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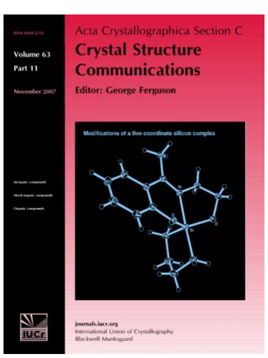

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Aqua(oxydiacetato-κ^3O,O',O'')(pyridine-3-carboxamide-κN^1)copper(II) sesquihydrate

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In the monomeric title compound, $[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)]\cdot 1.5H_2O$, the Cu^{II} cation is bound in a square-pyramidal coordination to a tridentate oxydiacetate (ODA) ligand, a monodentate pyridine-3-carboxamide (p3ca) ligand and one aqua ligand, where the two organic ligands form the basal plane and the water O atom occupies the unique apical site. The ODA ligand presents a slight out-of-plane puckering in its central ether O atom, while the p3ca ligand is essentially planar. The availability of efficient donors and acceptors for hydrogen bonding results in the formation of strongly linked hydrogen-bonded bilayers parallel to (101), with an interplanar distance of 3.18 (1) Å and a stacking separation between the bilayers of 3.10 (1) Å, both of them governed by extended π–π interactions. The disordered nature of the solvent water molecules around inversion centres is discussed. The monoaqua compound is compared with the octahedral diaqua analogue, $[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)_2]$, reported recently [Perec & Baggio (2009). *Acta Cryst.* **C65**, m296–m298].

Comment

The coordination flexibility of Cu^{II} centres, combined with the electronic and steric diversity of selected organic ligands, continues to lead to novel architectures and topologies in the field of copper(II) carboxylates (Perec *et al.*, 2010; Sartoris *et al.*, 2010, *etc.*). We recently reported a new ternary copper compound, $[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)_2]$, (II), isolated from the Cu^{II}–oxydiacetate (ODA)–pyridine-3-carboxamide (p3ca) system, with one tridentate ($\kappa^3O,O'O''$) ODA anion, one monodentate (κN) p3ca ligand and two aqua molecules bonded to the central Cu^{II} ion (Perec & Baggio, 2009). In this compound, the two organic ligands define the basal plane of an octahedral arrangement around the Cu^{II} cation, while two water ligands occupy the apical sites (see Scheme). By slightly changing the reaction conditions (a methanol–water ratio of 3:1 instead of 1:1), blue crystals were obtained of the title compound, $[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)]\cdot 1.5H_2O$, (I), a pentacoordinated Cu^{II} complex.

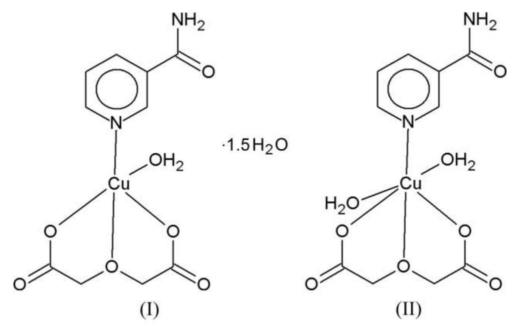

Fig. 1 shows ODA and p3ca coordination to Cu^{II} in (I) that is similar to that in (II), *viz.* a planar arrangement spanning a tight range of Cu—O/N distances [Cu—O = 1.9467 (15)–1.9561 (15) and 1.964 (2)–1.989 (2) Å in (I) and (II), respectively, and Cu—N = 1.9675 (18) and 1.989 (2) Å in (I) and (II), respectively]. The main structural difference resides in the apical water ligands: only one in (I), at a Cu1—O1*W* distance of 2.2684 (18) Å, to complete a square-pyramidal polyhedron, but two in (II), with Cu—O*W* distances of 2.359 (3) and 2.483 (2) Å, to generate an octahedral geometry.

