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A Chloro-Bridged Dinuclear Copper(II) Cationic Complex of a 15-Membered Tetraaza Macrocyclic Ligand

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Abstract

The title complex, μ-chloro-bis[(1*R**,4*R**)-5,5,7,13,15,15-hexamethyl-1,4,8,12-tetraazacyclopentadeca-7,12-diene-N^1,N^4,N^8,N^{12})(perchlorato-*O*)copper(II)] perchlorate, $[Cu_2Cl(ClO_4)_2(C_{17}H_{34}N_4)_2](ClO_4)$, has a chloride-bridged centrosymmetric confacial dinuclear cation. Each copper(II) ion has tetrahedrally twisted (±0.30 Å) planar coordination composed of the four N atoms of the macrocyclic ligand [mean Cu—N_{amine} 2.02 (1) and Cu—N_{imine} 1.99 (1) Å], with weak tetragonal chloride [Cu—Cl 2.83 (1) Å] and perchlorate O-atom [Cu—O 2.94 (1) Å] interactions. The Cu atom is displaced by 0.09 Å from the best N_4 plane towards the chloride ion.

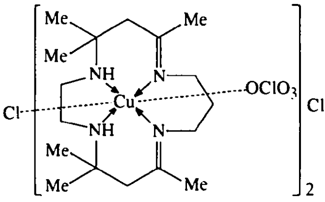
Comment

Preparations of the copper(II) and nickel(II) compounds of the 15-membered tetraaza macrocycle 6,8,8,13,13,15-hexamethyl-1,5,9,12-tetraazacyclopentadeca-5,15(1)-diene (*cis*-[15]diene) have been reported previously (Hedwig, Love & Powell, 1970; Love & Powell, 1968). The salt $[Cu(cis\text{-}[15]diene)](ClO_4)_2$ has also been described.

The *cis*-[15]diene ligand is a member of a sequence of hexamethyl-substituted diimine–diamine macrocycles of varying ring size formed by reaction of diamines of varying chain length with acetone, normally in the presence of nickel(II) or copper(II) (Curtis, 1968). Compounds of isomeric macrocycles of this type with the imine functions *cis* or *trans* have been prepared for 14-, 15-, 16- and 18-membered macrocycles, and the structures of the perchlorate salts of copper(II) cations with the *trans*-[14]diene [both *N-rac* (Lu, Lee, Liang & Chung, 1981) and *N-meso* (Lee, Lu, Chung & Lee, 1984)] and *cis*- and *trans*-[18]diene macrocycles (Timmons, Rudolph, Martell, Martin & Clearfield, 1980) have been determined, as well as those of the *cis*- and *trans*-[14]diene macrocycles with other metal ions (Curtis, 1979).

Comparison of the structures of members of the sequence enables evaluation of the structural consequences of changing the size of the macrocyclic ring. Most reported structures of 15-membered tetraaza macrocycles have an appreciable tetrahedral twisting of the N_4 coordination 'plane' (Curtis & Gainsford, 1986). Metal–nitrogen bond lengths in the reported structures of copper(II) diamine–diimine macrocycle compounds with 14–18-membered rings, however, are essentially independent of ring size.

The salt $[Cu(cis\text{-}[15]diene)](ClO_4)_2$ recrystallizes from water in the presence of chloride ions as a compound of composition $[Cu(cis\text{-}[15]diene)]_2Cl(ClO_4)_3$. Both the perchlorate and mixed chloride–perchlorate compounds are blue–violet in colour and are visually indistinguishable. The structure of the chloride–perchlorate compound has been established as (9*R**, 12*R**)-(6,8,8,13,13,15-hexamethyl-1,5,9,12-tetraazacyclopentadeca-5,15(1)-diene-N^1,N^5,N^9,N^{12})copper(II) chloride triperchlorate, or if weak axial interactions are considered as μ-chloro-bis{(9*R**,12*R**)-[6,8,8,13,13,15-hexamethyl-1,5,9,12-tetraazacyclopentadeca-5,15(1)-diene-N^1,N^5,N^9,N^{12}]perchlorato}dicopper(II) perchlorate, *i.e.* [*N-rac*-$\{CuCl(cis\text{-}[15]diene)(ClO_4)\}_2](ClO_4)$, (I). Tetraaza macrocyclic ligand copper(II) units are axially chloro-bridged [Cu—Cl 2.83 (1) Å] forming centrosymmetric confacial dinuclear cations having very long interactions with perchlorate O atoms [Cu—O 2.94 (1) Å], which complete a tetragonal coordination environment. The bridging Cl3 ion and Cl2 of the non-coordinated perchlorate ion lie on centres of symmetry.



