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Acta Cryst. (1998). C**54**, 574–576

Di-μ-chloro-bis[(2-ammoniobenzenethiolato-*S*)chloromercury(II)]

Naka Davidović,[a] Dubravka Matković-Čalogović,[a] Zora Popović[a] and Irena Vedrina-Dragojević[b]

[a]*Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8, HR-10000 Zagreb, Croatia, and* [b]*Department of Food Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Domagojeva 2, HR-10000 Zagreb, Croatia. E-mail: zpopovic@zagreb.zoak.pmf.hr*

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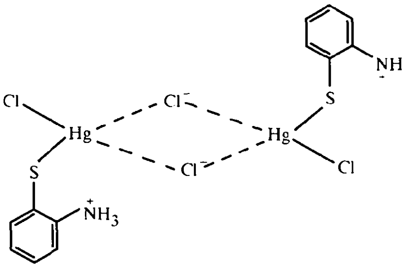
Abstract

The title compound, [$Hg_2Cl_4(C_6H_7NS)_2$], was obtained from the reaction of $HgCl_2$ with benzothiazole and studied by X-ray diffraction and IR spectroscopy. The molecule is centrosymmetric, with Hg—μ-Cl distances of 2.720 (1) and 2.976 (1) Å. The 2-aminobenzenethiol ligand (existing in a zwitterionic form) is bonded to mercury through the S atom, with an Hg—S distance of 2.340 (2) Å. There are N—H···Cl hydrogen bonds involving the bridging Cl atoms, as well as a bifurcated hydrogen bond involving the terminal Cl atoms.

Comment

As the activities of many enzymes depend upon the interaction of an imidazole or thiazole group with a metal ion, the coordination behaviour of benzothiazole towards mercury(II) is of particular interest since this molecule contains both S and N heteroatoms, and a π-donor aromatic system. The title compound, (I), was obtained from the reaction of $HgCl_2$ with benzothiazole. Ring opening of 2-(2-pyridyl)benzothiazoline by mercury(II) cations (Capitan *et al.*, 1979) and similar metal-ion-induced rearrangements of bis(benzothiazolines) to Schiff base chelates (Bayer, 1961; Jadamus *et al.*, 1964) have been reported. The reaction of 2-aminobenzenethiol and mercury(II) acetate gave bis(2-aminobenzenethiolato)mercury(II) (Jadamus *et al.*, 1964).



(I)

In (I), the 2-aminobenzenethiol ligand is bonded to mercury through the S atom. The Hg—S distance of 2.340 (2) Å is equal to the sum of the covalent radii of sulfur and two-coordinate mercury (Grdenić, 1981), but is the shortest of its kind found in the Cambridge Structural Database (1996) (Romero *et al.*, 1996; Brotherton *et al.*, 1974; Herbstein *et al.*, 1986). The Hg—Cl1 distance of 2.383 (1) Å is longer than expected for two-coordination, though it is comparable to that of 2.391 (2) Å found in $C_{24}H_{36}Cl_4Hg_2S_4$ (Romero *et al.*, 1996), and there is a large deviation from linearity [S—Hg—Cl1 148.31 (5)°]. These deformations are caused by two additional Hg···Cl interactions with distances shorter than the sum of the van der Waals radii [Hg···Cl2 2.720 (1) and Hg···Cl2^i 2.976 (1) Å; see Table 1 for symmetry code]. These two Cl atoms bridge the monomeric molecules related by a centre of symmetry. The Hg···Cl2 and Hg···Cl2^i distances fall within the range found for other chloro-bridged dimeric mercury structures (Biscarini & Pelizzi, 1988).

The molecules are interconnected by four hydrogen bonds of the N—H···Cl type, leading to an infinite two-dimensional network parallel to the (100) plane. Atom H13 forms a bifurcated hydrogen bond with two terminal Cl1 atoms. The geometries of the hydrogen bonds are given in Table 2.

The strong and broad absorption bands at 3300–2910 cm^{-1} in the IR spectrum are indicative of asymmetric and symmetric NH_3^+ stretching modes. Two main bands at 2830 (NH stretching vibrations) and 2566 cm^{-1} (deformation combination bands), as well as the complicated fine structure associated with NH stretching bands, are characteristic of amine salts. In addition, there are a number of weaker bands near 2000 cm^{-1} due to hydrogen bonds (Colthup *et al.*, 1964). The asymmetric and symmetric NH_3^+ deformation absorption bands are observed at 1654 and 1549 cm^{-1}, respectively.

