Chlorobis(clemizole)copper(II) chloride ethanol solvate

Kristin Braitenbach and Masood Parvez*

Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

Correspondence e-mail: parvez@ucalgary.ca

Key indicators

Single-crystal X-ray study

T = 293 K

Mean σ(C–C) = 0.010 Å

Disorder in solvent or counterion

R factor = 0.051

wR factor = 0.142

Data-to-parameter ratio = 8.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of chlorobis{[1-(p-chlorophenylmethyl)-2-(1-pyrrolidin-1-ylmethyl)-2,3-dihydro-1H-benzimidazole-N^2,-N^3]}copper(II) chloride ethanol solvate, [CuCl(C$_{19}$H$_{20}$ClN$_3$)$_2$]Cl·C$_2$H$_6$O, contains two molecules of clemizole bound in a bidentate manner to copper, with significantly different Cu—N distances; the pyrrolidinyl N—Cu and imidazole N—Cu distances are 1.959 (4) and 2.366 (5) Å for ligand 1, and 1.976 (4) and 2.193 (4) Å for ligand 2, respectively. The geometry around copper is distorted trigonal bipyramidal, with a Cu—Cl distance of 2.2699 (15) Å.

Comment

The crystal structures of clemizole hydrochloride (Parvez, 1996), clemizoledichlorozinc(II) (Parvez & Sabir, 1996a) clemizoledichlorocobalt(II), (Parvez & Braitenbach, 2000), clemizole as a free base (Parvez & Sabir, 1996b), clemizole tetrachlorocuprate(II) and clemizole tetrachlorocobaltate(II) (Parvez & Sabir, 1997) have been reported from our laboratory. This H$_1$ antihistamine has now been incorporated into a copper complex to investigate further the effects such complex formation may have on the conformation of the clemizole moiety. In this paper, we report the structure of bis-(clemizole)chlorocopper(II) chloride ethanol solvate, (I).
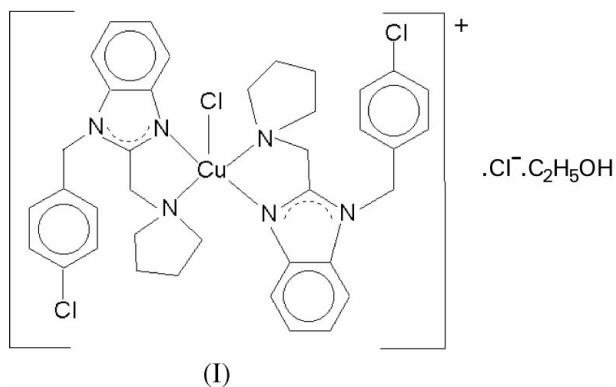

(I)

