Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Tetrameric dichloro(trimethylammonio-*p*-toluenesulfonamidate)mercury(II)

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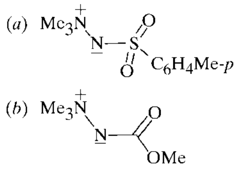
Received 21 November 2003
Accepted 10 December 2003
Online 17 January 2004

In the title compound, hexa-μ-chloro-dichlorotetrakis(*N*-trimethylammonio-*p*-toluenesulfonamidate-κ^2N,O)tetramercury(II), $[\mathrm{Hg}\{\mathrm{Me_3N(+)N(-)SO_2C_6H_4CH_3}\text{-}p\}\mathrm{Cl_2}]_4$ or $[\mathrm{Hg_4Cl_8(C_{10}H_{16}N_2O_2S)_4}]$, four nearly linear and parallel Cl—Hg—Cl units associate through pairwise Hg$\cdots$Cl interactions of 3.1–3.2 Å. Each Hg atom is also coordinated through N and O atoms to a ylide molecule. The available structural data indicate that coordination of a sulfonyl-stabilized nitrogen ylide to a metal atom (Hg or Ag) has no detectable effect on its geometry.

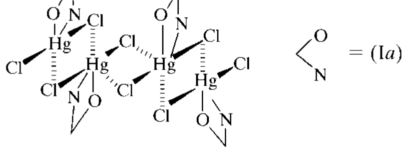
Comment

We have recently shown that trimethylammonio-stabilized nitrogen ylides, such as (I*a*) or (I*b*), can act as ligands, donating to silver(I) and mercury(II) through their negatively charged N atoms and sometimes also through an O atom (Morris *et al.*, 2003). In an extension of this work, we now report the structure of the title complex, (II), a 1:1 adduct of the sulfonyl-stabilized ylide (I*a*) with mercury(II) chloride.

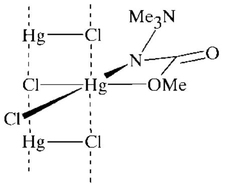
The asymmetric unit of (II) contains two HgCl$_2$*L* moieties [Fig. 1; *L* is (I*a*)]. The discrete centrosymmetric tetrameric molecule shown in Fig. 2 is formed from two such asymmetric units. Each metal atom is strongly bonded to two Cl atoms [Hg—Cl = 2.325 (1)–2.340 (1) Å; Table 1] and is thereby incorporated into a nearly linear Cl—Hg—Cl unit; the Cl11—Hg1—Cl12 and Cl21—Hg2—Cl22 angles are 167.6 (1) and 160.8 (1)°, respectively. The tetrameric molecule contains four such Cl—Hg—Cl units which are roughly parallel to one another, and they associate through pairs of weak Hg$\cdots$Cl interactions (3.07–3.22 Å). Each metal atom is also chelated by the N and O atoms of a ylide ligand, and the Hg—N and Hg—O distances [2.507 (2) and 2.831 (2) Å, respectively, for Hg1, and 2.492 (2) and 2.757 (2) Å, respectively, for Hg2] indicate that the stronger interaction is through the N atom. It is broadly true that, at each Hg atom, the Hg—N and Hg—O bonds are normal to the strong Hg—Cl bonds and coplanar with the weaker Hg$\cdots$Cl interactions. Atom Hg1 has a distorted octahedral coordination formed by strong bonds to atoms Cl11 and Cl12, and weaker bonds to atoms Cl11$^{\mathrm{i}}$ and Cl22 and to the N and O atoms of the ylide [symmetry code: (i) $-x, -y, -z$]. In contrast, atom Hg2 adopts a distorted square-pyramidal coordination, with atom N21 apical. The Hg2 coordination can be compared with that of Hg1 when the Hg1$\cdots$Cl11$^{\mathrm{i}}$ interaction is ignored. The average difference between corresponding angles subtended at Hg1 and Hg2 is then only 5°.



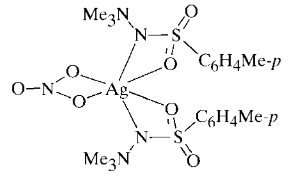
(I)



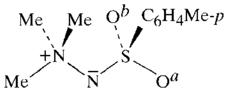
(II)



(III)



(IV)



(V)

The structure of (II) contrasts with that of the apparently analogous species (III), *viz*. HgCl$_2$*L* with *L* = (I*b*) (Morris *et al.*, 2003). In (III), linear Hg coordination is defined by strong Hg—N and Hg—Cl bonds of 2.154 (5) and 2.371 (2) Å, which are roughly normal to weak Hg—Cl bonds [2.596 (1) Å] and extremely weak Hg$\cdots$O interactions [2.847 (4) Å]. The weaker Hg—Cl bond associates further with the corresponding bonds in adjacent units so that a chain coordination polymer is produced. Each metal atom has the same [2,2,2] distorted-octahedral coordination. Although the variable and as yet unpredictable nature of mercury(II) coordination polyhedra is well known (House *et al.*, 1994), the difference of 0.35 Å between the Hg—N(ylide) bonds in (II) and (III) is particularly striking.

