Crystal Structure of Bis(N^1-isopropyl-2-methyl-1,2-propanediamine)isothiocyanatozinc(II) Thiocyanate

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The title compound crystallizes in the monoclinic space group $P2_1/C$, with $a = 13.339(2)$, $b = 12.066(1)$, $c = 14.572(3)$ Å, $\beta = 96.52(1)°$ and $Z = 4$. Using 3984 observed reflections the structure was refined to $R = 0.059$. The two non-planar N^1-isopropyl-2-methyl-1,2-propanediamine ligands display bond lengths and angles close to expected values. The Zn atom has a distorted trigonal-bipyramidal environment consisting of two primary N atoms [Zn–N(prim) = 2.094(3), 2.103(3) Å], and the N atom [Zn–N = 1.984(3) Å] of one isothiocyanate group in the basal plane and two secondary nitrogen atoms [Zn–N(sec) = 2.273(2), 2.229(3) Å] in the axial positions. The five-membered chelate rings are in the form of open envelopes and the conformation of the diamine chelate rings are δδ(λλ). One NCS⁻ anion does not enter the inner coordination sphere of the Zn(II) atom. A three-dimensional network of N–H···N and N–H···S hydrogen bonds stabilizes the crystal packing.

Crystal structures of several metal complexes, [NiL₂]Br₂·3H₂O, [NiL₂Br]Br, [NiL₂(NCS)₂] and [CdL₂(NCS)₂] (L = N^1-isopropyl-2-methyl-1,2-propanediamine) have recently been investigated in this laboratory.[1,2] The coordination geometry of the central atom with different counter anions varies, i.e. square-planar, trigonal-bipyramidal and octahedral with appreciable distortions. In the [CdL₂(NCS)₂] complex,[2] the two isothiocyanate groups are coordinated to the metal atom forming a distorted octahedral arrangement. To study the effect of substituents at N and C atoms in the diamine on the structures of the resulting Zn(II) complex, the ligand N^1-isopropyl-2-methyl-1,2-propanediamine (L), has been chosen. The ligand, L, is an asymmetrically C- and N-substituted 1,2-ethanediamine derivative forming a five-membered puckered chelate ring owing to its bidentate nature. The conformation of the diamine chelate rings are either δδ(λλ) or δλ.[3,4] As the isopropyl group in the diamine is very bulky, the zinc salt yields a bis diamine complex[5] in which the ligand-to-metal ratio is 2:1. In bis complexes the counter-anion is generally coordinated at the apical position, but in some special cases it is uncoordinated.

The present X-ray crystal structure study was undertaken to establish the coordination geometry of the title complex, to determine whether structural features of the title compound are similar to that in the cadmium com-

plex[2] and to study the nature of the Zn–N bonding and the bonding within the ligand molecule.

Experimental

The title compound was synthesized by adding the diamine ligand (2 mmol) dropwise with constant stirring to an ethanolic solution (10 cm³) of Zn(NCS)₂ (1 mmol). Transparent colourless crystals suitable for X-ray analysis were obtained on slow evaporation from methanol. Rotation and Weissenberg photographs showed the crystal to be monoclinic and gave approximate lattice constants. Accurate cell parameters were determined by least squares from the 2θ values of 25 randomly chosen reflections measured on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu K$_x$ radiation. Intensity data were collected at 293 K employing an ω-2θ scan. During data collection crystal stability was monitored by periodical measurement of three standard reflections (4 0 0; 4 − 1 1; 2 − 4 1); there was no evidence of crystal deterioration. Intensities were corrected for Lorentz, polarisation and absorption effects. Approximate coordinates of the Zn atom were obtained from un-sharpened three-dimensional Patterson map. Considering the contribution from Zn atoms only, Fourier synthesis revealed the positions of 18 atoms. The contribution of 19 atoms were then included in the structure factor calculation for the next weighted Fourier synthesis, and the E

