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Structure of the Red Macrocyclic Ligand Complex Diaqua[(1*SR*,2*SR*,4*RS*,7*RS*,8*RS*,9*RS*,11*SR*,14*SR*)-2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane)]copper(II) Perchlorate*

By Tsong-Jen Lee, Tseng-Yuh Lee, Wen-Bii Juang and Chung-Sun Chung

National Tsing Hua University, Hsinchu, Taiwan 300

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Abstract. $[Cu(C_{18}H_{40}N_4)(H_2O)_2](ClO_4)_2$, $M_r = 611{\cdot}03$, monoclinic, $P2_1/c$, $a = 8{\cdot}201\,(1)$, $b = 16{\cdot}082\,(3)$, $c = 10{\cdot}432\,(1)$ Å, $\beta = 103{\cdot}30\,(1)°$, $U = 1338{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}515$, $D_m = 1{\cdot}50\,(3)$ Mg m^{-3} (by flotation in CCl_4/hexane mixture), Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}105$ mm^{-1}, $F(000) = 647$, $T = 296\,(4)$ K, $R(F) = 0{\cdot}069$ for 2828 observed reflections $[I > 3\sigma(I)]$. The coordination about Cu^{II} is a tetragonally distorted octahedron with the macrocycle equatorial and the two water O atoms axial. This complex is centrosymmetric and has the (1*SR*,4*RS*,8*RS*,11*SR*) configuration for the chiral N centers. The six-membered chelate rings exhibit a chair form and the five-membered rings take *gauche* forms.

Introduction. There are four asymmetric C centers in the macrocyclic ligand 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (represented by '*L*'). The structure of a Ni^{II} complex of one of the diastereomers of this ligand, (2*SR*,7*SR*,9*RS*,14*SR*)-*L*, has recently been reported by Ito, Ito & Toriumi (1981). The present paper concerns the crystal structure of the most stable Cu^{II} complex of another diastereomer of this ligand, (2*SR*,7*RS*,9*RS*,14*SR*)-*L*.

Experimental. 2,5,5,7,9,12,12,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate was prepared using the procedure described by Curtis (1974). 37 g of this compound was added to 300 ml of methanol and stirred until it was completely dissolved, then 10 g of sodium borohydride was added slowly. The solution was stirred continuously for 1 h until no more bubbles appeared. 5 g of sodium hydroxide was added to the solution, and refluxed for 20 min. After the solution had cooled to room temperature, an aqueous solution of sodium hydroxide (10 g NaOH in 200 ml H_2O) was added and stirred; a precipitate subsequently occurred. The precipitate, which is a mixture of isomers, was washed with cold water and dried. These isomers were separated by the partial-crystallization method: 30 g of the product was dissolved in 300 ml methanol, then 200 ml of water was added and stirred; white crystals of (2*SR*,7*RS*,9*RS*,14*SR*)-*L* were obtained and recrystallized in methanol solution.

Copper(II) perchlorate (1·4 g) and (2*SR*,7*RS*,9*RS*,14*SR*)-*L* were mixed in 100 ml 50% (by weight) methanol–water mixture, heated to 313 K, and a solution of sodium hydroxide (10 ml of 1·0 *M*) rapidly added. After 2 h activated C was added, and the mixture brought to boiling and filtered using a filter aid. Sodium perchlorate (5 g) was added and the solution cooled. The red crystals were filtered, washed with cold water, recrystallized from 50% (by weight) methanol–water mixture, dried and used in the crystal structure analysis (Juang, 1984).

