

Crystal-to-crystal transformation upon dehydration of a copper(II) 2,2':6',2''-terpyridine complex

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The reaction of 2,2':6',2''-terpyridine (terpy) with CuCl_2 in the presence of sodium sulfite led to the synthesis of the ionic complex aquachlorido(2,2':6',2''-terpyridyl- κ^3N,N',N'')copper(II) chlorido(dithionato- κO)(2,2':6',2''-terpyridyl- κ^3N,N',N'')cuprate(II) dihydrate, $[\text{CuCl}(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{H}_2\text{O})][\text{CuCl}(\text{S}_2\text{O}_6)(\text{C}_{15}\text{H}_{11}\text{N}_3)] \cdot 2\text{H}_2\text{O}$, (I), and the *in situ* synthesis of the $\text{S}_2\text{O}_6^{2-}$ dianion. Compound (I) is composed of a $[\text{CuCl}(\text{terpy})(\text{H}_2\text{O})]^+$ cation, a $[\text{Cu}(\text{S}_2\text{O}_6)(\text{terpy})]^-$ anion and two solvent water molecules. Thermogravimetric analysis indicated the loss of two water molecules at *ca* 363 K, and at 433 K the weight loss indicated a total loss of 2.5 water molecules. The crystal structure analysis of the resulting pale-green dried crystals, μ -dithionato- $\kappa^2 O:O'$ -bis[chlorido(2,2':6',2''-terpyridyl- κ^3N,N',N'')copper(II)] monohydrate, $[\text{Cu}_2\text{Cl}_2(\text{S}_2\text{O}_6)(\text{C}_{15}\text{H}_{11}\text{N}_3)_2] \cdot \text{H}_2\text{O}$, (II), revealed a net loss of 1.5 water molecules and the formation of a binuclear complex with two $[\text{CuCl}(\text{terpy})]^+$ cations bridged by a dithionate dianion. The crystal-to-crystal transformation involved an effective reduction in the

unit-cell volume of *ca* 7.6%. In (I), the ions are linked by $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds involving the coordinated and solvent water molecules and O atoms of the dithionate unit, to form ribbon-like polymer chains propagating in [100]. These chains are linked by $\text{Cu} \cdots \text{Cl}$ interactions [3.2626 (7) Å in the cation and 3.3492 (7) Å in the anion] centred about inversion centres, to form two-dimensional networks lying in and parallel to (0 $\bar{1}$ 1). In (II), symmetry-related molecules are linked by $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds involving the partially occupied disordered water molecule and an O atom of the bridging thiosulfite anion, to form ribbon-like polymer chains propagating in [100]. These chains are also linked by $\text{Cu} \cdots \text{Cl}$ interactions [3.3765 (12) Å] centred about inversion centres to form similar two-dimensional networks to (I) lying in and parallel to (0 $\bar{2}$ 2), crosslinked into three dimensions by $\text{C} \cdots \text{H} \cdots \text{O}=\text{S}$ and $\text{C} \cdots \text{H} \cdots \text{O}(\text{water})$ interactions.

Comment

Crystal-to-crystal structural transformations are not uncommon and many of them are the result of dehydration of transition metal complexes or polymers (Habib *et al.*, 2008; Lin *et al.*, 2008; Mahmoudi & Morsali, 2008; Mobin *et al.*, 2009). Some of these structural transformations have been shown by *in situ* powder X-ray diffraction to be reversible on rehydration (Wang *et al.*, 2007; Aslani *et al.*, 2008; Sereda *et al.*, 2009). The ligand 2,2':6',2''-terpyridine (terpy) was first synthesized by Morgan & Burstall (1932). Since then, a very large number of transition metal complexes containing terpy have been synthesized and studied for their optical and electrochemical properties, *viz.* metal-to-ligand charge transfer (MLCT) in the visible-light region, reversible reduction and oxidation, and fairly intense luminescence. A search of the Cambridge Structural Database (CSD, Version 5.1, last update May 2010; Allen, 2002) revealed the presence of more than 1100 structures involving terpy, the majority being coordination complexes.

