Poly[[aqua-μ_3-2,2-dimethylmalonato-copper(II)] monohydrate] and poly[aqua-μ_3-2,2-dimethylmalonato-copper(II)]

Ming-Lin Guo* and Feng-Qin Wang

School of Environment and Chemical Engineering and Key Laboratory of Hollow Fiber Membrane Materials and Membrane Processes, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China
Correspondence e-mail: guomlin@yahoo.com

The coordination mode of the dimethylmalonate ligand in the two title Cu^{II} complexes, {[Cu(C$_5$H$_3$O$_4$)(H$_2$O)]·H$_2$O}$_n$, (I), and [Cu(C$_5$H$_3$O$_4$)(H$_2$O)]$_n$, (II), is the same, with chelated six-membered, bis-monodentate and bridging bonding modes. However, the coordination environment of the Cu^{II} atoms, the connectivity of their metal–organic frameworks and their hydrogen-bonding interactions are different. Complex (I) has a perfect square-pyramidal Cu^{II} environment with the aqua ligand in the apical position, and only one type of square grid consisting of Cu^{II} atoms linked *via* carboxylate bridges to three dimethylmalonate ligands, with weak hydrogen-bond interactions within and between its two-dimensional layers. Complex (II) has a coordination geometry that is closer to square pyramidal than trigonal bipyramidal for its Cu^{II} atoms with the aqua ligand now in the basal plane. Its two-dimensional layer structure comprises two alternating grids, which involve two and four different dimethylmalonate anions, respectively. There are strong hydrogen bonds only within its layers.

Comment

In complexes of copper with malonic acid, the malonate dianion and protonated malonate have proved to have great versatility. Structural complexity is associated with the simultaneous adoption of chelating bidentate and different carboxylate-bridging coordination modes (Pasan *et al.*, 2007; Rodriguez-Martin *et al.*, 2002; Delgado *et al.*, 2004; Gil de Muro *et al.*, 2004). For dimethylmalonate, however, in spite of this wealth of possibilities, no binary complexes with the Cu^{II} cation have been reported to date. Two related structural studies have been published, one containing the methylmalonate dianion (Pasan *et al.*, 2007) and the other involving our previously reported heterobimetallic complex, poly[di-aquabis(μ_3-2,2-dimethylpropanedioato)calcium(II)copper(II)]

(Guo & Wang, 2010). In the course of an attempt to obtain such a heterobimetallic complex, we also obtained the two title complexes, (I) and (II). Interestingly, both these complexes have the same coordination mode of the dimethylmalonate ligand, but the connectivity of their metal–organic frameworks is different and there are different hydrogen-bond interactions. A comparison with the previously reported methylmalonate Cu^{II} complexes (Pasan *et al.*, 2007) reveals that the presence of two methyl groups, due to geometric constraints that would contribute to the overall stability of the resulting complexes, induces different coordination geometries of the metal. We report here the crystal structures of (I) and (II).

(I)

(II)
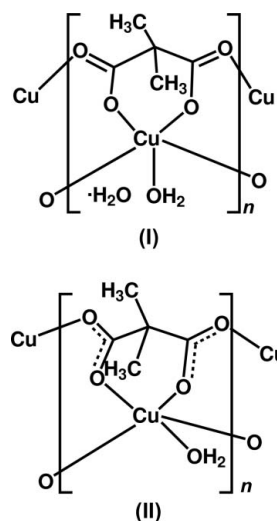
Apart from the solvent water molecule in (I), both asymmetric units comprise one Cu^{II} atom, one complete dimethylmalonate dianion and one coordinated water molecule (Figs. 1a and 1b). In (I), the Cu^{II} atom exhibits a perfect square-pyramidal coordination environment ($\tau = 0.023$; Addison *et al.*, 1984), with atoms O1, O3, O2^i and O4^{ii} (see Fig. 1a for symmetry codes) from three different dimethyl-malonate dianions forming the basal plane with a mean Cu—O(eq) bond distance of 1.964 (7) Å, comparable with that reported for poly[aqua(μ_3-methylmalonato-O,O',O'',O''')-copper(II)] (Pasan *et al.*, 2007). The apical position is occupied by a water molecule [Cu1—O5 = 2.306 (7) Å] and the Cu^{II} atom is shifted by 0.034 (3) Å from the plane defined by the basal O atoms towards the apical position. In the case of (II), the Cu^{II} atom has a coordination geometry that is closer to square pyramidal than trigonal bipyramidal ($\tau = 0.381$), with atoms O1, O3, O2^i of two different dimethylmalonate ligands and atom O5 of the aqua ligand (see Fig. 1b for symmetry codes) in a roughly square-planar arrangement and a mean Cu—O(eq) bond distance of 1.949 (2) Å. The apical position is occupied by atom O4^{ii} of a third dimethylmalonate ligand [Cu1—O4^{ii} = 2.251 (2) Å] and the Cu^{II} atom deviates by 0.2132 (5) Å from the least-squares plane defined by the basal O atoms towards apical atom O4^{ii}. The Cu—O(eq) bond lengths are somewhat longer than those reported [mean 1.913 (7) Å] for the square-planar Cu^{II} atom in poly[diaqua-bis(μ_3-2,2-dimethylpropanedioato)calcium(II)copper(II)]

