C20†	0.794 (2)	0.305 (2)	0.698 (2)	0.058 (6)
C21†	0.833 (3)	0.199 (2)	0.687 (2)	0.058 (6)
C22†	0.988 (3)	0.172 (2)	0.670 (1)	0.058 (6)
C23†	1.103 (2)	0.251 (3)	0.666 (1)	0.058 (6)
C24†	1.064 (2)	0.356 (3)	0.678 (1)	0.058 (6)
C25†	0.909 (2)	0.384 (2)	0.694 (2)	0.058 (6)
C30‡	0.813 (2)	0.333 (2)	0.696 (2)	0.050 (6)
C31‡	0.874 (3)	0.233 (2)	0.679 (1)	0.050 (6)
C32‡	1.034 (3)	0.222 (2)	0.665 (1)	0.050 (6)
C33‡	1.133 (2)	0.311 (2)	0.667 (1)	0.050 (6)
C34‡	1.072 (2)	0.410 (2)	0.683 (1)	0.050 (6)
C35‡	0.911 (2)	0.421 (2)	0.698 (1)	0.050 (6)
C40§	0.793 (2)	0.289 (2)	0.693 (2)	0.055 (6)
C41§	0.792 (2)	0.179 (2)	0.683 (2)	0.055 (6)
C42§	0.933 (3)	0.126 (2)	0.669 (1)	0.055 (6)
C43§	1.074 (2)	0.183 (2)	0.666 (1)	0.055 (6)
C44§	1.075 (2)	0.292 (2)	0.676 (2)	0.055 (6)
C45§	0.934 (3)	0.345 (2)	0.690 (2)	0.055 (6)

† Occupancy = 0.40 (3); $U_{\rm iso}$. ‡ Occupancy = 0.32 (3); $U_{\rm iso}$. § Occupancy = 0.30 (3); $U_{\rm iso}$.

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

Pt—Cl1	2.310 (3)	S2—O2	1.448 (7)
Pt—Cl2	2.307 (3)	S2—C10	1.81 (1)
Pt—S1	2.241 (2)	S2—C15	1.800 (9)
Pt—S2	2.233 (2)	C1—C2	1.49 (1)
S1—O1	1.479 (7)	C15—C20	1.45 (2)
S1—C1	1.828 (10)	C15—C30	1.55 (2)
S1—C8	1.79 (1)	C15—C40	1.55 (2)
Cl1—Pt—Cl2	87.8 (1)	Pt—S2—C10	109.3 (3)
Cl1—Pt—S1	177.31 (10)	Pt—S2—C15	110.4 (3)
Cl1—Pt—S2	88.56 (9)	O2—S2—C10	109.0 (4)
Cl2—Pt—S1	92.4 (1)	O2—S2—C15	109.5 (4)
Cl2—Pt—S2	176.0 (1)	C10—S2—C15	100.1 (5)
S1—Pt—S2	91.19 (9)	S1—C1—C2	112.8 (7)
Pt—S1—O1	115.7 (3)	S2—C15—C20	106 (1)
Pt—S1—C1	108.2 (3)	S2—C15—C30	108 (1)
Pt—S1—C8	112.6 (4)	S2—C15—C40	109 (1)
O1—S1—C1	110.6 (5)	C20—C15—C30	14 (1)
O1—S1—C8	107.5 (5)	C20—C15—C40	7 (1)
C1—S1—C8	101.4 (5)	C30—C15—C40	21 (1)
Pt—S2—O2	117.1 (3)		

