



# Crystal structure and characterization of a new one-dimensional copper(II) coordination polymer containing a 4-aminobenzoic acid ligand

Alisha Gogia,<sup>a\*</sup> Egor M. Novikov,<sup>a</sup> Ilia A. Guzei,<sup>b</sup> Marina S. Fonari<sup>c</sup> and Tatiana V. Timofeeva<sup>a</sup>

Received 17 November 2023

Accepted 9 February 2024

Edited by A. S. Batsanov, University of Durham, United Kingdom

**Keywords:** 4-aminobenzoic acid; pABA; one-dimensional coordination polymer; crystal structure.

**CCDC reference:** 2332153

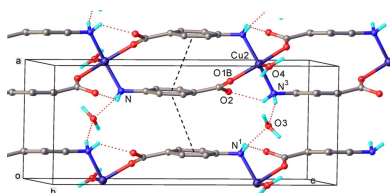
**Supporting information:** this article has supporting information at journals.iucr.org/e

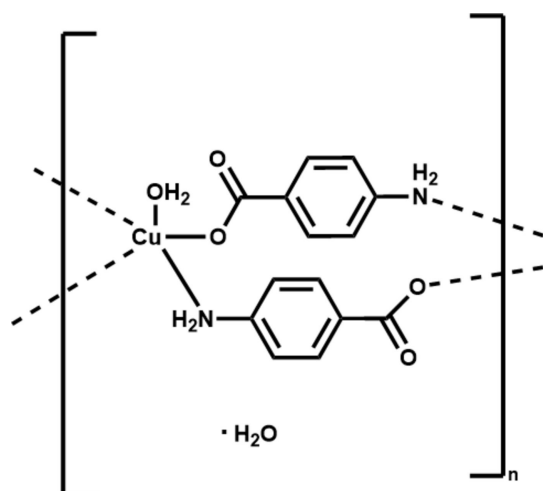
<sup>a</sup>Department of Chemistry, New Mexico Highlands University, Las Vegas, New Mexico, 87701, USA, <sup>b</sup>Chemistry Department, University of Wisconsin-Madison, 1101 University Ave, Madison, WI 53706, USA, and <sup>c</sup>Institute of Applied Physics, Moldova State University, Academy str., 5 MD2028, Chisinau, Moldova. \*Correspondence e-mail: alishagogia@nmhu.edu

A Cu<sup>II</sup> coordination polymer, *catena*-poly[[[aquacopper(II)]-bis( $\mu$ -4-aminobenzoato)- $\kappa^2N:O:\kappa^2O:N$ ] monohydrate], {[Cu(*p*ABA)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> (*p*ABA = *p*-aminobenzoate, C<sub>7</sub>H<sub>4</sub>NO<sub>2</sub><sup>−</sup>), was synthesized and characterized. It exhibits a one-dimensional chain structure extended into a three-dimensional supramolecular assembly through hydrogen bonds and  $\pi$ – $\pi$  interactions. While the twinned crystal shows a metrically orthorhombic lattice and an apparent space group *Pbcm*, the true symmetry is monoclinic (space group *P2/c*), with disordered Cu atoms and mixed roles of water molecules (aqua ligand/crystallization water). The luminescence spectrum of the complex shows an emission at 345 nm, *cf.* 349 nm for *p*ABA.

## 1. Chemical context

Coordination polymers (CPs), which can be categorized in the class of lower dimensional metal–organic frameworks (MOFs), have received great attention in the past few decades owing to the multitude of applications they offer, such as gas storage and separation (Férey, 2008), sensing (Horcajada *et al.*, 2012), drug delivery (Liu *et al.*, 2020), electrochemical applications (Morozan & Jaouen, 2012), adsorption and remediation (Baruah, 2022), magnetic properties (MasPOCH *et al.*, 2004), *etc.* Despite advancements, the anticipation of MOF structures remains an ongoing challenge. Even with reticular synthesis initiated by geometrically analogous ligands, the outcome of structures or ligand behaviors under elevated temperature and pressure conditions, prevalent during synthesis, remains complicated (Szczyński *et al.*, 2021). Occasionally, in the pursuit of creating porous architectures, our efforts yield coordination polymers with unexpected features. In the present work, we attempted to synthesize a porous metal–organic framework based on Cu<sup>II</sup> and a flexible tricarboxylic acid ligand, 4,4',4''-[[[1*E*,1'*E*,1''*E*]-benzene-1,3,5-triyltris(methaneylylidene)] tris(azaneylylidene)]tribenzoic acid (H<sub>3</sub>btta) (Fig. 1). Instead, we obtained a one-dimensional CP, {[Cu(*p*ABA)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O}<sub>n</sub> (I), with the anion of *p*-aminobenzoic acid (*p*ABA), the latter presumably formed by disintegration of H<sub>3</sub>btta in the course of hydrothermal synthesis. Subsequently we synthesized compound (I) from Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O and *p*ABA under the same synthetic conditions. Compound (I) was characterized by single-crystal X-ray diffraction, FTIR spectroscopy and thermogravimetric analysis (TGA).