(I)

The cation, complete with axial chloride and perchlorate groups, is shown in Fig. 1. Each copper(II) ion has tetrahedrally twisted planar coordination involving the four N atoms of the macrocycle. The N5—C6 and C15—N1 bond lengths of 1.27 (1) Å, and the *ca* 120° bond angles about these atoms confirm the *cis*-diimine structure of the macrocycle. The mean Cu—N_{amine} distance of 2.02 (1) Å is longer than the mean Cu—N_{imine} distance of 1.99 (1) Å, both values being typical of those reported for related macrocyclic compounds. The N_4 primary coordination plane shows ±0.30 Å tetrahedral twisting, with the Cu atom displaced by 0.09 Å from the best N_4 plane towards the chloride ion. The N9 and N12 amine groups of each coordinated macrocycle are on opposite sides of the molecular plane, *i.e.* the cation has an *N-rac* configuration, with inversion about the chloride bridging group resulting in an achiral dinuclear cation.

Each copper–macrocycle unit has approximate two-fold symmetry through atoms C3 and Cu, and the

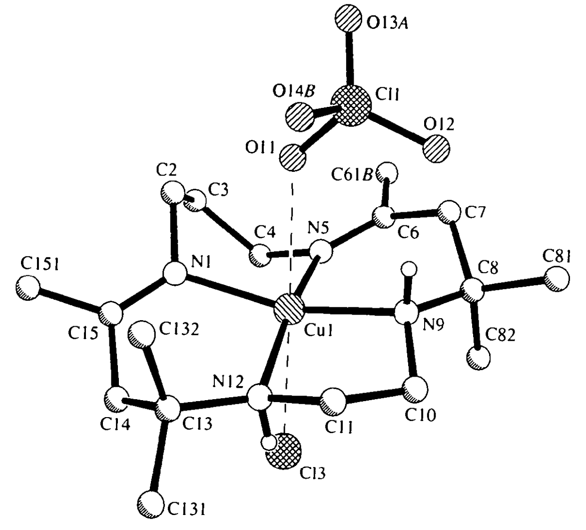


Fig. 1. The structure of half of the dinuclear complex cation showing interactions with axial chloride and perchlorate ions.

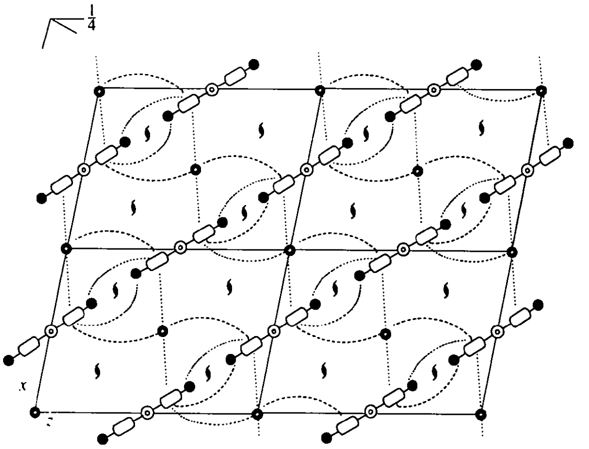


Fig. 2. A schematic representation of the unit-cell contents projected onto the *xz* plane. Shaded circles represent perchlorate ions and ovals the copper(II) macrocyclic ligand complex cation. Hydrogen bonds are indicated by dashed lines.

midpoint of C10—C11. The five-membered chelate ring (Cu, N9, C10, C11, N12) has a *gauche* conformation with displacements from the CuN_2 plane of −0.37 for C10 and 0.34 Å for C11. The two six-membered amine–imine chelate rings have similar 'twist–boat' conformations [deviations: C6 −0.24, C7 −0.56, C8 0.35 and C13 0.10, C14 −0.86, C15 −0.38 Å], while the six-membered Cu, N1, C2–C4, N5 ring has a twist conformation [deviations: C2 −0.81, C3 −0.02 and C4 0.80 Å].

