

A bis(amine–carboxylate) copper(II) coordination compound forms a two-dimensional metal–organic framework when crystallized from water and methanol

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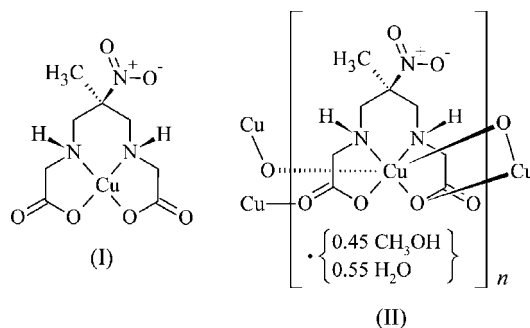
When {2,2'-[(2-methyl-2-nitropropane-1,3-diyl)diimino]diacetato}copper(II), [Cu(C₈H₁₃N₃O₆)] (I), was crystallized from a binary mixture of methanol and water, a monoclinic two-dimensional water- and methanol-solvated metal–organic framework (MOF) structure, distinctly different from the known orthorhombic one-dimensional coordination polymer of (I), was isolated, namely *catena*-poly[[copper(II)- μ_3 -2,2'-[(2-methyl-2-nitropropane-1,3-diyl)diimino]diacetato] methanol 0.45-solvate 0.55-hydrate], {[Cu(C₈H₁₃N₃O₆)]·0.45CH₃OH·0.55H₂O}_n (II). The monoclinic structure of (II) comprises centrosymmetric dimers stabilized by a dative covalent Cu₂O₂ core and intramolecular N–H···O hydrogen bonds. Each dimer is linked to four neighbouring dimers *via* symmetry-related (opposing) pairs of bridging carboxylate O atoms to generate a 'diamondoid' net or two-dimensional coordination network. Tight voids of 166 Å³ are located between these two-dimensional MOF sheets and contain a mixture of water and methanol with fractional occupancies of 0.55 and 0.45, respectively. The two-dimensional MOF sheets have nanometre-scale spacings (11.2 Å) in the crystal structure. Hydrogen-bonding between the methanol/water hydroxy groups and a Cu-bound bridging carboxylate O atom apparently negates thermal desolvation of the structure below 358 K in an uncrushed crystal of (II).

Comment

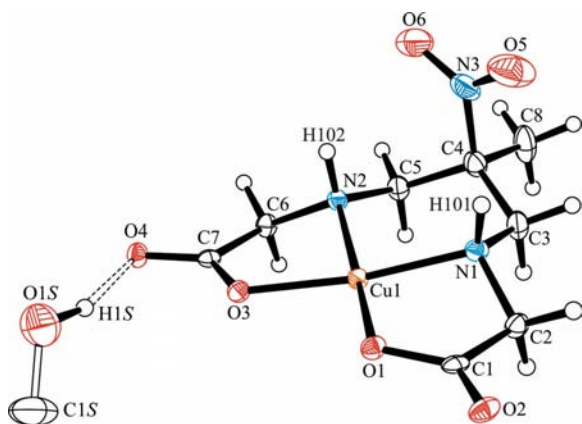
The reaction of Cu^{II} ions in methanol with two molar equivalents of an amino acid such as glycine (HL) in the presence of a base affords the nominally square-planar chelate CuL₂. The geometric isomer with *cis* amino groups is pre-organized for *N,N'*-chelate ring formation (*i.e.* ring closure) in the presence of excess formaldehyde, one molar equivalent of a diprotic carbon nucleophile such as nitroethane, and excess

base. This elegant template reaction, which links the *cis* metal-bound NH₂ groups with a three-carbon bridge, was developed by Comba and co-workers 23 years ago (Comba *et al.*, 1986) and then extended sometime later to include compound (I) and its derivatives (Comba *et al.*, 1991). More recent synthetic efforts by others with the same type of system have employed diethylmalonate as the carbon diacid for ring closure (Supriya *et al.*, 2007). The reduced ligand (in which the nitro group is converted into an amino group) has also been condensed with aldehydes to form Schiff base analogues of (I) with pendant noncoordinating base groups (Villanueva *et al.*, 1998).

