

catena-Poly[[[(di-2-pyridylamine- $\kappa^2N^2,N^{2'}$)copper(II)]- μ -benzene-1,3-dicarboxylato- $\kappa^3O^1,O^{1'}:O^3$] mono-hydrate], a zigzag coordination polymer with strong π - π interactions

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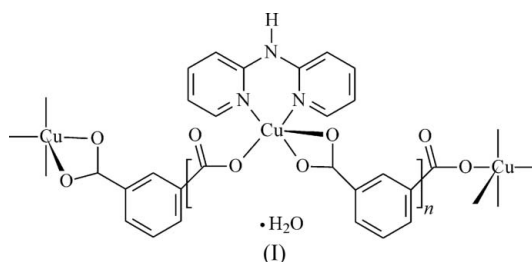
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The novel title coordination polymer, $\{[\text{Cu}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{10}\text{H}_9\text{N}_3)]\cdot\text{H}_2\text{O}\}_n$, synthesized by the slow-diffusion method, takes the form of one-dimensional zigzag chains built up of Cu^{II} cations linked by benzene-1,3-dicarboxylate (ipht) anions. An exceptional characteristic of this structure is that it belongs to a small group of metal-organic polymers where ipht is coordinated as a bridging tridentate ligand with monodentate and chelate coordination of individual carboxylate groups. The Cu^{II} cation has a highly distorted square-pyramidal geometry formed by three O atoms from two ipht anions and two N atoms from a di-2-pyridylamine (dipya) ligand. The zigzag chains, which run along the *b* axis, further construct a three-dimensional metal-organic framework *via* strong face-to-face π - π interactions and hydrogen bonds. A solvent water molecule is linked to the different carboxylate groups *via* hydrogen bonds. Thermogravimetric and differential scanning calorimetric analyses confirm the strong hydrogen bonding.

Comment

The design and synthesis of mixed metal-organic coordination polymers are of current interest in the fields of supramolecular chemistry and crystal engineering, not only for the fascinating architectures and structural diversity of these compounds, but also for their potential applications as functional materials (Li & Wei, 2007; Cui *et al.*, 2009; Du *et al.*, 2009; Shyu *et al.*, 2009; Huang *et al.*, 2010; Liu *et al.*, 2010). An effective approach for the synthesis of such complexes is the appropriate choice of aromatic polycarboxylate ligands as bridges with a variety of transition metal ions as nodes. During the past decade, there have been many reports of the synthesis of coordination compounds where dianions of benzene-1,3-dicarboxylic (iso-

phthalic) acid (H_2ipht) combined with aromatic N-containing chelating ligands have been used to assemble a wide range of coordination polymers from chains to sheets to networks (see, for example, Liu *et al.*, 2008; Ma, Liu *et al.*, 2010). The multi-dimensional framework structures formed by these combinations of aromatic ligands are often stabilized *via* noncovalent intermolecular forces, *viz.* hydrogen bonds and/or π - π interactions (Zhang *et al.*, 2003; Li & Wei, 2007; An *et al.*, 2008; Li *et al.*, 2009; Ma *et al.*, 2009; Guo *et al.*, 2010; He *et al.*, 2010). The title compound, $\{[\text{Cu}(\text{ipht})(\text{dipya})]\cdot\text{H}_2\text{O}\}_n$ (I), where dipya is di-2-pyridylamine, represents a new example, comprising a three-dimensional structure built up from one-dimensional zigzag polymeric chains.



In (I), Cu^{II} cations are surrounded by three O atoms from two carboxylate groups of neighbouring ipht anions and two N atoms from dipya ligands, forming a (4+1) coordination polyhedron, which can be described as a square pyramid with a tetrahedrally distorted basal plane (Fig. 1). The dihedral angle between coordinated carboxylate groups is $82.73(8)^\circ$. The bond distances between the Cu^{II} cation and atoms O1, O2 and O4 (Table 1) are within the usual ranges for complexes where monodentate and chelate carboxylate groups of ipht or substituted ipht are present (Li & Wei, 2007; Cui *et al.*, 2009; Du *et al.*, 2009; Su *et al.*, 2009; Zeng *et al.*, 2009; Al-Hashemi *et al.*, 2010; Guo *et al.*, 2010). The chelate O1-Cu1-O2 angle [$56.76(6)^\circ$] is also similar to those found in these related

