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Doxylaminium Tetrachlorozincate(II) and Doxylaminium Tetrachlorocobaltate(II)

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Abstract

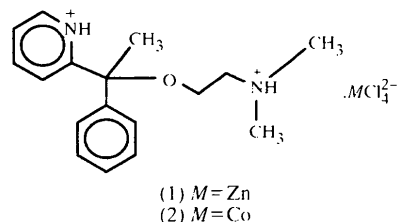
Doxylamine is an anti-allergic ether effective on H_1 -type receptors. The crystal structures of dihydro cationic salts of doxylamine {2-[1-(dimethylammonioethoxy)-1-phenylethyl]pyridinium} with the anions tetrachlorozincate(II), $(C_{17}H_{24}N_2O)[ZnCl_4]$, and tetrachlorocobaltate(II), $(C_{17}H_{24}N_2O)[CoCl_4]$, are isomorphous. The molecular dimensions in both structures are normal, and the anions and cations are hydrogen bonded, resulting in chain structures. The $ZnCl_4^{2-}$ and $CoCl_4^{2-}$ anions exhibit normal tetrahedral geometries.

Comment

Doxylamine, 2-[1-(dimethylaminoethoxy)-1-phenylethyl]pyridine, $C_{17}H_{22}N_2O$, is a chiral tertiary aminoalkyl ether which exhibits an antihistaminic action on the H_1 receptor site (Casy, 1991). The crystal structures of a number of compounds belonging to this class of ethers that possess anti-allergic activities have been

reported, *e.g.* diphenhydramine hydrochloride (Glaser & Maartmann-Moe, 1990), diphenhydramine thiourea complex (Wiedenfeld & Knoch, 1987), carbinoxamine maleate (Bertolasi *et al.*, 1980) and clemastine hydrogen fumarate (Parvez & Wendling, 1991). Glaser *et al.* (1992) have reported the crystal structure of orphenadrine hydrochloride, a skeletal muscle relaxant, which is also closely related to these compounds.

Our interest in the conformations of antihistamines effective on H_1 receptors has led to the preparation of dihydro cationic salts of doxylamine in order to investigate the influence of tetrachlorozinc(II) and tetrachlorocobalt(II) ions on the conformation of doxylamine. In this paper, we report the crystal structures of doxylaminium tetrachlorozincate(II), (1), and doxylaminium tetrachlorocobaltate(II), (2). The crystal structures of dihydro cationic salts of several antihistamines, *e.g.* clemizole. $CuCl_4^{2-}$ and clemizole. $CoCl_4^{2-}$ (Parvez & Sabir, 1997*a*), chlorpyramine. $CuCl_4^{2-}$ (Parvez & Sabir, 1997*b*), and triprolidine. $CuCl_4^{2-}$ (Parvez & Sabir, 1997*c*), have been reported recently by our laboratory.



Compounds (1) and (2) are isomorphous. An *ORTEP II* (Johnson, 1976) drawing of compound (1) is shown in Fig. 1. The molecular dimensions in the cations of both compounds are normal with the following respective mean bond distances: $C_{sp^3}-C_{sp^3}$ 1.517 (14) and 1.52 (2), $C_{sp^3}-C_{sp^2}$ 1.522 (4) and 1.527 (12), $O-C_{sp^3}$ 1.432 (5) and 1.438 (15), $N-C_{sp^3}$ 1.478 (9) and 1.484 (7), $N-C_{sp^2}$ 1.337 (4) and 1.350 (7), $C-C_{pyridyl}$ 1.372 (6) and 1.375 (11), and $C-C_{aromatic}$ 1.378 (11) and 1.382 (13) Å.

The ethereal O atom in each of (1) and (2) is not only hydrogen bonded to the ammonium H atom, but is also hydrogen bonded to the pyridinium H atom, *i.e.* both lone pairs of electrons of the ethereal O atom of the antihistamine in each of (1) and (2) are oriented towards H atoms bonded to N atoms. The $N\cdots O$ separations for these intramolecular interactions in the two structures lie between 2.513 (6) and 2.748 (7) Å. The N—H groups are also hydrogen bonded to the Cl atoms of two MCl_4^{2-} anions [$M = Zn$ in (1) and Co in (2)], with $N\cdots Cl$ separations in the range 3.211 (6)–3.265 (5) Å, thus forming hydrogen-bonded structures extending along the *a* axis, as observed in the structure of clemizole. $CoCl_4^{2-}$ (Parvez & Sabir, 1997*a*). Similar bifurcated hydrogen bonding has been reported for the dihydro cation of the antihistamine chlorpyramine

