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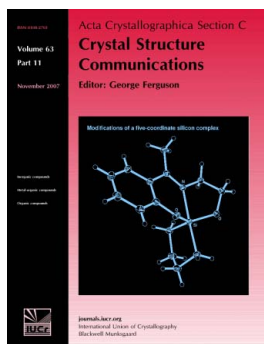
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metal-organic compounds

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

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In the mononuclear title compound, [Cu(C₄H₄O₅)(C₆H₆N₂O)(H₂O)₂], the Cu^{II} centre is bound to a chelating oxydiacetate ligand, a monodentate pyridine-3-carboxamide unit and two water molecules, defining an octahedral coordination where the first two ligands form the equatorial plane and the last two occupy the apical sites. The planar oxydiacetate ligand is slightly disordered at its central ether O atom. The availability of efficient donors and acceptors for hydrogen bonding results in a complex interaction scheme where each monomer links to six similar units to define a well connected three-dimensional structure. A comparison is made with related structures in the literature, and the reasons for their differences are discussed.

Comment

The coordination chemistry of Cu^{II} is a topic of current interest because of the relevance of such complexes as structural and spectroscopic models in biological systems and molecular-based magnet materials. In the mononuclear title compound, diaqua(oxydiacetato)(pyridine-3-carboxamide)-copper(II), (I) (Fig. 1), the copper cation is bound to a κ^3O,O',O''-chelating oxydiacetate (ODA) ligand, a κN-monodentate pyridine-3-carboxamide unit (p3ca) and two water molecules, defining an octahedral coordination geometry where the first two ligands form the equatorial plane and the last two occupy the apical sites. The basal atoms span a very tight range of coordination distances [1.964 (2)–1.989 (2) Å; Table 1]; the apical water molecules, in contrast, show a 5% difference in their Cu—O bonds. In general terms, however, and in spite of chelation, the average geometry of the octahedron is rather regular. The oxydiacetate (ODA) ligand is slightly disordered at its O31 central atom, split at both sides [0.36 (1) Å above/below] of the plane through the remaining atoms (the mean deviation from the least-squares

plane is < 0.001 Å). The p3ca unit shows a rotation around the C22—C62 bond of 10.1 (1)° between the planar pyridyl and amide groups
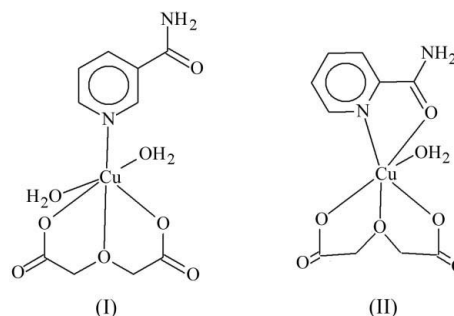

The availability of efficient donors and ready acceptors for hydrogen bonding, represented by water and amine H atoms on one side and carboxylate and amide O atoms on the other, results in a complex interaction scheme where each monomer links to six different similar units to define a well-connected three-dimensional structure. Fig. 2(a) shows a full packing view depicting the most conspicuous characteristics of this packing; the copper coordination polyhedra and the p3ca units (which stretch out from them) associate into two well differentiated types of planar arrays, which dispose parallel to (010) and are shown sideways in Fig. 2(a), labelled A and B, respectively. The B planes are formed by a conglomerate of p3ca units, which interact with each other in pairs through an N—H···O hydrogen bond (Table 1, first entry) around a symmetry centre defining a classical $R_2^2(8)$ loop (Bernstein et al., 1995); the interaction is marked as '(1)' in Fig. 2(b). The same figure shows how the two types of arrays (A and B) interconnect through a second N—H···O hydrogen bond [Table 1, second entry, and Fig. 2(b), site marked '(2)'].

