there is hydrogen bonding in the **c** direction between N(1) of one molecule and Cl(1) of a molecule related by the 2_1 axis at $x = \frac{1}{2}$, $z = \frac{1}{2}$. In this arrangement, however, hydrogen bonding cannot occur to the Cl(1) atoms in both molecules, above and below the first, at the same time. This means a choice has to be made and gives rise to the disorder in the ethylenediamine ring noted above.

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Structure of the Red Isomer of Aqua[(1SR,4RS,7RS,8SR,11RS,14RS)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) Perchlorate

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Abstract. $[Cu(H_2O)(C_{16}H_{36}N_4)](ClO_4)_2$, $M_r = 564 \cdot 5$, monoclinic, $C2/c$, $a = 11 \cdot 993$ (1), $b = 13 \cdot 057$ (2), $c = 15 \cdot 969$ (4) Å, $\beta = 92 \cdot 37$ (1)°, $V = 2498 \cdot 5$ (2) Å³, $Z = 4$, $D_x = 1 \cdot 50$, $D_m = 1 \cdot 49$ Mg m⁻³, $\lambda(Mo \, K\alpha) = 0 \cdot 7093$ Å, $\mu = 1 \cdot 14$ mm⁻¹, $F(000) = 1187 \cdot 8$, $T = 298$ K, $R = 0 \cdot 056$ for 3338 observed reflections. Cu^{II} is in a slightly distorted square pyramid with the macrocycle equatorial and the O atom of the aqua group axial. The four donor N atoms of the macrocyclic ligand form a buckled plane. The aqua group and the four H atoms of the NH groups are on the same side of this plane, and Cu^{II} is 0·10 Å out of this plane toward the aqua group. The configuration of the four chiral nitrogen centers is 1SR, 4RS, 8SR and 11RS. The ligand is in a planar coordination with both six-membered chelate rings in a stable chair form and both five-membered chelate rings in an unstable twist form. The two methyl groups attached to the asymmetric C atoms are equatorial.

Introduction. Copper(II) forms blue and red complexes with *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tet b). The blue complex is stable kinetically in acid solutions and it is converted at high pH to the thermodynamically more stable red one (Liang, Margerum & Chung, 1979). In a previous paper (Sheu, Lee, Lu, Liang & Chung, 1983) we have reported the X-ray structure analysis of the blue complex, blue-$[Cu(tet \, b)(H_2O)](ClO_4)_2$. The present paper concerns the structure of the red isomer, red-$[Cu(tet \, b)(H_2O)](ClO_4)_2$. Detailed structures of these red and blue isomers are compared.

Experimental. The macrocyclic ligand tet b was prepared using the procedures reported by Hay, Lawrance & Curtis (1975). Tet b (0·2 g, 0·66 mmol) was dissolved in 250 ml distilled water with the aid of a few drops of 1·0 *M* HClO₄. A 0·2 *M* solution of $Cu(ClO_4)_2.6H_2O$ (3·8 ml, 0·73 mmol) was added, then

the solution was made basic with 10 ml 1·0 M NaOH. The solution was filtered and evaporated to 100 ml. After the addition of NaClO$_4$ (2 g) the solution was allowed to stand for one day, then the red crystals were filtered off. The crystals were washed with 5 ml cold water, 10 ml ethanol and then recrystallized from HClO$_4$(10^{-4} M). A crystal of 0·6 × 0·7 × 0·8 mm was cut from the red thin plates. CAD-4 diffractometer, setting angles for 25 reflections (20 ≤ 2θ ≤ 28°) used to determine unit-cell constants and crystal orientation. D_m by flotation method. Max. $\sin\theta/\lambda = 0.81$ Å^{-1} ($-19 \leq h \leq 18$, $0 \leq k \leq 20$, $0 \leq l \leq 24$), ω–2θ scan, width $= 2 \times (0.75 + 0.35 \tan\theta)°$. Three standard reflections 283, 372, 556 monitored every 300 reflections, varied within $2\sigma(I)$. 5499 reflections collected, 3338 observed with $I \geq 2.5\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections $\overline{2}20$, $\overline{4}61$, $\overline{6}82$ (North, Phillips & Mathews, 1968). Patterson and difference Fourier syntheses used to locate heavy Cu atom and other atoms including H atoms, respectively. Function minimized in full-matrix least-squares fit $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ from counting statistics. 154 parameters with anisotropic temperature factors for non-H atoms, isotropic for H. $R = 0.056$, $wR = 0.051$, $S = 5.50$; $(\Delta/\sigma)_{max} = 0.4$ in final cycle. $(\Delta\rho)_{max}$ 0·96 e Å^{-3} (around perchlorate ion). Secondary-extinction coefficient 1·08 (length in μm).

