

METAL-ORGANIC COMPOUNDS

Acta Cryst. (1998). **C54**, 1748–1750

Tripelennamine Tetrachlorocobaltate(II)

MASOOD PARVEZ

*Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4.
E-mail: parvez@acs.ucalgary.ca*

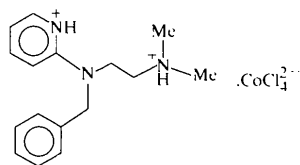
(Received 12 June 1998; accepted 13 July 1998)

Abstract

The crystal structure of the title compound, *N*-benzyl-*N*',*N*'-dimethyl-*N*-(2-pyridinio)-1,2-ethanediammonium tetrachlorocobaltate(II), (C₁₆H₂₃N₃)[CoCl₄], contains the dihydro cation of tripelennamine, an anti-allergic drug effective on H₁-type receptors. The molecular dimensions in the cation are normal. Two Cl atoms of the anion are involved in hydrogen bonds with different cations, with N...Cl distances of 3.099 (5) and 3.225 (5) Å. The CoCl₄²⁻ anion exhibits a slightly distorted tetrahedral geometry.

Comment

Tripelennamine, C₁₆H₂₁N₃, is a potent anti-allergic drug that is widely prescribed for hay fever and other allergies (Witiak, 1970). The reported crystal structures of antihistamines containing the *N*',*N*'-dimethyl-*N*-pyridylethanediamine moiety include those of histadyl (Clark & Palenik, 1972), tripelennamine-HCl (Parvez, 1987) and thonzylamine-HCl (Parvez, 1988). The crystal structures of several dihydro-cationic salts of antihistamines have been reported recently, *e.g.* those of clemizole-CuCl₄²⁻ and clemizole-CoCl₄²⁻ (Parvez & Sabir, 1997*a*), chloropyramine-CuCl₄²⁻ (Parvez & Sabir, 1997*b*), triprolidine-CuCl₄²⁻ (Parvez & Sabir, 1997*c*), and doxylamine-ZnCl₄²⁻ and doxylamine-CoCl₄²⁻ (Parvez & Sabir, 1998). Continuing interest in the conformations of antihistamines effective on H₁ receptors has led to the preparation of the dihydro-cationic salt of tripelennamine, in order to investigate the influence of tetrachlorocobaltate(II) ions on the conformation of tripelennamine. The crystal structure of tripelennamine tetrachlorocobaltate(II), (I), is presented in this paper.



(I)

An ORTEPII (Johnson, 1976) drawing of compound (I) is shown in Fig. 1. The molecular dimensions in the cation are normal, with mean bond distances as follows: N—C_{sp}³ 1.477 (13), N—C_{sp}² 1.357 (13), C—C_{pyridyl} 1.38 (2) and C—C_{aromatic} 1.379 (11) Å, while the C_{sp}³—C_{sp}³ and C_{sp}³—C_{sp}² distances are 1.519 (7) and 1.497 (8) Å, respectively. The CoCl₄²⁻ anion shows a slightly distorted tetrahedral geometry, with Co—Cl distances in the range 2.2404 (18)–2.2938 (15) Å; the longer bond distances are associated with those Cl atoms that are hydrogen bonded to the cations. The Cl—Co—Cl angles are in the range 103.88 (7)–120.33 (7)°.

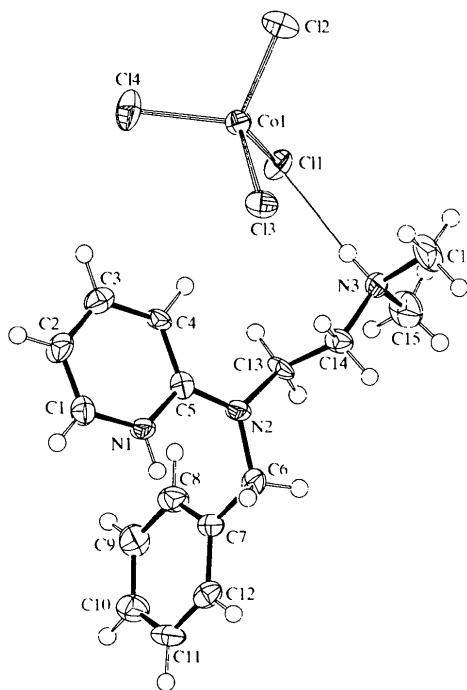


Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing the atomic numbering scheme. Displacement ellipsoids have been plotted at the 50% probability level and H atoms have been assigned arbitrary radii.

The pyridyl and phenyl rings in (I) are essentially planar and are inclined almost at right angles [79.58 (19)°] to each other. The side chain comprising N2, C13, C14, N3 and C16 is fully extended, while N2 and C15 lie 0.334 (10) and –1.198 (11) Å, respectively, out of the plane of atoms C13, C14, N3 and C16. A similar conformation of the side chain has been observed in the crystal structure of tripelennamine-HCl (Parvez, 1987), wherein the methyl group corresponding to C15 is *cis*-oriented with respect to the pyridyl group in both molecules of the asymmetric unit. In (I), the ammonium H atom is

cis oriented with respect to the pyridinium group, which may be the result of the bulky hydrogen-bonded anion. Another striking difference between the conformations of (I) and tripeleannamine·HCl is the C5—N2—C6—C7 torsion angle of 71.0(7)° in (I), which is significantly different from the corresponding angle in the two molecules of tripeleannamine·HCl [93.3(2) and -91.2(2)°].