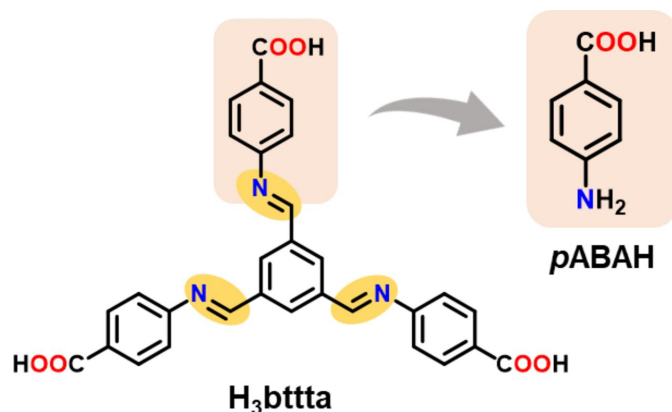




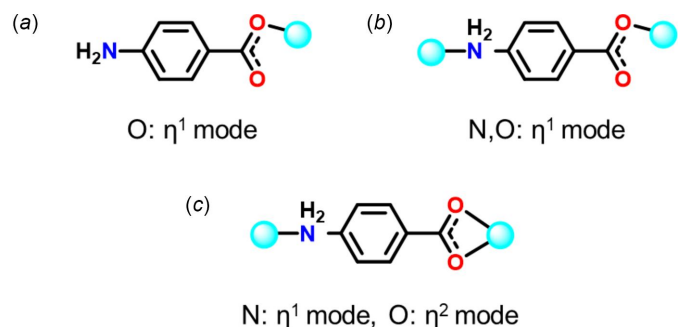
Its anion, *pABA*, is capable of versatile binding with metal ions *via* amino and carboxylic groups (Fig. 2), as well as strong hydrogen bonds and  $\pi$ - $\pi$  stacking interactions, enhancing the overall stability of the CP. Moreover, *pABA*H has a variety of applications, *viz.* as precursor in the synthesis of pharmaceutical compounds, UV absorbers, components in hair dyes, antioxidants, food additives, *etc.*

## 2. Structural commentary

Compound (I) crystallizes in a monoclinic space group  $P2_1/c$ , although the unit cell is metrically orthorhombic. The asymmetric unit comprises half of Cu atom, one *pABA* ligand and one water molecule. The Cu atom is disordered between two alternative sites, Cu1 and Cu2, both located on crystallographic twofold axes, with crystallographic occupancies of 0.3098 (8) and 0.1902 (8), respectively. The carboxylic group is also disordered, the atomic sites C1A and O1A are occupied simultaneously with Cu1 and have occupancies of 0.6196 (16), whereas C1B and O1B are occupied simultaneously with Cu2 and have occupancies of 0.3804 (16). The H atoms of the amino group are also disordered between two sets of positions with the same occupancies, depending on whether the adja-

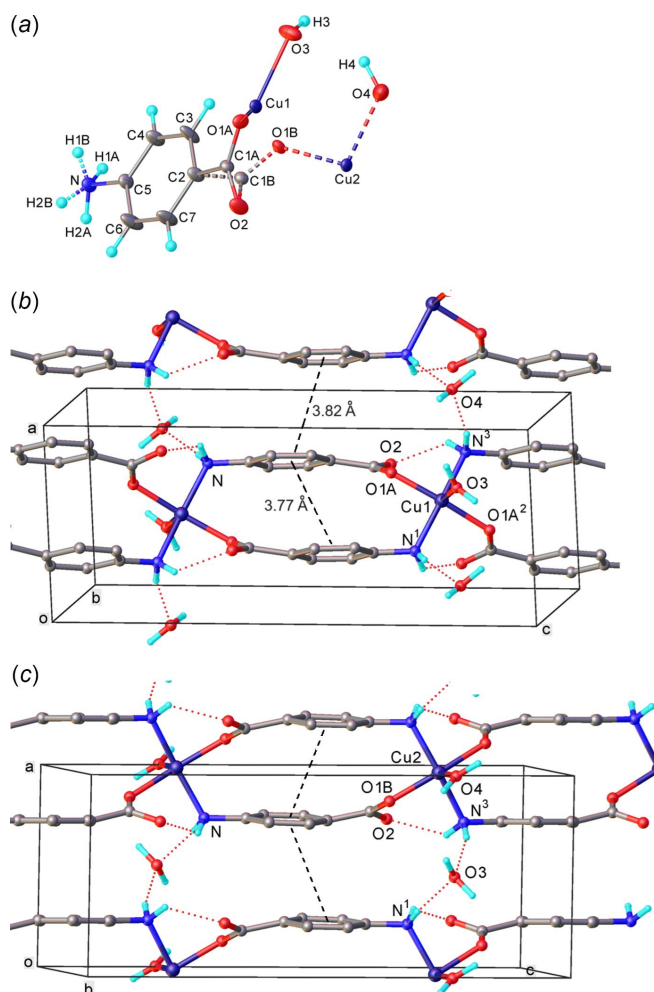


**Figure 1**  
Tricarboxylic ligand ( $H_3btta$ ) used and its fragmentation to *pABA*H under hydrothermal reaction conditions.



**Figure 2**  
Binding modes of the *pABA* ligand in coordination polymers with  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$ ,  $Zn^{II}$  or  $Cd^{II}$  (shown as blue spheres).

cent Cu1 or Cu2 site is occupied and coordinated with N1. The disorder is illustrated in Fig. 3.



