Poly[di-μ_3-hydroxymethanesulfinato-zinc(II)]

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(O–C) = 0.010 Å
R factor = 0.028
wR factor = 0.074
Data-to-parameter ratio = 6.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Zinc(II) formaldehyde sulfoxylate, [Zn(CH₃O₃S)₂], a widely marketed additive in the polymer and textile industry (under the registered trademarks Decroline, Decolin and Safolin, CAS 24887-06-7), possesses, in the solid state, a polymeric framework, with the Zn atoms octahedrally coordinated by six O atoms of four different hydroxymethanesulfinate groups. The latter are found to coordinate through all their O atoms, including the hydroxy ones, and possess a chelating nature. By contrast, in the structure of the only other commercially available salt of this ligand (dihydrated sodium formaldehyde sulfoxylate), the organic residue, being involved in an extensive network of hydrogen-bond contacts, is fully stretched and bridges two Na^I ions through a single O atom.

Comment

The long known (Meister *et al.*, 1905) zinc(II) formaldehyde sulfoxylate [or zinc(II) hydroxymethanesulfinate, CAS 24887-06-7], (I), crystallizes in the non-centrosymmetric, but achiral, space group *Cc*, with one crystallographically independent zinc(II) ion and two distinct hydroxymethanesulfinate groups per asymmetric unit. The latter act as chelating ligands as well as bridging groups within a three-dimensional complex and dense framework. The Zn—O bond distances fall in the 2.004 (5)–2.398 (6) Å range, with remarkably long Zn—O3 and Zn—O6 contacts (>2.20 Å), *i.e.* those involving hydroxy O atoms. Thus, as also indicated by the trans-O—Zn—O angles [in the 157.7 (2)–172.9 (2)° range], the coordination octahedron is heavily distorted, possibly through a combination of two different effects: the different Lewis basicity of hydroxy *versus* S-bound O atoms and the geometrical constraints imposed by periodicity in a three-dimensional polymeric system. Upon coordination, each ligand generates a (nearly planar) five-membered Zn/O/CH₂/S/O ring, with the H(O) and the S atoms lying slightly off the mean plane on the same side. The two crystallographically independent ligands can, however, be distinguished geometrically by the O—S—O—Zn torsion angles [99.7 (4) and −167.3 (3)°], leading to two very distinct Zn···Zn contacts of 5.087 (5) and 5.450 (5) Å. The only other known crystal structure of this type of compound is that of the dihydrated sodium salt (Truter, 1962; CAS 149-44-0), which, however, contains one-dimensional chains of six-coordinated Na^I ions, bound to two bridging water molecules (Na—O = 2.44–2.53 Å) and to a bridging, but monodentate, hydroxymethanesulfinate (Na—O = 2.46–2.52 Å). Both S=O and uncoordinated C—OH groups are, however, involved in an extensive network of hydrogen bonds within the polymer (S=O) and across parallel one-dimensional chains, giving the overall structure a three-dimensional nature.
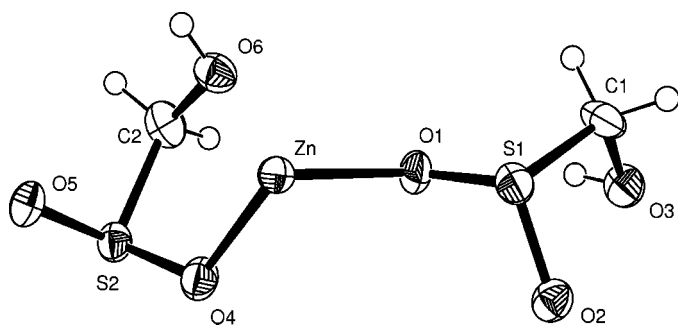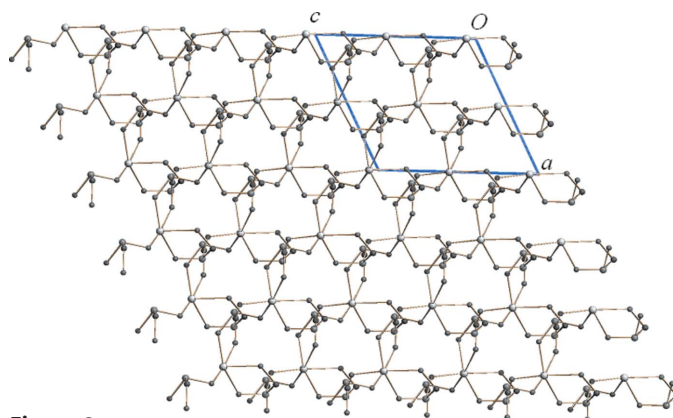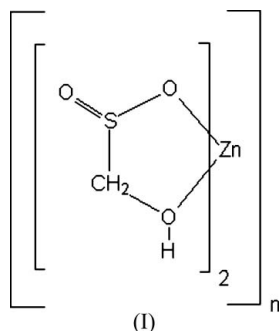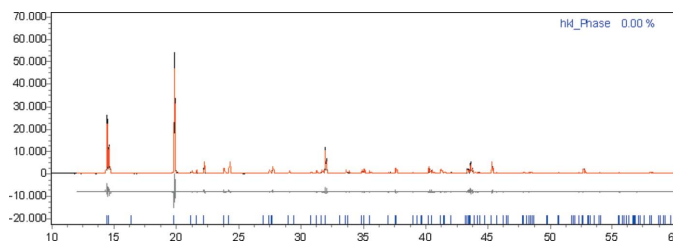
Figure 1
The asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are depicted as circles of arbitrary size.