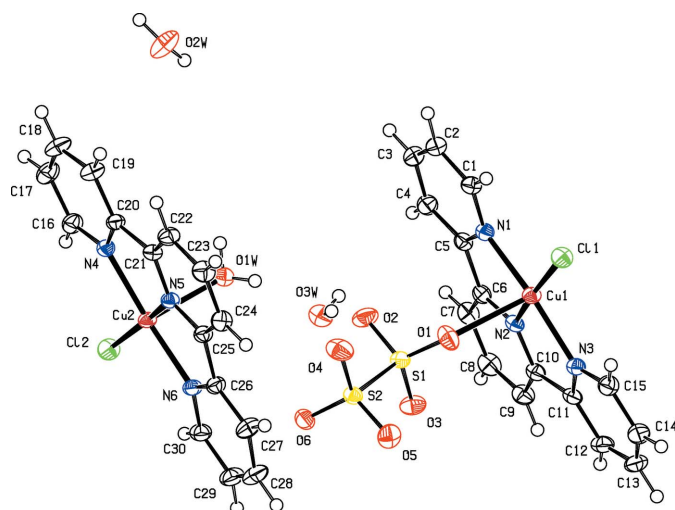
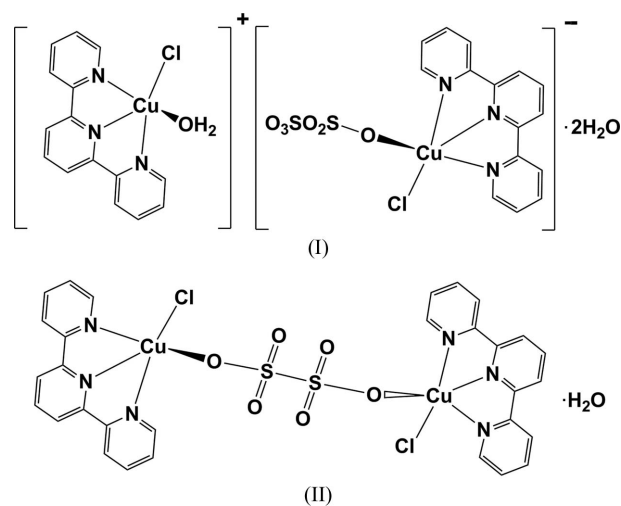


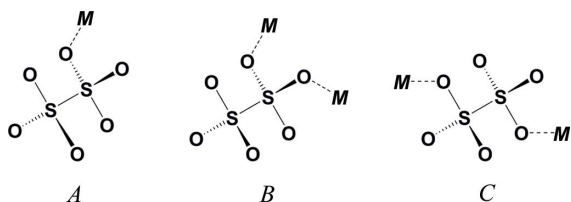
Figure 1

A view of the molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



The dithionate anion is a potentially useful component for the synthesis of multidimensional coordination polymers (Rusanov *et al.*, 2003; Neels *et al.*, 2003). A search of the CSD

revealed the presence of 119 transition metal complexes containing this anion. However, in the majority of cases it is not coordinated to the metal atom. Three coordination modes were found in this CSD search (see *A*, *B* and *C* in the Scheme below). Coordination mode *A* was observed for six compounds, of which four are copper(II) complexes (Bernhardt *et al.*, 2004; Ishii, 2001*a*; Donlevy *et al.*, 1990). Coordination mode *B* was observed for only two compounds, both of which are copper(II) complexes (Turba *et al.*, 2008; Ishii, 2001*a*); one of them, *catena*-poly[[μ -dithionato]aqua[2,6-bis(2-pyridyl)pyridine]copper(II)], also involves a terpyridine ligand (Ishii, 2001*a*). Bridging mode *C* was observed in seven compounds, of which three involve a Cu^{II} atom (Degtyarenko *et al.*, 2008; Kim *et al.*, 2003; Ishii, 2001*b*).



