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Complexes of HgCl₂ and HgBr₂ with Nitrilotriacetamide

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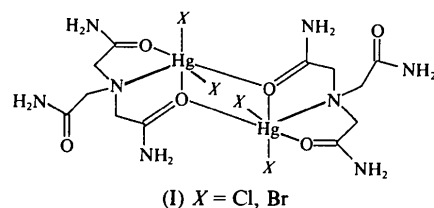
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Abstract

The two complexes bis(μ -nitrilo- κN -triacetamide)-1 κO ,1:2 $\kappa^2 O'$;2 κO ,1:2 $\kappa^2 O'$ -bis(dichloromercury), [HgCl₂(C₆H₁₂N₄O₃)₂]₂, and bis(μ -nitrilo- κN -triacetamide)-1 κO ,1:2 $\kappa^2 O'$;2 κO ,1:2 $\kappa^2 O'$ -bis(dibromomercury), [HgBr₂(C₆H₁₂N₄O₃)₂]₂, are isostructural, and represent the third case of metal complexes with nitrilotriacetamide [NTAM = N(CH₂CONH₂)₃]. [Pb and Co complexes have been reported by Sucheck, Finnen, Pinkerton, Skrzypczak-Jankun, Vijayakumar & Smith (1991). *Am. Crystallogr. Assoc. Meet.*, Toledo, Abstract PJ17.] The (NTAM:HgX₂)₂ complexes are centrosymmetric oxygen-bridged dimers. Each metal ion binds to six donors (2X, 1N, 3O; X = Br, Cl) at distances of 2.3–2.9 Å, although retaining the hexagonal bipyramidal configuration observed in complexes where Hg^{II} is eight-coordinate. Two 'empty sites' are occupied by donors from other molecules (X and N atoms) at distances of 3.7–4.1 Å. Two out of three amine groups of NTAM participate in hydrogen bonds, while the third is utilized as a ligand in the 'empty site' of the coordination sphere of the neighboring Hg^{II}.

Comment

In our continuing study of novel amide chelating ligands, we have prepared and characterized the symmetrical unalkylated nitrilotriacetamide and a variety of mono-, di- and trialkylated derivatives (Skrzypczak-Jankun & Smith, 1994; Smith, Cramer, Sucheck & Skrzypczak-Jankun, 1992). These compounds are obtained by divergent synthesis from nitrilotriacetic acid *via* transamidation and cyclization to the dioxopiperazineacetamide, followed by nucleophilic ring opening with primary amines. We have studied the coordination chemistry of these ligands with a variety of metals and have reported the first isolable crystalline complex of nitrilotriacetamide with lead, which is also the first example of both a completely acyclic ligand and a 2:1 ligand–metal ratio in a ten-coordinate lead complex (Smith, Sucheck & Pinkerton, 1992). In this paper we report the structure of the complexes (I) of nitrilotriacetamide with HgCl₂ and HgBr₂.



Two NTAM:HgX₂ moieties related by a center of symmetry form a dimer sharing O₃ atoms. However, this is not a typical bi-mercury complex. The Hg···Hg distance in typical bi-mercury complexes is about 2.5 Å (Taylor, 1977), while in the title complexes the shortest Hg···Hg distances are 4.4377 (3) and 4.4858 (5) Å within the chloride and bromide dimers, respectively, and 5.0284 (3) and 5.0989 (6) Å between dimers. In the Hg coordination sphere, a distorted hexagonal bipyramid, the halogen atoms, at distances of 2.3–2.5 Å, occupy axial sites with an average X—Hg—O,N,X angle of 88°; the average angle between bonds to atoms in the pyramid base is 61°. The distortion of the geometry of the coordination sphere seems to be normal for many organometallic complexes with transition metals (Brown & Kunz, 1992). Eight-coordinate Hg^{II} and the hexagonal bipyramidal coordination sphere have also been observed in bis(1-methylthymine)mercury(II) (Kosturko, Folzer & Stewart, 1974) and polyethers coordinated to mercury(II) halides (Bond & Rogers, 1993; Paige & Richardson, 1984; Kawasaki & Matsuura, 1984). Although the primary coordination number for Hg^{II} in (NTAM:HgX₂)₂ complexes is six, the molecule retains an arrangement of atoms around Hg^{II} based on a hexagonal bipyramid with two 'empty sites'. The deviation of the halogen atoms from the vertical axis of the pyramid and the lengthening of the Hg—X₂ bond in relation to Hg—X₁ are directly related to the nature of the intra-

and intermolecular interactions. The NH₂ groups form a three-dimensional hydrogen-bond network; distances are given in Table 2.

