

**(Acetato- $\kappa$ O)aqua(1*H*-imidazole- $\kappa$ N<sup>3</sup>)-  
(picolinato- $\kappa^2$ N,*O*)copper(II) 0.87-hy-  
drate: a  $Z' > 1$  structure****Anne-Christine Chamayou,<sup>a</sup> Chaitali Biswas,<sup>b</sup> Ashutosh  
Ghosh<sup>b\*</sup> and Christoph Janiak<sup>a\*</sup>**<sup>a</sup>Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany, and <sup>b</sup>Department of Chemistry, University College of Science and Technology, University of Calcutta, 92 APC Road, Kolkata 700 009, India

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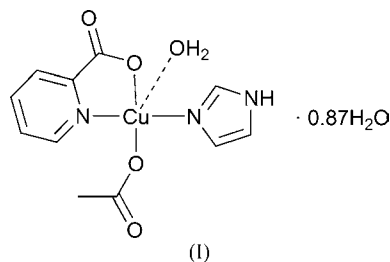
The crystal structure of the title compound, [Cu(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)(C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>)(H<sub>2</sub>O)]·0.87H<sub>2</sub>O, has a square-pyramidal-coordinated Cu<sup>II</sup> centre (the imidazole is *trans* to the picolinate N atom, the acetate is *trans* to the picolinate –CO<sub>2</sub> group and the aqua ligand is in a Jahn–Teller-elongated apical position) and has two symmetry-independent molecules in the unit cell ( $Z' = 2$ ), which are connected through complementary imidazole–picolinate N–H···O hydrogen bonding. The two partially occupied solvent water molecules are each disordered over two positions. The disordered solvent water molecules, together with pseudosymmetry elements, support the notion that a crystal structure with multiple identical chemical formula units in the structural asymmetric unit ( $Z' > 1$ ) can represent a crystal ‘on the way’, that is, a kinetic intermediate form which has not yet reached its thermodynamic minimum. Neighbouring molecules form  $\pi$ – $\pi$  stacks between their imidazole and picolinate N-heterocycles, with centroid–centroid distances in the range 3.582 (2)–3.764 (2) Å.

**Comment**

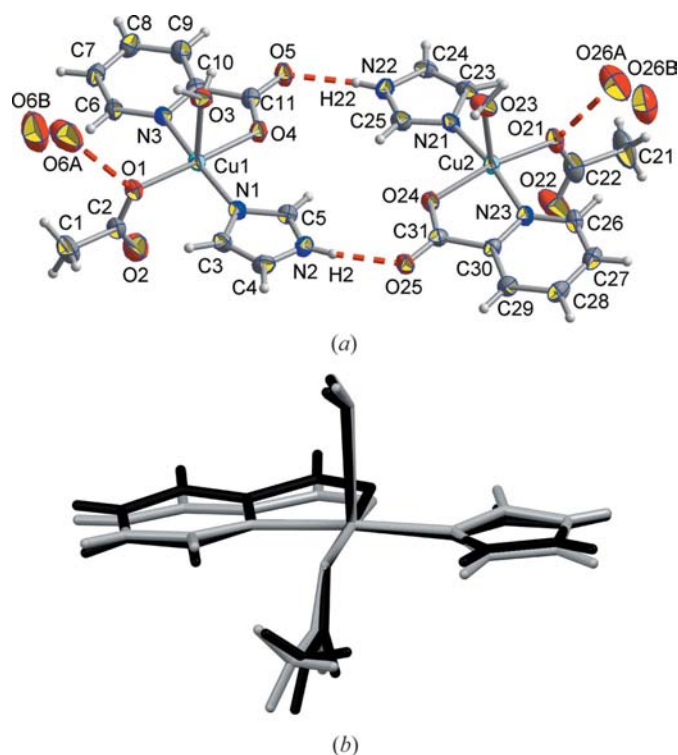
The asymmetric unit of the title complex, (I), has two identical chemical formula units ( $Z' = 2$ ), *i.e.* two symmetry-independent molecules including the partially occupied and disordered solvent water (Fig. 1*a*). The two independent molecules have similar structural data, hence there is no immediately apparent significant conformational difference (Fig. 1*b*). The Cu<sup>II</sup> centres are in square-pyramidal environments (Addison  $\tau$  parameter = 0.10; Addison *et al.*, 1984), with *trans* N- and *trans* O-donor atoms, respectively, and long apical Cu–OH<sub>2</sub> bonds due to the Jahn–Teller effect.

