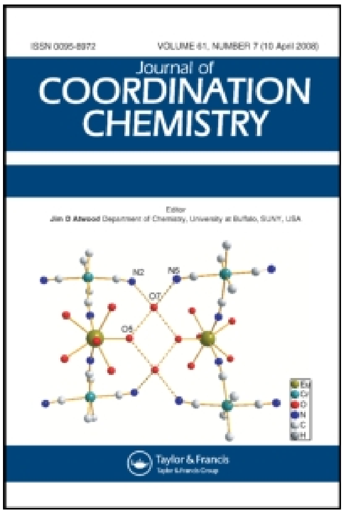

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Hydrothermal synthesis, crystal structure and fluorescence of a cyclic dimer copper compound constructed by 2-nitrobenzenedicarboxylate

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Hydrothermal synthesis, crystal structure and fluorescence of a cyclic dimer copper compound constructed by 2-nitrobenzenedicarboxylate

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The reaction of 2-nitro-1,4-benzenedicarboxylic acid (H_2nbdc) and 2,2′-bipyridine (2,2′-bipy) with $CuCl_2$ under hydrothermal conditions gives rise to a cyclic dimer $[Cu(nbdc)(2,2'\text{-bipy})(H_2O)]_2 \cdot 2H_2O$ (**1**). X-ray structural analysis revealed that **1** crystallizes in a monoclinic space group $P2_1/c$ with $a = 7.3801(13)$ Å, $b = 15.305(3)$ Å, $c = 16.333(3)$ Å, $\beta = 92.951(4)^\circ$, $V = 1842.5(6)$ Å^3, and $Z = 2$. Compound **1** represents the first cyclic dimeric example with 1,4-benzenedicarboxylate or its derivatives, in which two carboxylates of the nbdc are nearly perpendicular due to the steric effect by the nitro group. Compound **1** also displays strong fluorescent emission in the solid state.

Keywords: Synthesis; Cyclic dimer; Crystal structure; Copper compound; Fluorescent

1. Introduction

Over the past decade, a large number of 1,4-benzenedicarboxylate (bdc) compounds covering 0-D, 1-D, 2-D, and 3-D architectures with versatile topologies have been prepared for applications as functional materials [1–9]. Among these compounds, dimeric copper(II) species have received much attention and can be categorized into open and cyclic forms. All reported dimeric bdc compounds are open structures, constructed and controlled by the second anion to compensate the charge and/or complete the coordination [10–20]. We have been pursuing the construction of metal-organic frameworks with interesting topologies using 1,4-benzenedicarboxylate derivatives, such as 2-nitro-1,4-benzenedicarboxylic acid (H_2nbdc), and have found that the nitro substituent plays a key role in assembled architectures both in electronic and steric effects. The nitro group can repel neighboring carboxyl group of the nbdc rotating 90° around the benzyl ring, thus the nbdc ligand exhibits novel coordination modes. For example, following architectures have not been reported for the bdc compounds whereas in the case of nbdc we recently synthesized them,

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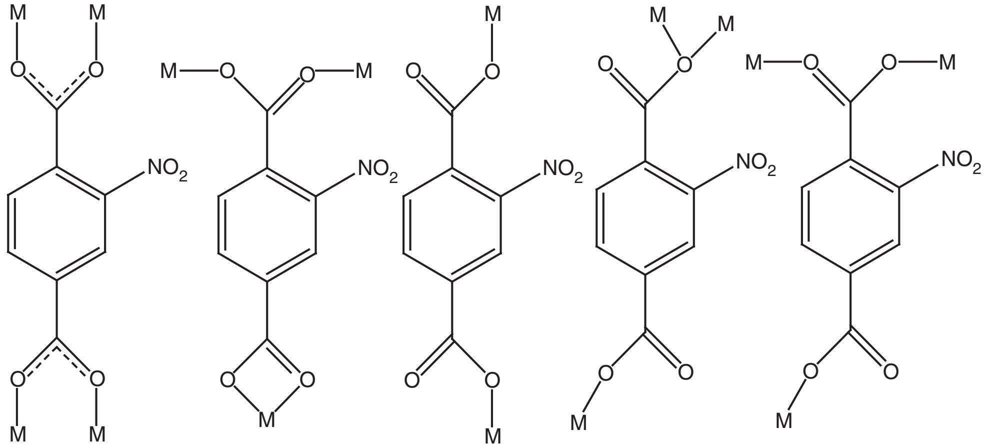