We report here the synthesis and crystal structure of a copper(II) terpy ionic complex, (I), with the *in situ* synthesis of the dithionate anion, which coordinates in mode *A*. On heating, (I) undergoes a crystal-to-crystal transformation to form a binuclear copper(II)–terpy dithionate-bridged complex, (II), with the anion coordinating in bridging mode *C*.

Complex (I) was synthesized by adding sodium sulfite to an aqueous solution of terpy and CuCl₂·2H₂O. It consists of a [CuCl(terpy)(H₂O)]⁺ cation, a [Cu(S₂O₆)(terpy)][−] anion and two solvent water molecules (Fig. 1). In the cation, atom Cu2 is coordinated to three N atoms of the terpy ligand and a chloride ion in the basal plane, and to a water molecule in the apical position. The coordination environment can be described as distorted square-pyramidal, with a τ value for Cu2 of 0.19 (where $\tau = 0$ for square-pyramidal and 1 for trigonal-pyramidal; Addison *et al.*, 1984; Spek, 2009). This cation has pseudo-mirror symmetry and is very similar to the same cation in aquachlorido(2,2':6',2''-terpyridyl)copper(II) chloride monohydrate, (III) (Schmitt *et al.*, 2010). The latter possesses crystallographic mirror symmetry and was produced as a by-product of the synthesis of (I). In the anion of (I), atom Cu1 is coordinated by the three N atoms of the terpy ligand and a chloride ion in the basal plane. The coordination geometry is completed by atom O3 from the dithionate anion in the apical position. The coordination environment is also distorted square-pyramidal, with a τ value for Cu1 of 0.18. The majority of the bond distances and angles in the cation and anion (Table 1) are similar to those found in (III). The main difference concerns the apical Cu–O distances: that involving an O atom of the dithionate anion, Cu1–O1, is 2.3901 (16) Å, while that involving the coordinated water molecule, Cu2–O1W, is 2.2816 (16) Å. Interestingly, in complex (III), the Cu–O(water) distance is significantly longer, at 2.3348 (19) Å.

In the crystal structure of (I), the ions are linked by O–H···O hydrogen bonds involving the coordinated and solvent

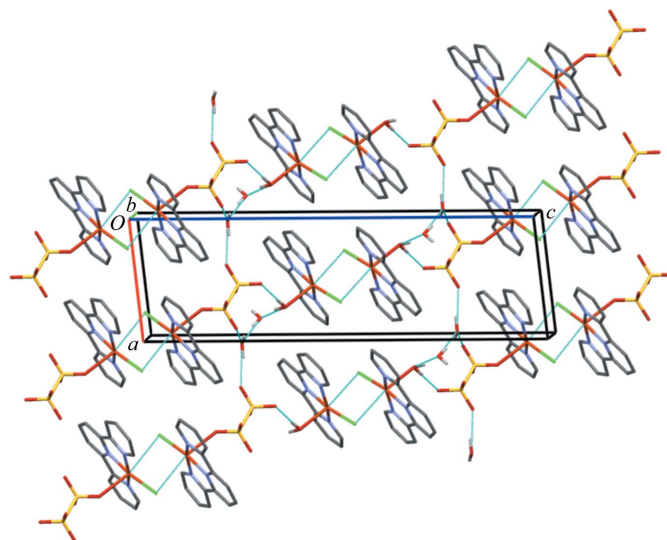


Figure 2
The crystal packing of complex (I), viewed along the *b* axis, showing the O–H···O hydrogen bonds and the Cu···Cl interactions as thin lines (see Tables 1 and 2 for details). H atoms not involved in hydrogen bonding have been omitted for clarity.

water molecules and O atoms of the dithionate unit (Table 2), to form ribbon-like polymer chains. These chains are linked by Cu···Cl interactions [3.2626 (7) Å in the cation and 3.3492 (7) Å in the anion, see Table 1] centred about inversion centres, to form two-dimensional networks lying in and parallel to (0 $\bar{1}$ 1), as shown in Fig. 2. The overall arrangement has pseudo-*I* centring (Spek, 2009). In the crystal structure, there is one significant S=O··· π interaction, involving the S2=O6 bond and the N4/C16–C20 pyridine ring of a neighbouring molecule at (*x*, 1 + *y*, *z*), with an O···centroid distance of 3.275 (2) Å and an S=O··· π angle of 134.8 (1)°. There is also a large number of C–H···O interactions involving both the water and the S=O O atoms, as well as a C–H···Cl interaction (Table 2), and these lead finally to the formation of a three-dimensional network.

