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Structure of a Red Macrocyclic Ligand Complex*

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Abstract. (1*RS*,4*RS*,5*SR*,7*RS*,8*SR*,11*SR*,12*RS*,14*SR*)-5,7,12,14-Tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) diperchlorate, $[Cu(C_{20}H_{44}N_4)](ClO_4)_2$, $M_r = 603{\cdot}00$, orthorhombic, *Pbca*, $a = 14{\cdot}516\ (6)$, $b = 11{\cdot}674\ (7)$, $c = 16{\cdot}225\ (9)$ Å, $V = 2749{\cdot}5\ (3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}47\ (3)$ (by flotation in CCl_4/hexane mixture), $D_x = 1{\cdot}457$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}070$ mm^{-1}, $F(000) = 1278$, $T = 296\ (4)$ K, $R(F) = 0{\cdot}069$ for 1516 observed reflections. The coordination about Cu$^{\rm II}$ is a tetragonally distorted centrosymmetric octahedron, with the macrocyclic ligand equatorial and the perchlorate ions axial. This complex has the 1*RS*, 4*RS*, 8*SR*, 11*SR* configuration at the chiral nitrogen centers; the six-membered chelate rings exhibit chair forms and the five-membered rings take *gauche* forms.

Introduction. The macrocyclic ligand (5*SR*,7*RS*,12*RS*,14*SR*)-5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradecane, $Et_4Me_2[14]aneN_4$, takes a variety of isomeric forms with transition-metal ions that exhibit a number of features that are of particular stereochemical interest. In a previous paper we have reported the crystal structure of a nickel(II) complex of this ligand (Lee, Lu, Liang, Chung & Lee, 1981). In this study, the title compound, $[Cu(Et_4Me_2[14]aneN_4)](ClO_4)_2$ has been synthesized and the three-dimensional structure determination by X-ray diffraction has been completed.

Experimental. *C-meso*-5,7,12,14-Tetraethyl-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydroperchlorate prepared with procedure described by Curtis (1974). 50 g of this compound added to 500 ml methanol and stirred until completely dissolved, then 10 g sodium borohydride added slowly. Solution stirred continuously for 2 h until no more bubbles occurred. 500 ml water added to solution and stirred again until room temperature reached. Solution cooled overnight to precipitate white product, $Et_4Me_2[14]aneN_4$, which was filtered, washed with water, and then recrystallized from methanol–water mixture. Copper(II) perchlorate (2·0 g) and $Et_4Me_2[14]aneN_4$ (2·0 g) mixed in 200 ml 50% (by weight) methanol–water mixture. Solution of sodium hydroxide (10 ml of 1·0 *M*) added. After 4 h, sodium perchlorate monohydrate added. Red crystals of $[Cu(Et_4Me_2[14]aneN_4)](ClO_4)_2$ filtered, washed with water, recrystallized from methanol–water mixture (50% by weight), and dried in vacuum oven at 323 K (Juang, 1984).

Experimental data and structure solution parameters together with the standard refinement procedures are listed in Table 1. In the last stage of least-squares refinement with coordinates and anisotropic temperature factors for non-hydrogen atoms, $R(F) = 0{\cdot}096$. The four perchlorate O atoms were disordered and each O atom is located at two positions with populations $P_{O(1)} = P_{O(2)} = P_{O(3)} = P_{O(4)} = 0{\cdot}81$ and $P_{O(1A)} = P_{O(2A)} = P_{O(3A)} = P_{O(4A)} = 0{\cdot}19$ respectively. With positions and isotropic temperature factors of these four additional oxygens included in the subsequent calculation, $R(F)$ reduced to 0·084. All 22 H atoms located in difference Fourier map. Temperature factors of H atoms assigned according to $B_H = B_n + 1$, where *n* is atom to which H is bonded (Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980). With these isotropic temperature factors and coordinates of H atoms refined in last cycle of least-squares calculation, $R(F)$ reduced to 0·069.