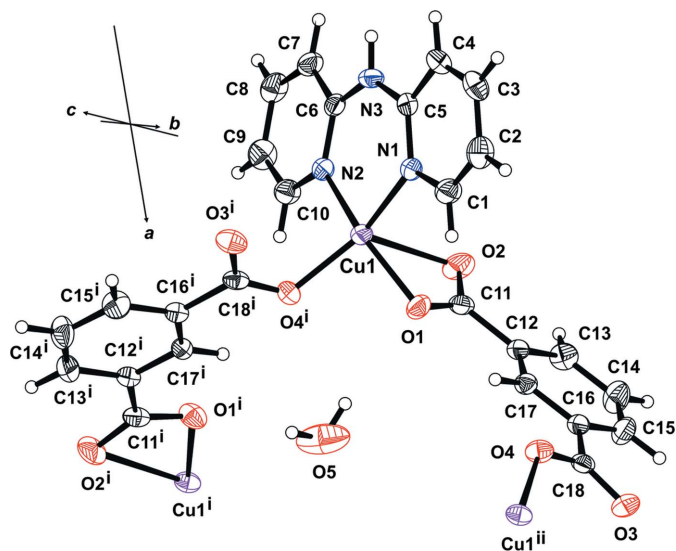


Figure 1
Part of the polymeric zigzag chain of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 40% probability level. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

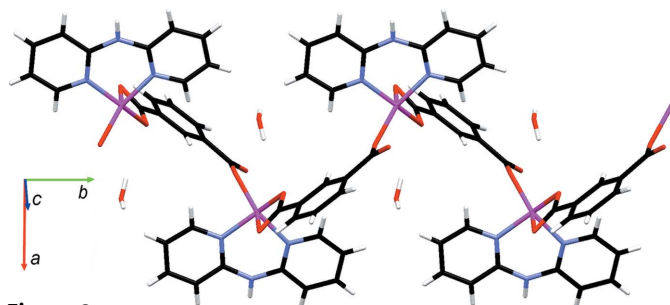


Figure 2
The zigzag chain of (I), running along the *b* axis.

structures. Due to the constraints imposed by chelation, the coordination polyhedron of Cu1 is highly distorted.

As expected, the apical Cu1–O2 bond distance [2.546 (2) Å] is significantly longer than the remaining four distances in the Cu1 coordination polyhedron (Table 1). Nevertheless, according to bond-valence analysis (Wills, 2009), atom Cu1 is oversaturated (2.21 bond valence units). A short Cu1–O3ⁱ contact of 3.0229 (18) Å [symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$], which is only slightly longer than the sum of the van der Waals radii (2.92 Å; Bondi, 1964), should also be mentioned. Since the O2–Cu1–O3ⁱ angle is 160.56 (5)°, the Cu1 environment could also be described as an extremely deformed very elongated octahedron.

As usual, dipya is a chelating ligand in (I), while the ipht anions act as bridging tridentate ligands with monodentate (C18/O3/O4) and chelating (C11/O1/O2) carboxylate groups, forming one-dimensional zigzag chains running along the *b* axis (Fig. 2). The distance between two Cu1 atoms bridged by the ipht anion is 11.7216 (5) Å, while the shortest interchain Cu1···Cu1 distance is 7.9931 (4) Å. Very similar zigzag chains are found in [Zn(ipht)(1-methylimidazole)₂]_n (Zhao, 2008*a*), [Co(ipht)(1-ethylimidazole)₂]_n (Zhao, 2008*b*), [Cu(tbipht)(bipy)]_n (bipy is 2,2'-bipyridine and tbipht is 5-*tert*-butylisophthalate; Li & Huang, 2008) and {[Mn(ipht)(bipy)(H₂O)₂·H₂O]_n (Ma, Hu *et al.*, 2010). In (I), the ipht aromatic ring and the entire dipya ligand are nearly perpendicular to each other [dihedral angle = 82.20 (6)°]. Considering the bridging role of the ipht anion, the value of this angle is probably the main reason for the existence of the zigzag chains.