Previous work on similar complexes has shown that, by careful heating, the solvent and coordinated water molecules can be eliminated. This leaves free coordination sites on the metal atom that can be filled by suitably positioned O or N atoms (Sereda *et al.*, 2008; Xue *et al.*, 2008; Zhang *et al.*, 2009). The emerald-green crystals of (I) were heated to 433 K by thermogravimetry, which indicated the loss of two water molecules at *ca* 363 K (weight loss of 3.94%, theoretical value 4.1%). The total weight loss at 433 K was 6.01% (equivalent to *ca* 2.5H₂O), whereas the theoretical value for the loss of three water molecules is 6.15%. The resulting material was found to be crystalline; the original crystals had retained their shape but were now pale-green in colour. X-ray diffraction analysis revealed that complex (I) had lost the coordinated water molecule in the cation and apparently only 1.5 solvent water molecules. Dehydration led to the formation of a centrosymmetric binuclear complex, (II), which is composed of two [CuCl(terpy)]⁺ cations bridged by a dithionate dianion and a partially occupied water molecule (Fig. 3). The crystal-to-

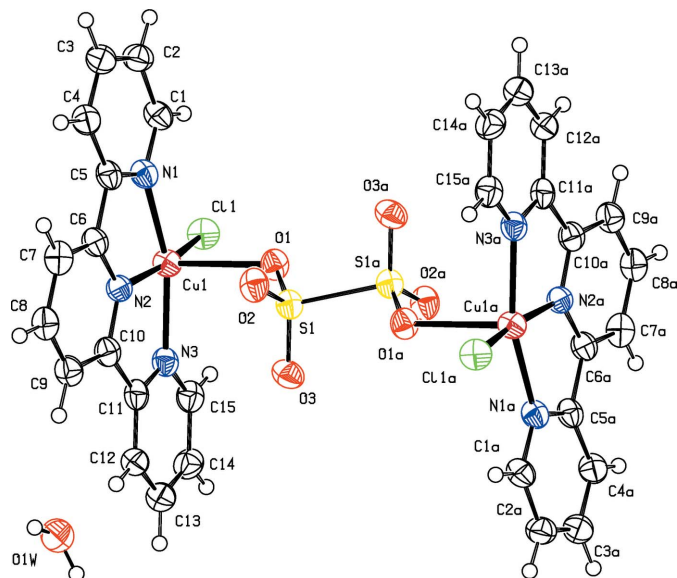


Figure 3

The molecular structure of complex (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The symmetry-related disordered water molecule is not shown. Atoms bearing the suffix 'a' are related to their unsuffixed equivalents by the symmetry operation $(2 - x, 2 - y, 1 - z)$.

crystal transformation resulted in an effective unit-cell volume contraction of *ca* 7.6%, considering that for (I) $Z = 2$ and $V = 1655.2(3) \text{ \AA}^3$, while for (II) $Z = 1$ and $V = 765.7(2) \text{ \AA}^3$.

