

There are no unusual intermolecular contacts within the crystal lattice. The closest intermolecular contact between Cu atoms is 4.049 Å.

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## Structure of the Copper(II) Complex of the Macrocycle 1-Thia-4,7-diazacyclononane with Two Pendant Pyridine Arms

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**Abstract.** [4,7-Bis(2-pyridyl- $\kappa N$ -methyl)-1-thia-4,7-diazacyclononane- $\kappa^2 N, N'$ ,  $\kappa S$ ]copper(II) diperchlorate, [Cu(C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>S)](ClO<sub>4</sub>)<sub>2</sub>,  $M_r = 590.9$ , orthorhombic, *Pnma*,  $a = 17.30$  (1),  $b = 11.937$  (7),  $c = 11.179$  (3) Å,  $V = 2308.8$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.68$ ,  $D_x = 1.73$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 13.2$  cm<sup>-1</sup>,  $F(000) = 1212$ ,  $T = 294$  K,  $R = 0.068$  for 1568 observed reflections. The copper coordination is square pyramidal with the S atom in an axial site. The Cu—S bond [2.496 (8) Å] is rather short. The basal plane is trapezoidally distorted. The ligand adopts a strained conformation to match the coordination properties of Cu<sup>II</sup>.

**Introduction.** Recently we reported the structure of several complexes of the mixed donor atom macrocyclic ligand 1-thia-4,7-diazacyclononane (L) (Hoffmann, Steinhoff & Mattes, 1987; Hoffmann & Mattes, 1988; Hoffman, Hermes & Mattes, 1988; Hoffmann & Mattes, 1989). In the course of our studies derivatives of this ligand with pendant amine and pyridyl arms were prepared and their complex chemistry investigated. During the progress of our work the preparation of 4,7-bis(3-aminopropyl)-1-thia-4,7-diazacyclononane and its copper(II) complex (Fortier & McAuley, 1989), and the structure of the copper(II) complex of dimethyl(1-thia-4,7-diaza-4,7-cyclononane)diacetate (Lac<sub>2</sub>) (Craig, Parker &

Ferguson, 1989) have been reported. In this paper we describe the structure of the copper(II) complex of the macrocycle 1-thia-4,7-diazacyclononane with two pendant pyridine arms.

**Experimental.** The ligand 4,7-bis(2-methylpyridyl)-1-thia-4,7-diaza-cyclononane (Lpy<sub>2</sub>) was prepared by reaction of 1-thia-4,7-diazacyclononane dihydrobromide (Hoffmann, Steinhoff & Mattes, 1987) and 2-picoly chloride in sodium hydroxide solution, evaporation of the solvent under reduced pressure and extraction with chloroform and ligroin. Dark-blue prismatic crystals of [4,7-bis(2-methylpyridyl)-1-thia-4,7-diazacyclononane]copper(II) diperchlorate were grown by slow evaporation of an aqueous solution containing the ligand, CuCl<sub>2</sub> and NaClO<sub>4</sub>.

Crystal sealed in Lindemann capillary and centered on an Enraf-Nonius CAD-4 diffractometer. Crystal size 0.8 × 0.1 × 0.1 mm; graphite-monochromated Mo  $K\alpha$  radiation. Cell dimensions and orientation matrix determined from 25 reflections ( $19.6 \leq 2\theta \leq 28.5^\circ$ ); intensities measured with indices  $h$  0 to 21,  $k$  0 to 14 and  $4 \leq 2\theta \leq 54^\circ$ ;  $\omega$ -2 $\theta$  scans, three standard reflections monitored every four hours showed no decay. 2921 reflections measured, 2640 were unique and 1570 with  $I \geq 1.96\sigma(I)$  were labelled observed and used in structure solution and refinement. Data were corrected for Lorentz,

