metal-organic compounds

Three novel non-centrosymmetric compounds of glycine: glycine lithium sulfate, glycine nickel dichloride dihydrate and glycine zinc sulfate trihydrate

Michel Fleck[a]* and Ladislav Bohatý[b]

[a]Universität Wien – Geozentrum, Institut für Mineralogie und Kristallographie, Althanstrasse 14, A-1090 Wien, Austria, and [b]Universität zu Köln, Institut für Kristallographie, Zülpicher Straße 49b, D 50674 Köln, Germany
Correspondence e-mail: michel.fleck@univie.ac.at

The crystal structures of three compounds of glycine and inorganic materials are presented and discussed. The orthorhombic structure of glycinesulfatodilithium(I), $[Li_2(SO_4)(C_2H_5NO_2)]_n$, consists of corrugated sheets of $[LiO_4]$ and $[SO_4]$ tetrahedra. The glycine molecules are located between these sheets. The main features of the monoclinic structure of diaquadichloroglycinenickel(II), $[NiCl_2(C_2H_5NO_2)(H_2O)_2]_n$, are helical chains of $[NiO_4Cl_2]$ octahedra connected by glycine molecules. The orthorhombic structure of triaquaglycinesulfatozinc(II), $[Zn(SO_4)(C_2H_5NO_2)(H_2O)_3]_n$, is made up of $[O_3SOZnO_5]$ clusters. These clusters are linked by glycine molecules into zigzag chains. All three compounds are examples of non-centrosymmetric glycine compounds.

Comment

In the course of our search for new non-centrosymmetric compounds, we have investigated compounds of glycine and inorganic materials. The Cambridge Structural Database (CSD; Allen, 2002) contains over 200 glycine compounds, nearly a third of which are non-centrosymmetric. However, in most of these substances, glycine is combined with other organic molecules. Only 20 compounds of glycine and inorganic materials were found. We focus here exclusively on such compounds, rather than on structures containing other organic molecules. In contrast to the chiral amino acids, non-chiral glycine (as a structural unit) cannot enforce non-centrosymmetry of a crystal structure. However, many compounds of glycine are polar [e.g. glycine sodium nitrate (space group Cc; Krishnakumar et al., 2001), glycine calcium dichloride (space group $Pb2_1a$; Ravikumar et al., 1986), glycine calcium dibromide (space group $Pbc2_1$; Mohana Rao & Natarajan, 1980) and glycine zinc chloride (space group $Pbn2_1$; Hariharan et al., 1989)]. Even two of the three polymorphs of pure glycine are

non-centrosymmetric, namely β-glycine (space group $P2_1$; Drebushchak et al., 2002) and γ-glycine (space group $P3_2$; Shimon et al., 1986). Since the glycine molecule as an amphoteric can assume cationic, anionic and zwitterionic forms, the molecule can combine with anionic, cationic and overall neutral chemical constituents, and thus a large number of possible glycine compounds exist. We have therefore started a study of such compounds of glycine and inorganic materials. We present here three new non-centrosymmetric structures of this type. All three represent new structure types, i.e. no isostructural compounds are known.
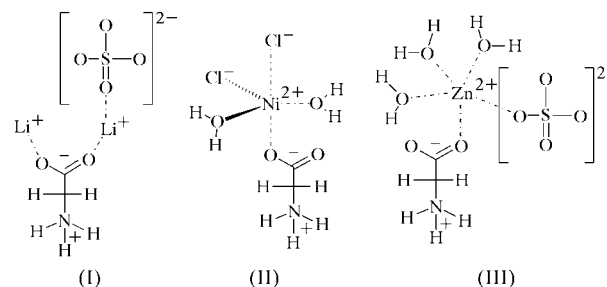
The structure of glycine lithium sulfate, (I) (Fig. 1), is composed of corrugated sheets of $[LiO_4]$ tetrahedra and $[SO_4]$ tetrahedra parallel to (001). These sheets consist of three crystallographically different tetrahedra (around atoms Li1, Li2 and S) that are connected by common corners (represented by atoms O2S, O3S and O4S; Fig. 4). The tip of each tetrahedron (i.e. the corner not connected to other tetrahedra) faces away from the sheet. Since the O atoms forming the tips of the Li1 and Li2 tetrahedra belong to the carboxyl group of the glycine molecule, these neighbouring tips are close to one another, twisting the polyhedra towards the glycine molecule and corrugating the sheets (Fig. 5). Consequently, the glycine molecules are located in the interstices between the sheets, and the sheets are connected only by weak hydrogen bonds (Table 2). The carboxyl groups, which effect the corrugation of the sheet, are more widely spread than usual; the O1—C1—O2 angle is 126.4 (2)° and the O1···O2 distance is 2.238 (2) Å, while the average values of these parameters based on literature data are 125.2° and 2.214 Å, respectively. A test for possible higher symmetry, using the program PLATON (Spek, 2000), suggests space group $Pnma$ with a probability of 92%.
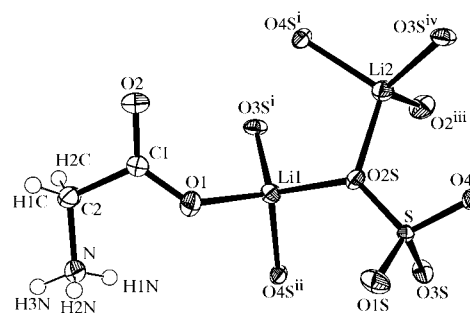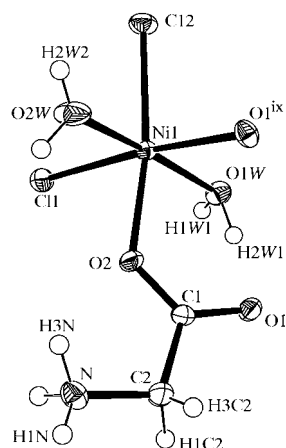