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

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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 42442 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Experimental data and structure refinement parameters for the red crystal of* $[Cu(Et_4Me_2[14]aneN_4](ClO_4)_2$

Crystal size	Sphere 0·4 mm diameter
Diffractometer and data collection technique used	ω–2θ scan, four-circle diffractometer (Syntex $P\bar{1}$) with graphite monochromator
Scan width	(2·0 + 0·7 tanθ)°; starting 1° below $K\alpha_1$ and 1° above $K\alpha_2$
Number and θ range used for measuring lattice parameters	15 reflections with $12 < 2\theta < 25°$
Absorption correction applied	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)
Transmission factor	0·652
Max. $(\sin\theta)/\lambda$ in intensity measurement	0·5947 Å^{-1}
Range of *hkl*	0,0,2 to 16,12,18
Standard reflections and intensity variation	200, 221, 111, variation ~3%
Number of reflections measured	5347
Number of unique reflections	1516 $[I > 3\sigma(I)]$
Method used to solve structure	Patterson and Fourier methods
Max. height in final difference Fourier synthesis	0·67 e Å^{-3}
Parameters refined, nonhydrogen atoms	Coordinates, occupancies and anisotropic temperature factors (189 parameters)
hydrogen atoms	Coordinates and isotropic temperature factors (88 parameters)
Atomic scattering factors, f' and f''	*International Tables for X-ray Crystallography* (1974)
Number of reflections per parameter	6
R and wR, $w = 1/\sigma^2(F)$	0·069 and 0·077
S	0·85
R_{int}	0·031
Max. Δ/σ	0·76
Program used	Tsing Hua University *XTAL* package and *ORTEP*II
Computer	CDC Cyber-172

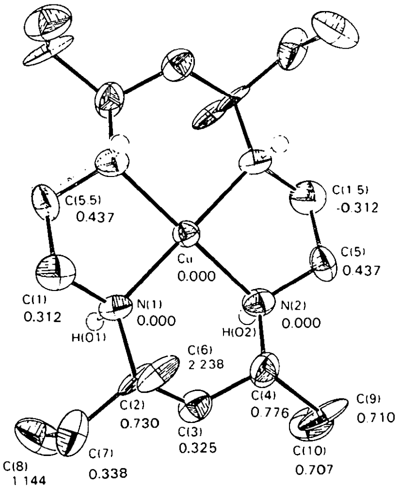

Fig. 1. Perspective view of the structure of $[Cu(Et_4Me_2[14]aneN_4)]^{2+}$, showing the atom numbering scheme and displacements of atoms from the plane through Cu, N(1) and N(2) (Å). The e.s.d.'s are around 0·009 Å. Thermal ellipsoids are depicted at the 50% probability level.

Table 2. *Atomic positional and thermal parameters of non-hydrogen atoms for the red crystal of* $[Cu(Et_4Me_2[14]aneN_4)](ClO_4)_2$ *with e.s.d.'s in parentheses*

The equivalent isotropic temperature factor* is calculated using the expression $B_{eq} = \frac{4}{3}\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j B_{ij}$, where the $\mathbf{a}_i$'s are the unit-cell edges in direct space.

	x	y	z	B_{eq}(Å^2)
Cu	0·0000	0·0000	0·0000	2·7 (1)
Cl(1)	0·0437 (2)	0·2560 (2)	0·1333 (1)	4·2 (2)
N(1)	0·0361 (4)	−0·1325 (5)	0·0747 (4)	2·7 (5)
N(2)	0·1142 (4)	−0·0149 (5)	−0·0713 (4)	2·8 (5)
O(1)	0·0067 (9)	0·1679 (9)	0·1871 (7)	8·5 (11)
O(1*A*)	−0·0350 (20)	0·2225 (25)	0·1639 (18)	3·0 (5)
O(2)	0·1163 (7)	0·3053 (9)	0·1813 (6)	6·4 (8)
O(2*A*)	0·0935 (16)	0·3402 (19)	0·1675 (15)	1·3 (4)
O(3)	0·0835 (7)	0·1841 (10)	0·0700 (6)	5·8 (9)
O(3*A*)	0·0659 (27)	0·2617 (39)	0·0470 (24)	5·3 (8)
O(4)	−0·0284 (10)	0·3256 (13)	0·1150 (10)	10·0 (15)
O(4*A*)	0·0258 (37)	0·3413 (46)	0·0616 (32)	7·8 (12)
C(1)	−0·0259 (6)	−0·1277 (7)	0·1476 (5)	4·3 (7)
C(2)	0·1351 (5)	−0·1566 (7)	0·0970 (5)	3·0 (7)
C(3)	0·1902 (5)	−0·1601 (7)	0·0158 (5)	3·2 (7)
C(4)	0·2031 (5)	−0·0481 (8)	−0·0310 (5)	3·3 (7)
C(5)	0·1209 (5)	0·0963 (7)	−0·1169 (5)	3·4 (6)
C(6)	0·1732 (7)	−0·0664 (9)	0·1557 (6)	3·7 (9)
C(7)	0·1439 (7)	−0·2756 (8)	0·1393 (6)	4·3 (9)
C(8)	0·0993 (9)	−0·3753 (10)	0·0970 (8)	6·3 (11)
C(9)	0·2826 (6)	−0·0529 (9)	−0·0924 (6)	5·0 (9)
C(10)	0·2642 (8)	−0·1314 (10)	−0·1641 (6)	5·5 (10)

