

[2,2'-(1,3,5,8,10,12-Hexaazacyclo- tetradecane-3,10-diyl)diethanol- $\kappa^4N^1,N^5,N^8,N^{12}$]bis(thiocyanato- κS)- copper(II)

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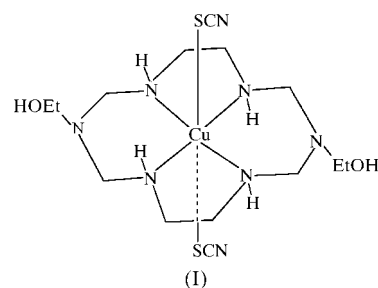
In the crystal structure of the title compound, $[\text{Cu}(\text{NCS})_2(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)]$, the Cu atom lies on an inversion centre and has an elongated octahedral coordination, with Cu—N distances of 2.004 (2) and 2.015 (2) Å, and a Cu—S distance of 2.9696 (10) Å. The 2,2'-ethanol chains are axially oriented. The molecules are linked to form a three-dimensional network via O—H...N, N—H...O and N—H...S hydrogen bonds.

Comment

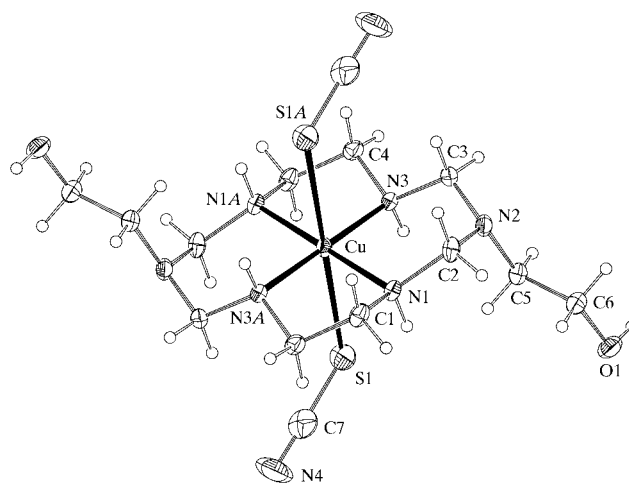
The synthesis of azamacrocyclic polydentate ligands and their interaction with metal ions have attracted a great deal of attention (Hancock & Martell, 1989; Bernhardt & Lawrance, 1990). Research on such systems may provide a basis for better knowledge of the biochemical function of these compounds. For instance, studies of the Ni^{III} complexes of pentaazacyclic ligands have shown that appropriately designed complexes may cause DNA scission under physiological conditions using only O_2 at ambient pressure (Cheng *et al.*, 1993). The *trans* isomer of $[\text{Fe}^{\text{III}}\text{LCl}_2]^+$ (*L* is 1,4,8,11-tetraazacyclotetradecane) was found to activate dioxygen in the presence of reducing agents (Nishida & Tanaka, 1994). Mimic studies have revealed that two Mn^{II} complexes with pentaazamacrocyclic ligands have high catalytic SOD (super-oxide dismutase) activity (Salvemini *et al.*, 1999). A series of Cu^{II} or Zn^{II} complexes with tetraazamacrocyclic ligands involving different substituents have been synthesized in order to study their EET (electronic energy transfer) properties (Bernhardt *et al.*, 2002). Attempts have been made to clarify the correlation between the structure and the biological and chemical properties of transition metal complexes with azamacrocyclic polydentate ligands. We report here the preparation and structure of the title novel Cu^{II} complex, (I), with the macrocyclic ligand 1,8-bis(2-hydroxyethyl)-1,3,6,8-, 10,13-hexaazacyclotetradecane.

Complex (I) possesses an inversion centre at the Cu atom, and thus the N donors of the macrocycle form a perfect plane

including the Cu^{II} cation. The Cu^{II} atom has an elongated octahedral coordination, as shown in Fig. 1. Four secondary N atoms of the macrocycle coordinate to the Cu^{II} atom in the equatorial plane. The axial positions are occupied by thiocyanate S atoms. The Cu—N bond distances are 2.004 (2) and 2.015 (2) Å, which are close to the values of 2.002 and 2.018 Å observed in $[\text{CuL}(\text{H}_2\text{O})]_n[(\text{CuL})\text{Fe}(\text{CN})_6]_{2n}$ [Lu *et al.* (2000); Cambridge Structural Database (Allen, 2002) refcode XASHOO]. The Cu—S bond distances of 2.9696 (10) Å are shorter than the sum of the van der Waals radii of Cu and S (3.4 Å; Pauling, 1960) and similar to the values found in other complexes in which S atoms adopt an axial position in a distorted octahedron around Cu^{II} (Ribas *et al.*, 1995; Vicente *et al.*, 1997; Ferlay *et al.*, 1998).



