Crystal Structure of (Diperchlorato-*O,O'*)(1,4,7,11-tetraazacyclotetradecane-*N,N',N'',N'''*)copper(II)

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The macrocyclic ligand, 1,4,7,11-tetraazacyclotetradecane (isocyclam) exists as the isomer of 1,4,8,11-tetraazacyclotetradecane (cyclam). Comparison of cyclam and isocyclam should allow one to evaluate how the sequence of rings affects coordinating tendencies of cyclic ligands of the same size.¹⁻³ The crystal structure of Cu(cyclam)(ClO₄)₂ has been reported.⁴ In present study, we determined the crystal structure of Cu(isocyclam)(ClO₄)₂.

The ligand, 1,4,7,11-tetraazacyclotetradecane (Fig.1) was prepared according to the literature methods.⁵

Fig. 1 Chemical structure.

Fig. 2 The structure of the title compound excluding H-atoms with the atom labeling. Thermal ellipsoids are drawn at the 30% probability level.

Equimolar quantities of Cu(ClO₄)₂·6H₂O and the ligand were mixed in methanol solution to react for 3 h on a water bath (*ca.* 60°C). The resulting solution was dried by rotary evaporator and the single crystals were obtained from water.

Two molecules of different orientations exist and were superposed in an asymmetric unit. The complex (Fig. 2) is monomeric, with the two perchlorates coordinated axially in a tetragonally distorted octahedral arrangement around the Cu(II) ion. The Cu(II) is located at the center of inversion. The N2 and C3 atoms are disordered with equal occupancy and form five- and six-membered rings alternatively. The bond lengths and angles (Table 3) involving N2 and C3 disordered atoms are slightly abnormal from tetrahedral geometry. Within the isocyclam moiety the six- and five-membered chelate rings adopt a flattened chair and a *gauche*

Table 1 Crystal and experimental data

Formula: C ₁₀ H ₂₄ N ₄ Cu(ClO ₄) ₂	
Formula weight=462.77	
Crystal system: triclinic	Z=1
Space group: <i>P</i> $\bar{1}$	
<i>a</i> =7.8871(5) Å	α =64.706(10)°
<i>b</i> =8.2290(6) Å	β =64.826(13)°
<i>c</i> =8.5054(11) Å	γ =87.892(6)°
<i>V</i> =444.55(7) Å ³	
<i>D</i> _x =1.729 g/cm ³	
μ (Mo K α)=1.576 mm ⁻¹	
<i>T</i> =293 K	
Color: blue	
<i>F</i> (0 0 0)=239	
0.187×0.147×0.141 mm	
Radiation=Mo K α (λ =0.71073 Å)	
<i>R</i> =0.056 (on <i>F</i>)	
<i>R</i> _w =0.171 (on <i>I</i>)	
No. of reflections used=2587	
No. of parameters=153	
Goodness-of-fit=1.11	
Measurement: Enraf-Nonius CAD4	
Program system: NRCVAX	
Structure determination: heavy atom methods (SHELXS-86)	
Refinement: full-matrix (SHELXL-93)	

Table 2 Final coordinates and equivalent temperature factors ($\text{\AA}^2$)

Atom	x	y	z	U_{eq}
Cu1	0.0000	0.0000	0.5000	0.040(1)
N1	0.1796(5)	0.2190(5)	0.4194(5)	0.047(1)
N2*	0.0552(8)	0.1564(7)	0.2095(8)	0.038(1)
N21*	-0.0877(9)	0.0967(8)	0.2871(8)	0.044(1)
C1	0.2884(6)	0.3235(6)	0.2039(6)	0.051(1)
C2	0.1525(7)	0.3556(5)	0.1165(6)	0.057(1)
C3*	-0.1132(11)	0.1467(9)	0.1764(12)	0.055(2)
C31*	0.0647(11)	0.2205(10)	0.0912(10)	0.055(2)
C4	-0.1932(7)	-0.0489(7)	0.2738(8)	0.063(1)
C5	-0.3068(6)	-0.1714(7)	0.4866(7)	0.053(1)
C11	0.3139(2)	-0.2637(2)	0.3083(2)	0.059(1)
O1	0.4957(6)	-0.3066(6)	0.2330(7)	0.084(1)
O2	0.3131(9)	-0.1129(7)	0.3461(9)	0.107(2)
O3	0.2012(12)	-0.4128(9)	0.4821(13)	0.199(5)
O4	0.2234(13)	-0.2393(14)	0.1960(16)	0.173(4)

*Occupancy 0.5.

$$U_{\text{eq}} = \sum \sum U_{ij} a_i^* a_j^* (\mathbf{a}_i \mathbf{a}_j).$$

conformation, respectively. The geometrical configuration of the four chiral nitrogens is the same as that found in Ni(isocyclam) $^{2+}$ (planar form).⁶ There are four hydrogen bonds between imido hydrogens and O atoms of perchlorato groups to help stabilize the crystal structure. The N...O distances are between 3.143(7) and 3.315(9) $\text{\AA}$.

