C20—W—C21	87.4 (3)	C18—Mo—W	89.7 (2)
C20—W—C23	84.1 (3)	C3—Mo—W	77.7 (2)
C21—W—C23	171.0 (3)	C17—Mo—W	153.4 (2)
C20—W—C22	88.4 (3)	C1—O1—C4	118.9 (5)
C21—W—C22	90.7 (3)	O1—C1—C2	119.8 (5)
C23—W—C22	86.3 (3)	O1—C1—Mo	125.8 (4)
C20—W—C19	85.1 (3)	C2—C1—Mo	71.6 (3)
C21—W—C19	91.2 (3)	O1—C1—W	110.9 (4)
C23—W—C19	90.9 (3)	C2—C1—W	127.7 (4)
C22—W—C19	173.2 (3)	Mo—C1—W	89.6 (2)
C20—W—C1	161.0 (2)	C3—C2—C1	116.9 (6)
C21—W—C1	76.6 (2)	C3—C2—Mo	73.2 (4)
C23—W—C1	112.3 (2)	C1—C2—Mo	71.9 (3)
C22—W—C1	101.8 (2)	C2—C3—Mo	70.7 (4)
C19—W—C1	85.1 (3)	O1—C4—C5	108.0 (6)
C20—W—Mo	152.0 (2)	C12—C11—C15	107.3 (6)
C21—W—Mo	120.6 (2)	C12—C11—C16	125.9 (7)
C23—W—Mo	68.1 (2)	C15—C11—C16	122.4 (6)
C22—W—Mo	92.7 (2)	C13—C12—C11	108.9 (7)
C19—W—Mo	92.0 (2)	C14—C13—C12	107.7 (7)
C1—W—Mo	44.69 (14)	C13—C14—C15	107.9 (7)
C18—Mo—C2	111.7 (3)	C11—C15—C14	108.2 (6)
C18—Mo—C1	123.6 (3)	C17—C16—C11	97.4 (5)
C18—Mo—C3	76.0 (3)	C16—C17—Mo	101.9 (5)
C18—Mo—C17	84.7 (3)	O18—C18—Mo	178.0 (7)
C2—Mo—C17	84.6 (3)	O19—C19—W	175.4 (6)
C1—Mo—C17	118.8 (2)	O20—C20—W	177.7 (6)
C3—Mo—C17	75.7 (3)	O21—C21—W	179.3 (6)
C12—Mo—C17	81.7 (3)	O22—C22—W	173.4 (6)
C11—Mo—C17	58.0 (2)	O23—C23—W	169.4 (6)

Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2).

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *XCAD4* (Harms & Wocadlo, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Bis(N¹-isopropyl-2-methylpropane-1,2-diamine)diisothiocyanatocadmium(II)

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Abstract

In the complex [Cd(NCS)₂(C₇H₁₈N₂)₂], the Cd atom lies on an inversion centre and has a distorted octahedral environment consisting of four amine N atoms from two bidentate N^1-isopropyl-2-methylpropane-1,2-diamine (N–N) ligands [Cd—N(primary) = 2.362 (3) Å, Cd—N(secondary) = 2.400 (3) Å] and two N atoms from two isothiocyanato groups [Cd—N = 2.378 (5) Å]. The conformation of the diamine chelate rings is $\delta\lambda$. Molecules are linked by N—H···S hydrogen bonds (N···S 3.665 Å).

Comment

The coordination geometry around a complexed metal ion is greatly influenced by the variation of substituents on the ethane-1,2-diamine as well as counteranions. The crystal structure of the title compound, (I), as found by X-ray analysis, clearly depicts the pattern of coordination and bonding in the molecule.

(I)

The Cd atom is octahedrally coordinated by the four amine N atoms of two bidentate *N–N* ligands, defining the equatorial plane, and the two N atoms of the isothiocyanato groups, coordinating in *trans* positions (Fig. 1). The orientation of the isothiocyanato group with respect to the metal ion [Cd—N—C = 144.3 (4)°] differs markedly from that reported for the analogous Ni complex [Ni—N—C = 170.2 (3)°] (Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Chaudhuri, 1994)]. The Cd—N(isothiocyanato) bond deviates from its expected perpendicular orientation to the equatorial plane of the octahedral molecule [N—Cd—N(1) = 97.1 (1) and N—Cd—N(2) = 85.1 (1)°]. The Cd—N(primary) lengths [2.362 (3) Å] and Cd—N(secondary) lengths [2.400 (3) Å] reveal a tendency for Cd—N(primary) to be shorter (0.04 Å) than Cd—N(secondary); similar behaviour has been observed in the analogous Ni complex (Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Chaudhuri, 1994). The relative shortness of the Cd—N(primary) bond compared with the Cd—N(secondary) bond may be a result of the bulky isopropyl substituent at N(secondary) or due to constraints involved in chelate-ring formation.
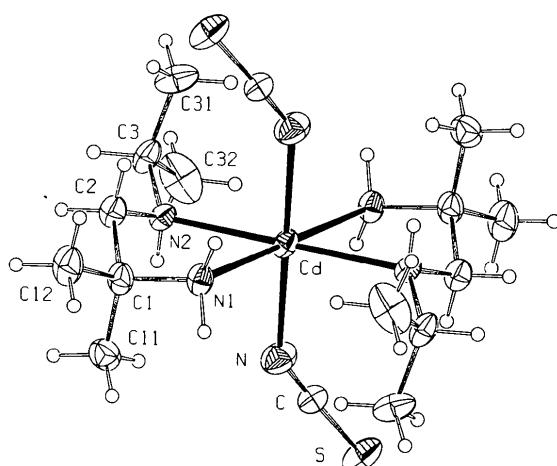
Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound showing the atom-numbering scheme. Ellipsoids are drawn at the 30% probability level.