All the dipya ligands in (I) are oriented approximately parallel to the (10 $\bar{2}$) plane (Fig. 3). This enables stacking of the chains by face-to-face π – π interactions between neighbouring dipya ligands. Although in mixed metal–organic complexes (Rogan *et al.*, 2006) the dihedral angle between the two pyridine rings of dipya can reach 29°, in (I) this angle is very small [7.68 (7)°] and both pyridine rings are involved in π – π interactions. The shortest distances between C atoms of neighbouring dipya ligands are 3.307 (4) Å for C5···C5^v and 3.303 (4) Å for C6···C6^v [symmetry code: (v) $-x, y, \frac{1}{2} - z$], with corresponding C_g···C_g^v separations between aromatic rings of 3.502 (7) and 3.678 (7) Å, respectively; these values confirm strong face-to-face π – π interactions (Janiak, 2000). In this way, hydrophilic and hydrophobic layers parallel to the *bc* plane are formed. With a few exceptions, *e.g.* where π – π interactions with centroid–centroid distances of around 3.2

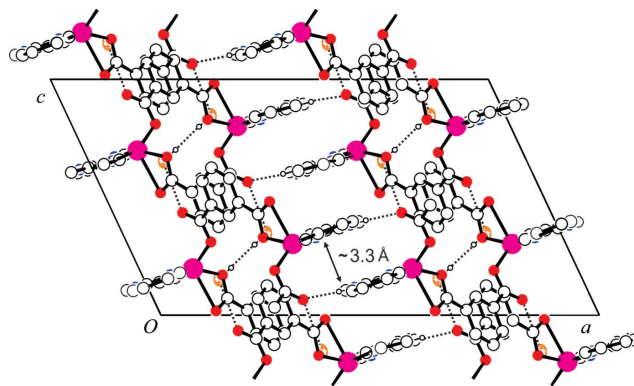


Figure 3
A projection of (I) along the *b* axis, showing the crystal packing, π – π interactions and hydrogen bonding (dashed lines). For emphasis, solvent water molecules are shown with displacement ellipsoids (orange in the electronic version of the paper).

(Guo *et al.*, 2010) and 3.3 Å (Zhang *et al.*, 2003; Li *et al.*, 2009) were found, in most reported ipht and substituted ipht complexes the π – π interactions are weaker and the distances are in the range 3.5–3.9 Å (Zhang *et al.*, 2003; Li & Wei, 2007; An *et al.*, 2008; Ma *et al.*, 2009; Guo *et al.*, 2010; He *et al.*, 2010).

In addition to π – π interactions, the zigzag chains in (I) are also interconnected *via* hydrogen bonding, yielding a three-dimensional metal–organic framework (Fig. 3). The hydrogen-bonding geometry is listed in Table 2. Three of the four hydrogen bonds are between the H₂O molecule and O atoms from different carboxylate groups, while the fourth is between amine atom H5 from dipya and uncoordinated atom O3 from the monodentate C18/O3/O4 group (Table 2). Atom O3 acts as a double hydrogen-bond acceptor from the already mentioned atom H5 and from atom H11 of the uncoordinated water molecule. The remaining H atom (H12) of the water molecule very likely participates in two hydrogen bonds, and therefore this bond can be described as bifurcated. The *D*···*A* distance for O5–H12···O1ⁱⁱⁱ is longer but the angle is acceptable, which is not the case for O5–H12···O4ⁱⁱⁱ, where the distance is suitable but a much smaller angle [127 (3)°] is found (distances and symmetry codes are in Table 2).

Since the initial positions of the H atoms were not found in ΔF maps but were generated using a combined geometric and force-field approach (Nardelli, 1999), they can not be considered as very reliable. For a better insight into the strength of the hydrogen bonding in (I), thermogravimetric and differential scanning calorimetric (TG and DSC) analyses were performed. It was found that the TG and DSC curves of (I) are practically identical to the recently published curves of the corresponding polycrystalline complex (Rogan *et al.*, 2011), so only dehydration will be discussed here. The dehydration is a single-step process and the mass loss of 4.5% between 396 and 450 K is attributed to the loss of the solvent H₂O molecule (calculated 4.3%). The endothermic peak in the DSC curve relating to the dehydration process gives a molar enthalpy of 50.4 kJ mol^{–1} which, together with the high final dehydration temperature, indicates strong hydrogen bonding. A similar value of the dehydration molar enthalpy was recently found for an Mn^{II} complex {[Mn(C₅O₅)(bipy)-

