

CRYSTALLOGRAPHIC  
COMMUNICATIONS

ISSN 2056-9890

Received 11 August 2016

Accepted 8 September 2016

Edited by M. Weil, Vienna University of  
Technology, Austria**Keywords:** crystal structure; glycine; zinc  
sulfate; zwitterion; dimer; neutron diffraction.**CCDC reference:** 1503478**Supporting information:** this article has  
supporting information at [journals.iucr.org/e](http://journals.iucr.org/e)

# Glycine zinc sulfate pentahydrate: redetermination at 10 K from time-of-flight neutron Laue diffraction

A. Dominic Fortes,<sup>a\*</sup> Christopher M. Howard,<sup>b</sup> Ian G. Wood<sup>b</sup> and Matthias J. Gutmann<sup>a</sup><sup>a</sup>ISIS Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation, Campus, Didcot, Oxfordshire OX11 0QX, England, and <sup>b</sup>Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, England. \*Correspondence e-mail: [dominic.fortes@stfc.ac.uk](mailto:dominic.fortes@stfc.ac.uk)

Single crystals of glycine zinc sulfate pentahydrate [systematic name: hexa-aquazinc tetraaquadiglycinezinc bis(sulfate)],  $[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}(\text{C}_2\text{H}_5\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{SO}_4)_2$ , have been grown by isothermal evaporation from aqueous solution at room temperature and characterized by single-crystal neutron diffraction. The unit cell contains two unique  $\text{ZnO}_6$  octahedra on sites of symmetry  $\bar{1}$  and two  $\text{SO}_4$  tetrahedra with site symmetry 1; the octahedra comprise one [tetraaqua-diglycine zinc]<sup>2+</sup> ion (centred on one Zn atom) and one [hexaaquazinc]<sup>2+</sup> ion (centred on the other Zn atom); the glycine zwitterion,  $\text{NH}_3^+\text{CH}_2\text{COO}^-$ , adopts a monodentate coordination to the first Zn atom. All other atoms sit on general positions of site symmetry 1. Glycine forms centrosymmetric closed cyclic dimers due to  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds between the amine and carboxylate groups of adjacent zwitterions and exhibits torsion angles varying from ideal planarity by no more than 1.2°, the smallest values for any known glycine zwitterion not otherwise constrained by a mirror plane. This work confirms the H-atom locations estimated in three earlier single-crystal X-ray diffraction studies with the addition of independently refined fractional coordinates and  $U_{ij}$  parameters, which provide accurate internuclear  $X-\text{H}$  ( $X = \text{N}, \text{O}$ ) bond lengths and consequently a more accurate and precise depiction of the hydrogen-bond framework.

## 1. Chemical context

Numerous coordination compounds of glycine (Glyc) with divalent metal sulfates are known. For the case of zinc, there is an anhydrous species,  $2\text{Glyc}\cdot\text{ZnSO}_4$  (Moldobaev & Nogoev, 1970) and two hydrates,  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 3\text{H}_2\text{O}$  and  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$ . The trihydrate is dimorphic, occurring either as an orthorhombic crystal (space group  $Pca2_1$ ) or as a monoclinic crystal ( $P2_1/n$ ) depending on the synthesis route (Fleck & Bohatý, 2004). The monoclinic form is isotypic with compounds of general formula  $\text{Glyc}\cdot M(\text{II})\text{SO}_4\cdot 3\text{H}_2\text{O}$  where  $M(\text{II}) = \text{Mg}, \text{Co}$  or  $\text{Fe}$  (Oguey *et al.*, 2013*a,b*, 2014). Compounds with the general formula  $\text{Glyc}\cdot M(\text{II})\text{SO}_4\cdot 5\text{H}_2\text{O}$  are known only as isotypic triclinic crystals ( $P\bar{1}$ ) for  $M(\text{II}) = \text{Mg}, \text{Mn}, \text{Co}, \text{Fe}$  and  $\text{Zn}$  (Lindqvist & Rosenstein, 1960; Elayaraja *et al.*, 2007; Fleck & Bohatý, 2006; Tepavitcharova *et al.*, 2012). Solubility data have been published for a purported  $\text{Glyc}\cdot\text{NiSO}_4\cdot 5\text{H}_2\text{O}$  (Moldobaev *et al.*, 1970; Alymkulova & Salyeva, 1987). We have collected as-yet unpublished X-ray powder-diffraction data from this species, showing that it is isotypic with the other known members of the series. The existence of  $\text{Glyc}\cdot\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  has been reported by Thilagavathi *et al.* (2012) but their work is in error, and quite unambiguously describes the well-known material  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ .

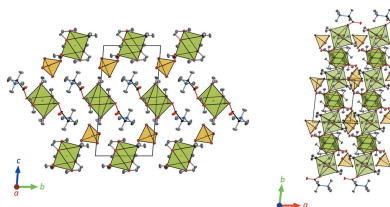
OPEN  ACCESS



Table 1

Comparison of bond lengths (Å), polyhedral volumes (Å<sup>3</sup>) and various distortion metrics (*cf.*, Robinson *et al.*, 1971) in Glyc·ZnSO<sub>4</sub>·5H<sub>2</sub>O from this work and the three preceding single-crystal X-ray diffraction studies.

The distortion index and quadratic elongation are dimensionless, whereas the bond-angle variance is in units of degrees squared.

	This work	Balamurugan <i>et al.</i> (2011)	Tepavitcharova <i>et al.</i> (2012)	Oguey <i>et al.</i> (2013c)
	Single-crystal neutron <i>T</i> = 10 K	Single-crystal X-ray <i>T</i> = 293 K	Single-crystal X-ray <i>T</i> = 150 K	Single-crystal X-ray <i>T</i> = 153 K
S—O1*	1.474 (5)	1.472 (2)	1.472 (1)	1.473 (2)
S—O2	1.484 (4)	1.478 (2)	1.482 (1)	1.485 (2)
S—O3*	1.473 (4)	1.472 (2)	1.477 (1)	1.481 (2)
S—O4	1.480 (5)	1.481 (2)	1.484 (1)	1.479 (2)
Mean S—O	1.478	1.476	1.479	1.479
SO <sub>4</sub> volume	1.656	1.649	1.659	1.661
Distortion index	0.0028	0.0025	0.0027	0.0022
Quadratic elongation	1.000	1.000	1.000	1.000
Bond-angle variance	0.410	0.268	0.320	0.420
Zn1—O5	2.039 (2)	2.024 (3)	2.032 (1)	2.035 (2)
Zn1—O6	2.093 (2)	2.101 (3)	2.098 (1)	2.098 (2)
Zn1—O7†	2.173 (2)	2.181 (3)	2.177 (1)	2.176 (2)
Mean Zn1—O	2.102	2.102	2.102	2.103
ZnO <sub>6</sub> volume	12.338	12.339	12.339	12.336
Distortion index	0.0227	0.0251	0.0238	0.0232
Quadratic elongation	1.003	1.003	1.003	1.003
Bond-angle variance	6.308	4.815	5.975	6.292
Zn2—O9	2.129 (3)	2.141 (3)	2.133 (1)	2.135 (2)
Zn2—O10	2.067 (3)	2.071 (3)	2.070 (1)	2.072 (2)
Zn2—O11	2.075 (2)	2.063 (3)	2.065 (2)	2.065 (2)
Mean Zn2—O	2.090	2.092	2.089	2.091
ZnO <sub>6</sub> volume	12.127	12.176	12.123	12.145
Distortion index	0.0124	0.0156	0.0139	0.0142
Quadratic elongation	1.003	1.002	1.002	1.002
Bond-angle variance	7.982	5.942	6.617	6.541
C1—O7	1.272 (4)	1.272 (5)	1.274 (2)	1.278 (3)
C1—O8	1.240 (3)	1.228 (5)	1.236 (2)	1.234 (3)
C1—C2	1.523 (4)	1.516 (5)	1.525 (3)	1.522 (3)
C2—N1	1.481 (2)	1.478 (5)	1.480 (2)	1.480 (3)

\*Denotes sulfate O atoms accepting two hydrogen bonds instead of three. †Denotes carboxylate oxygen ligand instead of water oxygen.

