In situ single-crystal to single-crystal (SCSC) transformation of the one-dimensional polymer *catena*-poly[[di-aqua(sulfato)copper(II)]- μ_2 -glycine] into the two-dimensional polymer poly[μ_2 -glycine- μ_4 -sulfato-copper(II)]

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The one-dimensional coordination polymer *catena*-poly[di-aqua(sulfato- κ O)copper(II)]- μ_2 -glycine- κ^2 O:O', [Cu(SO₄)(C₂H₅NO₂)(H₂O)₂]_n, (I), was synthesized by slow evaporation under vacuum of a saturated aqueous equimolar mixture of copper(II) sulfate and glycine. On heating the same blue crystal of this complex to 435 K in an oven, its aspect changed to a very pale blue and crystal structure analysis indicated that it had transformed into the two-dimensional coordination polymer poly[(μ_2 -glycine- κ^2 O:O')(μ_4 -sulfato- κ^4 O:O':O'':O'')-copper(II)], [Cu(SO₄)(C₂H₅NO₂)_n], (II). In (I), the Cu^{II} cation has a pentacoordinate square-pyramidal coordination environment. It is coordinated by two water molecules and two O atoms of bridging glycine carboxylate groups in the basal plane, and by a sulfate O atom in the apical position. In complex (II), the Cu^{II} cation has an octahedral coordination environment. It is coordinated by four sulfate O atoms, one of which bridges two Cu^{II} cations, and two O atoms of bridging glycine carboxylate groups. In the crystal structure of (I), the one-dimensional polymers, extending along [001], are linked *via* N—H...O, O—H...O and bifurcated N—H...O, O hydrogen bonds, forming a three-dimensional framework. In the crystal structure of (II), the two-dimensional networks are linked *via* bifurcated N—H...O, O hydrogen bonds involving the sulfate O atoms, forming a three-dimensional framework. In the crystal structures of both compounds, there are C—

H...O hydrogen bonds present, which reinforce the three-dimensional frameworks.

Keywords: crystal structure; crystal-to-crystal transformation; solid-state transformation; variable temperature; pentacoordinate; copper(II); glycine; sulfate; one-dimensional coordination polymers; two-dimensional coordination polymers; bioavailability; trace minerals; SCSC transformations.

1. Introduction

Trace minerals represent a tiny proportion of the body tissue of living organisms, but they play a major role in their metabolism. The chemical form of the trace mineral has a considerable influence on its stability towards dietary ingredients like phytic acids (Vohra *et al.*, 1965; Zhou *et al.*, 1992) or phenolic compounds (Cook, 1990; Hurrell, 1997). Interactions can occur between them to produce insoluble components which result in a decrease in absorption of the mineral. These reactions especially concern the inorganic forms of trace minerals, for example, sulfates and oxides. Organic trace mineral forms, such as chelates, proteinates, polysaccharides and complexes, can offer protection against antinutritional components, depending on the stability of the chemical bonding between the metal and the ligand(s). It has been shown (Wichert *et al.*, 2002; Spears *et al.*, 2004; Schlegel & Windisch, 2006) that the absorption of zinc(II), for example, is superior in the complexed form rather than simply using zinc(II) sulfate. The bioavailability of copper from copper glycinate in steers fed high dietary sulfur and molybdenum has also been shown to be more effective than using copper(II) sulfate (Hansen *et al.*, 2008). The critical part of the synthesis of such compounds lies in the manufacturing process used to obtain the correct hydrated form (Jacquier & Oguey, 2003; Meunier & Oguey, 2010). Their stability towards moist conditions is extremely important and, for practical purposes, a free-flowing powder must be obtained in order to avoid the so called 'caking phenomenon'. These crystalline organic trace mineral complexes were obtained by the reaction of metal sulfates with glycine. Two zinc(II) sulfate glycine complexes, formed under vacuum (Jacquier & Oguey, 2003), are in fact the product sold as an animal feed additive under the trade name of B-TRAXIM 2C (Pancosma SA) (Oguey *et al.*, 2008).

Recently, the equilibrium crystallization and characterization of a series of glycine metal sulfate complexes have been reported (Tepavitcharova *et al.*, 2012). The Gly-MSO₄-H₂O systems (*M* = Mn^{II}, Fe^{II}, Co^{II}, Zn^{II} and Mg^{II}) were studied by evaporation of supersaturated solutions at different fixed temperatures. They identified a number of complexes with varying water content and described the crystal structures of three ionic complexes involving magnesium(II), cobalt(II) and zinc(II), and a one-dimensional glycine cobalt(II) sulfate complex. Herein, we report the structure of a unique pentacoordinate copper(II) sulfate complex of glycine and its solid-state transformation, by heating/dehydration, from a one-dimensional to a two-dimensional coordination polymer, *viz.* complexes (I) and (II), respectively.