Bond lengths in the *L* = (I*a*) ligands of (II) and of (IV), [AgNO$_3$*L*$_2$] (Morris *et al.*, 2003), agree well with those in the monohydrate of (I*a*) (Cameron *et al.*, 1976), where the ylide N(−) atom is hydrogen bonded to a water molecule. These species all contain single N—N and S—C bonds [1.464 (3)–1.481 (6) and 1.761 (7)–1.782 (2) Å, respectively], whereas the S—N distances [1.592 (2)–1.616 (5) Å] imply some multiple-bond character. The S—O distances [1.434 (4)–1.452 (2) Å] do not appear to lengthen when the O atom is coordinated to Hg or Ag. Indeed, it is hard to find evidence that attachment of the ylide to Hg or Ag requires even a conformational change. The (I*a*) sulfonyl-ylide ligands in (II), in (IV) and in the monohydrate of (I*a*) all adopt the conformation (V), *i.e.* a roughly planar H$_3$C—N(+)—N(−)—S—O^a zigzag chain with

DOI: 10.1107/S0108270103028464

torsion angles of 156–173° across the N—N and N—S bonds [the superscript *a* refers to the (I*a*) ylide]. The N—S—O^a angles [103.0 (3)–104.1 (1)°] are invariably more acute than the N—S—O^b angles [113.0 (3)–115.4 (1)°]. In (II) and (IV), this could be ascribed to chelate ring formation. In the monohydrate of (I*a*), hydrogen bonding is a complicating factor. However, in *n*-$C_{16}H_{33}SO_2N(-)N(+)Me_3$ (Morris & Muir, 2004), the same ylide conformation [N—N and N—S torsion angles of 167 and 160°, respectively, N—S—O^a = 103.3 (3) and N—S—O^b = 114.5 (3)°] is found. This appears to be the stable conformation of an Me_3NNSO_2 ylide and we believe the near-eclipse implied by N—N—S—O^b torsion angles of 28–41° is responsible for the obtuseness of the N—S—O^b bond angles.

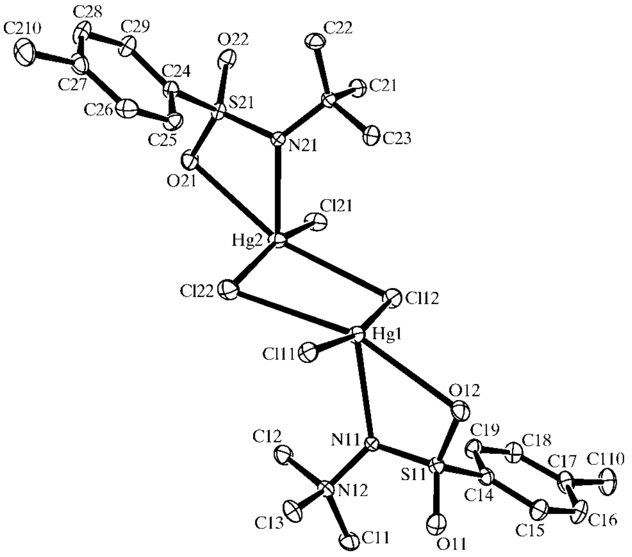


Figure 1
The asymmetric unit of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

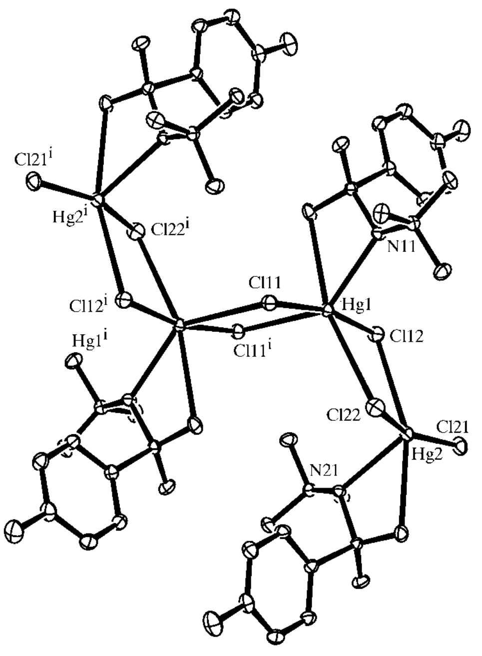


Figure 2
The tetrameric molecule of (II). H atoms have been omitted for clarity. [Symmetry code: (i) −*x*, −*y*, −*z*.]

