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Mercury(II) Chloride Adduct of a Betaine Derivative: Bis[(dimethyl)(2-dimethylaminoethyl)ammonioacetato]tetrakis[dichloromercury(II)]

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Abstract

The structure of a 4:2 adduct of mercury(II) chloride with a betaine derivative, di-μ-chloro-1:2κ^2Cl;3:4κ^2Cl-hexachloro-1κ^2Cl,2κCl,3κ^2Cl,4κCl-bis[μ_3-(dimethyl)(2-dimethylaminoethyl)ammonioacetato]-1κO:2$\kappa O'$:3$\kappa N'$;-1$\kappa N'$:2κO:3$\kappa O'$-tetramercury(II), [Hg$_4$(C$_8$H$_{18}$N$_2$O$_2$)$_2$-Cl$_8$], has been revealed as a centrosymmetric 16-membered macrocycle fused with two six-membered rings. Each of the two independent Hg^{II} atoms is in a highly distorted tetrahedral coordination environment.

Comment

The poor solubility of mercury(II) carboxylates in common solvents makes their structural characterization difficult. Accordingly, the crystal structures of only a few mercury(II) carboxylates and related complexes are known. Recent studies in our laboratory have demonstrated that betaine (Me$_3$N$^+$CH$_2$COO$^-$, IUPAC name trimethylammonioacetate, abbreviated to bet) and its derivatives, considered as neutral structural analogues of the corresponding carboxylate anions, can form soluble mercury(II) chloride adducts with the metal centre bearing additional anionic halide ligands and in different metal–betaine molar ratios (Chen & Mak, 1992). We now report the preparation and crystal structure of a mercury(II) chloride adduct of a betaine derivative, [Hg$_4$(C$_8$H$_{18}$N$_2$O$_2$)$_2$Cl$_8$], namely bis[(dimethyl)(2-dimethylaminoethyl)ammonioacetato]tetrakis[dichloromercury(II)], (I).

(I)
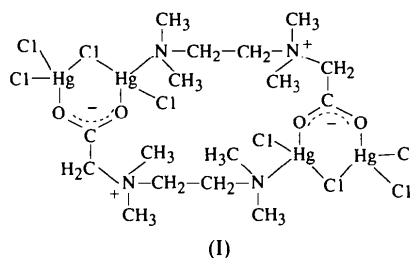
The structure of the title complex is based on a centrosymmetric macrocycle fused with two six-membered rings (Fig. 1). Most atoms of the 16-membered macrocyclic ring [—Hg(1)—O(1)—C(1)—C(2)—N(1)—C(5)—C(6)—N(2)—Hg(1a)—O(1a)—C(1a)—C(2a)—N(1a)—C(5a)—C(6a)—N(2a)—] are nearly coplanar. Each six-membered ring adopts a twist-boat conformation with C(1)—O(1) and Hg(2)—Cl(1) as the two sides of the boat. The mean plane containing atoms Hg(1), Cl(1), Hg(2) and O(2) is nearly orthogonal to the macrocycle. The carboxylate group functions in a *syn–anti* bridge mode, which is similar to that observed in [Hg(2-ClC$_6$H$_4$OCH$_2$CO$_2$)$_2$] (Mak, Yip, Kennard & Smith, 1990). The non-bonded distance of two Hg atoms bridged by the carboxylate group is 4.144 Å. The large inter-ring separations between the Hg^{II} atoms and the nearest uncoordinated Cl atoms [Hg(1)···Cl(3b) 3.54(1) Å, Hg(2)···Cl(2c) 3.43(1) Å, Hg(2)···Cl(4d) 3.63(1) Å] indicate that the bonding interactions are negligible (see Table 3 for symmetry relationships).

