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Synthesis and characterization of Cu(bpe)(ddc) [bpe = 1,2-bis(4-pyridyl)ethane, H₂ddc = 1,10-decanedicarboxylic acid]

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Abstract

A new 2D structure, Cu(bpe)(ddc) was synthesized by a reaction of hydrated cupric nitrate, 1,2-bis(4-pyridyl)ethane (bpe), 1,10-decanedicarboxylic acid (H₂ddc) and triethylamine (tea) via a room temperature diffusion method. The compound with chemical formula C₂₄H₃₂N₂CuO₄ crystallizes in triclinic space group $P\bar{1}$, $a = 7.944(3)$ Å, $b = 8.714(3)$ Å, $c = 9.366(3)$ Å, $\alpha = 64.55(3)^\circ$, $\beta = 86.72(2)^\circ$, $\gamma = 73.74(3)^\circ$, $V = 560.5(3)$ Å³ and $Z = 1$. Within the structure, each copper forms four equatorial bonds with two ddc and two axial bonds with two bpe to give rise to a distorted octahedron. The Cu–ddc connections generate a 1D zigzag chain. The chains are further connected via bpe nitrogen at Cu axial positions to result in a 2D layered structure. **To cite this article: B. Finkel et al., C. R. Chimie 8 (2005).**

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Résumé

Une nouvelle structure 2D Cu(bpe)(ddc) a été synthétisée par réaction d'hydratation du nitrate de cuivre, du 1,2-bis(4-pyridyl)éthane (bpe), de l'acide 1,10-décanedicarboxylique (H₂ddc) et de la triéthylamine (tea) par une méthode de diffusion à température ambiante. Le composé, de formule C₂₄H₃₂N₂CuO₄, cristallise dans le groupe d'espace triclinique $P\bar{1}$, avec $a = 7,944(3)$ Å, $b = 8,714(3)$ Å, $c = 9,366(3)$ Å, $\alpha = 64,55(3)^\circ$, $\beta = 86,72(2)^\circ$, $\gamma = 73,74(3)^\circ$, $V = 560,5(3)$ Å³ et $Z = 1$. Dans la structure, chaque cuivre forme quatre liaisons équatoriales avec deux ddc et deux liaisons axiales avec deux bpe pour donner un octaèdre déformé. Les enchaînements Cu–ddc produisent une chaîne en zigzag à une dimension. Les chaînes sont ensuite liées par l'intermédiaire de l'azote du bpe aux positions axiales du cuivre pour donner une structure en couches bidimensionnelle. **Pour citer cet article : B. Finkel et al., C. R. Chimie 8 (2005)**

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Keywords: Copper; 2D coordination polymer; Flexible ligand

Mots-clés : Cuivre ; Polymère en coordination bidimensionnelle ; Ligand flexible

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1. Introduction

Exploration and investigation of new metal–organic frameworks has increased extensively since 1990s because of their potential for applications, such as porous metal–organic frameworks as promising hydrogen storage materials [1,2], gas/liquid separation [3,4] and catalysis ability [5]. Many specific functions of these compounds could not be substituted by traditional inorganic or organic materials. In general, the strategy to design and construct metal–organic networks of a variety of structures is to elaborately select different metals with preferred coordination geometries and ligands with different shape, size and rigidity. In this paper, we report on a new compound synthesized using two flexible ligands 1,2-bis(4-pyridyl)ethane (bpe) and 1,10-decanedicarboxylic acid (H₂ddc).

Several chain-like alkyl dicarboxylate ligands, such as HOOC(CH₂)_nCOOH (*N* = 3–8) have been previously employed to build new metal–organic frameworks [6–9]. However, dicarboxylate ligands with *N* > 8 used to synthesize new structures are quite limited [10]. Herein, we report synthesis and structure analysis of a new copper coordination compound containing an unusually long alkyl dicarboxylate (ddc) and a flexible ligand (bpe).

2. Preparation

All chemicals were used as purchased. A 0.05 M acetonitrile solution of cupric nitrate, 0.1 M DMF solution of H₂ddc, 0.025 M ethanol solution of bpe and 0.1 M DMF solution of triethylamine (tea) were prepared. First, a buffer solution of 4 ml ethylene glycol was added into the bottom of U-type tube, then, solution was carefully added via disposable pipettes into both arms concurrently. The left arm the U-type was added 6 ml of acetonitrile cupric nitrate; the right arm was added 2 ml of H₂ddc/DMF, then 2 ml tea/DMF followed by 2 ml bpe/ethanol solution. After several weeks without disturbance, blue block-like crystals suitable for X-ray diffraction analysis were collected.