The structure of (I) crystallized from water has an unsolvated crystal structure (orthorhombic, *P*2₁2₁2₁) and has been reported previously (Comba *et al.*, 1991). In (I), the Cu^{II} ion is weakly bound to the carboxylate O atom of an adjacent molecule to form an extended one-dimensional coordination polymer in which the five-coordinate mononuclear repeat units are linked by long axial Cu–O bonds (2.60 Å). Although nominally five-coordinate, the coordination geometry at the Cu^{II} ion is closer to being square-planar than square-pyramidal, due to the in-plane location of the metal ion relative to the ligand donor atoms (Comba *et al.*, 1991). In the present study, we report the structure of compound (II), the monoclinic water/methanol solvate of (I). In (II), the copper chelate forms a novel MOF extended structure based on a half-solvated two-dimensional rhombus net of *C*₂-symmetry dimeric repeats. The markedly different extended structure of the material described here leads to significant structural differences for the metal centre that clearly reflect supramolecular control of the molecular geometry of the copper chelate.



The molecular structure of (II), *i.e.* the symmetry-unique monomer unit of the *C*₂-symmetry coordination dimer, is shown in Fig. 1. The Cu^{II} ion exhibits the expected four-coordinate geometry within the tetradentate chelate. The equatorial Cu–O and Cu–N distances average 1.955 (14) and 1.996 (4) Å, respectively. The mean Cu–O distance is within the normal range expected for terminal carboxylates bound to Cu^{II} [1.96 (2) Å; Orpen *et al.*, 1989]. It is, however, noteworthy that the Cu1–O1 distance is significantly shorter than the Cu1–O3 distance (Table 1), presumably because atom O1 is involved in bridging the two Cu^{II} ions of the dimeric structure (see below). Although the average equatorial Cu–O distance is normal, the mean Cu–N distance is compressed by the chelate ring and is thus shorter than that of a standard secondary amine bound to Cu^{II} [2.03 (3) Å; Orpen

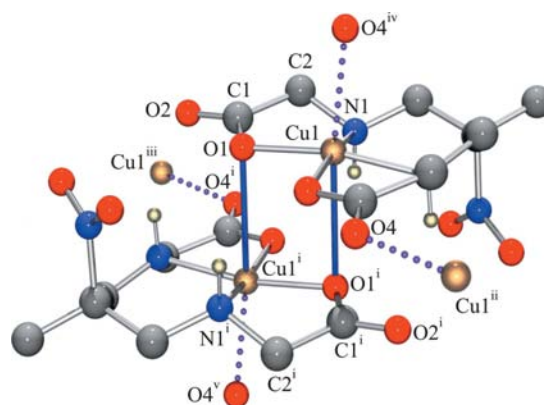

Figure 1

The structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of equal though arbitrary radii. The O atoms of the fractionally occupied methanol and water solvent molecules share the same site (O1S) and are hydrogen bonded to atom O4 *via* atom H1S (shared site). The partially occupied methanol atom C1S is shown with an open bond to atom O1S. The methyl-group H atoms were not located in the difference Fourier map.

et al., 1989]. The four ligand donor atoms lie exactly on the best-fit (least-squares) mean plane, with the Cu^{II} ion displaced by 0.179 (1) Å out of this plane in the direction opposite to that of the two N–H group bond vectors. Consequently, and in contrast with the orthorhombic structure of (I) reported previously (Comba *et al.*, 1991), the coordination geometry of the Cu^{II} ion in (II) is closest to being square-pyramidal if one considers all dative covalent bonds <2.5 Å in length to the Cu^{II} ion (see below).

