

Two-dimensional square-grid frameworks formed by self-associating copper(II) complexes with 1-(3-pyridyl)- and 1-(4-pyridyl)-substituted butane-1,3-diones

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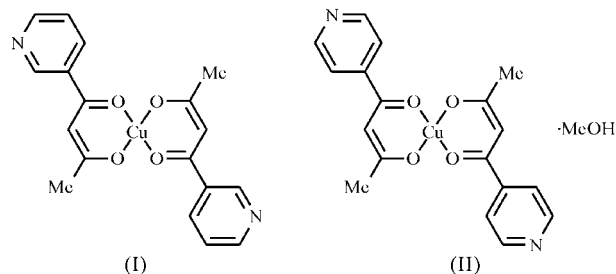
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In bis[1-(3-pyridyl)butane-1,3-dionato]copper(II) (the Cu atom occupies a centre of inversion), [Cu(C₉H₈NO₂)₂], (I), and bis[1-(4-pyridyl)butane-1,3-dionato]copper(II) methanol solvate, [Cu(C₉H₈NO₂)₂·CH₃OH], (II), the *O,O'*-chelating diketonate ligands support square-planar coordination of the metal ions [Cu—O = 1.948 (1)–1.965 (1) Å]. Weaker Cu···N interactions [2.405 (2)–2.499 (2) Å], at both axial sides, occur between symmetry-related bis(1-pyridylbutane-1,3-dionato)-copper(II) molecules. This causes their self-organization into two-dimensional square-grid frameworks, with uniform [6.48 Å for (I)] or alternating [4.72 and 6.66 Å for (II)] interlayer separations. Guest methanol molecules in (II) reside between the distal layers and form weak hydrogen bonds to coordinated O atoms [O···O = 3.018 (4) Å].

Comment

The assembly of complementary molecular components (for example, donors and acceptors of coordination or hydrogen bonds) into large well defined structures presents a basis for the concept of supramolecular synthesis. A special, though hitherto poorly recognized, issue of this approach is the self-organization of uniform 'building blocks' combining both donor and acceptor sites within a single molecular frame (Boldog *et al.*, 2003). In this way, four-connected coordination topologies may originate in a very illustrative self-organization of Lewis amphoteric molecular complexes preserving two unsaturated coordination positions at the metal ions and two outer donor groups, as provided by pyridyl- (Turner *et al.*, 1997) or nitrile-functionalized (Angelova *et al.*, 1989; Burdukov *et al.*, 2003) copper(II) diketonates. Such self-complementary species allow the one-component construction of extended solid-state architectures and the rational design of

inclusion compounds (Soldatov & Ripmeester, 2000) and polymorphs. Thus, despite the simplicity of its square-planar nodes, bis[3-(4-pyridyl)butane-1,3-dionato]copper(II) generates a variety of 4⁴ and NbO topologies, which can be efficiently controlled by choosing appropriate experimental conditions (*e.g.* solvent, temperature and guest molecules) (Chen *et al.*, 2003). From the design perspective, the inherent molecular geometry is also particularly prevalent, and the ligand structure offers rich possibilities for tuning the orientation of the diketonate and pyridyl binding sites. In this context, we have examined the mode of solid-state self-organization for two closely related copper(II) complexes with 1-(3-pyridyl)- [*viz.* (I)] and 1-(4-pyridyl)butane-1,3-dione [*viz.* (II)] (Faniran *et al.*, 1976), and we report their structures here.



The copper bis(diketonate) fragments in the structures of (I) and (II) are closely related and involve the organic ligands as *O,O'*-chelates towards the metal ions (Figs. 1 and 2), with a *trans* arrangement of the pyridyl groups. In (I), the Cu atom resides on a centre of inversion, while for (II), the evident inversion symmetry of the molecule is eliminated by hydrogen bonding with one equivalent of methanol solvent. The Cu—O bond lengths in both molecules range from 1.948 (1) to 1.965 (1) Å (Tables 1 and 2), in good agreement with those