It is interesting to compare the copper geometry observed here with that found in the structure of Cu(cyclam)(ClO $_4$) $_2$.⁴ The overall geometry about Cu(II) ion in this title complex is similar to that in Cu(cyclam)(ClO $_4$) $_2$. The averaged Cu-N bond length, ranging from 2.008(4) to 2.088(6) $\text{\AA}$, is 2.047 $\text{\AA}$ and is longer than that found in [Cu(cyclam)(ClO $_4$)] (2.02 $\text{\AA}$).⁴ The sequence of the chelate-ring size in the isocyclam complex leads to great differences in the Cu-N bonds. The elongation in the axial Cu-O bonds (2.607(5) $\text{\AA}$) is ascribable to Jahn-Teller effect and similar to that of [Cu(cyclam)(ClO $_4$) $_2$] (2.57(4) $\text{\AA}$)⁴, but longer than that in diperchlorato (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (2.539(2) $\text{\AA}$).⁷ The hydrogens attached to N1, C1 and C5 were located and refined with isotropic temperature factors.

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Table 3 Bond distances ($\text{\AA}$) and angles ($^\circ$)

Cu1 - N1	2.008(4)	Cu1 - N21	2.046(6)
Cu1 - N2	2.088(6)	Cu1 - O2	2.607(5)
N1 - C5 ¹	1.478(5)	N1 - C1	1.485(5)
N2 - C3	1.482(5)	N2 - C2	1.540(5)
N21 - C31	1.481(6)	N21 - C4	1.552(5)
C1 - C2	1.503(7)	C2 - C31	1.466(5)
C3 - C4	1.471(5)	C4 - C5	1.491(7)
C11 - O4	1.366(6)	C11 - O3	1.376(7)
C11 - O1	1.402(4)	C11 - O2	1.409(4)

N1 - Cu1 - N1 ¹	180.0	N1 - Cu1 - N21 ¹	78.4(2)
N1 - Cu1 - N21	101.6(2)	N21 - Cu1 - N21 ¹	180.0
N1 - Cu1 - N2 ¹	101.4(2)	N1 - Cu1 - N2	78.6(2)
N2 - Cu1 - N2 ¹	180.0	O2 - Cu1 - N1	83.5(1)
O2 - Cu1 - N2	83.3(2)	O2 - Cu1 - N21	103.3(2)
O2 - Cu1 - O2	180.0	C5 ¹ - N1 - C1	111.7(3)
C5 ¹ - N1 - Cu1	112.4(3)	C1 - N1 - Cu1	111.8(3)
C3 - N2 - C2	111.2(5)	C3 - N2 - Cu1	113.3(4)
C2 - N2 - Cu1	114.7(3)	C31 - N21 - C4	109.9(5)
C31 - N21 - Cu1	113.6(5)	C4 - N21 - Cu1	116.1(4)
N1 - C1 - C2	109.1(3)	C31 - C2 - C1	125.8(5)
C1 - C2 - N2	98.7(4)	N2 - C3 - C4	105.6(5)
C2 - C31 - N21	106.1(5)	C3 - C4 - C5	128.4(5)
C5 - C4 - N21	98.6(4)	N1 ¹ - C5 - C4	109.6(3)
O4 - C11 - O3	104.1(8)	O4 - C11 - O1	113.5(4)
O3 - C11 - O1	107.6(4)	O4 - C11 - O2	110.1(4)
O3 - C11 - O2	107.8(5)	O1 - C11 - O2	113.2(3)

Symmetry code: 1, -x, -y, -z.

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References

1. L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, **18**, 438 (1979).
2. V. J. Thom, C. C. Fox, J. C. A. Boeyens and R. D. Hancock, *J. Am. Chem. Soc.*, **106**, 5947 (1984).
3. R. C. Luckay and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, **1991**, 1491.
4. P. A. Tasker and L. Sklar, *J. Cryst. Mol. Struct.*, **5**, 329 (1975).
5. J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, **96**, 2268 (1974).
6. J. C. A. Boeyens, *Acta Crystallogr.*, **C39**, 846 (1983).
7. A. Wang, T. J. Lee, T. Y. Chi, G. S. Liu and C. S. Chung, *Acta Crystallogr.*, **C52**, 806 (1996).

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