Bond lengths and angles in (I) are as expected. The crystal packing is governed by O–H···O and N–H···O hydrogen

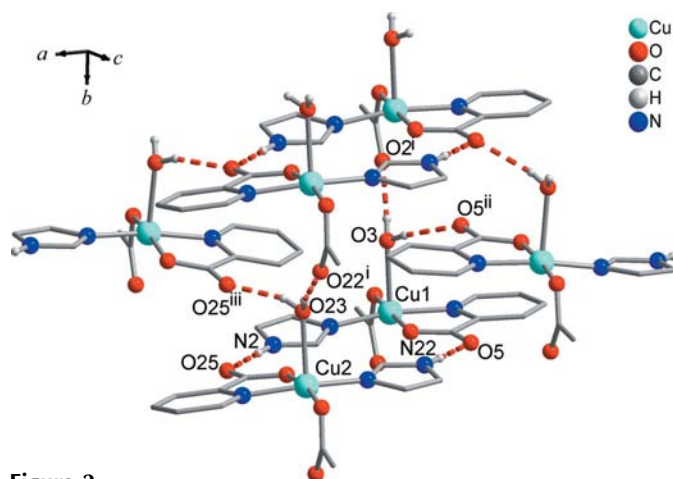
bonding (Table 1 and Fig. 2), the geometric parameters of which are within the normal range (Habib & Janiak, 2008; Wisser & Janiak, 2007*a,b*). Complementary N–H···O hydrogen bonds are formed between the two symmetry-independent complex molecules from their imidazole N–H to the uncoordinated picolinate carboxylate O atom (Fig. 1*a*). The aqua ligand forms hydrogen bonds to both uncoordinated carboxylate O atoms of the picolinate and acetate ligands



(Fig. 2). Together, these hydrogen bonds give a two-dimensional hydrogen-bonded double layer parallel to the *ab* plane (Fig. 2). Furthermore, the partially occupied solvent water atoms O6A and O26A form hydrogen bonds between acetate atoms O1 and O2, and O21 and O22, respectively, of two adjacent molecules along *b* (H atoms could not be found).  $\pi$ – $\pi$

**Figure 1**

(*a*) The asymmetric unit of (I), showing the atom-numbering scheme and the two identical chemical formula units, *i.e.* the two symmetry-independent molecules with their complementary hydrogen bonds (dashed lines; details in Table 1) and the disordered solvent water O atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (*b*) An overlay of the two symmetry-independent molecules in (I), by specifying Cu1/Cu2, acetate O1/O21 and picolinate N3/23 as pairs (r.m.s. deviation = 0.00464 Å). Molecule 1 (black) is that with atom Cu1 and molecule 2 (grey) that with atom Cu2.



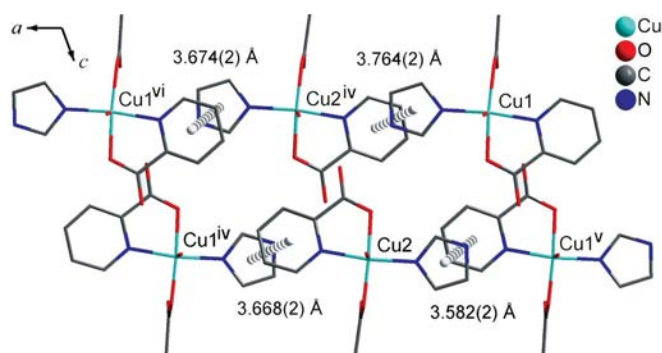
**Figure 2**

A packing diagram for (I), showing the hydrogen-bonding interactions (dashed lines) given in Table 1. C atoms are depicted in stick mode for clarity.

interactions between the picolinate and imidazole rings add to the supramolecular two-dimensional double layer parallel to the *ab* plane (Fig. 3). The  $\pi$ - $\pi$  stacking interactions can be viewed as strong because of the rather short centroid-centroid contacts [3.582 (2)–3.764 (2) Å], small slip angles (23–28°) and short interplanar separations [3.128 (1)–3.361 (1) Å], which translate into a sizeable overlap of the nearly parallel aromatic planes [interplanar angle = 4.83 (2) or 9.78 (2)°] (Janiak, 2000).

There is ongoing discussion of the origin of crystal structures with multiple identical molecules, *i.e.* formula units in the structural asymmetric unit or so-called  $Z' > 1$  structures (Gavezotti, 2008; van Eijck & Kroon, 2000). These can be regarded as a 'fossil relic' of a more stable form (Steed, 2003), as strong and special supramolecular interactions between the symmetry-independent units (Althoff *et al.*, 2006; Babu & Nangia, 2007; Hao *et al.*, 2005) or as a crystal 'on the way', that is, the crystal is the kinetic rather than thermodynamic product of the crystallization process (Desiraju, 2007; Nichol & Clegg, 2007; Ruiz *et al.*, 2008). The impossibility of packing chiral molecules in a centrosymmetric structure can also lead to the presence of two independent molecules (Anderson & Steed, 2007). A  $Z' > 1$  structure is also obtained when the molecule has different quasi-energetic conformations, with these conformations co-existing in the crystal structure (Hosseini Monfared *et al.*, 2009; Roy *et al.*, 2006).