In (II), atom Cu1 is coordinated to the three N atoms of the terpy ligand and a chloride ion in the basal plane, and to an O

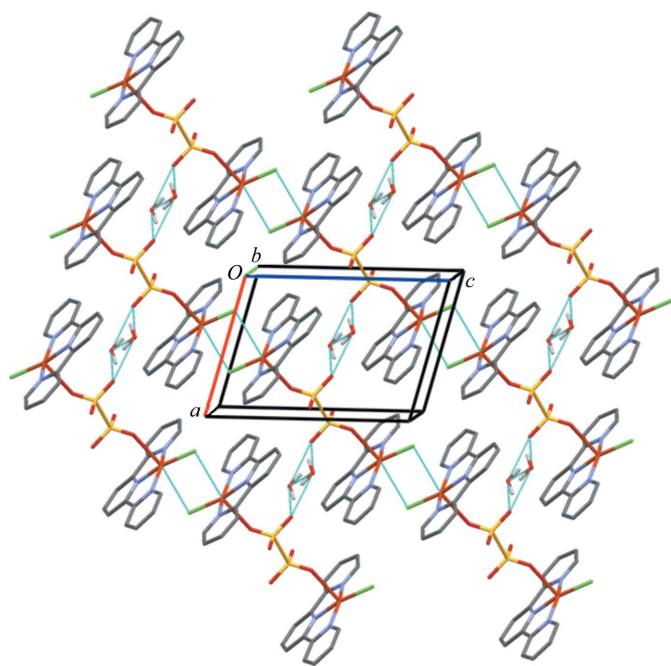


Figure 4

The crystal packing of complex (II), viewed along the *b* axis, showing the O—H...O hydrogen bonds and the Cu...Cl interactions as thin lines (see Tables 3 and 4 for details). H atoms not involved in hydrogen bonding have been omitted for clarity.

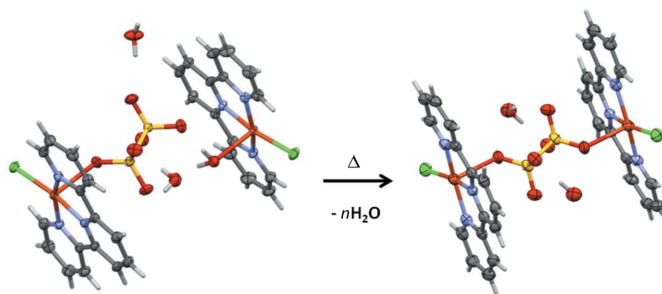


Figure 5

An illustration of the transformation of the ionic complex, (I), into the binuclear complex, (II). [Note that the water molecule is only partially occupied (0.5) in (II).]

atom of the dithionate anion in the axial position. Again, the coordination environment can be described as distorted square-pyramidal, with a τ value of 0.16. The Cu—Cl and Cu—N bond distances are similar to those in complexes (I) and (III) (Table 3). The main difference concerns the Cu—O(dithionate) bond distance, which is longer than in (I) by $0.083(2) \text{ \AA}$. These distances are comparable with the values observed in the copper(II) dithionate-bridged complex described by Ishii (2001*b*).

In the crystal structure of complex (II), molecules related by an inversion centre are linked by O—H...O hydrogen bonds involving the disordered water molecule and an O atom of the bridging thiosulfite anion, so forming a ribbon-like polymer chain (Table 4 and Fig. 4). These chains are linked by weak Cu...Cl interactions [$3.3765(12) \text{ \AA}$; see Table 3 for symmetry code] to form two-dimensional networks lying parallel to and in $(0\bar{2}2)$, as shown in Fig. 4. As in (I), there are a number of C—H...O interactions involving both the water and the S=O O atoms (Table 4), which lead finally to the formation of a three-dimensional network.

In conclusion, we have shown that, by careful drying, the water molecule coordinated to the cation in the ionic complex, (I), can be removed, and the vacant coordination site is then taken by an O atom of the thiosulfite ligand of the anion. This results in the transformation of the ionic complex (I) into a centrosymmetric binuclear complex, (II), as shown in Fig. 5.

Experimental

For the synthesis of complex (I), an aqueous solution (20 ml) of copper(II) chloride dihydrate (0.429 mmol, 75 mg) and 2,2':6',2''-terpyridine (0.429 mmol, 100 mg) was heated at 353 K for 1 h. After hot filtration, the green solution was cooled to room temperature and sodium sulfite (1.717 mmol, 216 mg) was added. The resulting solution was left in the fridge for two months and emerald-green block-like crystals of (I) were obtained (yield 38 mg, 20%).