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map showed the positions of all the remaining non-hydrogen atoms. The structure was finally refined by a full-matrix least-squares method with anisotropic thermal parameters for Zn, S, N and C atoms. All H atoms (except H2A and H4A) were included in calculated positions 'riding' on their bonded non-H atoms (C–H = 0.95 Å) and were kept fixed during refinement. Each atom is given the isotropic temperature factor of the associated non-H atom. A difference map at this stage revealed two peaks corresponding to H2A and H4A and were then included and refined with a fixed temperature factor. After the final cycle, the maximum shift was 0.5 and the residual electron density was 0.98 e Å^{-3} in the vicinity of the Zn atom. Finally, an isotropic extinction parameter, x, was varied where $F^1 = F[1 - (xF^2/\sin \theta)]$ for F_c; x was refined to a value of 0.011(1).The weighting scheme $w = 1/[\sigma^2(F_o) + 0.0059|F_o|^2]$ was used as give consistency of $w = \Delta F^2$ with $\sin \theta$ and $[F_o/F_{max}]^{1/2}$. Additional details concerning data collection and structure refinement are given find Table 1. The thermal motion of the diamine ligands is strongly anisotropic with U_{22} larger than the other components for most of the atoms. X-Ray scattering factors and anomalous dispersion corrections for Zn atom were taken from Ref. 6. All computations were carried out using Microvax II systems of D. I. C., Bose Institute, Calcutta. Program systems used were XRAYARC[7] for Patterson synthesis; NORMAL,

EXFFT and SEARCH sequences of MULTAN 78[8] for weighted Fourier synthesis, SHELX 76[9] for refinement and PARST 86[10] for the geometrical parameters of the molecule.

The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table 2. The relevant bond lengths and bond angles, selected torsion angles and hydrogen bonding geometry are presented in Table 3. Anisotropic displacement parameters, bond distances and bond angles involving H atoms and lists of observed and calculated structure amplitudes can be obtained from one of the authors (S. K. S.).

Results and discussion

Description of the structure. The crystal structure is formed by the $[ZnL_2(NCS)]^+$ cation and uncoordinated NCS^- anion. These moieties, which associate via interionic hydrogen bonds, give a pentacoordinated complex having the composition $[ZnL_2(NCS)](NCS)$. Figure 1 shows the ORTEP 11[11] diagram of the asymmetric unit along with the atom numbering scheme. The coordination polyhedron of the Zn(II) atom is best described as distorted trigonal-bipyramidal with one N atom of the isothiocyanate group and the two primary N atoms (N(1) and N(3)] of the bidentate ligands defining the basal plane

Table 1. Summary of crystal data intensity collection and structure refinement of $(C_8H_{18}N_3S)_2Zn$.

Chemical formula	$[Zn(C_7N_2H_{18})_2(NCS)]$ (NCS)
Formula weight	442.0
Crystal size/mm	0.10×0.06×0.05
Colour, habit	Colourless transparent, needle-shaped
Crystal system	Monoclinic
Space group	$P2_1/C$
Unit cell dimensions:	
$a/\text{Å}$	13.339(2)
$b/\text{Å}$	12.066(1)
$c/\text{Å}$	14.572(3)
$\beta/°$	96.52(1)
Volume/Å^3	2330.2(6)
Z	4
$F(000)/e$	944
$d_{calc}/\text{g cm}^{-3}$	1.26
$d_{meas}/\text{g cm}^{-3}$	1.28
Diffractometer type	CAD-4F Enraf-Nonius
Radiation; wavelength/Å	Cu K_α; 1.5418
Temperature/K	293
Monochromator	Graphite crystal
Absorption coefficient/mm^{-1}	3.21
Collection method	$\omega/2\theta$ scan mode
No. of reflections measured	4843
No. of independent reflections	4287
No. of observed reflections	3984 $[I > 3\sigma(I)]$
R_{int}	0.021
Absorption correction (T_{min}, T_{max})	0.7060, 0.9994
Index ranges	$-16 \leqslant h \leqslant 16, 0 \leqslant k \leqslant 14, 0 \leqslant l \leqslant 17$
2θ range/°	1–70
R	0.059
R_w	0.080
No. of variables	226
$S = \{\sum w\Delta F^2/(n-m)\}^{1/2}$	1.071

Table 2. Atomic positional parameters and equivalent isotropic or isotropic temperature factors for bis(N^1-isopropyl-2-methyl-1,2-propanediamine)isothiocyanatozinc(II) thiocyanate with their standard deviations in parentheses.

