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Diacetatobis(trimethylenethiourea)-zinc(II) monohydrate

Ibrahim Abdul Razak,[a] Anwar Usman,[a] Hoong-Kun Fun,[a]* Bohari M. Yamin[b] and Goh Wooi Keat[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Correspondence e-mail: hkfun@usm.my

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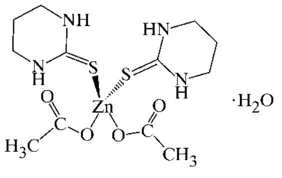
In the title compound, $[Zn(CH_3COO)_2(C_4H_8N_2S)_2]\cdot H_2O$, the Zn atom is tetrahedrally coordinated in the ZnO_2S_2 form. N—H···O and O—H···O intramolecular and intermolecular hydrogen bonds are formed by the four N atoms and the water molecule. N—H···O intermolecular hydrogen bonds and C—H···S and C—H···O intermolecular interactions interconnect columns formed by the molecules into layers. Adjacent layers are then linked by other N—H···O and O—H···O intermolecular hydrogen bonds to form a three-dimensional framework throughout the structure. The orientations of the acetate planes are such that the Zn atom lies within them.

Comment

Complexes of metal acetate with thioamides, such as bis(acetato)bis(ethylenethiourea)cobalt(II) (Holt *et al.*, 1970) and bis(acetato)bis(thiourea)zinc(II) (Cavalca *et al.*, 1967) show weak metal–oxygen interactions in addition to the normal metal–oxygen bond with the acetate group. Our interest in the structures of zinc(II) halides complexed with *S*-donor ligands led to the X-ray crystallographic investigation of the title complex, (I). It is also interesting to see the effects of the presence of the weak zinc–oxygen interactions and the water molecules on the structure.



(I)

The average lengths of the thioamide N—C [1.319 (4) Å] and S—C [1.734 (4) Å] bonds in the trimethylenethiourea ligands are comparable to the values reported for the free ligand [N—C = 1.334 (6) Å and S—C = 1.722 (7) Å; Dias & Truter, 1964]. The reduction of π-electron density in the exocyclic S—C bond for the S atom coordinated to a metal atom results in a lengthening of the S—C bond. This reduction contributes to increased π-electron density in the thioamide N—C bonds, and the corresponding shortening of these N—C bonds. The average Zn—S and Zn—O bond lengths, 2.333 (1) and 1.981 (3) Å, respectively, are comparable with the average values reported in the complexes $[Zn(C_2Cl_3O_2)_2(CH_4N_2S)_2]\cdot H_2O$ [Zn—S = 2.304 (2) Å and Zn—O = 2.006 (5) Å; Potočňák *et al.*, 1994], $[Zn\{SC(NHCH_2)_2\}_2(S_2O_3)]$ [Zn—S = 2.320 (8) Å and Zn—O = 2.022 (18) Å; Baggio *et al.*, 1974] and $[Zn(C_6H_5COO)_2\{CS(NH_2)_2\}_2]$ [Zn—S = 2.367 (1) Å and Zn—O = 1.964 (2) Å; Černák *et al.*, 1995].

The Zn atom is coordinated by an S atom from each of two trimetylenethiourea ligands and by one O atom from each of two acetate groups. This ZnO_2S_2 coordination forms a distorted tetrahedron with the angles around the Zn atom ranging from 93.48 (10) to 121.17 (8)°. This type of coordination is also observed in the structures reported by Černák *et al.* (1995) and Potočňák *et al.* (1994).

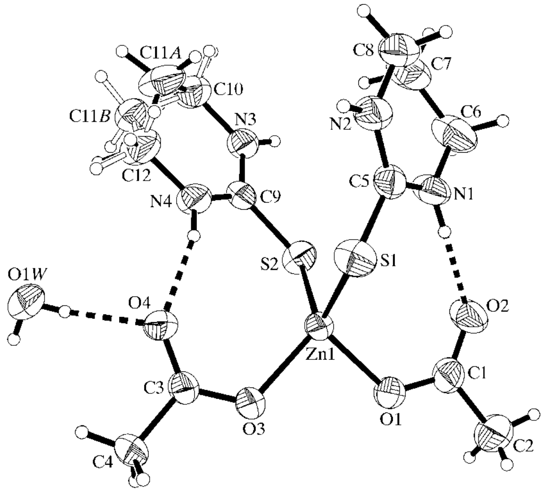


Figure 1
The structure of title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. The open bonds depict the alternate disordered arrangement involving C11.

In the crystal, all the N atoms of the thioamide ligands and the water molecules act as hydrogen donors, forming N—H···O and O—H···O intramolecular and intermolecular hydrogen bonds. There are also C—H···S and C—H···O intermolecular interactions observed in the crystal (Table 2). Within the asymmetric unit, the water molecule forms an intermolecular O1*W*—H2*W*1···O4 hydrogen bond with the Zn complex. The molecules are stacked into columns along the *a* axis. These columns are interconnected by an N3—H3*A*···O3$(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ hydrogen bond and by C4—H4*D*···S2$(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ and C10—H10*B*···O1$(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ interactions into layers which lie perpendicular to the *b* axis. The layers are then linked by the water molecules through N2—H2*A*···O1*W*$(1-x, 1-y, -z)$ and O1*W*—H1*W*1···O2$(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ interactions. These hydrogen bonds and interactions form a three-dimensional framework throughout the structure.

