Crystal Structure of (Diperchlorato-*O,O'*)(1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene-*N,N',N'',N'''*)copper(II)

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Preparations and the ultraviolet spectra of the copper(II) and nickel(II) complexes of the tetraaza macrocyclic ligand, 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene have been reported.¹ The present paper concerns the crystal structure of the copper(II) complex of this ligand.

The ligand of 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared according to the literature methods.¹ Equimolar

quantities of copper(II) acetate and 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate were dispersed in methanol. The suspension was heated under reflux for *ca.* 3 h, and then cooled to room temperature. A crop of red crystals was obtained and filtered off.

The structure of the title complex has an octahedral environment around the metal center. The Cu(II) ion is located at the center of symmetry and is surrounded by the four N atoms of the macrocyclic tetradentate ligand equatorial and the O atoms of two perchlorato groups axial. The Cu–O distance is 2.795(4) Å and is longer

Fig. 1 Chemical structural diagram.

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

Table 1 Crystal and experimental data

Formula:	[Cu(C ₁₄ H ₂₈ N ₄)(ClO ₄) ₂]
Formula weight:	514.84
Crystal system:	monoclinic
Space group:	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i> :	2
<i>a</i> :	7.6481(6) Å
<i>b</i> :	9.8618(8) Å
<i>c</i> :	14.191(1) Å
β :	99.764(1)°
<i>V</i> :	1054.8(4) Å ³
<i>D</i> _x :	1.621 g/cm ³
μ (Mo K α):	1.337 mm ⁻¹
<i>T</i> :	293 K
Color:	red
<i>F</i> (0 0 0):	534
Crystal size:	0.19×0.20×0.71 mm
Radiation:	Mo K α (λ =0.71073 Å)
2 θ _{max} :	51.0°
No. of reflections measured:	1730
<i>R</i> :	0.049 (on <i>F</i>)
<i>R</i> _w :	0.113 (on <i>I</i>)
(Δ / σ) _{max} final cycle:	0.001
($\Delta\rho$) _{max} :	0.53 eÅ ⁻³
($\Delta\rho$) _{min} :	-0.31 eÅ ⁻³
No. of reflections used:	1551 (>2 σ (<i>I</i>))
No. of parameters:	134
Goodness-of-fit:	1.126
Measurement:	Siemens SMART CCD
Program system:	NRCVAX
Structure determination:	heavy atom methods (SHELXS-97)
Refinement:	full matrix (SHELXL-97)

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Table 2 Final coordinates and equivalent temperature factors(Å²)

Atom	x	y	z	U _{eq}
Cu1	0.0000	0.0000	0.0000	0.0374(3)
Cl1	0.1701(1)	0.2606(1)	-0.1748(1)	0.0521(4)
N1	0.1664(4)	0.0808(4)	0.1124(2)	0.0395(8)
N2	0.1714(4)	-0.1527(4)	0.0086(2)	0.0399(8)
O1	0.1973(5)	0.1373(4)	-0.1187(3)	0.0716(11)
O2	0.3263(5)	0.3384(5)	-0.1570(4)	0.0933(14)
O3	0.0258(5)	0.3324(5)	-0.1479(3)	0.0904(14)
O4	0.1276(7)	0.2279(5)	-0.2731(3)	0.1070(16)
C1	0.3419(6)	0.0228(5)	0.1025(4)	0.0594(14)
C2	0.3266(6)	-0.1271(5)	0.0845(3)	0.0511(12)
C3	0.1595(6)	-0.2655(5)	-0.0346(3)	0.0473(11)
C4	0.0037(7)	-0.2987(5)	-0.1102(4)	0.0608(14)
C5	0.1739(7)	0.2290(5)	0.1041(4)	0.0590(13)
C6	0.1216(8)	0.0419(7)	0.2069(4)	0.0721(16)
C7	0.2967(7)	-0.3759(6)	-0.0149(4)	0.0676(15)

$$U_{eq} = \sum \sum U_{ij} a_i^* a_j^* (a_i^* a_j)$$

than the usual Cu-O (axial) distances found in Cu(II) macrocyclic complexes.² The Cu(II) ion and four ligand N atoms are exactly coplanar, satisfying the space group symmetry. The conformations of the five- and six-membered rings in the title complex are similar to those found in the related macrocyclic cations, *trans*-diisothiocyanato (5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) cobalt(III)³ and (C-*meso*-5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) nickel(II).⁴ The five-membered rings are close to an envelope conformation; the six-membered rings are in a chair conformation.⁵ The Cu-N distances can be classified into two types. They are between metal and amine N atoms, and between metal and imine N atoms. The two types of bond distances are generally in agreement with the results of previous investigations.^{2,6,7} The complex has a 1*RS*, 8*SR* configuration for the two chiral N-atom centers. The crystal structure is stabilized by coordination and van der Waals forces. All the H-atoms were fixed geometrically and refined using constraint with isotropic temperature factors (0.07 Å²).

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Table 3 Bond distances(Å) and angles(°)

Cu1 - N2	1.987(3)	Cu1 - N1	2.027(3)
Cu1 - O1	2.795(4)	Cl1 - O2	1.406(4)
Cl1 - O4	1.415(4)	Cl1 - O3	1.417(4)
Cl1 - O1	1.449(4)	N1 - C5	1.468(6)
N1 - C1	1.487(6)	N1 - C6	1.491(6)
N2 - C3	1.266(6)	N2 - C2	1.482(5)
C1 - C2	1.501(7)	C3 - C4	1.497(7)
C3 - C7	1.505(6)	C4 - C5 ¹	1.538(7)
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N2 - Cu1 - N2 ¹	180.0	N2 - Cu1 - N1	86.0(1)
N2 - Cu1 - N1 ¹	94.0(1)	N1 - Cu1 - N1 ¹	180.0
N2 - Cu1 - O1	89.2(1)	N1 - Cu1 - O1	87.3(1)
O1 - Cu1 - O1 ¹	180.0	O2 - Cl1 - O4	110.3(3)
O2 - Cl1 - O3	110.8(3)	O4 - Cl1 - O3	108.7(3)
O2 - Cl1 - O1	108.8(3)	O4 - Cl1 - O1	109.7(3)
O3 - Cl1 - O1	108.5(2)	C5 - N1 - C1	109.1(4)
C5 - N1 - C6	110.3(4)	C1 - N1 - C6	109.5(4)
C5 - N1 - Cu1	110.9(3)	C1 - N1 - Cu1	103.4(3)
C6 - N1 - Cu1	113.4(3)	C3 - N2 - C2	119.0(4)
C3 - N2 - Cu1	130.0(3)	C2 - N2 - Cu1	110.8(3)
N1 - C1 - C2	110.4(4)	N2 - C2 - C1	108.8(4)
N2 - C3 - C4	121.5(4)	N2 - C3 - C7	123.6(4)
C4 - C3 - C7	114.9(4)	C3 - C4 - C5 ¹	117.7(4)
N1 - C5 - C4	113.1(4)		

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

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