

Dichloro(ethylenediamine)copper(II)

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Abstract. $[\text{CuCl}_2(\text{C}_2\text{H}_8\text{N}_2)]$, $M_r = 194.55$, monoclinic, $P2_1/m$, $a = 8.219$ (2), $b = 5.747$ (1), $c = 6.776$ (1) Å, $\beta = 93.72$ (2)°, $V = 319.39$ Å³, $Z = 2$, $D_m = 2.03$ (1), $D_x = 2.02$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 105.58$ cm⁻¹, $F(000) = 194$, $T = 295$ K, $R = 0.0429$ for 812 unique reflections. The environment about the copper atom is square planar with the ethylenediamine ligand disordered between the λ and δ configurations. There are chlorine atoms from adjacent molecules above and below the square plane almost directly over the copper atom. These Cu–Cl distances are much longer than those in the plane [2.887 (2) Å vs 2.286 (2), 2.301 (2) Å].

Introduction. We wished to use dichloro(ethylenediamine)copper(II) as an agent in certain medical studies we are undertaking and it was necessary to have detailed structural information on the molecule. A brief note about the structure was published some time ago (Chiesi, Gaetani, Mangia, Nardelli & Pelizzi, 1969) but no details of the structure have been published. Although we anticipated a molecular structure akin to dichloro(ethylenediamine)platinum(II) (Iball, MacDougall & Scrimgeour, 1975), the difference in cell symmetry suggested that intermolecular interactions were different. Thus we have undertaken a redetermination of the structure.

Experimental. Cu(en)Cl_2 prepared from an equimolar mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ethylenediamine (Jonassen & Dexter, 1949). Pale blue powder recrystallized from water/ethanol mixture. Pale blue plates suitable for X-ray diffraction. Density determined by suspension in chloroform/bromoform mixture. Crystal $0.05 \times 0.22 \times 0.20$ mm; $P2_1$ diffractometer. Cell parameters from 15 reflections with $20 < 2\theta < 29^\circ$. Empirical absorption correction (Calabrese & Burnett, 1980): transmission factors 0.458–1.00; and data reduction, Lorentz and Bond absorption corrections (Stewart, 1976; Bond, 1972): transmission factors 7.0910–8.4631. Data collected in range $(\sin\theta/\lambda) < 0.6495$ Å⁻¹, $0 < h < 10$, $-7 < k < 7$, $-8 < l < 8$. Two standard reflections (203, 1.76% and $3\bar{2}1$, 1.47%). 1655 reflections measured, 812 unique, 17 unobserved with $l < 0$, $R_{\text{int}} = 0.0490$. Cu atom located from three-dimensional Patterson map and all other non-hydrogen

atoms found from electron density difference syntheses (SHELX76; Sheldrick, 1976). Hydrogen atoms bound to carbon atoms found on electron density difference map, even though hydrogen atoms H(5)[C(1)] and H(8)[C(2)] were disordered and off the mirror plane and thus had only half occupancy. Positional parameters of these hydrogen atoms refined but positions of hydrogen atoms on nitrogen atoms calculated and then fixed. Refinement on $|F|^2$'s to $R = 0.0429$, $wR = 0.0387$; 60 parameters, $w^{-1} = \sigma^2(F)$; secondary-extinction correction included in SHELX76 [$F' = F(1 - 0.0001x^2/\sin\theta)$, $x = 0.001$ (1)]; $S = 3.44$, max. (av.) $\Delta/\sigma = 2.145$ (0.207) [positional parameters for H(5), H(8) allowed to vary]; max. and min. heights in final $\Delta\rho$ map $+1.06$ and -0.45 e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Other programs used: NRC22 (Pippy & Ahmed, 1968) and ORTEPII (Johnson, 1976).*