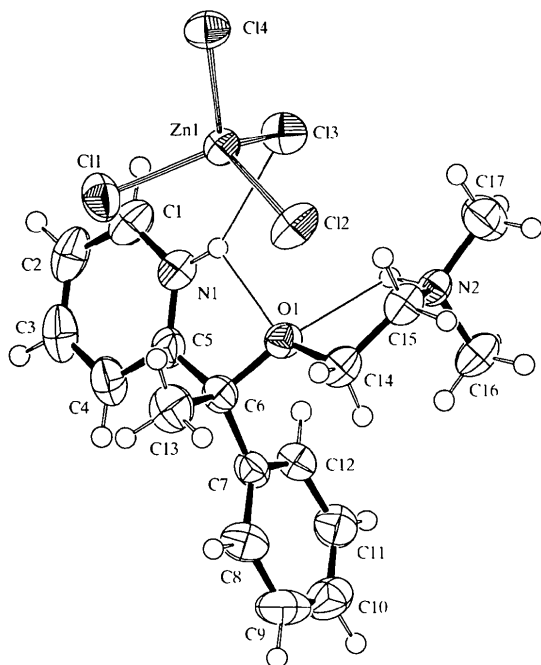


Fig. 1. ORTEP (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids have been plotted at the 50% probability level and H atoms assigned arbitrary radii.

(Parvez & Sabir, 1997*b*), where an ammonium H atom is hydrogen bonded to two Cl atoms of the same CuCl₄²⁻ anion. Details of the hydrogen bonds are presented in Tables 2 and 4 for (1) and (2), respectively.

The pyridyl and phenyl rings in (1) and (2) are essentially planar and are inclined at right angles with respect to each other [87.68(14) and 88.1(2)°, respectively], and the side chains comprising atoms O1, C5, C6, C14 and C15 in both are fully extended, wherein the atoms lie in planes with maximum deviations of 0.042(2) and 0.058(4) Å, respectively.

The ZnCl₄²⁻ and CoCl₄²⁻ anions show normal tetrahedral geometry with *M*—Cl distances in the range 2.2447(11)–2.2936(11) Å in (1) and 2.2538(18)–2.2994(16) Å in (2). The Cl—*M*—Cl angles are in the ranges 105.32(4)–113.54(5) and 104.98(7)–114.55(8)° in (1) and (2), respectively.

Experimental

For the preparation of compound (1), doxylaminium succinate (0.389 g, 1 mmol; Sigma Inc.) in concentrated HCl (8 ml) was mixed with ZnCl₂ (0.136 g, 1 mmol). On allowing the solution to stand overnight, colorless prisms of (1) were obtained. The crystals were washed with acetone. For the preparation of compound (2), doxylaminium succinate (0.389 g, 1 mmol; Sigma Inc.) in concentrated HCl (7 ml) was mixed with CoCl₂·6H₂O (0.238 g, 1 mmol). On allowing the solution to stand overnight, blue prisms of (2) were obtained, which were washed with acetone.

Compound (1)

Crystal data

(C₁₇H₂₄N₂O)[ZnCl₄]

M_r = 479.58

Monoclinic

*P*2₁/*n*

a = 9.5604(15) Å

b = 18.2218(17) Å

c = 12.782(3) Å

β = 107.536(17)°

V = 2123.3(7) Å³

Z = 4

D_i = 1.500 Mg m⁻³

D_m not measured

Data collection

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

ψ scan (3 reflections)

(North *et al.*, 1968)

T_{min} = 0.29, *T_{max}* = 0.32

4079 measured reflections

3852 independent reflections

Refinement

Refinement on *F*²

R(*F*) = 0.043

wR(*F*²) = 0.110

S = 1.001

3852 reflections

227 parameters

H atoms geometrically

idealized with C—H and

N—H = 0.95 Å

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 25 reflections

θ = 20.0–30.0°

μ = 6.301 mm⁻¹

T = 293(1) K

Block

0.22 × 0.20 × 0.18 mm

Colorless

2927 reflections with

I > 2σ(*I*)

