Structure of (4,7-Diazadecanediamide-*N*,*N'*,*O*)diisothiocyanatocopper(II)

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Abstract. [$Cu(C_8H_{18}N_4O_2)(NCS)_2$], $M_r = 381.95$, monoclinic, $P2_1/n$, $a = 9.548$ (2), $b = 15.814$ (3), $c = 10.660$ (2) Å, $\beta = 91.89$ (2)°, $V = 1608.5$ (5) Å^3, $Z = 4$, $D_x = 1.577$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7093 Å, $\mu = 1.63$ mm^{-1}, $F(000) = 788$, $T = 297$ (3) K, $R = 0.029$, $wR = 0.026$ for 1350 observed reflections. The Cu^{II} coordination is a distorted square pyramid. 4,7-Diazadecanediamide acts as a tridentate ligand through two amine N atoms and one amide O atom. Two isothiocyanato groups are bonded to Cu^{II} through the N atoms. The three ligating atoms of diazadecanediamide and an isothiocyanato N atom form a very slightly distorted plane; another isothiocyanato N atom occupies the axial position. Each isothiocyanato group is almost linear.

Introduction. Metal–thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanato group is bonded to the metal through the nitrogen atom (*M*—NCS), through the sulfur atom (*M*—SCN), or through both by means of bridging (*M*—NCS—*M*) (Mitchell & Williams, 1960). In order to expand the knowledge in this area, we have investigated the X-ray crystal structure of the title compound.

Experimental. Aqua[*N*,*N'*-bis(*β*-carbamoylethyl)-ethylenediamine]perchloratocopper(II) perchlorate monohydrate was prepared by the procedure described in a previous paper (Wei, Chao & Chung, 1979). 2.05 g of the complex in 25 ml of water was treated with 1.0 g KSCN in 10 ml of water. The blue solution which resulted was evaporated to dryness. It was then dissolved in 30 ml of CH_3NO_2, filtered and evaporated to yield 1.32 g of a blue solid. Single crystals were obtained from 50% aqueous methanol by slow evaporation. A crystal of size 0.32 × 0.45 × 0.59 mm was used for the X-ray structure determination by employing a Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Unit-cell parameters from 25 reflections with $20 < 2\theta < 27°$, data collected by ω–2θ scans with scan width of $2 \times (1.0 + 0.35\tan\theta)°$ and scan speed of 2.3 to 8.2° min^{-1}. Empirical absorption correction based on azimuthal rotation from three reflections ($\overline{3}6\overline{4}$, $\overline{3}3\overline{3}$, $\overline{5}8\overline{6}$) (North, Phillips & Mathews, 1968); the minimum, maximum and average correction factors were 0.8937, 0.9979 and 0.9605 respectively. Maximum $(\sin\theta)/\lambda = 0.59$ Å^{-1} ($-11 \leq h \leq 11$, $0 \leq k \leq 18$, $0 \leq l \leq 12$); standard reflections $\overline{2}4\overline{4}$, $03\overline{4}$ and $6\overline{2}\overline{1}$ checked every hour, varied within 1%; 3058 reflections collected, 1560 unique reflections ($R_{int} = 0.03$) and 1350 significant reflections with $I > 2.5\sigma(I)$ used for the structure determination. The heavy atom Cu was located by the Patterson function. Other atoms were located by alternate difference Fourier synthesis and least-squares fit. The function minimized in the full-matrix least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 209 parameters with anisotropic parameters for non-H atoms and isotropic ones for H atoms. $R = 0.029$, $wR = 0.026$, $S = 4.21$, $(\Delta/\sigma)_{max} = 0.04$, $(\Delta/\sigma)_{av} = 0.01$ in the final iteration, $(\Delta\rho)_{max} = 0.22$, $(\Delta\rho)_{min} = -0.27$ e Å^{-3}. Secondary-extinction coefficient 2.9 (2) × 10^{-5} (length in cm). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). NRCVAX programs (Gabe, Le Page, White & Lee, 1987) for the VAX compiler were used to solve the structure.