Discussion. The molecule possesses a C_2 axis along the Cu—O(W) bond. The atomic coordinates and isotropic temperature factors for non-H atoms are listed in Table 1. Fig. 1 shows a stereoview of the packing. A view along the b axis of the complex ion with the numbering scheme showing bond lengths and bond angles is shown in Fig. 2. Some other relevant bond distances and angles are listed in Table 2.*

This complex ion has a twofold rotation axis and belongs to the C_2 point group. Cu^{II} is in a slightly distorted square pyramid with the macrocycle equatorial and the O atom of the aqua group axial. The four donor N atoms of the macrocyclic ligand form a buckled plane. The aqua group and the four H atoms of the NH groups are on the same side of this plane, and Cu^{II} is 0·10 Å out of this plane toward the aqua group. The configuration of the four chiral nitrogen centers is 1SR, 4RS, 8SR and 11RS, which is also found in the thermodynamically most stable nickel(II) complex of this ligand (Curtis, Swann & Waters, 1973). The ligand is in a planar coordination with the six-membered chelate rings in a stable chair form and the five-membered ones in an unstable twist form. The two

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*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes for atoms around Cu have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42806 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
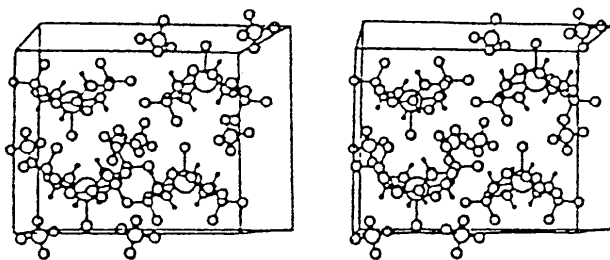
Table 1. *Atomic coordinates and isotropic thermal parameters*

E.s.d.'s refer to the last digit.

	x	y	z	B_{iso}*(Å²)
Cu	0	0.28299 (5)	$\frac{1}{4}$	2.985 (24)
O(W)	0	0.4694 (4)	$\frac{1}{4}$	9.5 (3)
N(1)	0.16606 (22)	0.29735 (22)	0.25143 (17)	3.50 (12)
N(2)	0.01211 (23)	0.25567 (20)	0.37275 (16)	3.36 (12)
C(1)	0.3542 (3)	0.2338 (5)	0.2118 (3)	6.9 (3)
C(2)	0.2272 (3)	0.2142 (3)	0.20750 (23)	4.32 (17)
C(3)	0.1979 (3)	0.3127 (3)	0.34156 (24)	4.67 (19)
C(4)	0.1322 (3)	0.2389 (3)	0.39419 (23)	4.37 (18)
C(5)	−0.0657 (3)	0.1759 (3)	0.40523 (22)	4.18 (17)
C(6)	−0.0414 (4)	0.0715 (3)	0.3679 (3)	5.56 (23)
C(7)	−0.0512 (4)	0.1697 (4)	0.5002 (3)	6.2 (3)
C(8)	0.1856 (3)	0.2094 (3)	0.11633 (22)	4.28 (17)
Cl	−0.16476 (11)	0.51960 (9)	0.42513 (8)	5.83 (6)
O(1)	−0.2286 (5)	0.5342 (4)	0.4947 (3)	14.2 (3)
O(2)	−0.2400 (3)	0.4915 (3)	0.35776 (20)	8.44 (19)
O(3)	−0.0906 (4)	0.4450 (3)	0.4403 (4)	18.4 (4)
O(4)	−0.1178 (3)	0.6131 (3)	0.4120 (3)	12.2 (3)

* B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s, not shown in Fig. 2*

Cu—O(W)	2.434 (4)	N(1)—H(5)	0.951 (3)
N(2)—H(10)	1.021 (3)	C(5)—C(6)	1.522 (6)
O(W)—H(W)	0.995 (3)	Cl—O(1)	1.388 (3)
Cl—O(2)	1.424 (1)	Cl—O(3)	1.334 (1)
Cl—O(4)	1.364 (1)		

O(W)—Cu—N(1)	84.6 (1)	O(W)—Cu—N(2)	100.3 (1)
C(6)—C(5)—N(2)	110.7 (3)	C(7)—C(5)—C(6)	109.1 (4)
C(8)—C(5)—C(6)	111.2 (3)	N(1)—Cu—N(1)A	169.2 (1)
N(2)—Cu—N(2)A	159.4 (1)	O(1)—Cl—O(2)	106.7 (3)
O(1)—Cl—O(3)	109.9 (4)	O(1)—Cl—O(4)	104.2 (3)
O(2)—Cl—O(3)	110.3 (2)	O(2)—Cl—O(4)	111.6 (2)
O(3)—Cl—O(4)	113.9 (3)	H(W)—O(W)—H(W)	102.6 (4)

methyl groups attached to the asymmetric C atoms are equatorial. Bond angles and distances of this complex are normal.