Atom	x	y	z	U_{eq} or $U/Å^2$
Zn	0.24760(3)	−0.00938(3)	0.18986(3)	0.038(0)
S	0.07222(11)	0.33069(10)	0.14282(9)	0.078(1)
C	0.1324(3)	0.2163(3)	0.1672(2)	0.049(1)
N	0.1750(3)	0.1344(3)	0.1821(2)	0.062(1)
N(1)	0.1608(2)	−0.1466(2)	0.2195(2)	0.041(1)
C(1)	0.1395(2)	−0.2208(3)	0.1375(2)	0.041(1)
C(2)	0.1166(2)	−0.1461(3)	0.0528(2)	0.044(1)
N(2)	0.1971(2)	−0.0662(2)	0.0432(2)	0.038(1)
N(3)	0.3989(2)	0.0029(2)	0.1632(2)	0.044(1)
C(4)	0.4696(3)	−0.0154(3)	0.2493(2)	0.043(1)
C(5)	0.4230(2)	0.0418(3)	0.3282(2)	0.049(1)
N(4)	0.3194(2)	0.0025(2)	0.3353(2)	0.038(1)
C(11)	0.0485(3)	−0.2941(4)	0.1458(3)	0.061(1)
C(12)	0.2329(3)	−0.2916(3)	0.1306(3)	0.055(1)
C(3)	0.1652(3)	0.0235(3)	−0.0258(2)	0.046(1)
C(31)	0.2552(3)	0.0993(4)	−0.0347(3)	0.068(1)
C(32)	0.1263(4)	−0.0223(4)	−0.1208(3)	0.069(2)
C(41)	0.4789(3)	−0.1411(3)	0.2633(3)	0.052(1)
C(42)	0.5718(3)	0.0360(4)	0.2407(3)	0.065(1)
C(6)	0.2672(3)	0.0674(3)	0.4022(2)	0.050(1)
C(61)	0.3263(3)	0.0690(4)	0.4994(2)	0.066(1)
C(62)	0.1618(3)	0.0215(4)	0.4052(3)	0.062(1)
S'	0.52788(9)	0.18216(11)	0.00351(7)	0.067(0)
C'	0.6336(3)	0.2243(3)	0.0642(2)	0.047(1)
N'	0.7061(2)	0.2536(3)	0.1067(2)	0.058(1)

^{a} $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

and the secondary N atoms [N(2) and N(4)] in axial positions. The Zn(II) atom deviates 0.017(1) Å from the basal plane. For the trigonal-bipyramidal system, the out-of-plane Zn–N(2) [2.273(2) Å] and Zn–N(4) [2.229(3) Å] distances are slightly different (average 2.251 Å) with the bonds being almost linear [N(2)–Zn–N(4) = 164.4(1)°]. The two in-plane Zn–N(1) [2.094(3) Å] and Zn–N(3) [2.103(3) Å] are almost similar and are on average shorter than the out-of-plane Zn–N distances by 0.153 Å, while the third in-plane Zn–N distance of 1.984(3) Å is significantly shorter (ca. 0.11 Å) than the other two. The out-of-plane angles are within 81–99°. These values agree well within experimental error with those reported for bis(N^1-isopropyl-2-methyl-1,2-propanediamine) [(S)-lactato]Zn (S)-lactate monohydrate,[12] Zn(acetylacetone)·2H$_2$O[13] and Zn(L-serinato)$_2$.[14] The bond angles in the equatorial plane are considerably distorted from the ideal trigonal angle of 120°, with two small angles of 113.6(1)° [α_1 = N–Zn–N(3)] and 115.2(1)° [α_2 = N–Zn–N(1)] and one large angle of 131.2(1)° [α_3 = N(1)–Zn–N(3)]. Thus, relative to a regular trigonal-bipyramidal ZnN$_5$ unit, the Zn–N bond shows a significant shortening and the angle α_3, which is opposite to the Zn–N bond, shows a widening by 11.2° relative to 120°. The sum of the bond angles in the equatorial plane amounts preciously to 360°, indicating co-planarity of the Zn(II) [maximum deviation 0.017(1) Å] atom with three coordinated N atoms. Thus the coordination polyhedron around Zn(II) can be described most

appropriately as trigonal bipyramidal, but the bond angles indicate appreciable distortion towards a square-pyramidal geometry.