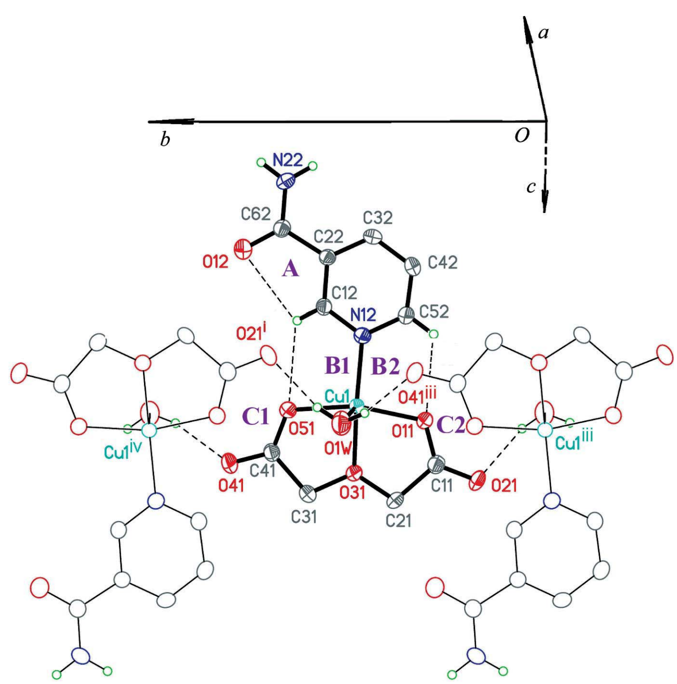

Figure 1
A molecular view of (I), showing the atom-labelling scheme used and the way in which different layers interact with each other *via* the aqua hydrogen bonds (dashed lines) to form structural bilayers parallel to (101). Displacement ellipsoids are drawn at the 50% probability level. Heavy lines represent molecules in the lower level and thin lines those in the upper level. Solvation water molecules O2*W* and O3*W* have been omitted for clarity. The symmetry codes are as in Table 2.

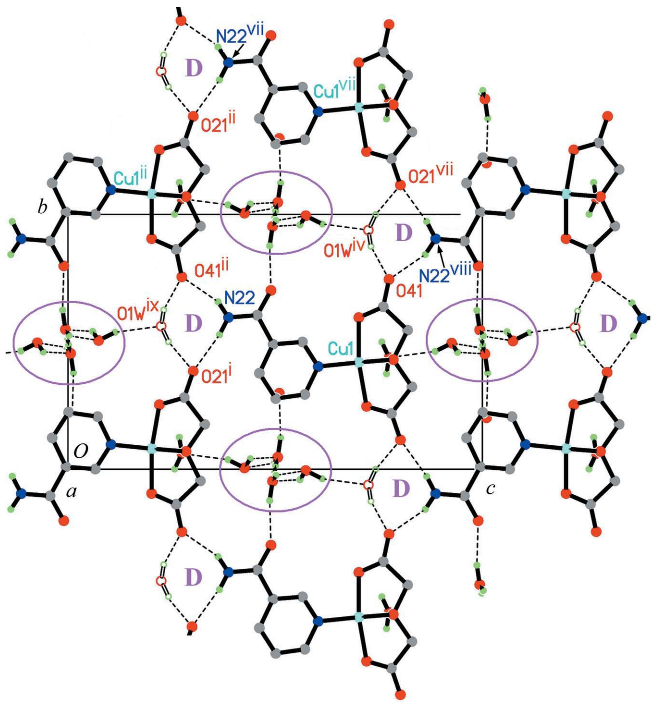

Figure 2
A packing view of (I), projected down [100], showing the way in which planar arrays of Cu coordination polyhedra are formed *via* the amide–ODA N—H···O hydrogen bonds. Hollow bonds denote solvent water molecules emerging from the lower planar arrays, about 3 Å below, interacting with the same ODA O atoms in the layer above to consolidate the structural bilayers (loop D). See Fig. 1 for a complete view of these latter interactions. Outlined by ellipses are the (disordered) solvent water systems (see Fig. 4 for details). Dashed lines indicate hydrogen bonds. [Symmetry codes as in Table 2; additionally; (vii) $x, y + 1, z$; (viii) $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ix) $-x + 2, -y + 1, -z + 1$.]

In (I), the ODA ligand presents a slight out-of-plane puckering at its central O31 atom [0.27 (1) Å out of the mean plane containing the remaining atoms, mean deviation from the least-squares plane < 0.02 (1) Å]. A similar effect, but disordered on both sides of the plane, was observed in (II). Also, as in (II), the terminal carboxylates in (I) present partial delocalization, with the coordinated O atoms showing a distinct lengthening in their C—O bonds [O11—C11 = 1.268 (3) Å and O51—C41 = 1.272 (3) Å] relative to those for noncoordinated O atoms [O21—C11 = 1.228 (3) Å and O41—C41 = 1.227 (3) Å].

