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Acta Cryst. (1997). **C53**, 1407–1409

Bis(piperidinium) Tetrachloromercurate

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(Received 14 April 1997; accepted 6 June 1997)

Abstract

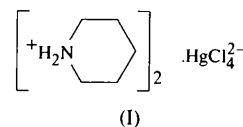
The title compound, (C₅H₁₂N)₂[HgCl₄], contains piperidinium cations and tetrachloromercurate anions, which are connected by N—H···Cl bonds *via* the Cl1, Cl2 and Cl3 atoms into a two-dimensional network in the (101) plane through the origin. The Hg—Cl bond lengths lie between 2.431 (3) and 2.515 (2) Å.

Comment

The reaction of substituted ammonium halides with metal halides leads to a series of compounds of the general formula (R_xNH_{4-x})₂MX₄, where *R* is an aliphatic or aromatic hydrocarbon, *M* is a divalent metal and *X* = Cl, Br or I.

These compounds show interesting structural and physical properties such as ferroelectricity, successive phase transitions and incommensurate phases, *e.g.* [N(CH₃)₄]₂[ZnCl₄] (*cf.* Mashiyama, 1980). An example of interesting physical properties is the compound [N(CH₃)₄]₂[MnCl₄], which was used by Dupas & Renard (1973) and Birgeneau, Shirane & Kitchens (1974) for studying low-dimensional magnetism.

Another point of interest is the investigation of the coordinative environment of Hg^{II} because of the closed shell and relatively large coordination distances. Coordination numbers can be three, four (tetrahedral) and five (trigonal bipyramidal); in the special case of (RNH₃)₂HgX₄, perovskite-like structures with MX₆ octahedra are found (Ben Salah, Daoud, Bats & Fuess, 1982).



The title compound, (I), contains two piperidinium cations and one tetrachloromercurate anion in the asymmetric unit (Fig. 1). The Hg atom is surrounded by four Cl atoms forming a slightly distorted tetrahedron. Three of the Cl atoms are connected to piperidinium cations by hydrogen contacts in the range from 2.27 to 2.47 Å, the Cl···N distances vary between 3.219 (4) and 3.395 (4) Å.

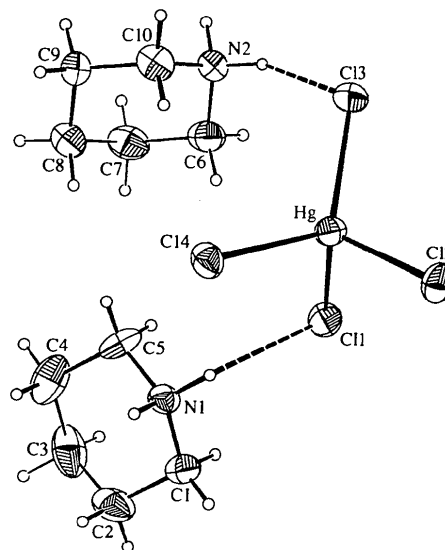


Fig. 1. Formula unit of the title compound in the crystal. Displacement ellipsoids correspond to 35% probability.

The base of the tetrahedron (Cl1, Cl2, Cl3) lies approximately in the glide plane *n*, *i.e.* ($x\frac{1}{4}y$), as do the atoms H3—N2—H4, setting up a zigzag chain in [101] direction: Cl3—Hg—Cl1—H4—N2—H3—Cl3—Hg—, and so on. The chain is augmented to a two-dimensional network close to the plane (101) by H1—N1—H2, which connects tetrahedra related by the centres of symmetry at (0 $\frac{1}{2}$ 0) and ($\frac{1}{2}$ $\frac{1}{2}$ 0), thus resulting in the translational repetition in the [010] direction (see Fig. 2 and Table 2). The hydrogen-bonding parameters are in good agreement with other experimental data (Ben

Salah, Bats, Fuess & Daoud, 1983; Ben Salah, Bats, Kalus, Fuess & Daoud, 1982).

No further interaction is present: the shortest intermolecular distances are longer than 3.6 Å (excluding H...H distances).