The difference between the Zn–N(prim) bonds and the Zn–N(sec) bonds are significantly larger (ca. 0.15 Å) than those observed in [CdL$_2$(NCS)$_2$]^2 and [NiL$_2$(NCS)$_2$]^1 complexes. The differences in the bonding to Zn of the two ligands and the isothiocyanato group are probably related to the internal geometry of the complex which was different in the [NiL$_2$(NCS)$_2$]^1 and [CdL$_2$(NCS)$_2$]^2 complexes.

The two non-planar diamine ligands are both chemically and crystallographically identical and display bond lengths and bond angles close to expected values with C–N and C–C single bond lengths varying from 1.476(4) to 1.505(4) Å and 1.516(5) to 1.540(5) Å and are in good agreement with those obtained in other metal complexes of this diamine.[1,2,12–17] The ligand bite angle (average 81.3°) of the five-membered chelate rings introduces a considerable distortion, and the ring is significantly puckered as indicated by the torsion angles presented in Table 3. Both the chelate rings are in the form of open envelopes with C(1) and C(5) atoms on the flaps, 0.521(3) and 0.502(4) Å away from the least-square plane through the remaining endocyclic atoms. The dihedral angle between the planes through Zn, N(1), N(2), C(2) and Zn, N(3), N(4), C(4) is 129.6(1)°. The uncoordinated diamine ligand has a synclinal conformation with a non-bonded N⋯N distance of 3.139(8) Å and a N–C–C–N

Table 3. Bond distances (in Å), bond angles (in °), some selected torsion angles (in °) and hydrogen-bonding geometry in [Zn(C₇N₂H₁₈)₂(NCS)](NCS).

Zn–N	1.984(3)	Zn–N(1)	2.094(3)
Zn–N(2)	2.273(2)	Zn–N(3)	2.103(3)
Zn–N(4)	2.229(3)	S–C	1.616(4)
C–N	1.148(5)	N(1)–C(1)	1.494(4)
C(1)–C(2)	1.530(4)	C(1)–C(11)	1.518(5)
C(1)–C(12)	1.523(5)	C(2)–N(2)	1.461(4)
N(2)–C(3)	1.505(4)	N(3)–C(4)	1.498(4)
C(4)–C(5)	1.532(5)	C(4)–C(41)	1.533(5)
C(4)–C(42)	1.516(5)	C(5)–N(4)	1.476(4)
N(4)–C(6)	1.484(4)	C(3)–C(31)	1.527(6)
C(3)–C(32)	1.526(5)	C(6)–C(61)	1.540(5)
C(6)–C(62)	1.517(6)	S′–C′	1.658(3)
C′–N′	1.143(4)		