* In the refinement processes, we assigned isotropic temperature factors to those atoms labeled *A*.

Table 3. *Bond lengths* (Å) *and angles* (°)

Cu–N(1)	2·034 (6)	C(2)–C(6)	1·524 (13)
Cu–N(2)	2·030 (6)	C(2)–C(7)	1·555 (13)
N(1)–C(1)	1·487 (10)	C(3)–C(4)	1·523 (12)
N(1)–C(2)	1·508 (10)	C(4)–C(9)	1·526 (12)
N(2)–C(4)	1·498 (10)	C(7)–C(8)	1·498 (15)
N(2)–C(5)	1·497 (10)	C(9)–C(10)	1·505 (15)
N(1)–O(3·5)*	2·981 (11)	Cl–O(1)	1·452 (11)
N(2)–O(1·5)	3·131 (13)	Cl–O(2)	1·431 (10)
C(5·5)–C(1)	1·512 (11)	Cl–O(3)	1·447 (11)
Cu–O(3)	2·716 (11)	Cl–O(4)	1·358 (15)
C(2)–C(3)	1·543 (11)		

N(2·5)–Cu–N(1)	86·3 (2)	C(2)–C(7)–C(8)	117·2 (8)
N(1)–Cu–N(2)	93·7 (2)	C(2)–C(3)–C(4)	117·8 (8)
		C(3)–C(4)–N(2)	109·5 (7)
N(1)–H(1)···O(3·5)	128·6 (6)	C(3)–C(4)–C(9)	112·7 (7)
N(2)–H(2)···O(1·5)	154·5 (6)	N(2)–C(4)–C(9)	112·0 (7)
		C(4)–C(9)–C(10)	113·1 (8)
C(5·5)–C(1)–N(1)	107·5 (6)	C(4)–N(2)–C(5)	112·6 (6)
C(1)–N(1)–C(2)	113·1 (6)	Cu–N(2)–C(4)	118·4 (5)
Cu–N(1)–C(1)	106·8 (5)	Cu–N(2)–C(5)	105·1 (4)
Cu–N(1)–C(2)	122·1 (5)	N(2)–C(5)–C(1·5)	108·3 (6)
N(1)–C(2)–C(3)	107·1 (6)	O(1)–Cl–O(2)	103·3 (6)
N(1)–C(2)–C(7)	110·5 (6)	O(1)–Cl–O(3)	99·4 (6)
N(1)–C(2)–C(6)	111·5 (7)	O(1)–Cl–O(4)	105·7 (8)
C(3)–C(2)–C(7)	108·1 (7)	O(2)–Cl–O(3)	109·0 (6)
C(3)–C(2)–C(6)	111·3 (7)	O(2)–Cl–O(4)	116·5 (8)
C(6)–C(2)–C(7)	108·2 (7)	O(3)–Cl–O(4)	119·9 (8)
O(3)–Cu–N(1)	103·8 (3)	O(3)–Cu–N(2)	86·7 (3)

* The number 5 after the decimal point in parentheses indicates the fifth equivalent atoms [symmetry code: $-x$, $-y$, $-z$; *International Tables for Crystallography* (1983), p. 287].