**Figure 3**  
Disorder in the crystal of (I). (a) The asymmetric unit, showing atomic displacement ellipsoids at the 30% probability level. The major (solid) and minor (stippled) components have occupancies of 0.6196 (16) and 0.3804 (16), respectively. (b), (c) Crystal packing for these components. In the former, molecule O4H<sub>2</sub> acts as an aqua ligand, O3H<sub>2</sub> as crystallization water, and *vice versa* in the latter. Hydrogen bonds are shown as dotted lines,  $\pi$ - $\pi$  stacking as dashed lines between the centroids of arene rings. Symmetry codes: (1)  $1 - x, 1 - y, 1 - z$ ; (2)  $1 - x, y, \frac{3}{2} - z$ ; (3)  $x, 1 - y, \frac{1}{2} + z$ .

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H3\cdots O2^i$	0.96 (1)	1.84 (1)	2.789 (3)	173 (2)
$O4-H4\cdots O2^i$	0.96 (1)	1.88 (2)	2.791 (3)	159 (3)
$N-H1A\cdots O2^{ii}$	0.91	2.26	2.954 (3)	133
$N-H2A\cdots O4^{iii}$	0.91	2.17	3.050 (4)	163
$N-H1B\cdots O2^{ii}$	0.91	2.26	2.954 (3)	133
$N-H2B\cdots O3^{iv}$	0.91	2.20	3.086 (4)	163

Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $x, -y + 1, z - \frac{1}{2}$ ; (iii)  $-x + 2, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y + 1, -z + 1$ .

It is noteworthy that the atomic positions (including those of the disordered atoms) approximately comply with the orthorhombic symmetry (apparent space group  $Pbcm$ ), but their occupancies do not, therefore refinement of the structure in this symmetry gives a computationally unstable, as well as chemically and crystallographically unreasonable, model.

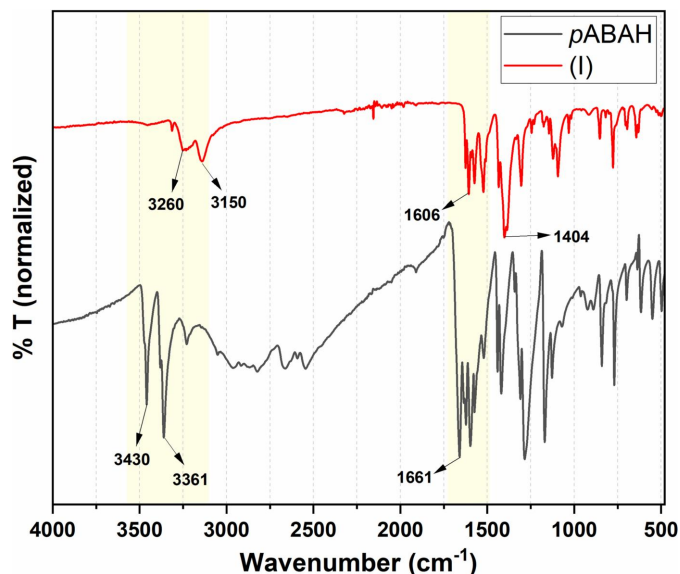
Both the Cu1 and Cu2 sites have an  $N_2O_3$  square-pyramidal coordination environment, in which the apical position is occupied by an aqua ligand (*i.e.* the O3 or O4 atom, respectively), also located on a twofold axis. Note that the water sites, unlike the Cu ones, are fully occupied. Thus, if the Cu1 site is occupied and Cu2 is vacant,  $O3H_2$  is an aqua ligand and  $O4H_2$  is a water molecule of crystallization and *vice versa* if the Cu2 site is occupied.

The *pABA* ligand bridges two adjacent Cu atoms (related by the  $c$  glide plane) through amine nitrogen and carboxylate oxygen atoms in a  $\mu_2-O:N$  binding mode. Thus each Cu atom is linked with two symmetry-equivalent ones by pairs of antiparallel *pABA* ligands (whose two O and two N atoms comprise the basal plane of the pyramid), to form a polymeric chain parallel to the  $c$  axis.

### 3. Supramolecular features

The one-dimensional *catena*-Cu(*pABA*) chains of (I) are combined into a three-dimensional supramolecular structure by a network of hydrogen bonds (Table 1). Both water molecules (whether coordinated or not) donate hydrogen bonds to the non-coordinated carboxylic atom O2 (and its equivalents), forming an infinite zigzag chain  $O2\cdots H-O3-H\cdots O2\cdots H-O4-H\cdots O2$  along the  $a$ -axis direction. The amino group, which is disordered over two orientations (see above), in either case donates one hydrogen bond to a trans-annular O2 and the other to the water molecule, which is not coordinated (the adjacent Cu site being vacant). Thus, while an aqua ligand donates two hydrogen bonds, the crystallization water at the same site donates two and accepts two, from different adjacent Cu(*pABA*) chains.