Two X-ray data sets were collected on two crystals of the title compound from two different batches to ascertain the  $Z' = 2$  phenomenon. One crystal was structurally investigated after drying and the other was taken directly from the mother liquor. Both data sets refined to the identical  $Z' = 2$  structure, including the same disordered and partially occupied solvent water molecules. The complementary N–H...O hydrogen-bonding interaction between the molecules containing atoms Cu1 and Cu2 may be viewed as a special supramolecular interaction which creates a 'dimer' and thereby gives a  $Z' = 2$  structure. However, the two independent molecules are superficially related by a pseudo- $C_2$  axis at ( $\frac{1}{2}$ ,  $y$ ,  $\frac{1}{4}$ ) (Fig. 1a) or



**Figure 3**

A packing diagram for (I) in wire-frame mode, with the  $\pi$ - $\pi$  stacking interactions in the supramolecular double-layer. Centroid-centroid contacts are indicated as thick dashed lines with their distances given. [Symmetry codes: (iv)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (v)  $-x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (vi)  $1 + x, y, z$ .]

a pseudo- $n$ -glide plane at ( $0, \frac{1}{2}, 0$ ), thus leading to a possible refinement in  $C2/c$  (see supplementary material, *\_refine\_special\_details* section). The only atoms with no symmetry-related counterpart are C8, C9, C28 and C29 from the aromatic ring of the picolinate group (Fig. 1a). It is here where the two molecules deviate most in their overlay and where a tilt disorder occurs upon refinement in  $C2/c$ . Based on this small conformational difference, the  $Z' = 2$  structure would then be due to two equi-energetic conformations with these conformations co-existing in the crystal. However, we view both the 'dimer' and the slight conformational difference, and hence the  $Z' = 2$  structure of (I), as consequences of partial crystal water loss, which apparently takes place when the compound is still in its mother liquor, thereby representing a 'crystal on the way' (Desiraju, 2007; Ruiz *et al.*, 2008).

## Experimental

A methanolic solution (10 ml) of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.40 g, 2.0 mmol) was mixed with a methanol solution (5 ml) of 2-picolinic acid (0.25 g, 2.0 mmol), followed by the addition of imidazole (0.14 g, 2.0 mmol) dissolved in methanol (5 ml). The resulting dark-blue solution was left to stand at room temperature. Dark-blue single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent over a period of several days (yield 82%). Elemental analysis calculated for  $\text{C}_{11}\text{H}_{14.74}\text{CuN}_3\text{O}_{5.87}$ : C 38.11, H 4.29, N 12.12; found: C 38.31, H 3.55, N 12.29%. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3432 (OH), 3135 (NH), 2939 (CH), 1623 (CO and CC), 1387 (CH).

### Crystal data

$[\text{Cu}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_3\text{H}_4\text{N}_2) \cdot (\text{H}_2\text{O})] \cdot 0.87\text{H}_2\text{O}$	$\beta = 110.333 (5)^\circ$
$M_r = 346.44$	$V = 2808.0 (4) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 8$
$a = 15.5708 (13) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 6.5334 (5) \text{ \AA}$	$\mu = 1.59 \text{ mm}^{-1}$
$c = 29.437 (2) \text{ \AA}$	$T = 203 \text{ K}$
	$0.21 \times 0.15 \times 0.04 \text{ mm}$

### Data collection

Bruker APEXII CCD area-detector diffractometer	30383 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5430 independent reflections
$T_{\min} = 0.731$ , $T_{\max} = 0.941$	3948 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

## Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.035$$

$$wR(F^2) = 0.096$$

$$S = 1.08$$

$$5430 \text{ reflections}$$

$$421 \text{ parameters}$$

$$2 \text{ restraints}$$

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$$

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H3A\cdots O2^i$	0.80 (3)	1.99 (3)	2.790 (3)	173 (4)
$O3-H3B\cdots O5^{ii}$	0.76 (3)	2.08 (3)	2.826 (3)	168 (4)
$N2-H2\cdots O25$	0.81 (3)	1.96 (3)	2.758 (3)	173 (3)
$O23-H23A\cdots O22^i$	0.79 (4)	2.01 (4)	2.792 (3)	169 (4)
$O23-H23B\cdots O25^{iii}$	0.78 (3)	2.02 (3)	2.765 (3)	161 (4)
$N22-H22\cdots O5$	0.81 (3)	1.96 (3)	2.767 (3)	173 (3)

Symmetry codes: (i)  $x, y-1, z$ ; (ii)  $-x, y-\frac{1}{2}, -z+\frac{3}{2}$ ; (iii)  $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$ .

Only positions O6A/O26A, O6A/O26B and O26A/O6B can be occupied simultaneously, but not O6A and O6B, O26A and O26B, or O6B and O26B. Occupation factors refined to about 0.63 (2) for the A and 0.24 (2) for the B positions, giving an occupancy of about 0.87 for each water molecule. H atoms were positioned geometrically (aromatic C—H = 0.94  $\text{\AA}$  and methyl C—H = 0.97  $\text{\AA}$ ) and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . H atoms on the aqua ligand and of the imidazole NH group were located and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O,N})$ . The O—H bond length of one H atom on each aqua ligand had to be controlled through a DFIX restraint (SHELXL97; Sheldrick, 2008), with O—H = 0.90 (5)  $\text{\AA}$ .

Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine

structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2009); software used to prepare material for publication: publCIF (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3110). Services for accessing these data are described at the back of the journal.

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