Two of the Cl atoms of the anion are hydrogen bonded to the ammonium and pyridinium H atoms of two different cations, with N···Cl distances of 3.099(5) and 3.225(5) Å, respectively; details of the hydrogen bonds are presented in Table 2.

Experimental

For the preparation of (I), tripeleannamine·HCl (0.224 g, 0.5 mmol; Sigma Inc.) in 6 M HCl (5 ml) was mixed with CoCl₂·6H₂O (0.119 g, 0.5 mmol). On allowing the solution to stand overnight, blue crystals of (I) were obtained, which were washed with absolute ethanol and recrystallized from CH₃CN at room temperature by slow evaporation.

Crystal data

(C₁₆H₂₃N₃)[CoCl₄]

M_r = 458.12

Monoclinic

*P*2₁/*n*

a = 11.670(3) Å

b = 9.780(2) Å

c = 17.777(5) Å

β = 90.37(2)°

V = 2028.9(9) Å³

Z = 4

D_x = 1.500 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 10–15°

μ = 1.376 mm⁻¹

T = 170(1) K

Prismatic

0.39 × 0.31 × 0.18 mm

Blue

Data collection

Rigaku AFC-6S diffractometer

ω/2θ scans

Absorption correction:

ψ scan (3 reflections)

(North *et al.*, 1968)

T_{min} = 0.617, *T_{max}* = 0.781

4932 measured reflections

4708 independent reflections

2049 reflections with

I > 2σ(*I*)

R_{int} = 0.050

θ_{max} = 27.5°

h = 0 → 15

k = 0 → 12

l = -23 → 23

3 standard reflections

every 200 reflections
intensity decay: none

Refinement

Refinement on *F*²

R [*F*² > 2σ(*F*²)] = 0.047

wR (*F*²) = 0.161

S = 0.980

4708 reflections

220 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0693*P*)² + 0.2191*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.684 e Å⁻³

Δρ_{min} = -0.780 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1—C11	2.2938 (15)	N2—C5	1.339 (6)
Co1—C12	2.2487 (17)	N2—C6	1.470 (7)
Co1—C13	2.2827 (16)	N2—C13	1.458 (6)
Co1—C14	2.2404 (18)	N3—C14	1.497 (6)
N1—C1	1.361 (7)	N3—C15	1.480 (7)
N1—C5	1.370 (6)	N3—C16	1.478 (7)
C12—Co1—C11	120.33 (7)	C5—N2—C6	120.9 (4)
C13—Co1—C11	105.28 (6)	C5—N2—C13	121.4 (4)
C14—Co1—C11	103.88 (7)	C13—N2—C6	116.8 (4)
C13—Co1—C12	105.16 (7)	C16—N3—C15	111.0 (5)
C14—Co1—C12	109.67 (7)	C16—N3—C14	110.7 (4)
C14—Co1—C13	112.64 (7)	C15—N3—C14	112.8 (4)
C1—N1—C5	123.3 (5)		

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

<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 ⁱ	0.86	2.42	3.225 (5)	155.3
N3—H3···Cl1	0.91	2.19	3.099 (5)	173.6

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

The space group *P*2₁/*n* was determined uniquely from the systematic absences. H atoms were placed in geometrically idealized positions.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

The author thanks 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: FG1505). Services for accessing these data are described at the back of the journal.

References

- Clark, G. R. & Palenik, G. J. (1972). *J. Am. Chem. Soc.* **94**, 4005–4009.
- Fan, H.-F. (1991). *SAPI91. Structure Analysis Program with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Parvez, M. (1987). *Acta Cryst.* **C43**, 1408–1410.
- Parvez, M. (1988). *Acta Cryst.* **C44**, 1433–1435.
- Parvez, M. & Sabir, A. P. (1997a). *Acta Cryst.* **C53**, 675–677.
- Parvez, M. & Sabir, A. P. (1997b). *Acta Cryst.* **C53**, 678–679.
- Parvez, M. & Sabir, A. P. (1997c). *Acta Cryst.* **C53**, 679–681.
- Parvez, M. & Sabir, A. P. (1998). *Acta Cryst.* **C54**, 933–935.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Witiak, D. T. (1970). *Medicinal Chemistry*, edited by A. Burger, pp. 1643–1668. New York: John Wiley.