Scheme 1. Coordination modes of nbdc in recent reported compounds.

i.e. tetra-nuclear $[Cu_4(nbdc)_4(phen)_4(H_2O)_4](H_2O)_4$ [21], 2-D polymer constructed by both μ_2 and μ_4 nbdc ligands in $\{[Cu(nbdc)(phen)](H_2O)\}_n$ [22] and $\{[Cu(nbdc)(2,2'\text{-bipy})](H_2O)\}_n$ [23], 3-D inorganic-organic layered compound $[Cu_2(nbdc)(OH)_2(H_2O)]_n$ [24], and 2-D compound with dimeric 4,4′-bipyridine $[Cu_2(nbdc)_2(4,4'\text{-bipy})(H_2O)]_n$ [25] where novel coordination modes of nbdc ligands are depicted in scheme 1. Herein we report the first cyclic dimer with H_2nbdc, namely $[Cu_2(nbdc)_2(2,2'\text{-bipy})_2(H_2O)_2]\cdot 2H_2O$ (**1**).

2. Experimental

2.1. *Materials and physical measurements*

All starting materials were purchased from Acros Organics and were of reagent grade. C, H, and N elemental analyses were carried out on a Perkin–Elmer analyzer model 1110. The infrared spectra were taken on a Nicolet Nexus 470 infrared spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Electronic spectra were recorded by SPECORD 2000 in the solid state. Thermogravimetric analysis (TGA) was carried out on a Delta Series TA-SDT Q600 under nitrogen in the temperature range 25 to 800°C (heating rate = $10°C\,min^{-1}$). The fluorescent study was carried out on powdered sample in the solid state at room temperature using a Hitachi 850 spectrometer.

2.2. *Preparation of the compound*

A mixture of $CuCl_2\cdot 2H_2O$ (0.034 g, 0.2 mmol), 2-nitro-1,4-benzenedicaroxylic acid (H_2nbdc, 0.021 g, 0.1 mmol), 2,2′-bipyridine (0.032 g, 0.2 mmol) and H_2O (8 mL) in the molar ratio ca 1 : 0.5 : 1 : 2220 was sealed in a 25 mL stainless-steel reactor with Teflon liner and was heated at 413 K for 3 h. After cooling, green needle-shaped crystals of **1** were collected by filtration. Yield: 87% with a little bit of blue crystals