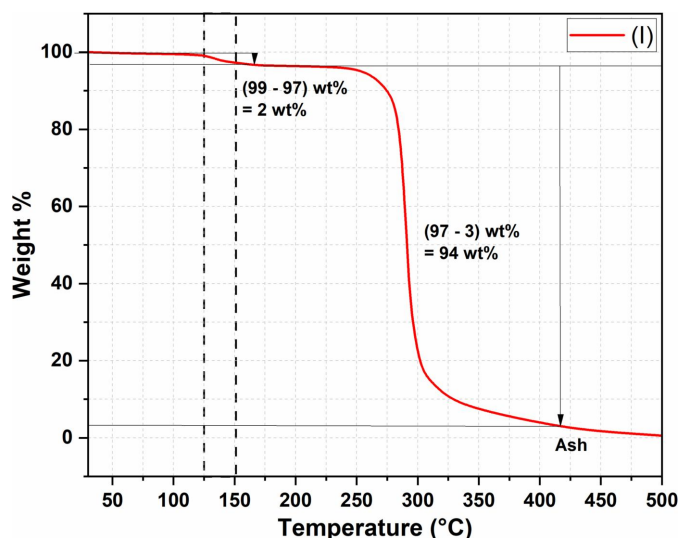
There is  $\pi$ - $\pi$  stacking of practically parallel arene rings of *pABA* (Fig. 3). Infinite stacks run parallel to the  $a$  axis, with alternating interplanar separations of 3.41 (6) and 3.49 (6) Å, lateral shifts between adjacent rings of 1.72 (8) and 1.42 (9) Å, and distances between ring centroids of 3.82 (4) and 3.77 (4) Å, respectively.



**Figure 4**  
FTIR spectra of *pABA* (black) and compound (I) (red).

### 4. Spectroscopic and thermal properties

The FTIR spectra of *pABA* and (I) (Fig. 4) demonstrated successful incorporation of the *pABA* ligand in (I). In comparison to the free ligand, *pABA*, the peaks corresponding to the amine group suffer a decrease in the wavenumber and intensity upon binding to the  $Cu^{II}$  atom in (I), similar to what is observed in other cases in the literature (Crisan *et al.*, 2019). In addition, the peak at  $1661\text{ cm}^{-1}$ , corresponding to the free carboxylic acid in *pABA* is diminished upon metal coordination in (I), Fig. 4. The strong bands at  $1606\text{ cm}^{-1}$  and  $1404\text{ cm}^{-1}$  correspond to the asymmetric ( $\nu_{\text{asym}}$ ) and symmetric ( $\nu_{\text{sym}}$ ) stretching vibrations of the carboxylate group of *pABA* in (I). The difference in the asymmetric and symmetric vibrations ( $\Delta\nu = 202\text{ cm}^{-1}$ ) corresponds to monodentate binding of the carboxylate which corroborates well with the structure of (I).



**Figure 5**  
Thermogravimetric analysis of (I).

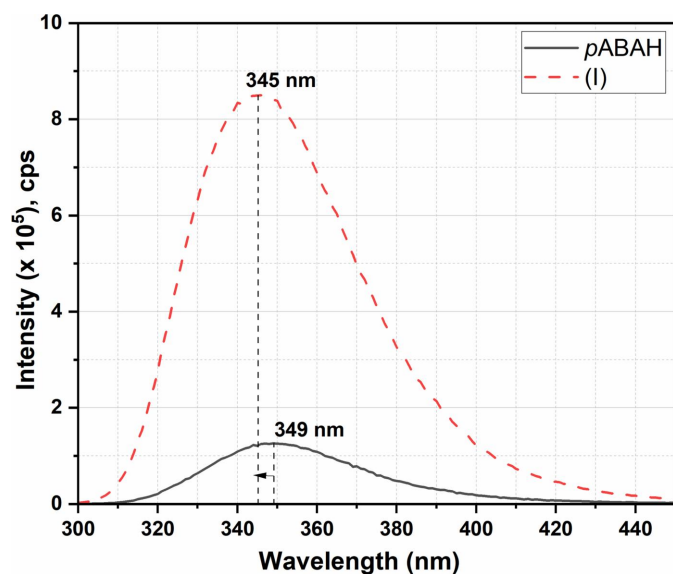
The stability of (I) was studied by thermal gravimetric analysis in the range of 30–500 °C, which shows that (I) is stable up to 300 °C. The initial loss of 2 wt% corresponds to the loss of coordinated water molecules, and the complete decomposition (94 wt%) corresponds to the evolution of CO<sub>2</sub> upon the decomposition of the carboxylate group in the ligand, *p*ABA, leaving behind metal oxide ash (Fig. 5). The percentage of ash left behind is surprisingly lower than expected and might be due to the heterogeneity of the material.

## 5. Luminescence properties

The emission spectra of (I) and the *p*ABA ligand were recorded at room temperature to assess the luminescence properties of the samples. For this, 1 mg of each sample was finely dispersed in 2 mL of water through ultrasonication. Their respective emission spectra were then recorded at an excitation wavelength of 280 nm, and excitation and emission slit widths of 1 and 1 nm, respectively, in the range 300 to 450 nm. It was found that the emission intensity of (I) is much more intense compared to the emission intensity of the pure *p*ABAH ligand in water. Compound (I) also undergoes a slight blue shift of  $\Delta\lambda = 4$  nm, which is representative of the binding of ligand (*p*ABA) with the metal center (Cu<sup>II</sup>) (Fig. 6).