The perchlorate ions are not within the bonding distance of the cation. As shown in Fig. 3, all C atoms lie on the lower side of the N$_4$ plane, while the Cu atom deviates slightly upward from the plane by 0·10 Å toward the water group. Bonding of a sixth ligand in the other axial position does not occur even in the presence of a strong coordinating monodentate ligand. As shown in Fig. 3, the two bulky axial methyl groups, C(6)H$_3$, as well as the protons attached to C(2), lie below the metal ion and hinder the axial position opposite the water group. Thus the coordination of a sixth ligand to this axial position is inhibited sterically by the 'picket fence'. The hydrogen-bond lengths of N(2)—H(10)$\cdots$O(3) and N(1)—H(5)$\cdots$O(W) are 2·99 (1) and 3·00 (1) Å respectively, and their bond angles are 170·1 (2) and 113·1 (2)° respectively. These hydrogen bonds contribute to the interactions between the complex cation, the aqua and perchlorate groups.

Fig. 1. A stereoview down c of the packing of molecules, excluding H atoms on methyl groups in the unit cell.
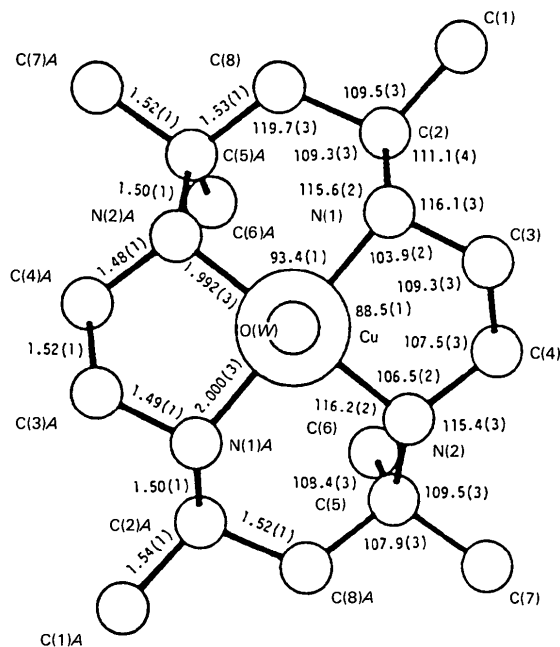

Fig. 2. Numbering scheme of the macrocyclic ligand, showing the bond distances (Å) and bond angles (°).
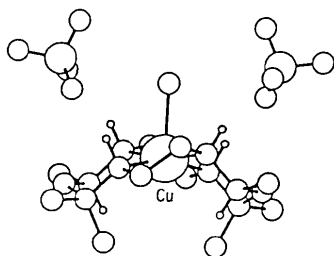

Fig. 3. Relation of the water molecule with the perchlorate ions and the macrocyclic ligand, showing the closeness of the two methyl groups C(6) and C(6)A.

Tet b forms blue and red complexes with copper(II) (Chung & Huang, 1976; Liang & Chung, 1979). The red isomer is more stable than the blue species (Liang & Chung, 1980). Comparing the molecular structures of these red and blue isomeric crystals, blue-[Cu(tet b)-(H$_2$O)](ClO$_4$)$_2$ and red-[Cu(tet b)(H$_2$O)](ClO$_4$)$_2$, we found the following significant results. (1) The structures of both complexes consist of five-coordinate copper(II) monomers with N$_4$O ligand donor sets. (2) For the red isomer, the macrocyclic tetraamine is in a planar coordination; for the blue isomer, the macrocyclic tetraamine is in a folded coordination. (3) The red complex has the (1SR,4RS,8SR,11RS) configuration of the chiral nitrogen centers while the blue complex has the (1RS,4RS,8RS,11RS) configuration of the nitrogen centers. (4) For the red complex, the coordination about the Cu^{II} atom is a distorted square pyramid with the aqua group axial; for the blue complex, the coordination is trigonal bipyramidal with the aqua group equatorial. The bond distance (2·43 Å) of Cu–O(W) in the red isomer is longer than that (2·23 Å) in the blue isomer. (5) For the red isomer, the two five-membered rings take an unstable twist form; for the blue isomer, they exhibit a stable gauche form. Both compounds have their six-membered rings in a stable chair form. (6) Both molecules have a C$_2$ axis. (7) The amine groups in both isomers form hydrogen bonds with the O atoms of the perchlorate ions, regardless of their configurations.

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