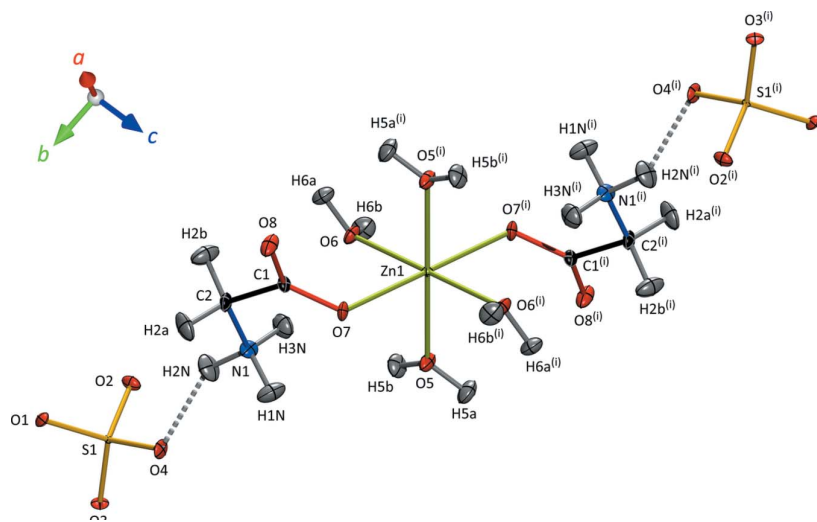


Figure 2

Local coordination environment of the Zn1 atom. Displacement ellipsoids are drawn at the 50% probability level for H and 90% for all other atoms. Dashed lines indicate N—H...O hydrogen bonds. [Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.]

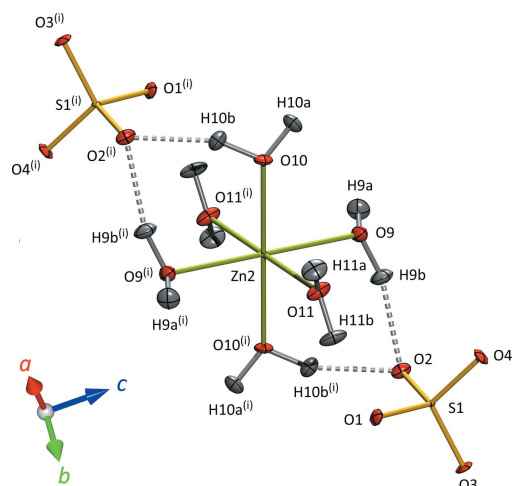


Figure 3

Local coordination environment of the Zn2 atom. Displacement ellipsoids are drawn at the 50% probability level for H and 90% for all other atoms. Dashed lines indicate O—H...O hydrogen bonds. [Symmetry code: (i) 1 - *x*, -*y*, 1 - *z*.]

Table 2

Comparison of  $X-H(D)$  bond lengths (Å) from earlier work (a–e) with our own (f).

Element symbols indicate the cation in each compound. ‘X-ray’ denotes single-crystal X-ray diffraction; ‘NPD’ denotes a neutron powder diffraction experiment on a deuterated analogue carried out at 10 K; ‘neutron’ indicates single-crystal neutron diffraction on a protonated analogue carried out at 10 K. Note that the atom symbols employed in our work are the same as those used by Elayaraja *et al.* (2007) and by Howard *et al.* (2016). Although other authors have used different atom labels – and indeed use them inconsistently in their own reports – we list equivalent contacts in this table.

	Mg, X-ray <sup>(a)</sup>	Mg, NPD <sup>(b)</sup>	Co, X-ray <sup>(c)</sup>	Mg, X-ray <sup>(e)</sup>	Zn, X-ray <sup>(c)</sup>	Zn, X-ray <sup>(d)</sup>	Zn, X-ray <sup>(e)</sup>	Zn, neutron <sup>(f)</sup>
N–H1N	0.87 (4)	1.008 (4)	0.847 (1)	0.849 (1)	0.881 (2)	0.85 (2)	0.910 (2)	1.033 (7)
N–H2N	0.87 (4)	0.982 (4)	0.907 (1)	0.898 (1)	0.904 (1)	0.83 (3)	0.911 (2)	1.028 (8)
N–H3N	0.87 (5)	0.991 (5)	0.904 (1)	0.902 (1)	0.946 (1)	absent	0.910 (2)	1.022 (6)
Average N–H	0.87	0.995	0.877	0.874	0.892	0.84	0.911	1.030
C–H2A	0.970 (4)	1.077 (4)	0.961 (1)	0.960 (1)	0.967 (2)	0.970 (3)	0.990 (2)	1.085 (6)
C–H2B	0.970 (3)	1.083 (4)	0.901 (1)	1.014 (1)	1.050 (2)	0.970 (3)	0.990 (2)	1.091 (7)
Average C–H	0.970	1.080	0.931	0.987	1.009	0.970	0.990	1.088
O5–H5A	0.84 (3)	0.975 (5)	0.880 (1)	0.789 (1)	0.879 (2)	0.85 (2)	0.83 (3)	0.973 (7)
O5–H5B	0.85 (3)	0.946 (5)	0.914 (1)	0.930 (1)	0.838 (1)	0.85 (3)	0.85 (3)	0.997 (7)
O6–H6A	0.84 (2)	0.987 (5)	0.964 (1)	0.875 (1)	0.864 (1)	0.83 (3)	0.86 (3)	0.981 (6)
O6–H6B	0.83 (3)	0.988 (5)	0.906 (1)	0.897 (1)	0.886 (1)	0.84 (3)	0.85 (2)	0.985 (6)
O9–H9A	0.83 (2)	0.977 (5)	0.864 (1)	0.871 (1)	0.881 (2)	0.87 (3)	0.86 (2)	0.979 (5)
O9–H9B	0.84 (2)	0.984 (4)	0.884 (1)	0.901 (1)	0.964 (1)	0.87 (2)	0.87 (3)	0.966 (6)
O10–H10A	0.84 (4)	0.954 (5)	0.972 (1)	0.911 (1)	0.887 (1)	0.82 (2)	0.87 (2)	0.977 (8)
O10–H10B	0.84 (3)	0.972 (5)	0.855 (1)	0.821 (1)	0.913 (1)	0.84 (2)	0.85 (2)	0.978 (6)
O11–H11A	0.84 (3)	1.002 (5)	0.822 (1)	0.884 (1)	0.808 (1)	0.83 (3)	0.86 (2)	0.966 (6)
O11–H11B	0.83 (3)	0.965 (5)	0.906 (1)	0.859 (1)	0.900 (1)	0.84 (2)	0.84 (2)	0.966 (6)
Average O–H	0.84	0.975	0.897	0.874	0.882	0.85	0.85	0.977

(a) Elayaraja *et al.* (2007); (b) Howard *et al.* (2016); (c) Tepavtcharova *et al.* (2012); (d) Balamurugan *et al.* (2011); (e) Oguey *et al.* (2013c); (f) this work.

where the glycine zwitterion lies on a mirror plane, are values of 180° realized (Fleck & Bohatý, 2005). In  $\alpha$ -glycine, the equivalent torsion angles are  $-19.60$  (3) and  $161.28$  (2)°.