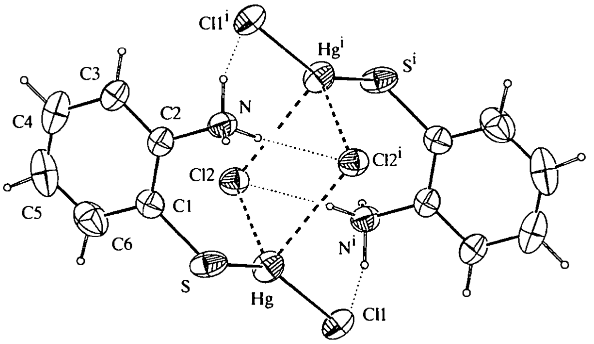


Fig. 1. View of the title molecule with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Intramolecular hydrogen bonds are indicated by dotted lines and the Cl bridges by dashed lines.

Experimental

Mercury(II) chloride (1.84 mmol) was dissolved in ethanol (60 ml). Into this solution, an ethanol solution of benzothiazole (4 mmol, 20 ml) was added with stirring. Slow evaporation of the solvent at room temperature yielded crystals suitable for X-ray structure determination. The IR spectrum in the region of 4000–450 cm^{-1} was recorded on a Perkin-Elmer FT-IR spectrophotometer Model 1600 using a KBr disk. IR max. (cm^{-1}): 3304 (*w*), 3120 (*s*), 3060 (*s*), 3001 (*s*), 2970 (*s*), 2910 (*s*), 2830 (*m*), 2590 (*m*), 2566 (*m*), 2100 (*w*), 2050 (*w*), 2010 (*w*), 1950 (*w*), 1930 (*w*), 1654 (*m*), 1604 (*w*), 1549 (*s*), 1496 (*s*), 1469 (*vs*), 1446 (*m*), 1302 (*m*), 1266 (*m*), 1162 (*w*), 1069 (*m*), 1133 (*w*), 1119 (*w*), 1043 (*w*), 1022 (*w*), 949 (*w*), 867 (*vw*), 825 (*vw*), 755 (*vs*), 675 (*m*), 551 (*w*), 515 (*vw*), 468 (*m*).

Crystal data

$[Hg_2Cl_4(C_6H_7NS)_2]$
M_r = 793.36
Orthorhombic
Pbca
a = 17.786 (2) Å
b = 14.504 (1) Å
c = 7.437 (3) Å
V = 1918.5 (8) Å^3
Z = 4
D_x = 2.747 Mg m^{-3}
D_m not measured

Mo *K*α radiation
λ = 0.71073 Å
Cell parameters from 39 reflections
θ = 11.1–18.7°
μ = 16.755 mm^{-1}
T = 295.0 (1) K
Prism
0.283 × 0.276 × 0.043 mm
Transparent

Data collection

Philips PW1100 diffractometer updated by Stoe
ω–2θ scans
Absorption correction: by integration
T_{min} = 0.015, T_{max} = 0.264
5516 measured reflections
2791 independent reflections
1857 reflections with $I > 2\sigma(I)$

R_{int} = 0.025
θ_{max} = 30.01°
h = 0 → 25
k = −1 → 20
l = −3 → 10
4 standard reflections
frequency: 90 min
intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.077$
S = 1.038
2791 reflections
127 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 1.4042P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 1.56 e Å^{-3} (0.86 Å from Hg)
$\Delta\rho_{min}$ = −0.84 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00278 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Hg—S	2.3404 (17)	Hg···Cl2^i	2.9762 (14)
Hg—Cl1	2.3834 (14)	S—C1	1.788 (5)
Hg···Cl2	2.7199 (14)	N—C2	1.459 (7)
S—Hg—Cl1	148.31 (5)	Cl1—Hg···Cl2^i	99.19 (5)
S—Hg···Cl2	115.99 (5)	Cl2—Hg···Cl2^i	81.29 (5)
Cl1—Hg···Cl2	94.05 (5)	C1—S—Hg	104.22 (19)
S—Hg···Cl2^i	95.36 (5)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H11···Cl2^i	0.96 (6)	2.42 (5)	3.377 (5)	174 (4)
N—H12···Cl2^{ii}	0.97 (3)	2.25 (4)	3.215 (5)	178 (5)
N—H13···Cl1^{iii}	0.97 (5)	2.42 (5)	3.254 (5)	144 (5)
N—H13···Cl1^i	0.97 (5)	2.65 (6)	3.218 (5)	118 (4)

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

The H atoms were found in the difference Fourier map and were refined isotropically with the C—H and N—H bond lengths restrained to be equal within an s.u. of 0.03.