3. Structural characterization

Data collection on a selected single crystal was carried out at 298 K on an automated Enraf-Nonius

CAD4 diffractometer equipped with graphite monochromatic Mo K α radiation (λ , 0.71073 Å). The cell parameters were obtained from least-squares analyses of 25 computer-centered reflections within a range of $4.86^\circ = \theta = 11.21^\circ$. The data collections were monitored by three standard reflections every four hours. No decay was observed except the statistic fluctuation. Data collections and reduction were controlled by the CAD4/PC [11], and XCAD4-PC [12], respectively. At the end of the systematic data collection the raw intensities were corrected for Lorentz and polarization effects. Direct phase determination and subsequent difference Fourier map synthesis yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. Hydrogen atoms were added geometrically with their thermal parameters set to $1.2 \times U_{eq}$ of the parent non-hydrogen atoms. The final full-matrix, least-squares refinement on F^2 was applied for all observed reflections [$I > 2 \sigma(I)$]. All calculations were performed by using the SHELX97 software package [13]. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated [14]. Crystal data and details of relevant parameters adopted in the data collection as well as crystal structure refinement are listed in Table 1. Additional materials have been deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK, as a supplementary publication No. 236288 available on request from the CCDC.

4. Results

The crystals of the title compound C₂₄H₃₂N₂CuO₄ were grown in a slowly diffusing solution of bpe, H₂ddc and tea into a methanol solution of Cu(NO₃)₂ through a ethylene glycol medium. C₂₄H₃₂N₂CuO₄ crystallizes in a triclinic space group *PT*. The atomic coordination, selected bond lengths and bond angles are listed in Tables 1 and 2, respectively. Fig. 1 shows the coordination environment of Cu(II). It has a distorted octahedral geometry and is situated at the inversion center, where two carboxylates groups of ddc ligands in the equatorial plane bond to Cu(II) in a bidentate mode, the bpe ligands bind to Cu(II) at two axial positions through their pyridine nitrogen atoms. The oxygens of

Table 1
Crystallographic data of Cu(bpe)(ddc)

Sample code	BF1-47A
Molecular formula	C ₂₄ H ₃₂ CuN ₂ O ₄
Molecular weight	476.06
Color and habit	Transparent blue, block-like
Crystal size	0.16 × 0.09 × 0.04 mm ³
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)
Unit cell parameters	$a = 7.944(3) \text{ \AA}$, $\alpha = 86.72(2)^\circ$ $b = 8.714(3) \text{ \AA}$, $\beta = 86.72(2)^\circ$ $c = 9.366(3) \text{ \AA}$, $\gamma = 86.72(2)^\circ$ $V = 560.5(3) \text{ \AA}^3$, $Z = 1$
$F(000)$	251
Density (calc.)	1.400 g cm ⁻³
Diffractometer	Enraf-Nonius CAD4
Radiation	Graphite-monochromatized Mo K α $\lambda = 0.71073 \text{ \AA}$
Refs. used for cell measurement	25, 4.86° = $\theta = 11.21^\circ$
Standard reflections	(-1, 1, -2); (1, 1, -4); (0, 0, -4)
Intensity variation	± 2.8%
Absorption coefficient	0.1007 mm ⁻¹
Transmission factor	0.879–1.000
Scan type and rate	ω scan
Scan range	(0.65 + 0.35 tan θ)°
Data collection range	0 = $h = 9$; -10 = $k = 10$; -11 = $l = 11$; 2.41° = $\theta = 25.97^\circ$
R_{int} (from merging of equiv. refls.)	None
Reflections measured	
Total	2203
Unique (n):	2203
Observed [$I \geq 2\sigma(I)$]:	1522
Number of variables, p	146
Extinction coefficient	None
Weighting scheme	$W = 1/\sigma^2 [F_o^2 + (0.0482 P)^2 + 0.1537 P]$, $P = (F_o^2 + 2 F_c^2)/3$
R_1^a	0.1109 (all data) 0.0560 (observed data)
WR_2^b	0.1275 (all data) 0.1108 (observed data)
Goof (S) ^c	1.052
Largest and mean Δ/σ	0.000, 0.000
Largest peak and hole	+ 0.372 to -0.324 e \AA^{-3}