It was possible to resolve three positions of the disordered phenyl group (see Table 1) using a rigid phenyl group in the refinement with C—C 1.40, C—H 0.95 Å and C—C—C 120°. An occupancy factor for each group was refined without restrictions: 0.40 (3), 0.32 (3) and 0.30 (3) resulted, giving a total occupancy for the phenyl group of 1.02 (5), which is an acceptable value. The H atoms of the disordered phenyl group were included in the rigid group and therefore refined with the whole group. The H atoms on C8, C10 and C15 were not included. The H atoms of the ordered benzyl group were included in calculated positions and included in the structure-factor calculations. The largest residual maxima and minima in the $\Delta\rho$ map were 0.92 Å from S1 and 1.55 Å from Cl(1), respectively.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*-4 (Enraf–Nonius, 1989). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (direct methods) (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1300). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Isothiocyanato)[(1*RS*,4*RS*,8*SR*,11*SR*)-1,4,8,11-tetraazacyclotetradecane]copper(II) Thiocyanate, [Cu(NCS)(cyclam)](SCN)

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Abstract

The crystal structure of the title compound, [Cu(NCS)-($C_{10}H_{24}N_4$)](SCN), has been determined by X-ray diffraction. A mirror plane passes through the metal atom and bisects the complex with the isothiocyanato ligand lying on the plane. The Cu$^{\rm II}$ ion is five-coordinate in a distorted square-pyramidal environment, with four amine N atoms in equatorial positions and the isothiocyanate N atom in an axial position; its coordination ge-

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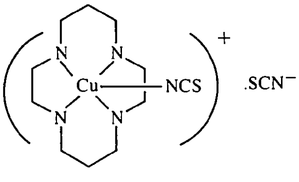
ometry is normal, with the equatorial Cu—N distances shorter than the axial one. The unbound SCN^- counter-ion is statistically disordered.

Comment

In the structure of $[Cu(cyclam)(ClO_4)_2]$, where cyclam is 1,4,8,11-tetraazacyclotetradecane (Tasker & Sklar, 1975), the Cu^{II} ion was found to be six-coordinate with a tetragonally distorted octahedral structure. In order to study the effect of a strong monodentate ligand on the structure of the tetraaza macrocyclic complex, the structure of the title compound, [Cu(NCS)(cyclam)](SCN), (I), has been determined.



(I)

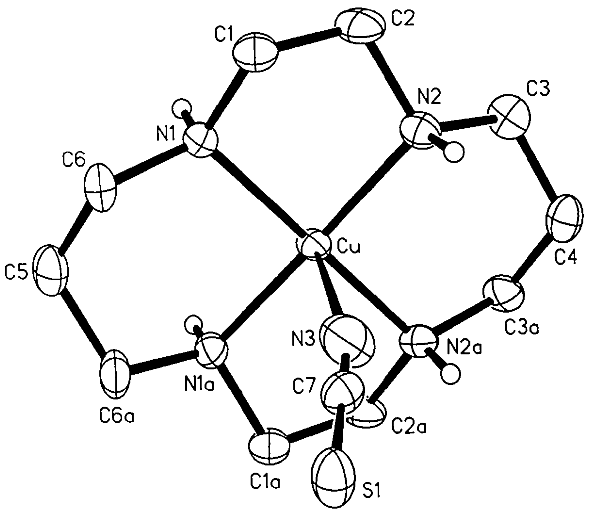


Fig. 1. A perspective view of the title molecule, with the atom-numbering scheme, excluding the unbound SCN^- group and the H atoms attached to the C atoms. Displacement ellipsoids are plotted at the 50% probability level.

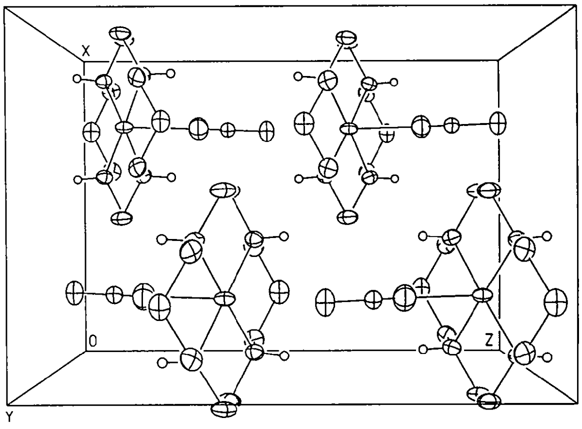


Fig. 2. A perspective view of the packing of the $[Cu(NCS)(cyclam)]^+$ cations in the unit cell.