That said, consideration of all metal–ligand interactions (first coordination sphere) less than the sum of the van der Waals radii of the pairwise interacting atoms (O···Cu = 2.92 Å and O···N = 2.95 Å; Bondi, 1964) suggests that the coordination geometry of each Cu^{II} centre is best described as a distorted octahedron with a significant axial displacement of the metal ion away from the Cu₂O₂ dimer core towards the closest axially coordinated (bridging) carboxylate O atom. The axial Cu–O distances of (II) are therefore markedly different, with the intra-dimer distance [Cu1–O1ⁱ = 2.7247 (15) Å] significantly longer than the inter-dimer distance [Cu–O4^{iv} = 2.3410 (15) Å], and both considerably longer than the equatorial Cu–O bonds [symmetry codes: (i) 1 – x, 1 – y, –z; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. Interestingly, the equatorial Cu–O and Cu–N distances of the present monoclinic structure, (II), are some 0.03 and 0.01 Å longer, respectively, than those of the orthorhombic crystalline form, (I) (Comba *et al.*, 1991). This clearly reflects the bond elongation required to support the out-of-plane displacement of the Cu^{II} ion in (II) and, ultimately, the markedly different extended structures of the two materials.

One intriguing hallmark of the molecular conformation of (II) is the approximate chair conformation of the six-membered chelate ring, in which the nitro group and amino group H atoms are positioned on the same side of the ring. (The ring-closing reaction could produce the alternative


Figure 2

Ball-and-cylinder representation of the C_7 -symmetry dimer that forms the repeat unit of the two-dimensional coordination polymer, or MOF structure, in water/methanol solvate (II). Bonds to atoms that lead to extension of the two-dimensional array are shown as dotted lines. H atoms (except those attached to N atoms) and solvent molecules have been omitted for clarity. [Symmetry codes: (i) 1 – x, 1 – y, –z; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (v) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

configurational isomer at C4 with the C8 methyl group axial, but does not.) Several noteworthy intramolecular hydrogen bonds appear to result from this particular chelate ring conformation (Table 2). More specifically, the nitro group O atoms (O5 and O6) are neatly hydrogen-bonded and thus ‘tethered’ to the closest amino group H atoms (H101 and H102). This may have some impact on transition-state geometries during the ring-closing reaction and certainly has some directional influence on thermal libration of the nitro group, as evidenced by the similar principal axes of displacement for the two O atoms. (The O-atom displacements are predominantly towards the amino group H atoms, as opposed to a more isotropic electron-density distribution which might be expected if rotational motion about the C4–N3 axis were favoured to a greater extent.) Perhaps more significant from the standpoint of conformational stability is the fact that the amino group H atoms of one chelate ring within the C_7 -symmetry dimer are hydrogen bonded to the closest carboxylate group O atoms of the second chelate. These hydrogen bonds clearly complement the structural stability associated with the Cu₂O₂ core of the dimer. On the whole, the six-membered chelate ring is somewhat flattened in the region of the Cu^{II} ion, such that the chelate-ring geometry tends towards being partly half-chair-like in conformation. This ring-flattening effect is highlighted by the fact that the Cu^{II} ion and the opposite C atom, C4, are displaced from the six-atom chelate ring mean plane (defined by atoms Cu1/N1/C3–C5/N2) by 0.127 (2) and 0.264 (2) Å, respectively.

The unit-cell packing shown in Fig. 3(a) clearly reveals the infinite two-dimensional network structure (or MOF architecture) of compound (II). As evidenced by the distinct arrangement of the C_7 -symmetry Cu₂O₂ dimer units in the structure, chains of interconnected dimers run parallel to, and include, the [1 $\bar{1}$ 0] plane. Furthermore, these chains are linked obliquely to adjacent chains *via* bridging Cu–O bonds, giving rise to a second series of parallel chains of interconnected