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}$
Cu(1)	1964 (1)	2500	1604 (1)	34 (1)
N(1)	2653 (3)	1150 (5)	1560 (5)	42 (2)
N(2)	1154 (3)	1357 (6)	2112 (7)	58 (2)
S(1)	1382 (2)	2500	-439 (3)	61 (1)
Cl(1)	4542 (2)	2500	8464 (3)	53 (1)
O(11)	5203 (5)	6641 (8)	2193 (12)	176 (6)
O(12)	6279 (4)	7500	1509 (7)	64 (3)
O(13)	5162 (6)	7500	470 (10)	259 (14)
Cl(2)	3333 (2)	2500	4432 (3)	59 (1)
O(14)	2558 (5)	2500	4098 (9)	105 (5)
O(15)	3472 (11)	2500	5556 (15)	335 (20)
O(16)	3694 (6)	1704 (12)	3930 (18)	298 (10)
C(1)	3332 (5)	1012 (7)	1027 (8)	55 (3)
C(2)	3732 (6)	34 (8)	1089 (10)	77 (4)
C(3)	3438 (7)	-840 (8)	1688 (11)	90 (5)
C(4)	2713 (6)	-731 (8)	2214 (10)	83 (4)
C(5)	2347 (5)	280 (6)	2152 (7)	54 (3)
Cl(6)	1586 (5)	489 (8)	2756 (9)	69 (3)
C(7)	753 (7)	900 (9)	1039 (11)	98 (5)
C(8)	809 (9)	1312 (14)	-44 (12)	163 (8)
C(9)	600 (7)	1882 (10)	2871 (12)	150 (6)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Cu(1)—N(1)	2.005 (8)	Cu(1)—N(2)	2.037 (8)
Cu(1)—S(1)	2.496 (8)	N(1)—C(1)	1.329 (10)
N(1)—C(5)	1.340 (10)	N(2)—C(6)	1.467 (12)
N(2)—C(7)	1.489 (15)	N(2)—C(9)	1.425 (14)
S(1)—C(8)	1.785 (17)	Cl(1)—O(11)	1.336 (12)
Cl(1)—O(12)	1.422 (8)	Cl(1)—O(13)	1.297 (12)
Cl(2)—O(14)	1.392 (10)	Cl(2)—O(15)	1.280 (17)
Cl(2)—O(16)	1.269 (16)	C(1)—C(2)	1.359 (13)
C(2)—C(3)	1.340 (15)	C(3)—C(4)	1.391 (17)
C(4)—C(5)	1.364 (13)	C(5)—C(6)	1.500 (13)
C(7)—C(8)	1.311 (19)	C(9)—C(9')	1.474 (24)
N(1)—Cu(1)—N(2)	83.0 (3)	N(1)—Cu(1)—S(1)	102.5 (2)
N(2)—Cu(1)—S(1)	88.7 (3)	N(1)—Cu(1)—N(1')	107.0 (4)
N(1)—Cu(1)—N(2')	162.6 (3)	N(2)—Cu(1)—N(2')	84.1 (4)
Cu(1)—N(1)—C(1)	129.5 (5)	Cu(1)—N(1)—C(5)	112.1 (5)
C(1)—N(1)—C(5)	118.4 (7)	Cu(1)—N(2)—C(6)	105.0 (5)
Cu(1)—N(2)—C(7)	109.9 (6)	C(6)—N(2)—C(7)	112.0 (7)
Cu(1)—N(2)—C(9)	109.5 (6)	C(6)—N(2)—C(9)	111.2 (8)
C(7)—N(2)—C(9)	109.1 (8)	Cu(1)—S(1)—C(8)	89.9 (5)
C(8)—S(1)—C(8')	105.2 (10)	O(11)—Cl(1)—O(11')	100.2 (10)
O(11)—Cl(1)—O(12)	110.0 (5)	O(11)—Cl(1)—O(13)	112.0 (6)
O(12)—Cl(1)—O(13)	112.0 (6)	O(14)—Cl(2)—O(15)	116.5 (10)
O(14)—Cl(2)—O(16)	110.9 (7)	O(15)—Cl(2)—O(16)	109.9 (10)
O(16)—Cl(2)—O(16')	97.0 (14)	N(1)—C(1)—C(2)	122.2 (8)
C(1)—C(2)—C(3)	120.1 (10)	C(2)—C(3)—C(4)	118.7 (9)
C(3)—C(4)—C(5)	118.7 (9)	N(1)—C(5)—C(4)	121.8 (8)
N(1)—C(5)—C(6)	116.1 (7)	C(4)—C(5)—C(6)	122.1 (8)
N(2)—C(6)—C(5)	110.1 (7)	N(2)—C(7)—C(8)	124.9 (11)
S(1)—C(8)—C(7)	124.6 (11)	N(2)—C(9)—C(9')	116.1 (6)

Symmetry operator for primed atoms:  $x, \frac{1}{2} - y, z$ .

polarization and absorption effects (azimuthal scans of nine reflections, max. and min. transmission factors 0.932 and 0.998). The systematic absences allow space groups  $Pn2_1a$  or  $Pnma$ . With  $Z = 4$  the latter would require the molecule to have mirror symme-

try. This seemed likely (see below) and was also indicated by the distribution of  $E^2$ . The structure was solved by direct methods and refined on  $F$  by routine Fourier and full-matrix least-squares methods, non-H atoms with anisotropic thermal parameters. Some H atoms were apparent in difference maps, but all were included as riding atoms in calculated positions with fixed isotropic  $U_{iso}$  of  $0.08 \text{\AA}^2$ . 167 variable parameters were used in the final cycles. Weighting scheme  $w^{-1} = \sigma(F_o) + 0.0003F_o^2$ .  $R = 0.068$ ,  $wR = 0.0793$ ;  $S = 2.51$ ,  $(\Delta/\sigma)_{max} = 0.12$ ; extreme values in final difference map  $+0.94 \text{ e \AA}^{-3}$  (close to a perchlorate oxygen) and  $-0.64 \text{ e \AA}^{-3}$ . Refinement in the non-centrosymmetric space group  $Pn2_1a$  was impossible due to strong correlations. Atomic coordinates and molecular parameters are given in Tables 1 and 2.\* Programs and scattering factors from *SHELXTL-Plus* (Sheldrick, 1989).

