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(*C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-N^1-acetato-N,N',N'',N''',O)copper(II) Bromide Monohydrate

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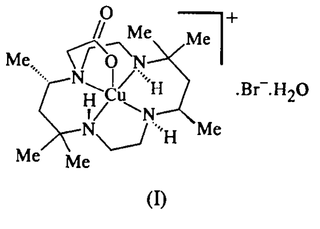
Abstract

The crystal structure of the title compound, $[Cu(C_{18}H_{37}N_4O_2)]Br.H_2O$, shows the Cu^{II} ion to be five-coordinate in a distorted square-pyramidal environment, with the four N atoms equatorial and the O atom axial. The Cu—O and average Cu—N bond lengths are 2.157 (3) and 2.050 (4) Å, respectively.

Comment

The coordination chemistry of macrocyclic ligands with pendant functional groups has attracted growing interest because of their potential biomedical applications (Bernhardt & Lawrance, 1990; Bünzli & Choppin, 1986; Kaden, 1984, 1993; Parker, 1990). However, the synthesis of these macrocyclic ligands is generally more complicated and necessitates several steps (Kaden, 1984). Previously, Xu, Ni & Lin (1986, 1988) presented a simple stereospecific synthesis of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid and discussed the crystal structures of its nickel(II) complexes. The crystal structure of the title complex, (I), has been determined and is presented here to expand the studies in this area.



(I)

The *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetate group coordinates the Cu^{II} ion as a pentadentate ligand. The complex cation has a distorted square-pyramidal environment around the Cu^{II} ion with the four N atoms equatorial and the O atom axial. The four N atoms of the macrocyclic ligand form a square plane [mean deviation 0.072 (2) Å], with the Cu^{II} ion lying 0.148 (2) Å out of this plane towards the carboxyl group. The macrocyclic moiety adopts the stable conformation with the two six-membered rings in chair conformations and the two five-membered rings in *gauche* conformations. The Cu—N distances range from 2.029 (4) to 2.088 (4) Å and the average Cu—N distance [2.050 (4) Å] in the title complex is longer than average Cu—N distances in the literature (2.03 Å) (Lu, Chung & Ashida, 1993). The bond distance of Cu—N(tertiary) [2.088 (4) Å] is longer than Cu—N(secondary) [2.029 (4)–2.046 (4) Å]. The four chiral N-atom centers have configurations 1*RS*, 4*SR*, 8*RS* and 11*RS*. The Cu—N(secondary) distance is shorter than that in the copper(II) complex with *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N,N''*-diacetic acid (2.070 Å; Belsky *et al.*, 1993). The axial Cu—O bond length [2.157 (3) Å] is shorter than those observed in copper(II) alkylcarboxylates (2.30–2.40 Å) (Orpen *et al.*, 1989). This arrangement of the four chiral N-atom centers is in the *trans*–III configuration according to the nomenclature of Bosnich, Poon & Tobe (1965), the same configuration found in the red isomer of copper(II) complexes of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Clay, Murray-Rust & Murray-Rust, 1979). The crystal structure is stabilized by a three-dimensional network of N—H···Br, N—H···O and O—H···Br hydrogen bonds (Table 2).

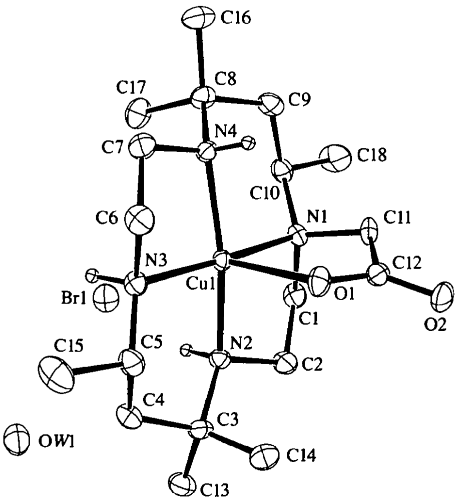


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been omitted, except those on N2, N3 and N4.

Experimental

The ligand *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid and the title complex were prepared according to literature methods (Xu, Ni & Lin, 1986, 1988). The complex was recrystallized from a methanol-*n*-butanol mixture by slow evaporation.

Crystal data

[$Cu(C_{18}H_{37}N_4O_2)$]$Br.H_2O$
$M_r = 502.98$
Triclinic
$P\bar{1}$
$a = 8.815\ (1)$ Å
$b = 10.905\ (1)$ Å
$c = 13.210\ (2)$ Å
$\alpha = 95.46\ (1)^\circ$
$\beta = 108.26\ (1)^\circ$
$\gamma = 107.74\ (1)^\circ$
$V = 1122.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.488$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.42\text{–}25.13^\circ$
$\mu = 2.777$ mm^{-1}
$T = 293\ (2)$ K
Pillar
0.49 × 0.32 × 0.14 mm
Blue