Fig. 1 shows an ORTEPII (Johnson, 1976) drawing of the cation bis(clemizole)chlorocopper(II) wherein two molecules of clemizole are coordinated in a bidentate mode to copper via pyrrolidinyl and imidazole N atoms with significantly different Cu—N distances of 1.959 (4) and 2.366 (5) Å for ligand 1, and 1.976 (4) and 2.193 (4) Å for ligand 2, respectively; the imidizole N atom, N3, of ligand 1 has an unusually long bond to copper. The Cu atom is also bound to Cl2, with a distance of 2.2699 (15) Å. The geometry around copper is distorted trigonal bipyramidal with an almost linear N1—Cu1—N1A angle, 172.84 (18)°. Similar distances and geometry have been
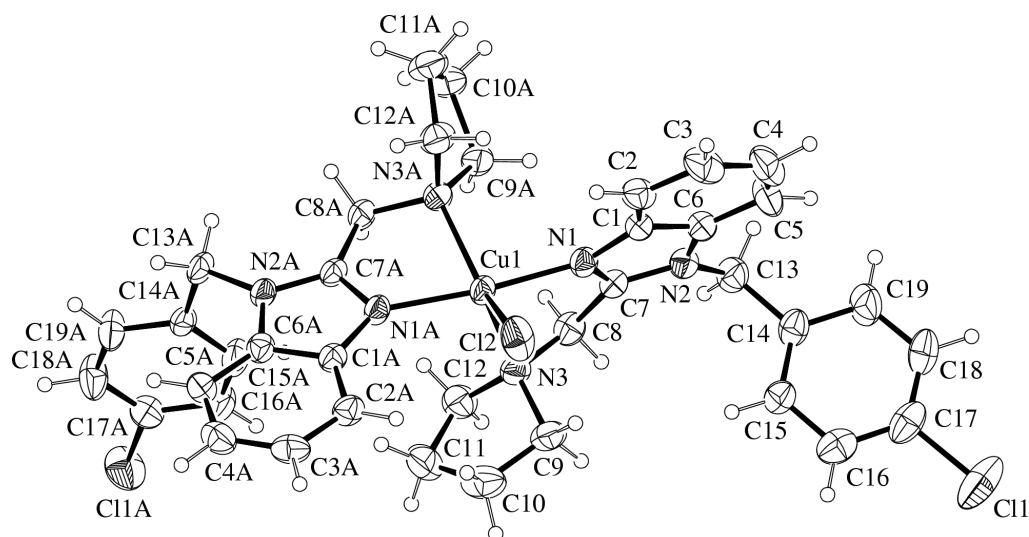
Figure 1
*ORTEP*II (Johnson, 1976) drawing of bis(clemizole)chlorocopper(II) with displacement ellipsoids plotted at the 30% probability level.

reported for a number of closely related copper complexes, *e.g.* chloro(2,5,8,11-tetraethyl-1,2,7,10-tetraazacyclododec-ane)copper(II) chloride hydrate (Sakurai *et al.*, 1982), chloro(1,4,7,10-tetrabenzyl-2,5,8,11-tetraethyl-1,4,7,10-tetra-azacyclododecane)copper(II) chloride (Sakurai *et al.*, 1982), chloro(*trans*-5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclo-tetradecane-6,13-dione dioxime)copper(II) chloride hepta-hydrate (Bernhardt & Sharpe, 1998), (4,11-dibenzyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)chlorocopper(II) chloride monohydrate (Weisman *et al.*, 1996), and (1,4,8,11-tetraaza-bicyclo[6.6.2]hexadecane)chlorocopper(II) chloride trihy-drate (Weisman *et al.*, 1996).

The molecular dimensions of the ligands are normal. The important mean bond distances are: C*sp*2—Cl 1.738 (9), C*sp*3—C*sp*3 1.519 (16), C*sp*3—C*sp*2 1.506 (5), N—C*sp*3 1.476 (11), N—C*sp*2 1.379 (10) and C—C$_{aromatic}$ 1.382 (18) Å. It is interesting to note that the N1—C7 and N1A—C7A bonds [1.336 (7) and 1.312 (6) Å, respectively] are much shorter than expected for a single bond and that the N2—C7 and N2A—C7A bonds [1.343 (7) and 1.348 (6) Å, respec-tively] are much longer than expected for a double bond; these bonds must represent a delocalized system with mean N—C distance of 1.334 (13) Å; the corresponding distances in the structure of clemizoledichlorozinc(II) (Parvez & Sabir, 1996a) were observed to be 1.357 (5) and 1.321 (5) Å, respectively.

The benzimidazole and phenyl rings are essentially planar with maximum deviations of atoms from the least-squares planes being 0.037 (5) and 0.021 (6) Å for ligand 1 and 0.020 (4) and 0.018 (6) Å for ligand 2, respectively. The dihe-dral angle between the least-squares planes of the benz-imidazole and phenyl rings is 81.38 (18)° for ligand 1 and 85.65 (18)° for ligand 2. The corresponding angle in the structures of clemizole dichlorozinc, clemizole hydrochloride, clemizole dichlorocobalt, clemizole as a free base, clemizole tetrachlorocuprate(II) and clemizole tetrachlorocobaltate(II) are 81.1 (4) (Parvez & Sabir, 1996a), 82.8 (9) (Parvez, 1996),

86.2 (2) (Parvez & Braitenbach, 2000), 68.8 (6) (Parvez & Sabir, 1996b), 70.5 (6) and 82.7 (9)° (Parvez & Sabir, 1997), respectively.