The bite distances of the five- and six-membered chelate rings are 2.742 (3) and 2.938 (3) Å, respectively, and the bite angles are 86.04 (9) and 93.96 (9)°, respectively. These data are also similar to those of $[\text{CuL}(\text{H}_2\text{O})]_n[(\text{CuL})\text{Fe}(\text{CN})_6]_{2n}$ (Lu *et al.*, 2000). The six-membered chelate rings adopt a chair conformation and the alkyl chains on the bridgehead N atoms are axial. The five-membered chelate rings assume a *gauche* conformation. The average N—C bond distance involving the bridged tertiary atom N2 is 1.445 (4) Å, which is shorter than the normal C—N single-bond distance, and the average C—N—C angle involving N2 is 115.6 (2)°.



The C–N [1.118 (6) Å] and C–S [1.626 (4) Å] distances, and N–C–S angles [174.6 (5)°] in the thiocyanate moiety of (I) are indicative of a normal thiocyanate structure.

Hydrogen-bonding interactions play an important role in the solid-state structure of (I). O–H···N and N–H···O hydrogen bonds link the molecules into sheets, in which there are centrosymmetric hydrogen-bonded rings (Fig. 2*a*). The

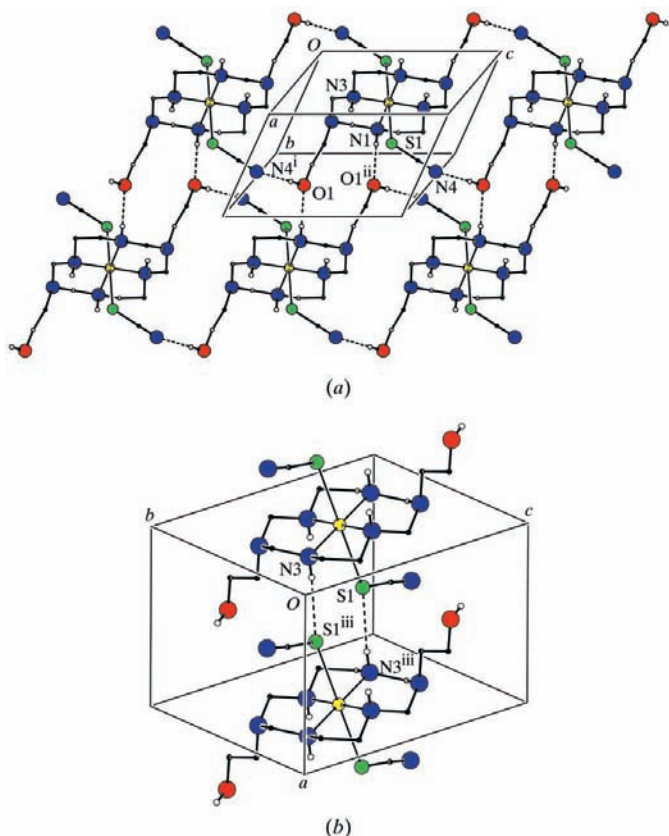


Figure 2

(*a*) Part of the crystal structure of (I), showing the formation of a two-dimensional net with centrosymmetric $R_4^2(16)$, $R_2^2(14)$ and $R_2^2(22)$ rings. (*b*) A diagram showing how the nets are linked in the *c* direction by pairs of N–H···S hydrogen bonds to generate $R_2^2(8)$ rings. In each case, hydrogen bonds are shown as dotted lines. The symmetry codes (i), (ii) and (iii) are as defined in Table 2.