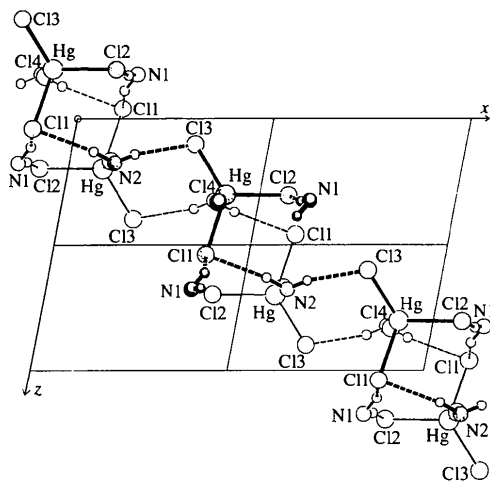


Fig. 2. Hydrogen contacts plotted along the [010] direction; only NH₂ groups of the cations are shown.

Experimental

The complex is obtained by mixing the solutions of piperidinium chloride and mercury chloride in an acetone-ethanol solution in the stoichiometric ratio 2:1. After a few weeks, colourless, non-hygroscopic crystals of C₁₀H₂₄Cl₄HgN₂ are obtained by slow evaporation. Chemical analysis is satisfactory. The determination of the crystal size and shape was performed by a self-constructed automated two-circle goniometer with CCD camera (Zimmermann, Lange & Burzlaff, 1995).

Crystal data

(C₅H₁₂N)₂[HgCl₄]

M_r = 514.72

Monoclinic

*P*2₁/*n*

a = 14.954 (2) Å

b = 12.157 (1) Å

c = 9.701 (1) Å

β = 100.76 (1)°

V = 1732.6 (3) Å³

Z = 4

D_x = 1.973 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 30 reflections

θ = 8.5–10.9°

μ = 9.491 mm⁻¹

T = 293 K

Prismatic

0.20 (1) × 0.15 (1) ×

0.10 (1)

Colourless

Data collection

Rebuilt Philips PW1100

diffractometer

(Gomm, 1993)

2311 reflections with

F > 2σ(*F*)

R_{int} = 0.061

θ/2θ scans

Absorption correction:

Gaussian by integration

(Busing & Levy, 1957)

T_{min} = 0.357, *T_{max}* = 0.418

5978 measured reflections

2726 independent reflections

θ_{max} = 24.0°

h = 0 → 17

k = -13 → 13

l = -11 → 11

4 standard reflections

every 100 reflections

intensity decay: 1.0%

Refinement

Refinement on *F*

R = 0.039

wR = 0.040

S = 1.38

2311 reflections

155 parameters

H atoms not refined

w = 1/[σ²(*F_{obs}*) + 0.015*F_{obs}*]

(Δ/σ)_{max} < 0.001

Δρ_{max} = 1.59 e Å⁻³

Δρ_{min} = -1.42 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray*

Crystallography (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

Hg—C11	2.515 (2)	Hg—C13	2.431 (3)
Hg—C12	2.485 (2)	Hg—C14	2.475 (3)
C14—Hg—C13	114.98 (8)	C11—Hg—C13	116.14 (9)
C12—Hg—C13	111.34 (9)	C11—Hg—C14	99.32 (8)
C12—Hg—C14	111.93 (8)	C11—Hg—C12	101.94 (8)

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...C11	0.96	2.46	3.242 (4)	138
N1—H2...C12 ⁱ	0.96	2.27	3.219 (4)	168
N2—H3...C13	0.96	2.36	3.239 (5)	153
N2—H4...C11 ⁱⁱ	0.96	2.47	3.395 (4)	161

Symmetry codes: (i) -*x*, 1 - *y*, -*z*; (ii) ½ + *x*, ½ - *y*, ½ + *z*.

All H-atom positions could be recognized in difference Fourier maps; calculated positional parameters for a distance of 0.96 Å, however, were used for the final refinement with a common isotropic displacement parameter for the H atoms since the calculated distances turned out to be more reasonable than the refined ones. The residual density shows six maxima with 1.3–1.6 e Å⁻³ at distances of 0.5–1.2 Å from the Hg atom. A similar situation is found for the minima. All refinements were carried out using a Levenberg–Marquardt least-squares algorithm (Spengler, Zimmermann & Burzlaff, 1994; Spengler & Zimmermann, 1995, 1996).

