

*Acta Cryst.* (1998). **C54**, 1071–1072

**(Isothiocyanato- $\kappa$ N)(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane- $\kappa^4$ N)-copper(II) Perchlorate**

TIAN-HUEY LU,<sup>a</sup> WEI-ZE SHUI,<sup>a</sup> SHU-FANG TUNG,<sup>b</sup>  
TA-YUNG CHI,<sup>c</sup> FEN-LING LIAO<sup>c</sup> AND CHUNG-SUN CHUNG<sup>c</sup>

<sup>a</sup>Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, <sup>b</sup>Southern Instrument Center, National Cheng Kung University, Tainan, Taiwan 701, and <sup>c</sup>Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300. E-mail: thlu@phys.nthu.edu.tw

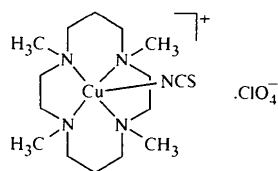
(Received 30 October 1997; accepted 27 January 1998)

**Abstract**

In  $[\text{Cu}(\text{NCS})(\text{C}_{14}\text{H}_{32}\text{N}_4)]\text{ClO}_4$ , the  $\text{Cu}^{\text{II}}$  ion is fivefold coordinated in a distorted trigonal-bipyramidal environment and the tetradentate macrocyclic ligand coordinates in a folded fashion. All four methyl groups of the macrocycle are disposed towards the same side as the isothiocyanato group.

**Comment**

The thiocyanate ion can act as an ambient ligand coordinating to a metal ion *via* the S or the N atom. According to Pearson's theory, the S atom in  $\text{SCN}^-$  is soft and prefers to coordinate to soft acids (class *b* metals), whereas the N atom in  $\text{SCN}^-$  is hard and coordinates to hard acids (class *a* metals) (Ahrland *et al.*, 1958; Pearson, 1963; Burmeister, 1990). The  $\text{Cu}^{\text{II}}$  ion is on the borderline between hard and soft. Thus, the nature of the other ligands attached to a  $\text{Cu}^{\text{II}}$  ion has a great effect on the coordination behaviour of a thiocyanato group (Lu *et al.*, 1996; Tahirov *et al.*, 1993, 1995). We report herein the crystal structure of the title complex, (I), in order to expand the knowledge in this area.



(I)

The  $\text{Cu}^{\text{II}}$  ion is five-coordinate in a distorted trigonal-bipyramidal environment. The macrocyclic ligand, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc), coordinates to the  $\text{Cu}^{\text{II}}$  ion in a folded fashion. The trigonal plane is formed by N1, N3 and N5. The N2 and N4 atoms occupy the apical positions.

Axial bonds [2.094 (4) and 2.097 (4) Å] are, on average, shorter than in-plane bonds [2.080 (4), 2.143 (4) and 2.116 (4) Å] because of the rigidity of the macrocyclic ligand. The N2—Cu—N4 angle [174.37 (15)°] deviates from linearity. The tetradentate ligand adopts a conformation in which the two six-membered rings have chair forms and the two five-membered rings have *gauche* forms. All four methyl groups of the macrocycle are disposed towards the same side as the isothiocyanato group. The chiral atoms N1, N2, N3 and N4 have the relative configurations 1*RS*, 4*SR*, 8*RS* and 11*SR*, respectively. The thiocyanate ion acts as a monodentate ligand and coordinates to the  $\text{Cu}^{\text{II}}$  ion *via* the N atom. Similar trigonal-bipyramidal coordination of tmc has been reported in the crystal structure of  $[\text{Zn}(\text{O}_2\text{COCH}_3)(\text{tmc})]\text{ClO}_4$  (Kato & Ito, 1985). The crystal structures of  $[\text{Fe}(\text{tmc})(\text{NO})](\text{BF}_4)_2$ ,  $[\text{Ni}(\text{tmc})(\text{N}_3)]\text{ClO}_4$  and  $[\text{Zn}(\text{tmc})\text{Cl}]\text{ClO}_4$  contain distorted square-pyramidal complexes (Alcock *et al.*, 1978; D'Aniello *et al.*, 1975; Hodges *et al.*, 1979). The perchlorate ion is not within bonding distance of the cation.

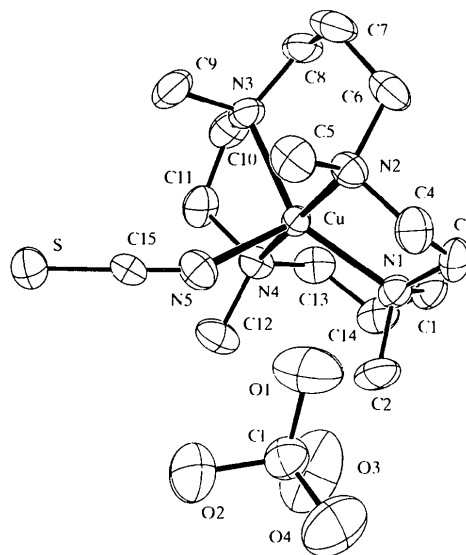


Fig. 1. A perspective view of the molecule of the  $\text{Cu}^{\text{II}}$  complex with the atom-numbering scheme, excluding H atoms. Displacement ellipsoids are drawn at the 50% probability level (ORTEPII; Johnson, 1976).