Discussion. Atom coordinates and temperature factors are given in Table 1, bond lengths and angles in Table 2. The Cu atom lies on the special position $x, \frac{1}{2}, z$, with crystallographic symmetry m . It is surrounded by two Cl atoms and two N atoms, also in the mirror plane, in a *cis* square-planar arrangement. The geometry about the Cu atom is, therefore, similar to the geometry of the Pt and Pd atoms in dichloro(ethylenediamine)metal(II) (metal = platinum or palladium) (Iball, MacDougall & Scrimgeour, 1975). There are, however, differences between the structures. In the copper complex there are additional chlorine atoms above and below the square plane at relatively long bonding distances [2.887 (2) Å] (Fig. 1). This type of severely tetragonally distorted octahedral structure, which is caused by the packing (see below), is well known for Cu^{II} and is supposed to arise from the Jahn–Teller effect. The Cu–Cl distances observed here are in good agreement with previous results (Cotton & Wilkinson, 1980). We assume the difference is carried into solution and that in water or

* 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 42761 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

3% saline solution the positions above and below the square plane of the copper complex are filled by weakly bonded molecules or chloride ions. Another difference between the copper and platinum/palladium complexes is that in the copper complex the ethylenediamine ring is disordered with equal amounts of the δ and λ configurations on each position. In the platinum and palladium structures, the δ and λ conformations lie on different positions. The difference is caused by the different crystal packing.

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} *
Cu	5403 (1)	2500	8485 (1)	291 (5)
Cl(1)	2922 (2)	2500	6754 (2)	362 (8)
Cl(2)	4251 (2)	2500	11490 (2)	338 (7)
N(1)	6684 (6)	2500	6056 (6)	340 (25)
N(2)	7616 (6)	2500	9959 (6)	385 (24)
C(1)†	8407 (10)	1940 (13)	6625 (12)	410 (39)
C(2)†	8845 (10)	3202 (14)	8547 (12)	432 (45)

$$* U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

† These carbon atoms are disordered and were given half-occupancy at these positions.

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

Cu—Cl(1)	2.286 (2)	Cu—Cl(2)	2.301 (2)
Cu—N(1)	2.010 (5)	Cu—N(2)	2.017 (5)
N(1)—C(1)	1.479 (9)	N(2)—C(2)	1.492 (10)
C(1)—C(2)	1.514 (11)	Cu...Cl(2')	2.887 (2)
Cl(1)—Cu—Cl(2)	92.84 (6)	N(1)—Cu—Cl(1)	94.4 (1)
N(1)—Cu—Cl(2)	172.8 (1)	N(2)—Cu—Cl(1)	178.8 (1)
N(2)—Cu—Cl(2)	88.4 (1)	N(1)—Cu—N(2)	84.4 (2)
C(1)—N(1)—Cu	109.3 (4)	C(2)—N(2)—Cu	108.0 (4)
N(1)—C(1)—C(2)	106.9 (6)	N(2)—C(2)—C(1)	106.8 (6)
Hydrogen bonds			
Cl(1)...N(1')	3.474 (3)	Cl(1)...H(1')	0.90
H(1')—N(1')	2.60	Cl(1)...H(1')—N(1')	164

The hydrogen-atom position H(1') is calculated by a 'tetrahedral geometry' program and was not refined. There are thus no calculated errors from the refinement associated with this atom.

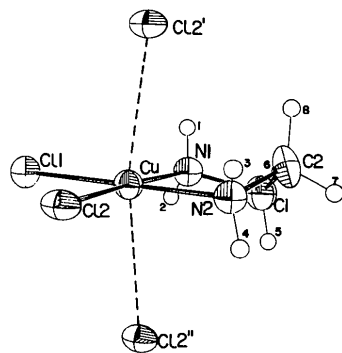


Fig. 1. The molecular structure of Cu(en)Cl_2 showing the atom numbering. Hydrogen atoms are indicated by affixes only in smaller print. Only one conformation of the disordered structure is shown for clarity.