(a)

(b)
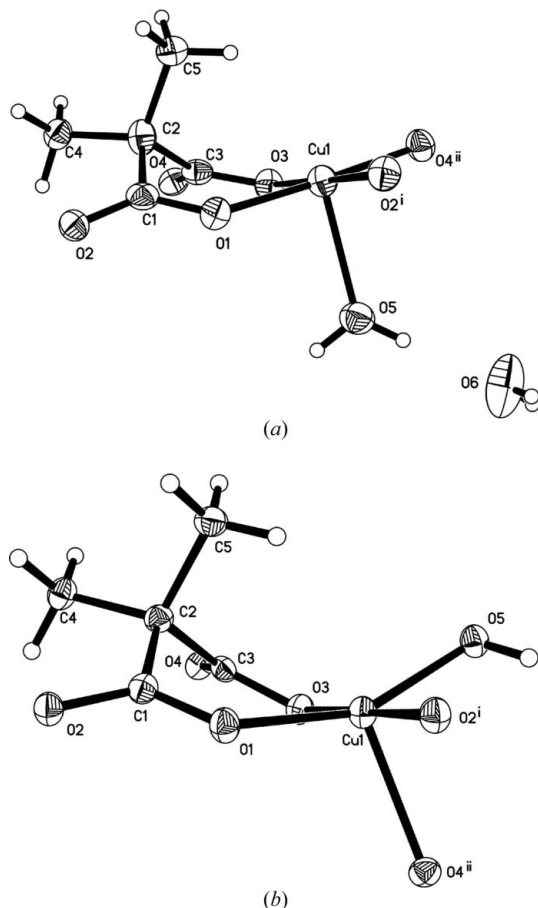
Figure 1
The structures of (*a*) (I) and (*b*) (II), showing the atom-numbering schemes and the Cu^{II} coordination environments. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes for (I): (i) $-x + 2, y + \frac{1}{2}, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + 1$. Symmetry codes for (II): (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.]

(Guo & Wang, 2010). There are no additional Cu—O contacts in (I) and (II) out to 3 Å.

The coordination behaviour of the dimethylmalonate ligands in (I) and (II) is the same, with chelated six-membered, bis-monodentate and bridging bonding modes, but the connectivity in their structures is different (Figs. 2*a* and 2*b*). In both complexes, there is one methyl group directed towards the open space opposite the apical Cu1—O bond. For (I), the coordinated water molecule, O5, is opposite this methyl group, while in the case of (II), it is the O4 atom from a different dimethylmalonate ligand which lies on the opposite side of the Cu1 atom from the methyl group. In (I), the basal plane of four O atoms (defined by O1/O3/O2^i/O4^{ii}) makes a dihedral angle of 81.8 (3)° with the corresponding plane in the next Cu^{II} square pyramid in the network (Fig. 2*a*). This value is very close to that observed in the cyclobutane-1,1-dicarboxylate Cu^{II} complex [82.2 (8)°; Pasan *et al.*, 2006], but it is somewhat smaller than that found in poly[aqua(μ_3-methylmalonato-*O,O′,O″,O‴*)copper(II)] [84.44 (9)°; Pasan *et al.*, 2007].