R_{int} = 0.057

θ_{max} = 68.0°

h = 0 → 11

k = 0 → 21

l = -15 → 14

3 standard reflections

every 200 reflections

intensity decay: 1.12%

$$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 1.605P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.626 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.487 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

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

Zn1—C11	2.2750(11)	N1—C1	1.341(5)
Zn1—C12	2.2858(11)	N1—C5	1.333(5)
Zn1—C13	2.2936(11)	N2—C15	1.488(4)
Zn1—C14	2.2447(11)	N2—C16	1.479(4)
O1—C6	1.437(4)	N2—C17	1.467(5)
O1—C14	1.427(4)		
C14—O1—C6	116.5(3)	C17—N2—C15	111.9(3)
C5—N1—C1	123.6(4)	C17—N2—C16	109.7(3)
C16—N2—C15	112.9(3)		

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Cl3	0.95	2.41	3.265(5)	150
N2—H2...Cl2'	0.95	2.43	3.222(4)	141
N1—H1...O1	0.95	2.08	2.513(6)	106
N2—H2...O1	0.95	2.32	2.748(7)	107

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

Compound (2)

Crystal data

(C₁₇H₂₄N₂O)[CoCl₄]

M_r = 473.13

Mo Kα radiation

λ = 0.71069 Å

Monoclinic

 $P2_1/n$ $a = 9.5279$ (12) Å $b = 18.229$ (3) Å $c = 12.7795$ (13) Å $\beta = 107.313$ (9)° $V = 2119.1$ (5) Å³ $Z = 4$ $D_x = 1.483$ Mg m⁻³ D_m not measured

Cell parameters from 25 reflections

 $\theta = 10.0\text{--}15.0^\circ$ $\mu = 1.322$ mm⁻¹ $T = 170$ (1) K

Prism

 $0.30 \times 0.30 \times 0.16$ mm

Blue

The authors thank the Natural Sciences and Engineering Research Council, Canada, for providing the diffractometer through an equipment grant to the University of Calgary, and the University of Calgary, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1429). Services for accessing these data are described at the back of the journal.

Data collection

AFC-6S diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scan (3 reflections)(North *et al.*, 1968) $T_{\min} = 0.63$, $T_{\max} = 0.81$

5172 measured reflections

4892 independent reflections

1836 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.061$ $\theta_{\max} = 27.5^\circ$ $h = 0 \rightarrow 12$ $k = 0 \rightarrow 23$ $l = -16 \rightarrow 15$

3 standard reflections

every 200 reflections

intensity decay: 0.43%

Refinement

Refinement on F^2 $R(F) = 0.048$ $wR(F^2) = 0.167$ $S = 0.953$

4892 reflections

227 parameters

H atoms geometrically

idealized with C—H and

N—H = 0.95 Å

 $w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.685$ e Å⁻³ $\Delta\rho_{\min} = -0.574$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

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

Co1—C11	2.2806 (19)	N1—C1	1.356 (8)
Co1—C12	2.2916 (18)	N1—C5	1.343 (8)
Co1—C13	2.2994 (16)	N2—C15	1.494 (7)
Co1—C14	2.2538 (18)	N2—C16	1.486 (7)
O1—C14	1.423 (7)	N2—C17	1.472 (8)
O1—C6	1.453 (7)		
C14—O1—C6	116.4 (4)	C17—N2—C15	111.4 (5)
C5—N1—C1	122.7 (6)	C17—N2—C16	110.8 (5)
C16—N2—C15	112.0 (5)		

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...C13	0.95	2.40	3.259 (7)	151
N2—H2...C12 ⁱ	0.95	2.43	3.221 (6)	141
N1—H1...O1	0.95	2.09	2.533 (8)	107
N2—H2...O1	0.95	2.33	2.747 (8)	106

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

For both (1) and (2), the space group $P2_1/n$ was determined uniquely from the systematic absences.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989) for (1); *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (2). Cell refinement: *CAD-4 Software* for (1); *MSC/AFC Diffractometer Control Software* for (2). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structures: *SAPI91* (Fan, 1991); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL97*.

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Chloro[2,3-dimethylbutane-2,3-diolato(2-)-O,O'] [2,3-dimethylbutane-2,3-diolato(1-)-O,O']oxotungsten(VI)

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Abstract

The title compound, [WOCl(C₆H₁₂O₂)(C₆H₁₃O₂)], is a neutral complex in which the central tungsten(VI) cation is bonded to one chloro, one oxo, one diolato