Table 1. *Experimental data and structure-refinement parameters*

Crystal size	Sphere 0·5 mm in diameter
Diffractometer and data collection technique used	ω–2θ scan; four circle diffractometer (Nonius CAD-4); graphite monochromator
Scan width	$(1{\cdot}6 + 0{\cdot}7\tan\theta)°$; starting 0·8° below $K\alpha_1$ and 0·8° above $K\alpha_2$
Number and θ range used for measuring lattice parameters	25 reflections with $26° < 2\theta < 42°$
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Transmission factor	0·576
Maximum value of $(\sin\theta)/\lambda$ reached in intensity measurements	0·7035 Å^{-1}
Range of h, k, l	0,0,−14 to 11,22,14
Standard reflections and their intensity variation	3 (< 3%)
Number of reflections measured	4579 $[I > 3\sigma(I)]$
Number of unique reflections	2828
Method used to solve the structure	Patterson and Fourier methods
Maximum height in final difference Fourier synthesis	0·81 e Å^{-3}
Parameters refined	
Non-H atoms	168 (coordinates, occupancies and anisotropic temperature factors)
H atoms	88 (coordinates and isotropic temperature factors)
Atomic scattering factors, f' and f''	*International Tables for X-ray Crystallography* (1974)
Number of reflections per parameter	11
R and wR $[w = 1/\sigma^2(F)]$	0·069 and 0·078
S	0·758
$R_{int}(I)$	0·012 for 186 reflections
$(\Delta/\sigma)_{max}$	0·76
Program used	Tsing Hua *XTAL* package* and *ORTEP*

* The user's guide and source program of this program package can be obtained from Professor T. Y. Lee, Computer Center, National Tsing Hua University, Taiwan.

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Experimental data and structure solution parameters together with the standard refinement procedures are listed in Table 1. H atoms of amines and water molecules were located on difference Fourier maps. Positions of other H atoms were calculated theoretically and treated in the same manner as in our previous work (Lee, Lu, Chung & Lee, 1984). The final $R(F) = 0{\cdot}069$.

Table 2. *Atomic positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j b_{ij}$, where the $\mathbf{a}_i$'s are the lattice vectors in direct space.

	x	y	z	B_{eq}(Å^2)
Cu(1)	0·0000	0·0000	0·0000	1·93 (5)
N(1)	0·0534 (4)	−0·0011 (2)	0·2004 (3)	2·3 (2)
N(2)	0·1066 (4)	−0·1125 (2)	−0·0154 (4)	2·5 (2)
Cl(1)	−0·2537 (2)	−0·3084 (1)	−0·1183 (2)	4·8 (1)
O(1)	−0·3551 (10)	−0·3365 (5)	−0·0338 (8)	13·5 (9)
O(2)	−0·2502 (12)	−0·3782 (5)	−0·1943 (8)	16 (1)
O(3)	−0·1023 (7)	−0·2864 (4)	−0·0378 (9)	12·7 (7)
O(4)	−0·3430 (11)	−0·2393 (4)	−0·1735 (7)	12·8 (8)
O(5)	0·2540 (5)	−0·1107 (3)	0·0312 (5)	5·9 (4)
C(1)	0·0303 (6)	0·0860 (3)	0·2423 (5)	2·8 (3)
C(2)	0·2120 (6)	−0·0419 (3)	0·2775 (4)	2·5 (3)
C(3)	0·2187 (6)	−0·1302 (3)	0·2245 (5)	2·8 (3)
C(4)	0·2546 (6)	−0·1407 (3)	0·0894 (5)	3·0 (3)
C(5)	0·1260 (6)	−0·1229 (3)	−0·1537 (4)	2·9 (3)
C(6)	0·2047 (8)	−0·0483 (4)	0·4231 (5)	4·0 (4)
C(7)	0·3648 (6)	0·0088 (3)	0·2653 (5)	3·4 (4)
C(8)	0·2989 (8)	−0·2316 (3)	0·0692 (6)	4·1 (4)
C(9)	0·2864 (7)	−0·0825 (4)	0·1749 (6)	3·9 (4)

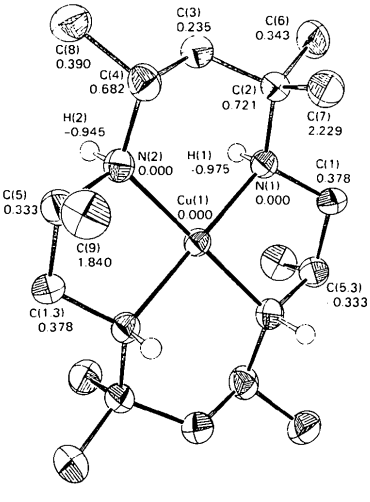

Fig. 1. Perspective view showing the atom-numbering scheme and displacements (Å) of atoms from the least-squares plane of Cu(1),N(1),N(2). E.s.d.'s are estimated to be in the range 0·005 to 0·006 Å. Thermal ellipsoids are depicted at the 50% probability level.