An interesting feature of the packing is the way in which type A planes build up through the interaction of CuO₃N-
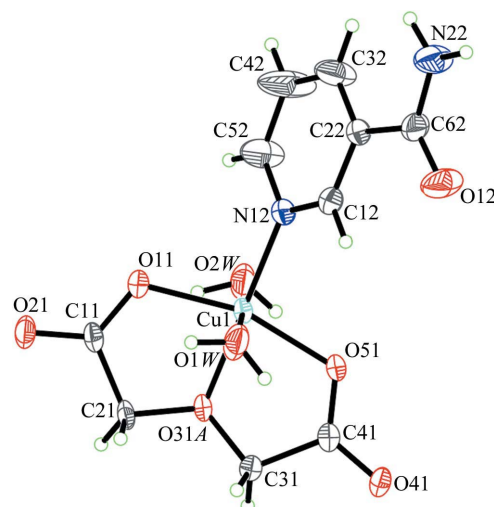
Figure 1
A view of the molecule of (I), showing the labelling scheme used (the minor component of the disordered groups has been omitted). Displacement ellipsoids are shown at the 50% probability level.
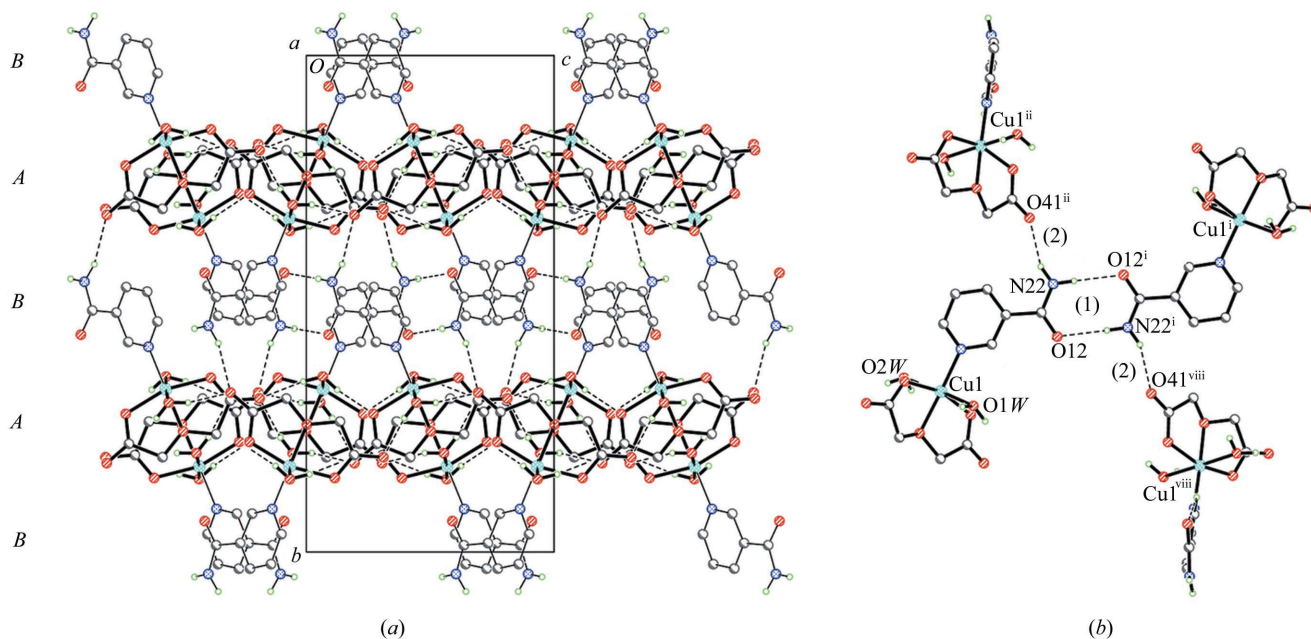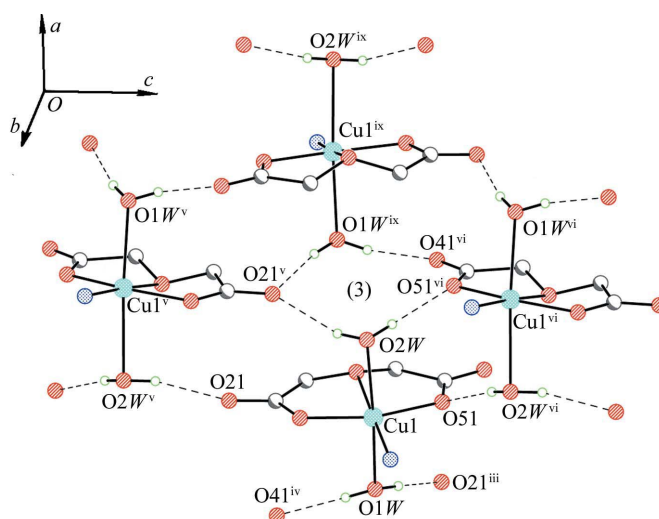
Figure 2
(*a*) A full packing diagram of (I) projected along the *a* axis, showing the way in which planar arrays of copper coordination polyhedra (in heavy lining) and p3ca (in light lining), respectively, stack along the *b* axis. (*b*) A detailed view of the latter, showing the hydrogen-bonded loops formed at the p3ca planes and the interaction with ODA ligands in the copper polyhedra. Nonrelevant H atoms have been omitted. See *Comment* for details of '(1)' and '(2)' labelling. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.]

