18	1.253(3)	C18-C18	1.535(5)
O2-Cu-O1	85.08(8)	O2-Cu-N2	166.06(10)
O1-Cu-N2	96.33(10)	O2-Cu-N1	92.56(9)
O1-Cu-N1	166.41(9)	N2-Cu-N1	82.82(11)
O2-Cu-N3	95.25(9)	O1-Cu-N3	94.48(9)
N2-Cu-N3	98.46(10)	N1-Cu-N3	99.06(10)
Specified hydrogen bonds (with esds except fixed and riding H)			
Donor-H...acceptor	D-H	H...A	D...A
C2-H2...O5	0.93	2.61	3.321(16)
C3-H3...O4 ⁱ	0.93	2.37	3.205(8)
C13-H13...O5 ⁱⁱ	0.93	2.56	3.386(16)
C14-H14...O2 ⁱⁱⁱ	0.93	2.56	3.266(4)
C16-H16...O1 ^{iv}	0.93	2.46	3.369(4)

Symmetry codes: (i) $-x + 1, y, -z + 1/2$, (ii) $x, y + 1, z$, (iii) $-x + 3/2, y + 1/2, -z + 1/2$, (iv) $-x + 3/2, y - 1/2, -z + 1/2$.

Results and Discussion

Description of the structures. The structure of **1** consists of cationic dinuclear species, $[\text{Cu}_2(\text{ox})(4,4'\text{-bpy})(\text{phen})_2]^{2+}$ and two nitrate anions (Fig. 1(a)). The dication has an inversion center at the midpoint of the C-C bond of the bridging oxalate.

In the dication, the Cu²⁺ environment is that of a distorted square pyramid composed of two phen N atoms (Cu-N1 = 2.000(3), Cu-N2 = 1.997(3) Å) and two O atoms (Cu-O1 = 1.989(2), Cu-O2 = 1.969(2) Å) of bridging oxalates at the corners of the basal square, and a fifth weakly coordinated N3 atom (Cu-N3 = 2.236(3) Å) of the 4,4'-bpy at the apical position. The Cu(II) ion is slightly displaced by 0.235(1) Å from the N1N2O1O2 mean plane (mean deviation, 0.001(1) Å) toward apical N3 atom. Two copper ions, symmetrically bridged by oxalate, are separated by 5.148(1) Å, comparable to that of 5.739(1) Å found in the mono- and bi-dentate fashion $\{[\text{Cu}(\text{H}_2\text{O})_4][\text{Cu}(\text{mal})_2(\text{H}_2\text{O})_2]\}$ complex.²⁸ The $[\text{Cu}_2(\text{ox})(\text{phen})_2]^{2+}$ unit was also bridged by 4,4'-bpy to establish 1D zig-zag chain structure (Fig. 1(b)). The distance between two copper atoms is 11.584(1) Å. The zig-zag chain structure is further extended by the inter-phen ring π - π stacking (the interplanar distance = 3.445 Å, the angle made by ring normal and the vector between the ring centroids = 1.82°) to form 2D layers, as illustrated in Fig. 1(c). In addition, the compound is further stabilized by hydrogen bonding between the coordinated oxalate-O atoms and the carbon atoms of 4,4'-bpy, and between nitrate oxygen atoms and the carbon atoms of 4,4'-bpy or 1,10-phen, respectively (Table 2, Fig. 2). The phen molecules are nearly planar [mean deviation is 0.046(3) Å]. The intra-ring C-N [mean value 1.345(4) Å] and C-C [mean value 1.397(5) Å] bond distances are as expected.²⁹ The angles subtended by the bidentate phen ligand at the copper atoms are N1-Cu-N2 = 82.82(11)°.