Table 3. *Bond distances* (Å) *and bond angles* (°)

Cu(1)–N(1)	2·035 (3)	C(2)–C(7)	1·524 (7)
Cu(1)–N(2)	2·031 (4)	C(3)–C(4)	1·514 (7)
Cu–O(5)	2·815 (5)	C(4)–C(8)	1·532 (7)
N(1)–C(1)	1·492 (6)	C(5)–C(9)	1·528 (8)
N(1)–C(2)	1·513 (5)	C(5)–C(1^{ii})	1·518 (6)
N(2)–C(4)	1·505 (5)	Cl(1)–O(1)	1·418 (10)
N(2)–C(5)	1·498 (6)	Cl(1)–O(2)	1·379 (8)
C(5^{ii})–C(1)	1·518 (6)	Cl(1)–O(3)	1·376 (6)
C(2)–C(3)	1·531 (7)	Cl(1)–O(4)	1·382 (7)
C(2)–C(6)	1·537 (7)		
N(1)–Cu(1)–N(2)	94·5 (1)	C(8)–C(4)–N(2)	111·4 (4)
N(2)–Cu(1)–N(1^{ii})	85·5 (1)	C(4)–N(2)–Cu(1)	120·1 (3)
C(3)–C(4)–N(2)	110·2 (4)	C(4)–N(2)–C(5)	114·8 (4)
C(3)–C(4)–C(8)	109·7 (4)	C(5)–N(2)–Cu(1)	108·6 (3)
C(5^{ii})–C(1)–N(1)	109·6 (3)	N(2)–C(5)–C(9)	112·2 (4)
C(1)–N(1)–C(2)	113·8 (3)	N(2)–C(5)–C(1^{ii})	106·3 (4)
C(1)–N(1)–Cu(1)	106·3 (3)	C(9)–C(5)–C(1^{ii})	112·3 (4)
C(2)–N(1)–Cu(1)	120·4 (3)	O(1)–Cl(1)–O(2)	101·0 (5)
N(1)–C(2)–C(3)	107·9 (3)	O(1)–Cl(1)–O(3)	106·2 (5)
N(1)–C(2)–C(6)	109·3 (4)	O(1)–Cl(1)–O(4)	100·7 (5)
N(1)–C(2)–C(7)	110·3 (4)	O(2)–Cl(1)–O(3)	115·2 (5)
C(3)–C(2)–C(6)	107·9 (4)	O(2)–Cl(1)–O(4)	119·6 (4)
C(3)–C(2)–C(7)	111·6 (4)	O(3)–Cl(1)–O(4)	111·4 (4)
C(6)–C(2)–C(7)	109·8 (4)	O(5)–Cu(1)–N(1)	82·3 (1)
C(2)–C(3)–C(4)	118·1 (4)	O(5)–Cu(1)–N(2)	77·8 (1)

Symmetry code: (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Discussion. The atomic coordinates and isotropic temperature factors are listed in Table 2.* A perspective view of the molecule with the numbering scheme and deviations from the plane through Cu—N(1)—N(2) are shown in Fig. 1. The bond distances and angles are listed in Table 3.

This compound is a six-coordinate octahedral complex, with the macrocycle equatorial and two axial water O atoms in the *trans* axial positions; it belongs to the '4+2' type (Lee, Lu, Chung & Lee, 1984; Pavkovic & Brown, 1982). The 14-membered rings have the zigzag shape and the four N chiral centers are in the (1*SR*,4*RS*,8*RS*,11*SR*) configuration, with two NH groups on one side of the coordination plane and the other two on the other side; the two methyl groups on the five-membered rings are disposed on opposite sides of the macrocyclic plane, and have an axial orientation. Each of these two methyl groups is *trans* to the H atom of the neighboring amine group. In contrast, in the Ni^{II} complex of the diastereomer, (2*SR*,7*SR*,9*RS*,14*SR*)-*L*, the macrocyclic ligand is in a basket conformation and the four NH groups and two methyl groups on the five-membered rings are all on the same side of the macrocyclic plane (Ito *et al.*, 1981). For the title complex, four of the six methyl groups on the six-membered rings are in the equatorial plane and lie away from the metal-ion center. The ligand is in its most stable, planar configuration with both six-membered rings in a chair form and both five-membered rings in a *gauche* form.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42379 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Possible hydrogen bonds*

Donor (D)		Acceptor (A)	$D\cdots A$ (Å)	D—H$\cdots A$ (°)
N(1)	H(1)	O(5)	3·245 (5)	121·9 (2)
N(2)	H(2)	O(5)	3·105 (5)	118·3 (2)
O(5)	H(4)	O(4)	2·942 (8)	159·6 (4)
O(5)	H(3)	O(2^{i})	2·861 (10)	138·8 (3)

Symmetry code: (i) $-x, -y, -z$.

