X-Ray Crystal Structure of [(*1SR,4RS,7RS,8SR,11RS,14RS*)-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane]thiocyanatocopper(II) Perchlorate Dihydrate†

Tian-Huey Lu
Department of Physics, National Tsing Hua University, Hsinchu Taiwan 30043, Republic of China
Der-Thin Wu and Chung-Sun Chung *
Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

The crystal structure of [CuL(SCN)]$ClO_4\cdot 2H_2O$ (L = *C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) has been determined by *X*-ray crystallography: space group $P2_1/n$, $a = 8.016(3)$, $b = 30.109(8)$, $c = 10.865(2)$ Å, $\beta = 104.93(2)°$, $Z = 4$, and $R = 0.084$ for 3 751 observed reflections [$I \geqslant 2.5\sigma(I)$]. The co-ordination about Cu^{II} is a distorted square pyramid with the macrocycle equatorial and the sulphur atom of the thiocyanato group axial. The four NH groups are on the same side of the CuN_4 plane and are close to the S-bonded thiocyanato group. The two six-membered chelate rings exhibit a stable chair form and the two five-membered rings an unstable twist form. Intermolecular hydrogen bonds play an important role.

The chemistry of macrocyclic compounds has undergone spectacular growth recently due to their distinctive co-ordination and biological significance. The extreme kinetic inertness and very high thermodynamic stability of tetra-amine macrocyclic ligand complexes are of particular stereochemical interest, since they greatly enhance the number of potentially isolable isomers.[1-4] Copper(II) salts react with *C*-*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (L) in basic solution to form initially a blue complex which is readily converted into a more stable red complex.[5] The crystal structure of the blue complex has been reported previously.[6] The present paper concerns the crystal structure of the red complex.

Experimental

The macrocyclic ligand L was prepared by using the procedure of Hay *et al.*[7] It (0.2 g, 0.66 mmol) was dissolved in distilled water (250 cm^3) with the aid of a few drops of 1.0 mol dm^{-3} $HClO_4$. A 0.2 mol dm^{-3} solution of $Cu(ClO_4)_2$ (3.8 cm^3, 0.73 mmol) was added, then the solution was made basic with 1.0 mol dm^{-3} NaOH (10 cm^3). The solution was filtered and evaporated to 100 cm^3. After addition of $NaClO_4$ (2 g), the solution was allowed to stand for 1 d, whereupon the red crystals were filtered off. This complex (0.3 g) and sodium thiocyanate (1.0 g) were dissolved in distilled water (150 cm^3) by stirring and heating the solution. Crystals of (red) [CuL(SCN)]ClO_4 were formed upon slow evaporation of the solution and were used for the *X*-ray structure determination.

X-Ray Crystallography.—Crystal data. [CuL(SCN)]$ClO_4\cdot 2H_2O$, $M = 541.63$, monoclinic, $a = 8.016(3)$, $b = 30.109(8)$, $c = 10.865(2)$ Å, $\beta = 104.93(2)°$ (from least-squares fit to CAD4 diffractometer co-ordinates of 25 reflections), $U =$ 2 533.9 Å^3, space group $P2_1/n$, $D_m = 1.42$ by flotation, $Z = 4$, $D_c = 1.42$ Mg m^{-3}, $T = 298(3)$ K, $\lambda(Cu\text{-}K_\alpha) = 1.5405$ Å, $\mu(Cu\text{-}K_\alpha) = 3.29$ mm^{-1}, $F(000) = 1\,145.6$.

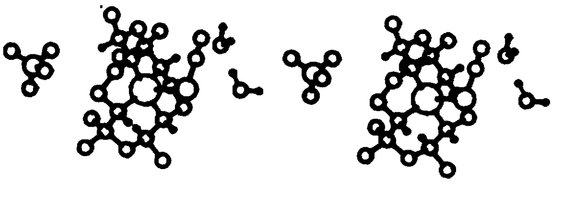

Figure 1. Stereoview of the molecule along an axis perpendicular to the macrocyclic plane

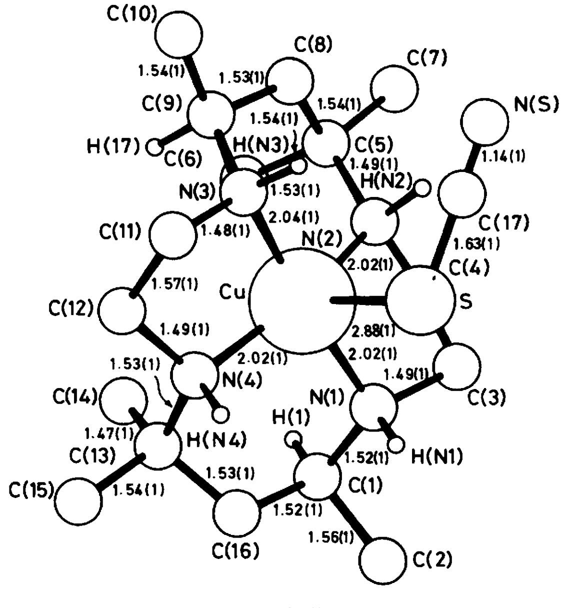

Figure 2. Molecular structure, excluding water and perchlorate ion, showing the bond lengths (Å) and their estimated errors

