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**Crystal Structure
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Bis(*N*,*N*′-dimethylimidazol-2-ylidene)mercury chlorotriiodomercury dimethyl sulfoxide solvate

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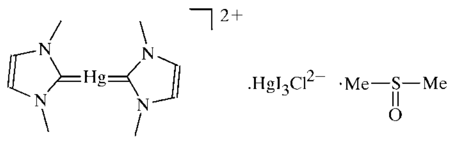
The double mercury salt $[Hg(C_5H_8N_2)_2][HgClI_3]\cdot C_2H_6OS$ was prepared and its structure characterized. The $[Hg(C_5H_8N_2)_2]^{2+}$ cation lies about an inversion centre and the $[HgClI_3]^{2-}$ anion lies on a mirror plane. Cations and anions are linked to form a one-dimensional polymer by weak Hg$\cdots$Cl interactions [Hg$\cdots$Cl 3.3744 (3) Å]. The mercury–carbene bond distance [2.076 (7) Å] is typical of a dicationic mercury–carbene species.

Comment

There has been considerable interest recently in *N*,*N*′-dialkylimidazol-2-ylidene ligands as they bind strongly to a number of transition metals, in some cases forming complexes that are unusually robust for carbene ligands (Regitz, 1996; Herrmann *et al.*, 1996; Herrmann & Köcher, 1997).

Whilst attempting to prepare a bis(*N*,*N*′-dimethylimidazol-2-ylidene)mercury salt for possible use as a transmetallation reagent, we produced the mercury double salt which has the formulation (*N*,*N*′-dimethylimidazol-2-ylidene)$_2$Hg$\cdot$HgClI$_3$ and crystallizes with one disordered molecule of dimethyl sulfoxide, (I). The salt contains two separate mercury-containing moieties. The organometallic part features the two carbene ligands coordinated to the central Hg atom in a strictly linear arrangement which is enforced by crystallographic inversion symmetry. This linear coordination has also been observed in related structures, such as that of (*N*,*N*′-diphenyimidazol-2-ylidene)$_2$Hg$\cdot$(ClO$_4$)$_2$, (II) (Luger & Ruban, 1971), in which the perchlorate anions do not distort the preferred linear coordination of the Hg atom. A different arrangement is found in the case of (*N*,*N*′-dimethylimidazol-2-ylidene)$_2$HgCl$_2$, (III) (Arduengo *et al.*, 1996), wherein the two chloride anions are coordinated to mercury, and the metal coordination is distorted toward tetrahedral.



(I)

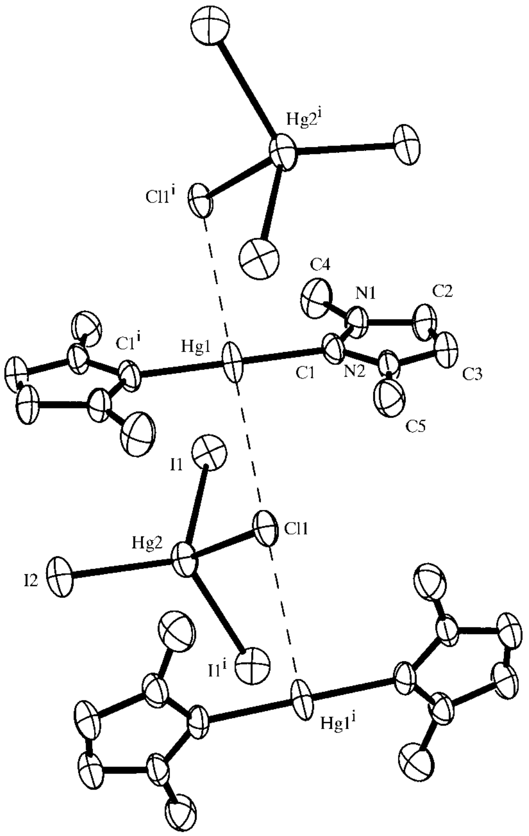


Figure 1
The extended structure of (I) showing the linking of cations and anions (50% probability displacement ellipsoids). H atoms and solvent of crystallization have been omitted for clarity.

The $[HgClI_3]^{2-}$ counter-ion lies on a crystallographic mirror plane and exhibits distorted tetrahedral geometry in which the Cl—Hg—I angles are reduced and the I—Hg—I angles increased compared with regular tetrahedral angles to accomodate the larger I atoms. The structure is polymeric through weak interactions between the carbene Hg and the Cl atoms, which make an approach of 3.3744 (3) Å, with the Cl atom bridging two Hg centres. The weak interactions show the organometallic moiety to be close to square planar, C1—Hg—Cl1 89.5 (2)°. The Hg1—Cl1—Hg1(x, $\frac{1}{2}+y$, z) angle is 177.85 (9)°.