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The Zn1 atom is also involved in weaker interactions with the other two O atoms, O2 and O4, of the carboxylate ligands (Table 3). The Zn1—O1—C1 and Zn1—O3—C3 bond angles are 124.4 (2) and 119.7 (2)°, respectively. The orientation of the planes of the two acetates are determined by the Zn1—O1, Zn1—O2, Zn1—O3 and Zn1—O4 interactions (Cavalca *et al.*, 1967). The two acetate groups are nearly coplanar, the dihedral angle between them being 11.1 (3)°. The Zn1 atom lies 0.116 (1) and 0.075 (1) Å from the acetate planes defined by atoms O1, O2, C1 and C2, and O3, O4, C3 and C4, respectively. As a result, the orientations of the acetate planes are such that Zn1 lies virtually on them. This observation was also reported by Cavalca *et al.* (1967) [Zn···O = 2.996 (5) and 2.891 (9) Å, Zn—O—C = 119.4 (6) and 118.2 (7)°, and Zn—plane$_{\rm acetates}$ = 0.095 and 0.036 Å]. Other short contacts observed in the structure are listed in Table 3.

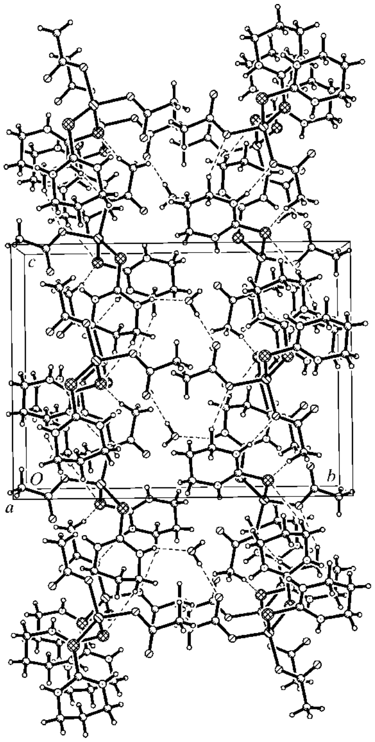

Figure 2
The three-dimensional framework viewed down the *a* axis, showing the hydrogen-bonding and intermolecular contacts.

Experimental

Solutions of zinc acetate (0.257 g, 1.17 mmol) and tetrahydropyrimidine-2-thione (0.271 g, 2.34 mmol) in acetonitrile were mixed in a 1:2 molar ratio in a 50 ml flask and the mixture was stirred for about 30 min. The solution was then filtered into another flask and left to evaporate slowly. After a few days, some single crystals were collected, washed with hexane and dried (m.p. 400 K).

Crystal data

$[Zn(C_2H_3O_2)_2(C_4H_8N_2S)_2]\cdot H_2O$
M_r = 433.84
Monoclinic, $P2_1/n$
a = 8.7517 (1) Å
b = 17.3654 (2) Å
c = 13.0543 (2) Å
β = 90.837 (1)°
V = 1983.74 (4) Å^3
Z = 4
D_x = 1.453 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
θ = 2.0–29.4°
μ = 1.48 mm^{-1}
T = 293 (2) K
Slab, colourless
0.16 × 0.12 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\rm min}$ = 0.798, $T_{\rm max}$ = 0.867
11 176 measured reflections
3495 independent reflections
2645 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.097
$\theta_{\rm max}$ = 25.0°
$h = -9 \rightarrow 10$
$k = -20 \rightarrow 19$
$l = -15 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.138
S = 0.98
3495 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.54 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.37 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0165 (16)

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.978 (2)	S2—C9	1.729 (3)
Zn1—O3	1.984 (2)	N1—C5	1.322 (4)
Zn1—S1	2.328 (1)	N2—C5	1.324 (4)
Zn1—S2	2.337 (1)	N3—C9	1.326 (4)
S1—C5	1.739 (4)	N4—C9	1.305 (4)
O1—Zn1—O3	93.48 (10)	O1—Zn1—S2	103.74 (8)
O1—Zn1—S1	114.42 (8)	O3—Zn1—S2	121.17 (8)
O3—Zn1—S1	110.28 (8)	S1—Zn1—S2	112.22 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O2	0.86	1.96	2.801 (4)	166
N4—H4*A*···O4	0.86	1.93	2.752 (4)	160
O1*W*—H2*W*1···O4	0.78 (5)	2.05 (5)	2.823 (4)	167 (5)
N2—H2*A*···O1*W*$^{\rm i}$	0.86	2.04	2.846 (5)	156
N3—H3*A*···O3$^{\rm ii}$	0.86	2.14	2.974 (4)	164
O1*W*—H1*W*1···O2$^{\rm iii}$	0.86 (6)	1.97 (6)	2.818 (5)	167 (6)
C4—H4*D*···S2$^{\rm iv}$	0.96	2.86	3.615 (5)	137
C10—H10*B*···O1$^{\rm ii}$	0.97	2.45	3.315 (5)	149

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

Table 3
Short contacts observed in the structure (Å).

Zn1···C3	2.842 (4)	Zn1···C9	3.346 (3)
Zn1···C1	2.886 (4)	Zn1···N4	3.469 (3)
Zn1···O4	3.018 (3)	S1···N2	2.658 (3)
Zn1···O2	3.150 (3)	S1···N1	2.681 (4)
Zn1···C5	3.153 (4)	S2···N3	2.625 (3)
Zn1···N1	3.340 (4)	S2···N4	2.667 (3)

After checking their presence in a difference map, the positions of all H atoms of the Zn complex were geometrically idealized and allowed to ride on their parent atoms, with C—H distances in the range 0.96–0.97 Å, N—H distances of 0.88 Å and fixed displacement parameters defined by $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom) or 1.5$U_{\rm eq}$($\rm C_{methyl}$). The H atoms of the water molecule were refined isotropically. The highest peak and the deepest hole are 0.97 and 1.03 Å from O3 and Zn1, respectively. Atom C11 in one of the trimethylenethiourea rings is disordered and was refined with an occupancy ratio of 0.75:0.25.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1123). Services for accessing these data are described at the back of the journal.

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