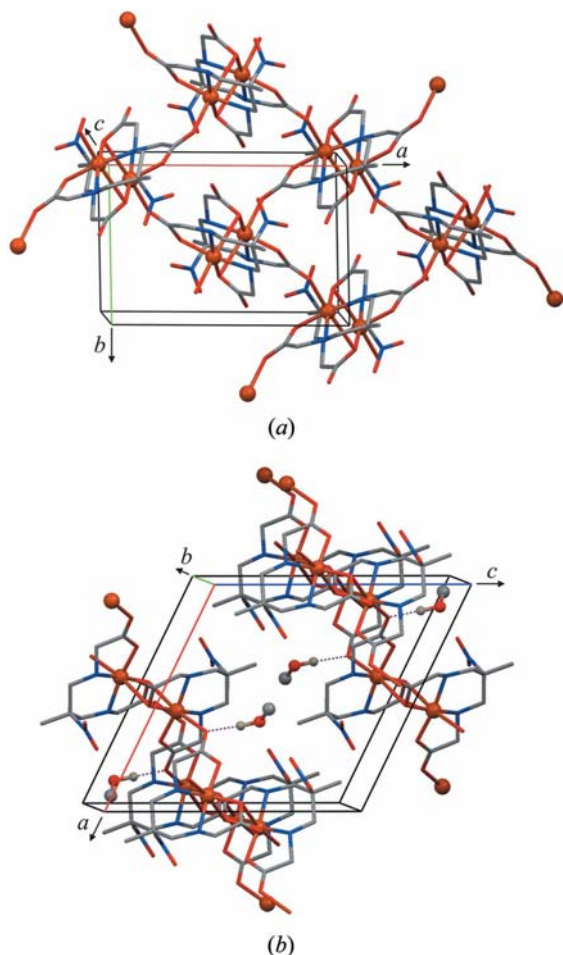


Figure 3

Views of part of the unit-cell contents of (II). (a) Projection approximately down the *c* axis. Methanol solvent molecules and H atoms have been omitted for clarity. (b) Projection approximately down the *b* axis, highlighting the location of the solvent-containing sites between the two-dimensional MOF layers. Intermolecular hydrogen bonds are indicated by dashed lines. Cu^{II} ions and solvent atoms are represented by spheres; all other atoms and bonds are represented as cylinders, or as end-capped cylinders in the case of terminal atoms. H atoms not involved in hydrogen bonding have been omitted for clarity.

dimers running parallel to, and including, the [110] plane. In effect, the two-dimensional coordination framework creates a 'diamondoid' or rhombus-like two-dimensional net. This net lies in the $[\bar{2}02]$ plane and, together with its translational repeats, generates parallel stacks of rather unusual metal-organic sheets in the crystal structure. The distance between parallel metal-organic sheets, e.g. that between the $[\bar{2}02]$ and $[20\bar{2}]$ planes, is 11.18 (1) Å.

The interesting layered crystal structure of (II), with a reasonably large nanometre-scale interlayer separation, creates solvent-accessible voids of 166 Å³ in the crystal structure. Upon closer inspection (PLATON; Spek, 2009), these voids comprise two 83 Å³ voids centred at $(\frac{1}{2}, 0.0, \frac{1}{2})$ and $(0.0, \frac{1}{2}, 1.0)$. The cavities are just large enough to accommodate methanol molecules (molecular volume ~71 Å³) or water molecules (molecular volume ~30 Å³), and compound (I) was,

not surprisingly, isolated as the mixed water/methanol solvate, (II), with a fractional composition ratio (from electron-density maxima) of 0.55:0.45 (Fig. 3*b*). The methanol and water O atoms are located at the same coordinates in the structure and OH groups of both solvents are clearly hydrogen bonded to bridging carboxylate group atoms O4 (Table 2). Although the unit-occupancy solvent atom H1S was cleanly located in a difference Fourier map, the remaining water H atom and the H atoms belonging to the methyl group of the methanol solvent molecule were not located and were omitted from the structural model during refinement. A full unit-occupancy methanol molecule can not be accommodated, as the methanol methyl C atom is too close [2.343 (3) Å] to the inversion-related methyl C atom at $(2 - x, 1 - y, -z)$.