In the case of (II), if its configuration is visualized as being a considerably distorted trigonal bipyramid, with atoms O1, O4^{ii}

and O5 in the equatorial plane (symmetry code as in Fig. 1*b*), the Cu^{II} atom deviates by 0.0078 (4) Å from the least-squares plane of those atoms. The value of the dihedral angle between the equatorial planes of adjacent Cu^{II} atoms being 75.35 (13)°. This is larger than the value found in the isotypic complex ($\tau =$ 0.58) poly[aqua-μ_3-2,2-dimethylmalonato-zinc(II)] [68.70 (8)°; Guo & Zhao, 2006].

The O—C—O angles for the four carboxylate groups of (I) and (II) are close to 120° (Tables 1 and 3). The values of the C—O bond distances in these carboxylate groups indicate that the mesomeric effect for the carboxylate groups of (II) is larger than that of the carboxylate groups of (I). In the structures of (I) and (II), each dimethylmalonate dianion binds to three Cu^{II} atoms, and each group of four Cu^{II} atoms

(a)

(b)
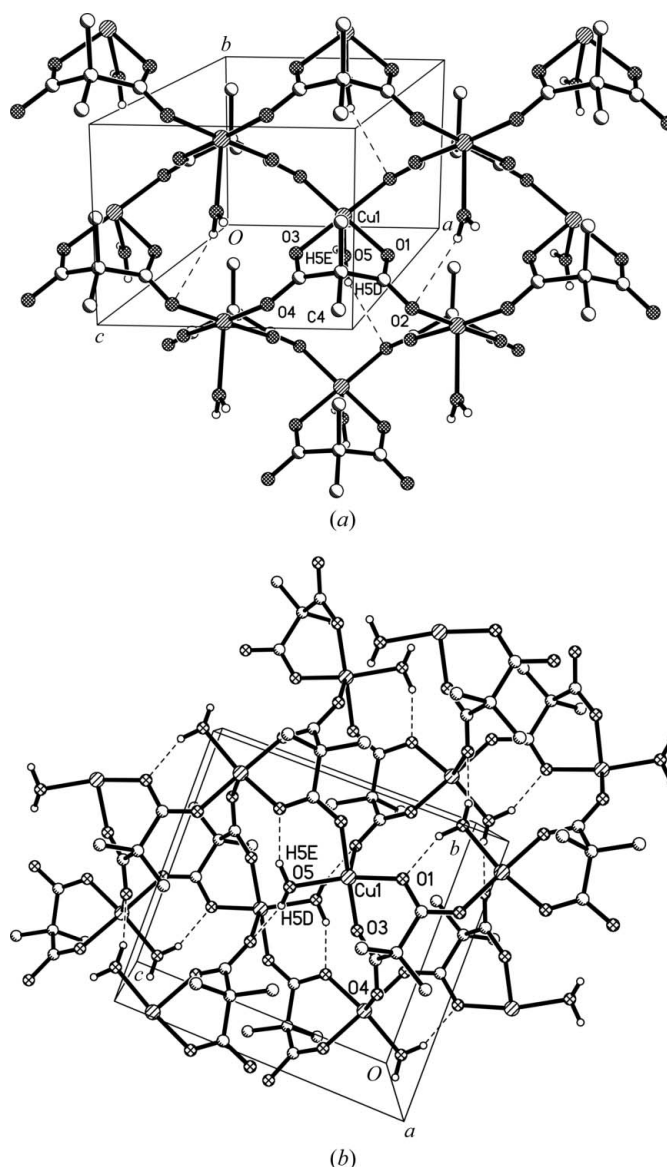
Figure 2
The two-dimensional extended structure of (*a*) (I), parallel to the *ab* plane and viewed approximately down the *c* axis, and (*b*) (II), parallel to the *bc* plane and viewed down the *a* axis, showing the two-dimensional polymeric layers. Hydrogen-bonding interactions are shown as dashed lines for the intralayers.
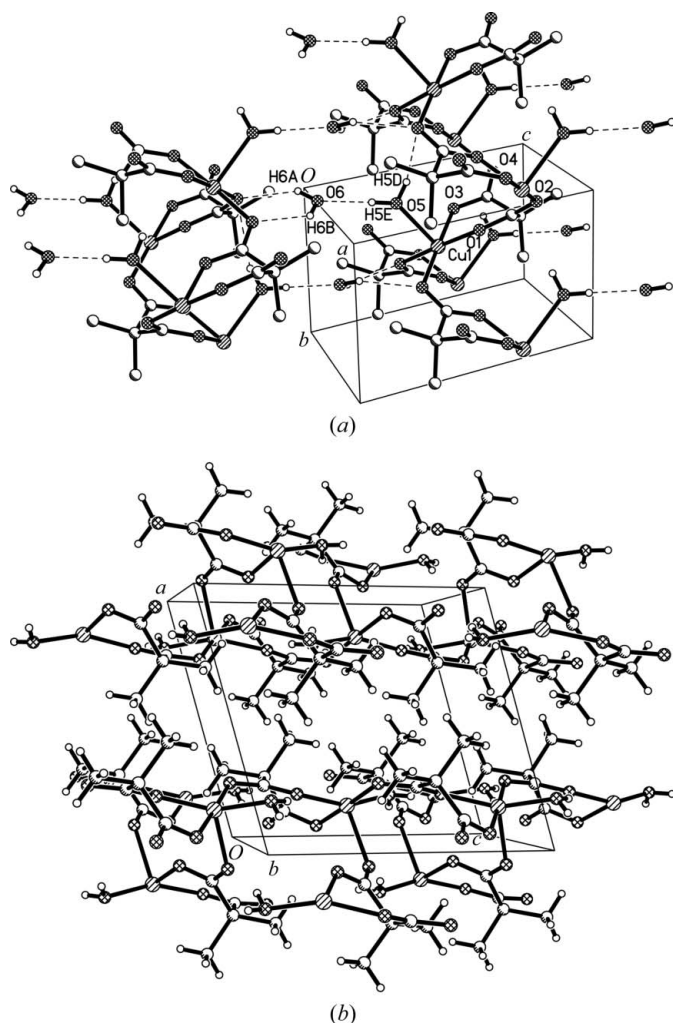
Figure 3
(*a*) A packing diagram for (I), viewed approximately down the *a* axis, showing the hydrogen-bonding interactions as dashed lines for the interlayers. The H atoms of the methyl groups have been omitted for clarity. (*b*) A packing diagram for (II), viewed approximately down the *b* axis, showing how the interlayer spaces are occupied alternately by a methyl group of the upper layer and another one from the layer below.