The coordinated Cl1 perchlorate ion forms an intramolecular N9—H···O12 hydrogen bond and also participates in a C14—H···O14 interaction that, together with the Cu···Cl interactions, forms layers parallel to the (101) plane. The non-coordinated Cl2 perchlorate ion is located between these layers and interconnects them *via* C—H···O interactions. These interactions are listed in Table 3 and shown schematically in Fig. 2.

Three structures have been reported previously for compounds of 15-membered tetraaza macrocycles with copper(II). The cyclic amine compound (1,4,9,12-tetraazacyclopentadecane)copper(II) perchlorate has tetrahedrally twisted planar coordination of the macrocycle (deviations from the best N_4 plane of ±0.21 Å), with Cu—N distances of 2.08, 2.06, 1.98 and 2.01 Å, and tetragonal interactions with perchlorate O atoms at a distance of 2.59 Å. The chelate rings have *gauche*, twist, flattened chair and twist conformations. The 10-methyl-10-nitro-substituted analogue, as the perchlorate salt, has the substituted six-membered chelate ring in a boat conformation, with a nitro group O atom in one axial site (Cu—O 2.44 Å) and a perchlorate O atom (Cu—O 2.58 Å) in the other, with Cu—N distances close to the mean value of 2.04 Å and tetrahedral twisting of the N_4 plane of ±0.14 Å (Comba, Curtis, Lawrance, O'Leary, Skelton & White, 1988*b*). The chloride salt of this cation has chloride ions coordinated tetragonally (Cu—Cl 2.699 and 2.806 Å), Cu—N distances close to the mean value of 2.06 Å, with smaller tetrahedral twisting of the N_4 plane of ±0.11 Å, and the substituted chelate ring in a skew-boat conformation (Comba, Hambley, Hitchman & Stratemeier, 1995).

(1*R**,8*S**)-5,7,7,13,15,15-Hexamethyl-1,4,8,12-tetraazacyclopentadeca-4,12-diene)nickel(II) perchlorate hydrate has a macrocyclic ligand geometrically isomeric with *cis*-[15]diene (Curtis & Gainsford, 1986). μ-Chloro-1,1,1-trichloro-2-(12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane)dicopper(II) has one copper(II) ion, Cu1, with square-planar coordination involving the 13-membered macrocycle, with one chlorine of a $(Cu_2Cl_4)^{2-}$ anion interacting axially in a square-pyramidal arrangement [Cu1—Cl 2.266 (2), Cu2—Cl 2.246 (1) Å and Cu1—Cl—Cu2 98.85 (4)°; Comba, Curtis, Lawrance, O'Leary, Skelton & White, 1988*a*]. The Cu1—Cl distance is appreciably shorter and the Cu1—Cl—Cu2 bond angle quite different from the values found for the *cis*-[15]diene compound.

Experimental

[Cu(*cis*-[15]diene)]$(ClO_4)_2$ was prepared by reaction of 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione diperchlorate (Curtis, 1982) with propane-1,3-diamine and reaction of the resulting solution with basic copper(II) carbonate (Hedwig, Love & Powell, 1970). The yield was improved by substitution of the methanol solvent in the original preparation by acetonitrile. Slow evaporation of an aqueous solution of this compound and excess lithium chloride resulted in crystallization of blue-violet crystals of the title chloride–triperchlorate compound, [Cu(*cis*-[15]diene)]$_2$Cl$(ClO_4)_3$.

Crystal data

$[Cu_2Cl(ClO_4)_2(C_{17}H_{34}N_4)_2]$-$(ClO_4)$

Mo $K\alpha$ radiation
λ = 0.71073 Å

$M_r = 524.92$
Monoclinic
$P2_1/n$
$a = 11.379\ (3)$ Å
$b = 12.708\ (2)$ Å
$c = 16.241\ (3)$ Å
$\beta = 100.11\ (2)°$
$V = 2312.1\ (7)$ Å^3
$Z = 4$
$D_x = 1.508$ Mg m^{-3}
D_m not measured

Cell parameters from 27 reflections
$\theta = 2–22.5°$
$\mu = 1.216$ mm^{-1}
$T = 141\ (2)$ K
Block
0.48 × 0.38 × 0.28 mm
Dark blue

Data collection

Siemens diffractometer
ω scans
Absorption correction: none
3160 measured reflections
2668 independent reflections
1740 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0974$