This complex has a center of symmetry. Copper(II) is in a severely tetragonally distorted octahedron with the macrocycle equatorial and perchlorate ions axial. Hence, copper(II) is six-coordinate of '4 + 2' type (Lee, Lu, Liu, Chung & Lee, 1984; Pavkovic & Brown, 1982), as would be expected on the basis of the Jahn–Teller effect. The configuration of the four chiral nitrogen centers is 1*RS*, 4*RS*, 8*SR*, 11*SR*, which is also found in the most stable nickel(II) complex of this ligand (Lee, Lu, Liang, Chung & Lee, 1981). The ligand is in its most stable planar conformation with both six-membered chelate rings in a chair form and both five-membered chelate rings in a *gauche* form. The four ethyl groups attached to the asymmetric carbons are equatorial.

The coordination bond distances, 2·034 (6) Å [Cu—N(1)] and 2·030 (6) Å [Cu—N(2)], are normal for planar Cu^{II}–tetraamine and –diamine complexes. As seen from Table 4, these distances are relatively insensitive to ring strain and the number of chelate rings. The chelate angles subtended at Cu^{II}, 86·3 (2)° for the five-membered and 93·7 (2)° for the six-membered rings, are normal for planar tetraamine 14-membered macrocyclic ligand complexes of copper(II), with alternating five- and six-membered chelate rings. These angles are a compromise between the optimum value of the bond angle at Cu^{II}, 90°, the Cu—N bond distances and the preferred 'bite' of the chelate. The Cu—O (apical) distances, 2·716 (11) Å for the two symmetric pairs, are slightly longer than the typical value for Cu^{II} complexes with tetragonal N_4O_2 ligand donor sets (Table 4). This distortion is mainly due to the steric effect of the substituents of the macrocycle, as shown in Fig. 2.

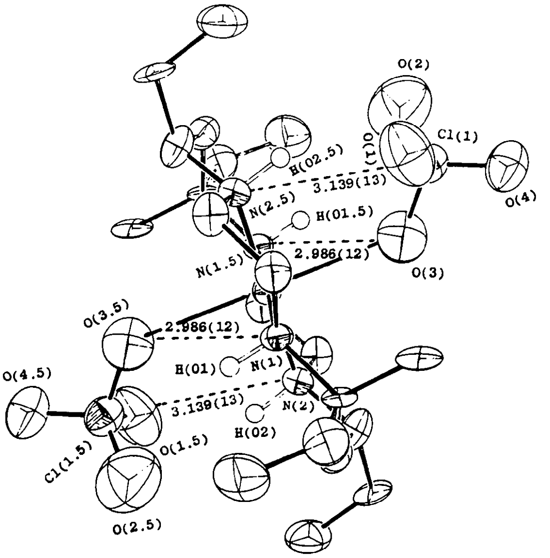

Fig. 2. *ORTEP*II (Johnson, 1976) drawing of $[Cu(Et_4Me_2N_4)](ClO_4)_2$ illustrating the intermolecular hydrogen bonds (dashed lines) between the perchlorate ions and the macrocyclic ligand. The axial coordination bonds between Cu and O atoms are indicated by solid lines. Unshaded ellipsoids are carbon atoms; each amine hydrogen is plotted as a circle. The ethyl groups are a hindrance to the perchlorate ions.

Table 4. *Selected structural data for* Cu^{II}*–tetraamine and –diamine complexes*