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum w(F_o^2)^2}}$$

$$^c \text{Goof} = S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{n-p}}$$

Table 2
Atomic coordinates and thermal parameters for Cu(bpe)(ddc). Estimated standard deviations are given in parentheses

Atoms	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	$U_{\text{eq}}(\sigma)$
Cu	0	0	0	0.039(1)
O(1)	-0.662(4)	0.1449(4)	-0.2229(3)	0.044(1)
O(2)	0.1665(4)	-0.0558(5)	-0.2348(4)	0.066(1)
N	-0.1466(5)	-0.1582(5)	0.0083(4)	0.041(1)
C(1)	-0.0983(7)	-0.3322(6)	0.1024(6)	0.058(1)
C(2)	-0.2020(8)	-0.4388(7)	0.1171(6)	0.072(2)
C(3)	-0.3649(8)	-0.3700(7)	0.0366(6)	0.068(2)
C(4)	-0.4118(6)	-0.1926(7)	-0.0632(6)	0.059(1)
C(5)	-0.2999(6)	-0.0923(6)	-0.0751(5)	0.048(1)
^a C(6 A)	-0.5017(12)	-0.4727(11)	0.0652(9)	0.066(2)
^b C(6B)	-0.4130(40)	-0.5210(30)	0.0160(30)	0.066(2)
C(7)	0.0493(6)	0.0846(6)	-0.2987(6)	0.047(1)
C(8)	0.0349(6)	0.1976(6)	-0.4769(5)	0.053(1)
C(9)	0.1979(6)	0.1681(7)	-0.5614(6)	0.058(1)
C(10)	0.3569(6)	0.1993(6)	-0.5098(6)	0.061(1)
C(11)	0.3350(6)	0.3819(6)	-0.5225(6)	0.060(1)
C(12)	0.5060(6)	0.4082(6)	-0.4873(6)	0.061(1)
H(1 A)	0.0102	-0.3826	0.1602	0.069
H(2 A)	-0.1619	-0.5596	0.1824	0.086
H(4 A)	-0.5191	-0.1397	-0.1229	0.071
H(5 A)	-0.3338	0.0274	-0.1451	0.057
^a H(6AA)	-0.4736	-0.5763	0.1666	0.079
^a H(6AB)	-0.6177	-0.3982	0.0662	0.079
^b H(6BA)	-0.3511	-0.5399	-0.0703	0.079
^b H(6BB)	-0.3757	-0.6304	0.1120	0.079
H(8 A)	-0.0570	0.1766	-0.5239	0.063
H(8B)	-0.0024	0.3212	-0.4962	0.063
H(9 A)	0.1697	0.2449	-0.6737	0.069
H(9B)	0.2299	0.0468	-0.5489	0.069
H(10 A)	0.3920	0.1148	-0.4003	0.073
H(10B)	0.4525	0.1741	-0.5729	0.073
H(11 A)	0.2508	0.4027	-0.4489	0.072
H(11B)	0.2875	0.4687	-0.6287	0.072
H(12 A)	0.5475	0.3282	-0.3778	0.074
H(12B)	0.5931	0.3756	-0.5538	0.074

^a U_{eq} defined as one third of the trace of the orthogonalized U tensor.

^b The S.O.F.s for a and b are 0.765 and 0.235, respectively.

the carboxylate groups are asymmetrically coordinated to the Cu with a short bond distance of 1.928 Å (Cu–O1) and longer bond distance 2.655 Å (Cu–O2). Pyridine groups coming from bpe at the apical positions give an identical C–N distance of 2.015 Å. The bond angles of O–Cu–N and N–Cu–N are 91.23° and 180°, respectively, and the bite angles of the carboxylate at the copper metal is 54.52° (Table 3). All bond