In respect of the heavy atoms, agreement in the interatomic distances and angles between the single-crystal X-ray and single-crystal neutron refinements (Table 1) is excellent, with some differences emerging in respect of the room-temperature refinement by Balamurugan *et al.* (2011). However, the neutron data provide a substantial improvement in accuracy with respect to the X-ray data in the hydrogen atom’s frac-

tional coordinates and  $U_{ij}$  parameters. This is not surprising since neutrons are sensitive to the nuclear positions and X-rays to the electron density; in the covalent  $X-H$  bond the centroid of the H-atom’s electron-density distribution is displaced towards the heavy atom by 0.1 Å, yielding  $X-H$  distances from 10–15% shorter than the true internuclear separation (Coppens, 1997). Table 2 compares  $X-H$  bond lengths from a range of Gly·M(II)SO<sub>4</sub>·5H<sub>2</sub>O crystals obtained by single-crystal X-ray diffraction and by neutron powder diffraction. In the work of Elayaraja *et al.* (2007), methyl

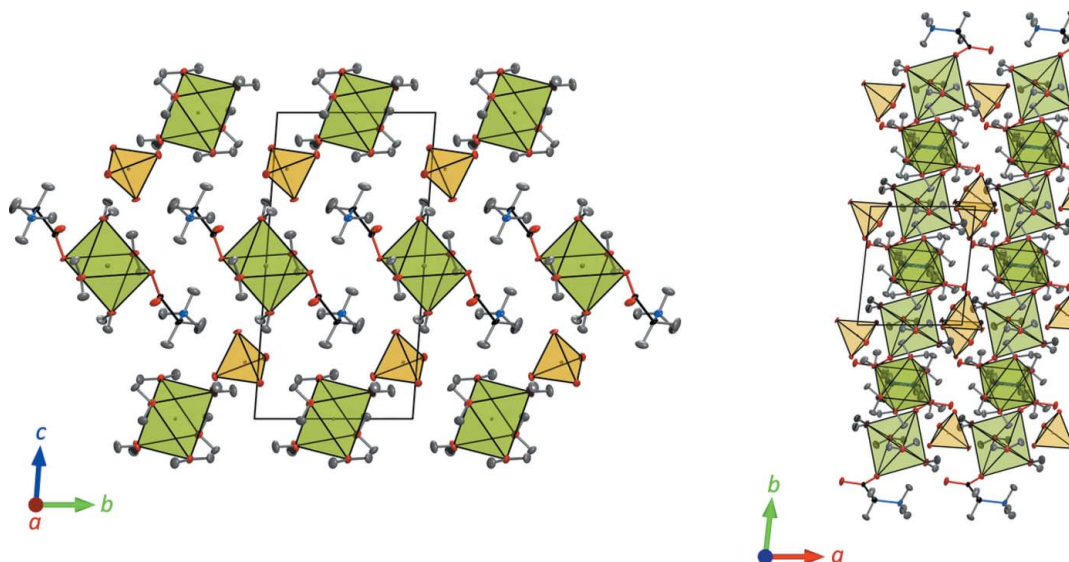


Figure 4

Packing of polyhedra in the structure of Glyc·ZnSO<sub>4</sub>·5H<sub>2</sub>O viewed along  $a$  (left) and along  $c$  (right). ZnO<sub>6</sub> octahedra are green, SO<sub>4</sub> tetrahedra are yellow.

**Table 3**  
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A···O4 <sup>i</sup>	0.973 (7)	1.793 (7)	2.755 (4)	169.0 (7)
O5—H5B···O8 <sup>ii</sup>	0.997 (7)	1.656 (8)	2.642 (4)	168.9 (6)
O6—H6A···O3 <sup>iii</sup>	0.981 (6)	1.722 (6)	2.696 (3)	170.8 (5)
O6—H6B···O4 <sup>iv</sup>	0.985 (6)	1.751 (5)	2.729 (3)	171.8 (7)
O9—H9A···O1 <sup>iv</sup>	0.979 (5)	1.732 (5)	2.707 (3)	173.8 (6)
O9—H9B···O2	0.966 (6)	1.895 (6)	2.811 (3)	157.2 (6)
O10—H10A···O3 <sup>iii</sup>	0.977 (8)	1.740 (8)	2.713 (4)	173.0 (7)
O10—H10B···O2 <sup>v</sup>	0.979 (6)	1.811 (7)	2.745 (4)	158.5 (7)
O11—H11A···O2 <sup>vi</sup>	0.966 (6)	1.772 (6)	2.726 (3)	168.6 (6)
O11—H11B···O1	0.966 (6)	1.824 (6)	2.750 (3)	159.5 (7)
C2—H2A···O2 <sup>vi</sup>	1.085 (6)	2.682 (9)	3.351 (4)	119.4 (6)
C2—H2A···O5 <sup>vii</sup>	1.085 (6)	2.716 (8)	3.489 (3)	127.9 (6)
C2—H2B···O10	1.091 (7)	2.579 (8)	3.649 (4)	166.7 (7)
N1—H1N···O7 <sup>vii</sup>	1.033 (7)	1.853 (7)	2.848 (3)	160.8 (7)
N1—H2N···O4	1.027 (8)	1.961 (7)	2.877 (3)	147.0 (7)
N1—H3N···O6	1.022 (6)	2.216 (7)	3.066 (3)	139.5 (5)

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

hydrogens were positioned geometrically and allowed to ride with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ; water hydrogen atoms were refined with restraints; the N—H bond lengths were all restrained to be equal. Balamurugan *et al.* (2011) placed the majority of their hydrogen atoms geometrically, although failed to identify the third amine hydrogen atom; water and the two amine H atoms were refined isotropically whereas the two methyl hydrogen atoms were riding on the C atom. Tepavitcharova *et al.* (2012) placed the hydrogen atoms in Gly·ZnSO<sub>4</sub>·5H<sub>2</sub>O geometrically and treated all of them as riding on their associated heavy atom during refinement. Oguey *et al.* (2013c) allowed all water hydrogen atoms to refine isotropically but fixed the methyl and amine hydrogens to ride on C and N, respectively. The coordinates of hydrogen atoms in this work were unrestrained and allowed to refine anisotropically.

Our values for the N—H and C—H bond lengths are in excellent agreement with other single-crystal neutron diffraction work, as noted in the preceding paragraph. Our values for the O—H bond lengths also agree well with those found in similar environments in hydrated  $M(\text{II})$  coordination compounds, such as MgSO<sub>4</sub>·11H<sub>2</sub>O and MgCrO<sub>4</sub>·11H<sub>2</sub>O where the average O—H = 0.974 Å (Fortes *et al.*, 2013), MgSeO<sub>4</sub>·9H<sub>2</sub>O, O—H<sub>av</sub> = 0.972 Å (Fortes *et al.*, 2015), and MgSeO<sub>4</sub>·7H<sub>2</sub>O, O—H<sub>av</sub> = 0.974 Å (Fortes & Gutmann, 2014).