A view of the molecular structure is shown in Fig. 1. A mirror plane passes through the Cu, C(4) and C(5) atoms and the isothiocyanate ligand and bisects the macrocyclic complex. Cu^{II} has two coordination spheres; the first involves five N atoms on the apices of the square pyramid, with the cyclam equatorial and the isothiocyanate ligand axial, while the second is a square bipyramid with a second axial position occupied by the S atom of the neighbouring thiocyanate ion, with a $Cu\cdots S(1^{ii})$ distance of 3.015 (1) Å [symmetry code: (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$], which is shorter than the sum of the Cu and S van der Waals radii (3.2 Å; Huheey, 1983). The resulting $[Cu(SCN)(cyclam)]^+$ cations, linked through $Cu\cdots S$ interactions, form chains parallel to the *c* axis (Fig. 2).

The structure of the title compound is favourably five-coordinate owing to the strong ligand-field effect of the isothiocyanate ion. The deviation of the Cu atom from the equatorial plane composed of the four tetraamine N atoms is 0.040 (1) Å towards the isothiocyanate ion. The axial Cu—N bond is about 0.42 Å longer than the equatorial Cu—N bonds and is 0.14 Å shorter than the axial Cu—O bond in the $[Cu(cyclam)(ClO_4)_2]$ complex. The equatorial Cu—N distances are comparable to the reported average value (Lu, Chung & Ashida, 1991) within standard deviation. The two pairs of *trans* H atoms on the amine groups are in a *trans* configuration. The configurations of the four chiral N-atom centres are 1*RS*, 4*RS*, 8*SR* and 11*SR*. The two six-membered chelate rings are in chair forms and the two five-membered chelate rings in *gauche* forms. Both the title compound and $[Cu(cyclam)(ClO_4)_2]$ contain the γ form of the coordinated macrocycle and hence the conformation, bond lengths and angles of the macrocyclic ligands of both complexes compare well with one another. The bond angles at the metal are, as usual, less than 90° in the five-membered chelate rings and a little greater than 90° in the six-membered rings.

The S(1)—C(7)—N(3) angle is approximately 180°. The uncoordinated SCN^- anion also adopts a linear conformation, is statistically disordered and participates in hydrogen bonds with the N(1) amine group. The $N(1)—H(N1)\cdots N(4^{iii})$ intermolecular hydrogen bond of 3.15 (1) Å [symmetry code: (iii) $1-x, 1-y, -z$] helps stabilize the crystal structure.

Experimental

(1,4,8,11-Tetraazacyclotetradecane)copper(II) perchlorate was prepared by the literature method of Fabbrizzi & Poggi (1983). 1 g of this complex in 25 ml of water was treated with 0.5 g of KSCN in 10 ml of water. The resulting blue solution was evaporated to dryness and the solid obtained was dissolved in 30 ml of CH_3NO_2, filtered and evaporated to yield a blue solid. Single crystals were obtained from methanol solution by slow evaporation.

Crystal data

$[Cu(NCS)(C_{10}H_{24}N_4)](SCN)$
$M_r = 380.02$
Orthorhombic
Pmcn
$a = 9.358\,(1)$ Å
$b = 13.408\,(1)$ Å
$c = 13.755\,(1)$ Å
$V = 1725.9\,(3)$ Å^3
$Z = 4$
$D_x = 1.463$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.64$–$16.12°$
$\mu = 1.50$ mm^{-1}
$T = 298\,(3)$ K
Parallelepiped
0.47 × 0.44 × 0.34 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.676$, $T_{\max} = 0.680$
5183 measured reflections
2645 independent reflections
1778 observed reflections $[I > 2.5\sigma(I)]$