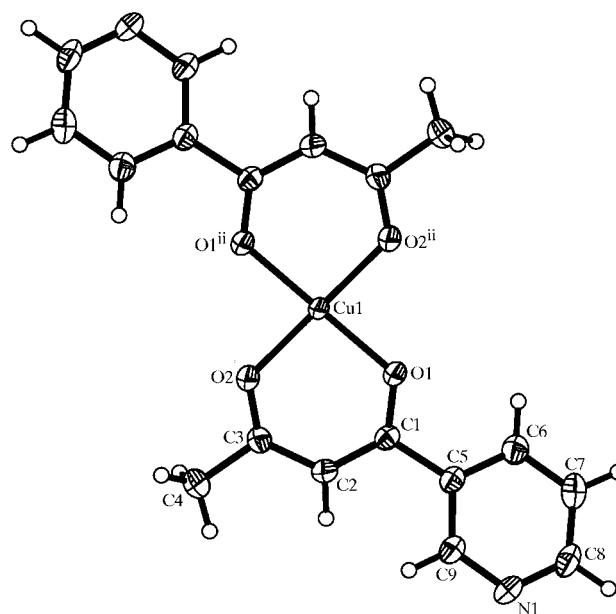


Figure 1

The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (ii) $-x, -y, -z$.]

reported for the related complexes of bis(1-phenylbutane-1,3-dionato)copper(II) with azo 3- and 4-pyridines [1.919 (8)–2.017 (3) Å; Li *et al.*, 2003]. The six-membered metallochelatone rings are planar to within *ca* 0.17 Å in both compounds, while the dihedral angles between the mean planes of the chelate fragments [0° in (I) and 6.33 (3)° in (II)] have normal values found also for the square-planar complex bis(1-phenyl-1,3-butanedionato)copper (Hon *et al.*, 1966), as well as for octahedral copper diketonates. The C–O [1.258 (3)–1.274 (2) Å] and C–C [1.382 (3)–1.409 (3) Å] distances within the metalcycles are intermediate between single and double bonds and suggest a significant delocalization of π -electron density, whereas the C–C bonds between diketonate and pyridyl

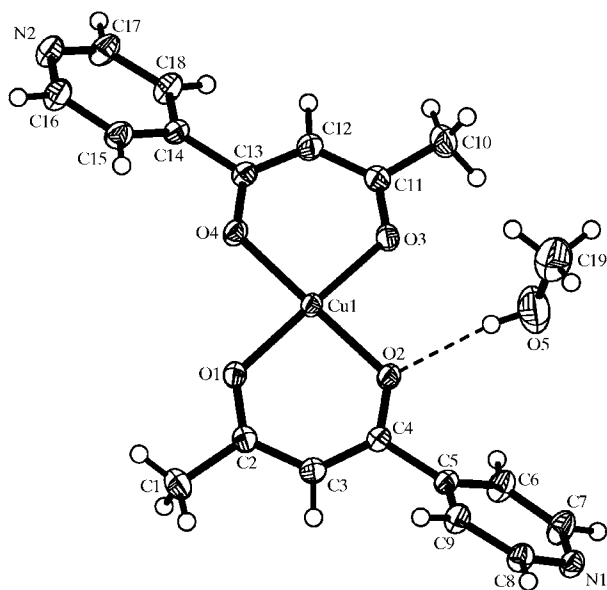


Figure 2
The structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line represents an intermolecular hydrogen bond.

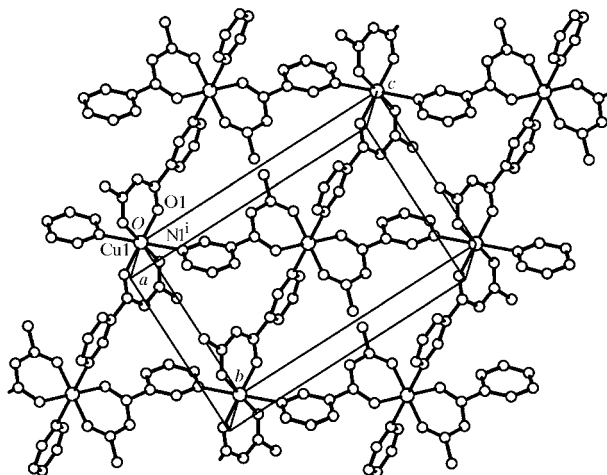


Figure 3
The two-dimensional network of (I). H atoms have been omitted for clarity. [Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