**Experimental**

The tmc ligand and  $[\text{Cu}(\text{tmc})](\text{ClO}_4)_2$  were prepared according to literature methods (Barefield & Wagner, 1973; Lee *et al.*, 1986).  $[\text{Cu}(\text{tmc})](\text{ClO}_4)_2$  (0.03 g) and KSCN (0.05 g) were mixed in aqueous solution (10 ml) and allowed to react for 3 h at room temperature. Acetone was added to the resulting solution until the solution became clear. The solution was allowed to stand in air overnight whereupon blue crystals suitable for crystallographic analysis were obtained.

**Crystal data**

[Cu(NCS)(C <sub>14</sub> H <sub>32</sub> N <sub>4</sub> )]ClO <sub>4</sub>	Mo K $\alpha$ radiation
$M_r = 477.50$	$\lambda = 0.7107 \text{ \AA}$
Monoclinic	Cell parameters from 22 reflections
$P2_1/c$	$\theta = 5.45\text{--}15.74^\circ$
$a = 8.9245 (10) \text{ \AA}$	$\mu = 1.30 \text{ mm}^{-1}$
$b = 14.9611 (10) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.7331 (13) \text{ \AA}$	Cubic
$\beta = 96.184 (10)^\circ$	$0.25 \times 0.13 \times 0.12 \text{ mm}$
$V = 2088.5 (3) \text{ \AA}^3$	Light blue
$Z = 4$	
$D_x = 1.519 \text{ Mg m}^{-3}$	
$D_m$ not measured	

**Data collection**

Nonius CAD-4 diffractometer	2514 reflections with $I > 1.5\sigma(I)$
$\theta/2\theta$ scans	$R_{\text{int}} = 0.019$
Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968)	$\theta_{\text{max}} = 24.93^\circ$
$T_{\text{min}} = 0.703$ , $T_{\text{max}} = 0.867$	$h = -10 \rightarrow 10$
3926 measured reflections	$k = 0 \rightarrow 17$
3675 independent reflections	$l = 0 \rightarrow 18$
	3 standard reflections
	frequency: 60 min
	intensity decay: 1.0%

**Refinement**

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
$R = 0.041$	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
$wR = 0.052$	Extinction correction: Larson (1970)
$S = 1.13$	Extinction coefficient: $8 (2) \times 10^3$
2513 reflections	Scattering factors from <i>International Tables for X-ray Crystallography</i> (Vol. IV)
245 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F) + 0.001F^2]$	
$(\Delta/\sigma)_{\text{max}} = 0.002$	

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cu—N1	2.080 (4)	Cu—N4	2.097 (4)
Cu—N2	2.094 (4)	Cu—N5	2.116 (4)
Cu—N3	2.143 (4)	S—C15	1.628 (5)
N1—Cu—N2	85.45 (15)	Cu—N1—C3	106.4 (3)
N1—Cu—N3	145.46 (15)	Cu—N2—C4	104.4 (3)
N1—Cu—N4	92.40 (15)	Cu—N2—C5	115.3 (3)
N1—Cu—N5	114.57 (16)	Cu—N2—C6	112.1 (3)
N2—Cu—N3	92.80 (16)	Cu—N3—C8	112.1 (3)
N2—Cu—N4	174.37 (15)	Cu—N3—C9	114.7 (3)
N2—Cu—N5	93.53 (15)	Cu—N3—C10	103.8 (3)
N3—Cu—N4	86.02 (15)	Cu—N4—C11	103.0 (3)
N3—Cu—N5	99.98 (16)	Cu—N4—C12	115.7 (3)
N4—Cu—N5	92.09 (16)	Cu—N4—C13	112.8 (3)
Cu—N1—C1	114.0 (3)	Cu—N5—C15	144.6 (4)
Cu—N1—C2	111.2 (3)	S—C15—N5	178.9 (4)

Data reduction: *NRCVAX DATRD2* (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES*.

The authors thank the National Science Council, Republic of China, for support under grants NSC87-2112-M007-009 and NSC87-2113-M007-041.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1047). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). **C54**, 1072–1074

**Bis[*N*-(2-bromo-4-methylphenyl)-naphthalidinato]copper(II)**

YALÇIN ELERMAN,<sup>a</sup> AYHAN ELMALI<sup>a</sup> AND SÜHEYLA ÖZBEY<sup>b</sup>

<sup>a</sup>Department of Physics Engineering, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and <sup>b</sup>Department of Physics Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey. E-mail: elmali@science.ankara.edu.tr

(Received 6 November 1997; accepted 24 February 1998)

**Abstract**

The title compound, bis[1-(2-bromo-4-methylphenyl)iminomethyl]-2-naphtholato-*N,O*]copper(II), [Cu(C<sub>18</sub>H<sub>13</sub>-BrNO)<sub>2</sub>], has crystallographic inversion symmetry. The Cu<sup>II</sup> ion shows a pseudo-square-planar coordination. The Cu—N and Cu—O distances are 1.990 (4) and 1.880 (4) Å, respectively. The Cu<sup>II</sup> ion is in an approximate octahedral environment if bromine is included in