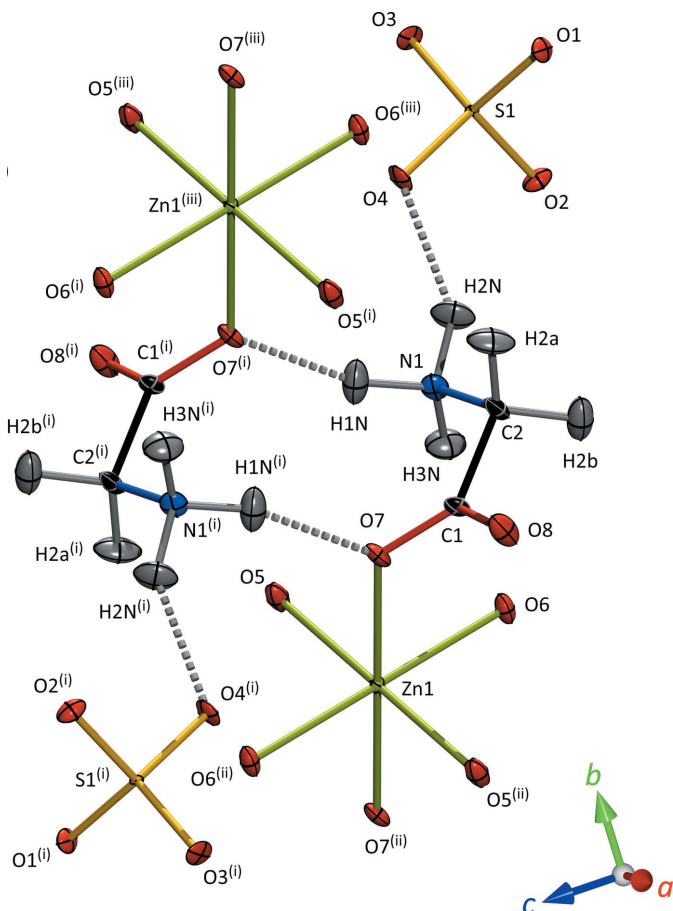
### 3. Supramolecular features

The overall three-dimensional framework is completed by a variety of hydrogen bonds with a range of strengths (Table 3). Fig. 4 shows the spatial relationship of the main structural elements. The majority of the hydrogen bonds are O—H···O contacts of medium strength ( $1.66 < H\cdots O < 1.90$  Å) and high linearity ( $\angle \text{O—H}\cdots\text{O} > 157^\circ$ ), characteristic of two-centred interactions. As expected, the N—H···O hydrogen bonds are weaker (*i.e.*, longer,  $1.85 < H\cdots O < 2.22$  Å) and more strained ( $\angle \text{N—H}\cdots\text{O}$  between approx.  $140$ – $160^\circ$ ). The methyl groups appear to participate in weak C—H···O hydrogen bonds (*cf.*,

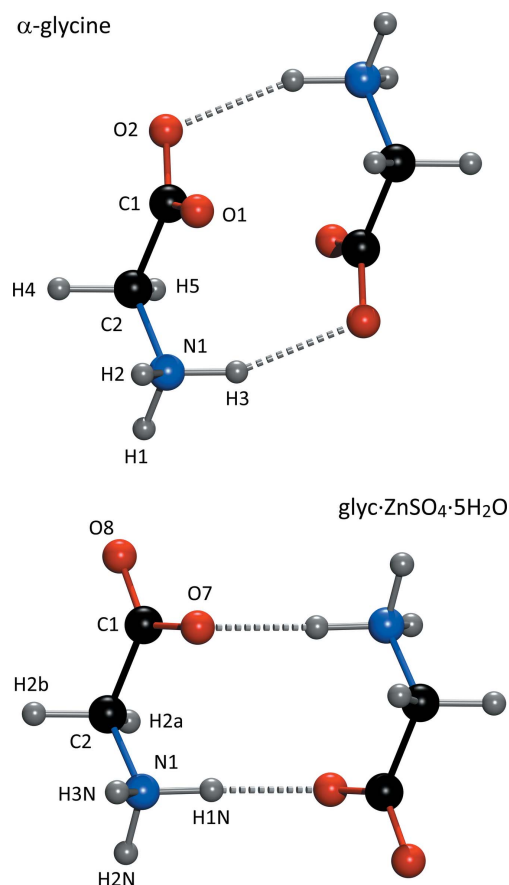
Steiner & Desiraju, 1998). One C—H···O bond is evidently a two-centred interaction, being the shortest and most of linear contact of this kind, with  $H\cdots O = 2.58$  (1) Å and  $\angle \text{C—H}\cdots\text{O} = 167$  (1)°. The other, involving C—H2A, is clearly a two-centred interaction (*i.e.*, a bifurcated hydrogen bond) with ‘arms’ of roughly equal length,  $H\cdots O \simeq 2.7$  Å and C—H···O angles of 119 and 128° involving O2 and O5, respectively.

#### 3.1. Glycine dimers

A hitherto unrecognized aspect of the supramolecular structure of Glyc· $M(\text{II})\text{SO}_4\cdot 5\text{H}_2\text{O}$  compounds is the presence of glycine dimers (Fig. 5). These occur as closed cyclic structures formed by N—H···O hydrogen bonds between the amine group of one glycine zwitterion and the Zn-coordinating carboxylate oxygen (O7) of another zwitterion, related to the first by an inversion centre. A similar cyclic dimer occurs in the structure of  $\alpha$ -glycine. A direct comparison between the dimers in Glyc·ZnSO<sub>4</sub>·5H<sub>2</sub>O and in  $\alpha$ -glycine is shown in Fig. 6; clearly, the main difference between these two dimers is the orientation of the carboxylate group, which is presumably due to the influence of a divalent metal being coordinated by



**Figure 5**  
 Connectivity between adjacent Zn1 octahedra is *via* a closed cyclic glycine dimer. As before, displacement ellipsoids are drawn at the 50% probability level for H and 90% for all other atoms. Dashed lines indicate N—H···O hydrogen bonds. [Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $x, 1+y, z$ .]



**Figure 6**  
Comparison of the closed cyclic dimers involving zwitterionic glycine that occur in the crystal structures of  $\alpha$ -glycine (top) and in Glyc·ZnSO<sub>4</sub>·5H<sub>2</sub>O (bottom).

the O7 carboxylate oxygen. Experimental studies of aqueous solutions indicate that only glycine monomers exist in the liquid phase (Huang *et al.*, 2008). However, there has been widespread disagreement on this matter from computational studies, which indicate either that there are no dimers (Hamad & Catlow, 2011), substantial quantities of closed zwitterionic dimers (Friant-Michel & Ruiz-López, 2010), or a small fraction of open dimers (Yani *et al.*, 2012) present in saturated solutions. The presence or absence of glycine polymerization in coordination compounds such as these may be useful in understanding the association of glycine in saturated aqueous solutions during nucleation and the role of solvated metal ions in polymerizing amino acids in Earth's Hadean oceans (Kitadai *et al.*, 2011, 2016) or in extraterrestrial oceans elsewhere in our solar system (Kimura & Kitadai, 2015).

#### 4. Database survey

A search of the Cambridge Structural Database (Groom *et al.*, 2016) identified the following directly relevant entries:

Glyc·M(II)SO<sub>4</sub> pentahydrates: 672589 (Mg); 857075 (Mg); 1451396 (Mg); 296329 (Co); 857073 (Co); 806684 (Zn); 857076 (Zn); 936400 (Zn).

**Table 4**

Raman vibrational frequencies and mode assignments of  $\alpha$ -glycine (*cf.*, Stenbäck, 1976; Rosado *et al.*, 1998; Yang *et al.*, 2008), Glyc·MgSO<sub>4</sub>·5H<sub>2</sub>O (Howard *et al.*, 2016) and the title compound.

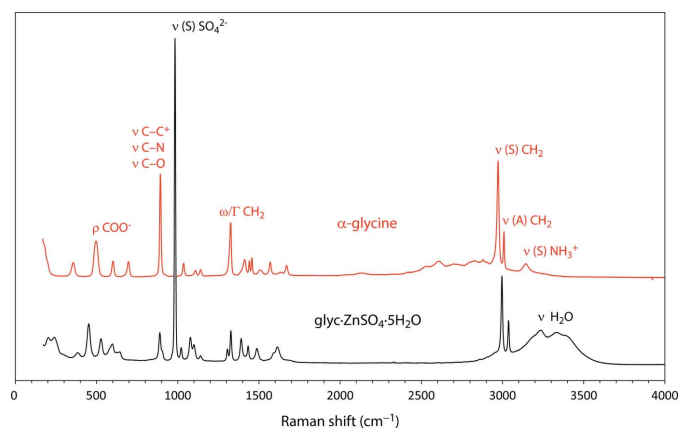
Meaning of symbols:  $\nu$  = stretch;  $\delta$  = deformation;  $\rho$  = rock;  $\omega$  = wag;  $\Gamma$  = twist; (A) = asymmetric; (S) = symmetric.