groups [*e.g.* C1–C5 in (I), and C4–C5 and C13–C14 in (II); 1.504 (3)–1.509 (3) Å] are typical for C–C single bonds in metal acetylacetonates (1.518 Å; Orpen *et al.*, 1989) and indicate lack of any conjugation between the fragments (Turner *et al.*, 1997).

Unlike the simpler complex bis(1-phenylbutane-1,3-dionato)copper (Hon *et al.*, 1966), in the structures of (I) and (II) the molecular complexes retain additional coordination functionality in the form of two outer pyridyl N-donor groups. Their combination with unsaturated axial coordination positions at the metal ion clearly provides a mechanism for intermolecular interactions and the generation of crystal packing by total interconnection (Cu–N) of the available binding sites. In both structures, the Cu atoms additionally form two weak axial bonds with N atoms from neighbouring symmetry-related diketonates [Cu–N = 2.4987 (17) Å in (I), and 2.4045 (17) and 2.4532 (19) Å in (II)]. These elongated Cu–N bonds are only slightly shorter than those found for Cu[MeCOC(4-py)COCMe]₂ [2.567 (9) Å; Turner *et al.*, 1997], and the coordination geometry around the metal centre can be described as 4O+2N octahedral with an obvious Jahn–Teller distortion.

The aggregation of self-complementary molecules therefore results in the generation of flat square-grid frameworks (Figs. 3 and 4). However, the shapes and metrics of such square grids are not uniform for (I) and (II), as they are dictated by the mutual orientation of the binding directions provided by the molecules. The pyridyl and chelate fragments are not coplanar and, for the 3-pyridyl-substituted diketonate, *viz.* (I), the rotation around the C1–C5 single bond predetermines the orientation of the lone pairs of the N atoms with respect to the CuO₄ plane. Since the resulting angle between the Cu1–N1ⁱ and N1–Cuⁱⁱⁱ [symmetry codes: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $-x, \frac{1}{2} + y,$

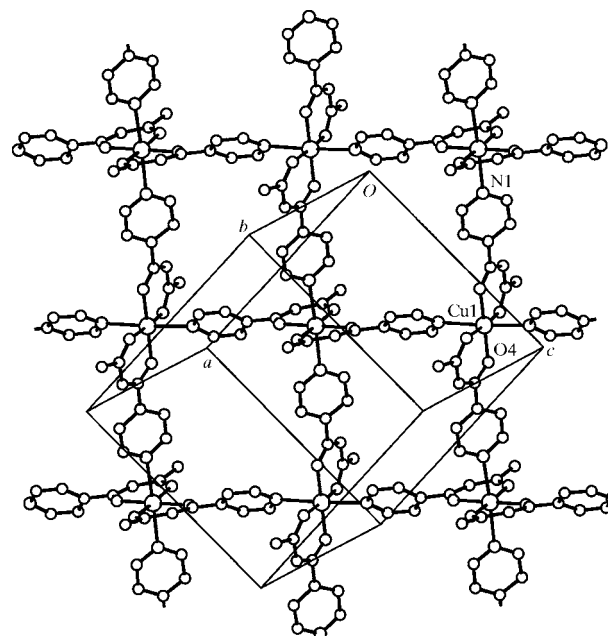


Figure 4
The two-dimensional network in the structure of (II). H atoms and methanol solvent molecules have been omitted for clarity.

$-\frac{1}{2} + z]$ vectors is nearly a function of the C2—C1—C5—C9 torsion angle [$-28.6(3)^\circ$], the self-organization of the molecules of (I) cannot afford rectangles and leads to rhombic grids (Cu···Cu···Cu angles are 66.87 and 113.13°) (Fig. 3). Such a collapse of the grids results in elimination of any internal cavities and facilitates dense packing of the molecules within the coordination layer. Successive layers of the structure are related by simple translation along the a axis.