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In recent years, there have been a number of reports of *in situ* single-crystal to single-crystal (SCSC) transformations (He *et al.*, 2014; Uchida *et al.*, 2013; Halasz, 2010; Li *et al.*, 2009), and the subject of SCSC [2+2] photodimerizations has been reviewed by Friscic & MacGillivray (2005). Recently, reversible SCSC [2,2]-cycloaddition reactions have also been reported (Park *et al.*, 2014). We have, for example, described the transformation 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 into the binuclear complex (μ -dithionato- $\kappa^2 O:O'$)bis-[chlorido(2,2':6',2''-terpyridyl- κ^3N,N',N'')copper(II)] monohydrate (Schmitt *et al.*, 2010). On heating the crystal, the coordinated water molecule of the cation was lost and the vacant site on the Cu^{II} cation atom was occupied by an O atom of the adjacent dithionate anion.

2. Experimental

2.1. Synthesis and crystallization

Complex (I) was synthesized by slow evaporation of a saturated equimolar mixture of copper(II) sulfate and glycine in water under vacuum, using the technique developed by Pancosma SA (Jacquier & Oguey, 2003). A differential scanning calorimetry (DSC) measurement (Fig. S1 in the *Supporting information*) indicated that an endothermic transformation takes place at *ca* 433 K. As our cryosystem did not allow us to heat the crystal on the diffractometer above 393 K, the same blue crystal used for the X-ray diffraction analysis of (I) was heated to 435 K in an oven and was found to transform into a very pale-blue crystal of (II), as shown in Fig. 1. The same transformation was also followed by variable-temperature powder X-ray diffraction (VT-PXRD), as shown in Fig. 2.

Figure 1

Crystals and diffraction images of: (a) a blue crystal of (I); (b) a pale-blue crystal of (II); (c) a typical diffraction image for (I); (d) a typical diffraction image for (II) – notice the presence of the powder diffraction rings.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. While (I) crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, compound (II) crystallized as a nonmerohedral twin in the noncentrosymmetric monoclinic space group $P2_1$. Both general twinning and inversion twinning for both components were refined for (II) with the instructions TWIN $-1\ 0\ 0\ 0\ -1\ 0\ 1\ 0\ 1\ -4$ and BASF $0.20\ (8)\ 0.30\ (10)\ 0.20\ (9)$ (*SHELXL2014*; Sheldrick, 2008), implying a 180° rotation about the c^* axis. These are the final refined values; the first parameter is the general twinning factor, while the second and third are the first and second component inversion twin factors, respectively. Correction for twinning reduced the *R* factor for the observed data [$I > 2\sigma(I)$] from 0.124 to 0.056. For (I), the H atoms of the water molecules and the NH_3^+ group were located in a difference Fourier map and freely refined. For (II), the NH_3^+ H atoms were included in calculated positions and treated as riding, with $\text{N}—\text{H} = 0.91\ \text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. In both (I) and (II), the methylene H atoms were included in calculated positions and treated as riding, with $\text{C}—\text{H} = 0.93\ \text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

3. Results and discussion

The asymmetric unit of (I) consists of a Cu^{II} cation, a glycine molecule present in the zwitterionic form, a sulfate anion and two water molecules (Fig. 3), and forms a one-dimensional zigzag coordination polymer (Fig. 4). Atom Cu1 is penta-coordinate and has an almost perfect square-pyramidal geometry, with a τ value of 0.06 (Addison *et al.*, 1984; $\tau = 0$ for a perfect square-pyramid and $\tau = 1$ for a perfect triangular-

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	[Cu(SO ₄)(C ₂ H ₅ NO ₂)(H ₂ O) ₂]	[Cu(SO ₄)(C ₂ H ₅ NO ₂)]
<i>M</i> _r	270.70	234.67
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.6347 (8), 12.3140 (9), 8.3675 (8)	4.8131 (8), 7.787 (1), 7.9262 (11)
β (°)	90.855 (8)	107.729 (12)
<i>V</i> (Å ³)	786.57 (13)	282.96 (7)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	3.06	4.21
Crystal size (mm)	0.42 × 0.30 × 0.21	0.42 × 0.30 × 0.21
Data collection		
Diffractometer	Stoe IPDS 2 diffractometer	Stoe IPDS 2 diffractometer
Absorption correction	Multi-scan (<i>MULABS</i> in <i>PLATON</i> ; Spek, 2009)	Multi-scan (<i>MULABS</i> in <i>PLATON</i> ; Spek, 2009)
<i>T</i> _{min} , <i>T</i> _{max}	0.850, 1.000	0.646, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5320, 1481, 1352	3296, 1065, 862
<i>R</i> _{int}	0.027	0.110
(sin θ/λ) _{max} (Å ⁻¹)	0.608	0.609
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.055, 1.13	0.056, 0.132, 0.98
No. of reflections	1481	1065
No. of parameters	147	104
No. of restraints	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.76, -0.33	0.82, -0.71

Computer programs: *X-AREA* (Stoe & Cie, 2009), *X-RED32* (Stoe & Cie, 2009), *SHELXS2013* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

based pyramid). In the basal plane it is coordinated by two water molecules (atoms O1W and O2W) and an O atom from each of two bridging glycine carboxylate groups (atoms O1 and O2), and in the apical position by a sulfate O atom (O11). Atom Cu1 is displaced by 0.1856 (2) Å from the mean plane

through atoms O1W/O2W/O1/O2 [mean deviation = 0.033 (2) Å] towards sulfate O atom O11. The Cu—O(water) bonds are slightly longer than the Cu—O(carboxylate) bonds (Table 2), while the apical Cu1—O11 bond is longer, at 2.2179 (17) Å. The intra-chain Cu···Cu distance is

Figure 2
Variable-temperature powder diffractograms for the transformation of the copper glycine complex (I) to (II); the transformation takes place at *ca* 433 K.