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.257$, $T_{\max} = 0.678$
4729 measured reflections
3888 independent reflections
2738 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\max} = 25.00^\circ$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 15$
3 standard reflections every 197 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.123$
$S = 1.024$
3888 reflections
361 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.060$
$\Delta\rho_{\max} = 0.557$ e Å^{-3}
$\Delta\rho_{\min} = -0.849$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N3	2.029 (4)	O2—C12	1.231 (6)
Cu1—N2	2.038 (4)	C1—C2	1.499 (8)
Cu1—N4	2.046 (4)	C3—C14	1.513 (8)
Cu1—N1	2.088 (4)	C3—C13	1.514 (8)
Cu1—O1	2.157 (3)	C3—C4	1.540 (7)
N1—C11	1.487 (6)	C4—C5	1.524 (8)
N1—C1	1.493 (6)	C5—C15	1.545 (8)
N1—C10	1.511 (6)	C6—C7	1.519 (8)
N2—C2	1.484 (6)	C8—C9	1.523 (8)
N2—C3	1.511 (6)	C8—C17	1.533 (7)
N3—C6	1.483 (7)	C8—C16	1.537 (8)
N3—C5	1.489 (7)	C9—C10	1.508 (8)
N4—C7	1.480 (6)	C10—C18	1.531 (8)
N4—C8	1.499 (6)	C11—C12	1.543 (7)
O1—C12	1.266 (6)		
N3—Cu1—N2	93.8 (2)	N2—C2—C1	108.6 (4)
N3—Cu1—N4	85.5 (2)	N2—C3—C14	110.1 (4)
N2—Cu1—N4	167.6 (2)	N2—C3—C13	109.7 (4)
N3—Cu1—N1	175.7 (2)	C14—C3—C13	111.0 (5)
N2—Cu1—N1	86.6 (2)	N2—C3—C4	107.6 (4)
N4—Cu1—N1	93.2 (2)	C14—C3—C4	110.6 (5)
N3—Cu1—O1	100.5 (2)	C13—C3—C4	107.8 (5)
N2—Cu1—O1	96.01 (15)	C5—C4—C3	119.0 (5)
N4—Cu1—O1	96.30 (15)	N3—C5—C4	109.0 (4)
N1—Cu1—O1	83.71 (14)	N3—C5—C15	111.1 (5)
C11—N1—C1	110.3 (4)	C4—C5—C15	109.9 (5)
C11—N1—C10	111.8 (4)	N3—C6—C7	106.2 (4)
C1—N1—C10	109.1 (4)	N4—C7—C6	109.1 (4)
C11—N1—Cu1	106.5 (3)	N4—C8—C9	108.5 (4)
C1—N1—Cu1	104.1 (3)	N4—C8—C17	109.8 (4)
C10—N1—Cu1	114.8 (3)	C9—C8—C17	110.8 (5)
C2—N2—C3	114.0 (4)	N4—C8—C16	109.7 (4)
C2—N2—Cu1	105.7 (3)	C9—C8—C16	108.0 (5)
C3—N2—Cu1	123.2 (3)	C17—C8—C16	109.9 (5)
C6—N3—C5	113.6 (4)	C10—C9—C8	118.6 (4)
C6—N3—Cu1	103.2 (3)	C9—C10—N1	114.2 (4)
C5—N3—Cu1	117.4 (3)	C9—C10—C18	110.2 (5)
C7—N4—C8	114.5 (4)	N1—C10—C18	112.1 (5)
C7—N4—Cu1	107.1 (3)	N1—C11—C12	115.1 (4)
C8—N4—Cu1	119.7 (3)	O2—C12—O1	126.6 (5)
C12—O1—Cu1	111.5 (3)	O2—C12—C11	116.0 (5)
N1—C1—C2	111.1 (4)	O1—C12—C11	117.3 (4)
N2—Cu1—N1—C1	10.1 (3)	Cu1—N4—C7—C6	30.5 (5)
Cu1—N1—C1—C2	−37.2 (5)	N3—Cu1—N4—C7	−0.8 (3)
N1—C1—C2—N2	55.8 (6)	N1—Cu1—N4—C8	42.6 (3)
Cu1—N2—C2—C1	−42.9 (5)	Cu1—N4—C8—C9	−56.9 (5)
N1—Cu1—N2—C2	17.8 (3)	N4—C8—C9—C10	66.8 (6)
N3—Cu1—N2—C3	−32.9 (4)	C8—C9—C10—N1	−68.3 (6)
Cu1—N2—C3—C4	45.9 (5)	Cu1—N1—C10—C9	53.5 (5)
N2—C3—C4—C5	−65.8 (6)	N4—Cu1—N1—C10	−38.2 (3)
C3—C4—C5—N3	74.9 (6)	O1—Cu1—N1—C11	−10.0 (3)
Cu1—N3—C5—C4	−58.5 (5)	N1—Cu1—O1—C12	−4.8 (3)
N2—Cu1—N3—C5	37.7 (4)	Cu1—O1—C12—C11	18.8 (5)
N4—Cu1—N3—C6	−28.9 (3)	N1—C11—C12—O1	−29.3 (7)
Cu1—N3—C6—C7	52.7 (5)	Cu1—N1—C11—C12	22.1 (5)
N3—C6—C7—N4	−57.0 (6)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1N2···Br1	0.84 (6)	2.62 (6)	3.440 (4)	166 (6)
N3—H1N3···O*W*1$^{\rm i}$	0.89 (6)	2.10 (6)	2.976 (7)	167 (6)
N4—H1N4···O2$^{\rm ii}$	0.92 (6)	2.00 (6)	2.885 (5)	159 (5)
O*W*1—H1O*W*···Br1$^{\rm i}$	0.69 (7)	2.65 (7)	3.338 (5)	172 (8)
O*W*1—H2O*W*···Br1	0.83 (7)	2.51 (7)	3.337 (5)	173 (6)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, -y, -z$.