	$\alpha$ -Glycine <sup>a</sup>	Glyc·MgSO <sub>4</sub> ·5H <sub>2</sub> O <sup>a</sup>	Glyc·ZnSO <sub>4</sub> ·5H <sub>2</sub> O
Vibrational mode	180 s, 18 mW	1400 s, 18 mW	540 s, 18 mW
$\delta M^{2+}-O$ (?)	–	208 236	203 220
$\delta CCN^+$ $\rho COO^-$	356	361	382
$\delta(S) SO_4^{2-}$ $\rho COO^-$ $\omega COO^-$	– 497 601	453 522 597	451 527 582 599
$\delta(A) SO_4^{2-}$	–	623 645	626 644
$\delta COO^-$ unknown	696 –	– 794	– –
$\nu C-C^+$ $\nu C-N$ $\nu C-O$	893	890 905	890 906
$\rho CH_2$ $\nu(S) SO_4^{2-}$ $\nu C-N$	922 – 1036	– 983.8 1020	– 983.2 1021
$\nu(A) SO_4^{2-}$	–	1077 1100	1078 1101
$\rho NH_3^+$	1108 1140	1139	1141
$\omega CH_2$ $\Gamma CH_2$	1325	1305 1328	1306 1327
$\nu(S) COO^-$	1410	1395	1391
$\delta(S) CH_2$	1441 1457	1434	1433
$\delta(A) NH_3^+$ $\delta(S) NH_3^+$	1502 1516 1569	1488	1488
$\nu C-C^+$ $\omega CH_2$	1634	1597	1590
$\nu(A) COO^-$ $\nu(S) CH_2$ $\nu(A) CH_2$ $\nu(S) NH_3^+$	1670 2972 3009 3143	1631 2997 3038 –	1614 2996 3037 –
$\nu(S) H_2O$	–	3248	3204 3233
$\nu(A) H_2O$	–	3384	3331 3405

<sup>a</sup>Howard *et al.* (2016).

Glyc·M(II)SO<sub>4</sub> trihydrates: 989590 (Mg); 1451397 (Mg); 857074 (Co); 936396 (Fe); 243588 (Zn, orthorhombic); 936394 (Zn, monoclinic).

Glyc·M(II)SO<sub>4</sub> hexahydrates: 1285639 (Ni).



**Figure 7**  
Raman spectra of  $\alpha$ -glycine (top) and  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$  (bottom). Selected vibrational modes are labelled and a complete quantitative listing is given in Table 4.

### 5. Vibrational spectroscopy

Laser-stimulated Raman spectra were measured using a portable B&W Tek *i*-Raman Plus spectrometer equipped with a 532 nm laser ( $P_{\text{max}} = 37$  mW at the probe tip) that records spectra over the range 171–4002  $\text{cm}^{-1}$  with an optimal resolution of 3  $\text{cm}^{-1}$ . Measurements were carried out on powdered specimens of  $\alpha$ -glycine and  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$ . Samples were measured in thin-walled glass vials using the BC100 fibre-optic coupled Raman probe; the total integration time and laser power for each sample is provided with the tabulated results (see supplementary material).

The Raman spectrum of  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$  (Fig. 6) is virtually identical with that of  $\text{Glyc}\cdot\text{MgSO}_4\cdot 5\text{H}_2\text{O}$  reported in Howard *et al.* (2016) and is in excellent agreement with the spectrum shown in Tepavitcharova *et al.* (2012). Numerical data of the Raman spectrum are provided as an electronic supplement; peak positions and vibrational mode assignments are given in Table 4. The main differences between the two divalent-metal-substituted compounds include the blue-shifting of octahedral deformation modes and blue-shifting of both symmetric and asymmetric  $\text{COO}^-$  stretching modes. A large blue-shift of  $\nu(A)$  and  $\nu(S)$   $\text{COO}^-$  occurs when glycine coordinates to  $\text{Mg}^{2+}$  and the shift increases when glycine coordinates to  $\text{Zn}^{2+}$ . Raman spectra of  $\alpha$ -glycine and  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$  are shown in Fig. 7.

### 6. Synthesis and crystallization

$\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$  was crystallized by evaporation at room temperature of an equimolar aqueous solution of  $\alpha$ -glycine (Alfa Aesar A13816) and  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  (Sigma Aldrich Z4750) in deionized water (Alfa Aesar 36645). Unlike the  $\text{MgSO}_4$ -bearing analogue,  $\text{Glyc}\cdot\text{ZnSO}_4\cdot 5\text{H}_2\text{O}$  forms large well-faceted crystals that are both amenable to morphological study and suitably large for single-crystal neutron diffraction analysis. Fig. 1 shows photographs of a representative crystal

viewed along its *a* axis and series of drawings with indexed crystal faces.

### 7. Data collection and refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. Data were collected from a pair of single crystals at a series of four discrete rotational positions about the vertical axis, each frame being counted for 5 h, equivalent to 800  $\mu\text{Ahr}$  of ISIS proton beam current per frame. The structure of  $\text{Glyc}(d_5)\cdot\text{MgSO}_4\cdot 5\text{D}_2\text{O}$  at 10 K reported by Howard *et al.* (2016) was used as a starting point for the refinement. A total of eleven peaks, with the largest  $\sigma(F_{\text{obs}} - F_{\text{calc}})$  values were omitted from the refinement; such outliers are fairly common in SXD measurement when peaks occur close to the edges of detectors. A mild restraint on the  $U_{ij}$  parameters of the sulfur atom was imposed (*SHELX* ISOR command) in order to avoid a slightly non-positive-definite displacement ellipsoid. Since sulfur has the smallest neutron scattering cross section of any atom in the structure, and since it is both comparatively heavy and the temperature is very low, it is not surprising that – within errors – the effective  $U_{\text{iso}}$  parameter should refine to a small negative value.

**Table 5**  
Experimental details.

Crystal data	
Chemical formula	$[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}(\text{C}_2\text{H}_5\text{NO}_2)_2\cdot (\text{H}_2\text{O})_4](\text{SO}_4)_2$
$M_r$	653.20
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	10
$a, b, c$ (Å)	5.9601 (15), 6.7670 (17), 13.112 (4)
$\alpha, \beta, \gamma$ (°)	84.955 (18), 83.25 (2), 83.042 (19)
$V$ (Å <sup>3</sup> )	519.8 (2)
$Z$	1
Radiation type	Neutron, $\lambda = 0.48\text{--}7.0$ Å
$\mu$ (mm <sup>-1</sup> )	$5.02 + 0.0182 * \lambda$
Crystal size (mm)	$4 \times 2.5 \times 1$
Data collection	
Diffractometer	SXD
Absorption correction	Numerical. The linear absorption coefficient is wavelength dependent and is calculated as: $\mu = 5.0165 + 0.0182 * \lambda$ [ $\text{cm}^{-1}$ ] as determined by Gaussian integration in <i>SXD2001</i> (Gutmann, 2005)
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	8296, 8296, 8296
$R_{\text{int}}$	0.089
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.089, 0.246, 1.09
No. of reflections	8296
No. of parameters	291
No. of restraints	12
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	3.20, -3.47

Computer programs: *SXD2001* (Gutmann, 2005), *SHELXT2014* (Sheldrick, 2015a; Gruene *et al.*, 2014), *SHELXL2014* (Sheldrick, 2015b; Gruene *et al.*, 2014), *DIAMOND* (Putz & Brandenburg, 2006) and *publCIF* (Westrip, 2010).

## Acknowledgements

The authors thank the STFC ISIS facility for beam-time access. IGW acknowledges a grant from STFC, No. ST/K000934/1; CMH is similarly supported by a postgraduate studentship from STFC.