## 6. Database survey

Although *p*ABA is widely used as a ligand in the synthesis of coordination polymers and metal–organic frameworks, a survey of the Cambridge Structural Database (version 5.45, updated on 01/01/2024; Groom *et al.*, 2016) revealed no Cu complexes containing only *p*ABA ligands and coordinated or crystallization water, while such complexes are known for Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup> and Cd<sup>II</sup>. Most of these are one-dimensional coordination polymers, although [Co(*p*ABA)(H<sub>2</sub>O)<sub>4</sub>]



**Figure 6**  
Luminescence emission spectra of pure *p*ABAH and (I) measured at room temperature in water ( $\lambda_{\text{excitation}} = 280$  nm).

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Cu(C <sub>7</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O
<i>M<sub>r</sub></i>	371.83
Crystal system, space group	Monoclinic, <i>P2/c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.9143 (14), 6.2111 (12), 17.169 (3)
$\beta$ (°)	90.05 (3)
<i>V</i> (Å <sup>3</sup> )	737.3 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.52
Crystal size (mm)	0.3 × 0.2 × 0.2
Data collection	
Diffractometer	Bruker SMART APEXII
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.618, 0.745
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	8617, 1477, 1311
<i>R<sub>int</sub></i>	0.027
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.642
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.033, 0.087, 1.09
No. of reflections	1477
No. of parameters	131
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.37, -0.29

Computer programs: *APEX2* (Bruker, 2019), *SAINT-Plus* (Bruker, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

(ABZACO10; Amiraslanov *et al.*, 1979a) crystallizes as discrete molecular units, [Zn(*p*ABA)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O (IWORET; Ibragimov *et al.*, 2016) as a two-dimensional polymer, and [Zn(*p*ABA)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O (RUPZIM; Li *et al.*, 2009) as a three-dimensional MOF. The carboxylic group of *p*ABA is usually monodentate (Amiraslanov *et al.*, 1978; Prondzinski & Merz, 2008), except in Cd<sup>II</sup> complexes ABZCUH (Amiraslanov *et al.*, 1979b) and BESRAS (Turner, *et al.*, 1982), where it is bidentate, and in RUPZIM where both mono- and bidentate coordination is present. Thus, compound (I) shows the most typical structural features, being a 1D coordination polymer with the *p*ABA bridge coordinated *via* the amino group and one carboxylic O atom (Fig. 2b).

It is noteworthy that an isomer of the two-dimensional polymer IWORET (IWORET01; Crisan *et al.*, 2019) is one-dimensional and essentially isostructural with (I), with the same space group *P2/c* and similar unit-cell parameters, *a* = 7.0013 (4), *b* = 6.1301 (2), *c* = 17.1919 (7) Å,  $\beta$  = 92.148 (4)°, albeit without disorder. Another isomer of these, YIMDEO (Prondzinski & Merz, 2008) is 1D-polymeric, but with a tetrahedral (O<sub>3</sub>N) metal coordination and different *p*ABA modes (Fig. 2a,b).

## 7. Synthesis and crystallization

**Synthesis of (I).** A mixture of Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (117 mg, 0.5 mmol), *p*ABAH (68.6 mg, 0.5 mmol) and 10 mL of H<sub>2</sub>O was placed in a 15 mL stainless steel-jacketed Teflon reactor.



The reactor was carefully sealed, placed in the center of a programmable oven (Nabertherm 30–3000°C, S/N. 432847, 2022), and subjected to heating at a gradual rate of 0.1 K min<sup>-1</sup> to 358 K, kept at the same temperature for a duration of 24 h, followed by gradual cooling of K min<sup>-1</sup> to 298 K over 12 h. This afforded green block-shaped clear crystals. The obtained crystals were collected *via* filtration, washed with water (3 × 4 mL), then with ethanol (2 × 4 mL) and air-dried. Yield: 58 mg (65%), based on metal salt. Selected FTIR peaks (KBr, cm<sup>-1</sup>): 3250 (*br*), 3139 (*br*), 1606 (*s*), 1576 (*s*), 1304 (*s*), 1092 (*m*), 854 (*w*), 775 (*m*). The reaction synthesis is similar to that synthesized with H<sub>3</sub>btta, except that 0.034 mmol (174 mg) of H<sub>3</sub>btta were used instead of 0.5 mmol (34.8 mg) of pABAH.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal studied was a merohedral twin with the twin components of equal size related by a 180° rotation about the *c* axis. The water H atoms were refined in isotropic approximation, other H atoms as riding in idealized positions, with  $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}$  of the bearing C or N atom.

## Funding information

Funding for this research was provided by: NSF (grant No. DMR-2122108 (PREM)).

## References

Amiraslanov, I. R., Mamedov, K. S., Movsumov, E. M., Musaev, F. N., Magerramov, A. I. & Nadzhafov, G. N. (1979*b*). *Zh. Strukt. Khim.* **20**, 498–503.

Amiraslanov, I. R., Mamedov, K. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1978). *Zh. Strukt. Khim.* **19**, 1129–1137.

Amiraslanov, I. R., Mamedov, K. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979*a*). *Zh. Strukt. Khim.* **20**, 1075–1080.