Figure 3

A view of the asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$]

Figure 4

A view, along the a axis, of the one-dimensional polymeric structure of (I).

4.7498 (6) Å, while the shortest inter-chain $\text{Cu} \cdots \text{Cu}$ distance is 5.6118 (7) Å.

In the crystal structure of (I), the one-dimensional polymer chains that propagate in the [001] direction are linked *via* $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ and by bifurcated $\text{O}-\text{H}, \text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}, \text{O}$ hydrogen bonds, forming a three-dimensional framework (Fig. 5 and Table 3). There is also a $\text{C}-\text{H} \cdots \text{O}$ hydrogen bond present that consolidates the three-dimensional structure (Table 3).

After heating the same crystal of (I) to 435 K in an oven, it was remounted on the diffractometer and a full data set was measured at 173 K. It can be seen that the quality of the crystal was not as good as before (Fig. 1). When comparing typical diffraction images for the two crystals it is seen that, for (II), there are a significant number of powder diffraction lines

Table 2

Selected bond lengths (Å) for (I).

$\text{Cu1}-\text{O1}$	1.9438 (17)	$\text{Cu1}-\text{O2W}$	1.9960 (17)
$\text{Cu1}-\text{O2}^i$	1.9477 (17)	$\text{Cu1}-\text{O11}$	2.2179 (17)
$\text{Cu1}-\text{O1W}$	1.9979 (17)		

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

Figure 5

A view, along the c axis, of the crystal packing of (I). The hydrogen bonds are shown as pale-turquoise dashed lines (see Table 3 for details). C-bound H atoms have been omitted for clarity.

present. However, the data were good enough to determine the crystal structure.

The asymmetric unit of (II) consists of a Cu^{II} cation, a glycine molecule present in the zwitterionic form and a sulfate anion (Fig. 6). The two water molecules present in (I) have been lost and the polymeric chains of (I) have reorganized themselves to form a two-dimensional network (Fig. 7). The coordination sites on the Cu^{II} cation in (I) liberated by the water molecules are now occupied by sulfate O atoms.

One possible explanation for the transformation pathway is illustrated in Fig. 8. Comparing Figs. 8(a) and 8(b), it can be seen that the zigzag chains in (I) are now horizontal in (II). We propose that the coordinated sulfate O atom in (I), *viz.* O11, moves to coordinate the adjacent Cu^{II} cation, so forming a $\text{Cu}-\text{O}-\text{Cu}$ bridge. This involves a twisting of the chains, resulting in a change in the intra-chain $\text{Cu1} \cdots \text{Cu1}$ distance from 4.7498 (6) Å in (I) to 3.8998 (6) Å in (II). The sulfate group is then in a position where atoms O12 and O13 can coordinate and bridge two Cu^{II} cations of the adjacent chain,

Table 3

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O1W}^{\text{ii}}$	0.87 (3)	2.08 (3)	2.917 (3)	161 (3)
$\text{N1}-\text{H1B} \cdots \text{O2W}^{\text{iii}}$	0.86 (4)	2.42 (3)	3.068 (3)	133 (3)
$\text{N1}-\text{H1B} \cdots \text{O13}^{\text{iii}}$	0.86 (4)	2.16 (3)	2.923 (3)	147 (3)
$\text{N1}-\text{H1C} \cdots \text{O12}^{\text{iv}}$	0.88 (4)	1.87 (4)	2.754 (3)	175 (3)
$\text{O1W}-\text{H1WA} \cdots \text{O14}^{\text{ii}}$	0.76 (4)	1.96 (4)	2.716 (3)	179 (3)
$\text{O1W}-\text{H1WB} \cdots \text{O14}^{\text{v}}$	0.80 (4)	1.87 (4)	2.667 (3)	170 (3)
$\text{O2W}-\text{H2WA} \cdots \text{O12}^{\text{vi}}$	0.83 (4)	1.90 (4)	2.732 (2)	174 (3)
$\text{O2W}-\text{H2WB} \cdots \text{O13}^{\text{iii}}$	0.85 (4)	1.82 (4)	2.676 (2)	177 (3)
$\text{C2}-\text{H2A} \cdots \text{O12}^{\text{iii}}$	0.99	2.64	3.422 (3)	137

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

Figure 6
A view of the asymmetric unit of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + 1$; (ii) $x - 1, y, z$; (iii) $-x + 1, y + \frac{1}{2}, -z + 1$.]

Figure 7
A view, along the c axis, of the two-dimensional polymeric structure of (II). C-bound H atoms have been omitted for clarity.

so forming a two-dimensional network. One problem that we have not, as yet, been able to explain is the change from a centrosymmetric arrangement in (I) to a noncentrosymmetric arrangement in (II).