Figure 1
The connectivity in (I), with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (ii) $x, 1 + y, z$; (iii) $\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $\frac{3}{2} - x, y - \frac{1}{2}, z + \frac{1}{2}$.]

metal-organic compounds

However, refinement in this space group shows that the position of the NH₃ group does not suit this symmetry (imagine these alleged mirror planes horizontally in Fig. 5).

The crystal structure of glycine nickel dichloride dihydrate, (II) (Fig. 2), is altogether different. It is composed of distorted [NiO₄Cl₂] octahedra, with atoms Cl1 and Cl2 located at adjacent corners. The two opposite corners are occupied by O atoms from the carboxyl group of the glycine molecule (O1 and O2). The two remaining corners are occupied by O atoms of water molecules (O1W and O2W). Atoms O1 and O2 of one Ni coordination sphere belong to two different glycine molecules. Thus, each molecule connects two Ni polyhedra, forming infinite chains along [010]. Each chain is actually a left-handed helix around a 2_1 screw axis (Fig. 6). These chains are connected to one another by hydrogen bonds (Table 4). Similar chains are common in L-malates, *e.g.* copper dihydrogen dimalate (Fleck *et al.*, 2004).

Glycine zinc sulfate trihydrate, (III) (Fig. 3), can also be described as having a chain structure. Slightly irregular [ZnO₆] octahedra are connected to [SO₄] tetrahedra by one common corner, namely atom O3S, thus forming [O₃SOZnO₅] clusters (Fig. 7). Three corners of the [ZnO₆] octahedra are occupied by O atoms of water molecules. The remaining two corners are occupied by O atoms from the carboxyl group of the glycine molecules. Thus, these [O₃SOZnO₅] zinc sulfate clusters are connected to one another by the glycine molecules, forming zigzag chains along [100]. The chain is not a spiral, unlike that reported for the above nickel compound, but can be described by means of the *a*-glide plane in (010). The chains are connected to each other by medium to long hydrogen bonds (Table 6). More than 70 years ago, Dubský & Rabas (1931) described a pentahydrate, (C₂H₅NO₂)ZnSO₄·5H₂O. However, in our experiments, we obtained only the trihydrate, which in turn was not reported by Dubský & Rabas (1931).

