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Clemizole Tetrachlorocuprate(II) and Clemizole Tetrachlorocobaltate(II)

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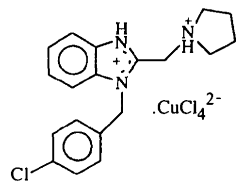
Abstract

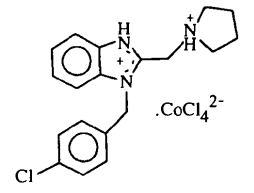
The crystal structures of 3-[4-(chlorophenyl)methyl]-2-(1-pyrrolidiniomethyl)-1*H*-benzimidazolium tetrachlorocopper(II), $(C_{19}H_{22}ClN_3)[CuCl_4]$, and 3-[4-(chlorophenyl)methyl]-2-(1-pyrrolidiniomethyl)-1*H*-benzimidazolium tetrachlorocobalt(II), $(C_{19}H_{22}ClN_3)[CoCl_4]$, show different conformations of the free radical dihydro cations of clemizole, a potent anti-allergic agent. The anions, $CuCl_4^{2-}$ and $CoCl_4^{2-}$, exhibit flattened and normal tetrahedral geometries, respectively.

Comment

Our continued interest in the conformations of antihistamines effective on H_1-receptors has led to the preparation of free radical dihydro cations of clemizole in order to investigate the influence of tetrachlorocopper(II) and tetrachlorocobalt(II) ions on the conformation of clemizole. In this paper, we report the crystal structures of clemizole tetrachlorocopper(II), (1), and clemizole tetrachlorocobalt(II), (2); the crystal structures of clemizole in its free form, (3) (Parvez & Sabir, 1996*a*), clemizole hydrochloride, (4) (Parvez, 1996), and a transition metal complex of clemizole, clemizoledichlorozinc(II), (5) (Parvez & Sabir, 1996*b*), have been reported recently from this laboratory.



(1)



(2)

The *ORTEP*II (Johnson, 1976) drawings of (1) and (2) are shown in Figs. 1 and 2, respectively. The molecular dimensions of the dihydro cations in (1) and (2) are normal, with identical corresponding bond distances and angles. The C1—N1 and C1—N2 distances in the two cations are equivalent, indicating electron delocalization in the imidazole rings. The remaining bond distances and angles are not very different from those observed in compounds (3)–(5).

The benzimidazole and phenyl rings are individually planar in the two cations and are inclined at angles of 70.5 (6) and 82.7 (9)° in (1) and (2), respectively; the corresponding angles in the crystal structures of (3)–(5) are 68.8 (6), 82.8 (9) and 81.1 (4)°, respectively.

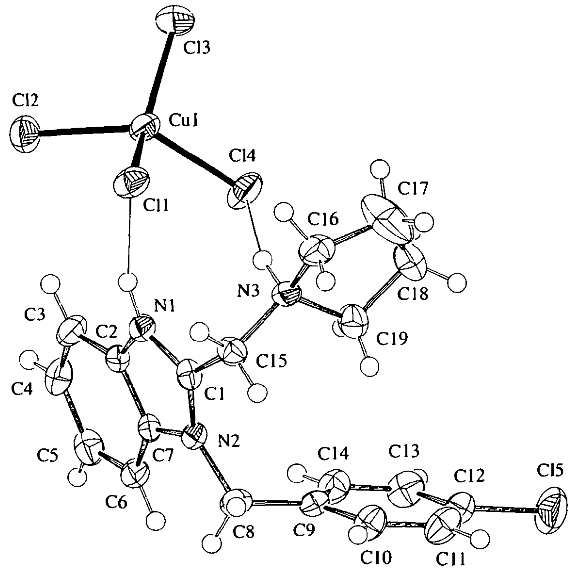


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been assigned arbitrary radii.