Data collection: local software (Gomm, 1993). Cell refinement: local software. Data reduction: local software. Program(s) used to solve structure: *CRYSTAN* (Burzlaff & Rothammel, 1988). Program(s) used to refine structure: *CRYSTAN* (Spengler & Zimmermann, 1996). Molecular graphics: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1222). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1409–1411

Monodentate Ligation of Tetracyanonickelate(II): (2-Aminoethanol)[N-(2-aminoethyl)-1,2-ethanediamine][tetracyanonickelato(II)]copper(II)–Water (1/2)†

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(Received 4 March 1997; accepted 24 April 1997)

Abstract

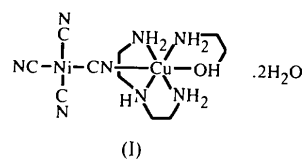
In the title complex, [CuNi(CN)₄(C₄H₁₃N₃)(C₂H₇NO)]·2H₂O, the Cu atom, chelated by a terdentate dien [dien = N-(2-aminoethyl)-1,2-ethanediamine] and a bidentate mea (mea = 2-aminoethanol) ligand, is ligated additionally with [Ni(CN)₄]²⁻ monodentately at the N atom of one CN group; the three other N atoms are free from ligation. This is a rare example of tetracyanonickelate(II) bridging to another coordination centre through only one CN group.

Comment

A tetracyanomethylate anion centred by a divalent *d*⁸ transition metal, Ni, Pd or Pt, can behave as a

† Systematic name: (2-aminoethanol)-2κN,2κO-[N-(2-aminoethyl)-1,2-ethanediamine]-2κ³N-μ-cyano-1κC:2κN-tricyano-1κ³C-coppernickel dihydrate.

bridging ligand to other coordination centres via the cyano N atoms, as can *d*¹⁰ cyanometallates such as [Cd(CN)₄]²⁻, [Cu(CN)₄]³⁻ and [Ag(CN)₂]⁻ (Iwamoto, 1996*a,b*). A variety of multidimensional structures have been obtained in which [Ni(CN)₄]²⁻ forms a tetramonodentate cross joint, by using all the N atoms, or a di-monodentate bridge, by using the N atoms of *trans* or *cis* CN groups, to other coordination centres. Recently, a T-1D (T-shaped one-dimensional extension) catenation (Iwamoto, 1996*a,b*), *i.e.* a one-dimensional ladder structure, involving the tri-monodentate [Ni(CN)₄]²⁻ or [Pt(CN)₄]²⁻ moieties using three of the four CN groups to bridge three Eu^{II} atoms successively, has been reported (Knoepfel & Shore, 1996). Another example of T-type three-handed coordination exists for two polymorphs of [Cu(tn)Ni(CN)₄] (tn = 1,3-propanediamine), in which [Ni(CN)₄]²⁻ is linked to three Cu^{II} atoms (Černák, Lipkowski & Hudak, 1996). Thus, four-, three- and two-handed coordination structures with tetracyanonickelate(II) as a bridging ligand have been demonstrated, as is illustrated in Fig. 1. Monodentate ligation has been found in the crystal structure of the title complex, (I).



As shown in Fig. 2, the neutral discrete molecule of (I) is binuclear. One of the coordination centres, the octahedral Cu^{II}, is chelated with the terdentate dien and bidentate mea ligands, N atoms of both ligands being on the equatorial plane; the O atom of the mea is in the axial position. The other side of the axial position is coordinated monodentately by the N1 atom of [Ni(CN)₄]²⁻, leaving three of the CN groups free from coordination. To the authors' knowledge, this is the first case of monodentate ligation of [Ni(CN)₄]²⁻ in a well defined crystal structure.

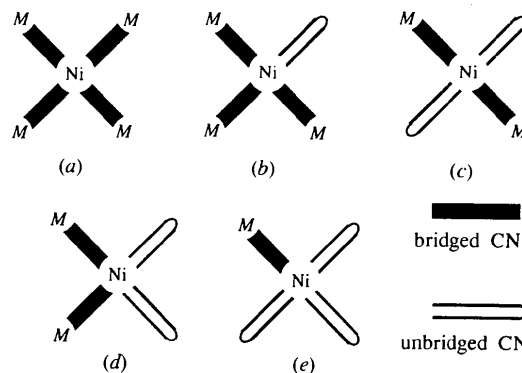


Fig. 1. Coordination modes of square-planar [Ni(CN)₄]²⁻ as a bridging ligand: (a) four-handed, (b) three-handed, (c) two-handed in *trans*, (d) two-handed in *cis*, (e) one-handed.