(H₂O)]·H₂O)_n (Chen *et al.*, 2010), where the solvent H₂O molecule participates in two hydrogen bonds but with significantly shorter *D*···*A* distances (2.88–2.98 Å). At the same time, a detailed analysis of analogous terephthalate complexes (Rogan & Poleti, 2004) showed that the mean energy of a hydrogen bond should be about 16 kJ mol⁻¹ or slightly higher. Therefore, the hydrogen bonds in (I) are stronger than expected and it is evident that all three hydrogen bonds in which the solvent H₂O molecule participates really exist.

Metal-organic polymers where ipht is coordinated as a bridging tridentate ligand with monodentate and chelate carboxylate groups are quite rare among the numerous ipht complexes. To the best of our knowledge, in total four such transition metal complexes have been described so far (Li & Wei, 2007; Cui *et al.*, 2009; Su *et al.*, 2009; Al-Hashemi *et al.*, 2010), but two of them (Su *et al.*, 2009; Al-Hashemi *et al.*, 2010) contain two chemically different ipht anions, *i.e.* one anion is not a bridging tridentate ligand. In addition, five complexes are known containing derivatives of ipht coordinating in the same mode to Cu^{II} (Guo *et al.*, 2010) or Co^{II} (Du *et al.*, 2009; Zeng *et al.*, 2009) as the central atoms. The predominant coordination number of the transition metal atoms in these complexes is 6.

The similarities in geometry between (I) and comparable metal-organic polymers are related to the dihedral angle between the plane of the benzene ring of the polycarboxylate ligand and the chelate or monodentate carboxylate group, as well as that between the planes of the chelate and monodentate carboxylate group. With one exception (Table 3), these angles do not exceed 25°. Accordingly, a general characteristic of (I) and related complexes containing ipht or its derivatives is that these kinds of ligands do not deviate very much from planarity. It seems that higher dihedral angles in several complexes (Table 3) are associated with the bulkiness of the second ligand (Al-Hashemi *et al.*, 2010), the bulkiness of the substituent on the ipht ligand (Du *et al.*, 2009) or the overall bulkiness of the complex unit (Guo *et al.*, 2010). The same coordination mode for polycarboxylate ligands is presumably the main explanation for the minor deviations between the stated dihedral angles.

Experimental

Single crystals of (I) were obtained by a modification of the slow-diffusion method. A mixture containing Cu(NO₃)₂·3H₂O (60 mg, 0.25 mmol), di-2-pyridylamine (43 mg, 0.25 mmol) and H₂ipht (42 mg, 0.25 mmol) was dissolved in dimethyl sulfoxide (12 ml). The mixture was stirred for 10 min and then transferred to a small test tube. A dilute solution of Na₂ipht in H₂O (0.05 M) was then layered on top carefully and very slowly in order to minimize mixing of the solutions. The first prismatic green crystals of (I) appeared within 24 h, but single crystals of a suitable size for analysis were filtered off after about 10 d. The complex is stable in air and insoluble in all common solvents. The thermal properties of (I) were examined from room temperature up to 973 K on an SDT Q600 TGA/DSC instrument (TA Instruments). The heating rate was 20 K min⁻¹ using less than 10 mg sample mass. The furnace atmosphere consisted of dry nitrogen at a flow rate of 100 cm³ min⁻¹.

Table 1
Selected bond lengths (Å).