Experimental

N,*N*′-Dimethylimidazolium iodide (prepared as described by Sarasin, 1923) (5.3 g) was dissolved in dimethyl sulfoxide (25 ml), to which was added HgCl$_2$ (3.0 g) with stirring. A solution of sodium bicarbonate (1 g) in water (40 ml) was added, followed by ethanol (30 ml). The solution was allowed to stand overnight, during which time a considerable amount of white precipitate formed which was collected by filtration to give the pure title compound (8.7 g, 68% based on the organic starting material). ^{1}H NMR: δ 7.62 (*s*, 4H, H3 + H4), 3.98 (*s*, 12H, N—CH$_3$). Analysis calculated for [Hg(C$_5$H$_8$N$_2$)$_2$][HgClI$_3$]·C$_2$H$_6$OS: C, 13.27; H, 2.04; N, 5.15%; found: C, 13.50; H, 1.71; N, 4.79%. Crystals were grown by dissolving a small amount of the substrate in dimethyl sulfoxide (70%) and ethanol (30%). Each day a small portion of ethanol (*ca* 5%) was added, and crystals formed gradually as the overall proportion of ethanol increased.

Crystal data

[Hg(C$_5$H$_8$N$_2$)$_2$][HgClI$_3$]·C$_2$H$_6$OS
M_r = 1087.73
Orthorhombic, *Pnma*
a = 9.6119 (1) Å
b = 13.4954 (1) Å
c = 18.514 (3) Å
V = 2401.57 (5) Å^3
Z = 4
D_x = 3.008 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 7498 reflections
θ = 1.87–28.31°
μ = 16.833 mm^{-1}
T = 203 (2) K
Needle, colourless
0.38 × 0.18 × 0.05 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min}$ = 0.060, $T_{\rm max}$ = 0.487
14 997 measured reflections

2937 independent reflections
2317 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.0513
$\theta_{\rm max}$ = 28.31°
$h = -11 \rightarrow 12$
$k = -16 \rightarrow 17$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0383
$wR(F^2)$ = 0.1099
S = 1.050
2937 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 11.9641P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.018
$\Delta\rho_{\rm max}$ = 1.328 e Å^{-3}
$\Delta\rho_{\rm min}$ = −2.282 e Å^{-3}

The dimethyl sulfoxide molecule is disordered with the C and O atoms lying on the mirror plane and the S atom disordered either side of the mirror plane. The maxima and minima in the difference map are 0.79 Å from Hg2 and 0.58 Å from I1, respectively.

Data collection: *SMART* (Siemens, 1994*a*); cell refinement: *SAINT* (Siemens, 1994*a*); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *SHELXTL* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

Hg1—C1	2.076 (7)	N2—C5	1.449 (11)
N1—C1	1.355 (10)	C2—C3	1.360 (15)
N1—C2	1.367 (11)	Hg2—Cl1	2.680 (3)
N1—C4	1.470 (12)	Hg2—I2	2.6863 (9)
N2—C1	1.340 (10)	Hg2—I1	2.7602 (7)
N2—C3	1.359 (11)		
Cl1—Hg2—I2	105.72 (6)	Cl1—Hg2—I1	97.87 (4)
Cl1—Hg2—I1^{i}	97.87 (4)	I2—Hg2—I1	119.263 (19)
I2—Hg2—I1^{i}	119.262 (18)	I1^{i}—Hg2—I1	111.44 (3)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1265). Services for accessing these data are described at the back of the journal.

References

Arduengo, J. A., Harlow, L. H., Marshall, W. J. & Prakasha, T. K. (1996). *Heteroatom Chem.* **7**, 421–426.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Herrmann, W. A., Elison, M., Fischer, J., Köcher, C. & Artus, G. R. J. (1996). *Chem. Eur. J.* **2**, 772–780.
Herrmann, W. A. & Köcher, C. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 2163–2187.
Luger, V. P. & Ruban, G. (1971). *Acta Cryst.* B**27**, 2276–2279.
Regitz, M. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 725–728.
Sarasin, J. (1923). *Helv. Chim. Acta*, **6**, 370–376.
Sheldrick, G. M. (1997*a*). *SHELXS*97. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXL*97. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994*a*). *SMART* and *SAINT*. *Area Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *SHELXTL.* Release 5.03. Siemens Analytical X-ray Instruments Inc.. Madison, Wisconsin, USA.

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