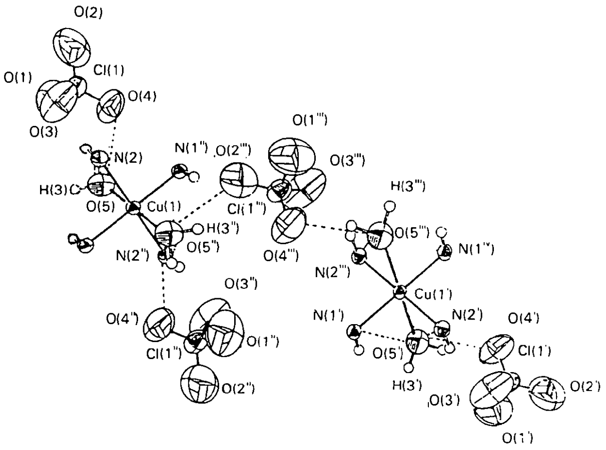

Fig. 2. *ORTEP* drawing (Johnson, 1976) of $[Cu(Me_8[14]aneN_4)(H_2O)_2](ClO_4)_2$ illustrating the intramolecular and intermolecular hydrogen bonds (broken lines, see Table 4) for the perchlorate ions, water molecules and macrocyclic ligands. Symmetry code: (i) $-x, -y, -z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-x, \frac{1}{2}-y, \frac{1}{2}+z$.

The coordination bond lengths in the equatorial plane, 2·035 (3) and 2·031 (4) Å, are longer than those of the Ni complex of the same ligand and consistent with those of $Cu(Et_4Me_2[14]aneN_4)(ClO_4)_2$ (Lee, Lee, Juang & Chung, 1985). The Cu—O(axial) distance, 2·815 (5) Å, is longer than the typical value for Cu^{II} complexes and is significantly longer than the Cu—N(equatorial) distances. Each of these water molecules forms intramolecular hydrogen bonds with one H of an amino group and one O of the perchlorate ion, as well as an intermolecular hydrogen bond with the perchlorate O of a neighboring molecule. The possible hydrogen-bond distances and angles are listed in Table 4 and shown in Fig. 2.

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Structures of Monomethylcarbonato- and Hydrogencarbonato(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)cadmium(II) Perchlorate, $[Cd(O_2COCH_3)(Me_4[14]aneN_4)](ClO_4)$ (I) and $[Cd(O_2COH)(Me_4[14]aneN_4)](ClO_4)$ (II)

By Haruko Ito* and Tasuku Ito†

Department of Applied Molecular Science, Institute for Molecular Science, Okazaki National Research Institutes, Okazaki 444, *Japan*

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Abstract. Compound (I), $[Cd(C_{14}H_{32}N_4)(C_2H_3O_3)]ClO_4$, $M_r = 543·33$, monoclinic, Pa, $a = 15·926$ (2), $b = 8·414$ (1), $c = 8·497$ (1) Å, $\beta = 98·21$ (1)°, $V = 1126·9$ (3) Å^3, $Z = 2$, $D_m = 1·56$ (by flotation in CCl_4/hexane, at 293 K),‡ $D_x = 1·60$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 1·13$ mm^{-1}, $F(000) = 560$, $T = 184$ K, final $R = 0·022$ and $wR = 0·029$ for 2566 observed reflections; compound (II), $[Cd(C_{14}H_{32}N_4)(CHO_3)]$-

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* Aichi Kyoiku University, Kariya 448, Japan.

† To whom correspondence should be addressed.

‡ At 293 K, $a = 16·049$ (2), $b = 8·462$ (1), $c = 8·549$ (1) Å, $D_x = 1·57$ Mg m^{-3}.

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