Experimental

The methods of Morris *et al.* (2003) were used for the preparation of the ylide ligand and its complexation to mercury(II) chloride. Crystals of the title compound, (II), were obtained from an aqueous solution.

Crystal data

$[Hg_4Cl_8(C_{10}H_{16}N_2O_2S)_4]$
$M_r = 1999.2$
Monoclinic, $P2_1/c$
$a = 7.9948$ (1) Å
$b = 21.6336$ (2) Å
$c = 17.2957$ (1) Å
$\beta = 93.3241$ (3)°
$V = 2986.37$ (5) Å^3
$Z = 2$
$D_x = 2.223$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 596 reflections
$\theta = 1.0$–35.0°
$\mu = 10.8$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
0.35 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Thick-slice ω and φ scans
Absorption correction: Gaussian quadrature algorithm in *WinGX* KappaCCD processing package (Farrugia, 1999)
$T_{min} = 0.119$, $T_{max} = 0.479$
59 772 measured reflections
12 956 independent reflections
11 417 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 35.0°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 34$
$l = 0 \rightarrow 27$

Refinement

Refinement on F^2
$R(F) = 0.026$
$wR(F^2) = 0.068$
$S = 1.04$
12 956 reflections
326 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 2.14P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.54$ e Å^{-3}
$\Delta\rho_{min} = -3.59$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00064 (5)

Table 1
Selected geometric parameters (Å, °).

Hg1—Cl11	2.3323 (5)	N11—N12	1.464 (3)
Hg1—Cl12	2.3403 (5)	Hg2—Cl21	2.3254 (6)
Hg1—N11	2.507 (2)	Hg2—Cl22	2.3336 (6)
Hg1—O12	2.831 (2)	Hg2—N21	2.492 (2)
Hg1—Cl11^i	3.0896 (6)	Hg2—O21	2.757 (2)
Hg1—Cl22	3.2160 (7)	S21—O22	1.452 (2)
Cl12—Hg2	3.0654 (6)	S21—O21	1.454 (2)
S11—O11	1.447 (2)	S21—N21	1.600 (2)
S11—O12	1.450 (2)	S21—C24	1.771 (2)
S11—N11	1.598 (2)	N21—N22	1.465 (3)
S11—C14	1.775 (2)		
Cl11—Hg1—Cl12	167.59 (2)	Cl21—Hg2—Cl22	160.75 (2)
N11—Hg1—Cl11^i	135.22 (4)	O21—Hg2—Cl12	159.72 (4)
O12—Hg1—Cl22	162.36 (4)	O22—S21—N21	114.72 (10)
O11—S11—N11	115.36 (10)	O21—S21—N21	104.12 (11)
O12—S11—N11	103.34 (11)	N22—N21—S21	118.46 (15)
N12—N11—S11	119.48 (15)		
O11—S11—N11—N12	−28.0 (2)	O22—S21—N21—N22	27.3 (2)
O12—S11—N11—N12	−157.36 (17)	O21—S21—N21—N22	156.35 (16)
O12—S11—N11—Hg1	−2.21 (12)	O21—S21—N21—Hg2	6.54 (11)
S11—N11—N12—C12	−165.10 (17)	S21—N21—N22—C23	163.75 (17)

Symmetry code: (i) −*x*, −*y*, −*z*.

H-atom positions were initially obtained from difference syntheses. Subsequently, all H atoms were allowed to ride on their parent C atoms; for methyl H atoms, C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C), while for phenyl H atoms, C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The final difference synthesis indicated some inadequacy in the absorption correction; all regions with $|\Delta\rho| > 1.5$ e Å^{-3} are within 1 Å of an Hg atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the EPSRC and the University of Glasgow for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1143). Services for accessing these data are described at the back of the journal.

References

Cameron, A. F., Duncanson, F. D. & Morris, D. G. (1976). *Acta Cryst.* B**32**, 1987–1989.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

House, D. A., Robinson, W. T. & McKee, V. (1994). *Coord. Chem. Rev.* **135–136**, 533–590.

Morris, D. G. & Muir, K. W. (2004). Unpublished results.

Morris, D. G., Muir, K. W. & Chii, C. O. W. (2003). *Polyhedron*, **22**, 3345–3353.

Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.