N–Zn–N(1)	115.2(1)	N–Zn–N(2)	96.9(1)
N–Zn–N(3)	113.6(1)	N–Zn–N(4)	98.8(1)
N(1)–Zn–N(2)	81.0(1)	N(1)–Zn–N(3)	131.2(1)
N(1)–Zn–N(4)	92.5(1)	N(2)–Zn–N(3)	92.1(1)
N(2)–Zn–N(4)	164.4(1)	N(3)–Zn–N(4)	81.6(1)
S–C–N	178.2(4)	Zn–N–C	172.4(3)
Zn–N(1)–C(1)	111.6(2)	N(1)–C(1)–C(12)	107.8(3)
N(1)–C(1)–C(11)	111.5(3)	N(1)–C(1)–C(2)	107.1(2)
C(11)–C(1)–C(12)	110.3(3)	C(2)–C(1)–C(12)	111.5(3)
C(2)–C(1)–C(11)	108.6(3)	C(1)–C(2)–N(2)	112.6(3)
Zn–N(2)–C(2)	104.6(2)	C(2)–N(2)–C(3)	112.6(2)
Zn–N(2)–C(3)	116.2(2)	Zn–N(3)–C(4)	111.2(2)
N(3)–C(4)–C(42)	110.9(3)	N(3)–C(4)–C(41)	106.9(3)
N(3)–C(4)–C(5)	106.9(3)	C(41)–C(4)–C(42)	110.8(3)
C(5)–C(4)–C(42)	108.9(3)	C(5)–C(4)–C(41)	112.3(3)
C(4)–C(5)–N(4)	111.8(3)	Zn–N(4)–C(5)	105.0(2)
C(5)–N(4)–C(6)	112.9(3)	Zn–N(4)–C(6)	118.4(2)
N(2)–C(3)–C(32)	112.8(3)	N(2)–C(3)–C(31)	108.8(3)
C(31)–C(3)–C(32)	109.3(3)	N(4)–C(6)–C(62)	109.3(3)
N(4)–C(6)–C(61)	112.4(3)	C(61)–C(6)–C(62)	111.0(3)
S′–C′–N′	179.4(3)		

Selected torsion angles

N(1)–Zn–N(2)–C(2)	12.9(2)	N(3)–Zn–N(4)–C(5)	14.9(2)
Zn–N(1)–C(1)–C(2)	−40.5(3)	Zn–N(3)–C(4)–C(5)	−39.2(3)
C(1)–C(2)–N(2)–Zn	−39.7(3)	C(4)–C(5)–N(4)–Zn	−41.6(3)
N(4)–Zn–N(3)–C(4)	13.9(2)	N(2)–Zn–N(1)–C(1)	15.7(2)
N(3)–C(4)–C(5)–N(4)	55.2(3)	N(1)–C(1)–C(2)–N(2)	55.0(3)

Hydrogen bonding geometry

D	H	A	D–H	H···A	D···A	D–H···A
N(2)	H2A	N(3)⁽ⁱ⁾	0.78(3)	2.53(3)	3.152(4)	138(3)
N(4)	H4A	N(1)⁽ⁱ⁾	0.84(3)	2.51(3)	3.123(4)	130(2)
N(4)	H4A	N′ ⁽ⁱⁱ⁾	0.84(3)	2.40(3)	3.148(4)	148(3)
N(1)	H1B	N′ ⁽ⁱⁱ⁾	0.95(0)	2.23(0)	3.163(3)	167.2(2)
N(3)	H3B	S′ ⁽ⁱⁱⁱ⁾	0.95(0)	2.58(0)	3.519(4)	171.0(2)

Symmetry code: (i) x, y, z; (ii) $-x+1$, $y-1/2$, $-z+1/2$; (iii) $-x+1$, $-y$, $-z$.

torsion angle of 73.7(5)°, while for the coordinated amine molecule, these values differ significantly (average 2.836 Å, 55.1°).[18] The two diamine chelate rings are in the same conformation (λ) as in the corresponding [NiL₂Br]Br[1], Cu(II)[19] and Zn(II)[12] complexes. The conformations of the diamine chelate rings are δδ(λλ).[3,4]