are linked together *via* carboxylate bridges, forming a 16-membered ring, but there is only one such connectivity in (I), while there are two in (II). An alternative description, perhaps more revealing from the viewpoint of crystal engineering, is as follows. The structure of (I) consists of one type of square grid of Cu^{II} atoms linked parallel to the *ab* plane *via* three different dimethylmalonate anions (Fig. 2*a*), and the intralayer Cu1$\cdots$Cu1^{iii} and Cu1$\cdots$Cu1^{iv} (see Table 1 for symmetry codes) separations through the carboxylate bridges are 4.8583 (18) and 4.8847 (18) Å, respectively, while the structure of (II) comprises two different alternating grids parallel to the *bc* plane, one involving two different dimethylmalonate anions and the other containing four. The intralayer Cu1$\cdots$Cu1^{iii} and Cu1$\cdots$Cu1^{iv} (see Table 3 for symmetry codes) separations through the carboxylate bridges are 5.052 (1) and 5.310 (1) Å, respectively.

Within the two-dimensional layer of (I), atom O2 of the dimethylmalonate dianion, acting as hydrogen-bond acceptor,

is involved in a weak intermolecular hydrogen-bonding interaction with atom H5*D* of the coordinated water molecule (Table 2 and Fig. 2*a*). Between the two-dimensional layers, solvent water molecule O6 is responsible for the formation of a six-membered hydrogen-bonded ring of graph set $R_2^2(6)$ (Bernstein *et al.*, 1995) (Fig. 3*a*). Furthermore, the hydrogen bonds formed by aqua ligand O5 are also engaged in forming a chain of edge-shared 12-membered hydrogen-bonded rings of graph set $R_5^4(12)$ along the *b* direction. In contrast, within the two-dimensional layer of (II), there are two strong intermolecular hydrogen-bonding interactions (Brown, 1976) involving symmetry-related positions of atoms O1, O4 and aqua ligand O5 (Table 4). These hydrogen bonds play an important role in the propagation of the two-dimensional layer structure, due to their formation of different hydrogen-bonded rings with graph sets $R(6)$, $R_2^2(10)$ and $R_2^2(8)$, which is formed *via* Cu1 and O5—H5*D*$\cdots$O4^v hydrogen bonds (Fig. 2*b*). No hydrogen bonds are observed between the two-dimensional layers; the interlayer spaces are occupied alternately by a methyl group of the upper layer and another one from the layer below (Fig. 3*b*).