Acta Cryst. (1998). **C54**, 1750–1752

Hexakis(μ -*N*-ethylthiourea-*S*)tetrakis[iodo-copper(I)] Monohydrate

CHAVENG PAKAWATCHAI,^a YUPA THANYASIRIKUL,^a
 TAPANEE SAEPAE,^a SUWALUK PANSOOK,^a HOONG-KUN
 FUN^b† AND KANDASAMY CHINNAKALI^b‡

^aDepartment of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai 90112, Thailand, and
^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: chaveng@ratree.psu.ac.th

(Received 6 January 1998; accepted 3 August 1998)

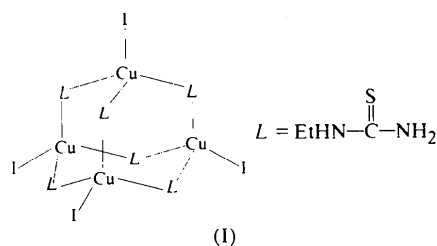
Abstract

In the title compound, $[Cu_4I_4(N\text{-ethylthiourea})_6]\cdot H_2O$ (*N*-ethylthiourea = $C_3H_8N_2S$), a hexanuclear copper(I) cluster complex, the Cu atoms have tetrahedral coordination. Four such tetrahedra share corners to form a tetrahedral assembly. This cage structure results in the formation of four six-membered Cu—S—Cu—S—Cu—S rings all in the chair conformation.

Comment

Reactions between copper(I) halides and thiourea (tu) or substituted thioureas frequently generate a variety of complexes which have unpredictable stoichiometry and stereochemistry. The substituted thiourea ligands generally coordinate to the Cu atom through the S atom as terminal ligands or bridging ligands or both. Terminal coordination is reported in the complexes $[Cu(dmtu)_3Cl]$ (dmtu = *N,N'*-dimethylthiourea) (Girling & Amma, 1971) and $[Cu(detu)_3I]$ (detu = diethylthiourea) (Fun *et al.*, 1998), whereas in the complexes $[Cu(tu)_2Cl]$ (Spofford & Amma, 1968), $[Cu(tu)_3Cl]$ (Okaya & Knobler, 1964) and $[Cu_2(etu)_4Cl_2]$ (etu = ethylenethiourea) (Battaglia *et al.*, 1976), the ligands have both terminal and bridging coordination. The crystal structure determination of the title compound, (I), was carried out to establish the coordination environment.

The stoichiometric ratio of CuI and *N*-ethylthiourea in the title complex (I) is 1:1.5. Each Cu atom



is coordinated tetrahedrally by three S atoms and an I atom. Four such tetrahedra are held together by corner sharing at sulfur positions to form a tetrahedral array. This arrangement defines four six-membered Cu_3S_3 rings, all adopting a chair conformation. In these rings, the substituent I atoms occupy equatorial positions and of the three $C(NH_2)(NHCH_2CH_3)$ substituents, one is in an axial position and the remaining two are in equatorial positions. The Cu—I distances vary from 2.623 (2) to 3.081 (2) Å and the Cu—S distances range from 2.259 (3) to 2.386 (3) Å. The overall complex has an adamantane-like cluster structure with *N*-ethylthiourea as bridging and I as terminal ligands. Similar adamantane structures have been reported for $Cu_4(tu)_6(NO_3)_4\cdot 4H_2O$ and $Cu_4(tu)_9(NO_3)_4\cdot 4H_2O$, with trigonal planar Cu atoms in the former, but with three tetrahedral and one trigonal planar Cu atom in the latter (Griffith *et al.*, 1976). For the sulfate analogue, structures have been reported for $[Cu_4(tu)_6](SO_4)_4\cdot 2H_2O$ (Declercq *et al.*, 1978), $[Cu_8(tu)_{15}](SO_4)_4\cdot xH_2O$ (Declercq *et al.*, 1978) and $[Cu_4(tu)_7](SO_4)_2\cdot H_2O$ (Bott *et al.*, 1998).

The geometry of short $N-H\cdots O$ and $N-H\cdots I$ intra- and intermolecular contacts is given in Table 2. The water in the structure comes from the undried ethanol solvent.

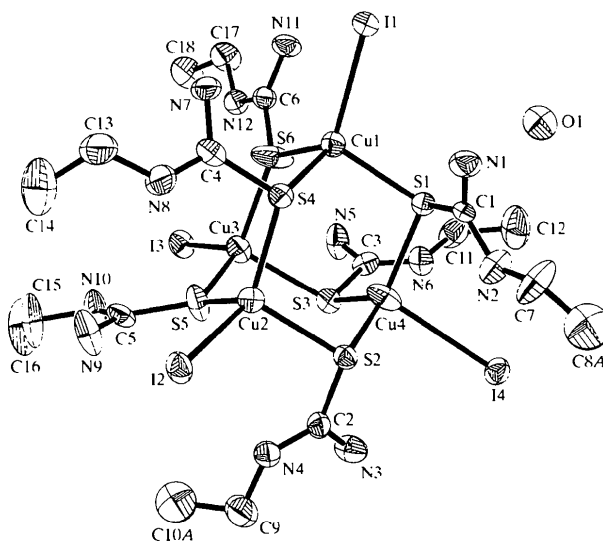


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. The H atoms have been omitted for clarity.

† On sabbatical leave at: Department of Chemistry, Prince of Songkla University, Hat Yai, Thailand.

‡ On leave from: Department of Physics, Anna University, Chennai 600 025, India.