Discussion. The atomic coordinates and isotropic temperature factors are listed in Table 1.* Table 2 lists bond lengths and bond angles. The numbering scheme and the displacements of the atoms from the equatorial plane are shown in Fig. 1. A stereoview of the molecular packing is shown in Fig. 2. The Cu^{II} coordination is a distorted square pyramid. 4,7-

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Table 1. *Atomic parameters and equivalent isotropic thermal parameters (e.s.d.'s refer to the last digit printed)*

B_{eq} is the mean of the principal axes of the thermal ellipsoids.

	x	y	z	$B_{eq}(\text{Å}^2)$
Cu	0.89044 (6)	0.23159 (3)	0.03849 (6)	2.58 (3)
S(1)	0.83532 (16)	0.01348 (7)	0.33278 (12)	4.00 (7)
S(2)	1.25255 (17)	0.38912 (8)	0.27988 (16)	4.86 (8)
O(1)	0.6919 (3)	0.2699 (2)	0.0607 (3)	3.2 (2)
O(2)	1.3448 (4)	0.1751 (2)	0.1299 (3)	3.0 (2)
N(1)	0.4868 (4)	0.3356 (2)	0.0257 (5)	2.9 (2)
N(2)	0.9094 (4)	0.3126 (2)	-0.1003 (4)	2.4 (2)
N(3)	1.0870 (4)	0.1919 (2)	-0.0077 (4)	2.8 (2)
N(4)	1.5122 (5)	0.1124 (2)	0.0199 (5)	3.4 (3)
N(5)	0.8537 (4)	0.1367 (2)	0.1506 (4)	3.3 (2)
N(6)	1.0006 (5)	0.3177 (2)	0.1887 (4)	4.6 (3)
C(1)	0.6200 (5)	0.3260 (3)	0.0032 (5)	2.3 (2)
C(2)	0.6792 (5)	0.3804 (3)	-0.0954 (5)	3.1 (3)
C(3)	0.8384 (5)	0.3943 (3)	-0.0877 (5)	2.8 (3)
C(4)	1.0621 (6)	0.3237 (3)	-0.1229 (6)	3.3 (3)
C(5)	1.1259 (6)	0.2354 (3)	-0.1246 (5)	3.7 (3)
C(6)	1.1204 (5)	0.1004 (3)	-0.0065 (6)	3.4 (3)
C(7)	1.2744 (5)	0.0804 (3)	-0.0368 (6)	3.3 (3)
C(8)	1.3784 (6)	0.1275 (3)	0.0471 (6)	2.5 (3)
C(9)	0.8468 (5)	0.0859 (2)	0.2259 (4)	2.4 (2)
C(10)	1.1031 (6)	0.3464 (3)	0.2271 (5)	3.4 (3)

Table 2. *Bond lengths (Å) and bond angles (°)*

Cu—O(1)	2.012 (4)	N(2)—C(4)	1.497 (8)
Cu—N(2)	1.971 (4)	N(3)—C(5)	1.485 (8)
Cu—N(3)	2.054 (5)	N(3)—C(6)	1.482 (6)
Cu—N(5)	1.962 (4)	N(4)—C(8)	1.344 (9)
Cu—N(6)	2.328 (4)	N(5)—C(9)	1.137 (6)
S(1)—C(9)	1.619 (5)	N(6)—C(10)	1.141 (7)
S(2)—C(10)	1.661 (6)	C(1)—C(2)	1.484 (9)
O(1)—C(1)	1.269 (5)	C(2)—C(3)	1.536 (8)
O(2)—C(8)	1.211 (8)	C(4)—C(5)	1.531 (7)
N(1)—C(1)	1.312 (8)	C(6)—C(7)	1.547 (9)
N(2)—C(3)	1.467 (6)	C(7)—C(8)	1.512 (6)