In (II), atom Cu1 now has an octahedral coordination environment and exhibits a typical pseudo-Jahn–Teller

Table 4
Selected bond lengths (Å) for (II).

Cu1—O1	1.95 (2)	Cu1—O13 ⁱ	1.94 (2)
Cu1—O2 ⁱ	1.97 (2)	Cu1—O14 ⁱⁱ	2.50 (2)
Cu1—O11	1.93 (2)	Cu1—O14 ⁱⁱⁱ	2.50 (2)

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

Figure 8
A view of the possible pathway for the transformation of (a) complex (I) into (b) complex (II). Generic atom labels without symmetry codes have been used. In part (a), the dashed, dashed-dotted and long-dashed arrows represent the movement of atoms O11, O12 and O13, respectively, towards the Cu atoms to which they are coordinated in complex (II).

distortion. In the equatorial plane it is coordinated by an O atom from each of two bridging glycine carboxylate groups, *i.e.* O1 and O2ⁱ [symmetry code: (i) $-x, y + \frac{1}{2}, -z + 1$], and an O atom from each of two sulfate groups, *i.e.* O13ⁱ and O11, with similar C—O bond lengths (Table 4). The axial positions are occupied by an O atom from each of two additional bridging

Figure 9

A view, along the *a* axis, of the crystal packing of (II). The hydrogen bonds are shown as pale-turquoise dashed lines (see Table 5 for details). C-bound H atoms have been omitted for clarity.

sulfate groups [O14ⁱⁱ and O14ⁱⁱⁱ; symmetry codes: (ii) $x - 1, y, z$; (iii) $-x + 1, y + \frac{1}{2}, -z + 1$], with Cu—O bond lengths of 2.50 (2) Å (Table 4).

In the crystal structure of (II), the two-dimensional networks lie parallel to (001) and are linked *via* bifurcated N—H...O and N—H...O...O hydrogen bonds, forming a three-dimensional framework (Fig. 9 and Table 5). There is also a C—H...O hydrogen bond present that consolidates the three-dimensional structure (Table 5).

A search of the Cambridge Structural Database (CSD; Version 5.35, last update May 2014; Allen, 2002) for transition metal complexes of glycine gave 400 hits. However, restricting the search to glycine (NH₂CH₂COO⁻; with any type of C—O bond), sulfate, Mg^{II} and first-row transition metals indicated the presence of only 14 complexes, some of which have been reported more than once. These include a number of ionic complexes, such as tetraaquabis(glycine- κ O)iron(II) hexaaquairon(II) bis(sulfate) (Lindqvist & Rosenstein, 1960), one-dimensional coordination polymers, for example, *catena*-poly[triaqua(μ_2 -glycine)sulfatozinc(II)] (Fleck & Bohatý, 2004) and *catena*-poly[hexaaquabis(μ_2 -glycine)disulfatodibicobalt(II)] (Tepavitcharova *et al.*, 2012), and a two-dimensional Mn^{II} coordination polymer (Weng *et al.*, 2009). In all of these complexes, the glycine molecule exists in the zwitterionic form and coordinates the metal *via* the carboxylate group, the amine group always being protonated.

Complex (I) is the only copper(II) sulfate–glycine coordination polymer to have been synthesized to date. It is isotypic with the zinc(II) complex *catena*-poly[diaqua(μ_2 -glycine)sulfatozinc(II)] (Oguey *et al.*, 2013a). These two complexes are unique, in as much as the Cu^{II} and Zn^{II} cations have fivefold coordination environments. Complex (II) is isotypic with the two-dimensional Mn^{II} coordination polymer mentioned above

Table 5

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>
N1—H1N...O1 ^{iv}	0.91	2.47	3.10 (3)	127
N1—H1N...O12 ^v	0.91	2.11	2.78 (3)	130
N1—H2N...O12 ^{vi}	0.91	2.09	2.92 (3)	152
N1—H2N...O13 ^{vi}	0.91	2.31	3.08 (3)	143
N1—H3N...O11 ^{vii}	0.91	2.07	2.94 (3)	161
N1—H3N...O12 ^{vii}	0.91	2.44	3.13 (3)	133
C2—H2A...O1 ^{viii}	0.99	2.65	3.62 (4)	168
C2—H2A...O13 ⁱⁱⁱ	0.99	2.63	3.29 (4)	124

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

that was prepared hydrothermally and which crystallized in the centrosymmetric space group $P2_1/m$.

It is interesting that, on studying single-crystal to single-crystal (SCSC) transformations of a number of these ionic complexes, different results were obtained. For example, on heating, in a capillary on the diffractometer, a crystal of the zinc(II) ionic complex tetraaquabis(glycine- κ O)zinc(II) hexaaquazinc(II) bis(sulfate) (Tepavitcharova *et al.*, 2012), two successive SCSC transformations were observed. At *ca* 343 K it transformed into a one-dimensional polymer isotypic with (I), with a loss of eight water molecules (Oguey *et al.*, 2013a). On continued heating at *ca* 393 K, two further water molecules were lost and a two-dimensional polymer isostructural with (II) was obtained (Oguey *et al.*, 2014a). These two successive SCSC transformations have also been followed by variable-temperature powder X-ray diffraction (see Fig. S2 in the *Supporting information*).