In contrast to the situation in (II), the p3ca unit in (I) is nearly planar, with a dihedral angle of 2.7 (1)° between the pyridyl and amide planes, smaller than the value in (II) [10.1 (1)°]. The free rotation of the amide planar group appears to be hindered by the intramolecular C12—H12···O12 hydrogen bond linking both subunits (Table 2, first entry, and Fig. 2), which gives rise to an *S*(5) motif (Bernstein *et al.*, 1995), labelled 'A' in Fig. 1. There are two further weak nonconventional intramolecular C—H···O interactions restraining the free rotation of the pyridyl ring around the Cu—N11 bond, which generate two more *S*(5) motifs, labelled B1 and B2 in Fig. 1, which in turn link this group to the coordinated O atoms in ODA (O11 and O51) (Table 2, entries 2 and 3).

In addition to these weak C—H···O interactions influencing the molecular geometry of (I), there are a number of strong hydrogen bonds, having water and amine H-atom donors and carboxylate and amide O-atom acceptors, which define the main aspects of the crystal structure. Through these, each monomer interacts with six different symmetry-related analogues, similar to what was found for (II). However, the two packing schemes are quite different. Fig. 2 shows a view of (I), parallel to (101) and displaying the planar array determined by just one specific type of hydrogen bond, those involving the amide N—H group as donors and the uncoordinated ODA O atoms (O21 and O41) as acceptors (Table 2, entries 4 and 5). These bonds, and the resulting large $R_4^4(32)$ loops which they generate (in Fig. 2, those involving amides N22, N22^{i} and N22^{ii}), define almost planar two-dimensional arrays [mean square deviation from the least-squares plane = 0.12 (1) Å, with apical ligands excluded from the calculation]. A characteristic of these structures is that they have all their Cu—O$_{water}$ apical bonds pointing in the same direction (downwards in the case represented in Fig. 2).

Since the inversion centres in the structure of (I) are located at (x, y, z), with x, y and z either 0 or $\frac{1}{2}$, we can arbitrarily define two possible families, those with $x + z = \frac{1}{2}, \frac{3}{2}$, *etc.*, denoted type *a*, and a complementary set with $x + z = 0, 1$, *etc.*, denoted type *b*. These two families have different effects when operating on the above-mentioned planes: type *a* centres generate structures which oppose apical Cu—O$_{water}$ vectors in related planes, so that water molecules corresponding to monomers in one plane in fact end up appearing very near the neighbouring plane, at hydrogen-bonding distances, and *vice versa*. This is shown in Figs. 1 and 2, which show the connectivity resulting from water–ODA O—H···O hydrogen bonds (Table 2, entries 6 and 7). It is relevant for the discussion below to note that these hydrogen bonds are, as for those previously discussed, almost parallel to the planar structure they help to build. The bonds give rise to tight $R_4^2(8)$ in-plane loops (labelled D in Fig. 2) and large $R_2^2(12)$ out-of-plane loops (labelled C1 and C2 in Fig. 1), which help to clamp the two planar structures into a thick bilayer with a separation d_1 = 3.18 (1) Å. On the other hand, inversion centres of type *b* relate the basal planes of the Cu coordination polyhedra in a back-to-back fashion (Fig. 3) with only weak interactions between them, basically the hydrogen bonds involving the disordered solvent water molecules O2*W* and O3*W* (see encircled zones in Fig. 2 and related discussion below), at an interplanar distance d_2 = 3.10 (1) Å.

This similarity ($d_1 \sim d_2$) in interplanar separation at a graphitic distance strongly suggests a dominant π–π interaction, which is compatible with the fact that all the strong hydrogen bonds in the structure are in-plane and thus contribute mainly to the lateral coherence between monomers rather than to the interaction between planes. The solvent water molecules correspond to one fully occupied (O2*W*) and one half-occupied (O3*W*); the latter is disordered around a type *a* inversion centre, thus providing for a $\overline{1}$ local symmetry