O(1)—Cu—N(2)	90.2 (2)	Cu—N(5)—C(9)	170.6 (3)
O(1)—Cu—N(3)	172.9 (1)	Cu—N(6)—C(10)	147.3 (5)
O(1)—Cu—N(5)	88.3 (2)	O(1)—C(1)—N(1)	120.2 (6)
O(1)—Cu—N(6)	98.5 (2)	O(1)—C(1)—C(2)	122.5 (6)
N(2)—Cu—N(3)	85.0 (2)	N(1)—C(1)—C(2)	117.2 (4)
N(2)—Cu—N(5)	168.5 (1)	C(1)—C(2)—C(3)	116.3 (4)
N(2)—Cu—N(6)	94.9 (2)	N(2)—C(3)—C(2)	109.2 (4)
N(3)—Cu—N(5)	95.4 (2)	N(2)—C(4)—C(5)	106.6 (4)
N(3)—Cu—N(6)	87.1 (2)	N(3)—C(5)—C(4)	107.5 (5)
N(5)—Cu—N(6)	96.6 (2)	N(3)—C(6)—C(7)	113.8 (4)
Cu—O(1)—C(1)	130.5 (4)	C(6)—C(7)—C(8)	112.7 (5)
Cu—N(2)—C(3)	116.8 (4)	O(2)—C(8)—N(4)	123.2 (4)
Cu—N(2)—C(4)	108.2 (3)	O(2)—C(8)—C(7)	123.6 (6)
C(3)—N(2)—C(4)	111.4 (4)	N(4)—C(8)—C(7)	113.2 (6)
Cu—N(3)—C(5)	108.5 (3)	S(1)—C(9)—N(5)	179.4 (4)
Cu—N(3)—C(6)	119.7 (4)	S(2)—C(10)—N(6)	178.6 (6)
C(5)—N(3)—C(6)	113.5 (5)		

Diazadecanediamide acts as a tridentate ligand bonding to the Cu^{II} ion through the two amine N atoms and one amide O atom as shown in Fig. 2. In addition to this ligand, two isothiocyanato groups are bonded to the metal through the N atoms. The two donor N atoms and a donor O atom of 4,7-diazadecanediamide and the isothiocyanato N atom form a very slightly distorted plane; another isothiocyanato N atom occupies the axial position. The intrusion of one equatorial isothiocyanate group makes the nearby bond lengths Cu—O(1) and

Cu—N(3) longer than those of the other equatorial bonds Cu—N(2) and Cu—N(5) and keeps the fifth bond, Cu—N(6), longest as usual. The bond length Cu—N(6) of the isothiocyanato group in the axial position, 2.328 (4) Å, is significantly longer than the Cu—N(5) bond of the isothiocyanato group in the equatorial position, 1.962 (4) Å. The maximum deviation of the four atoms from the best plane for the four equatorial atoms is 0.059 (6) Å. The Cu^{II} atom is 0.140 (2) Å out of the best plane and is directed towards the axial ligand. The two H atoms on the two amino groups, N(2) and N(3), are *trans* to each other with respect to the basal plane of the square pyramid. The coordinated isothiocyanato groups are almost linear. The five-membered chelate ring is in a *gauche* form; the six-membered chelate ring is in a twist form. Our present bond lengths and bond angles for Cu—N≡C—S correspond to the data for other isothiocyanato complexes of Cu^{II} (Burmeister, 1990). Three intermolecular hydrogen-bond lengths are N(1)—H⋯O(2) 3.099 (8), N(2)—H⋯O(2) 2.928 (8) and N(4)—H⋯O(1) 3.049 (9) Å.

According to Pearson's theory, S in SCN⁻ is soft and prefers to coordinate with soft acids (class *b* metals), whereas N in SCN⁻ is hard and coordinates
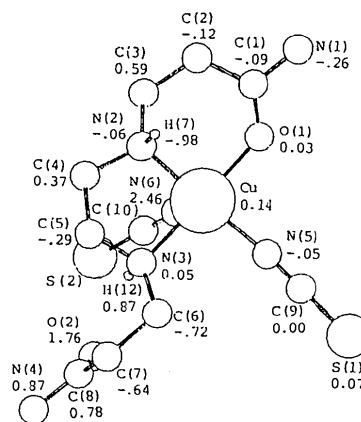

