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Bis(thiosemicarbazide-*S*,*N*)zinc(II) dinitrate

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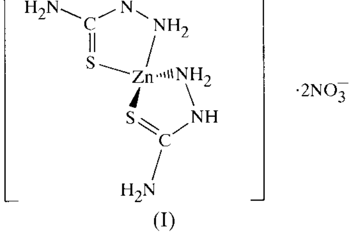
In the title compound, $[Zn(CH_5N_3S)_2](NO_3)_2$, the zinc(II) ion is located on the twofold axis and chelated by two thiosemicarbazide ligands with Zn—S and Zn—N distances of 2.0904 (17) and 2.2672 (6) Å, respectively. Thus the central zinc(II) is four-coordinated and in a distorted tetrahedral geometry. The inter- and intramolecular hydrogen bonds formed between thiosemicarbazide ligands and nitrate anions assemble the molecules into a one-dimensional chain.

Comment

As a ligand with potential S and N donors, thiosemicarbazide is interesting not only because of the structural chemistry of its multifunction coordination modes, but also because of the formation of complexes with biological activities. The biological activities of complexes with thiourea derivatives have been well documented (Shen *et al.*, 1998) and thiourea derivatives have been successfully screened for various biological actions (Antholine & Taketa, 1982). We are interested in the crystal engineering of metal complexes with various intra- and intermolecular interactions (Su *et al.*, 1998; Su, Kang *et al.*, 1999; Su, Zhou *et al.*, 1999), and now report the crystal structure of $[Zn(CH_5N_3S)_2](NO_3)_2$, (I).



(I)

The structure of the title compound consists of a cation $[Zn(CH_5N_3S)_2]^{2+}$ and two nitrate anions, which are joined together by two sets of intramolecular cyclic hydrogen bonding as shown in Fig. 1. The cation of the complex contains a distorted tetrahedral zinc(II) ion which is chelated by two bidentate thiosemicarbazide ligands through their S and N atoms. There is a crystallographically imposed twofold axis passing through the central zinc(II) ion [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. The Zn—S and Zn—N distances show no remarkable features [2.0904 (17) and 2.2672 (6) Å, respectively], and the greatest deviation from normal tetrahedral geometry was found from the N1—Zn1—S1 and S1^i—Zn1—S1 angles [88.33 (5) and 134.26 (3)°, respectively].

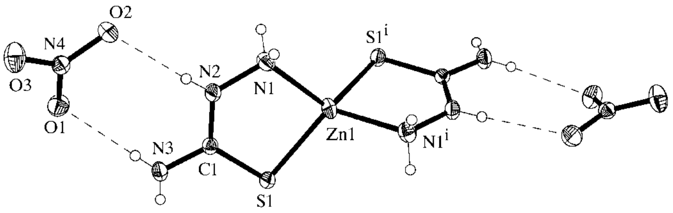


Figure 1
The molecular structure of (I) with displacement ellipsoids at the 30% probability level.

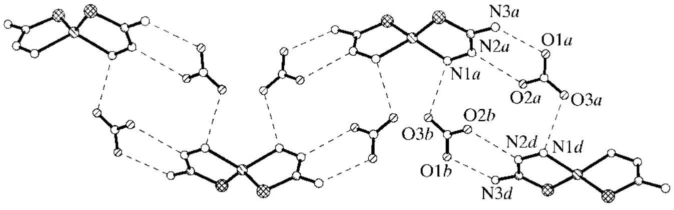


Figure 2
The one-dimensional chain assembled from intra- and intermolecular hydrogen bonds.

It is interesting that hydrogen bonding plays an important role in the crystal packing. Both the coordinated and uncoordinated NH_2 group, and the NH group of the thiosemicarbazide ligands are involved in hydrogen bonding acting as hydrogen-bond donors with three O atoms of nitrate as potential hydrogen-bond acceptors. As shown in Fig. 1, the N2 and N3 atoms form intramolecular cyclic hydrogen bonds with the O2 and O1 atoms, and the N1 atom forms an intermolecular hydrogen bond with O3^{ii} (Table 1) as shown in Fig. 2. So the two nitrate anions bridge two $[Zn(CH_5N_3S)_2]^{2+}$ cations to form a tricyclic hydrogen-bonding motif which assembles the molecules into a one-dimensional chain.

Experimental

The deep red crystals of the title compound were obtained from the reaction of hydrated $Zn(NO_3)_2$ with thiosemicarbazide in a molar ratio of 1:2 in H_2O–ethanol mixed solution at room temperature. The yield was 55%. Found: C 6.39, H 2.79, N 30.12%; analysis calculated for $C_2H_{10}N_8O_6S_2Zn$: C 6.46, H 2.71, N 30.15%. IR (KBr): 3367 (*s*), 3295 (*s*), 3288 (*s*), 3142 (*s*), 2987 (*m*), 2945 (*m*), 2635 (*w*), 2425 (*w*), 1771 (*w*), 1630 (*s*), 1447 (*m*), 1391 (*s*), 1349 (*s*), 1285 (*s*), 1215 (*m*), 1131 (*s*), 1046 (*m*), 1018 (*m*), 814 (*m*), 716 (*m*), 688 (*s*), 629 (*w*), 561 (*s*), 456 (*w*) cm^{-1}.

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*B*···O1	0.73 (3)	2.14 (3)	2.866 (3)	175 (3)
N2—H2···O2	0.74 (3)	2.22 (3)	2.955 (2)	174 (3)
N1—H1*B*···O3^{ii}	0.86 (3)	2.16 (3)	2.948 (2)	151 (3)

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

Crystal data

$[Zn(CH_5N_3S)_2](NO_3)_2$
$M_r = 371.67$
Monoclinic, $C2/c$
$a = 11.165$ (2) Å
$b = 7.605$ (2) Å
$c = 14.167$ (3) Å
$\beta = 102.02$ (3)°
$V = 1176.5$ (4) Å^3
$Z = 4$

$D_x = 2.098$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.0$–12.5°
$\mu = 2.484$ mm^{-1}
$T = 293$ (2) K
Block, dark red
0.42 × 0.40 × 0.38 mm

Data collection

Siemens *R*3*m* diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.28, T_{\max} = 0.39$
1808 measured reflections
1728 independent reflections
1497 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\max} = 30.07$°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections every 197 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.08$
1728 reflections
108 parameters
H-atom parameters are refined independently

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 0.5812P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0257 (12)

The H atoms were located in a difference electron-density map and were included in the refinement independently.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*96 (Sheldrick, 1996); software used to prepare material for publication: *SHELXTL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1501). Services for accessing these data are described at the back of the journal.

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