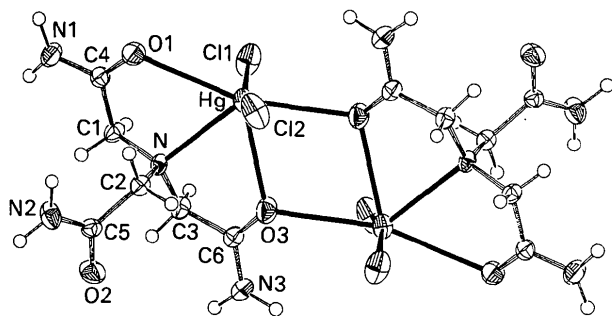


Fig. 1. ORTEP (Johnson, 1976) drawing of the NTAM:HgCl₂ molecule with 50% probability displacement ellipsoids. NTAM:HgBr₂ is very similar and the numbering scheme used is the same.

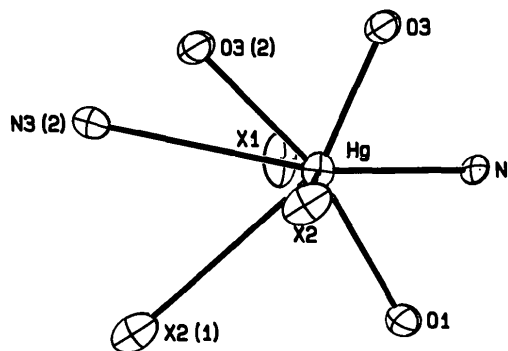
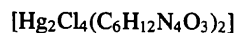


Fig. 2. Coordination sphere of the Hg atom [where X2(1) = X2ⁱ, N3(2) = N3ⁱⁱ, O3(2) = O3ⁱⁱ; symmetry codes as in Table 2].

Experimental

NTAM:HgCl₂

Crystal data



M_r = 919.4

Triclinic

P $\bar{1}$

a = 8.124 (2) Å

b = 8.393 (2) Å

c = 10.122 (2) Å

α = 78.03 (1)°

β = 78.74 (2)°

γ = 64.05 (2)°

V = 603 (1) Å³

Z = 1

D_x = 2.53 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
diffractometer

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 9–18°

μ = 13.21 mm⁻¹

T = 294 K

Prism

0.20 × 0.20 × 0.10 mm

Colorless

Crystal source: crystallized
from water

*R*_{int} = 0.020

θ _{max} = 25.98°

$\theta/2\theta$ scans

Absorption correction:

empirical

*T*_{min} = 0.608, *T*_{max} =
0.999

2495 measured reflections

2355 independent reflections

2184 observed reflections

[*I* > 3.0σ(*I*)]

Refinement

Refinement on *F*

R = 0.034

wR = 0.042

S = 1.5

2184 reflections

145 parameters

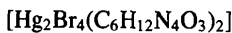
H atoms riding

$w = 4F_o^2/\sigma^2(F_o^2)$

(Δ/σ)_{max} = 0.01

NTAM:HgBr₂

Crystal data



M_r = 1097.2

Triclinic

P $\bar{1}$

a = 8.135 (2) Å

b = 8.558 (3) Å

c = 10.337 (3) Å

α = 78.94 (3)°

β = 78.81 (2)°

γ = 64.92 (2)°

V = 635 (1) Å³

Z = 1

D_x = 2.87 Mg m⁻³

Data collection

Enraf-Nonius CAD-4
diffractometer

$\theta/2\theta$ scans

Absorption correction:

empirical

*T*_{min} = 0.145, *T*_{max} =
0.997

2627 measured reflections

2481 independent reflections

2244 observed reflections

[*I* > 3.0σ(*I*)]