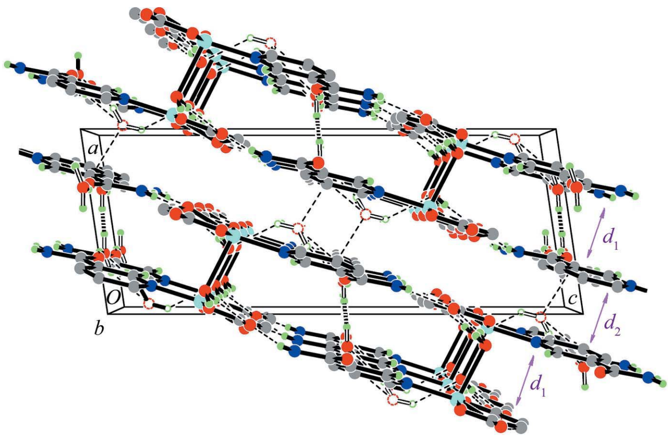

Figure 3
A complementary view to Fig. 2, projected at right angles to the latter, showing the (101) bilayers and the way in which they interact. Dashed lines indicate hydrogen bonds. d_1 and d_2 indicate the interplanar separations (see *Comment*).

in an 'average' sense, *i.e.* when one half is present, the remaining one must be absent and *vice versa*. Molecule O2*W* is also placed near a type *a* inversion centre, generating a symmetric image with which it could only co-exist through some kind of disorder of the H atoms involved (in order to give short H···H contacts). In spite of the disordered nature of the hydrate system, the difference map allowed the detection of three 'H-like' peaks around O2*W* and two in the neighbourhood of O3*W*, giving on average the model displayed in Fig. 4(*a*), and which could be consistently interpreted as explained in Figs. 4(*b*) and 4(*c*). These models present two mutually exclusive but complementary motifs: both of them are present at random in the structure with a 50% probability, and when added together they make up the 'average' structure represented in Fig. 4(*a*) and described by the centrosymmetric space group $P2_1/n$. The interaction takes the form of a column, climbing along [100] and linking alternate planes, anchored at the aldehyde O atom (O12) and the aqua ligand (O1*W*).

In spite of the structural differences between (I) and (II), the X-ray powder diffraction diagrams showed that both compounds transform to a similar crystalline dehydration product when the thermally driven dehydration process is conducted up to a maximum of 450 K. Mass-loss calculations [found/expected: 12.6/12.39% for (I) and 10.4/10.19% for (II)] suggest a formula for the common dehydration product of [Cu(ODA)(p3ca)].

A final word of caution: although there is clear synthetic and analytical evidence for the composition of (I), nevertheless significantly lower *R* indices were obtained when the structure was refined as an Ni complex rather than as a Cu complex. However, despite the *R* factor indications, the Hirshfeld tests implemented in *PLATON* checkCIF (Spek, 2009) generated a significant number of alerts for the Ni refinement but none for the Cu version, indicating an incorrect assignment of atom type in the case of Ni. We can propose no simple explanation for this apparent paradox.

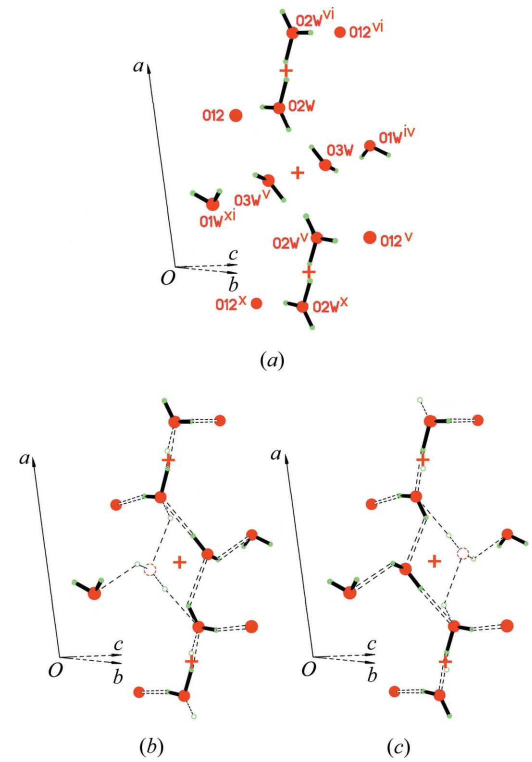

Figure 4
The disordered solvent water molecules and their columnar interaction, viewed at right angles to the orientation in Fig. 2. The type *a* inversion centres, represented as crosses, align along [100] at $y = 1$, $z = \frac{1}{2}$. (*a*) The centrosymmetric model, disordered around type *a* inversion centres. (*b*) and (*c*) Two physically plausible alternatives for the atomic distribution along the columns. Even though they violate the space group centrosymmetry, their co-existence would explain the centrosymmetric disordered model. Solid spheres, heavy bonds and hydrogen bonds as double broken lines correspond to 'existing' atoms, and hollow bonds (including hydrogen bonds as single broken lines) represent absent atoms. [Symmetry codes as in Table 2; additionally; (x) $x - 1, y, z$; (xi) $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.]