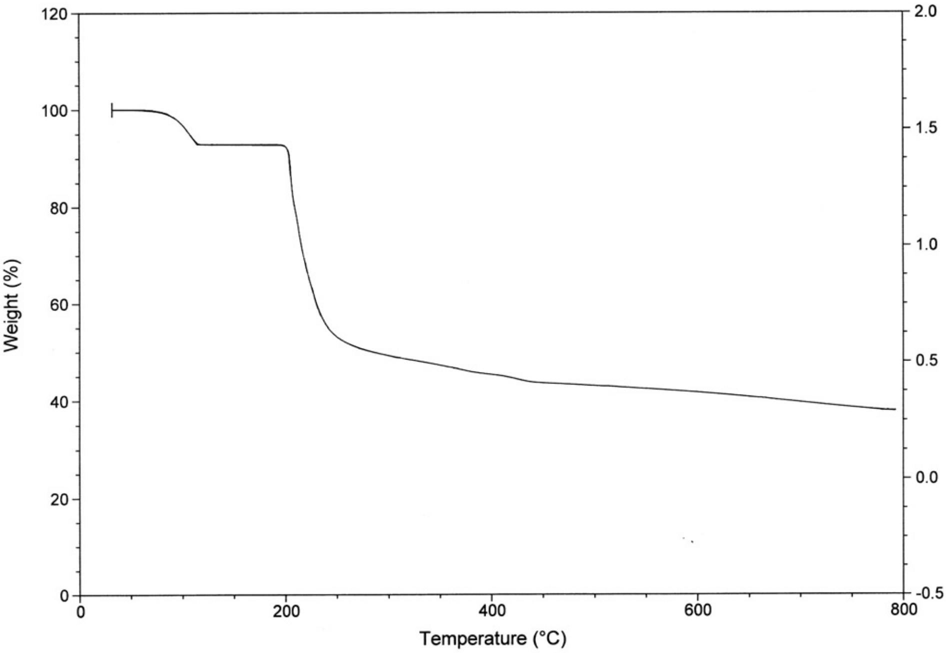

Figure 1. The TG spectrum of **1**.

reported in our previous work [23], [Cu(nbdc)(2,2′-bipy)](H_2O)]$_n$ (**2**). Anal. Calcd for $C_{36}H_{30}Cu_2N_6O_{16}$ of **1** (%): C, 46.51; H, 3.25; N, 9.04. Found: C, 46.45; H, 3.24; N, 9.05. Thermogravimetric analysis of **1** (figure 1) shows that in the range 82°C to 135°C, weight loss is 7.64% (Calcd 7.75%), which corresponds to the loss of four water molecules. The compound cannot dissolve in water and common organic solvents such as methanol, ethanol, benzene, tetrahydrofuran, dimethylformamide, and chloroform.

2.3. *Crystallography*

A green needle crystal with approximate dimensions $0.09 \times 0.10 \times 0.17\,mm^3$ was used for data collection on a Bruker SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The data were integrated by use of the SAINT program [26], with the intensities corrected for Lorentz factor polarization and absorption. The structures were solved by direct methods and successive Fourier syntheses. Full-matrix least squares refinements on F^2 were carried out using SHELXL-97 [27]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms on carbon were placed in idealized positions and refined as riding atoms, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Hydrogen atoms bound to oxygen were located in difference Fourier maps and refined with distance restraints of O–H = 0.85(1) Å and fixed isotropic displacement parameter of $U_{iso}(H) = 0.08$ Å^2. All the programs used are included in the WinGX Suite with version 1.70 [28].

Table 1. Crystallographic data for $[Cu_2(nbdc)_2(2,2'\text{-bipy})_2(H_2O)_2] \cdot 2H_2O$ (**1**).

Formula	$C_{36}H_{30}Cu_2N_6O_{16}$
F_w	929.74
Crystal color, habit	Green, needle
Crystal size (mm^3)	0.09 × 0.10 × 0.17
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	7.3801(13)
b(Å)	15.305(3)
c(Å)	16.333(3)
β(°)	92.951(4)
V(Å^3)	1842.5(6)
Z	2
D g (cm^{-3})	1.676
T (K)	295 ± 2
μ (mm^{-1})	1.241
Measured reflections	9093
Unique reflections	3267
R_1 and wR_2 ($I > 2\sigma(I)$)	0.055, 0.073
Number of variables	283
Goodness of fit (GOF)	0.816
Largest difference peak and hole (e Å^{-3})	0.488, −0.407

Information concerning the crystallographic data collection and structure refinements is summarized in table 1.