Complex*	Cu—N (Å)	Cu—O (Å)	N—Cu—N for five-membered ring (°)	N—Cu—N for six-membered ring (°)	*trans* N—Cu—N (°)	References
$Cu(en)_2(BF_4)_2$	2·02 (1) 2·03 (1)		86·4 (5)		180†	Brown, Lee & Melson (1968)
Cu(2,3,2-tet)-$(ClO_4)_2$	2·016 (6) 2·032	2·667 (5) 2·527 (5)	85·3 (2) 85·2 (2)	93·9 (2)	176·4 (3) 178·5 (4)	Fawcett *et al.* (1980)
$Cu(pn)_2(ClO_4)_2$	2·01 (3) 2·03 (3)	2·61 (2)	86·0		180†	Pajunen & Lehtonen (1972)
$Cu(tn)_2(ClO_4)_2$	2·027 (7) 2·031 (7)	2·676 (10)		93·3 (2)	180†	Pajunen, Smolander & Belinskij (1972)
Cu(2,2,2-tet)-$(SCN)_2$	2·008 (7) 2·030 (5)		84·6 (3) 84·3 (2) 84·7 (3)		154·0 161·0	Marongiu, Lingafelter & Paoletti (1969)
Cu([14]aneN_4)-$(ClO_4)_2$	2·02 (2) 2·04 (4)	2·547 (4)	86·0 (2)	94·0 (2)	180†	Tasker & Sklar (1969)
Cu(tet a)-$(ClO_4)_2$(red)	2·022 (2) 2·063 (3)	2·594 (5)	85·7 (10)			Clay, Murray-Rust & Murray-Rust (1979)
Cu(Et_4Me_2-[14]aneN_4)-$(ClO_4)_2$	2·030 (6) 2·034 (6)	2·716 (11)	86·3 (2)	93·7 (2)	180†	Present work

* Abbreviations: en: ethylenediamine, $NH_2CH_2CH_2NH_2$; pn: 1,2-propanediamine, $NH_2CH_2CH(CH_3)NH_2$; tn: 1,3-butanediamine, $NH_2CH_2CH_2CH(CH_3)NH_2$; tet: [14]aneN_4, 1,4,8,11-tetraazacyclotetradecane; tet a: Me_6[14]aneN_4, *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; 2,3,2-tet: 1,4,8,11-tetraazaundecane; 2,2,2-tet: 1,4,7,10-tetraazadecane; 3,2,3-tet: 1,5,8,12-tetraazadodecane.

† Required by symmetry operation and yielding planar CuN_4 unit.

Intramolecular hydrogen bonds between N—H groups and O atoms of the perchlorate ions are shown in Fig. 2. The hydrogen-bonding network is in a fairly symmetric arrangement and contributes a significant stabilizing effect in the whole molecule.

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cis-Dichlorobis(methyldiphenylphosphine)palladium(II)

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Abstract. $[PdCl_2\{P(CH_3)(C_6H_5)_2\}_2]$, $M_r = 577\cdot7$, orthorhombic, $P2_12_12_1$, $a = 10\cdot010$ (2), $b = 14\cdot542$ (3), $c = 17\cdot028$ (4) Å, $V = 2478\cdot7$ (9) Å^3, $Z = 4$, $D_x = 1\cdot55$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 10\cdot95$ cm^{-1}, $F(000) = 1168$, $T = 290$ K, $R = 0\cdot030$ for 1919 unique observed reflections. The homogeneous crystals contain the *cis*-isomer, although in solution the title compound exists as a mixture of *cis*- and *trans*-isomers. The square-planar palladium coordination has P—Pd—P [98·9 (1)°] slightly larger than the Cl—Pd—Cl angle [89·9 (1)°]. Bond distances are Pd—P 2·265 (2) Å and Pd—Cl 2·341 (2) Å.

Introduction. The title compound was prepared by the method of Grim & Keiter (1970). It was dissolved in $CHCl_3$ to give a yellow solution and a solution of excess $SnCl_2.2H_2O$ in ethanol was added. This produced a deep-red colour, believed to be due to (Ph_2MeP)-$Pd[SnCl_2]_2$. Slow evaporation at ambient temperature gave large yellow crystals, which were shown by the X-ray determination to be unchanged starting material.

Experimental. Crystal character: well shaped blocks. Data collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ 50°, with scan range $\pm0\cdot9°$ (2θ) around $K\alpha_1 - K\alpha_2$ angles, scan speed 2–29° min^{-1}, depending on intensity of a 2 s pre-scan; backgrounds measured at each end of scan for 0·25 of scan time. *hkl* ranges: 0–11, 0–17, 0–20. Three standard reflections monitored every 200 reflections, and rescaled following a very slight decrease during data collection; unit-cell dimensions and standard deviations obtained by least-squares fit to 15 reflections $(20 < 2\theta < 22°)$. Reflections processed using profile analysis to give 2519 unique reflections; 1919 considered observed $[I/\sigma(I) \geq 3\cdot0]$ and used in refinement, corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970), maximum and

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