For (II), the dihedral angles between the planes of the pyridyl and diketonate groups are even larger (30.7 and 46.5°). However, any orientation of the pyridyl-4 substituent does not alter the nearly orthogonal binding directions, and this predetermines the generation of approximately square grids (Cu···Cu···Cu angles 81.1 and 99.0°) (Fig. 4). This shape maximizes the internal cages of the grids, which became large enough ($4.5 \times 4.5 \text{ \AA}$) to sustain certain guest molecules. Each mesh of the network houses the methyl group from an adjacent layer (Fig. 5), which leads to the formation of an interdigitated pattern by dual population of all available grid cages. The latter has a clear chemical significance, since the tightness of the packing of the two-dimensional coordination nets within and between such double layers is different [interlayer separations of 4.72 and 6.66 \AA , compared with the uniform interlayer distance of 6.48 \AA for (I)] (Fig. 6) and this may favour an effective accommodation of guest molecules between pairs of weakly bonded layers, in the same way as occurs for clays or organic clay mimics (Biradha *et al.*, 1998). In (II), the free space between the interlocked double layers is filled by methanol solvent molecules, which act as hydrogen-bond donors to O2 atoms of the coordinated diketonate, and

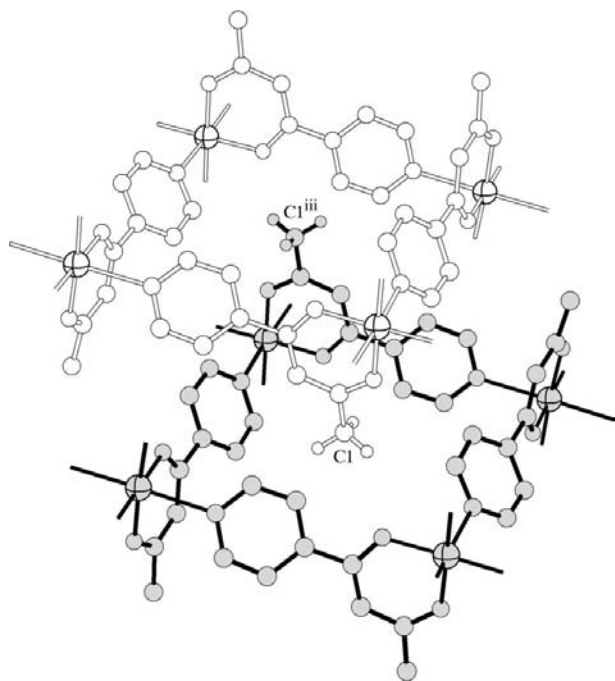


Figure 5
Self-inclusion of coordination layers in the structure of (II). Aromatic H atoms have been omitted for clarity. The methyl group resides exactly inside the rectangular cage (atom C1 deviates from the corresponding Cu₄ plane by 0.47 \AA). [Symmetry code: (iii) $-x, -y, 1 - z$.]

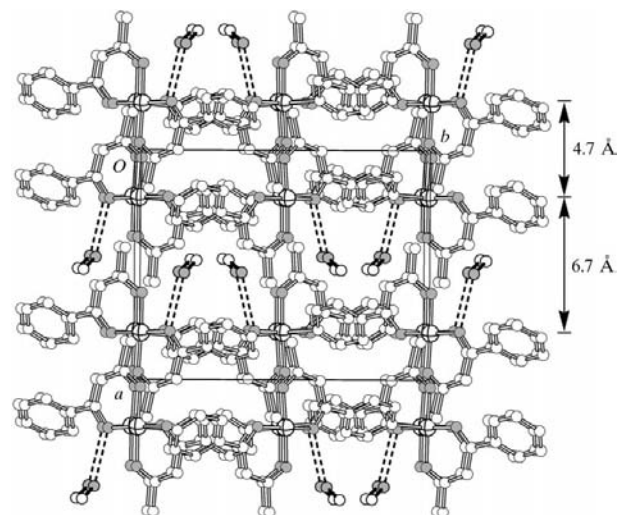


Figure 6
A perspective view of the structure of (II), showing two kinds of interlayer separations and how the guest methanol molecules are accommodated between pairs of closely separated layers. H atoms have been omitted and O atoms are shaded grey.

also as acceptors of a typical weak hydrogen bond, namely C18^{iv}—H···O [symmetry code: (iv) $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$; Table 3] (Desiraju & Steiner, 1999).