Pale-green crystals of (II) were obtained after thermogravimetric analysis of compound (I); see *Comment*. A sample of (I) (*ca* 20 mg) was heated to 433 K in a closed aluminium oxide crucible at a rate of 2 K min^{-1} (gas flow 150 ml min^{-1}) at atmospheric pressure.

A small quantity of blue-green crystals were obtained as a by-product during the synthesis of (I). They were identified by X-ray crystallographic analysis to be the mononuclear complex aquachlorido(2,2':6',2''-terpyridyl)copper(II) chloride monohydrate

Table 1
Selected interatomic distances (Å) for (I).

Cu1—Cl1	2.2203 (6)	Cu2—Cl2	2.2284 (6)
Cu1—O1	2.3901 (16)	Cu2—O1W	2.2816 (16)
Cu1—N1	2.0368 (17)	Cu2—N4	2.0216 (17)
Cu1—N2	1.9342 (16)	Cu2—N5	1.9447 (16)
Cu1—N3	2.0322 (17)	Cu2—N6	2.0245 (17)
Cu1···Cl1 ⁱ	3.2626 (7)	Cu2···Cl2 ⁱⁱ	3.3492 (7)

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

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

<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>
O1W—H1WA···O6 ⁱⁱⁱ	0.84 (3)	1.95 (3)	2.787 (2)	176 (3)
O1W—H1WB···O3W	0.89 (3)	2.06 (3)	2.918 (2)	162 (3)
O2W—H2WA···O3 ^{iv}	0.88 (3)	2.01 (3)	2.831 (2)	154 (3)
O2W—H2WB···O4 ⁱⁱⁱ	0.85 (2)	1.95 (2)	2.785 (2)	169 (4)
O3W—H3WA···O2W ^v	0.83 (3)	2.00 (3)	2.811 (2)	166 (3)
O3W—H3WB···O2	0.82 (3)	2.24 (3)	3.052 (2)	168 (3)
C4—H4A···O2W ^v	0.95	2.47	3.407 (3)	169
C7—H7A···O2W ^v	0.95	2.43	3.347 (3)	162
C8—H8A···O5 ^{vi}	0.95	2.34	3.217 (3)	154
C9—H9A···O2 ^w	0.95	2.56	3.496 (3)	171
C12—H12A···O1 ^v	0.95	2.56	3.335 (3)	139
C18—H18A···O1W ^{vii}	0.95	2.57	3.213 (3)	126
C19—H19A···O3W ^{vii}	0.95	2.50	3.446 (3)	178
C22—H22A···O3W ^{vii}	0.95	2.51	3.452 (3)	175
C24—H24A···O6	0.95	2.43	3.363 (3)	167
C27—H27A···O6	0.95	2.19	3.141 (3)	179
C29—H29A···Cl2 ^{viii}	0.95	2.74	3.690 (3)	174

Symmetry codes: (iii) $x, y - 1, z$; (iv) $x - 1, y - 1, z$; (v) $x + 1, y, z$; (vi) $x + 1, y - 1, z$; (vii) $x - 1, y, z$; (viii) $-x + 2, -y + 1, -z + 1$.

(Schmitt *et al.*, 2010), *i.e.* compound (III) mentioned in the *Comment*. The analytical and spectroscopic data for (I) and (II) are available in the archived CIF.