Fig. 1. Perspective view of the atom-numbering scheme of the molecule excluding the H atoms except those attached to the amino groups, N(2) and N(3). The displacements from the best plane formed by the four nearest atoms coordinated to the Cu^{II} atom are indicated.
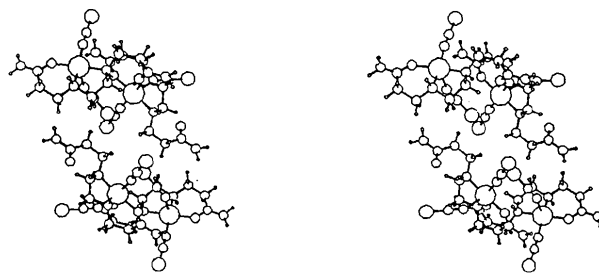

Fig. 2. A stereoview of the molecular packing.

with hard acids (class *a* metals) (Pearson, 1963; Ahrland, Chatt & Davies, 1958). Cu^{II} is on the borderline between hard and soft (Yingst & McDaniel, 1967), thus, the nature of the other ligands attached to it has a very great effect on the coordination behaviour of the thiocyanato group (Wu & Chung, 1986; Bennett, Clark & Goodwin, 1967). It is interesting that a thiocyanato group is bonded to a Cu^{II} ion through the S atom in four Cu^{II} complexes of open-chain tetraamines (Wu & Chung, 1986; Marongiu, Lingafelter & Paoletti, 1969); however, in this complex, the two isothiocyanato groups are bonded in Cu^{II} through the N atoms.

The basicity of the polydentate ligand has a very important effect on the coordination behaviour of the thiocyanato group. It has been suggested (Burmeister & Basolo, 1964) that the bonding *M*—SCN is stabilized by π bonding which is formed between the *d* electrons of the metal and an empty antibonding π orbital located on the S atom of the thiocyanato group. The availability of the metal *d* electrons for *M*—SCN π bonding will, however, be increased by the basicity of the other ligands (Bertini & Sabatini, 1966). A structural change from N-bonded to S-bonded thiocyanates may therefore be expected if the basicity of the polydentate organic ligand is increased.

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Structure of *N,N*-Bis(2-aminoethyl)diethylenetriamine(chloro)cobalt(III) Chloride Perchlorate Hydrate

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Abstract. $[Co(C_8H_{23}N_5)Cl]Cl(ClO_4).H_2O$, $M_r = 436.6$, monoclinic, $P2_1/n$, $a = 14.769\,(3)$, $b = 13.558\,(1)$, $c = 9.056\,(2)$ Å, $\beta = 105.281\,(3)°$, $V = 1749\,(1)$ Å^3, $Z = 4$, $D_m = 1.66\,(1)$, $D_x = 1.658$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.7107$ Å, $\mu = 14.67$ cm^{-1}, $F(000) = 904$, $T = 293$ K, final $R = 0.046$ for 5092 counter-measured reflections. The structure consists of octahedral cations $[Co(trenen)Cl]^{2+}$ with one chloride and one perchlorate ion together with one water molecule involved in hydrogen bonding in the gross structure. The mean Co—N distance is 1.960 (18) and Co—Cl is 2.267 (1) Å. The Co—

N(sec) distance [1.932 (3) Å] is significantly shorter than the other Co—N distances and indicates stronger binding to the secondary N atom.

Introduction. Recently Gatehouse, McLachlan, Martin, Martin & Spiccia (1991) reported the synthesis, properties and X-ray structure of the peroxo-bridged Co^{III} complex, $[(trenen)CoO_2Co(trenen)](ClO_4)_4$, where trenen = *N,N,N'*-tris(2-aminoethyl)-ethane-1,2-diamine (1). An interesting structural feature of this complex is the short Co—N distance *trans* to the bridging peroxo group, *viz.* 1.928 (6) Å compared with the average Co—N distance of 1.952 (21) Å. This is unusual for peroxo-bridged