Similar trends are also observed in other metal complexes of this diamine (Kansikas, 1987; Kansikas & Pajunen, 1980; Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Chaudhuri, 1994; Ahlgren, Turpeinen & Hamalainen, 1982; Kansikas & Hamalainen, 1978). The coordinated *N–N* ligand displays bond lengths and angles close to expected values, in good agreement with those obtained for other metal complexes with *N–N* ligands. The bite angle [N(1)—Cd—N(2) = 75.2 (1)°] of the five-membered chelate ring introduces a considerable in-plane distortion in the coordination octahedron. The chelate ring is significantly puckered as indicated by the torsion angles given in Table 2 and is in the form of an open envelope with C(2) on the flap, −0.57 (5) Å away from the least-squares plane through the remaining endocyclic atoms. Due to the presence of a centre of inversion in the molecule, the diamine chelate-ring conformation is $\delta\lambda$. The non-bonded N(1)$\cdots$N(2) distance of 2.906 (5) Å and torsion angle N(1)—C(1)—C(2)—N(2) of 59.8 (5)° are significantly different for the uncoordinated *N–N* ligand where a synclinal conformation (Kansikas, 1985) is observed. A similar conformation was observed in [Ni(*N–N*)₂(NCS)₂] (Pariya, Ghosh, Ghosh, Mukherjee, Mukherjee & Chaudhuri, 1994).

Experimental

The title compound was conveniently synthesized by slow addition of the diamine ligand (2 mmol) to an ethanolic solution (10 ml) of $Cd(SCN)_2$ (1 mmol). The colourless compound separated out slowly on keeping the above mixture in a P_4O_{10} desiccator for several days. Fine colourless single crystals were obtained by slow evaporation of the crude compound in methanol. It is very interesting to note that if excess diamine is added to $Cd(SCN)_2$ in aqueous medium at 278 K, the polymeric form of the title compound is separated out, as is evident from its IR spectrum (Pariya, Ghosh, Ganguli & Chaudhuri, 1994). The above polymeric species on crystallization from methanol/ethanol also yields the title compound which indicates that the monomeric form of the title compound is the thermodynamically stable isomer at room temperature (298 K). The crystal density D_m was measured by flotation in xylene–chloroform.

Crystal data

[Cd(NCS)₂(C₇H₁₈N₂)₂]	Cu *K*α radiation
$M_r = 489.02$	$\lambda = 1.5418$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 8.027 (1)$ Å	$\theta = 28.2–41.1°$
$b = 12.368 (1)$ Å	$\mu = 9.26$ mm⁻¹
$c = 12.017 (1)$ Å	$T = 293$ K
$\beta = 102.55 (1)°$	Needle, cut as block
$V = 1164.5 (2)$ Å³	$0.10 \times 0.08 \times 0.06$ mm
$Z = 2$	Colourless
$D_x = 1.395$ Mg m⁻³	
$D_m = 1.41$ Mg m⁻³	

Data collection

Enraf–Nonius CAD-4F diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan (Kopfmann & Huber, 1968)
  $T_{min} = 0.744$, $T_{max} = 0.998$
2488 measured reflections
2082 independent reflections

1856 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.021$
$\theta_{max} = 69.74°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 14$
3 standard reflections
  frequency: 60 min
  intensity decay: 3.4%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.059$
$S = 1.086$
1855 reflections
116 parameters
H atoms: x, y, z, U of only amine H atoms refined
$w = 3.1793/[\sigma^2(F_o) + 0.003451F_o^2]$
$(\Delta/\sigma)_{max} = 0.145$