Data collection: *STADI*4 (Stoe & Cie, 1995*a*). Cell refinement: *STADI*4. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON*97 (Spek, 1997) and *PLUTON*96 (Spek, 1996). Software used to prepare material for publication: *PLATON*97.

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[$Er_2Al_2(O^iPr)_{12}(HO^iPr)_2$], a Novel Heterobimetallic Alkoxide

Mikael Kritikos,[a] Maria Wijk[b] and Gunnar Westin[b]

[a]*Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden, and* [b]*Department of Inorganic Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden. E-mail: mkr@struc.su.se*

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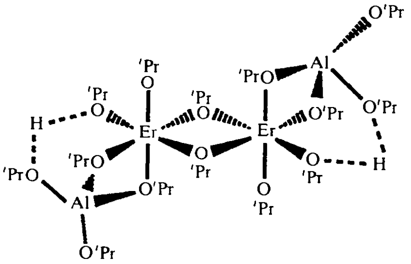
Abstract

A new heterobimetallic tetranuclear alkoxide of the Er–Al system, [$Al_2Er_2(C_3H_7O)_{12}(C_3H_8O)_2$], has been synthesized and characterized by single-crystal X-ray diffraction and IR spectroscopy. Hexakis(μ_2-isopropoxo)hexakis(isopropoxo)bis(2-propanol)dialuminiumdierbium has the linear composition [$(O^iPr)_2Al$]-(μ_2-$O^iPr)_2$-[$(HO^iPr)Er(O^iPr)$]-(μ_2-$O^iPr)_2$-[$(O^iPr)Er(HO^iPr)$]-(μ_2-$O^iPr)_2$-[$Al(O^iPr)_2$]. The inner pair of Er atoms are each sixfold coordinated and the outer Al atoms are each fourfold coordinated by O atoms. Two intramolecular hydrogen bonds exist between the 2-propanol group at the Er atom and the monodentate isopropoxo ligand at the adjacent Al atom. The adopted chain geometry of four alkoxo-bridged metal atoms is a rather unusual structural feature for heterobimetallic ($M_2M'_2$) alkoxides.

Comment

Alkoxides are important precursors in the organic sol–gel process for the preparation of, for example, construction, opto- and electroceramics (Chandler *et al.*, 1993). The present study is part of a program involving rare earth alkoxides as precursors for anionic conductor ceramics and optical materials for, for example, laser amplifiers and frequency up-conversion devices (Desurvire, 1991). We are presently investigating the formation of alkoxides with various Er-to-Al ratios in the Er–Al–isopropoxide system. These alkoxides are to be used as precursors for the above-mentioned materials. The compounds that have been investigated so far are [$ErAl_3(O^iPr)_{12}$] and [$Er_5O(O^iPr)_{13}$] (Wijk *et al.*, 1996, 1998). The title heterobimetallic alkoxide, (I), having an Er:Al composition of 2:2, consists of a linear tetranuclear Al···Er···Er···Al array, with half of the molecule in the asymmetric unit. The central pair of Er atoms are doubly bridged by two isopropoxo groups. Each end of the Er pair is connected to an Al atom *via* bridging isopropoxo groups, forming an $Er_2Al_2O_6$ core in the molecule.



(I)

Although rare, other linear $M_2M'_2$ alkoxides have been characterized by single-crystal X-ray diffraction, namely those of the series $M_2Ge_2(OBu)_8$, M = Co, Ni (Veith *et al.*, 1992). However, these compounds have *tert*-butoxo ligands and tetrahedral coordination around the inner pair of transition metal atoms. Another example of this type of metal-atom arrangement is found in the mixed-valence compound $W_4(\mu\text{-}H)_2(O^iPr)_{14}$ (Akiyama *et al.*, 1981), in which the inner pair of W atoms are octahedrally coordinated in the same way as the Er atoms in the title compound.

The metal-chain structural fragment exhibited by the present compound is not usually adopted by hetero-