In brief, self-associating copper(II) complexes with 1-pyridyl-substituted butane-1,3-diones reveal a potential for one-component supramolecular synthesis of two-dimensional coordination frameworks with tuneable metrics. Structure (II) suggests the existence of new families of inclusion compounds, in which the guest species are accommodated in the interlayer space provided by the self-assembled coordination layers.

Experimental

The ligands 1-(3-pyridyl)butane-1,3-dione (HL¹) and 1-(4-pyridyl)butane-1,3-dione (HL²) were synthesized according to the literature method of Levine & Sneed (1951). For the preparation of complex (I), Cu(OAc)₂·H₂O (0.050 g, 0.25 mmol) in methanol (5 ml) was added to a solution of HL¹ (0.086 g, 0.52 mmol) in dimethylformamide (5 ml). Slow evaporation of the solvent over a period of 10–15 d gave green prismatic crystals of the product in 23% yield. In the same manner, (II) was synthesized in 36% yield, starting with a solution of Cu(OAc)₂·H₂O (0.050 g, 0.25 mmol) in methanol (5 ml) and HL² (0.086 g, 0.52 mmol) in CHCl₃ (5 ml). Compound (II) readily loses the methanol solvent in air within minutes, with loss of crystallinity. For X-ray analysis, the crystal was sealed in a capillary under the mother solution.

Compound (I)

Crystal data

[Cu(C₉H₈NO₂)₂]
M_r = 387.87
 Monoclinic, $P2_1/c$
a = $6.6044(11) \text{ \AA}$
b = $9.2107(15) \text{ \AA}$
c = $13.950(2) \text{ \AA}$
 β = $101.217(3)^\circ$
V = $832.4(2) \text{ \AA}^3$

Z = 2
D_x = 1.547 Mg m^{-3}
 Mo $K\alpha$ radiation
 μ = 1.34 mm^{-1}
T = $223(2) \text{ K}$
 Prism, green
 $0.35 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	5845 measured reflections
ω scans	2001 independent reflections
Absorption correction: empirical (using intensity measurements) (<i>SADABS</i> ; Sheldrick, 1996)	1725 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.645$, $T_{\max} = 0.768$	$R_{\text{int}} = 0.018$
	$\theta_{\text{max}} = 28.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.3834P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.36 \text{ e } \text{Å}^{-3}$
2001 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{Å}^{-3}$
115 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1—O2	1.9485 (13)	C1—C5	1.504 (2)
Cu1—O1	1.9645 (12)	C2—C3	1.403 (2)
Cu1—N1 ⁱ	2.4896 (17)	C3—C4	1.510 (3)
O1—C1	1.271 (2)	C5—C9	1.391 (3)
O2—C3	1.264 (2)	C5—C6	1.391 (3)
N1—C9	1.338 (2)	C6—C7	1.390 (3)
N1—C8	1.339 (3)	C7—C8	1.382 (3)
C1—C2	1.395 (3)		
O2—Cu1—O1	93.51 (5)	O1—C1—C2	125.94 (16)
O2—Cu1—O1 ⁱⁱ	86.49 (5)	O1—C1—C5	115.74 (15)
O2—Cu1—N1 ⁱ	85.28 (6)	C2—C1—C5	118.31 (16)
O1—Cu1—N1 ⁱ	91.29 (5)	C1—C2—C3	124.77 (17)
O2—Cu1—N1 ⁱⁱⁱ	94.72 (6)	O2—C3—C2	125.90 (17)
O1—Cu1—N1 ⁱⁱⁱ	88.71 (5)	O2—C3—C4	115.97 (16)
C1—O1—Cu1	124.42 (11)	C2—C3—C4	118.12 (17)
C3—O2—Cu1	124.97 (12)		
C2—C1—C5—C9	−28.6 (3)		