distances and angles around the Cu center are consistent with those reported for similar structures [15,16]. Each metal center is connected to four adjacent metal centers by two bpe and dcc ligands to generate a 2D structure. Although there are two conformations (*anti* and *gauche*) of bpe existing in various structures [17], only the *anti* structure has been found in the title compound. It is interesting to note that every chelating carboxylate group of the long alkyl chain is bent to coordinate the metal resulting in carbon backbone in dcc with torsion angles of C7–C8–C9–C10 (59.79°), and C8–C9–C10–C11 (58.72°), whereas the average torsion angle in the rest of alkyl chain is ca. 175°. Due to the bending manner of the flexible dcc ligands, the alternating Cu and dcc zigzag chains are formed along <111> axis. Due to such a bending, the shape of the resultant 2D structure is quite different from those of normal grids [18] or parquet (basket weave) pattern [19,20] (see Fig. 2). Within the 2D net, each rectangle grid is 52-membered ring deformed to two ‘fused’ rectangles. In this grid, the distances between two adjacent copper centers separated by bpe and dcc are 13.67 and 13.34 Å, respectively. The fact that long alkyl chain of dcc is bent significantly to comply with the crystal architecture is quite different from the structure arrangement of the dicarboxylate ligands reported previously [10]. The 2D net is compressed significantly leaving no space for guest molecules to enter. Fig. 3 shows the packing of 2D nets, with a separation of adjacent nets ca. 2.5 Å.

5. Conclusion

In this paper, we describe the crystal growth of a new Cu-containing coordination polymer using diffusion method. We show that the crystal structure of Cu(bpe)(dcc) has an unusual shape due to the incorporation of a lengthy and flexible ligand, 1,10-H₂dcc. The new structure consists of distorted octahedral of copper metal bound to two bpe as *anti* mode to form a linear chain propagating approximately along the b axis. The other coordination positions are chelated by dcc. The resultant structure is a 2D net. It is interesting to note each grid comprises of two fused rectangle-shipped rings as a result of dcc bending.

Table 3
Selected bond distances (Å) and bond angles (°) for Cu(bpe)(ddc)

Cu–O(1)#1	1.928(3)	C(3)–C(4)	1.371(7)
Cu–O(1)	1.928(3)	C(3)–C(6 A)	1.536(7)
Cu–N#1	2.015(3)	C(3)–C(6B)	1.557(16)
Cu–N	2.015(3)	C(4)–C(5)	1.381(6)
Cu–O(2)	2.655(4)	C(6 A)–C(6 A)#2	1.486(17)
Cu–O(2)#1	2.655(4)	C(6B)–C(6B)#2	1.35(6)
O(1)–C(7)	1.265(5)	C(7)–C(8)	1.521(6)
O(2)–C(7)	1.232(5)	C(8)–C(9)	1.497(6)
N–C(5)	1.324(5)	C(9)–C(10)	1.510(6)
N–C(1)	1.337(5)	C(10)–C(11)	1.504(6)
C(1)–C(2)	1.367(6)	C(11)–C(12)	1.516(6)
C(2)–C(3)	1.375(7)	C(12)–C(12)#3	1.487(9)
O(1)#1–Cu–O(1)	180.0(3)	N–C(1)–C(2)	122.5(5)
O(1)#1–Cu–N#1	91.23(12)	C(1)–C(2)–C(3)	120.9(5)
O(1)–Cu–N#1	88.77(12)	C(4)–C(3)–C(2)	116.3(4)
O(1)#1–Cu–N	88.77(12)	C(4)–C(3)–C(6 A)	118.8(6)
O(1)–Cu–N	91.23(12)	C(2)–C(3)–C(6 A)	124.5(5)
N#1–Cu–N	180.0(2)	C(4)–C(3)–C(6B)	128.0(12)
O(1)#1–Cu–O(2)	125.48(12)	C(2)–C(3)–C(6B)	108.2(13)
O(1)–Cu–O(2)	54.52(12)	C(6 A)–C(3)–C(6B)	34.8(10)
N#1–Cu–O(2)	90.48(12)	C(3)–C(4)–C(5)	120.0(4)
N–Cu–O(2)	89.52(12)	N–C(5)–C(4)	123.2(4)
O(1)#1–Cu–O(2)#1	54.52(12)	C(6 A)#2–C(6 A)–C(3)	107.8(8)
O(1)–Cu–O(2)#1	125.48(12)	C(6B)#2–C(6B)–C(3)	110(3)
N#1–Cu–O(2)#1	89.52(12)	O(2)–C(7)–O(1)	123.2(5)
N–Cu–O(2)#1	90.48(12)	O(2)–C(7)–C(8)	121.4(5)
O(2)–Cu–O(2)#1	180.00(14)	O(1)–C(7)–C(8)	115.4(4)
C(7)–O(1)–Cu	107.6(3)	C(9)–C(8)–C(7)	116.5(4)
C(7)–O(2)–Cu	74.2(3)	C(8)–C(9)–C(10)	116.9(4)
C(5)–N–C(1)	116.9(4)	C(11)–C(10)–C(9)	116.4(4)
C(5)–N–Cu	121.1(3)	C(10)–C(11)–C(12)	112.8(4)
C(1)–N–Cu	122.0(3)	C(12)#3–C(12)–C(11)	114.7(5)