3. Results and discussion

3.1. *Synthesis and IR*

The system $Cu^{2+}/H_2nbdc/2,2'$-bipy reacted under hydrothermal conditions giving two products, **1** (green needle) and previously reported compound **2** (deep blue, block). Further exploring the reaction indicated that the ratio of the products depends on the reaction temperature. With increasing reaction time, **2** dominates after heating for six hours. At present procedure the heating of three hours is suitable for **1** with only minor mixture of **2**, and both products are easily separated as they differ in color and habits. These investigations of **1** and **2** indicate that **2** is more stable than **1**, confirmed by TG analyses. After removal of water, **1** decomposes at 203°C, whereas **2** decomposes at 224°C. Compared with the tetra-nuclear 1,10-phenanthroline compound synthesized by typical mixed solution method [21], cyclic dimer **1** is more thermally stable.

IR spectra clearly indicate **1** and **2** are different. The IR of **1** shows typical chelating carboxylate antisymmetric and symmetric stretching bands at 1565 cm^{-1} and 1395 cm^{-1}, which suggest monodentate coordination.

3.2. *Structural description*

A single crystal X-ray analysis of **1** revealed that it is a cyclic dimer (figure 2 and table 2), in which there is one crystallographically independent copper. The local

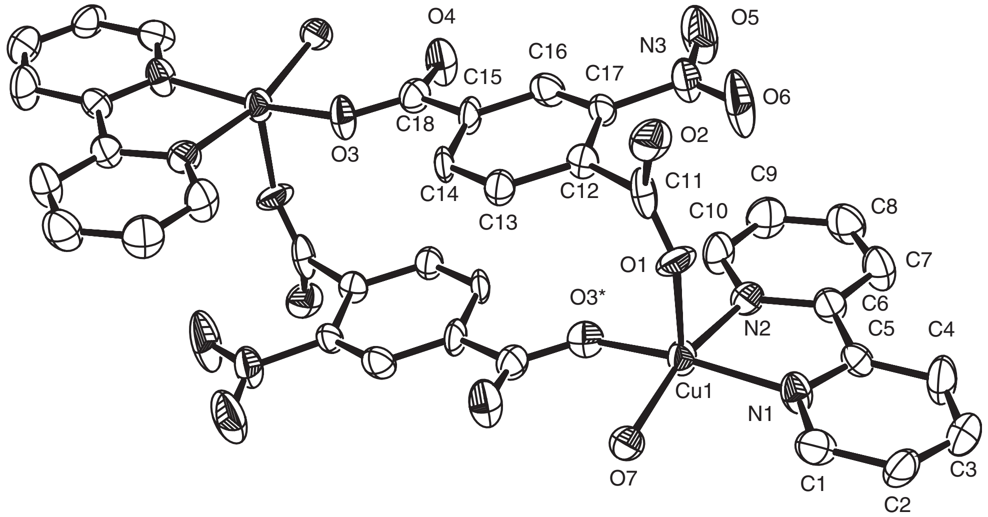

Figure 2. Perspective view of the dimer showing the atom labeling. Thermal ellipsoids are drawn at the 40% probability level.

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

Cu1–O1	2.172(4)	Cu1–O3*	1.957(4)
Cu1–O7	1.978(5)	Cu1–N1	2.004(5)
Cu1–N2	1.992(5)		
O1–Cu1–O3*	104.8(2)	O1–Cu1–O7	93.0(2)
O1–Cu1–N1	90.7(2)	O1–Cu1–N2	99.4(2)
O3*–Cu1–O7	93.5(2)	O3*–Cu1–N1	163.3(2)
O3*–Cu1–N2	89.6(2)	O7–Cu1–N1	92.0(2)
O7–Cu1–N2	166.1(2)	N1–Cu1–N2	81.5(2)

Symmetry code, *: $-x$, $1-y$, $1-z$.

coordination geometry around Cu1 is a square pyramid completed by two N-donors from one 2,2′-bipyridine, two carboxyl oxygens from two nbdc ligands, and one water. The two nitrogens (N1 and N2), O3* (symmetry code, *: $-x$, $1-y$, $1-z$), and O7 comprise the basal plane, while O1 occupies the apical position with Cu–O1 distance of 2.172(4) Å. The Cu–N bond lengths are similar to those of open dimers containing 2,2′-bipyridine ligands. The Cu–O(COO$^-$) bond lengths are divided into two types, shorter distance in the basal plane, and longer distance in the apical direction. The geometry of Cu^{II} in **1** is similar to that in tetra-nuclear species [23] which consists of two cyclic subunits. The two pyridyl rings of the 2,2′-bipyridine in **1** are nearly co-planar with dihedral angle of 2.0(3)°. Although two nbdc ligands are face-to-face parallel in the dimer, there is no stacking interaction.