Compound (I)

Crystal data

[CuCl(C₁₅H₁₁N₃)(H₂O)]·
[CuCl(S₂O₆)(C₁₅H₁₁N₃)]·2H₂O
M_r = 878.68
 Triclinic, *P*1̄
a = 8.0705 (10) Å
b = 8.589 (1) Å
c = 25.177 (3) Å
 α = 83.096 (10)°
 β = 82.870 (11)°
 γ = 73.675 (11)°
V = 1655.2 (3) Å³
Z = 2
 Mo *K*α radiation
 μ = 1.64 mm⁻¹
T = 173 K
 0.50 × 0.37 × 0.20 mm

Data collection

Stoe IPDS II diffractometer
 Absorption correction: multi-scan
 (MULABS in PLATON; Spek,
 2009)
T_{min} = 0.254, *T_{max}* = 1.00
 25099 measured reflections
 8888 independent reflections
 8053 reflections with *I* > 2σ(*I*)
R_{int} = 0.073

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.116$
S = 1.06
 8888 reflections
 485 parameters
 6 restraints
 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\max} = 0.95 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.47 \text{ e \AA}^{-3}$

Table 3
Selected interatomic distances (Å) for (II).

Cu1—Cl1	2.2220 (11)	Cu1—N2	1.934 (3)
Cu1—O1	2.473 (2)	Cu1—N3	2.041 (3)
Cu1—N1	2.030 (3)		
Cu1···Cl1 ⁱ	3.3765 (12)		

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

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

<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>
O1W—H1WA···O2 ⁱⁱ	0.88 (8)	2.05 (8)	2.803 (7)	142 (8)
O1W—H1WB···O2 ⁱⁱⁱ	0.89 (9)	1.94 (10)	2.759 (7)	153 (10)
C7—H7···O3 ^{iv}	0.95	2.40	3.342 (5)	174
C8—H8···O3 ⁱⁱ	0.95	2.47	3.421 (5)	176
C9—H9···O1W	0.95	2.47	3.404 (7)	168
C12—H12···O1W	0.95	2.31	3.253 (7)	172
C13—H13···O1 ⁱⁱⁱ	0.95	2.60	3.429 (5)	146

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, y - 1, z$; (iv) $x - 1, y, z$.

Compound (II)

Crystal data

[Cu₂Cl₂(S₂O₆)(C₁₅H₁₁N₃)₂]-H₂O
M_r = 842.65
 Triclinic, *P*1̄
a = 8.1961 (13) Å
b = 8.6029 (15) Å
c = 12.2566 (19) Å
 α = 107.927 (13)°
 β = 99.171 (13)°
 γ = 105.244 (13)°
V = 765.7 (2) Å³
Z = 1
 Mo *K*α radiation
 μ = 1.76 mm⁻¹
T = 173 K
 0.21 × 0.13 × 0.11 mm

Data collection

Stoe IPDS II diffractometer
 Absorption correction: multi-scan
 (MULABS in PLATON; Spek,
 2009)
T_{min} = 0.846, *T_{max}* = 1.00
 8262 measured reflections
 2724 independent reflections
 2001 reflections with *I* > 2σ(*I*)
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.079$
S = 0.89
 2724 reflections
 232 parameters
 2 restraints
 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.48 \text{ e \AA}^{-3}$

In a difference Fourier map for compound (II), a peak of 2.0 e Å⁻³ was observed near an inversion centre. It was refined as a partially occupied solvent water molecule (O1W) with an occupancy of 0.5. For compound (I), the water H atoms were located in a difference electron-density map and refined isotropically, with O—H distance restraints of 0.84 (2) Å. For compound (II), the water H atoms could also be located in a difference electron-density map and they were refined with O—H distance restraints of 0.84 (2) Å and *U_{iso}*(H) = 1.5*U_{eq}*(O). For both (I) and (II), C-bound H atoms were included in calculated positions and treated as riding, with C—H = 0.95 Å and *U_{iso}*(H) = 1.2*U_{eq}*(C). For compound (I), 16 strong reflections were excluded from the structure factor file. This was due to the fact that the crystal exposure time was too long and this caused overloads on the image plate. The individual intensities of these reflections could not be measured accurately and they were omitted from the final

