

[*N*-(2-Hydroxyethyl)ethylenediamine- κ^3N,N',O]-*cis*-bis(isothiocyanato- κN)-copper(II)

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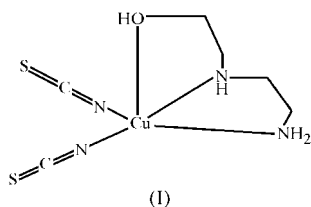
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In the novel transition metal isothiocyanate complex of *N*-(2-hydroxyethyl)ethylenediamine (hydet-en) with copper, [Cu(NCS)₂(C₄H₁₂N₂O)], the Cu atom lies in a distorted square-pyramidal environment, coordinated by four N atoms in the basal plane and an apical O atom. The hydet-en ligand is *N,N,O*-tridentate, in contrast to the disposition in previously studied complexes, while the isothiocyanate ions act as N-atom donor ligands. The monomeric units are linked to one another by hydrogen bonds.

Comment

Studies of the syntheses, structures and properties of metal complexes containing ambidentate ligands are of interest for a number of reasons, some of which involve controlling the reactivities of the coordination sites in the metal complexes. Many transition metal complexes of this type have been synthesized, and their structures and physical properties, as well as the linkage isomerization reactions of the ambidentate units, have been investigated (Kabsova *et al.*, 1995; Buckingham, 1994; Burmeister, 1990). The coordination mode of an



ambidentate ligand depends strongly on the nature of the central metal and the adjacent ligands. In this context, we have undertaken a study of the effect of the ligand *N*-(2-hydroxyethyl)ethylenediamine (hydet-en) on the coordination behavior of thiocyanate ions in copper complexes. Hydet-en, with three donor sites, has been the subject of few studies (Yılmaz *et al.*, 2002; Karadađ *et al.*, 2004), and its coordination behavior is, therefore, not well characterized. The present paper reports

the synthesis and crystal structure determination of the compound [Cu(NCS)₂(hydet-en)], (I).

An *ORTEP* (Burnett & Johnson, 1996) view of the molecular structure of (I) is shown in Fig. 1. The structure consists of monomeric units, which are connected by hydrogen bonds.

Each Cu^{II} ion has square-pyramidal geometry and is coordinated by one hydet-en ligand and two isothiocyanate ions, which are mutually *cis*. The hydet-en ligand chelates through its two amine N atoms and the O atom of the ethanol group, an arrangement that is different from those observed in the copper and cadmium saccharin complexes with the hydet-en ligand (Yılmaz *et al.*, 2002), the cyano-bridged Zn^{II}/Ni^{II} complex (Karadađ, Paşaođlu, Kaştaş & Büyükgüngör, unpublished results) and the nickel isothiocyanate complex (Karadađ *et al.*, 2004).

A topological ambiguity exists in the structure, in that it would have been possible to assign atoms N4 and O1 either as shown in Fig. 1 or with their identities reversed. The possibility of disorder also had to be considered. However, since atom N4 donates two hydrogen bonds while atom O1 donates one, the correct assignment was clear.

The square-pyramidal coordination shell consists of two five-membered chelate rings, *viz.* *A* (Cu1/O1/C3/C4/N3) and *B* (Cu1/N3/C5/C6/N4), with a dihedral angle between the mean planes through rings *A* and *B* of 70.20 (11)°. The isothiocyanate ions act as N-atom donor ligands, as reported in related studies (Xu *et al.*, 2003; Yılmaz *et al.*, 2000). The coordinated amine N atoms of the hydet-en ligands and the N atoms of two isothiocyanate ions form the basal plane (N1–N4), while the O atom of the ethanol group of the hydet-en ligand is located in the axial position. The Cu–N distances are comparable to those in a previously reported Cu–hydet-en complex (Yılmaz *et al.*, 2002). The bite angles of rings *A* and *B* are 77.70 (14) and 83.84 (15)°, respectively. The other *cis* angles around the Cu atom deviate slightly from 90°, completing the basal plane along with the bite angle of ring *A*. The isothiocyanate groups are almost linear; the S–C and C–N distances (Table 1) agree with previously reported values (Yılmaz *et al.*, 2000). Other than the chelate bite angles, the bond angles around the Cu^{II} center deviate only slightly from the ideal angles for square-pyramidal geometry.

The molecule, which constitutes the asymmetric unit, is linked to surrounding molecules *via* hydrogen bonds (N3–