Data collection and processing. CAD4 diffractometer, ω—2θ scan with width = 2(0.8 + 0.15tanθ), scan speed = 1.0—6.7°

---

† *Supplementary data available* (No. SUP 56579, 6 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic parameters for $[CuL(SCN)]ClO_4\cdot2H_2O$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	0.098 73(13)	0.116 97(3)	0.163 81(9)
Cl	0.131 0(3)	0.316 33(8)	0.280 69(22)
S	−0.232 2(3)	0.073 45(9)	0.107 32(22)
O(1)	−0.041 4(8)	0.310 39(23)	0.222 4(6)
O(2)	0.230 9(10)	0.314 8(3)	0.193 9(7)
O(3)	0.161 3(13)	0.354 0(3)	0.350 7(10)
O(4)	0.188 9(11)	0.280 9(3)	0.365 5(7)
O(w1)	0.103 7(9)	−0.021 8(3)	0.385 3(6)
O(w2)	0.159 8(9)	−0.066 77(19)	0.180 5(5)
N(1)	0.158 1(7)	0.077 47(19)	0.033 4(5)
N(2)	0.239 1(7)	0.076 01(19)	0.301 2(5)
N(3)	−0.001 4(8)	0.152 22(19)	0.290 7(5)
N(4)	0.054 4(8)	0.170 69(18)	0.050 6(5)
N(S)	−0.177 5(11)	0.042 0(3)	0.354 5(7)
C(1)	0.281 2(10)	0.097 8(3)	−0.036 5(7)
C(2)	0.309 7(12)	0.064 7(3)	−0.139 4(8)
C(3)	0.217 3(11)	0.035 58(24)	0.103 5(7)
C(4)	0.336 4(11)	0.047 4(3)	0.234 0(7)
C(5)	0.336 9(10)	0.097 1(3)	0.422 2(7)
C(6)	0.472 3(11)	0.129 0(3)	0.396 2(8)
C(7)	0.427 2(12)	0.061 1(3)	0.517 7(7)
C(8)	0.205 7(10)	0.121 3(3)	0.480 5(7)
C(9)	0.120 0(10)	0.163 5(3)	0.415 1(7)
C(10)	0.022 0(14)	0.186 0(3)	0.503 2(8)
C(11)	−0.094 9(11)	0.189 6(3)	0.215 9(7)
C(12)	0.020 9(12)	0.208 1(3)	0.131 1(8)
C(13)	0.193 4(10)	0.181 0(3)	−0.018 5(7)
C(14)	0.360 8(11)	0.190 3(3)	0.072 0(8)
C(15)	0.134 9(12)	0.221 4(3)	−0.106 7(8)
C(16)	0.202 6(10)	0.140 5(3)	−0.101 3(7)
C(17)	−0.200 6(10)	0.054 1(3)	0.251 8(8)

Table 2. Other bond lengths (Å) and angles (°)

C(3)–C(4)	1.53(1)	C(4)–N(2)	1.48(1)
C(9)–N(3)	1.49(1)	Cl–O(1)	1.38(1)
Cl–O(2)	1.39(1)	Cl–O(3)	1.35(1)
Cl–O(4)	1.41(1)		
N(1)–Cu–N(3)	170.4(2)	N(2)–Cu–N(4)	156.1(3)
N(1)–Cu–N(2)	88.3(2)	Cu–N(2)–C(4)	105.2(4)
S–Cu–N(3)	83.5(1)	S–Cu–N(4)	102.8(1)
S–C(17)–N(S)	177.6(8)	C(1)–N(1)–C(3)	115.8(6)
C(4)–N(2)–C(5)	117.5(6)	C(9)–N(3)–C(11)	116.5(6)
Cu–N(4)–C(13)	115.7(4)	N(1)–C(1)–C(16)	109.0(6)
N(1)–C(3)–C(4)	108.5(6)	N(2)–C(4)–C(3)	108.1(6)
N(2)–C(5)–C(8)	107.7(6)	C(6)–C(5)–C(7)	109.4(7)
C(6)–C(5)–C(8)	111.8(7)	N(3)–C(9)–C(8)	110.0(6)
N(3)–C(9)–C(10)	110.2(7)	N(4)–C(13)–C(14)	111.5(6)
N(4)–C(13)–C(15)	108.8(6)	C(14)–C(13)–C(16)	111.7(7)
O(1)–Cl–O(2)	111.8(5)	O(1)–Cl–O(3)	112.4(5)
O(1)–Cl–O(4)	109.0(5)	O(2)–Cl–O(3)	111.0(6)
O(2)–Cl–O(4)	105.6(5)	O(3)–Cl–O(4)	106.6(6)