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

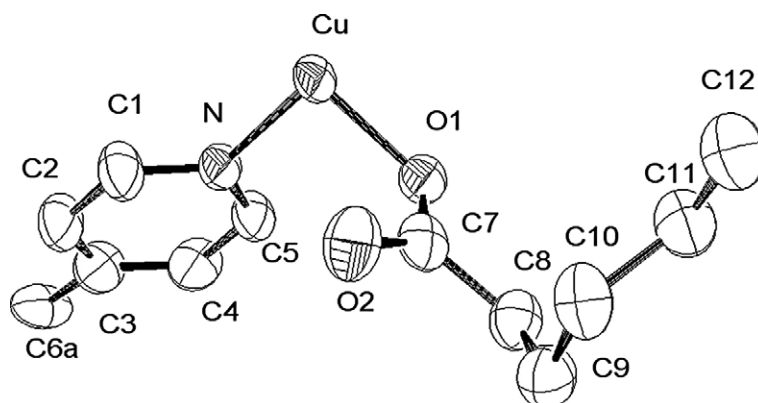


Fig. 1. ORTEP (50% probability) drawing and atom labeling diagram for Cu(bpe)(ddc).

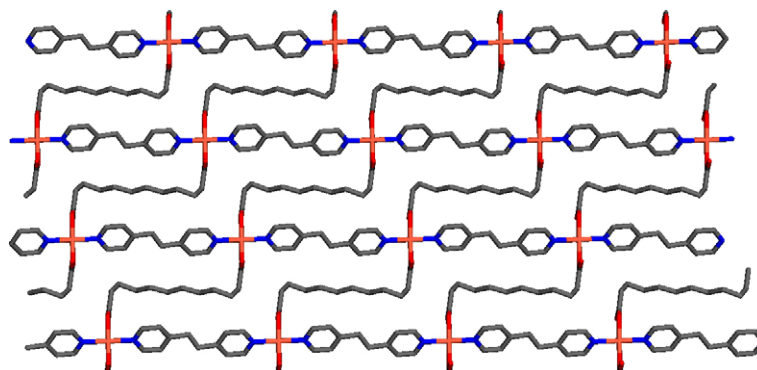


Fig. 2. View of a single 2D net of Cu(bpe)(dde) along *a*-axis.

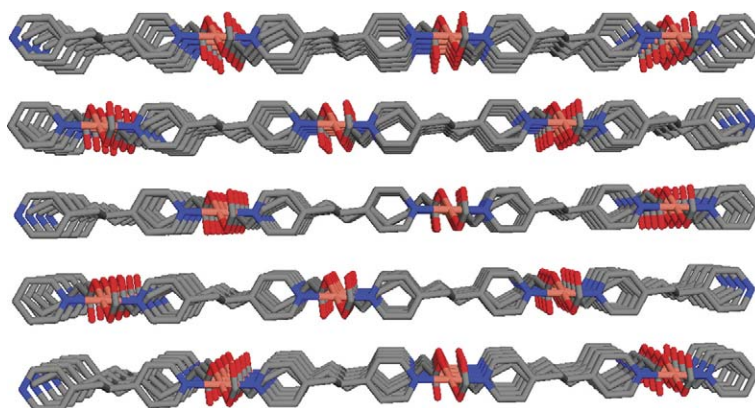


Fig. 3. Perspective view of the crystal structure of Cu(bpe)(dde) showing the packing of 2D nets.

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