In contrast, for the magnesium(II) ionic complex (Elayaraja *et al.*, 2007), heating a crystal in a capillary on the diffractometer resulted in the loss of four water molecules at *ca* 363 K and its SCSC transformation into the one-dimensional polymer *catena*-poly[hexaaquabis(μ_2 -glycine)disulfatodimagnesium(II)] (Oguey *et al.*, 2014b). Further heating gave an amorphous powder. This last structure is isostructural with the cobalt(II) (Tepavitcharova *et al.*, 2012), the iron(II) (Oguey *et al.*, 2013b) and the zinc(II) (Oguey *et al.*, 2013c) analogues.

The reversibility of the SCSC transformation of (I) into (II) was examined by immersing a powder sample of (II) in water at room temperature. A clear pale-blue solution was obtained, indicating that (II) had dissolved. The aqueous solution was allowed to evaporate in air and yielded blue crystals of (I).

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supporting information

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***In situ* single-crystal to single-crystal (SCSC) transformation of the one-dimensional polymer catena-poly[[diaqua(sulfato)copper(II)]- μ_2 -glycine] into the two-dimensional polymer poly[μ_2 -glycine- μ_4 -sulfato-copper(II)]**

Helen Stoeckli-Evans, Olha Sereda, Antonia Neels, Sebastien Oguey, Catherine Ionescu and Yvan Jacquier

Computing details

For both compounds, data collection: *X-Area* (Stoe & Cie, 2009); cell refinement: *X-Area* (Stoe & Cie, 2009); data reduction: *X-Red32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2014/6* (Sheldrick, 2008) for (I); *SHELXL2013* (Sheldrick, 2008) for (II). For both compounds, molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008). Software used to prepare material for publication: *SHELXL2014/6* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010) for (I); *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010) for (II).

(I) catena-Poly[diaqua(sulfato- κ O)copper(II)]- μ_2 -glycine- κ^2 O:O']

Crystal data

[Cu(SO₄)(C₂H₅NO₂)(H₂O)₂]

$M_r = 270.70$

Monoclinic, $P2_1/c$

$a = 7.6347$ (8) Å

$b = 12.3140$ (9) Å

$c = 8.3675$ (8) Å

$\beta = 90.855$ (8)°

$V = 786.57$ (13) Å³

$Z = 4$

$F(000) = 548$

$D_x = 2.286$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6664 reflections

$\theta = 2.4\text{--}26.1^\circ$

$\mu = 3.06$ mm⁻¹

$T = 173$ K

Prism, blue

$0.42 \times 0.30 \times 0.21$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

$\varphi + \omega$ scans

Absorption correction: multi-scan

(*MULABS* in *PLATON*; Spek, 2009)

$T_{\min} = 0.850$, $T_{\max} = 1.000$

5320 measured reflections

1481 independent reflections

1352 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 25.6^\circ$, $\theta_{\min} = 2.7^\circ$

$h = -9 \rightarrow 9$

$k = -14 \rightarrow 14$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.055$

$S = 1.13$

1481 reflections

147 parameters
 0 restraints
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 0.3965P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.76 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL2014/6*
 (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0046 (8)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.28498 (3)	0.84131 (2)	0.35769 (3)	0.00946 (12)
O1W	0.5449 (2)	0.82336 (15)	0.3700 (2)	0.0136 (4)
H1WA	0.579 (4)	0.824 (2)	0.456 (4)	0.018 (8)*
H1WB	0.585 (4)	0.773 (3)	0.321 (4)	0.023 (8)*
O2W	0.0255 (2)	0.83224 (15)	0.3800 (2)	0.0130 (3)
H2WA	−0.022 (5)	0.771 (3)	0.387 (4)	0.036 (10)*
H2WB	−0.007 (4)	0.864 (3)	0.465 (4)	0.025 (8)*
O1	0.3000 (2)	0.91826 (12)	0.56027 (19)	0.0107 (3)
O2	0.2793 (2)	0.75656 (13)	0.6748 (2)	0.0121 (3)
N1	0.2361 (3)	1.03136 (17)	0.8164 (3)	0.0140 (4)
H1A	0.314 (4)	1.061 (2)	0.755 (4)	0.012 (7)*
H1B	0.138 (4)	1.030 (3)	0.764 (4)	0.023 (8)*
H1C	0.213 (4)	1.064 (3)	0.908 (4)	0.022 (8)*
C1	0.2875 (3)	0.85914 (19)	0.6815 (3)	0.0109 (5)
C2	0.2819 (3)	0.91600 (19)	0.8415 (3)	0.0126 (5)
H2A	0.1937	0.8810	0.9100	0.015*
H2B	0.3976	0.9105	0.8960	0.015*
S1	0.21315 (7)	1.09071 (4)	0.24529 (7)	0.00928 (15)
O11	0.3070 (2)	0.98928 (13)	0.2082 (2)	0.0148 (4)
O12	0.1499 (2)	1.13996 (13)	0.0921 (2)	0.0143 (4)
O13	0.0632 (2)	1.06845 (14)	0.3485 (2)	0.0144 (4)
O14	0.3330 (2)	1.16977 (13)	0.3236 (2)	0.0147 (4)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01192 (16)	0.00816 (17)	0.00830 (17)	−0.00001 (10)	0.00031 (10)	−0.00131 (11)
O1W	0.0151 (8)	0.0130 (9)	0.0127 (10)	0.0021 (7)	−0.0006 (7)	−0.0032 (8)
O2W	0.0150 (8)	0.0104 (8)	0.0137 (9)	−0.0024 (7)	0.0012 (7)	−0.0033 (7)
O1	0.0135 (8)	0.0097 (8)	0.0089 (8)	0.0000 (6)	0.0002 (6)	0.0017 (6)
O2	0.0171 (8)	0.0089 (8)	0.0102 (8)	0.0005 (6)	−0.0010 (6)	0.0002 (6)
N1	0.0193 (11)	0.0119 (11)	0.0109 (11)	−0.0001 (8)	0.0023 (9)	−0.0022 (9)