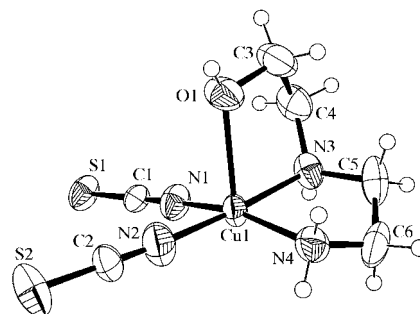


Figure 1

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

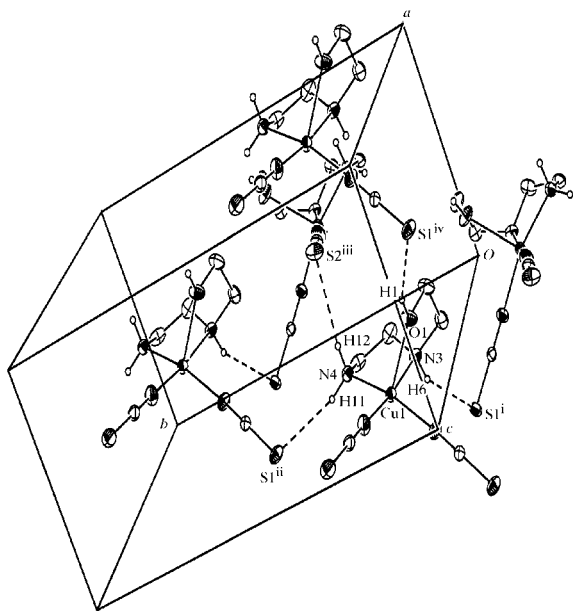


Figure 2
The packing of (I), with hydrogen bonds shown as dashed lines.

H6...S1ⁱ, N4—H11...S1ⁱⁱ, N4—H12...S2ⁱⁱⁱ and O1—H1...S1^{iv}; see Table 2 and Fig. 2).

Experimental

CuCl₂·H₂O (0.17 g, 1 mmol) in water (10 ml) was mixed with KSCN (0.197 g, 2 mmol) for 5 min. Hydret-en (0.105 g, 1 mmol) in ethanol (10 ml) was added to the mixture, which was stirred well at room temperature. On slow evaporation of the resulting violet solution, single crystals suitable for X-ray diffraction analysis were obtained within a week and were separated by filtration, washed and air dried.

Crystal data

[Cu(NCS) ₂ (C ₄ H ₁₂ N ₂ O)]	<i>D_x</i> = 1.607 Mg m ⁻³
<i>M_r</i> = 283.86	Mo Kα radiation
Monoclinic, <i>C</i> ₂	Cell parameters from 7025 reflections
<i>a</i> = 7.312 (5) Å	<i>θ</i> = 2.8–26.3°
<i>b</i> = 14.774 (5) Å	<i>μ</i> = 2.19 mm ⁻¹
<i>c</i> = 10.902 (5) Å	<i>T</i> = 293 (2) K
<i>β</i> = 95.076 (5)°	Prism, violet
<i>V</i> = 1173.1 (10) Å ³	0.40 × 0.35 × 0.28 mm
<i>Z</i> = 4	

Data collection

Stoe IPDS-II diffractometer	1795 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>ω</i> scans	<i>R</i> _{int} = 0.067
Absorption correction: integration	<i>θ</i> _{max} = 26.0°
(<i>X-RED32</i> ; Stoe & Cie, 2002)	<i>h</i> = -9 → 9
<i>T</i> _{min} = 0.433, <i>T</i> _{max} = 0.541	<i>k</i> = -18 → 18
7769 measured reflections	<i>l</i> = -13 → 12
2231 independent reflections	

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0234 <i>P</i>) ²]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.031	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.059	(Δ/σ) _{max} = 0.001
<i>S</i> = 0.90	Δ <i>ρ</i> _{max} = 0.30 e Å ⁻³
2231 reflections	Δ <i>ρ</i> _{min} = -0.27 e Å ⁻³
131 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1074 Friedel pairs
	Flack parameter: -0.014 (16)

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.952 (4)	S1—C1	1.626 (5)
Cu1—N1	1.963 (4)	S2—C2	1.608 (4)
Cu1—N4	2.000 (3)	C1—N1	1.154 (6)
Cu1—N3	2.013 (3)	C2—N2	1.155 (5)
Cu1—O1	2.331 (4)		
N2—Cu1—N1	92.02 (17)	N2—Cu1—O1	96.70 (16)
N2—Cu1—N4	93.29 (16)	N4—Cu1—O1	103.77 (15)
N1—Cu1—N4	162.99 (15)	N3—Cu1—O1	77.70 (14)
N2—Cu1—N3	172.84 (17)	N1—C1—S1	178.3 (4)
N1—Cu1—N3	92.59 (15)	N2—C2—S2	179.6 (5)
N4—Cu1—N3	83.84 (15)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H6...S1 ⁱ	0.91	2.66	3.505 (4)	155
N4—H11...S1 ⁱⁱ	0.90	2.73	3.562 (4)	155
N4—H12...S2 ⁱⁱⁱ	0.90	2.65	3.514 (4)	162
O1—H1...S1 ^{iv}	0.82 (4)	2.49 (5)	3.260 (4)	155 (4)

Symmetry codes: (i) *x*, -*y*, *z* - ½; (ii) *x* + ½, *y* + ½, *z*; (iii) *x* + ½, -*y* + ½, *z* - ½; (iv) *x* + 1, *y*, *z*.

All H atoms, except H1, were placed in calculated positions and refined as riding [C—H = 0.97 Å, N—H = 0.90–0.91 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C,N)]. Atom H1 was allowed to refine freely.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1084). Services for accessing these data are described at the back of the journal.

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