## References

- Alymkulova, K. & Salyeva, N. V. (1987). *Koordinatsionnye Soedineniya Metallov s Bioligandami, Institut Neorganicheskoy i Fizicheskoy Khimii* pp. 77–79. Kyrgyz SSR Ilimder Akademijasy. (In Russian).
- Balakrishnan, T. & Ramamurthy, K. (2007). *Spectrochim. Acta A*, **68**, 360–363.
- Balamurugan, M. S., Subramanian, P. & Rao, P. S. (2011). Private communication (Deposition number CCDC 8606684). CCDC, Cambridge, England. DOI: 10.5517/ccw2f2f.
- Coppens, P. (1997). *X-ray Charge Density and Chemical Bonding*. Oxford University Press, Oxford, England.
- Elayaraja, K., Parthiban, S. P., Ramalingom, S., Bocelli, G. & Kalkura, S. N. (2007). *Acta Cryst. E* **63**, m2901–m2902.
- El-Fadl, A. A. & Abdulwahab, A. M. (2010). *Physica B*, **405**, 3421–3426.
- Fleck, M. & Bohatý, L. (2004). *Acta Cryst. C* **60**, m291–m295.
- Fleck, M. & Bohatý, L. (2005). *Acta Cryst. C* **61**, m412–m416.
- Fleck, M. & Bohatý, L. (2006). *Acta Cryst. C* **62**, m22–m26.
- Fortes, A. D., Alfè, D., Hernández, E. R. & Gutmann, M. J. (2015). *Acta Cryst. B* **71**, 313–327.
- Fortes, A. D. & Gutmann, M. J. (2014). *Acta Cryst. E* **70**, 134–137.
- Fortes, A. D., Wood, I. G. & Gutmann, M. J. (2013). *Acta Cryst. C* **69**, 324–329.
- Friant-Michel, P. & Ruiz-López, M. F. (2010). *ChemPhysChem*, **11**, 3499–3504.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.
- Gruene, T., Hahn, H. W., Luebben, A. V., Meilleur, F. & Sheldrick, G. M. (2014). *J. Appl. Cryst.* **47**, 462–466.
- Gutmann, M. J. (2005). *SXD2001*. ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire, England.
- Hamad, S. & Catlow, C. R. A. (2011). *CrystEngComm*, **13**, 4391–4399.
- Howard, C., Wood, I. G., Knight, K. S. & Fortes, A. D. (2016). *Acta Cryst. C* **72**, 203–216.
- Huang, J., Stringfellow, T. C. & Yu, L. (2008). *J. Am. Chem. Soc.* **130**, 13973–13980.
- Jönsson, P.-G. & Kvick, Å. (1972). *Acta Cryst. B* **28**, 1827–1833.
- Kaminsky, W. (2005). *J. Appl. Cryst.* **38**, 566–567.
- Kaminsky, W. (2007). *J. Appl. Cryst.* **40**, 382–385.
- Kimura, J. & Kitadai, N. (2015). *Astrobiology*, **15**, 430–441.
- Kitadai, N. (2016). *Orig. Life Evol. Biosph.* **10**, 1007s11084-016-9510-5.
- Kitadai, N., Yokoyama, T. & Nakashima, S. (2011). *Geochim. Cosmochim. Acta*, **75**, 6285–6299.
- Lindqvist, I. & Rosenstein, R. (1960). *Acta Chem. Scand.* **14**, 1228–1229.
- Moldobaev, S. & Noguev, K. (1970). *Materialy Nauchnoi Konferentsii Posvyashchennoy 100-letiyu Periodicheskogo Zakona D. I. Mendeleeva*, C-29. (In Russian).
- Moldobaev, S., Noguev, K. & Ismailov, T. (1970). *Materialy Nauchnoi Konferentsii Posvyashchennoy 100-letiyu Periodicheskogo Zakona D. I. Mendeleeva*, C-120. (In Russian).
- Oguey, S., Jacquier, Y., Neels, A. & Stoeckli-Evans, H. (2013a). Private communication (deposit number CCDC 936393). CCDC, Cambridge, England. DOI: 10.5517/cc10fd72
- Oguey, S., Jacquier, Y., Neels, A. & Stoeckli-Evans, H. (2013b). Private communication (deposit number CCDC 936394). CCDC, Union Road, Cambridge, England. DOI: 10.5517/cc10fd83
- Oguey, S., Jacquier, Y., Neels, A. & Stoeckli-Evans, H. (2013c). Private communication (deposit number CCDC 936400). CCDC, Cambridge, England. DOI: 10.5517/cc10fdg9
- Oguey, S., Jacquier, Y., Sereda, O., Neels, A. & Stoeckli-Evans, H. (2014). Private communication (deposit number CCDC 989590). CCDC, Cambridge, England. DOI: 10.5517/cc126r89
- Power, L. F., Turner, K. E. & Moore, F. H. (1976). *Acta Cryst. B* **32**, 11–16.
- Putz, H. & Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.
- Rosado, M. T., Duarte, M. L. T. S. & Fausto, R. (1998). *Vib. Spectrosc.* **16**, 35–54.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.
- Stenbäck, H. (1976). *J. Raman Spectrosc.* **5**, 49–55.
- Tepavitcharova, S., Rabadjieva, D., Havlíček, D., Němec, I., Vojtíšek, P., Plocek, J. & Koleva, Z. (2012). *J. Mol. Struct.* **1018**, 113–121.
- Thilagavathi, R., Selvarajan, P. & Kumari, V. V. (2012). *Int. J. Adv. Sci. Tech. Res.* **2**, 164–183.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yang, X., Lu, J., Wang, X. & Ching, C. B. (2008). *J. Raman Spectrosc.* **39**, 1433–1439.
- Yani, Y., Chow, P. S. & Tan, R. B. H. (2012). *Cryst. Growth Des.* **12**, 4771–4778.



## supporting information

*Acta Cryst.* (2016). E72, 1438-1445 [doi:10.1107/S2056989016014304]

## Glycine zinc sulfate pentahydrate: redetermination at 10 K from time-of-flight neutron Laue diffraction

A. Dominic Fortes, Christopher M. Howard, Ian G. Wood and Matthias J. Gutmann

### Computing details

Data collection: *SXD2001* (Gutmann, 2005); cell refinement: *SXD2001* (Gutmann, 2005); data reduction: *SXD2001* (Gutmann, 2005); program(s) used to solve structure: *SHELXT2014* (Sheldrick, 2015a; Gruene *et al.*, 2014); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b; Gruene *et al.*, 2014); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2006); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

### Hexaaquazinc(II) tetraaquadiglycinezinc(II) bis(sulfate)

#### Crystal data

$[\text{Zn}(\text{H}_2\text{O})_6][\text{Zn}(\text{C}_2\text{H}_5\text{NO}_2)_2(\text{H}_2\text{O})_4](\text{SO}_4)_2$

$M_r = 653.20$

Triclinic,  $P\bar{1}$

$a = 5.9601$  (15) Å

$b = 6.7670$  (17) Å

$c = 13.112$  (4) Å

$\alpha = 84.955$  (18)°

$\beta = 83.25$  (2)°

$\gamma = 83.042$  (19)°

$V = 519.8$  (2) Å<sup>3</sup>

$Z = 1$

$F(000) = 336$

$D_x = 2.086$  Mg m<sup>-3</sup>

Neutron radiation,  $\lambda = 0.48\text{--}7.0$  Å

Cell parameters from 550 reflections

$\mu = 5.02 + 0.0182 * \lambda$  mm<sup>-1</sup>

$T = 10$  K

Tabular, colourless

$4 \times 2.5 \times 1$  mm

#### Data collection

SXD

diffractometer

Radiation source: ISIS neutron spallation source

time-of-flight LAUE diffraction scans

Absorption correction: numerical

The linear absorption coefficient is wavelength dependent and is calculated as:  $\mu = 5.0165 + 0.0182 * \lambda$  [cm<sup>-1</sup>] as determined by Gaussian integration in *SXD2001* (Gutmann, 2005)

8296 measured reflections

8296 independent reflections

8296 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.089$

$\theta_{\text{max}} = 87.4^\circ$ ,  $\theta_{\text{min}} = 8.2^\circ$

$h = -15 \rightarrow 15$

$k = -18 \rightarrow 16$

$l = -28 \rightarrow 29$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.089$

$wR(F^2) = 0.246$

$S = 1.09$

8296 reflections

291 parameters

12 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1376P)^2 + 36.2519P]$

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

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 3.20$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -3.47$  e Å<sup>-3</sup>