Experimental

Copper(II) oxydiacetate hemihydrate (0.01 mol) and pyridine-3-carboxamide (0.02 mol) were added to a methanol–water solution (3:1 *v*/*v*, 100 ml). The mixture was heated at 333 K with stirring for 1 h, filtered, and the solution left to stand at ambient temperature. After a few days, large blue crystals of (I) were separated. Analysis found: C 33.1, H 4.1, N 7.7, Cu 17.1%; $C_{20}H_{30}Cu_2N_4O_{17}$ requires: C 33.1, H 4.1, N, 7.7, Cu 17.5%. EDAX analysis on a Philips 515 microscope (Philips Export BV, Eindhoven, The Netherlands) equipped with an EDAX PV9100 probe (EDAX International Inc., Prairie View, Illinois, USA) showed that Cu was the only metallic element present.

Crystal data

$[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)]\cdot 1.5H_2O$	$\beta = 98.349$ (3)°
$M_r = 725.58$	$V = 1415.25$ (7) Å^3
Monoclinic, $P2_1/n$	$Z = 2$
$a = 7.1545$ (2) Å	Mo $K\alpha$ radiation
$b = 11.0251$ (3) Å	$\mu = 1.59$ mm^{-1}
$c = 18.1342$ (5) Å	$T = 294$ K
	0.35 × 0.30 × 0.20 mm

Table 1
Selected bond lengths (Å).

Cu1—O11	1.9467 (15)	Cu1—N12	1.9675 (18)
Cu1—O31	1.9547 (16)	Cu1—O1*W*	2.2684 (19)
Cu1—O51	1.9561 (15)		

Data collection

Oxford Gemini CCD S Ultra diffractometer
Absorption correction: multi-scan (*CrysAlis Pro*; Oxford Diffraction, 2009)
T_{min} = 0.54, T_{max} = 0.73
6237 measured reflections
3194 independent reflections
2408 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.089
S = 0.92
3194 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···O12	0.93	2.43	2.761 (3)	101
C12—H12···O51	0.93	2.57	3.099 (3)	116
C52—H52···O11	0.93	2.39	2.972 (3)	121
N22—H22*A*···O21^{i}	0.86	2.17	2.998 (2)	163
N22—H22*B*···O41^{ii}	0.86	2.11	2.930 (2)	158
O1*W*—H1*WA*···O41^{iii}	0.85	1.90	2.726 (2)	163
O1*W*—H1*WB*···O21^{iv}	0.85	2.00	2.835 (2)	167
O2*W*—H2*WA*···O12	0.85	1.94	2.771 (3)	164
O2*W*—H2*WB*···O3*W*	0.85	1.94	2.700 (5)	148
O2*W*—H2*WB*···O3*W*^{v}	0.85	2.13	2.747 (5)	129
O2*W*—H2*WC*···O2*W*^{vi}	0.85	1.89	2.738 (5)	175
O3*W*—H3*WA*···O1*W*^{iv}	0.85	2.11	2.804 (4)	138
O3*W*—H3*WB*···O2*W*	0.85	1.94	2.700 (5)	149

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

The solvent water molecules appear disordered around inversion centres: molecule O2*W* with a fully occupied O atom but disordered H atoms, and the remaining molecule, O3*W*, split into two halves (at collision distance from each other), the occupancy of which refined freely to a value slightly larger than a half [0.58 (4)]. The parameter was finally fixed at 0.50, as an 'anticollision' condition limiting the simultaneous presence of both otherwise colliding centrosymmetrically related images. This fact, in turn, in conjunction with the requirements posed by a feasible hydrogen-bonding scheme, forced the occupancy of the remaining disordered H atoms (H2*W* and H3*W*) to be 0.50 also. All the H atoms attached to O atoms (even those in the problematic solvent water molecules) could be located in a difference Fourier map. They were further idealized, with O—H = 0.85 Å and H···H = 1.35 Å, and finally allowed to ride. Those attached to C and N atoms were placed in calculated positions, with pyridine C—H = 0.93 Å, methine C—H = 0.97 Å and amine N—H = 0.86 Å, and allowed to ride. Displacement parameters were taken as $U_{iso}(H) = 1.2U_{eq}$(carrier).

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3364). Services for accessing these data are described at the back of the journal.

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