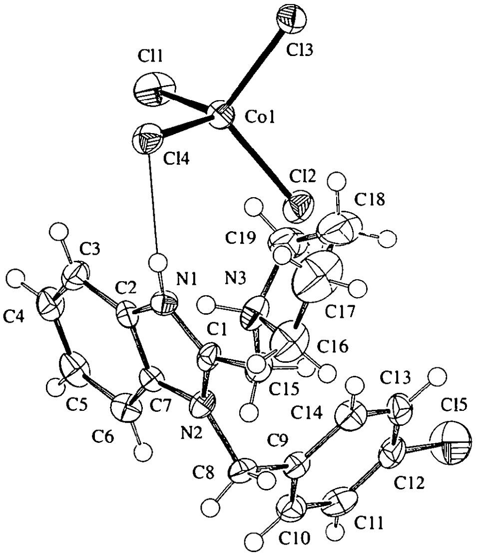


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of (2) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been assigned arbitrary radii.

The pyrrolidinyl ring in (1) has the usual N3-envelope conformation as observed in (3)–(5) with N3 0.493 (5) Å out of the plane of the remaining four C atoms of the ring. However, the corresponding ring in (2) has a C17-envelope conformation with C17 0.499 (6) Å out of the plane of the remaining four atoms of the ring.

The $CuCl_4^{2-}$ anion in (1) is a flattened tetrahedron with Cu—Cl distances in the range 2.197 (2)–2.289 (2) Å; four Cl—Cu—Cl angles are in the range 97.07 (7)–100.88 (7)° and the remaining two are 131.44 (7) and 137.99 (7)°. Similar geometry for $CuCl_4^{2-}$ has been reported in a number of structures, *e.g.* dicytosinium tetrachlorocuprate(II) (Ogawa, Nishitani, Fujiwara, Shirotake & Tomita, 1979), chlorpromazine tetrachlorocopper(II) (Obata, Kawazura & Miyamae, 1984), promazine tetrachlorocopper(II) (Von Dreele & Harris, 1983) and fenethazine tetrachlorocopper(II) (Obata, Yoshimori, Yamada & Kawazura, 1985). The $CoCl_4^{2-}$ anion in (2), on the other hand, has a normal tetrahedral geometry with Co—Cl distances 2.234 (2)–2.312 (2) Å and Cl—Co—Cl angles in the range 104.48 (7)–114.36 (8)°. A similar geometry has been reported for the anion in the structures of histamine tetrachlorocobalt(II) (Bonnet & Jeannin, 1972) and bis(lignocaine) tetrachlorocobalt(II) (Indira, Babu, Bellad, Sridhar & Prasad, 1992).

It is interesting to note that in (1), the anions are hydrogen-bonded through two Cl atoms to the same cation, forming independent anion–cation pairs with N···Cl interactions of 3.175 (4) and 3.157 (5) Å. On the other hand, in (2), the anions are linked to two different cations through Cl atoms, with N···Cl separations of 3.167 (5) and 3.128 (5) Å, thus resulting in a hydrogen-bonded chain structure along the *a* axis.

Experimental

Clemizole hydrochloride (0.362 g, 1 mmol; Sigma Inc.) in 15 ml of concentrated HCl was mixed with $CuCl_2.2H_2O$ (0.171 g, 1 mmol) and boiled for 10 min. On allowing the solution to stand overnight, orange prismatic crystals of (1) were obtained. The crystals were washed with acetone. For compound (2), clemizole hydrochloride (0.362 g, 1 mmol; Sigma Inc.) in 30 ml of concentrated HCl was mixed with $CoCl_2.6H_2O$ (0.238 g, 1 mmol) and boiled for 10 min. On allowing the solution to stand overnight, blue needles of (2) were obtained and washed with acetone.

Compound (1)

Crystal data

($C_{19}H_{22}ClN_3$)[$CuCl_4$]
M_r = 533.21
Triclinic
$P\bar{1}$
a = 9.595 (5) Å
b = 14.008 (4) Å
c = 9.413 (5) Å
α = 93.53 (3)°
β = 117.14 (4)°
γ = 85.03 (3)°
V = 1121.3 (10) Å^3
Z = 2
D_x = 1.579 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 21 reflections
θ = 10–15°
μ = 1.581 mm^{-1}
T = 296 K
Prismatic
0.30 × 0.20 × 0.13 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.72, T_{max} = 0.81
4228 measured reflections
3971 independent reflections

2420 reflections with $I > 2\sigma(I)$
R_{int} = 0.0327
θ_{max} = 25°
$h = 0 \rightarrow 11$
$k = -16 \rightarrow 16$
$l = -11 \rightarrow 9$
3 standard reflections every 200 reflections intensity decay: 0.78%