Each nbdc^{2-} ligand acts as a bridge linker in bis-monodentate mode and connects two coppers with distance of 9.076(2) Å. In bdc compounds, two carboxylate groups of each bdc are nearly coplanar with benzene. In contrast to bdc compounds, two carboxylates of each nbdc in **1** are nearly perpendicular; one carboxylate is nearly co-planar with the benzyl ring (the dihedral angle is 6.4(7)°), while the other adopts a perpendicular orientation to the benzyl ring (the dihedral angle is 86.1 (3)°).

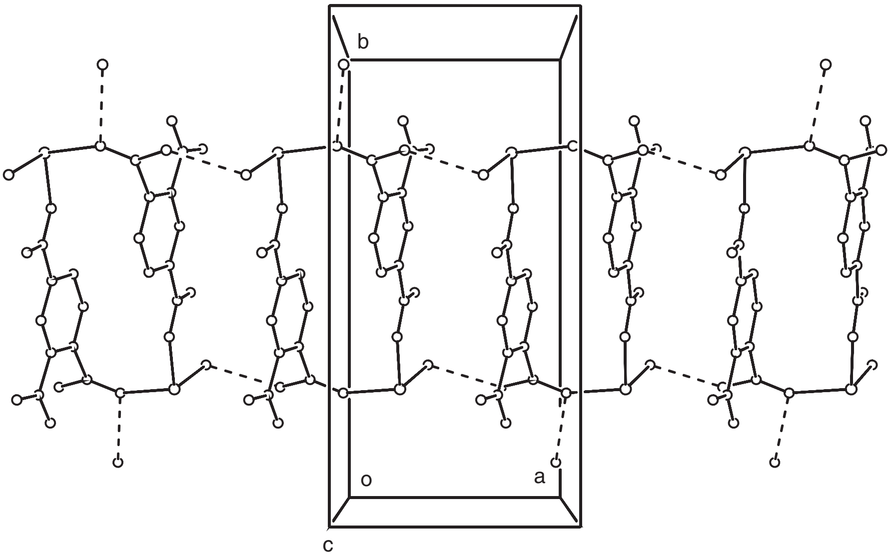

Figure 3. A view of the one-dimensional network for **1**.

Therefore, nbdc ligands are cyclic dimeric linkers. Yaghi and co-workers have proven that the dihedral angle between planes of the benzene and carboxylate groups plays a determining role in the formation of the paddle-wheel motif [29]. In fact, the large dihedral angle is difficult for formation of the paddle wheel motif, while in our system the large dihedral angle caused by the nitro group is essential for the formation of cyclic dimeric compounds, explaining why 1,4-benzenedicarboxylate compounds could not form cyclic dimeric compounds. The cyclic dimer architecture of $[Cu_2\mu_2\text{-nbdc})_2]$ is created without 2,2′-bipy, but the addition of 2,2′-bipyridine is necessary since the reaction of Cu^{II} ion with H_2nbdc affords no cyclic dimer.

In the title compound the nitro group is ordered, also found in the tetra-nuclear compound and 2-D manganese compound, while in other nbdc compounds the nitro groups exist in disordered forms.