hydroxy group O1–H1 at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the thiocyanate atom N4 at (*x*, *y*, *z* – 1), while O1–H1 at (*x*, *y*, *z* – 1) acts as a donor to atom N4 at (1 – *x*, 2 – *y*, 1 – *z*). In this way, an $R_4^2(16)$ ring (Bernstein *et al.*, 1995) is generated about the inversion centre at ($\frac{1}{2}$, 1, 0). The N1–H1A moiety at (*x*, *y*, *z*) acts as a hydrogen-bond donor to the hydroxyl atom O1 at (1 – *x*, 2 – *y*, 1 – *z*) and, coupled with the inversion centre at ($\frac{1}{2}$, 1, $\frac{1}{2}$), an $R_2^2(14)$ ring is generated. Also generated is an $R_2^2(22)$ ring with its centre at the inversion centre at (0, $\frac{1}{2}$, 0). These sheets are then linked to generate a three-dimensional network *via* pairs of N–H···S hydrogen bonds (Fig. 2*b*), which generates an $R_2^2(8)$ ring centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), with N3–H3 acting as a donor to atom S1 at (1 – *x*, 1 – *y*, 1 – *z*).

Experimental

To a suspension of bis(ethanediamine)copper(II) perchlorate (5.0 g, 13 mmol) in methanol (100 ml) were added 2-hydroxyethylamine (2.5 ml) and triethanolamine (2.5 ml). A solution of formaldehyde (2.5 ml, 37% aqueous solution) in methanol (8 ml) was then added dropwise to the refluxing suspension over a period of 1 h. The solution was refluxed for a further 4 h and then cooled in an ice bath, whereupon a purple–red product was collected. Purple single crystals of (I) were obtained after recrystallization from water containing NaNCS.

Crystal data

[Cu(NCS)₂(C₁₂H₃₀N₆O₂)]
 $M_r = 470.12$
 Triclinic, *P1*
 $a = 7.118$ (1) Å
 $b = 9.328$ (1) Å
 $c = 9.483$ (1) Å
 $\alpha = 111.00$ (1)°
 $\beta = 106.80$ (1)°
 $\gamma = 103.85$ (1)°
 $V = 519.65$ (15) Å³

$Z = 1$
 $D_x = 1.502$ Mg m^{–3}
 Mo *K*α radiation
 Cell parameters from 30 reflections
 $\theta = 2.5$ – 15.4 °
 $\mu = 1.28$ mm^{–1}
 $T = 296$ (2) K
 Prism, purple
 0.56 × 0.56 × 0.40 mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: empirical (North *et al.*, 1968)
 $T_{\min} = 0.451$, $T_{\max} = 0.600$
 1903 measured reflections
 1747 independent reflections
 1639 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$
 $\theta_{\max} = 25$ °
 $h = 0 \rightarrow 8$
 $k = -9 \rightarrow 9$
 $l = -11 \rightarrow 10$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.089$
 $S = 1.08$
 1747 reflections
 126 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.5754P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.73$ e Å^{–3}
 $\Delta\rho_{\min} = -0.37$ e Å^{–3}
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.117 (7)

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|----------|-------------|
| Cu–N1 | 2.004 (2) | S1–C7 | 1.626 (4) |
| Cu–N3 | 2.015 (2) | N4–C7 | 1.118 (5) |
| Cu–S1 | 2.9696 (10) | | |
| N1–Cu–N3 | 93.96 (9) | C7–S1–Cu | 115.95 (13) |
| N1–Cu–S1 | 86.56 (7) | N4–C7–S1 | 174.6 (5) |
| N3–Cu–S1 | 83.78 (6) | | |

Table 2

Hydrogen-bonding 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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O1–H1···N4 ⁱ | 0.82 | 2.03 | 2.850 (5) | 175 |
| N1–H1A···O1 ⁱⁱ | 0.91 | 2.22 | 2.951 (3) | 137 |
| N3–H3···S1 ⁱⁱⁱ | 0.91 | 2.56 | 3.381 (2) | 150 |

Symmetry codes: (i) *x*, *y*, *z* – 1; (ii) 1 – *x*, 2 – *y*, 1 – *z*; (iii) 1 – *x*, 1 – *y*, 1 – *z*.

The H atoms were visible in difference maps and were allowed for as riding atoms, with C—H = 0.97, N—H = 0.91 and O—H = 0.82 Å.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990a); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1669). Services for accessing these data are described at the back of the journal.

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