Cu1—O4 ⁱ	1.9250 (15)	Cu1—N1	1.9806 (18)
Cu1—O1	1.9356 (15)	Cu1—O2	2.546 (2)
Cu1—N2	1.9650 (17)	Cu1—O3 [†]	3.0229 (18)

Symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O5—H11···O3 ⁱ	0.84 (3)	2.21 (3)	3.017 (4)	159 (2)
O5—H12···O1 ⁱⁱ	0.85 (2)	2.51 (3)	3.346 (3)	167 (3)
O5—H12···O4 ⁱⁱⁱ	0.85 (2)	2.53 (4)	3.117 (4)	127 (3)
N3—H5···O3 ^{iv}	0.86	1.95	2.813 (3)	178

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

Crystal data

[Cu(C ₈ H ₄ O ₄)(C ₁₀ H ₉ N ₃)]·H ₂ O	<i>V</i> = 3394.1 (3) Å ³
<i>M_r</i> = 416.87	<i>Z</i> = 8
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 23.2351 (11) Å	<i>μ</i> = 1.32 mm ⁻¹
<i>b</i> = 11.7216 (4) Å	<i>T</i> = 295 K
<i>c</i> = 13.7825 (7) Å	0.29 × 0.16 × 0.10 mm
<i>β</i> = 115.285 (6)°	

Data collection

Oxford Gemini-S diffractometer	8071 measured reflections
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	3214 independent reflections 2473 reflections with <i>I</i> > 2σ(<i>I</i>) <i>R</i> _{int} = 0.021
<i>T</i> _{min} = 0.700, <i>T</i> _{max} = 0.879	

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.030	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.076	Δρ _{max} = 0.45 e Å ⁻³
<i>S</i> = 0.96	Δρ _{min} = -0.34 e Å ⁻³
3214 reflections	
250 parameters	
2 restraints	

C-bound H atoms and amine atom H5 of the dipya ligand were positioned geometrically and refined as riding, with C—H = 0.93 Å and N—H = 0.86 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N). The initial positions of water atoms H11 and H12 were calculated using the program *HYDROGEN* (Nardelli, 1999) and then refined with O—H restrained to 0.85 (1) Å and with *U*_{iso}(H) = 1.5*U*_{eq}(O5).

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *PARST* (Nardelli, 1995).

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Table 3

Selected dihedral angles (°) for (I) and some related compounds.

3-bpo is 2,5-bis(3-pyridyl)-1,3,4-oxadiazole, miphth is 5-methylisophthalate, moiphth is 5-methoxyisophthalate, 5-NH₂-iphth is 5-aminoisophthalate, phen is 1,10-phenanthroline, tbiphth is 5-*tert*-butylisophthalate, dm4bt is 2,2'-dimethyl-4,4'-bithiazole and tib is 1,3,5-triimidazol-1-ylbenzene.

Compound	Benzene ring–chelate COO [−] group	Benzene ring–monodentate COO [−] group	Chelate–monodentate COO [−] group
(I)	9.37	6.07	9.34
{[Cu(iphth)(C ₆ H ₅ N ₃)(H ₂ O)]·C ₆ H ₅ N ₃] _n ^a	6.43	12.64	13.65
[Ni(iphth)(2,4'-bipyridine) ₂ (H ₂ O)] _n ^b	0.81	7.80	8.61
{[Cu(miphth)(3-bpo)(H ₂ O)]·0.5H ₂ O] _n ^c	7.23	17.92	25.15
{[Cu(moiphth)(3-bpo)(H ₂ O)]·0.5H ₂ O] _n ^c	7.98	12.24	20.12
{[Co(5-NH ₂ -iphth)(4,4'-bipyridine) _{0.5} (H ₂ O)]·2H ₂ O] _n ^d	9.10	3.15	11.50
{[Co(tbiphth)(H ₂ O)(phen)]·H ₂ O] _n ^e	18.89	2.79	21.64
{[Cu(iphth)(dm4bt)(H ₂ O)] ₄ ·2H ₂ O] _n ^f	12.88	23.45	23.69
{[Zn ₂ (iphth) ₂ (H ₂ O)(tib)]·2H ₂ O] _n ^g	4.75	5.51	9.04
[Co ₄ (tbiphth) ₄ (2,2'-bipyridine) ₄ (H ₂ O)] _n ^e	26.16	6.38	32.48

References: (a) Li & Wei (2007); (b) Cui *et al.* (2009); (c) Guo *et al.* (2010); (d) Zeng *et al.* (2009); (e) Du *et al.* (2009); (f) Al-Hashemi *et al.* (2010); (g) Su *et al.* (2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3138). Services for accessing these data are described at the back of the journal.

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