The Cu—N distances [2.010 (5), 2.017 (5) \AA] are insignificantly different and fall between the Pd—N [1.98 (1) \AA] and Pt—N [2.08 (3) \AA] distances and agree with other Cu—N(alkylamine) distances (Brown & Lingafelter, 1964). The Cu—Cl distances are different, however, the longer Cu—Cl(2) distance of 2.301 (2) \AA being associated with the chlorine atom which interacts weakly with another copper atom (see below). Both Cu—Cl distances lie between the Pd—Cl and Pt—Cl distances [2.288 (8), 2.309 (3) \AA] and are consistent with other Cu—Cl distances (Cotton & Wilkinson, 1980). Angles within the square plane are close to those in the Pd and Pt complexes and differ from 90 and 180 $^\circ$ in the expected manner. The carbon atoms are asymmetric about the N—Cu—N plane, with one carbon atom -1.10 (1) \AA from the plane and the other 0.21 (1) \AA from the plane. This asymmetry is very marked and lies outside the limits $+0.37$ to -0.68 \AA observed in other Cu—en complexes (Brown & Lingafelter, 1964). The asymmetry is caused by hydrogen bonding and has been discussed previously (Corey & Bailar, 1959; Britten & Lock, 1980).

The crystal packing of the copper complex is completely different from the Pt and Pd complexes. In the case of the Pt and Pd complexes, the metal ions are on a 2₁ axis and the molecules form a chain along the *b* axis, such that in a given molecule each chlorine atom is hydrogen bonded to a nitrogen atom of the ethylenediamine ligand in molecules above and below the first. These distances are ~ 3.4 \AA so that the *b* axis is 6.761 \AA . In the copper complex, molecules are still arranged in chains along the *b* axis (Fig. 2), but the copper atoms no longer lie on the 2₁ axis at $x = \frac{1}{2}$, $z = \frac{1}{2}$. Displacement from the axis allows Cl(2) to lie directly above and below the copper atoms in adjacent molecules in the *b* direction, with a Cu...Cl(2) separation of ~ 2.9 \AA , as noted above. This means the molecules are closer together than in the Pd and Pt cases and the *b* axis is shortened to 5.747 (1) \AA . Most interactions between molecules are van der Waals but

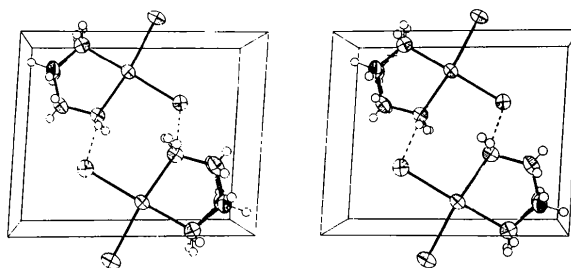


Fig. 2. The packing of the molecule in the unit cell. Hydrogen bonds are shown by dotted lines. *a* and *c** are horizontal and vertical, respectively and the view is down *b*. Both orientations are shown for the ethylenediamine ring giving rise to the extra carbon and hydrogen atoms.

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[(1*SR*,4*RS*,7*RS*,8*SR*,11*RS*,14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) Perchlorate

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Abstract. [Cu(H₂O)(C₁₆H₃₆N₄)](ClO₄)₂, $M_r = 564.5$, monoclinic, $C2/c$, $a = 11.993$ (1), $b = 13.057$ (2), $c = 15.969$ (4) Å, $\beta = 92.37$ (1)°, $V = 2498.5$ (2) Å³, $Z = 4$, $D_x = 1.50$, $D_m = 1.49$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 1.14$ mm⁻¹, $F(000) = 1187.8$, $T = 298$ K, $R = 0.056$ 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 1*SR*, 4*RS*, 8*SR* and 11*RS*. 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-tetraazacyclotetradecane (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)(H₂O)](ClO₄)₂. The present paper concerns the structure of the red isomer, red-[Cu(tet b)(H₂O)](ClO₄)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(ClO₄)₂·6H₂O (3.8 ml, 0.73 mmol) was added, then