$(H_2O)_2$ units, interwoven into a two-dimensional network of large $R_4^4(10)$ loops, shown as '(3)' in Fig. 3, where both types of water molecules participate with all their H atoms (Table 1, entries 3–6). There are also some weak C—H···O contacts completing the interaction scheme.

A search of the 2009 version of the Cambridge Structural Database (CSD; Allen, 2002) showed a closely related structure to (I), *viz.* aqua(ODA-$\kappa^3 O, O', O''$)(p2ca-$\kappa^2 N, O$)copper(II), (II) (Sieroń, 2007), where the only *a priori* difference between intervening units resides in the position of the carboxamide substituent. In (I), the group is bound to pyridine at site 3, the next nearest neighbour to the coordinated N atom, and the result is that the amide O atom is positioned too far away to make chelation feasible; in (II), however, the group attaches at site 2, nearest neighbour to N, thus configuring an adequate geometry for a bidentate coordination. This results in two completely different coordination modes for the pca ligands, $\kappa^1 N$-monodentate (p3ca) in (I) and $\kappa^2 N, O$-chelating (p2ca) in (II) (see scheme). However, this also has a profound influence on the remaining ligands, *viz.* the ODA group, which in (I) adopts its usual planar meridional coordination mode, in (II) 'breaks' around the central O_{ether}—Cu bond into two quasi-perpendicular 'butterfly' wings binding in a facial mode, a fact that positions the ether O atom in one apical coordination site. The remaining apical site is occupied by the unique water molecule in the structure.

The simultaneous reduction of the number of potential hydrogen-bonding donors (now the amine group and only one water molecule) and acceptors (through the involvement of the amide O atom in coordination) drastically modifies the noncovalent interaction scheme by decreasing the number of strong hydrogen bonds in (II) to basically three.

The coordination modes to copper discussed herein appear to be quite typical for both cpa groups; all entries found in the CSD for Cu–c2pa complexes (15 in all) show the ligand behaving in a chelating manner; on the other side, 41 out of a total of 45 Cu–p3ca complexes show the ligand acting in a monodentate mode, the exceptions [refcodes BENQAM (Kozlevcar *et al.*, 1999), ESAFEJ (Cakir *et al.*, 2003), PEPJOK (Valigura *et al.*, 2006) and TIMXIX (Monfared *et al.*, 2007)]

Figure 3
The two-dimensional hydrogen-bonded structure involving copper coordination polyhedra, drawn parallel to (010), at right angles to the view in Fig. 2. Note the $R_4^4(10)$ loop at '(3)'. For clarity, p3ca molecules are represented only by their coordinated N atom and nonrelevant H atoms have been omitted. [Symmetry codes: (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $-x, y, -z - \frac{1}{2}$; (vi) $-x, y, -z + \frac{1}{2}$; (ix) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.]

metal-organic compounds

showing the ligand in the role of a bridge, either in dimeric or polymeric compounds.