In the cyclic dimer, coordinated water forms strong intra-molecular hydrogen bonds with uncoordinated carboxyl oxygen ($O2^i$) [$O7\cdots O2^i = 2.589(6)$ Å, i: $x+1$, y, z]. The coordinated water molecule further forms hydrogen bonds with the carboxyl O atom ($O4^{ii}$) [$O7\cdots O4^{ii} = 2.598(6)$ Å, ii: $-x$, $-y+1$, $-z+1$] from adjacent dimers and such interactions extend the structure into one-dimensional hydrogen bonding ladder-like chain (figure 3). The lattice water affords terminal hydrogen bond with carboxyl O atom (O1) [$O8\cdots O1 = 2.961(6)$ Å]. Unexpectedly, there is no aromatic-aromatic interaction between dimers. Hence, the crystal packing is stabilized by intra and inter-molecular hydrogen bonds.

3.3. *UV–Vis and fluorescence*

The UV–Vis spectrum of **1** (figure 4) exhibits two high-energy absorptions at 225 nm and 305 nm in the solid state; the latter can be assigned to ligand-to-metal charge transfer. The electronic properties of **1** are very different from **2**. An intense fluorescent

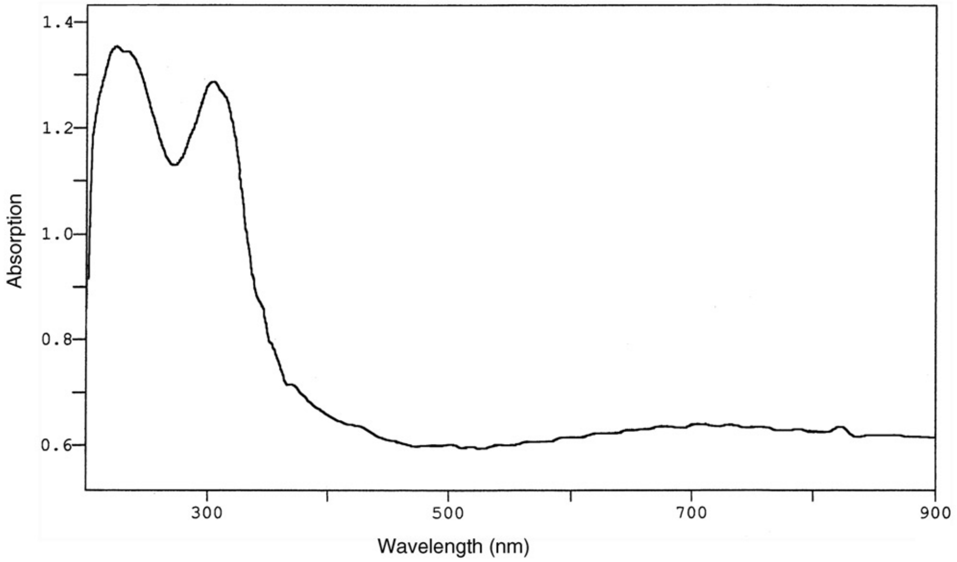

Figure 4. The electronic spectrum of **1** in the solid state.

emission of **1** at 472 nm ($\lambda_{ex} = 230$ nm) was observed in the solid state at room temperature and is assigned to the ligand-to-metal charge transfer band and some σ-donations from cooperation of 2,2′-bipy and nbdc ligands. This information suggests that **1** might be a photoactive material.

4. Conclusion

In summary, we have synthesized $[Cu_2(nbdc)_2(2,2'\text{-bipy})_2(H_2O)_2]\cdot(2H_2O)$ constructed from 2-nitro-1,4-benzenedicarboxylic acid and 2,2′-bipyridine with fluorescence. The single crystal X-ray diffraction analysis shows that the structure is a cyclic dimer which is a first example for 1,4-benzenedicarboxylate or its derivative compounds. The rotation of the carboxylate group opposed to the benzene ring is driven by the substituent group, which plays a key role in the formation of the cyclic dimer.

Supplementary material

Crystallographic data for the structures reported in the paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-602810. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44–1223/336033; Email: deposit@ccdc.cam.ac.uk].

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