**Discussion.** The copper coordination (see Fig. 1) is best described as square pyramidal  $\text{CuN}_4\text{S}$  with the Cu atom lying out of the  $\text{N}_4$  plane  $0.22 \text{\AA}$  towards the S atom. Copper interacts weakly with a perchlorate ion [ $\text{Cu}\cdots\text{O}(14) = 2.955 (6) \text{\AA}$ ]. The basal plane is strongly trapezoidally distorted with parallel edges of  $2.73$  and  $3.23 \text{\AA}$ ; the latter edge is occupied by the pyridine moieties. The Cu—S bond [ $2.496 (8) \text{\AA}$ ] is one of the shortest so far observed for axial Cu—S bonds (Hartmann & Cooper, 1986). Structural data on  $\text{CuN}_4\text{S}$  systems are very rare. A second example is the structure of 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane copper perchlorate (Fortier & McAuley, 1989) with Cu—S =  $2.549 (2) \text{\AA}$ . In the related  $\text{Cu}^{\text{II}}$  complex  $[\text{CuLac}_2]^{2+}$ , the metal center is octahedrally coordinated with the

\* Lists of structure factors, thermal parameters and calculated H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53016 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

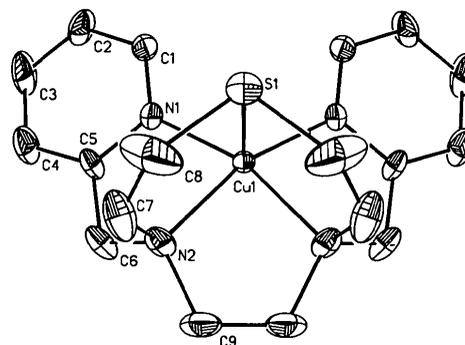


Fig. 1. Structure and atom-numbering scheme of the  $[\text{Cu}(\text{Lpy}_2)]^{2+}$  cation (ellipsoids at the 50% probability level).

axial bond length Cu—S = 2.635 (2) Å and Cu...O = 2.554 (4) Å. The short Cu—S bond distance in the present complex and the strong distortion of the basal plane show clearly that the ligand Lpy<sub>2</sub> adopts a rather strained conformation. [CuLpy<sub>2</sub>]<sup>2+</sup> has the crystallographically required mirror symmetry. But C(7), C(8), and to a much lesser extent C(9) are statistically disordered, manifested by large anisotropic thermal parameters approximately rectangular to their respective chelate rings. One has to assume, therefore, that the conformation of the chelate rings is either λλλ or δδδ. The macrocycle then adopts the [333] conformation. A similar situation is frequently observed for 1,4,7-triazacyclononane complexes (Drüeke, Wiegardt, Nuber & Weiss, 1989).

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## Synthesis and Structure of Aquabis(2,2'-bipyrimidine-*N,N'*)copper(II) Hexafluorophosphate Dihydrate

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**Abstract.** [Cu(C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)](PF<sub>6</sub>)<sub>2</sub>·2H<sub>2</sub>O, *M<sub>r</sub>* = 723.84, monoclinic, *I*2/*c*, *a* = 18.862 (2), *b* = 7.699 (1), *c* = 17.090 (2) Å, β = 95.44 (2)°, *V* = 2470.6 (5) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.95 g cm<sup>-3</sup>, *Mo Kα*, λ = 0.71069 Å, μ = 10.9 cm<sup>-1</sup>, *F*(000) = 1444, *T* = 298 K, final *R* = 0.039 and *wR* = 0.039 for 1833 reflections with *I* > 3σ(*I*). The compound is formed by [Cu(2,2'-bipyrimidine)<sub>2</sub>(H<sub>2</sub>O)]<sup>2+</sup> cationic units, uncoordinated PF<sub>6</sub><sup>-</sup> anions and crystallization water molecules. The Cu atom is coordinated to four N atoms of two bipyrimidine molecules and to an O atom of a water molecule in a distorted trigonal bipyramidal geometry. The bipyrimidine acts as a bidentate ligand.

**Introduction.** Polynuclear complexes, which contain ligands able to act as bridges between paramagnetic centers, have been studied during the last two decades in order to correlate structure and magnetic properties (Gatteschi, Kahn & Willett, 1985). The 2,2'-bipyrimidine ligand (bpm) is able to form magnetically coupled systems and, for this reason, particular attention was devoted to the synthesis of their metal complexes (Brewer & Sinn, 1985; Brewer, Murphy & Petersen, 1987; Kaim & Kholmann, 1987). Fe<sup>II</sup> and Cu<sup>II</sup> bipyrimidine (bpm) mixed complexes have been studied as models for binuclear metalloenzyme centers (Petty, Welch, Wilson, Bottomley & Kadish, 1980). We examined the