In summary, a comparison with the previously reported methylmalonate Cu complex (Pasan *et al.*, 2007) reveals that (I) has some similarities in the connectivity of its two-dimensional layered structure, but its interlayer structure is different. Not only the methyl groups, but also hydrogen bonds separate the layers. The interlayer spaces are occupied by methyl groups of the layers above and below and by water molecules. The chemically similar complex poly[aqua-μ_3-2,2-dimethylmalonato-zinc(II)] (Guo & Zhao, 2006) and (II) are isotypic, and they both have the same structure topology. It might be possible that the differences in conditions during the synthesis and the packing efficiency requirements of the different extended structures are responsible for the different coordination environments of the two complexes.

Experimental

Complex (I) was prepared under continuous stirring, with successive addition of dimethylmalonic acid (0.53 g, 4 mmol), CaCO$_3$ (0.30 g, 3 mmol) and Cu(NO$_3$)$_2$·6H$_2$O (0.48 g, 2 mmol) to distilled water (25 ml) at room temperature. After filtration, slow evaporation over a period of 2 d at room temperature provided blue prismatic crystals of (I). Complex (II) was prepared under continuous stirring, with successive addition of dimethylmalonic acid (0.53 g, 4 mmol), Na$_2$CO$_3$ (0.22 g, 2 mmol), Cu(NO$_3$)$_2$·6H$_2$O (0.48 g, 2 mmol) and barium nitrate (0.52 g, 2 mmol) to distilled water (20 ml) at room temperature. After filtration, slow evaporation over a period of 3 d at room temperature provided blue prismatic crystals of (II).

Compound (I)

Crystal data

[Cu(C$_5$H$_3$O$_4$)(H$_2$O)]·H$_2$O	$V = 379.76$ (13) Å^3
$M_r = 229.67$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.0202$ (14) Å	$\mu = 2.86$ mm^{-1}
$b = 5.6645$ (11) Å	$T = 294$ K
$c = 9.938$ (2) Å	$0.18 \times 0.06 \times 0.04$ mm
$\beta = 106.06$ (3)°	

metal-organic compounds

Data collection

Rigaku Saturn CCD area-detector diffractometer

Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.793$, $T_{max} = 0.887$

3098 measured reflections
1467 independent reflections
1177 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.152$
$S = 1.01$
1467 reflections
112 parameters
2 restraints

H-atom parameters constrained
$\Delta\rho_{max} = 1.22$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}
Absolute structure: Flack (1983), with 506 Friedel pairs
Flack parameter: -0.02 (7)

Compound (II)

Crystal data

[Cu(C5H3O4)(H2O)]
$M_r = 211.65$
Monoclinic, $P2_1/c$
$a = 8.7697$ (18) Å
$b = 8.5492$ (17) Å
$c = 9.3313$ (19) Å
$\beta = 105.42$ (3)°

$V = 674.4$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.21$ mm^{-1}
$T = 294$ K
$0.12 \times 0.08 \times 0.08$ mm

Data collection

Rigaku Saturn CCD area-detector diffractometer

Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.745$, $T_{max} = 0.773$

4871 measured reflections
1183 independent reflections
1083 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.086$
$S = 1.11$
1183 reflections

100 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Initially, the structure of (I) refined poorly, with $R_1 = 0.115$ [$I > 2\sigma(I)$] and 0.119 (all data), $wR_2 = 0.260$, highest peak = 5.50 e Å^{-3} and deepest hole = -0.77 e Å^{-3}. The TwinRotMat routine in *PLATON* (Spek, 2009) indicated the presence of nonmerohedral twinning in the data, with a twin law of (-1 0 0/0 -1 0/0.783 0 1), which corresponds to a twofold rotation about (001). A reflection file in HKLF 5 format (*SHELXL97*; Sheldrick, 2008) with twin contributions to overlapping reflections added to the original reflection file was used in the final refinement. 813 of the 1507 reflections had contributions from both twin components. The twin fraction refined to 0.330 (1).

The H atoms of the water molecules were found in difference Fourier maps. However, during refinement they were fixed at O—H = 0.85 Å, with $U_{iso}(H) = 1.2U_{eq}(O)$. The H atoms of the methyl groups were placed in geometrically idealized positions and treated as riding, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The initial refinement of (I) led to a C2—C5 bond length of 1.576 (11) Å, so a bond-length restraint of 1.540 (4) Å was applied to this bond in the final refinement.