$\theta_{\max} = 24.01°$
$h = -8 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0560$
$wR(F^2) = 0.1567$
$S = 1.009$
2668 reflections
333 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -3.767$ (for x of H12)
$\Delta\rho_{\max} = 0.542$ e Å^{-3}
$\Delta\rho_{\min} = -0.616$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	0.48241 (7)	0.17937 (7)	0.10028 (6)	0.0246 (4)
N1	0.3078 (5)	0.2035 (5)	0.0708 (4)	0.029 (2)
C2	0.2804 (8)	0.3116 (7)	0.0394 (7)	0.048 (3)
C3	0.3004 (8)	0.3183 (7)	−0.0501 (7)	0.048 (3)
C4	0.4127 (7)	0.2589 (6)	−0.0657 (5)	0.037 (2)
N5	0.5095 (6)	0.2701 (5)	0.0056 (4)	0.029 (2)
C6	0.5975 (8)	0.3313 (6)	0.0029 (6)	0.038 (2)
C61*A*†	0.646 (3)	0.389 (3)	−0.075 (2)	0.041 (9)
C61*B*†	0.592 (2)	0.405 (2)	−0.069 (2)	0.038 (6)
C7	0.6946 (8)	0.3406 (6)	0.0788 (6)	0.039 (2)
C8	0.7437 (6)	0.2390 (6)	0.1213 (5)	0.030 (2)
C81	0.8558 (7)	0.2634 (7)	0.1862 (5)	0.045 (3)
C82	0.7736 (7)	0.1600 (7)	0.0561 (6)	0.046 (3)
N9	0.6500 (5)	0.1940 (5)	0.1646 (4)	0.026 (2)
C10	0.6759 (7)	0.1010 (6)	0.2163 (5)	0.035 (2)
C11	0.5677 (7)	0.0713 (6)	0.2521 (5)	0.030 (2)
N12	0.4662 (5)	0.0638 (5)	0.1821 (4)	0.024 (2)
C13	0.3478 (6)	0.0334 (6)	0.2002 (5)	0.027 (2)
C131	0.3514 (8)	−0.0764 (7)	0.2361 (7)	0.058 (3)
C132	0.3084 (7)	0.1121 (6)	0.2612 (5)	0.035 (2)
C14	0.2617 (7)	0.0343 (7)	0.1170 (6)	0.039 (2)
C15	0.2260 (7)	0.1385 (7)	0.0790 (5)	0.037 (2)
C151	0.0956 (7)	0.1564 (10)	0.0532 (6)	0.071 (4)
Cl1	0.5325 (2)	0.4117 (2)	0.2795 (2)	0.0464 (7)
O11	0.4629 (5)	0.3518 (5)	0.2167 (5)	0.066 (2)
O12	0.6533 (5)	0.3755 (5)	0.2953 (4)	0.052 (2)
O13*A*†	0.5117 (17)	0.5116 (13)	0.2782 (13)	0.022 (6)
O13*B*†	0.547 (2)	0.5105 (19)	0.227 (3)	0.165 (16)
O14*A*†	0.5027 (16)	0.471 (3)	0.341 (2)	0.085 (17)
O14*B*†	0.4751 (12)	0.3724 (15)	0.3540 (9)	0.067 (6)
Cl3	1/2	0	0	0.0238 (7)
Cl2	0	1/2	0	0.0289 (8)
O21	0.1242 (8)	0.5121 (8)	0.0296 (8)	0.042 (3)
O22	−0.0668 (10)	0.5286 (9)	0.0589 (7)	0.041 (3)
O23	−0.0341 (10)	0.5542 (8)	−0.0780 (7)	0.046 (4)
O24	−0.0185 (10)	0.3861 (8)	−0.0215 (9)	0.064 (4)

† Partial occupancy (see below).