min^{-1}, graphite-monochromated Cu-K_α radiation. 4 308 Measured reflections ($1 \leqslant \theta \leqslant 65°$, −9,0,0 to 9,35,12) were reduced to 3 751 [$I \geqslant 2.5\sigma(I)$]. Three strong reflections (2,7,0; 3,2,$\bar{4}$; and $\bar{1}$,9,4) were remeasured every 2 h as a check on the crystal and instrument stability. Systematic extinctions (0*k*0, *k* odd; *h*0*l*, *h* + *l* odd) uniquely determined the space group $P2_1/n$. With azimuthal rotation[8] about three strong reflection axes, (0,0.4), ($\bar{2}$,0,10), and ($\bar{1}$,2,12), the averaged intensity curve was normalized for absorption correction by interpolation.

Structure analysis and refinement. The position of the Cu atom was determined by the heavy-atom method. Other atoms were located by successive Fourier difference syntheses and full-matrix least-squares fit. The function minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$, where weighting factors of $1/\sigma^2(F_o)$ were employed, $\sigma(F_o)$ being taken from counting statistics. Final values of R and R' $\{= [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}\}$, were 0.084 and 0.082 respectively. Absorption and Lorentz polarization corrections were applied. The range of standard deviations of bond lengths was from 0.005 to 0.011 Å, and that for bond angles from 0.2 to 0.8°.

Results and Discussion

The atomic parameters are listed in Table 1. Figure 1 shows a stereoscopic view of the molecule, Figure 2 the bond lengths, and Figure 3 the bond angles. Other relevant bond lengths and angles are listed in Table 2.

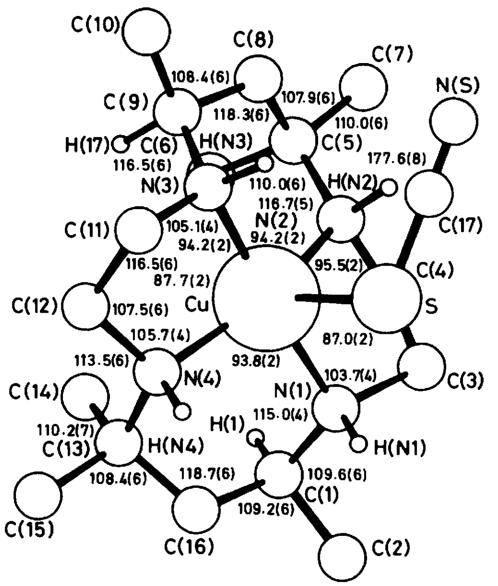

Figure 3. Molecular structure, excluding water and perchlorate ion, showing the bond angles (°) and their estimated errors

The copper(II) co-ordination is a buckled square pyramid with the macrocycle equatorial and S-bonded SCN^- axial as shown in Figure 4. The macrocyclic ligand is co-ordinated in a square-planar manner with slight tetrahedral distortions. All four hydrogens of the N–H groups are on the same side of the metal–nitrogen plane. This set of nitrogen and carbon configurations (1*SR*,4*RS*,7*RS*,8*SR*,11*RS*,14*RS*), designated as the *trans* I form by Bosnich *et al.*,[9] is also the thermodynamically most stable for $[NiL][ClO_4]_2$.[10]

The unidentate ligand SCN^- is S-bonded to the metal ion on the same side as the four hydrogens of the N–H groups. The four donor nitrogen atoms of the macrocyclic ligand form a buckled plane, the copper(II) lying 0.13 Å out of this plane toward the thiocyanato group. The perchlorate ion is not within bonding distance of the cation. Bonding of a sixth ligand in the other axial position does not occur even in the presence of a strongly co-ordinating unidentate ligand. As shown in Figure 4, the two bulky axial-methyl groups, $C(6)H_3$ and $C(14)H_3$, as well as the protons attached to C(1) and C(9), lie below the metal ion and hinder the axial position opposite the thiocyanato group, thus bonding of a sixth ligand in this position is impossible.