We have compared the geometry of the glycine molecules in the title compounds and in α-glycine (Legros & Kvick, 1980), β-glycine (Drebushchak *et al.*, 2002), γ-glycine (Shimon *et al.*, 1986), glycine nickel sulfate hydrate (Peterková *et al.*, 1991) and glycine zinc chloride (Hariharan *et al.*, 1989). Obviously, the molecular conformation is the geometric feature with the highest degree of freedom. Comparing the O—C1—C2—N torsion angles (assuming no chemical difference between the two O atoms of the carboxyl group) we found more or less antiperiplanar (*i.e. trans*) conformations. In some compounds, large deviations from the ideal *trans* conformation (*i.e.* a torsion angle of 180°) were observed [*e.g.* −157.4 (2)° in
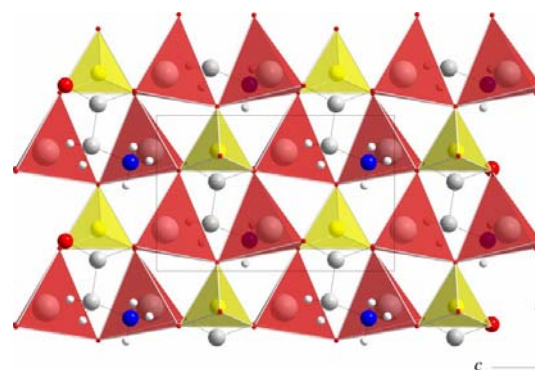
Figure 2
The connectivity in (II), with displacement ellipsoids at the 50% probability level. [Symmetry code: (ix) $2 - x, \frac{1}{2} + y, 1 - z$.]
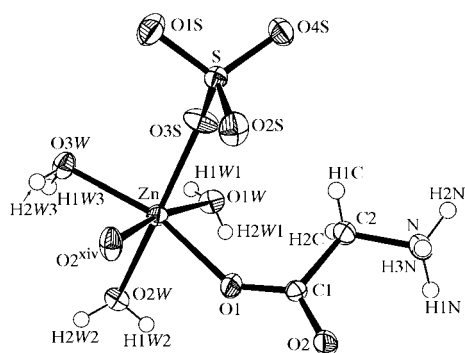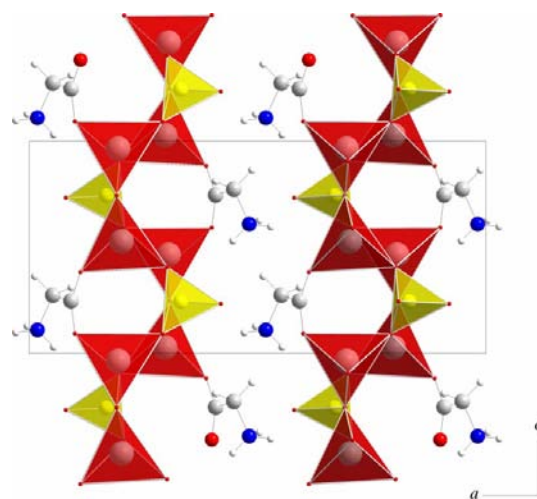
Figure 3
The connectivity in (III), with displacement ellipsoids at the 50% probability level. [Symmetry code: (xiv) $x - \frac{1}{2}, -y, z$.]

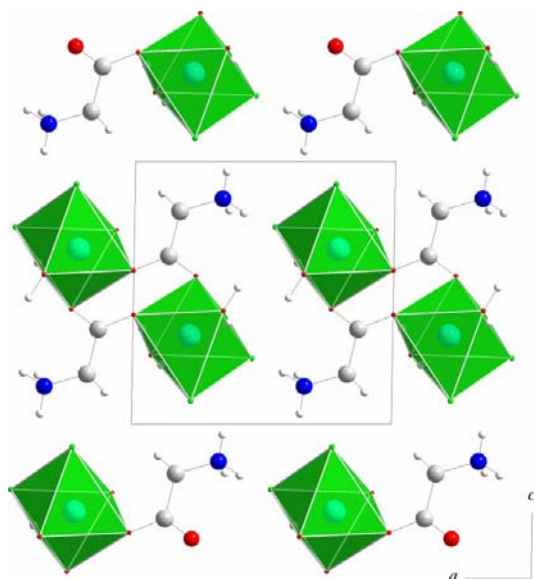**Figure 4**
The crystal structure of (I), in a view perpendicular to the sheets. The [LiO₄] tetrahedra are dark and the [SO₄] tetrahedra are light.

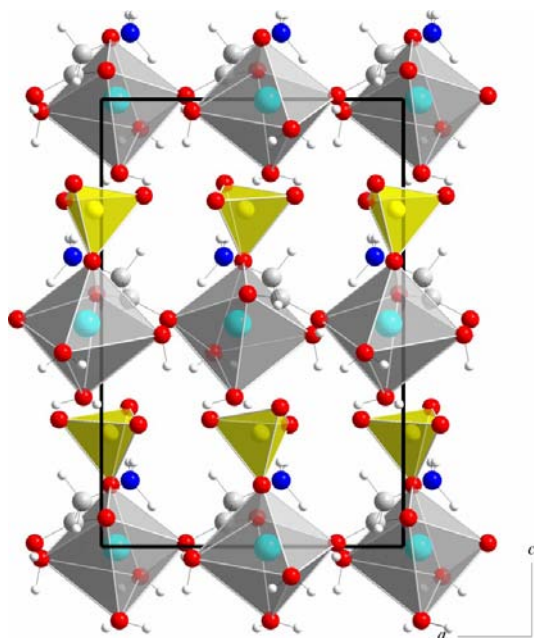**Figure 5**
The crystal structure of (I), viewed along [010]. The corrugated sheets are oriented vertically. Note the position of the acid group, forcing the tips of the Li1 and Li2 tetrahedra together. The tetrahedra are represented as in Fig. 4.