C1	0.0088 (10)	0.0133 (12)	0.0106 (12)	0.0010 (8)	−0.0003 (8)	0.0003 (9)
C2	0.0175 (11)	0.0117 (11)	0.0086 (12)	0.0007 (9)	0.0002 (9)	−0.0003 (9)
S1	0.0117 (3)	0.0076 (3)	0.0085 (3)	0.0002 (2)	0.0006 (2)	0.0003 (2)
O11	0.0203 (8)	0.0096 (8)	0.0147 (9)	0.0034 (6)	0.0053 (7)	0.0020 (7)
O12	0.0210 (9)	0.0124 (8)	0.0095 (8)	0.0038 (7)	−0.0023 (7)	0.0003 (7)
O13	0.0132 (8)	0.0157 (9)	0.0144 (9)	−0.0021 (6)	0.0029 (6)	−0.0013 (7)
O14	0.0170 (8)	0.0132 (8)	0.0139 (9)	−0.0050 (6)	−0.0012 (7)	0.0005 (7)

Geometric parameters (Å, °)

Cu1—O1	1.9438 (17)	N1—C2	1.477 (3)
Cu1—O2 ⁱ	1.9477 (17)	N1—H1A	0.87 (3)
Cu1—O1W	1.9979 (17)	N1—H1B	0.86 (4)
Cu1—O2W	1.9960 (17)	N1—H1C	0.88 (4)
Cu1—O11	2.2179 (17)	C1—C2	1.512 (3)
O1W—H1WA	0.76 (4)	C2—H2A	0.9900
O1W—H1WB	0.80 (4)	C2—H2B	0.9900
O2—C1	1.266 (3)	S1—O13	1.4699 (17)
O2—Cu1 ⁱⁱ	1.9477 (17)	S1—O11	1.4752 (17)
O2W—H2WA	0.83 (4)	S1—O14	1.4820 (17)
O2W—H2WB	0.85 (4)	S1—O12	1.4921 (17)
O1—C1	1.253 (3)		
O1—Cu1—O2 ⁱ	170.76 (7)	H1A—N1—H1B	108 (3)
O1—Cu1—O2W	89.52 (7)	C2—N1—H1C	111 (2)
O2 ⁱ —Cu1—O2W	91.61 (7)	H1A—N1—H1C	118 (3)
O1—Cu1—O1W	87.88 (7)	H1B—N1—H1C	105 (3)
O2 ⁱ —Cu1—O1W	89.02 (8)	O1—C1—O2	123.2 (2)
O2W—Cu1—O1W	167.31 (7)	O1—C1—C2	116.8 (2)
O1—Cu1—O11	95.01 (6)	O2—C1—C2	119.9 (2)
O2 ⁱ —Cu1—O11	93.80 (7)	N1—C2—C1	109.23 (19)
O2W—Cu1—O11	100.51 (7)	N1—C2—H2A	109.8
O1W—Cu1—O11	92.10 (7)	C1—C2—H2A	109.8
Cu1—O1W—H1WA	112 (2)	N1—C2—H2B	109.8
Cu1—O1W—H1WB	117 (2)	C1—C2—H2B	109.8
H1WA—O1W—H1WB	111 (3)	H2A—C2—H2B	108.3
C1—O2—Cu1 ⁱⁱ	125.60 (15)	O13—S1—O11	110.52 (10)
Cu1—O2W—H2WA	119 (2)	O13—S1—O14	110.12 (10)
Cu1—O2W—H2WB	111 (2)	O11—S1—O14	110.53 (10)
H2WA—O2W—H2WB	103 (3)	O13—S1—O12	109.62 (10)
C1—O1—Cu1	114.73 (14)	O11—S1—O12	108.38 (10)
C2—N1—H1A	108.9 (19)	O14—S1—O12	107.61 (10)
C2—N1—H1B	105 (2)	S1—O11—Cu1	122.40 (10)
Cu1—O1—C1—O2	5.2 (3)	O2—C1—C2—N1	−161.8 (2)
Cu1—O1—C1—C2	−174.63 (15)	O13—S1—O11—Cu1	−20.93 (15)
Cu1 ⁱⁱ —O2—C1—O1	173.00 (16)	O14—S1—O11—Cu1	101.23 (12)