The coordination geometry about each Hg^{II} atom is distorted tetrahedral. Hg(1) is coordinated by carboxy O atom O(1), tertiary amine atom N(2a), bridging Cl atom Cl(1) and terminal Cl atom Cl(2); the four bond lengths are nearly equal [Hg(1)—O(1) 2.43(2) Å, Hg(1)—N(2a) 2.43(2) Å, Hg(1)—Cl(1) 2.435(10) Å, Hg(1)—Cl(2) 2.394(11) Å]. The bond angles range from 87.6(8) for O(1)—Hg(1)—N(2a) to
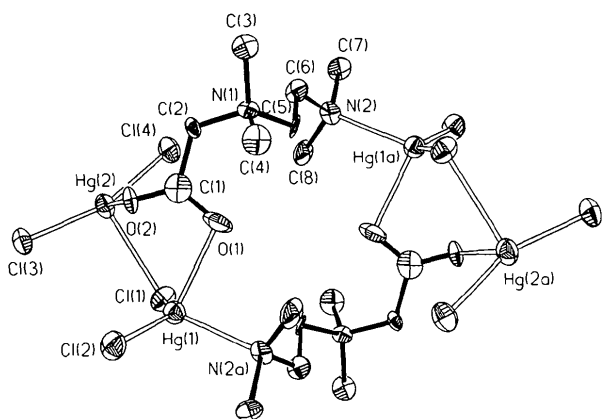
Fig. 1. Molecular structure (35% displacement ellipsoids) of the title complex with the atom-numbering scheme excluding the H atoms. The peculiar shape of the displacement ellipsoid of C(5) may be due to positional disorder.

135.4 (3)° for Cl(1)—Hg(1)—Cl(2). The marked difference between the strong [Hg(2)—Cl(3) 2.305 (9), Hg(2)—Cl(4) 2.309 (9) Å] and the weak [Hg(2)—Cl(1) 2.891 (9), Hg(2)—O(2) 2.68 (2) Å] bonds about Hg(2) results in an even more distorted tetrahedral geometry with bond angles ranging from 79.4 (4) for Cl(1)—Hg(2)—O(2) to 160.4 (3)° for Cl(3)—Hg(2)—Cl(4). The tetrahedral geometry about Hg^{II} is common in mercury(II) betaine complexes [for example $[Hg_2bet_2Cl_4.2HgCl_2]$ (Chen & Mak, 1992) and $[Hg_2\{cis\text{-}(p\text{-}Me_2NC_5H_4N)_2C_2(COO)_2\}X_4.6HgX_2]$ (X = Cl, Br) (Wu & Mak, 1994a)], whereas such a coordination mode is rare in their anionic carboxylates, in which the Hg^{II} atoms generally exhibit linear (Allmann, 1973), planar trigonal (Mak et $al.$, 1990) or irregular pentahedral coordination (Roberts, Ferguson, Goel, Ogini & Restivo, 1978).

Experimental

The betaine derivative was obtained as a by-product in our attempt (Wu & Mak, 1994b) to prepare the double betaine N,N'-dicarboxymethyl-N,N,N',N'-tetramethyl-ethylenediammonium according to the literature procedure (Lloyd, Baker, Smith, Olliff & Rutt, 1992). The crude product without recrystallization (126 mg, 0.50 mmol, calculated as pure double betaine) was mixed with $HgCl_2$ (535 mg, 2.0 mmol) in 15 ml of boiling distilled water; after the clear solution was cooled to room temperature, the resulting white precipitate was removed by filtration. Slow evaporation of the filtrate in air at room temperature for several days yielded a large quantity of colourless plate-like crystals and a small amount of colourless prismatic crystals. The former compound turned out to be a mercury chloride adduct of the double betaine (Wu & Mak, 1994c), and the latter was the title complex.

Crystal data

$[Hg_4(C_8H_{18}N_2O_2)_2Cl_8]$
$M_r = 1434.4$
Monoclinic
$P2_1/n$
$a = 8.106 (2)$ Å
$b = 20.135 (4)$ Å
$c = 10.399 (2)$ Å
$\beta = 102.77 (3)°$
$V = 1655.3 (8)$ Å^3
$Z = 2$
$D_x = 2.878$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$11°$
$\mu = 19.17$ mm^{-1}
$T = 293$ K
Prism
$0.20 \times 0.18 \times 0.10$ mm
Colourless

Data collection

Siemens $R3m/V$ diffractometer
ω scans
Absorption correction:
 ψ scan (Kopfmann & Huber, 1968)
 $T_{min} = 0.036$, $T_{max} = 0.110$
2349 measured reflections
2180 independent reflections