structure factor file. A comparison of similar bond lengths in the two crystal structures shows that this has little effect on the final structure analysis.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*, *PLATON* and *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3158). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, T. N., Reedijk, J. V.-R., Jacobus, V. & Gerrig, C. (1984). *J. Chem. Soc. Dalton Trans.* **7**, 1349–1355.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Aslani, A., Morsali, A. & Zeller, M. (2008). *Dalton Trans.* pp. 5173–5177.
- Bernhardt, P. V., Dyahningtyas, T. E., Han, S. C., Harrowfield, J. M., Kim, I. C., Kim, Y., Koutsantonis, G. A., Rukmini, E. & Thury, P. (2004). *Polyhedron*, **23**, 869–877.
- Degtyarenko, A. S., Solntsev, P. V., Krautscheid, H., Rusanov, E. B., Chernega, A. N. & Domasevitch, K. V. (2008). *New J. Chem.* **32**, 1910–1918.
- Donlevy, T. M., Gahan, L. R., Hambley, T. W., Hanson, G. R., Markiewicz, A., Murray, K. S., Swann, L. L. & Pickering, S. R. (1990). *Aust. J. Chem.* **43**, 1407–1419.
- Habib, H. A., Sanchiz, J. & Janiak, C. (2008). *Dalton Trans.* pp. 1734–1744.
- Ishii, M. (2001a). *Bull. Yamagata Univ. Nat. Sci.* **15**, 1–6.
- Ishii, M. (2001b). *Bull. Yamagata Univ. Nat. Sci.* **15**, 7–12.
- Kim, Y., Skelton, B. W. & White, A. H. (2003). *Acta Cryst.* **C59**, m546–m548.
- Lin, J.-G., Xu, Y.-Y., Qiu, L., Zang, S.-Q., Lu, C.-S., Duan, C.-Y., Li, Y.-Z., Gao, S. & Meng, Q.-J. (2008). *Chem. Commun.* pp. 2659–2662.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Mahmoudi, G. & Morsali, A. (2008). *Cryst. Growth Des.* **8**, 391–394.
- Mobin, S. M., Srivastava, A. K., Mathur, P. & Lahiri, G. K. (2009). *Inorg. Chem.* **48**, 4652–4654.
- Morgan, G. T. & Burstall, F. H. (1932). *J. Chem. Soc.* pp. 20–30.
- Neels, A., Alfonso, M., Gonzalez Mantero, D. & Stoeckli-Evans, H. (2003). *Chimia (Aarau)*, **57**, 619–622.
- Rusanov, E. B., Ponomarova, V. V., Komarchuk, V. V., Stoeckli-Evans, H., Fernandez-Ibanez, E., Stoeckli, F., Sieler, J. & Domasevitch, K. V. (2003). *Angew. Chem. Int. Ed.* **42**, 2499–2501.
- Schmitt, L., Labat, G. & Stoeckli-Evans, H. (2010). *Acta Cryst.* **E66**, m1169.
- Sereda, O., Neels, A., Stoeckli, F., Stoeckli-Evans, H. & Filinchuk, Y. (2008). *Cryst. Growth Des.* **8**, 2307–2311.
- Sereda, O., Stoeckli-Evans, H., Dolomanov, O., Filinchuk, Y. & Pattison, P. (2009). *Cryst. Growth Des.* **9**, 3168–3176.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2006). *X-AREA* (Version 1.35) and *X-RED32* (Version 1.31). Stoe & Cie GmbH, Darmstadt, Germany.
- Turba, S., Walter, O., Schindler, S., Nielsen, L. P., Hazell, A., McKenzie, C. J., Loret, F., Cano, J. & Julve, M. (2008). *Inorg. Chem.* **47**, 9612–9623.
- Wang, X.-Y., Scancella, M. & Sevov, S. C. (2007). *Chem. Mater.* **19**, 4506–4513.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Xue, D.-X., Zhana, W.-X., Chen, X.-M. & Wang, H.-Z. (2008). *Chem. Commun.* pp. 1551–1553.
- Zhang, Y.-J., Liu, T., Kanegawa, S. & Sato, O. (2009). *J. Am. Chem. Soc.* **131**, 7942–7943.