For both compounds, data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*;

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—O1	1.958 (7)	C1—O2	1.231 (13)
Cu1—O2^i	1.981 (7)	C1—O1	1.270 (13)
Cu1—O4^{ii}	1.961 (7)	C3—O4	1.246 (13)
Cu1—O3	1.958 (8)	C3—O3	1.278 (14)
Cu1—O5	2.306 (7)		
O3—Cu1—O1	89.8 (2)	O3—Cu1—O5	90.8 (3)
O3—Cu1—O4^{ii}	89.8 (3)	O1—Cu1—O5	89.8 (3)
O1—Cu1—O4^{ii}	177.3 (4)	O4^{ii}—Cu1—O5	92.9 (3)
O3—Cu1—O2^i	178.7 (4)	O2^i—Cu1—O5	90.5 (3)
O1—Cu1—O2^i	90.3 (3)	O2—C1—O1	123.2 (10)
O4^{ii}—Cu1—O2^i	90.1 (2)	O4—C3—O3	119.9 (9)
O1—C1—O2—Cu1^{iii}	-14.3 (14)	O3—C3—O4—Cu1^{iv}	18.2 (14)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6$B\cdots$O4^v	0.86	2.34	3.009 (13)	135
O6—H6$A\cdots$O2^{vi}	0.85	2.18	2.907 (13)	143
O5—H5$E\cdots$O6	0.85	1.89	2.745 (13)	179
O5—H5$D\cdots$O2^{iii}	0.85	2.54	3.310 (11)	151

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

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—O3	1.928 (2)	O1—C1	1.268 (4)
Cu1—O1	1.937 (2)	O2—C1	1.256 (4)
Cu1—O5	1.961 (2)	O3—C3	1.271 (4)
Cu1—O2^i	1.969 (2)	O4—C3	1.252 (4)
Cu1—O4^{ii}	2.251 (2)		
O3—Cu1—O1	89.50 (10)	O3—Cu1—O4^{ii}	95.83 (10)
O3—Cu1—O5	88.54 (10)	O1—Cu1—O4^{ii}	106.50 (10)
O1—Cu1—O5	155.47 (11)	O5—Cu1—O4^{ii}	98.02 (10)
O3—Cu1—O2^i	178.31 (11)	O2^i—Cu1—O4^{ii}	85.06 (10)
O1—Cu1—O2^i	88.87 (11)	O2—C1—O1	123.2 (3)
O5—Cu1—O2^i	92.76 (10)	O4—C3—O3	122.1 (3)
Cu1^{iii}—O2—C1—O1	-23.1 (5)	Cu1^{iv}—O4—C3—O3	16.4 (5)

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5$D\cdots$O4^v	0.85	1.85	2.678 (3)	164
O5—H5$E\cdots$O1^i	0.85	1.82	2.604 (3)	153

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

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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3385). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brown, I. D. (1976). *Acta Cryst.* A**32**, 24–31.

Delgado, F. S., Sanchiz, J., Ruis-Perez, C., Lloret, F. & Julve, M. (2004). *CrystEngComm*, **6**, 443–450.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gil de Muro, I., Lezama, L., Insausti, M. & Rojo, T. (2004). *Polyhedron*, **23**, 929–936.

Guo, M.-L. & Wang, F.-Q. (2010). *Acta Cryst.* C**66**, m184–m187.

Guo, M.-L. & Zhao, Y.-N. (2006). *Acta Cryst.* C**62**, m563–m565.

Pasan, J., Sanchiz, J., Lloret, F., Julvec, M. & Ruiz-Perez, C. (2007). *CrystEngComm*, **9**, 478–487.

Pasan, J., Sanchiz, J., Ruiz-Perez, C., Campo, J., Lloret, F. & Julvec, M. (2006). *Chem. Commun.* pp. 2857–2859.

Rigaku/MSC (2005). *CrystalClear.* Version 1.3.6. Rigaku/MSC, The Woodlands, Texas, USA.

Rodriguez-Martin, Y., Hernandez-Molina, M., Delgado, F. S., Jorge Pasan, J., Ruiz-Perez, C., Sanchiz, J., Lloretc, F. & Julve, M. (2002). *CrystEngComm*, **4**, 522–535.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.