Experimental

Copper(II) oxydiacetate hemihydrate (0.01 mol) and pyridine-3-carboxamide (0.02 mol) were added to a methanol–water solution (1:1, 100 ml). The mixture was heated at 333 K under stirring for 1 h and then filtered and left to stand at ambient temperature. After a few days, blue crystals of the title compound had separated.

Crystal data

$[Cu(C_4H_4O_5)(C_6H_6N_2O)(H_2O)_2]$	$V = 2724.2\ (10)$ Å^3
$M_r = 353.77$	$Z = 8$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 12.498\ (3)$ Å	$\mu = 1.65$ mm^{-1}
$b = 20.899\ (4)$ Å	$T = 295$ K
$c = 10.430\ (2)$ Å	$0.22 \times 0.18 \times 0.12$ mm

Data collection

Rigaku AFC-6 diffractometer	2287 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.120$
$T_{min} = 0.68$, $T_{max} = 0.82$	3 standard reflections
11251 measured reflections	every 150 reflections
2685 independent reflections	intensity decay: <2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	3 restraints
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.90$ e Å^{-3}
2685 reflections	$\Delta\rho_{min} = -0.66$ e Å^{-3}
195 parameters	

The ether O atom in ODA appeared disordered at both sides of the least-squares plane defined by the other ODA atoms, with occupation factors which refined to 0.900 (6) and 0.100 (6). Similarity restraints were applied to bond distances and displacement parameters involving the disordered atoms. The concomitant disorder in the H atoms of the adjacent methylene groups was modelled using the same occupation factors. Water H atoms were found in a difference Fourier map, further idealized (O—H = 0.85 Å) and finally allowed to ride. Those attached to C and N atoms were placed at calculated positions [C—H = 0.93 (CH) or 0.97 Å (CH$_2$) and N—H = 0.90 Å] and allowed to ride; U_{iso}(H) values were taken as $1.2U_{eq}$(C) and $1.5U_{eq}$(N,O).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC*

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N22—H22B$\cdots$O12[i]	0.90	2.13	3.031 (4)	177
N22—H22A$\cdots$O41[ii]	0.90	2.14	2.993 (3)	157
O1W—H1WA$\cdots$O21[iii]	0.85	1.93	2.771 (3)	169
O1W—H1WB$\cdots$O41[iv]	0.85	1.89	2.720 (3)	166
O2W—H2WA$\cdots$O21[v]	0.85	2.13	2.947 (3)	163
O2W—H2WB$\cdots$O51[vi]	0.85	1.98	2.820 (3)	170
C21—H21A$\cdots$O51[iv]	0.97	2.57	3.393 (3)	143
C32—H32$\cdots$O11[vii]	0.93	2.49	3.158 (4)	129

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

Diffractometer Control Software; 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: *SHELXTL* and *PLATON* (Spek, 2009).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3105). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cakir, S., Bulut, I. & Aoki, K. (2003). *J. Chem. Crystallogr.* **33**, 875–884.
Kozlevcar, B., Leban, I., Turel, I., Segedin, P., Petric, M., Pohleven, F., White, A. J. P., Williams, D. J. & Sieler, J. (1999). *Polyhedron*, **18**, 755–762.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, The Woodlands, Texas, USA.
Monfared, H. H., Kalantari, Z., Kamyabi, M.-A. & Janiak, C. (2007). *Z. Anorg. Allg. Chem.* **633**, 1945–1948.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sieroń, L. (2007). *Acta Cryst.* E**63**, m3087.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Valigura, D., Moncol, J., Korabik, M., Pucekova, Z., Lis, T., Mrozinski, J. & Melnik, M. (2006). *Eur. J. Inorg. Chem.* pp. 3813–3817.