β-glycine and $-163.4\,(2)^{\circ}$ in glycine zinc chloride]. In the title compounds, the torsion angles are $-170.98\,(15)$ [in (I)], $-178.78\,(13)$ [in (II)] and $-176.85\,(18)^{\circ}$ [in (III)]. The differences in the interatomic distances and angles are much smaller. None of the distances and angles deviate significantly from the average values calculated from the structural data of the above compounds [$C1-O1 = 1.25\,(2)$ Å, $C1-O2 = 1.26\,(2)$ Å, $C1-C2 = 1.52\,(2)$ Å, $C2-N = 1.48\,(1)$ Å and $O1-C1-O2 = 125.7\,(19)^{\circ}$; cf. Tables 1, 3 and 5]. The only noteworthy deviation from these values occurs in glycine zinc chloride, where both carboxyl O atoms are virtually equi-

distant from the C atom. Obviously, the mesomeric effect is more pronounced in this salt than in the other compounds.

Experimental

Crystals of the title compounds were grown from aqueous solutions of glycine and lithium sulfate, nickel dichloride and zinc sulfate, respectively, in a stoichiometric ratio. The solutions were evaporated slowly at a temperature of approximately 295 K over a period of four months. The syntheses yielded crystals of up to several millimetres in diameter.

Compound (I)

Crystal data

[Li$_2$(SO$_4$)(C$_2$H$_5$NO$_2$)]	Mo $K\alpha$ radiation
$M_r = 185.01$	Cell parameters from 1054
Orthorhombic, $Pna2_1$	reflections
$a = 16.423\,(3)$ Å	$\theta = 4.1$–30.0°
$b = 5.005\,(1)$ Å	$\mu = 0.49$ mm^{-1}
$c = 7.654\,(2)$ Å	$T = 293\,(2)$ K
$V = 629.1\,(2)$ Å^3	Prism, colourless
$Z = 4$	$0.40 \times 0.20 \times 0.20$ mm
$D_x = 1.953$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	1653 independent reflections
φ and ω scans	1582 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$\theta_{max} = 30.0^{\circ}$
(Otwinowski & Minor, 1997)	$h = -22 \rightarrow 23$
$T_{min} = 0.827$, $T_{max} = 0.908$	$k = -7 \rightarrow 7$
1653 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
$wR(F^2) = 0.066$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
$S = 1.09$	Extinction correction: *SHELXL*97
1653 reflections	Extinction coefficient: 0.013 (7)
130 parameters	Absolute structure: Flack (1983),
H-atom parameters refined	675 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2$	Flack parameter = 0.021 (4)
$+ 0.088P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

Li1—O1	1.911 (4)	S—O4S	1.4796 (9)
Li1—O3S^{i}	1.958 (4)	S—O3S	1.4837 (17)
Li1—O2S	1.968 (4)	O3S—Li2^{vi}	1.950 (4)
Li1—O4S^{ii}	1.980 (4)	O3S—Li1^{iii}	1.958 (4)
Li2—O2^{iii}	1.878 (4)	O4S—Li2^{iii}	1.973 (5)
Li2—O3S^{v}	1.950 (4)	O1—C1	1.258 (3)
Li2—O4S^{i}	1.973 (5)	O2—C1	1.249 (3)
Li2—O2S	1.976 (4)	C1—C2	1.517 (2)
S—O1S	1.4573 (11)	C2—N	1.470 (2)
S—O2S	1.4732 (17)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N—H1N$\cdots$O1S^{ii}	0.84 (3)	2.32 (4)	3.066 (4)	147 (3)
N—H2N$\cdots$O2^{vii}	0.92 (4)	2.14 (4)	2.816 (2)	130 (3)
N—H3N$\cdots$O1S^{viii}	0.83 (3)	2.07 (3)	2.868 (2)	160 (3)

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

Figure 6
The crystal structure of (II), in a view along [010], along the chains.

