

## METAL-ORGANIC COMPOUNDS

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## (Diethylenetriamine)bis(isothiocyanato)-zinc(II)

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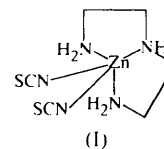
## Abstract

In the X-ray crystal structure of the title complex, [*N*-(2-aminoethyl)-1,2-ethanediamine- $\kappa^3N$ ]bis(isothiocyanato)zinc(II), [Zn(NCS)<sub>2</sub>(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)], the Zn<sup>II</sup> ion and the two isothiocyanate groups lie on a mirror plane and the diethylenetriamine ligand is disordered. The Zn<sup>II</sup> ion is coordinated to the three N atoms of the diethylenetriamine ligand and to the N atoms of two isothiocyanate ions. The primary coordination sphere about the Zn<sup>II</sup> ion can be regarded as a symmetric trigonal bipyramid. The ordered Zn—N distances range from 1.984 (7) to 2.252 (8) Å.

## Comment

Linkage isomers of metal complexes of the type *M*—NCS (isothiocyanato) and *M*—SCN (thiocyanato) have been extensively studied (Burmeister, 1990). The S atom in SCN<sup>−</sup> is soft and prefers to coordinate with soft acids (class *b* metals), whereas the N atom in SCN<sup>−</sup> is hard and coordinates with hard acids (class *a* metals) (Pearson, 1987, 1988). Iron(III) and cobalt(III) complexes have the normal *M*(hard)—NCS bonding pattern. The crystal structures of iron(III)- and cobalt(III)-isothiocyanato complexes with other ligands have been reported, for example, *trans*-[Fe(pyridine)(octaethylporphinate)(NCS)] (Scheidt *et al.*, 1982) and *trans*-[Co(ethylenediamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>(NCS)] (Grenthe & Nordin, 1979). Crystal structures with the *M*(soft)—SCN bonding pattern that have been reported include [HgPh<sub>2</sub>{Hg(SCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] (Lobana *et al.*, 1989) and [Au(PPh<sub>3</sub>)<sub>2</sub>(SCN)] (Muir *et al.*, 1982). It is interesting that 'borderline' metals have been found to coordinate the SCN<sup>−</sup> ion through either the S or N atom depending on the nature of the other ligands present (Tahirov *et al.*,

1995). In order to study the bond type of borderline zinc complexes with the thiocyanate ion, we have prepared and studied the structure of the title complex, (I).



The molecular structure and atom-labelling scheme for the five-coordinate title complex are shown in Fig. 1. The two five-membered rings are disordered with equal occupancy; atoms C3 and C31, and N4 and N41 have occupancies of 0.5. H atoms could not be located because of the disordered N and C atoms. The bond length from the central N atom of the diethylenetriamine ligand to the Zn atom is longer than those involving the terminal N atoms (Table 1). Viewed as a symmetric trigonal bipyramid, with the N1 and N3 atoms apical, the N1—Zn—N3 angle is 170.8 (3)° and the intra-equatorial angles range from 107.3 (4) to 135.7 (7)°. The two Zn—N(isothiocyanato) bonds are non-equivalent, with the apical bond length being longer than the equatorial bond length. These non-equivalent bond lengths have also been observed in the analogous complex bis(isothiocyanato)(1,5,9-triazacyclododecane)-zinc(II) (Kimura *et al.*, 1992).

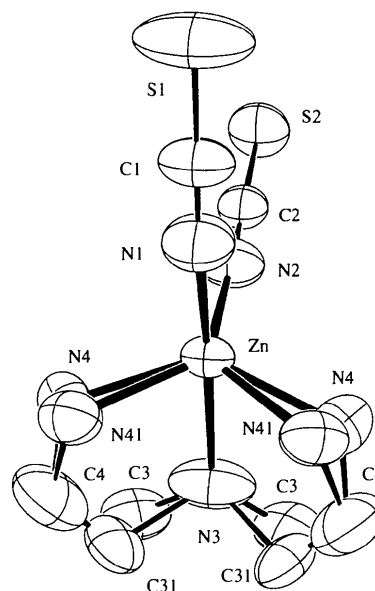


Fig. 1. A perspective view of the molecular structure of (I) with the atom-numbering scheme, excluding the H atoms attached to the N and C atoms. Displacement ellipsoids are drawn at the 50% probability level (ORTEPII; Johnson, 1976).