Table 2. *Selected geometric parameters (Å, °)*

Cu1—N1	1.984 (6)	Cu1—N9	2.016 (6)
Cu1—N5	1.988 (6)	N1—C15	1.27 (1)
Cu1—N12	2.011 (6)	N5—C6	1.27 (1)
N1—Cu1—N5	90.4 (3)	C2—N1—Cu1	111.6 (6)
N1—Cu1—N12	93.9 (3)	C6—N5—C4	121.3 (7)
N5—Cu1—N12	168.3 (3)	C6—N5—Cu1	127.6 (6)
N1—Cu1—N9	158.0 (3)	C4—N5—Cu1	111.1 (5)
N5—Cu1—N9	95.0 (3)	N1—C15—C151	125.7 (9)
N12—Cu1—N9	85.0 (2)	N1—C15—C14	118.2 (7)
C15—N1—C2	121.8 (7)	C151—C15—C14	116.1 (8)
C15—N1—Cu1	126.5 (6)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H···O12	0.91	2.23	3.13 (1)	171
C14—H···O14*A*$^{\rm i}$	0.99	2.36	3.30 (1)	159
C131—H···O23$^{\rm ii}$	0.98	2.19	3.08 (1)	152
C151—H···O24	0.98	2.40	3.34 (1)	160

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

The structure of the title compound was solved by heavy-atom methods and refined with anisotropic displacement parameters for non-H atoms. Neutral-atom scattering factors were from Ibers & Hamilton (1992). Rotational disorder of the Cl1 perchlorate ion was modelled with two O atoms each occupying two half-weighted sites. The Cl2 perchlorate ion occupies alternating half-weighted sites and this modulates the location of one imine methyl group, which was modelled with C atoms occupying half-weighted C61*A* and C61*B* sites. Non-H-atom parameters were refined anisotropically and H-atom positions were calculated and their parameters refined in isotropic approximation, omitting the H atoms associated with the disordered C61 atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XPMA* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

Collection of the diffraction data by Professor W. T. Robinson, Chemistry Department, University of Canterbury, New Zealand, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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{2-[Bis(1-methyl-2-benzimidazolylmethyl)-amino]ethanol}chlorocopper(II) Chloride Hydrate

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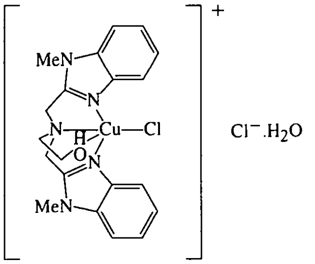
Abstract

During the multi-step synthesis of a novel and potentially binucleating ligand, the title complex, $[CuCl(C_{20}H_{23}N_5O)]Cl.H_2O$, was obtained and structurally characterized. The analysis revealed distorted five-coordinate square-pyramidal coordination geometry about Cu, with three N atoms and one Cl ion in the basal plane and the hydroxy group, which remains protonated, at the apical position [Cu—O 2.278 (2) Å].

Comment

The design, synthesis and characterization of ligands that offer coordination environments similar to those identified in metalloproteins and enzymes is an ongoing ambition of our research. The title complex, (I), displays two benzimidazole groups, a tertiary aliphatic amine and an ethyl alcohol group. Benzimidazole is an excellent model for the amino acid histidine because, in addition to structural similarities, it has a similar pK_a.



(I)

There is five-coordinate distorted square-pyramidal coordination geometry about the Cu atom, with the alcohol group in the apical position at a distance of 2.278 (2) Å from Cu. A feature of particular interest is that the alcohol group remains protonated although coordinated to the copper centre. This relatively unusual feature offers a structural model for a putative intermediate in the reduction of dioxygen for blue copper oxidases. During enzymic function a hydroperoxide is postulated to be stabilized by coordination to the Type III copper centre prior to complete reduction of the substrate. This complex represents effectively half of the Type III copper centre for the blue copper oxidases, and as such is a

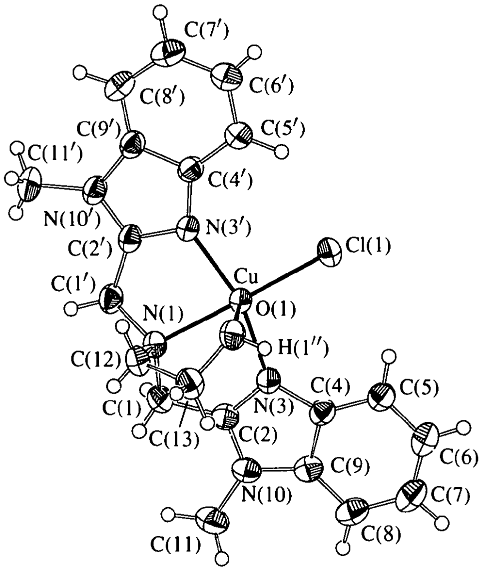


Fig. 1. A view of the cation with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as circles with arbitrary radii.

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