An examination of the torsion angle N2—C13—C14—C19 in ligand 1 [-123.4 (7)°] and N2A—C13A—C14A—C19A in ligand 2 [146.7 (6)°] shows that the orientation of the phenyl ring with respect to the imidazole ring in ligand 1 in (I) is somewhat similar to the orientation of these rings in clemizole tetrachlorocobaltate (−116°; Parvez & Sabir, 1997) and the orientation of these rings in ligand 2 in (I) is somewhat similar to the orientation of these rings in clemizole tetrachloro-cuprate (133°; Parvez & Sabir, 1997) and clemizole hydro-chloride (153°; Parvez, 1996). The pyrrolidinyl rings in each ligand have an N-envelope conformation with N3 0.627 (9) Å out of the plane of the C9–C12 atoms and N3A 0.582 (9) Å out of the plane of the C9A–C12A atoms; similar conformations of the five-membered ring have been observed in the crystal structures mentioned above.

The structure is composed of independent cations of the complex separated by normal van der Waals distances. The hydrogen bonding interactions exist between Cl⁻ ions and the ethanol molecules of solvation, both the distances O1H1···Cl3 and O1H1A···Cl3 are 2.73 Å. The benzimidazole moieties of the complex molecules which lie about the inver-sion centers are stacked parallel to each other.

Experimental

The title compound was synthesized by adding 1.0 mmol of $CuCl_2 \cdot 2H_2O$ to 2.0 mmol of clemizole hydrochloride (Sigma Inc.) in 20 ml of ethanol. NH_4OH was added until the pH was 8–9. The solution was evaporated slowly at room temperature and blue pris-matic crystals separated after a few days.

Crystal data

[CuCl(C$_{19}$H$_{20}$ClN$_3$)$_2$]Cl·C$_2$H$_6$O
$M_r = 832.17$
Monoclinic, Pn
$a = 12.809$ (3) Å
$b = 8.608$ (2) Å
$c = 19.482$ (4) Å
$\beta = 95.81$ (2)°
$V = 2137.0$ (8) Å^3
$Z = 2$

$D_x = 1.293$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25
  reflections
$\theta = 15.0–40.0°$
$\mu = 3.31$ mm^{-1}
$T = 293$ (2) K
Prismatic, blue
$0.48 \times 0.45 \times 0.40$ mm

Data collection

Enraf–Nonius CAD-4 diffract-
  ometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ
  scan (3 reflections) (North *et al.*,
  1968)
$T_{min} = 0.299$, $T_{max} = 0.351$
7860 measured reflections
4073 independent reflections

3871 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 68.0°$
$h = 0 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = -23 \rightarrow 23$
3 standard reflections
  every 200 reflections
  intensity decay: 32%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.142$
$S = 1.03$
4073 reflections
469 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1112P)^2$
  $+ 0.3126P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0054 (7)
Absolute structure: Flack (1983)
Flack parameter = 0.08 (2)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Cl3^i	0.82	2.73	3.061 (10)	106
O1A—H1$A\cdots$Cl3^{ii}	0.82	2.73	3.16 (2)	114

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

Based on the systematic absences: $h0l$, $h + l = 2n + 1$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be Pn. The asymmetric unit contains a bis-(clemizole)chlorocopper(II) cation, a Cl$^-$ anion and two half molecules of ethanol of solvation. The C and O atoms of the solvent molecules were refined with isotropic displacement parameters while the rest of the non-H atoms were allowed anisotropic vibrations. The partial occupancy factors for the solvents were determined during the initial rounds of calculations and were fixed at 0.50 at the final stages of the refinements. A small degree of disorder was also evident in the solvent molecules, therefore, C—O and C—C distances were constrained. The H atoms were included in the refinements in a riding mode with O—H = 0.82 Å and C—H = 0.93–0.97 Å. The non-methyl and methyl H atoms were allowed isotropic displacement parameters 1.2 and 1.5 times the displacement parameters of the atoms to which they were attached.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1994); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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