The normal geometry of the isothiocyanate group and the metal–N–C angle 172.4(3)° is similar to that found in [NiL₂(NCS)₂].[1] Bond distances and the N–C–S angle in the uncoordinated thiocyanate anion are also within the expected range. The central ion is coordinated by only one NCS⁻ ion, while the other acts simply as a counter-anion probably due to the steric hindrance of the bulky isopropyl group resulting in a pentacoordinate geometry.
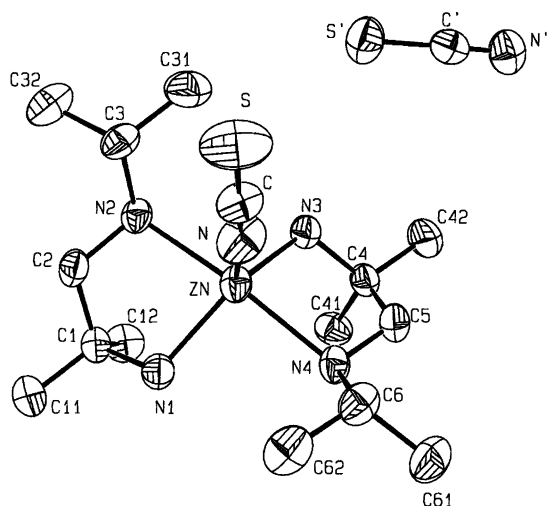
Fig. 1. ORTEP drawing of the title compound showing the atom-numbering scheme. For non-H atoms, 50% probability ellipsoids are shown; H atoms are omitted for clarity.
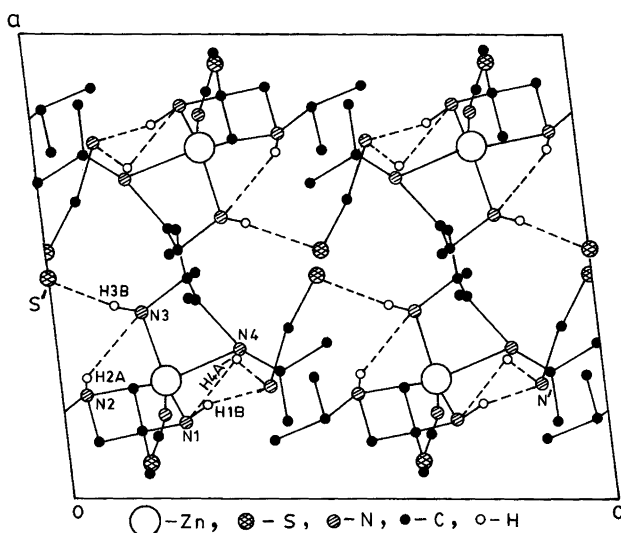
Crystal packing. Figure 2 shows the content of the unit cell projected along b. In the molecule, secondary nitrogens of one diamine ligand are hydrogen bonded to the primary nitrogens of the other ligand. The close contacts {N(2)···N(3) [N(2)–H(2A)···N(3)] of 3.152(4) Å and N(4)···N(1) [N(4)–H(4A)···N(1)] of 3.123(4) Å} may indicate very weak intramolecular hydrogen bonds. The diamine molecule is linked to the other NCS⁻ anion by N(4)–H(4A)···N ($-x+1$, $y-1/2$, $-z+1/2$), N(1)–H(1B)···N ($-x+1$, $y-1/2$, $-z+1/2$) and N(3)–H(3B)···S ($-x+1$, $-y$, $-z$) interionic hydrogen bonds (Table 3) and stabilize the crystal packing. A stereographic view of the unit-cell contents is presented in Fig. 3. Layers of molecules are displaced with respect to one another to relieve short intermolecular contacts. There are no unusually short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to an appreciable extent.

Conclusions

The diamine, N^1-isopropyl-2-methyl-1,2-propanediamine forms five coordinate, trigonal-bipyramidal complex with Zn^{II} isothiocyanate in the solid state. Conversely, corresponding nickel and cadmium salts give six-coordinate, octahedral complexes. The smaller size of the coordinating atom (N) of the isothiocyanate ion (NCS⁻) typically matches with the size, electrostatic forces and covalent bonding forces of the Zn^{2+} ion, which are just sufficient to overcome the steric hindrance caused by the bulky diamines in accommodating only one NCS⁻ ion in the axial position. Thus, the five coordination around Zn(II) in the presence of this diamine maintains a delicate balance between four- and six-coordination.

Fig. 2. The packing of the molecules viewed down the b-axis. H atoms which are involved in hydrogen bonding (dotted lines) are shown and others are omitted for clarity.

Fig. 3. A stereographic packing diagram showing the contents of one unit cell of the title compound.

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