## Experimental

The title complex, [Zn(NCS)<sub>2</sub>(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)], was prepared by the reaction of zinc chloride (30 mmol), diethylenetriamine (30 mmol) and sodium thiocyanate (60 mmol) in ethanol (60 ml). Crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of an acetonitrile solution of the product.

### Crystal data

[Zn(NCS) <sub>2</sub> (C <sub>4</sub> H <sub>13</sub> N <sub>3</sub> )]	Mo K $\alpha$ radiation
$M_r = 284.70$	$\lambda = 0.7107 \text{ \AA}$
Orthorhombic	Cell parameters from 25 reflections
$Cmc2_1$	$\theta = 6.18\text{--}16.33^\circ$
$a = 8.6388 (8) \text{ \AA}$	$\mu = 2.285 \text{ mm}^{-1}$
$b = 12.9233 (11) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 11.1300 (13) \text{ \AA}$	Parallelepiped
$V = 1242.6 (2) \text{ \AA}^3$	$0.45 \times 0.31 \times 0.25 \text{ mm}$
$Z = 4$	Colourless
$D_x = 1.522 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Enraf–Nonius CAD-4 diffractometer	806 reflections with $I > 2\sigma(I)$
$\theta/2\theta$ scans	$R_{int} = 0.026$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$\theta_{max} = 29.90^\circ$
$T_{min} = 0.467$ , $T_{max} = 0.565$	$h = 0 \rightarrow 12$
2006 measured reflections	$k = 0 \rightarrow 18$
1004 independent reflections	$l = 0 \rightarrow 15$
	3 standard reflections frequency: 60 min intensity decay: 1.0%

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{max} = -0.002$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{max} = 0.428 \text{ e \AA}^{-3}$
$wR(F^2) = 0.098$	$\Delta\rho_{min} = -0.650 \text{ e \AA}^{-3}$
$S = 1.071$	Extinction correction: none
1004 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
94 parameters	Absolute structure: Flack (1983)
H atoms not located	Flack parameter = 0.00 (3)
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.0611P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Zn—N1	2.103 (7)	Zn—N3	2.252 (8)
Zn—N2	1.984 (7)	S1—C1	1.629 (7)
Zn—N4	2.054 (10)	S2—C2	1.616 (7)
Zn—N41	2.084 (10)		
N2—Zn—N1	94.7 (3)	C3—N3—Zn	116.3 (6)
N2—Zn—N3	94.5 (3)	C3 <sup>1</sup> —N3—Zn	116.3 (6)
N1—Zn—N3	170.8 (3)	N1—C1—S1	179.8 (8)
C1—N1—Zn	165.8 (8)	N2—C2—S2	178.2 (7)
C2—N2—Zn	174.7 (7)		

Symmetry code: (i)  $-x, y, z$ .

The 2006 diffraction data were initially collected in a monoclinic  $P$  lattice. About half of the data were absent after data reduction and the cell dimensions were then transformed into the orthorhombic crystal system. Systematic absences of  $h +$

$k = 2n + 1$  indicated a C-centered lattice. Three possible space groups ( $Cmc2_1$ ,  $Cmcm$  and  $C2cm$ ) pertained to the same systematic absences of  $hkl$ :  $h + k = 2n + 1$ ;  $h0l$ :  $l = 2n + 1$ . The crystal density and the molecular symmetry excluded the centrosymmetric space group  $Cmcm$ . Unreasonable interatomic distances due to mirror or twofold symmetry in space group  $C2cm$  excluded this. Space group  $Cmc2_1$  was thus used for the subsequent analysis.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRC-VAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1401). Services for accessing these data are described at the back of the journal.

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