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: *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1176). Services for accessing these data are described at the back of the journal.

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Platinum(II) Complexes of Piperazine (and Derivatives): *trans*-Dichlorobis(*N*-methylpiperazine-*N*′)platinum(II)

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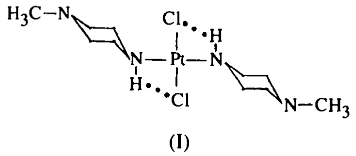
Abstract

The neutral title complex, *trans*-[PtCl$_2$(C$_5$H$_{12}$N$_2$)$_2$], has been synthesized in the course of our studies on piperazine derivative complexes with platinum(II). This complex is square planar and isomorphous with the analogous palladium(II) complex, and exhibits the same molecular, but not crystallographic, structure as *trans*-[PtCl$_2$(C$_5$H$_{13}$N$_2$)$_2$]Cl$_2$.2H$_2$O, [(C$_5$H$_{13}$N$_2$) is *N*-methylpiperazinium(1+)]. The six-membered ring is in the chair conformation and binds platinum(II) through the unmethylated N1—H nitrogen, which is sterically less hindered than the methylated one. The molecule has a local pseudo-mirror plane nearly coincident with the square-planar coordination plane and nearly bisecting the piperazine ring.

Comment

The cyclic diamine piperazine (H$_2$ppz) contains a non-planar six-membered ring formed by four C and two basic N atoms. Piperazine and its derivatives, *N*-methylpiperazine (HMeppz) and *N*,*N*′-dimethylpiperazine (Me$_2$ppz), can act as monodentate, bidentate or bidentate chelate ligands. The six-membered ring commonly displays a chair and less frequently a boat conformation, the former conformation being 17.2 kJ mol^{-1} more stable (Niemeyer, 1979). However, the boat conformation occurs when *N*-methylpiperazine forms a bidentate chelate complex with one platinum(II) ion (Marzotto, Clemente & Valle, 1998), when *N*,*N*′-dimethylpiperazine forms a chelate complex with one palladium(II) ion (Hassel & Pedersen, 1959) or when the piperazine ring is forced to form a macrocyclic ligand capable of chelating selectively one metal ion (Wade *et al.*, 1990). Other interesting platinum(II) coordination compounds of *N*-methylpiperazine and *N*,*N*′-dimethylpiperazine, with potential antitumoral activity, will be published soon (Ciccarese *et al.*, 1998).

The X-ray analysis of the title complex, (I), shows that the platinum(II) ion has a distorted square-planar coordination geometry (Table 1), with the two Cl and the two *N*-methylpiperazine ligands each in *trans* positions, as found in *trans*-[PdCl$_2$(HMeppz)$_2$] (Ivanova *et al.*, 1991) and in *trans*-[PtCl$_2$(H$_2$Meppz)$_2$]Cl$_2$.2H$_2$O (Ciccarese *et al.*, 1998) [H$_2$Meppz is *N*-methylpiperazinium(1+), *i.e.* a cationic ligand]. The piperazine ring possesses a chair conformation and is coordinated through the secondary amine N1 atom which is sterically less hindered than the methylated N2 atom. The Pt—N1 and N2—CH$_3$ bonds lie in equatorial positions, while the N1—H1 bond is in an axial position for steric reasons. In this way, N1 can form a strong intramolecular hydrogen bond with the Cl1 atom (Table 2). In fact, the decrease of the N1—Pt—Cl1 angle from 90 to 87.84 (11)° indicates that this hydrogen bond stabilizes the molecule. The angle between the Pt, Cl1, N1 plane and the C1, C2, C3, C4 plane is 89.06 (16)°, very near to 90°. This angle is very likely imposed by the abovementioned strong intramolecular N1—H1···Cl1 hydrogen bond. In fact, only if this angle is 90° does the H1 atom lie exactly in the square-planar coordination plane which favours the formation of a strong hydrogen bond. The entire molecule possess a pseudo-mirror plane, practically coincident with the square-planar coordination plane [the dihedral angle is 0.49 (7)°], and bisects the piperazine ring passing through the N1, N2 and C5 atoms.



(I)