Cu1 ⁱⁱ —O2—C1—C2	−7.1 (3)	O12—S1—O11—Cu1	−141.07 (11)
O1—C1—C2—N1	18.0 (3)		

Symmetry codes: (i) $x, -y+3/2, z-1/2$; (ii) $x, -y+3/2, z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O1W ⁱⁱⁱ	0.87 (3)	2.08 (3)	2.917 (3)	161 (3)
N1—H1B $\cdots$ O2W ^{iv}	0.86 (4)	2.42 (3)	3.068 (3)	133 (3)
N1—H1B $\cdots$ O13 ^{iv}	0.86 (4)	2.16 (3)	2.923 (3)	147 (3)
N1—H1C $\cdots$ O12 ^v	0.88 (4)	1.87 (4)	2.754 (3)	175 (3)
O1W—H1WA $\cdots$ O14 ⁱⁱⁱ	0.76 (4)	1.96 (4)	2.716 (3)	179 (3)
O1W—H1WB $\cdots$ O14 ^{vi}	0.80 (4)	1.87 (4)	2.667 (3)	170 (3)
O2W—H2WA $\cdots$ O12 ^{vii}	0.83 (4)	1.90 (4)	2.732 (2)	174 (3)
O2W—H2WB $\cdots$ O13 ^{iv}	0.85 (4)	1.82 (4)	2.676 (2)	177 (3)
C2—H2A $\cdots$ O12 ^{iv}	0.99	2.64	3.422 (3)	137

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

(II) Poly[(μ_2 -glycine- $\kappa^2 O:O'$)(μ_4 -sulfato- $\kappa^4 O:O':O'':O''$)copper(II)],

Crystal data

[Cu(SO₄)(C₂H₅NO₂)]

$M_r = 234.67$

Monoclinic, $P2_1$

$a = 4.8131$ (8) $\text{\AA}$

$b = 7.787$ (1) $\text{\AA}$

$c = 7.9262$ (11) $\text{\AA}$

$\beta = 107.729$ (12) $^\circ$

$V = 282.96$ (7) $\text{\AA}^3$

$Z = 2$

$F(000) = 234$

$D_x = 2.754$ Mg m^{−3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ $\text{\AA}$

Cell parameters from 2571 reflections

$\theta = 2.6\text{--}25.9^\circ$

$\mu = 4.21$ mm^{−1}

$T = 173$ K

Prism, very pale blue

$0.42 \times 0.30 \times 0.21$ mm

Data collection

Stoe IPDS 2

diffractometer

Radiation source: fine-focus sealed tube

Plane graphite monochromator

$\varphi + \omega$ scans

Absorption correction: multi-scan

(*MULABS* in *PLATON*; Spek, 2009)

$T_{\min} = 0.646$, $T_{\max} = 1.000$

3296 measured reflections

1065 independent reflections

862 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.110$

$\theta_{\max} = 25.7^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -5 \rightarrow 5$

$k = -9 \rightarrow 9$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.132$

$S = 0.98$

1065 reflections

104 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.043$

$\Delta\rho_{\max} = 0.82$ e $\text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.71$ e $\text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 4-component inversion twin.

TWIN -1 0 0 0 -1 0 1 0 1 -4 BASF 0.20187 0.30116 0.19949 (e.s.d. 0.08667 0.10598 0.08668)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	−0.0044 (16)	0.7841 (9)	0.4855 (3)	0.0239 (6)
S1	0.3739 (11)	0.5278 (11)	0.3240 (6)	0.0240 (12)
O1	0.256 (5)	0.680 (3)	0.699 (3)	0.032 (5)
O2	0.274 (5)	0.388 (3)	0.727 (3)	0.035 (6)
O11	0.199 (6)	0.693 (3)	0.329 (3)	0.031 (5)
O14	0.660 (3)	0.533 (3)	0.4498 (16)	0.028 (3)
O12	0.377 (4)	0.516 (4)	0.1411 (19)	0.030 (5)
O13	0.208 (5)	0.379 (3)	0.358 (3)	0.032 (5)
N1	0.779 (6)	0.396 (2)	0.980 (3)	0.035 (5)
H1N	0.6478	0.3636	1.0364	0.052*
H2N	0.9566	0.4117	1.0616	0.052*
H3N	0.7916	0.3123	0.9027	0.052*
C1	0.385 (4)	0.535 (5)	0.762 (2)	0.023 (4)
C2	0.682 (7)	0.557 (4)	0.883 (3)	0.027 (6)
H2A	0.8155	0.5887	0.8149	0.032*
H2B	0.6843	0.6513	0.9680	0.032*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0296 (14)	0.0212 (8)	0.0212 (11)	0.0043 (13)	0.008 (2)	0.0041 (16)
S1	0.033 (3)	0.0187 (19)	0.021 (2)	0.001 (6)	0.009 (2)	0.004 (2)
O1	0.027 (12)	0.030 (12)	0.029 (10)	0.023 (9)	−0.008 (9)	−0.004 (9)
O2	0.048 (14)	0.023 (12)	0.032 (11)	0.015 (11)	0.011 (9)	−0.003 (9)
O11	0.047 (14)	0.024 (11)	0.025 (9)	0.008 (11)	0.016 (9)	0.000 (8)
O14	0.030 (6)	0.028 (7)	0.026 (9)	−0.008 (13)	0.006 (6)	0.002 (13)
O12	0.050 (10)	0.028 (12)	0.017 (6)	−0.003 (12)	0.019 (7)	−0.006 (8)
O13	0.034 (13)	0.027 (10)	0.039 (11)	−0.006 (11)	0.017 (10)	0.004 (9)
N1	0.050 (15)	0.019 (8)	0.035 (10)	−0.004 (12)	0.012 (12)	−0.003 (7)
C1	0.035 (11)	0.022 (10)	0.015 (9)	0.016 (18)	0.013 (8)	0.001 (12)
C2	0.033 (12)	0.014 (16)	0.030 (10)	0.002 (16)	0.006 (14)	0.010 (10)