1265 observed reflections
 $[F > 6.0\sigma(F)]$
$R_{int} = 0.030$
$\theta_{max} = 24.0°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 21$
$l = -11 \rightarrow 10$
2 standard reflections
 monitored every 100 reflections
 intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.063$
$wR = 0.074$
$S = 1.25$
1265 reflections
164 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.002F^2]$

$(\Delta/\sigma)_{max} = 0.086$
$\Delta\rho_{max} = 2.33$ e Å^{-3}
$\Delta\rho_{min} = -1.59$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from $International$ $Tables$ for X-ray $Crystallography$ (1974, Vol. IV)

Table 1. $Fractional$ $atomic$ $coordinates$ and $equivalent$ $isotropic$ $displacement$ $parameters$ ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg(1)	0.5476 (2)	0.6498 (1)	0.3021 (1)	0.046 (1)
Hg(2)	0.0657 (2)	0.6048 (1)	0.0887 (2)	0.053 (1)
Cl(1)	0.2580 (11)	0.6734 (4)	0.3174 (10)	0.058 (3)
Cl(2)	0.7322 (13)	0.6880 (5)	0.1670 (9)	0.063 (3)
Cl(3)	0.0623 (13)	0.6880 (4)	−0.0640 (10)	0.061 (3)
Cl(4)	−0.0092 (12)	0.5100 (4)	0.1870 (9)	0.059 (3)
O(1)	0.506 (3)	0.530 (1)	0.300 (3)	0.069 (4)
O(2)	0.376 (2)	0.556 (1)	0.097 (2)	0.042 (4)
N(1)	0.498 (3)	0.391 (1)	0.236 (2)	0.030 (4)
N(2)	0.241 (3)	0.365 (1)	0.495 (3)	0.038 (4)
C(1)	0.432 (4)	0.516 (2)	0.182 (3)	0.052 (4)
C(2)	0.406 (3)	0.442 (1)	0.148 (3)	0.029 (4)
C(3)	0.465 (4)	0.327 (1)	0.161 (3)	0.052 (4)
C(4)	0.683 (4)	0.409 (2)	0.252 (4)	0.060 (4)
C(5)	0.455 (3)	0.389 (1)	0.373 (3)	0.042 (4)
C(6)	0.291 (4)	0.356 (2)	0.369 (3)	0.049 (4)
C(7)	0.095 (4)	0.313 (2)	0.493 (4)	0.066 (4)
C(8)	0.166 (4)	0.431 (2)	0.497 (3)	0.071 (4)

Table 2. $Selected$ $bond$ $lengths$ (Å) and $angles$ (°)

Hg(1)—Cl(1)	2.435 (10)	Hg(1)—Cl(2)	2.394 (11)
Hg(1)—O(1)	2.43 (2)	Hg(1)—N(2a)	2.43 (2)
Hg(2)—Cl(1)	2.891 (9)	Hg(2)—Cl(3)	2.305 (9)
Hg(2)—Cl(4)	2.309 (9)	Hg(2)—O(2)	2.68 (2)
O(1)—C(1)	1.28 (4)	O(2)—C(1)	1.21 (4)
N(1)—C(2)	1.47 (3)	N(1)—C(3)	1.49 (4)
N(1)—C(4)	1.51 (4)	N(1)—C(5)	1.54 (4)