Refinement

Refinement on *F*

R = 0.045

wR = 0.060

S = 2.24

2244 reflections

146 parameters

H atoms riding

$w = 4F_o^2/[\sigma^2(F_o^2)$

+ 0.00148*F*_o⁴]

(Δ/σ)_{max} = 0.01

h = 0 → 9

k = -8 → 10

l = -11 → 12

3 standard reflections
monitored every 100

reflections

intensity variation:

-0.80%

$\Delta\rho$ _{max} = 1.3 (3) e Å⁻³

$\Delta\rho$ _{min} = -0.5 (3) e Å⁻³

Extinction correction:

not applied

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 22
reflections

θ = 10–15°

μ = 18.37 mm⁻¹

T = 294 K

Prism

0.23 × 0.18 × 0.10 mm

Colorless

Crystal source: crystallized
from water

*R*_{int} = 0.023

θ _{max} = 25.97°

h = -10 → 9

k = -10 → 10

l = -12 → 0

3 standard reflections
monitored every 100

reflections

intensity variation:

-0.30%

$\Delta\rho$ _{max} = 3.8 (4) e Å⁻³

$\Delta\rho$ _{min} = -0.8 (4) e Å⁻³

Extinction correction:

isotropic (Zachariasen,
1963)

Extinction coefficient: 1.5

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$B_{\text{eq}} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	x	y	z	B_{eq}
NTAM:HgCl ₂				
Hg	0.23477 (3)	0.01614 (2)	0.11971 (2)	2.093 (5)
Cl1	0.4045 (3)	-0.2652 (2)	0.2342 (2)	3.73 (4)
Cl2	0.0373 (2)	0.2357 (3)	-0.0315 (2)	3.39 (4)
O1	-0.0697 (5)	0.0994 (5)	0.3240 (4)	2.67 (9)
O2	0.3453 (6)	0.3299 (5)	0.4858 (4)	2.95 (9)
O3	0.5214 (5)	0.0960 (5)	0.1078 (4)	2.69 (9)
N	0.1920 (5)	0.2415 (6)	0.2762 (4)	1.59 (9)
N1	-0.2834 (7)	0.3389 (7)	0.4183 (5)	2.8 (1)
N2	0.2184 (7)	0.1625 (7)	0.6318 (5)	2.8 (1)
N3	0.5951 (6)	0.3195 (7)	0.1222 (5)	2.8 (1)
C1	-0.0024 (7)	0.3546 (7)	0.3101 (6)	1.9 (1)
C2	0.2764 (7)	0.1223 (7)	0.3992 (5)	1.8 (1)
C3	0.2848 (7)	0.3551 (7)	0.2004 (5)	1.9 (1)
C4	-0.1209 (7)	0.2502 (7)	0.3533 (5)	1.9 (1)
C5	0.2804 (6)	0.2170 (7)	0.5097 (5)	1.7 (1)
C6	0.4808 (7)	0.2421 (7)	0.1409 (5)	1.9 (1)
NTAM:HgBr ₂				
Br1	0.4015 (2)	-0.2677 (1)	0.2380 (1)	3.97 (3)
Br2	0.0380 (1)	0.2405 (1)	-0.0371 (1)	3.39 (2)
O1	-0.0759 (8)	0.1051 (7)	0.3252 (7)	2.9 (1)
O2	0.3369 (9)	0.3337 (8)	0.4848 (7)	3.2 (1)
O3	0.5152 (8)	0.0954 (8)	0.1118 (7)	3.0 (1)
N	0.1901 (8)	0.2383 (8)	0.2813 (6)	1.6 (1)
N1	-0.286 (1)	0.341 (1)	0.4153 (8)	3.0 (2)
N2	0.225 (1)	0.160 (1)	0.6295 (8)	3.2 (2)
N3	0.593 (1)	0.314 (1)	0.125 (1)	3.5 (2)
C1	-0.001 (1)	0.351 (1)	0.3150 (9)	2.2 (2)
C2	0.275 (1)	0.1269 (9)	0.3976 (8)	1.8 (2)
C3	0.285 (1)	0.3483 (9)	0.2044 (9)	2.1 (2)
C4	-0.123 (1)	0.251 (1)	0.3534 (9)	2.1 (2)
C5	0.280 (1)	0.218 (1)	0.5085 (9)	2.2 (2)
C6	0.476 (1)	0.238 (1)	0.1453 (9)	2.0 (2)