Extinction correction: SHELXL,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0386 (18)

*Special details*

**Experimental.** For peak integration a local UB matrix refined for each frame, using approximately 50 reflections from each of the 11 detectors. Hence `_cell_measurement_reflns_used` 550 For final cell dimensions a weighted average of all local cells was calculated Because of the nature of the experiment, it is not possible to give values of `_theta_min` and `_theta_max` for the cell determination. The same applies for the wavelength used for the experiment. The range of wavelengths used was 0.48–7.0 Angstroms, BUT the bulk of the diffraction information is obtained from wavelengths in the range 0.7–2.5 Angstroms. The data collection procedures on the SXD instrument used for the single-crystal neutron data collection are most recently summarized in the Appendix to the following paper Wilson, C.C. (1997). *J. Mol. Struct.* 405, 207–217

**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.** The variable wavelength nature of the data collection procedure means that sensible values of `_diffn_reflns_theta_min` & `_diffn_reflns_theta_max` cannot be given instead the following limits are given `_diffn_reflns_sin(theta)/lambda_min` 0.06 `_diffn_reflns_sin(theta)/lambda_max` 1.38 `_refine_diff_density_max/min` is given in Fermi per angstrom cubed not electrons per angstrom cubed. Another way to consider the `_refine_diff_density_` is as a percentage of the scattering density of a given atom: `_refine_diff_density_max` = 5.7 % of hydrogen `_refine_diff_density_min` = -6.1 % of hydrogen Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.0141 (6)	0.9128 (6)	0.1847 (4)	0.0008 (6)
O1	0.1809 (4)	1.0196 (3)	0.1159 (2)	0.0036 (4)
O2	-0.0249 (4)	0.7303 (3)	0.1375 (2)	0.0037 (4)
O3	-0.2027 (4)	1.0416 (3)	0.2010 (2)	0.0040 (4)
O4	0.1050 (4)	0.8522 (4)	0.2845 (2)	0.0038 (3)
Zn1	0.5000	0.0000	0.5000	0.0017 (4)
O5	0.1954 (4)	0.1618 (4)	0.5392 (2)	0.0049 (4)
H5A	0.0913 (11)	0.1389 (11)	0.6009 (6)	0.0198 (11)
H5B	0.0998 (10)	0.2109 (9)	0.4826 (6)	0.0170 (10)
O6	0.4360 (4)	0.0464 (4)	0.3456 (2)	0.0043 (4)
H6A	0.5654 (10)	0.0305 (9)	0.2922 (5)	0.0162 (10)
H6B	0.3082 (10)	-0.0116 (10)	0.3229 (6)	0.0179 (11)
O7	0.6512 (4)	0.2793 (4)	0.4768 (2)	0.0037 (3)
O8	0.9812 (4)	0.3195 (4)	0.3809 (2)	0.0060 (4)
N1	0.3991 (2)	0.5025 (2)	0.34432 (14)	0.0044 (2)
H1N	0.3634 (11)	0.5559 (12)	0.4165 (6)	0.0218 (13)
H2N	0.3159 (12)	0.6073 (10)	0.2963 (7)	0.0212 (12)
H3N	0.3294 (11)	0.3719 (9)	0.3435 (6)	0.0199 (12)
C1	0.7711 (3)	0.3465 (3)	0.39746 (19)	0.0029 (3)
C2	0.6484 (3)	0.4781 (3)	0.3163 (2)	0.0041 (3)
H2A	0.7111 (11)	0.6233 (9)	0.3086 (7)	0.0220 (13)
H2B	0.6871 (11)	0.4134 (12)	0.2420 (6)	0.0222 (13)
Zn2	0.5000	0.5000	0.0000	0.0008 (3)

O9	0.2958 (4)	0.3897 (3)	0.1320 (2)	0.0045 (4)
H9A	0.2434 (11)	0.2593 (8)	0.1279 (6)	0.0175 (11)
H9B	0.1606 (10)	0.4824 (9)	0.1443 (6)	0.0190 (11)
O10	0.7911 (4)	0.3443 (4)	0.0509 (2)	0.0048 (4)
H10A	0.7828 (12)	0.2322 (9)	0.1030 (6)	0.0180 (10)
H10B	0.8989 (11)	0.2959 (10)	-0.0061 (6)	0.0197 (11)
O11	0.5434 (4)	0.7298 (4)	0.0881 (2)	0.0054 (4)
H11A	0.6938 (9)	0.7484 (9)	0.1036 (6)	0.0182 (11)
H11B	0.4422 (10)	0.8523 (8)	0.0915 (7)	0.0200 (12)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0006 (10)	0.0009 (11)	0.0010 (18)	0.0001 (8)	-0.0003 (9)	0.0000 (11)
O1	0.0027 (6)	0.0037 (7)	0.0038 (10)	-0.0006 (5)	0.0016 (5)	0.0001 (7)
O2	0.0029 (6)	0.0028 (6)	0.0058 (11)	-0.0007 (5)	-0.0007 (6)	-0.0012 (7)
O3	0.0017 (6)	0.0040 (7)	0.0053 (11)	0.0018 (5)	0.0010 (6)	0.0000 (7)
O4	0.0039 (6)	0.0054 (7)	0.0018 (10)	0.0001 (5)	-0.0015 (6)	0.0011 (7)
Zn1	0.0015 (4)	0.0017 (4)	0.0017 (5)	-0.0001 (3)	-0.0001 (3)	0.0000 (3)
O5	0.0036 (7)	0.0071 (8)	0.0032 (11)	0.0014 (5)	-0.0002 (6)	0.0011 (7)
H5A	0.015 (2)	0.028 (3)	0.014 (3)	-0.0027 (18)	0.0046 (18)	0.002 (2)
H5B	0.015 (2)	0.019 (2)	0.016 (3)	0.0017 (15)	-0.0065 (17)	0.004 (2)
O6	0.0041 (7)	0.0064 (7)	0.0021 (11)	-0.0005 (5)	-0.0004 (6)	0.0002 (7)
H6A	0.0142 (18)	0.021 (2)	0.013 (3)	-0.0020 (15)	0.0034 (16)	-0.005 (2)
H6B	0.017 (2)	0.023 (2)	0.017 (3)	-0.0076 (17)	-0.0052 (18)	-0.005 (2)
O7	0.0042 (6)	0.0041 (7)	0.0026 (10)	-0.0011 (5)	-0.0004 (6)	0.0014 (7)
O8	0.0028 (7)	0.0091 (9)	0.0050 (12)	0.0008 (5)	0.0001 (6)	0.0022 (8)
N1	0.0030 (4)	0.0057 (5)	0.0041 (7)	0.0012 (3)	-0.0013 (4)	0.0004 (5)
H1N	0.017 (2)	0.033 (3)	0.015 (3)	0.002 (2)	0.0004 (19)	-0.009 (3)
H2N	0.019 (2)	0.020 (2)	0.025 (4)	0.0015 (18)	-0.011 (2)	0.006 (2)
H3N	0.018 (2)	0.015 (2)	0.027 (4)	-0.0066 (16)	-0.001 (2)	0.001 (2)
C1	0.0020 (5)	0.0034 (6)	0.0032 (9)	0.0000 (4)	-0.0011 (5)	0.0007 (6)
C2	0.0042 (6)	0.0047 (6)	0.0030 (9)	-0.0002 (4)	-0.0004 (5)	0.0017 (6)
H2A	0.020 (2)	0.013 (2)	0.033 (4)	-0.0078 (17)	-0.005 (2)	0.007 (2)
H2B	0.018 (2)	0.035 (3)	0.013 (3)	0.007 (2)	-0.0031 (19)	-0.006 (3)
Zn2	0.0008 (4)	0.0008 (4)	0.0009 (5)	-0.0001 (3)	-0.0001 (3)	0.0001 (3)
O9	0.0045 (7)	0.0035 (7)	0.0050 (11)	-0.0005 (5)	0.0005 (6)	0.0004 (7)
H9A	0.021 (2)	0.0115 (17)	0.021 (3)	-0.0064 (15)	-0.001 (2)	-0.001 (2)
H9B	0.0135 (19)	0.016 (2)	0.024 (4)	0.0064 (14)	0.0009 (18)	-0.001 (2)
O10	0.0039 (7)	0.0047 (7)	0.0050 (11)	0.0019 (5)	-0.0012 (6)	0.0010 (7)
H10A	0.024 (3)	0.015 (2)	0.013 (3)	0.0011 (17)	0.0002 (19)	0.0054 (19)
H10B	0.020 (2)	0.020 (2)	0.016 (3)	0.0065 (17)	0.0040 (19)	-0.002 (2)
O11	0.0033 (6)	0.0048 (7)	0.0086 (12)	0.0002 (5)	-0.0015 (6)	-0.0033 (8)
H11A	0.0091 (16)	0.022 (2)	0.025 (3)	-0.0030 (15)	-0.0057 (17)	-0.004 (2)
H11B	0.017 (2)	0.0118 (18)	0.031 (4)	0.0059 (14)	-0.003 (2)	-0.006 (2)