N(2)—C(6)	1.47 (4)	N(2)—C(7)	1.57 (4)
N(2)—C(8)	1.48 (4)	C(1)—C(2)	1.52 (4)
C(5)—C(6)	1.47 (4)		
Cl(1)—Hg(1)—Cl(2)	135.4 (3)	Cl(1)—Hg(1)—O(1)	93.5 (6)
Cl(2)—Hg(1)—O(1)	114.6 (7)	Cl(1)—Hg(1)—N(2a)	118.1 (6)
Cl(2)—Hg(1)—N(2a)	98.0 (6)	O(1)—Hg(1)—N(2a)	87.6 (8)
Cl(1)—Hg(2)—Cl(3)	98.2 (3)	Cl(1)—Hg(2)—Cl(4)	100.2 (3)
Cl(3)—Hg(2)—Cl(4)	160.4 (3)	Cl(1)—Hg(2)—O(2)	79.4 (4)
Cl(3)—Hg(2)—O(2)	99.0 (5)	Cl(4)—Hg(2)—O(2)	91.1 (5)
Hg(1)—Cl(1)—Hg(2)	101.8 (3)	Hg(1)—O(1)—C(1)	106 (2)
Hg(2)—O(2)—C(1)	118 (2)	C(2)—N(1)—C(3)	106 (2)
C(2)—N(1)—C(4)	105 (2)	C(3)—N(1)—C(4)	109 (2)
C(2)—N(1)—C(5)	114 (2)	C(3)—N(1)—C(5)	114 (2)
C(4)—N(1)—C(5)	109 (2)	C(6)—N(2)—C(7)	105 (2)
C(6)—N(2)—C(8)	109 (2)	C(7)—N(2)—C(8)	107 (2)
C(6)—N(2)—Hg(1a)	119 (2)	C(7)—N(2)—Hg(1a)	109 (2)
C(8)—N(2)—Hg(1a)	108 (2)	O(1)—C(1)—O(2)	124 (3)
O(1)—C(1)—C(2)	117 (2)	O(2)—C(1)—C(2)	118 (2)
N(1)—C(2)—C(1)	121 (2)	N(1)—C(5)—C(6)	112 (2)
N(2)—C(6)—C(5)	110 (2)		

Symmetry code: (a) $1 - x, 1 - y, 1 - z$.

Table 3. Contact distances (Å)

Hg(1)· · ·Hg(2)	4.144	Hg(1)· · ·Cl(3b)	3.54 (1)
Hg(2)· · ·Cl(2c)	3.43 (1)	Hg(2)· · ·Cl(4d)	3.63 (1)

Symmetry codes: (b) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (c) $x-1, y, z$; (d) $-x, 1-y, -z$.

The structure was solved by direct and Fourier methods and refined by full-matrix least squares using the *SHELXTL/PC* program (Sheldrick, 1990). H atoms were placed in their idealized locations and included in structure-factor calculations.

Data collection: Siemens *P3* software. Cell reduction: Siemens *P3* software. Data reduction: *SHELXTL-Plus XDISK* (Sheldrick, 1987). Structure solution: *SHELXTL/PC XS*. Structure refinement: *SHELXTL/PC XLS*. Molecular graphics: *SHELXTL/PC XP*. Preparation of material for publication *SHELXTL/PC XPBUL*.

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cis-Dipyridine Complex of Bis(ω-nitroacetophenonato)zinc(II)

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Abstract

The title compound, bis(ω-nitroacetophenonato-*O*,*O'*)-bis(pyridine)zinc(II), [Zn(C$_5$H$_5$N)$_2$(C$_8$H$_6$NO$_3$)$_2$], was synthesized by the reaction of zinc acetate dihydrate with ω-nitroacetophenone (ω-nap) in ethanol, followed by warming of the resulting product in pyridine. The ω-nap ligands chelate the Zn center forming six-membered rings with a bite angle of 83.23 (8)°. The distance from Zn to the nitro O atom [2.152 (2) Å] is longer than that from Zn to the carbonyl O atom [2.039 (2) Å], indicating that the latter is more strongly bound and suggesting a keto–enol mechanism preceding the binding of ω-nap to the Zn atom.

Comment

The pyridine complex of bis(ω-nitroacetophenonato)-zinc(II) was synthesized as part of a wider study of complexes of first-row *d*-block elements with polyfunctional ligands and of their packing arrangements in the solid state in the presence of hydrogen bonding. The ω-nitroacetophenone (ω-nap) ligand is capable of acting as an acceptor, but not as a donor, in hydrogen-bonding interactions and thus a secondary ligand or unligated moiety capable of hydrogen-bond donation is necessary for studies of the topological response of compounds of ω-nap to the presence of hydrogen-bonded networks. In addition, as was pointed out by Bonamico, Dessy, Fares & Scaramuzza (1972), stabilization of complexes of ω-nap is aided by the presence of an additional ligand because of the weakly ligating nature of ω-nap. The present complex, (I), synthesized as a molecular prototype, cannot alone form hydrogen bonds in a crystalline environment. It is expected that the molecular structure of this complex is determined by intramolecular energetics in the absence of strong interactions with the crystalline surroundings.