Baruah, J. B. (2022). *Coord. Chem. Rev.* **470**, 214694–214723.

Bruker (2019). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2020). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.

Crisan, M. E., Gorobet, A., Siminel, A. V., Bourosh, P. N. & Croitor, L. (2019). *Polyhedron*, **171**, 502–507.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Férey, G. (2008). *Coord. Chem. Rev.* **37**, 191–214.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.

Horcajada, P., Gref, R., Baati, T., Allan, P. K., Maurin, G., Couvreur, P., Férey, G., Morris, R. E. & Serre, C. (2012). *Chem. Rev.* **112**, 1232–1268.

Ibragimov, A. B., Ashurov, J. M. & Zakirov, B. S. (2016). *J. Chem. Crystallogr.* **46**, 352–363.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Li, L., Sun, D., Wang, Z., Song, X. & Sun, S. (2009). *Solid State Sci.* **11**, 1040–1043.

Liu, J. Q., Luo, Z. D., Pan, Y., Kumar Singh, A., Trivedi, M. & Kumar, A. (2020). *Coord. Chem. Rev.* **406**, 213145–213190.

Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2004). *J. Mater. Chem.* **14**, 2713–2723.

Moroza, A. & Jaouen, F. (2012). *Energy Environ. Sci.* **5**, 9269–9290.

Prondzinski, N. V. & Merz, K. (2008). *Z. Anorg. Allg. Chem.* **634**, 555–558.

Sheldrick, G. M. (2015*a*). *Acta Cryst.* **A71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.

Szczypliński, F. T., Bennett, S. & Jelfs, K. E. (2021). *Chem. Sci.* **12**, 830–840.

Turner, R. W., Charles, N. G. E. & Amma, L. (1982). *Cryst. Struct. Commun.* **11**, 241–242.

## supporting information

*Acta Cryst.* (2024). E80, 330-334 [https://doi.org/10.1107/S2056989024001336]

## Crystal structure and characterization of a new one-dimensional copper(II) coordination polymer containing a 4-aminobenzoic acid ligand

Alisha Gogia, Egor M. Novikov, Ilia A. Guzei, Marina S. Fonari and Tatiana V. Timofeeva

### Computing details

*catena*-Poly[[[aquacopper(II)]-bis( $\mu$ -4-aminobenzoato)- $\kappa^2$ N:O; $\kappa^2$ O:N] monohydrate]

#### Crystal data

[Cu(C<sub>7</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O

$M_r = 371.83$

Monoclinic,  $P2_1/c$

$a = 6.9143$  (14) Å

$b = 6.2111$  (12) Å

$c = 17.169$  (3) Å

$\beta = 90.05$  (3)°

$V = 737.3$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 382$

$D_x = 1.675$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2372 reflections

$\theta = 3.0$ – $26.0$ °

$\mu = 1.52$  mm<sup>-1</sup>

$T = 100$  K

Block, clear dark green

$0.3 \times 0.2 \times 0.2$  mm

#### Data collection

Bruker SMART APEXII  
diffractometer

Radiation source: sealed X-ray tube,  
EIGENMANN GmbH

Graphite monochromator

Detector resolution: 7.9 pixels mm<sup>-1</sup>

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.618$ ,  $T_{\max} = 0.745$

8617 measured reflections

1477 independent reflections

1311 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.1$ °,  $\theta_{\min} = 1.2$ °

$h = -8 \rightarrow 8$

$k = -7 \rightarrow 4$

$l = -20 \rightarrow 21$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.087$