## Geometric parameters (Å, °)

S1—O3	1.473 (4)	N1—H1N	1.033 (7)
S1—O1	1.474 (5)	N1—C2	1.481 (2)
S1—O4	1.480 (6)	C1—C2	1.523 (4)
S1—O2	1.484 (4)	C2—H2A	1.085 (6)
Zn1—O5	2.039 (2)	C2—H2B	1.091 (7)
Zn1—O5 <sup>i</sup>	2.039 (2)	Zn2—O10	2.067 (3)
Zn1—O6	2.093 (3)	Zn2—O10 <sup>ii</sup>	2.067 (3)
Zn1—O6 <sup>i</sup>	2.094 (3)	Zn2—O11 <sup>ii</sup>	2.075 (2)
Zn1—O7 <sup>i</sup>	2.173 (2)	Zn2—O11	2.075 (2)
Zn1—O7	2.173 (2)	Zn2—O9	2.129 (3)
O5—H5A	0.973 (7)	Zn2—O9 <sup>ii</sup>	2.129 (3)
O5—H5B	0.997 (7)	O9—H9B	0.966 (6)
O6—H6A	0.981 (6)	O9—H9A	0.979 (5)
O6—H6B	0.985 (6)	O10—H10A	0.977 (8)
O7—C1	1.272 (4)	O10—H10B	0.979 (6)
O8—C1	1.240 (3)	O11—H11B	0.966 (6)
N1—H3N	1.022 (6)	O11—H11A	0.966 (6)
N1—H2N	1.027 (8)		
O3—S1—O1	110.2 (3)	O8—C1—O7	126.0 (3)
O3—S1—O4	110.1 (3)	O8—C1—C2	116.2 (2)
O1—S1—O4	109.5 (3)	O7—C1—C2	117.7 (2)
O3—S1—O2	109.3 (3)	H2A—C2—H2B	107.9 (7)
O1—S1—O2	109.3 (3)	H2A—C2—N1	109.5 (4)
O4—S1—O2	108.4 (3)	H2B—C2—N1	109.5 (4)
O5—Zn1—O5 <sup>i</sup>	180.0	H2A—C2—C1	108.5 (5)
O5—Zn1—O6	88.59 (11)	H2B—C2—C1	109.7 (4)
O5 <sup>i</sup> —Zn1—O6	91.41 (11)	O10—Zn2—O10 <sup>ii</sup>	180.0
O5—Zn1—O6 <sup>i</sup>	91.41 (11)	O10—Zn2—O11 <sup>ii</sup>	91.57 (10)
O5 <sup>i</sup> —Zn1—O6 <sup>i</sup>	88.59 (11)	O10 <sup>ii</sup> —Zn2—O11 <sup>ii</sup>	88.43 (10)
O6—Zn1—O6 <sup>i</sup>	180.0	O10—Zn2—O11	88.43 (10)
O5—Zn1—O7 <sup>i</sup>	92.01 (9)	O10 <sup>ii</sup> —Zn2—O11	91.57 (10)
O5 <sup>i</sup> —Zn1—O7 <sup>i</sup>	87.99 (9)	O11 <sup>ii</sup> —Zn2—O11	180.0
O6—Zn1—O7 <sup>i</sup>	93.38 (10)	O10—Zn2—O9	91.52 (11)
O6 <sup>i</sup> —Zn1—O7 <sup>i</sup>	86.62 (10)	O10 <sup>ii</sup> —Zn2—O9	88.48 (11)
O5—Zn1—O7	87.99 (9)	O11 <sup>ii</sup> —Zn2—O9	94.16 (10)
O5 <sup>i</sup> —Zn1—O7	92.01 (9)	O11—Zn2—O9	85.84 (10)
O6—Zn1—O7	86.62 (10)	O10—Zn2—O9 <sup>ii</sup>	88.48 (11)
O6 <sup>i</sup> —Zn1—O7	93.38 (10)	O10 <sup>ii</sup> —Zn2—O9 <sup>ii</sup>	91.52 (11)
O7 <sup>i</sup> —Zn1—O7	180.0	O11 <sup>ii</sup> —Zn2—O9 <sup>ii</sup>	85.84 (10)
H5A—O5—H5B	106.7 (6)	O11—Zn2—O9 <sup>ii</sup>	94.16 (10)
H6A—O6—H6B	108.1 (6)	O9—Zn2—O9 <sup>ii</sup>	180.00 (12)
C1—O7—Zn1	128.26 (18)	H9B—O9—H9A	106.2 (6)
H3N—N1—H2N	107.6 (6)	H10A—O10—H10B	106.1 (6)

H3N—N1—H1N	109.8 (7)	H11B—O11—H11A	111.4 (6)
H2N—N1—H1N	105.0 (6)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O5—H5A...O4 <sup>iii</sup>	0.973 (7)	1.793 (7)	2.755 (4)	169.0 (7)
O5—H5B...O8 <sup>iv</sup>	0.997 (7)	1.656 (8)	2.642 (4)	168.9 (6)
O6—H6A...O3 <sup>v</sup>	0.981 (6)	1.722 (6)	2.696 (3)	170.8 (5)
O6—H6B...O4 <sup>vi</sup>	0.985 (6)	1.751 (5)	2.729 (3)	171.8 (7)
O9—H9A...O1 <sup>vi</sup>	0.979 (5)	1.732 (5)	2.707 (3)	173.8 (6)
O9—H9B...O2	0.966 (6)	1.895 (6)	2.811 (3)	157.2 (6)
O10—H10A...O3 <sup>v</sup>	0.977 (8)	1.740 (8)	2.713 (4)	173.0 (7)
O10—H10B...O2 <sup>ii</sup>	0.979 (6)	1.811 (7)	2.745 (4)	158.5 (7)
O11—H11A...O2 <sup>vii</sup>	0.966 (6)	1.772 (6)	2.726 (3)	168.6 (6)
O11—H11B...O1	0.966 (6)	1.824 (6)	2.750 (3)	159.5 (7)
C2—H2A...O2 <sup>vii</sup>	1.085 (6)	2.682 (9)	3.351 (4)	119.4 (6)
C2—H2A...O5 <sup>viii</sup>	1.085 (6)	2.716 (8)	3.489 (3)	127.9 (6)
C2—H2B...O10	1.091 (7)	2.579 (8)	3.649 (4)	166.7 (7)
N1—H1N...O7 <sup>viii</sup>	1.033 (7)	1.853 (7)	2.848 (3)	160.8 (7)
N1—H2N...O4	1.027 (8)	1.961 (7)	2.877 (3)	147.0 (7)
N1—H3N...O6	1.022 (6)	2.216 (7)	3.066 (3)	139.5 (5)

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