Figure 7
The crystal structure of (III), in a view along [010]. The chains are oriented horizontally. [ZnO$_6$] groups are octahedral and [SO$_4$] groups are tetrahedral.

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

Ni—O2W	2.0457 (14)	Ni—Cl1	2.4688 (6)
Ni—O2	2.0658 (11)	O1—C1	1.2582 (17)
Ni—O1W	2.0732 (12)	O2—C1	1.2534 (18)
Ni—O1^{ix}	2.0762 (11)	C1—C2	1.512 (2)
Ni—Cl2	2.3677 (6)	C2—N	1.477 (2)

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

Compound (II)

Crystal data

[NiCl$_2$(C$_2$H$_5$NO$_2$)(H$_2$O)$_2$]	$D_x = 2.142$ Mg m^{-3}
$M_r = 240.71$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1197
$a = 8.203$ (2) Å	reflections
$b = 5.475$ (1) Å	$\theta = 4.1–30.0°$
$c = 8.311$ (2) Å	$\mu = 3.27$ mm^{-1}
$\beta = 90.97$ (3)°	$T = 293$ (2) K
$V = 373.21$ (14) Å^3	Prism, green
$Z = 2$	$0.20 \times 0.10 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	2170 independent reflections
ω scans	2142 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$\theta_{max} = 30.0°$
(Otwinowski & Minor, 1997)	$h = -11 \rightarrow 11$
$T_{min} = 0.561$, $T_{max} = 0.736$	$k = -7 \rightarrow 7$
2170 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.003$
$R[F^2 > 2\sigma(F^2)] = 0.016$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$wR(F^2) = 0.038$	$\Delta\rho_{min} = -0.34$ e Å^{-3}
$S = 1.13$	Extinction correction: *SHELXL*97
2170 reflections	Extinction coefficient: 0.127 (3)
128 parameters	Absolute structure: Flack (1983),
H-atom parameters refined	972 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0166P)^2$	Flack parameter = 0.002 (8)
$+ 0.065P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H1N$\cdots$Cl1^{x}	0.86 (3)	2.58 (3)	3.4296 (17)	167 (3)
N—H2N$\cdots$Cl1^{xi}	0.96 (4)	2.37 (4)	3.2372 (16)	150 (4)
N—H3N$\cdots$Cl1^{xii}	0.91 (4)	2.55 (4)	3.4042 (17)	156 (4)
O1W—H1W1$\cdots$Cl2^{xiii}	0.85 (4)	2.49 (4)	3.3304 (14)	174 (3)
O1W—H2W1$\cdots$O1	0.92 (3)	1.86 (3)	2.7451 (17)	161 (3)
O2W—H1W2$\cdots$Cl1^{xii}	0.89 (3)	2.24 (3)	3.1226 (16)	172 (3)
O2W—H2W2$\cdots$Cl1^{ii}	0.75 (3)	2.43 (3)	3.1756 (15)	176 (3)

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

Table 5
Selected interatomic distances (Å) for (III).

Zn—O3S	2.0507 (16)	S—O2S	1.4675 (16)
Zn—O1	2.0584 (13)	S—O3S	1.4857 (17)
Zn—O2^{xiv}	2.1229 (15)	S—O4S	1.4888 (16)
Zn—O1W	2.1238 (16)	O1—C1	1.249 (2)
Zn—O3W	2.1290 (16)	O2—C1	1.248 (2)
Zn—O2W	2.1449 (18)	C1—C2	1.524 (3)
S—O1S	1.4642 (18)	C2—N	1.467 (3)

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

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H1N$\cdots$O3W^{xv}	0.95 (4)	2.00 (4)	2.929 (3)	164 (3)
N—H2N$\cdots$O4S^{xvi}	0.88 (5)	2.11 (5)	2.967 (3)	165 (4)
N—H3N$\cdots$O2W^{xvii}	0.75 (6)	2.49 (6)	3.151 (3)	148 (5)
O1W—H1W1$\cdots$O4S^{xviii}	0.71 (3)	2.04 (4)	2.744 (2)	171 (4)
O1W—H2W1$\cdots$O4S^{xix}	0.72 (5)	2.12 (5)	2.815 (2)	164 (5)
O2W—H1W2$\cdots$O2S^{xix}	0.79 (4)	2.01 (4)	2.802 (2)	177 (4)
O2W—H2W2$\cdots$O2S^{xx}	0.85 (5)	1.88 (5)	2.714 (2)	167 (5)
O3W—H1W3$\cdots$O1S^{xxi}	0.89 (5)	1.93 (5)	2.747 (2)	152 (5)
O3W—H2W3$\cdots$O1^{xiv}	0.80 (5)	1.97 (5)	2.746 (2)	164 (4)

Symmetry codes: (xiv) $x - \frac{1}{2}, -y, z$; (xv) $1 + x, y, z$; (xvi) $\frac{1}{2} + x, 1 - y, z$; (xvii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (xviii) $-x, 1 - y, z - \frac{1}{2}$; (xix) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (xx) $-x, -y, z - \frac{1}{2}$; (xxi) $-\frac{1}{2} - x, y, z - \frac{1}{2}$.