Refinement

Refinement on F^2
$R(F)$ = 0.0572
$wR(F^2)$ = 0.0747
S = 1.96
3963 reflections
253 parameters
H atoms geometrically idealized, with C—H and N—H 0.95 Å

$w = 1/[\sigma^2(F_o) + 0.01F_o^2]$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

Cu1—Cl1	2.289 (2)	N2—C1	1.342 (6)
Cu1—Cl2	2.276 (2)	N2—C7	1.395 (6)
Cu1—Cl3	2.197 (2)	N2—C8	1.493 (6)
Cu1—Cl4	2.251 (2)	N3—C15	1.495 (6)
Cl5—C12	1.747 (6)	N3—C16	1.519 (7)
N1—C1	1.344 (6)	N3—C19	1.503 (7)
N1—C2	1.380 (6)		

Cl1—Cu1—Cl2	97.39 (6)	C1—N2—C7	108.4 (4)
Cl1—Cu1—Cl3	137.99 (7)	C1—N2—C8	126.1 (5)
Cl1—Cu1—Cl4	97.07 (7)	C7—N2—C8	125.4 (4)
Cl2—Cu1—Cl3	100.88 (7)	C15—N3—C16	114.6 (4)
Cl2—Cu1—Cl4	131.44 (7)	C15—N3—C19	115.2 (4)
Cl3—Cu1—Cl4	98.50 (7)	C16—N3—C19	105.5 (4)
C1—N1—C2	110.1 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.95	2.28	3.175 (4)	157
N3—H3···Cl4	0.95	2.26	3.157 (5)	157

Compound (2)

Crystal data

$(C_{19}H_{22}ClN_3)[CoCl_4]$
$M_r = 528.60$
Monoclinic
$P2_1/c$
$a = 7.040$ (1) Å
$b = 23.282$ (3) Å
$c = 13.730$ (1) Å
$\beta = 91.11$ (1)°
$V = 2250.0$ (4) Å^3
$Z = 4$
$D_x = 1.560$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–20°
$\mu = 1.367$ mm^{-1}
$T = 200$ K
Needle
0.30 × 0.16 × 0.15 mm
Blue

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min} = 0.75$, $T_{\max} = 0.81$
4465 measured reflections
4116 independent reflections

2129 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0855$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 27$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: 1.39%

Refinement

Refinement on F^2
$R(F) = 0.0566$
$wR(F^2) = 0.0809$
$S = 1.67$
3992 reflections
253 parameters
H atoms geometrically idealized, with C—H and N—H 0.95 Å

$w = 1/[\sigma^2(F_o) + 0.014F_o^2]$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Co1—Cl1	2.234 (2)	N2—C1	1.339 (8)
Co1—Cl2	2.282 (2)	N2—C7	1.405 (7)
Co1—Cl3	2.312 (2)	N2—C8	1.469 (7)
Co1—Cl4	2.291 (2)	N3—C15	1.483 (8)
Cl5—C12	1.743 (7)	N3—C16	1.518 (8)
N1—C1	1.337 (7)	N3—C19	1.512 (9)
N1—C2	1.400 (7)		
Cl1—Co1—Cl2	114.36 (8)	C1—N2—C7	108.4 (5)
Cl1—Co1—Cl3	110.70 (8)	C1—N2—C8	126.9 (5)
Cl1—Co1—Cl4	108.99 (8)	C7—N2—C8	124.7 (5)
Cl2—Co1—Cl3	104.48 (7)	C15—N3—C16	109.6 (5)
Cl2—Co1—Cl4	109.94 (7)	C15—N3—C19	115.5 (5)
Cl3—Co1—Cl4	108.16 (7)	C16—N3—C19	107.4 (5)
C1—N1—C2	109.1 (5)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl4	0.95	2.35	3.167 (5)	144
N3—H3···Cl3^{i}	0.95	2.21	3.128 (5)	162

Symmetry code: (i) $x - 1, y, z$.

Based on statistical analysis, intensity distribution, successful solution and refinement of the structure, the space group $P\bar{1}$ was assigned to (1). For (2), the space group $P2_1/c$ was determined uniquely from the systematic absences of $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SAPI*91 (Fan, 1991); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1248). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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