$S = 1.09$

1477 reflections

131 parameters

4 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.5003P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.37$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.29$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.500000	0.70928 (13)	0.750000	0.0206 (2)	0.6196 (16)
Cu2	1.000000	0.7095 (2)	0.750000	0.0204 (4)	0.3804 (16)
O1A	0.6443 (6)	0.6835 (6)	0.6512 (2)	0.0262 (8)	0.6196 (16)
O1B	0.8560 (9)	0.6813 (9)	0.6519 (4)	0.0243 (13)	0.3804 (16)
O2	0.7512 (5)	0.3523 (3)	0.68132 (10)	0.0363 (5)	
O3	0.500000	1.0567 (5)	0.750000	0.0468 (9)	
H3	0.586 (4)	1.1507 (11)	0.7225 (18)	0.070*	
O4	1.000000	1.0536 (5)	0.750000	0.0450 (9)	
H4	0.933 (5)	1.1481 (11)	0.7152 (15)	0.067*	
N	0.7528 (6)	0.3218 (3)	0.30662 (11)	0.0259 (5)	
H2A	0.820104	0.197454	0.299519	0.031*	0.6196 (16)
H1A	0.820685	0.428119	0.282487	0.031*	0.6196 (16)
H1B	0.684525	0.428327	0.282761	0.031*	0.3804 (16)
H2B	0.685060	0.197642	0.299792	0.031*	0.3804 (16)
C1A	0.7092 (8)	0.5003 (14)	0.6330 (5)	0.0224 (11)	0.6196 (16)
C1B	0.7949 (14)	0.492 (3)	0.6320 (9)	0.0224 (11)	0.3804 (16)
C2	0.7486 (7)	0.4541 (4)	0.54737 (13)	0.0284 (6)	
C3	0.7403 (8)	0.6201 (4)	0.49334 (15)	0.0424 (8)	
H3A	0.731206	0.764858	0.510783	0.051*	
C4	0.7451 (8)	0.5766 (4)	0.41429 (14)	0.0344 (7)	
H4A	0.742225	0.691677	0.377838	0.041*	
C5	0.7542 (8)	0.3680 (4)	0.38847 (13)	0.0268 (5)	
C6	0.7623 (8)	0.2011 (4)	0.44200 (17)	0.0494 (10)	
H6	0.768947	0.056284	0.424427	0.059*	
C7	0.7608 (8)	0.2452 (4)	0.52089 (16)	0.0420 (8)	
H7	0.768247	0.130184	0.557248	0.050*	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0307 (4)	0.0221 (4)	0.0090 (3)	0.000	-0.0030 (12)	0.000
Cu2	0.0274 (7)	0.0220 (6)	0.0119 (6)	0.000	-0.005 (2)	0.000
O1A	0.038 (2)	0.031 (2)	0.0097 (17)	0.0077 (18)	0.0008 (19)	0.0004 (17)
O1B	0.037 (3)	0.016 (3)	0.020 (3)	-0.005 (3)	-0.002 (4)	0.000 (3)
O2	0.0657 (13)	0.0277 (8)	0.0155 (8)	0.0000 (13)	0.001 (2)	0.0047 (7)
O3	0.0460 (19)	0.0244 (16)	0.070 (2)	0.000	0.017 (4)	0.000
O4	0.0417 (18)	0.0358 (18)	0.057 (2)	0.000	-0.017 (4)	0.000
N	0.0398 (13)	0.0253 (9)	0.0127 (9)	0.0015 (17)	-0.001 (2)	-0.0010 (8)

C1A	0.027 (3)	0.0214 (14)	0.0188 (14)	0.002 (4)	0.002 (4)	-0.0026 (11)
C1B	0.027 (3)	0.0214 (14)	0.0188 (14)	0.002 (4)	0.002 (4)	-0.0026 (11)
C2	0.0508 (16)	0.0221 (12)	0.0121 (11)	0.002 (2)	0.004 (3)	-0.0001 (9)
C3	0.093 (3)	0.0178 (12)	0.0171 (12)	-0.006 (3)	-0.002 (3)	-0.0025 (10)
C4	0.066 (2)	0.0218 (11)	0.0155 (11)	0.000 (2)	0.003 (3)	0.0031 (9)
C5	0.0412 (14)	0.0268 (12)	0.0123 (10)	0.002 (2)	0.000 (2)	-0.0026 (9)
C6	0.107 (3)	0.0222 (13)	0.0189 (13)	0.008 (3)	0.000 (3)	-0.0037 (10)
C7	0.090 (3)	0.0196 (11)	0.0167 (13)	0.004 (2)	-0.001 (2)	0.0046 (10)

*Geometric parameters (Å, °)*

Cu1—O1A <sup>i</sup>	1.975 (4)	N—H2A	0.9100
Cu1—O1A	1.975 (4)	N—H1A	0.9100
Cu1—O3	2.158 (3)	N—H1B	0.9100
Cu1—N <sup>ii</sup>	2.009 (4)	N—H2B	0.9100
Cu1—N <sup>iii</sup>	2.009 (4)	N—C5	1.434 (3)
Cu2—O1B	1.964 (6)	C1A—C2	1.523 (9)
Cu2—O1B <sup>iv</sup>	1.964 (6)	C1B—C2	1.506 (16)
Cu2—O4	2.137 (3)	C2—C3	1.388 (3)
Cu2—N <sup>ii</sup>	1.976 (4)	C2—C7	1.377 (3)
Cu2—N <sup>v</sup>	1.976 (4)	C3—H3A	0.9500
O1A—C1A	1.262 (9)	C3—C4	1.384 (3)
O1B—C1B	1.294 (17)	C4—H4A	0.9500
O2—C1A	1.272 (9)	C4—C5	1.371 (3)
O2—C1B	1.251 (16)	C5—C6	1.386 (4)
O3—H3 <sup>i</sup>	0.957 (3)	C6—H6	0.9500
O3—H3	0.957 (3)	C6—C7	1.382 (4)
O4—H4	0.958 (3)	C7—H7	0.9500
O4—H4 <sup>iv</sup>	0.958 (3)		
O1A <sup>i</sup> —Cu1—O1A	170.7 (2)	C5—N—Cu2 <sup>v</sup>	119.8 (3)
O1A—Cu1—O3	94.66 (12)	C5—N—H2A	107.4
O1A <sup>i</sup> —Cu1—O3	94.66 (12)	C5—N—H1A	107.4
O1A <sup>i</sup> —Cu1—N <sup>ii</sup>	90.96 (15)	C5—N—H1B	107.4
O1A <sup>i</sup> —Cu1—N <sup>iii</sup>	88.14 (15)	C5—N—H2B	107.4
O1A—Cu1—N <sup>iii</sup>	90.96 (15)	O1A—C1A—O2	124.8 (7)
O1A—Cu1—N <sup>ii</sup>	88.14 (15)	O1A—C1A—C2	118.3 (7)
N <sup>iii</sup> —Cu1—O3	95.52 (6)	O2—C1A—C2	116.9 (6)
N <sup>ii</sup> —Cu1—O3	95.52 (6)	O1B—C1B—C2	117.8 (12)
N <sup>iii</sup> —Cu1—N <sup>ii</sup>	168.96 (12)	O2—C1B—O1B	122.1 (13)
O1B <sup>iv</sup> —Cu2—O1B	169.8 (3)	O2—C1B—C2	119.5 (11)
O1B—Cu2—O4	95.11 (17)	C3—C2—C1A	119.8 (4)
O1B <sup>iv</sup> —Cu2—O4	95.11 (17)	C3—C2—C1B	122.4 (7)
O1B <sup>iv</sup> —Cu2—N <sup>ii</sup>	90.4 (2)	C7—C2—C1A	120.5 (4)
O1B—Cu2—N <sup>ii</sup>	88.6 (2)	C7—C2—C1B	117.0 (6)
N <sup>ii</sup> —Cu2—O4	95.64 (7)	C7—C2—C3	118.8 (2)
N <sup>v</sup> —Cu2—O4	95.64 (7)	C2—C3—H3A	119.7
N <sup>ii</sup> —Cu2—N <sup>v</sup>	168.72 (13)	C4—C3—C2	120.6 (2)