Compound (III)

Crystal data

[Zn(SO$_4$)(C$_2$H$_5$NO$_2$)(H$_2$O)$_3$]	Mo $K\alpha$ radiation
$M_r = 290.55$	Cell parameters from 2456
Orthorhombic, $Pca2_1$	reflections
$a = 8.440$ (2) Å	$\theta = 3.5–37.8°$
$b = 8.278$ (2) Å	$\mu = 3.08$ mm^{-1}
$c = 12.521$ (3) Å	$T = 293$ (2) K
$V = 874.8$ (4) Å^3	Prism, colourless
$Z = 4$	$0.10 \times 0.05 \times 0.05$ mm
$D_x = 2.206$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	4460 independent reflections
ω scans	3901 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$\theta_{max} = 37.8°$
(Otwinowski & Minor, 1997)	$h = -14 \rightarrow 14$
$T_{min} = 0.748$, $T_{max} = 0.861$	$k = -14 \rightarrow 14$
4460 measured reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$\Delta\rho_{max} = 0.64$ e Å^{-3}
$wR(F^2) = 0.067$	$\Delta\rho_{min} = -0.47$ e Å^{-3}
$S = 1.02$	Extinction correction: *SHELXL*97
4460 reflections	Extinction coefficient: 0.0018 (8)
172 parameters	Absolute structure: Flack (1983),
H-atom parameters refined	2027 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0230P)^2$	Flack parameter = 0.006 (3)
$+ 0.336P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

All H atoms were refined isotropically: C—H = 0.95 (3) and 0.94 (3) Å, and N—H = 0.83 (3)–0.92 (4) Å in (I); C—H = 0.86 (3) and 1.04 (4) Å, N—H = 0.86 (3)–0.96 (4) Å and O—H = 0.75 (3)–0.92 (3) Å in (II); C—H = 0.93 (4) and 1.03 (4) Å, N—H = 0.75 (6)–0.95 (4) Å and O—H = 0.71 (3)–0.89 (5) Å in (III).

For all compounds, data collection: *COLLECT* (Nonius, 2003); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff *et al.*, 1997) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1004). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bergerhoff, G., Berndt, M. & Brandenburg, K. (1997). *J. Res. NIST*, **101**, 221–225.
Drebushchak, T. N., Boldyreva, E. V. & Shutova, E. S. (2002). *Acta Cryst.* E**58**, o634–o636.
Dubský, J. V. & Rabas, A. (1931). *Collect. Trav. Chim. Tchecosl.* **3**, 135–154.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1977). *Acta Cryst.* A**33**, 890–898.
Fleck, M., Bohatý, L., Tillmanns, E. & Held, P. (2004). *Z. Kristallogr.* **219**, 101–111.
Hariharan, M., Rajan, S. S. & Srinivasan, R. (1989). *Z. Kristallogr.* **188**, 217–222.
Krishnakumar, R. V., Subha Nandhini, M., Natarajan, S., Sivakumar K. & Varghese, B. (2001). *Acta Cryst.* C**57**, 1149–1150.
Legros, J. P. & Kvick, Å. (1980). *Acta Cryst.* B**36**, 3052–3059.
Mohana Rao, J. K. & Natarajan, S. (1980). *Acta Cryst.* B**36**, 1058–1061.
Nonius (2003). *COLLECT.* Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Peterková, J., Podlahova, J., Loub, J. & Micka, Z. (1991). *Acta Cryst.* C**47**, 2664–2666.
Ravikumar, K., Rajan, S. S., Natarajan, S., Ponnuswamy, M. N. & Trotter, J. (1986). *Z. Kristallogr.* **175**, 217–225.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Shimon, L. J. W., Lahav, M. & Leiserowitz, L. (1986). *New J. Chem.* **10** 723–729.
Spek, A. L. (2000). *PLATON.* Utrecht University, The Netherlands.