Finally, other somewhat more simple Cu^{II} coordination compounds based on 4,4'-bipyridine linking ligands have been described with two-dimensional MOF sheet-like structures that form clathrates with small molecules such as CO₂ (Kondo *et al.*, 2006). This particular material exhibits reversible sorption/desorption of guest molecules with varying CO₂ partial pressure. Given the increasing likelihood that MOFs may become the materials of choice for gas-storage applications (Czaja *et al.*, 2009), we attempted to desolvate the crystal of (II), *i.e.* (I)·0.55H₂O·0.45CH₃OH, used for X-ray data collection. This crystal was neatly glued to a glass microfibre through only a very small area of the largest crystal face, thereby exposing >90% of the crystal surface to the atmosphere. Furthermore, the crystal faces were clean and uncovered by inert mounting oil. The glass-mounted crystal was warmed and maintained at 358 K in a thermal convection oven for 3 d. However, complete desolvation was not observed under the conditions tested (as judged from a post-warming X-ray data set), possibly due to the tight solvent-binding cavities, and to hydrogen-bonding between the solvent guests and the rigid host MOF.

Experimental

Compound (I) was synthesized according to a literature method (Comba *et al.*, 1991). X-ray quality crystals of (II) were grown by slow diffusion of methanol into a solution of (I) in distilled water at room temperature over a period of 3 d.

Crystal data

[Cu(C ₈ H ₁₃ N ₃ O ₆)]·0.45CH ₃ O·0.55H ₂ O	$\beta = 115.726 (16)^\circ$
$M_r = 335.08$	$V = 1266.9 (3) \text{ \AA}^3$
Monoclinic, $P2_1/n$	$Z = 4$
$a = 13.0407 (16) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.0578 (15) \text{ \AA}$	$\mu = 1.76 \text{ mm}^{-1}$
$c = 13.383 (2) \text{ \AA}$	$T = 200 \text{ K}$
	$0.55 \times 0.45 \times 0.38 \text{ mm}$

Data collection

Oxford Xcalibur2 diffractometer	mented in SCALE3 ABSPACK
Absorption correction: multi-scan	scaling algorithm]
[CrysAlis RED (Oxford	$T_{\min} = 0.387, T_{\max} = 0.511$
Diffracton, 2006); empirical	13298 measured reflections
(using intensity measurements)	2974 independent reflections
absorption correction using	2401 reflections with $I > 2\sigma(I)$
spherical harmonics, imple-	$R_{\text{int}} = 0.023$

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9453 (14)	Cu1—N2	1.9934 (18)
Cu1—O1 ⁱ	2.7247 (15)	Cu1—N1	1.9988 (18)
Cu1—O3	1.9644 (14)	Cu1—O4 ^{iv}	2.3410 (15)
O1—Cu1—O3	94.11 (6)	O3—Cu1—N2	83.69 (6)
O1—Cu1—N2	169.44 (7)	O3—Cu1—O4 ^{iv}	99.85 (6)
O1—Cu1—N1	83.80 (7)	N1—Cu1—O4 ^{iv}	90.53 (6)
O1—Cu1—O4 ^{iv}	97.44 (6)	N2—Cu1—N1	96.50 (7)
O3—Cu1—N1	169.60 (7)	N2—Cu1—O4 ^{iv}	93.11 (7)

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

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>
O1S—H1S···O4	0.95	1.96	2.823 (3)	163
N1—H101···O5	0.93	2.42	2.984 (3)	119
N1—H101···O3 ⁱ	0.93	2.37	3.101 (3)	135
N2—H102···O6	0.93	2.43	3.017 (3)	121
N2—H102···O2 ⁱ	0.93	2.15	2.912 (3)	138

Symmetry code: (i) $-x + 1, -y + 1, -z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	186 parameters
$wR(F^2) = 0.085$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\max} = 0.44 \text{ e } \text{Å}^{-3}$
2974 reflections	$\Delta\rho_{\min} = -0.37 \text{ e } \text{Å}^{-3}$

All H atoms of the metal complex of (II) were clearly visible in difference maps and then allowed for as riding atoms, with N—H = 0.93 Å, methylene C—H = 0.99 Å and methyl C—H = 0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N or methylene C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. One of

the H atoms belonging with the water/methanol O atom was included at the position found in the difference map.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3106). Services for accessing these data are described at the back of the journal.

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