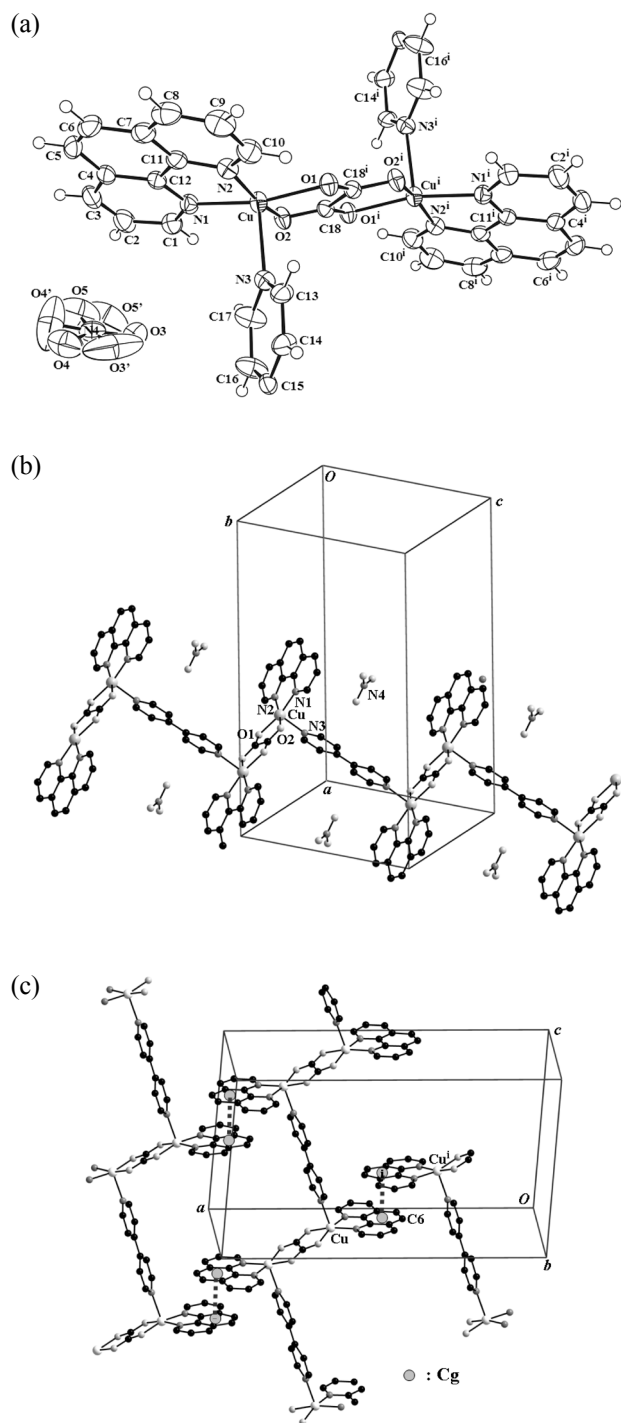


Figure 1. (a) ORTEP view (50%) of coordination environments of Cu(II) ion with atom labeling for **1**. [Symmetry code: (i) $-x + 3/2, -y + 3/2, z$]. (b) One-dimensional structure of **1**. (c) $\pi \cdots \pi$ interaction (dotted lines) in **1**. Cg is the centroids of the C4-C7, C11, C12 ring. [Symmetry code: (i) $-x + 1, y, -z + 1/2$].

The oxalate ligand adopts simultaneously bidentate coordination modes at both Cu ions. The angle subtended at Cu by the chelating oxalate group (O2-Cu-O1) is $85.08(8)^\circ$. The average C-O bond distances and O2-C18-O1 bond angles are $1.254(3) \text{ \AA}$ and $125.9(3)^\circ$, respectively. These structural data are in good agreement with those in the copper(II) complexes,

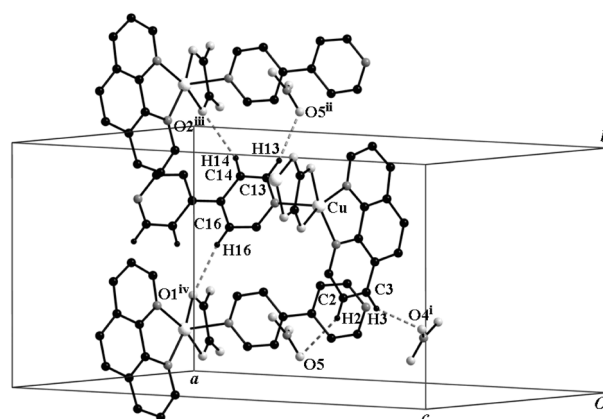


Figure 2. Hydrogen bonding of **1**.

$[\text{Cu}_2(\text{ox})(\text{phen})(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ³⁰ and $[\text{Cu}_2(\text{ox})(\text{phen})(\text{NO}_3)_2]$ ³¹.

The IR spectra of the bis-bidentate oxalate-bridging ligand: $1609(\text{w}) (\nu_{\text{as}}\text{CO}_2)$, $1383(\text{s}), 1310(\text{s}) (\nu_{\text{s}}\text{CO}_2)$, and $851(\text{m}) \text{ cm}^{-1}$ (δCO_2). The peaks at $3190(\text{w})$ and $3060(\text{w}) \text{ cm}^{-1}$ and $1631 - 1429 \text{ cm}^{-1}$ are attributable to the C-H, aromatic C-C, and C=N stretching frequencies of the aromatic group.³²

TG-DTA curves have been obtained in flowing N_2 atmosphere for crystalline samples of **1** in the temperature range of $30 - 800^\circ\text{C}$. The TG curve of complex **1** shows that it is thermally stable up to 133°C and upon further heating it undergoes three consecutive steps of decomposition processes up to 500°C (87.69%). This is assigned to the removal of one oxalate, one 4,4'-bpy, two phen, and two nitrate per formula unit (calculated: 85.14%). The DTA curve exhibits one endothermic peak at 146°C and three exothermic processes with maximum at $319, 370, \text{ and } 478^\circ\text{C}$, respectively.

In conclusion, by self-assembly reactions of Cu(II) ion, oxalate, 4,4'-bpy, and 1,10-phen ligands under ambient conditions, one new Cu(II)-oxalate complex $[\text{Cu}_2(\text{Ox})(4,4'\text{-bpy})(\text{phen})_2](\text{NO}_3)_2$ (**1**) was successfully isolated. The compound consists of 1D zig zag chain of $[\text{Cu}(\text{phen})]^{2+}$ units bridged alternately by oxalate and 4,4'-bpy. To the best of our knowledge, the title compound is the first example of copper(II) oxalate with mixed-ligand of 1,10-phen and 4,4'-bpy. It has been shown that the oxalate dianion in combination with organic spacers such as bis(4-pyridyl) derivatives is an excellent ligand for constructing 1D metal-organic framework structures with transition metal ions.

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