$R_{\rm int} = 0.03$
$\theta_{\max} = 29.9°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 3 reflections frequency: 60 min intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.048$
$S = 1.53$
1778 reflections
170 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.34\,(7)$ e Å^{-3}
$\Delta\rho_{\min} = -0.40\,(7)$ e Å^{-3}
Extinction correction: none
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)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu	3/4	0.29737 (3)	0.12977 (3)	3.72 (2)
S(1)	3/4	0.08827 (7)	0.44108 (8)	5.51 (5)
S(2)	0.6417 (6)	0.7923 (4)	0.1264 (4)	7.60 (19)
N(1)	0.5930 (2)	0.21194 (14)	0.07476 (18)	4.06 (9)
N(2)	0.5924 (2)	0.38608 (16)	0.17990 (18)	4.27 (9)
N(3)	3/4	0.2171 (4)	0.2882 (3)	8.1 (3)
N(4)	0.5725 (11)	0.8391 (8)	0.1180 (5)	8.3 (5)
C(1)	0.4607 (3)	0.2426 (3)	0.1235 (3)	5.63 (15)
C(2)	0.4603 (3)	0.3553 (3)	0.1290 (3)	5.75 (16)
C(3)	0.6145 (4)	0.4950 (2)	0.1788 (2)	5.05 (13)
C(4)	3/4	0.5251 (3)	0.2303 (4)	5.4 (2)
C(5)	3/4	0.0720 (3)	0.0270 (4)	5.8 (2)
C(6)	0.6146 (4)	0.10278 (19)	0.0784 (3)	5.38 (14)
C(7)	3/4	0.1650 (3)	0.3509 (3)	4.28 (16)
C(8)	0.6874 (17)	0.8200 (10)	0.1241 (12)	5.9 (5)

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

Cu—N(1)	2.011 (2)	N(2)—C(2)	1.479 (4)
Cu—N(2)	2.016 (2)	N(2)—C(3)	1.476 (3)
Cu—N(3)	2.430 (4)	N(3)—C(7)	1.110 (6)
S(1)—C(7)	1.612 (4)	C(1)—C(2)	1.513 (5)
N(1)—C(1)	1.467 (4)	C(3)—C(4)	1.508 (4)
N(1)—C(6)	1.478 (3)	C(5)—C(6)	1.508 (4)
S(2)—C(8')	1.642 (18)	N(4)—C(8)	1.11 (2)
N(1)—Cu—N(1')	93.88 (9)	Cu—N(2)—C(3)	118.57 (18)
N(1)—Cu—N(2)	86.00 (9)	C(2)—N(2)—C(3)	112.8 (2)
N(1)—Cu—N(2')	177.71 (10)	N(1)—C(1)—C(2)	107.8 (2)
N(2)—Cu—N(2')	94.02 (9)	N(2)—C(2)—C(1)	107.5 (2)
N(1)—Cu—N(3)	94.89 (11)	N(2)—C(3)—C(4)	112.2 (3)
N(2)—Cu—N(3)	87.39 (11)	C(3)—C(4)—C(3')	114.5 (3)
Cu—N(1)—C(1)	106.55 (17)	C(6)—C(5)—C(6')	114.3 (4)
Cu—N(1)—C(6)	116.85 (19)	N(1)—C(6)—C(5)	111.7 (3)
C(1)—N(1)—C(6)	112.2 (2)	S(1)—C(7)—N(3)	179.3 (4)
Cu—N(2)—C(2)	106.53 (18)	S(2')—C(8)—N(4)	176.7 (15)
Cu—N(3)—C(7)	167.3 (4)		

Symmetry code: (i) $\frac{3}{2} - x, y, z$.

H atoms were located from a difference Fourier synthesis. Refinement was by full-matrix least squares, with H atoms refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1986). Software used to prepare material for publication: *NRCVAX*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: KH1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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