Figure 2
Schematic drawing of the packing environment of the complex three-dimensional polymer, highlighting the nearly octahedral coordination environment of the Zn^{II} ions. For clarity, H atoms have been omitted.

(I)

Figure 3
A full-profile structureless refinement performed by *TOPAS* (Bruker, 2003), showing that the bulk material is indeed monophasic, with narrow powder diffraction peaks and no splitting in the 2θ axis. Although affected by some residual texture effects, these powder data confirm the *C*-centred monoclinic unit cell derived from single-crystal analysis, and indicate that all 'single crystals' tested by us were indeed multiple aggregates, some only a few degrees displaced from each other.

Experimental

The title compound was obtained from Transpek Silox Industry Ltd, Vadodara, India, and used as supplied. Recrystallization from aqueous solutions, with the aim of obtaining better crystals, was found to be unsuccessful. From the many available batches, several crystals were tested, all showing extreme mosaicity and heavily broadened multiple peaks in the ω axis. Eventually, a (nearly) single-crystal specimen was found, which allowed a satisfactory unit-cell determination and data collection.

Crystal data

[Zn(CH$_3$O$_3$S)$_2$]
$M_r = 255.56$
Monoclinic, Cc
$a = 8.332$ (5) Å
$b = 10.797$ (10) Å
$c = 8.939$ (2) Å
$\beta = 116.56$ (3)°
$V = 719.3$ (8) Å^3
$Z = 4$

$D_x = 2.360$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9$–12°
$\mu = 3.97$ mm^{-1}
$T = 295$ K
Prism, colourless
$0.12 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scan
Absorption correction: none
653 measured reflections
653 independent reflections
652 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$

$\theta_{max} = 25.3°$
$h = -10 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 10$
3 standard reflections
    frequency: 180 min
    intensity decay: 5.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.074$
$S = 1.15$
653 reflections
108 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 8.9338P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.013$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Zn—O2^i	2.004 (5)	Zn—O3^i	2.398 (6)
Zn—O4	2.031 (5)	S1—O2	1.524 (5)
Zn—O5^{ii}	2.040 (5)	S1—O1	1.535 (6)
Zn—O1	2.053 (5)	S2—O4	1.518 (5)
Zn—O6	2.219 (5)	S2—O5	1.539 (5)
O2^i—Zn—O4	157.7 (2)	O1—Zn—O6	90.5 (2)
O2^i—Zn—O5^{ii}	96.0 (2)	O2^i—Zn—O3^i	75.7 (2)
O4—Zn—O5^{ii}	93.5 (2)	O4—Zn—O3^i	84.9 (2)
O2^i—Zn—O1	97.3 (2)	O5^{ii}—Zn—O3^i	86.2 (2)
O4—Zn—O1	102.3 (2)	O1—Zn—O3^i	172.9 (2)
O5^{ii}—Zn—O1	93.4 (2)	O6—Zn—O3^i	90.79 (19)
O2^i—Zn—O6	90.6 (2)	O2—S1—O1	109.1 (3)
O4—Zn—O6	78.6 (2)	O4—S2—O5	107.6 (3)
O5^{ii}—Zn—O6	171.8 (2)		

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

Of the several data collections performed with increasing ω scan width, the best results, reported here, were obtained by the ω scan method with an unconventional scan angle of $\Delta\omega = (6.0 + 0.35\tan\theta)°$, 150 s per reflection. Given the very long acquisition times required by such an unconventional scan angle, Friedel pairs were not collected. However, the Flack (1983) parameter for the proposed enantiomer achieved an almost ideal zero value. Powder diffraction data (Cu $K\alpha$ radiation) were collected (on a Bruker AXS D8 Advance $\theta{:}\theta$ diffractometer) on the bulk sample, in order to test sample purity, crystal mosaicity and to confirm the unit cell proposed above. The relevant comments are reported in the caption to Fig. 3. Although all H atoms could be located in difference Fourier maps, those attached to C atoms were eventually positioned geometrically (C—H = 0.97 Å) and refined using a riding model, with $U_{iso}(H)$ equal to $1.2U_{eq}(C)$. The hydroxy H atoms were refined with an O—H distance restraint of 0.82 (1) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: local programs; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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