As shown in Figure 1, both six-membered rings are in the

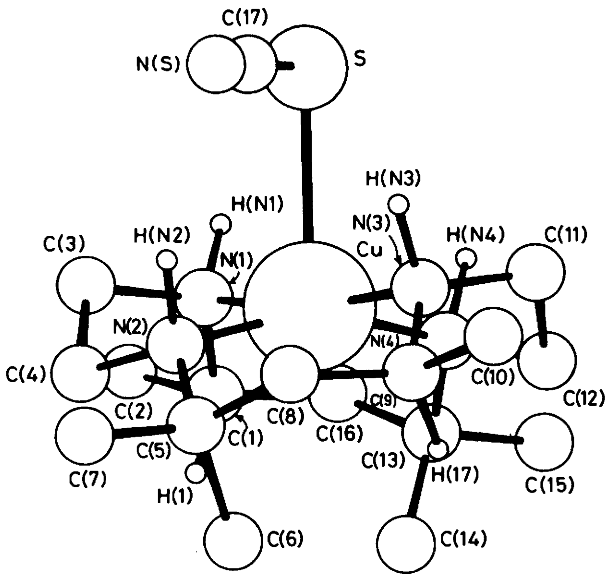

Figure 4. A view of the macrocyclic molecule, including the thiocyanate group, showing the approach of two methyl groups, $C(6)H_3$ and $C(14)H_3$

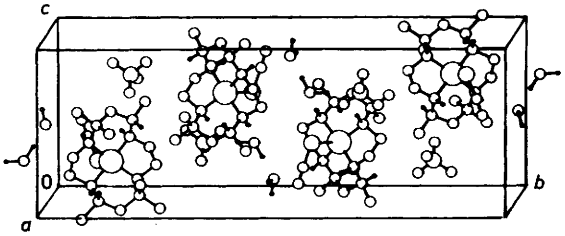

Figure 5. Packing of the four equivalent molecules in the unit cell

stable chair conformation and both five-membered rings have the unfavourable nitrogen configuration pertaining to the unstable twist form. The torsion angles of bond N(1)–C(3) to bond C(4)–N(2) and of N(3)–C(11) to C(12)–N(4) are both 58°. All the bond angles and distances are normal for planar tetra-amine 14-membered macrocyclic ligand complexes of copper(II), with alternating five- and six-membered chelate rings. The Cu–S bond distance [2.88(1) Å] is significantly smaller than that (3.27 Å) found in $[Cu(en)_2][SCN]_2$ (en = ethylenediamine)[11] and is comparable to that (3.0 Å) in $[Cu(py)_2(NCS)_2]$ (py = pyridine).[12]

With respect to the macrocyclic plane, the hydrogen atoms attached to C(1) and C(6) are opposite to the four amine hydrogens. Figure 5 shows the unit-cell packing. Intermolecular hydrogen bonds exist between nitrogen atom N(S) of the thiocyanato group and water molecule O(w1), 2.92 Å, and between O(w1) and O(w2), 2.73 Å; also between molecule O(w1) and N(S) at the position (0.1775, −0.420, 0.6455), 2.80 Å, and between amine group N(1) and water molecule O(w2) at (−0.1598, 0.0668, −0.1805), 2.99 Å. These hydrogen bonds play an important role in the crystal structure.

Acknowledgements

We thank Mr. Hsi-Chi Shan for help in figure plotting, Professor E. J. Gabe, Chemistry Division, National Research Council, Canada for providing the computing programs run on the VAX/VMS 11/750 computer, and are indebted to the National Science Council for a research grant and the use of the CAD4 diffractometer.

References

1 C-S. Lee, S-Y. Wu, and C-S. Chung, *Inorg. Chem.*, 1984, **23**, 1298.
2 T-H. Lu, T-J. Lee, B-F. Liang, and C-S. Chung, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2333.
3 T-H. Lu, T-J. Lee, and C-S. Chung, Abstracts of the Twelfth International Congress of Crystallography, Ottawa, Canada, 1981, C-231.
4 T-J. Lee, T-H. Lu, C-S. Chung, and T. Y. Lee, *Acta Crystallogr., Sect. C*, 1984, **40**, 70.
5 B-F. Liang, D. W. Margerum, and C-S. Chung, *Inorg. Chem.*, 1979, **18**, 2001.
6 H-R. Sheu, T-J. Lee, T-H. Lu, B-F. Liang, and C-S. Chung, *Proc. Natl. Sci. Counc. B, Rep. China*, 1983, **7**, 113.
7 R. W. Hay, G. A. Lawrance, and N. F. Curtis, *J. Chem. Soc., Perkin Trans. 1*, 1975, 591.
8 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
9 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
10 N. F. Curtis, D. A. Swann, and T. N. Waters, *J. Chem. Soc., Dalton Trans.*, 1973, 1963.
11 B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 254.
12 M. A. Porai-Koshits and G. N. Tishchenko, *Sov. Phys.-Crystallogr.*, 1959, **4**, 216.

Received 24*th September* 1985; *Paper* 5/1656