Geometric parameters ($\text{\AA}$, $^\circ$)

Cu1—O1	1.95 (2)	S1—O11	1.55 (2)
Cu1—O2 ⁱ	1.97 (2)	O1—C1	1.31 (4)
Cu1—O11	1.93 (2)	O2—C1	1.25 (4)

Cu1—O13 ⁱ	1.94 (2)	N1—C2	1.48 (3)
Cu1—O14 ⁱⁱ	2.50 (2)	N1—H1N	0.9100
Cu1—O14 ⁱⁱⁱ	2.50 (2)	N1—H2N	0.9100
O2—Cu1 ^{iv}	1.97 (2)	N1—H3N	0.9100
O13—Cu1 ^{iv}	1.94 (2)	C1—C2	1.47 (3)
S1—O14	1.432 (13)	C2—H2A	0.9900
S1—O12	1.457 (15)	C2—H2B	0.9900
S1—O13	1.48 (2)		
O11—Cu1—O13 ⁱ	179.0 (14)	C2—N1—H1N	109.5
O11—Cu1—O1	95.1 (10)	C2—N1—H2N	109.5
O13 ⁱ —Cu1—O1	85.5 (10)	H1N—N1—H2N	109.5
O11—Cu1—O2 ⁱ	86.0 (10)	C2—N1—H3N	109.5
O13 ⁱ —Cu1—O2 ⁱ	93.4 (10)	H1N—N1—H3N	109.5
O1—Cu1—O2 ⁱ	178.7 (13)	H2N—N1—H3N	109.5
O14—S1—O12	113.4 (9)	O2—C1—O1	125.4 (18)
O14—S1—O13	110.6 (13)	O2—C1—C2	121 (3)
O12—S1—O13	107.7 (14)	O1—C1—C2	114 (3)
O14—S1—O11	112.0 (15)	N1—C2—C1	109 (3)
O12—S1—O11	104.3 (13)	N1—C2—H2A	109.8
O13—S1—O11	108.6 (8)	C1—C2—H2A	109.8
C1—O1—Cu1	142.7 (17)	N1—C2—H2B	109.8
C1—O2—Cu1 ^{iv}	133.7 (16)	C1—C2—H2B	109.9
S1—O11—Cu1	134.9 (13)	H2A—C2—H2B	108.3
S1—O13—Cu1 ^{iv}	145.3 (16)		
O14—S1—O11—Cu1	−76 (2)	Cu1 ^{iv} —O2—C1—O1	35 (3)
O12—S1—O11—Cu1	161 (2)	Cu1 ^{iv} —O2—C1—C2	−146 (2)
O13—S1—O11—Cu1	46 (2)	Cu1—O1—C1—O2	−38 (4)
O14—S1—O13—Cu1 ^{iv}	73 (3)	Cu1—O1—C1—C2	142 (3)
O12—S1—O13—Cu1 ^{iv}	−163 (2)	O2—C1—C2—N1	−14 (3)
O11—S1—O13—Cu1 ^{iv}	−51 (3)	O1—C1—C2—N1	166 (2)

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

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O1 ^v	0.91	2.47	3.10 (3)	127
N1—H1N $\cdots$ O12 ^{vi}	0.91	2.11	2.78 (3)	130
N1—H2N $\cdots$ O12 ^{vii}	0.91	2.09	2.92 (3)	152
N1—H2N $\cdots$ O13 ^{vii}	0.91	2.31	3.08 (3)	143
N1—H3N $\cdots$ O11 ^{viii}	0.91	2.07	2.94 (3)	161
N1—H3N $\cdots$ O12 ^{viii}	0.91	2.44	3.13 (3)	133
C2—H2A $\cdots$ O1 ^{ix}	0.99	2.65	3.62 (4)	168
C2—H2A $\cdots$ O13 ⁱⁱⁱ	0.99	2.63	3.29 (4)	124

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