$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -2.89$ e Å^{-3}
Extinction correction: SHELX76 (Sheldrick, 1976)
Extinction coefficient: 0.019 (2)
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cd	0	0	0	0.0394 (2)
S	0.2049 (2)	0.1058 (1)	−0.3382 (1)	0.0721 (6)
C	0.1965 (5)	0.0812 (3)	−0.2075 (4)	0.045 (1)
N	0.1868 (6)	0.0612 (4)	−0.1156 (3)	0.065 (2)
N(1)	0.1183 (5)	0.1033 (3)	0.1634 (3)	0.043 (1)
C(1)	0.2851 (6)	0.0599 (4)	0.2255 (4)	0.047 (2)
C(2)	0.2747 (7)	−0.0644 (4)	0.2161 (4)	0.046 (2)
N(2)	0.2406 (4)	−0.1033 (2)	0.0981 (3)	0.038 (1)
C(11)	0.4226 (6)	0.1055 (4)	0.1697 (4)	0.057 (2)
C(12)	0.3159 (7)	0.0905 (4)	0.3504 (4)	0.066 (2)
C(3)	0.2533 (6)	−0.2229 (3)	0.0926 (4)	0.051 (1)
C(31)	0.0999 (8)	−0.2768 (4)	0.1223 (4)	0.065 (2)
C(32)	0.2732 (7)	−0.2573 (4)	−0.0246 (4)	0.064 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cd—N	2.378 (5)		N(2)—C(3)	1.486 (5)
Cd—N(2)	2.400 (3)		C(1)—C(2)	1.542 (7)
S—C	1.615 (5)		C(1)—C(12)	1.516 (7)
N(2)—C(2)	1.466 (6)		C(3)—C(32)	1.512 (7)
Cd—N(1)	2.362 (3)		C(1)—C(11)	1.519 (8)
N—C	1.150 (6)		C(3)—C(31)	1.509 (8)
N(1)—C(1)	1.485 (6)			
N—Cd—N(1)	97.1 (1)		C(2)—C(1)—C(12)	108.4 (4)
N(1)—Cd—N(2)	75.2 (1)		Cd—N(2)—C(3)	124.3 (2)
Cd—N—C	144.3 (4)		N(2)—C(3)—C(31)	111.2 (3)
Cd—N(2)—C(2)	105.2 (3)		C(31)—C(3)—C(32)	110.6 (4)
C(1)—C(2)—N(2)	113.2 (4)		N(1)—C(1)—C(11)	107.8 (4)
N—Cd—N(2)	85.1 (1)		C(2)—C(1)—C(11)	111.8 (4)
S—C—N	177.8 (4)		C(11)—C(1)—C(12)	111.5 (4)
Cd—N(1)—C(1)	112.2 (3)		C(2)—N(2)—C(3)	111.7 (3)
N(1)—C(1)—C(2)	107.2 (4)		N(2)—C(3)—C(32)	110.1 (3)
N(1)—C(1)—C(12)	110.0 (4)			
N(1)—Cd—N(2)—C(2)	20.9 (3)		C(2)—N(2)—C(3)—C(31)	74.8 (5)
Cd—N(1)—C(1)—C(2)	−35.8 (4)		C(2)—N(2)—C(3)—C(32)	−162.2 (4)
C(1)—C(2)—N(2)—Cd	−49.8 (4)		N—Cd—N(2)—C(3)	−110.3 (3)

N(2)—Cd—N(1)—C(1)	8.9 (3)	N—Cd—N(2)—C(2)	119.5 (3)
N(1)—C(1)—C(2)—N(2)	59.8 (5)	N(2)—Cd—N—C	139.2 (7)
N(1)—Cd—N(2)—C(3)	151.4 (3)	Cd—N(1)—C(1)—C(11)	84.7 (4)
N—Cd—N(1)—C(1)	−74.1 (3)	C(12)—C(1)—C(2)—N(2)	178.5 (4)
N(1)—Cd—N—C	−146.4 (6)	C(1)—C(2)—N(2)—C(3)	172.7 (4)
Cd—N(1)—C(1)—C(12)	−153.6 (3)	Cd—N(2)—C(3)—C(31)	−53.0 (4)
C(11)—C(1)—C(2)—N(2)	−58.2 (5)	Cd—N(2)—C(3)—C(32)	70.0 (4)

The thermal motion of the molecule is strongly anisotropic with U_{11} larger than the other components for all atoms except for C(11).

Program systems used: *XRAYARC* (Vickery, Bright & Mallinson, 1971) for Patterson synthesis, *NORMAL*, *EXFFT* and *SEARCH* sequences of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) for weighted Fourier syntheses and *SHELX*76 (Sheldrick, 1976) for refinement, *PARST* (Nardelli, 1983) for the geometrical parameters of the molecule, and *ORTEP*II (Johnson, 1976) for molecular graphics. All computations were carried out using MicroVAX II systems of DIC, Bose Institute, Calcutta.

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