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

Compound (II)

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_8\text{NO}_2)_2] \cdot \text{CH}_4\text{O}$	$Z = 4$
$M_r = 419.91$	$D_x = 1.436 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.3492$ (12) Å	$\mu = 1.16 \text{ mm}^{-1}$
$b = 14.1993$ (13) Å	$T = 293$ (2) K
$c = 12.1291$ (12) Å	Prism, green
$\beta = 96.410$ (3)°	$0.14 \times 0.14 \times 0.12 \text{ mm}$
$V = 1942.4$ (3) Å ³	

Data collection

Stoe IPDS diffractometer	3072 reflections with $I > 2\sigma(I)$
φ oscillation scans	$R_{\text{int}} = 0.038$
12732 measured reflections	$\theta_{\text{max}} = 27.9^\circ$
4578 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4578 reflections	$\Delta\rho_{\text{max}} = 0.27 \text{ e } \text{Å}^{-3}$
244 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{Å}^{-3}$

Table 2

Selected geometric parameters (Å, °) for (II).

Cu1—O3	1.9559 (15)	C1—C2	1.499 (4)
Cu1—O1	1.9560 (15)	C2—C3	1.409 (3)
Cu1—O4	1.9584 (13)	C3—C4	1.384 (3)
Cu1—O2	1.9653 (13)	C4—C5	1.506 (3)
Cu1—N1 ⁱ	2.4045 (17)	C8—C9	1.386 (3)
Cu1—N2 ⁱⁱ	2.4531 (18)	C10—C11	1.501 (3)
O1—C2	1.258 (3)	C11—C12	1.406 (3)
O2—C4	1.272 (2)	C12—C13	1.382 (3)
O3—C11	1.261 (3)	C13—C14	1.509 (3)
O4—C13	1.274 (2)		
O3—Cu1—O1	176.10 (6)	O4—Cu1—N2 ⁱⁱ	90.20 (7)
O3—Cu1—O4	92.66 (6)	O2—Cu1—N2 ⁱⁱ	89.59 (7)
O1—Cu1—O4	87.55 (6)	N1 ⁱ —Cu1—N2 ⁱⁱ	176.67 (7)
O3—Cu1—O2	86.35 (6)	C2—O1—Cu1	125.33 (14)
O1—Cu1—O2	93.42 (6)	C4—O2—Cu1	123.11 (13)
O4—Cu1—O2	179.00 (6)	C11—O3—Cu1	124.98 (14)
O3—Cu1—N1 ⁱ	94.05 (6)	C13—O4—Cu1	123.18 (13)
O1—Cu1—N1 ⁱ	89.83 (6)	O1—C2—C3	125.0 (2)
O4—Cu1—N1 ⁱ	92.96 (6)	O2—C4—C3	126.83 (18)
O2—Cu1—N1 ⁱ	87.27 (6)	O3—C11—C12	124.7 (2)
O3—Cu1—N2 ⁱⁱ	86.86 (7)	C13—C12—C11	125.0 (2)
O1—Cu1—N2 ⁱⁱ	89.24 (7)	O4—C13—C12	126.56 (18)
O2—C4—C5—C6	−45.0 (3)	O4—C13—C14—C15	29.3 (3)

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

Table 3

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O5—H1 ⁱⁱⁱ ···O2	0.85	2.17	3.018 (3)	172
C18—H18A···O5 ⁱⁱⁱ	0.96	2.47	3.416 (4)	171

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

H atoms were located in a difference map and treated as riding, with C—H distances of 0.96 Å and an O—H distance of 0.85 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$, or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *SMART-NT* (Bruker, 1998) for (I); *IPDS Software* (Stoe & Cie, 2000) for (II). Cell refinement: *SMART-NT* for (I); *IPDS Software* for (II). Data reduction: *SMART-NT* for (I); *IPDS Software* for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.700.00; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3015). Services for accessing these data are described at the back of the journal.

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