C1A—O1A—Cu1	117.8 (5)	C4—C3—H3A	119.7
C1B—O1B—Cu2	118.2 (8)	C3—C4—H4A	119.9
Cu1—O3—H3 <sup>i</sup>	127.6 (4)	C5—C4—C3	120.2 (2)
Cu1—O3—H3	127.6 (4)	C5—C4—H4A	119.9
H3—O3—H3 <sup>i</sup>	104.8 (8)	C4—C5—N	120.4 (2)
Cu2—O4—H4	127.8 (4)	C4—C5—C6	119.6 (2)
H4—O4—H4 <sup>iv</sup>	104.4 (8)	C6—C5—N	120.0 (2)
Cu1 <sup>iii</sup> —N—H2A	107.4	C5—C6—H6	120.0
Cu1 <sup>iii</sup> —N—H1A	107.4	C7—C6—C5	120.1 (2)
Cu2 <sup>v</sup> —N—H1B	107.4	C7—C6—H6	120.0
Cu2 <sup>v</sup> —N—H2B	107.4	C2—C7—C6	120.7 (2)
H2A—N—H1A	106.9	C2—C7—H7	119.6
H1B—N—H2B	106.9	C6—C7—H7	119.6
C5—N—Cu1 <sup>iii</sup>	119.9 (3)		
Cu1—O1A—C1A—O2	-26.2 (8)	O2—C1B—C2—C3	161.0 (7)
Cu1—O1A—C1A—C2	156.5 (4)	O2—C1B—C2—C7	-34.5 (11)
Cu1 <sup>iii</sup> —N—C5—C4	-86.6 (6)	N—C5—C6—C7	-179.1 (5)
Cu1 <sup>iii</sup> —N—C5—C6	92.6 (5)	C1A—C2—C3—C4	-169.7 (5)
Cu2—O1B—C1B—O2	30.0 (12)	C1A—C2—C7—C6	168.5 (5)
Cu2—O1B—C1B—C2	-159.1 (6)	C1B—C2—C3—C4	163.9 (6)
Cu2 <sup>v</sup> —N—C5—C4	93.1 (5)	C1B—C2—C7—C6	-165.9 (7)
Cu2 <sup>v</sup> —N—C5—C6	-87.7 (5)	C2—C3—C4—C5	1.4 (9)
O1A—C1A—C2—C3	9.4 (9)	C3—C2—C7—C6	-0.8 (8)
O1A—C1A—C2—C7	-159.8 (5)	C3—C4—C5—N	178.0 (5)
O1B—C1B—C2—C3	-10.2 (12)	C3—C4—C5—C6	-1.3 (9)
O1B—C1B—C2—C7	154.3 (7)	C4—C5—C6—C7	0.2 (9)
O2—C1A—C2—C3	-168.2 (5)	C5—C6—C7—C2	0.9 (9)
O2—C1A—C2—C7	22.7 (8)	C7—C2—C3—C4	-0.3 (8)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 $\cdots$ O2 <sup>vi</sup>	0.96 (1)	1.84 (1)	2.789 (3)	173 (2)
O4—H4 $\cdots$ O2 <sup>vi</sup>	0.96 (1)	1.88 (2)	2.791 (3)	159 (3)
N—H1A $\cdots$ O2 <sup>vii</sup>	0.91	2.26	2.954 (3)	133
N—H2A $\cdots$ O4 <sup>v</sup>	0.91	2.17	3.050 (4)	163
N—H1B $\cdots$ O2 <sup>vii</sup>	0.91	2.26	2.954 (3)	133
N—H2B $\cdots$ O3 <sup>iii</sup>	0.91	2.20	3.086 (4)	163

Symmetry codes: (iii)  $-x+1, -y+1, -z+1$ ; (v)  $-x+2, -y+1, -z+1$ ; (vi)  $x, y+1, z$ ; (vii)  $x, -y+1, z-1/2$ .