Table 2. Selected geometric parameters (\AA , $^\circ$)

	NTAM:HgCl ₂	NTAM:HgBr ₂
N—C1	1.461 (6)	1.45 (1)
N—C2	1.495 (7)	1.47 (1)
N—C3	1.473 (8)	1.48 (1)
C1—C4	1.517 (8)	1.51 (1)
C2—C5	1.513 (8)	1.52 (1)
C3—C6	1.529 (8)	1.51 (1)
O1—C4	1.229 (8)	1.22 (1)
O2—C5	1.236 (9)	1.23 (1)
O3—C6	1.230 (8)	1.23 (1)
N1—C4	1.316 (8)	1.33 (1)
N2—C5	1.309 (8)	1.32 (1)
N3—C6	1.315 (8)	1.33 (1)
Hg—X1	2.337 (1)	2.451 (1)
Hg—X2	2.348 (1)	2.465 (1)
Hg—N	2.580 (5)	2.597 (7)
Hg—O1	2.823 (4)	2.874 (6)
Hg—O3	2.666 (5)	2.613 (7)
Hg—O3 ⁱ	2.757 (4)	2.877 (7)
Hg—N3 ⁱ	3.738 (4)	3.825 (9)
Hg—X2 ⁱⁱ	3.974 (2)	4.033 (1)
C1—N—C2	111.3 (4)	112.6 (6)
C1—N—C3	108.8 (5)	108.0 (7)
C2—N—C3	115.6 (4)	114.9 (7)
N—C1—C4	113.1 (5)	112.6 (6)
N—C2—C5	115.5 (5)	116.8 (6)
N—C3—C6	111.2 (5)	111.1 (6)
C1—C4—N1	114.0 (6)	113.5 (8)
C2—C5—N2	114.3 (5)	115.4 (9)
C3—C6—N3	114.5 (6)	114.2 (8)
C1—C4—O1	121.8 (5)	122.7 (7)
C2—C5—O2	121.9 (5)	121.0 (8)

C3—C6—O3	121.3 (5)	122.4 (9)
N1—C4—O1	124.2 (6)	123.7 (9)
N2—C5—O2	123.7 (5)	123.5 (9)
N3—C6—O3	124.1 (6)	123.3 (7)
Hg—N—C1	111.4 (3)	112.6 (6)
Hg—N—C2	102.7 (3)	103.9 (5)
Hg—N—C3	106.9 (3)	104.5 (5)
X1—Hg—X2	159.9 (1)	158.9 (1)
X1—Hg—N	105.2 (1)	105.0 (2)
X1—Hg—O1	94.7 (1)	94.2 (1)
X1—Hg—O3	88.2 (1)	89.1 (2)
X1—Hg—O3 ⁱ	86.4 (1)	87.1 (1)
X1—Hg—N3 ⁱ	71.5 (1)	53.6 (1)
X1—Hg—X2 ⁱⁱ	83.2 (1)	80.9 (1)
X2—Hg—N	93.6 (1)	94.8 (2)
X2—Hg—O1	87.7 (1)	89.2 (1)
X2—Hg—O3	107.0 (1)	106.1 (2)
X2—Hg—O3 ⁱ	86.3 (1)	84.4 (2)
X2—Hg—N3 ⁱ	91.7 (1)	90.5 (1)
X2—Hg—X2 ⁱⁱ	77.7 (1)	79.4 (1)
O1—Hg—N	61.8 (2)	60.7 (2)
O1—Hg—X2 ⁱⁱ	78.4 (1)	78.7 (2)
O3—Hg—N	64.2 (1)	65.0 (2)
O3—Hg—O3 ⁱ	70.2 (1)	70.5 (2)
O3 ⁱ —Hg—N3 ⁱ	36.6 (1)	35.8 (2)
X2 ⁱⁱ —Hg—N3 ⁱ	53.0 (1)	53.2 (1)
N2...O1 ⁱⁱⁱ	2.863 (8)	2.923 (10)
N1...O2 ^{iv}	2.937 (8)	2.992 (11)
N1...O2 ^v	2.991 (7)	3.036 (11)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, y, -z$; (iii) $-x, -y, 1-z$; (iv) $-x, 1-y, 1-z$; (v) $-1+x, y, z$.

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The structures were solved by Patterson techniques and difference Fourier syntheses. Data collection: CAD-4 software (Enraf-Nonius, 1977). Cell refinement: CAD-4 software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF*.

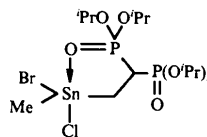
We thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The donor character of the Sn1—O6 [2.427 (2) Å] and Sn1—O1ⁱ [2.497 (2) Å] bonds [symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$] results in a lengthening effect (typical Sn—O single bonds = 2.15 Å; Harrison, 1989), and in accordance with this, the double-bond character of the bonds P1—O1 [1.472 (2) Å] and P2—O6 [1.484 (2) Å] is stronger than for the other P—O bonds [P1—O2 1.566 (2), P1—O3 1.567 (2), P2—O4 1.558 (2), P2—O5 1.568 (2) Å]; a typical P—O single bond = 1.62 Å (Rademacher, 1987). The bridging O atom O1 is almost linearly coordinated [Sn1—O1ⁱ—P1ⁱ 174.69 (15)°]. In most of the compounds with an Sn—O—P unit, this angle adopts values between 125 and 170° (Cambridge Structural Database; Allen *et al.*, 1979). The Sn—O—P angle in (1) is in the upper range, which is rarely observed. A similar structure to that of (1) is adopted by Me₂SnClCH₂CH[P(O)(OⁱPr)₂][P(O)Ph₂] (Richter, Weichmann, Freitag & Herbst-Irmer, 1994), in which the Sn atom is five-coordinate and no dimerization is found. Since the Lewis acidity resulting from an Sn—Br bond is greater than that from an Sn—Me bond, compound (1) displays sixfold coordination.

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Tetraisopropyl 2-[(Bromo)(chloro)(methyl)-stannyl]-1,1-ethanediphosphonate at 153 K

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Abstract

The structure of the title compound, [SnBrCl(CH₃)(C₁₄H₃₁O₆P₂)], is reported. As a result of an Sn—O interaction, dimers are formed in the crystal. The bridging O atom is almost linearly coordinated.

Comment

Syntheses and NMR studies of tetraisopropyl 2-[(bromo)(chloro)(methyl)stannyl]-1,1-ethanediphosphonate, (1), are discussed elsewhere (Richter, Weichmann, Krug, Hartung & Zeigan, 1994). The crystal structure of (1) consists of dimeric molecules, with an inversion centre in the middle of each dimer. The Sn atoms are coordinated by two C, two O, one Cl and one Br atom, forming distorted octahedra. As a result of the donor interaction of O6 with Sn1, a five-membered ring is formed. This ring adopts a twist conformation in which C2 lies 0.310 (6) Å above and C3 0.214 (6) Å below the plane formed by Sn1, P2 and O6.

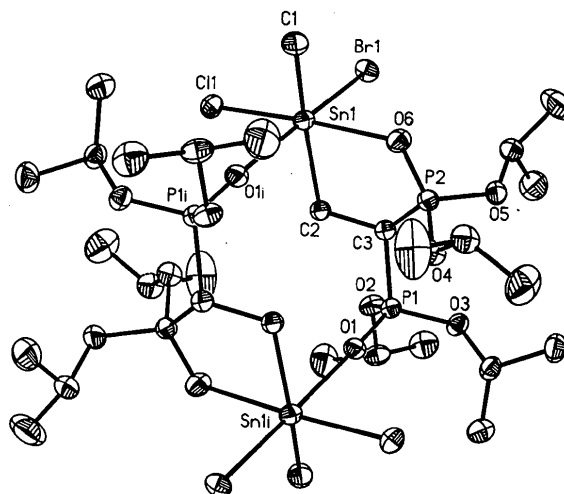


Fig. 1. Structure of (1) showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity. Atoms of the ⁱPr groups are not labelled.

Experimental

Crystal data

[SnBrCl(CH₃)(C₁₄H₃₁O₆P₂)]
M_r = 606.41

Mo *K*α radiation
λ = 0.71073 Å