

From La—C distances (Table 2) it can be concluded that each La atom is coordinated to three cyclopentadienyl rings in a pentahapto fashion and to one other from a neighbouring molecule though only one carbon atom. Indeed the average La—C bond length for the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> rings is 2.85 (8) Å with a maximum deviation from this mean value of only 0.05 Å.

This value compares favourably with those reported for several pentahapto-cyclopentadienyl lanthanum complexes (Rogers, Atwood, Emad, Sikora & Rausch, 1981; Xing-Fu, Eggers, Kopf, Jahn, Fischer, Apostolidis, Kanellakopoulos, Benetollo, Polo & Bombieri, 1985; Spirlet, Rebizant, Apostolidis & Kanellakopoulos, 1987). The interactions La(1)—C(20) and La(2)—C(1) are only about 0.13 Å greater than the  $\eta^5$  bonds. They can therefore be considered as  $\eta^1$  bonds. The next closer La—C approaches differ by 0.55 and 0.48 Å respectively for La(1) and La(2). The coordination polyhedra about the metal ions can be described as distorted tetrahedra, as shown by the angles subtended at the La atoms (Table 2).

The mean C—C bond lengths and the mean C—C—C bond angles in each C<sub>5</sub> ring agree with known values. The bridging C<sub>5</sub>H<sub>5</sub> group does not differ from the terminal group with respect to either bond distances and angles.

The first structure reported, by Eggers *et al.* (1986), for (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>La differs markedly, not only in the cell dimensions and the space group but also in the

molecular geometry and the packing arrangement. In this earlier structure a much wider range of La—C distances [2.560 (6) to 2.999 (6) Å] is observed for the  $\eta^5$ -cyclopentadienyl ligands. Moreover there are two (instead of one in the present structure analysis) La...C short contacts between adjacent molecules so that the crystal is described as made of zigzag chains of (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>La( $\mu$ - $\eta^5$ : $\eta^2$ -C<sub>5</sub>H<sub>5</sub>) units.

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*Acta Cryst.* (1988). **C44**, 616–618

## Structure of Chloromercury(II) Saccharinate

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(Received 6 July 1987; accepted 18 November 1987)

**Abstract.** C<sub>7</sub>H<sub>4</sub>ClHgNO<sub>3</sub>S, *M*<sub>r</sub> = 418.22, orthorhombic, *Pca*2<sub>1</sub>, *a* = 20.530 (5), *b* = 4.767 (2), *c* =

9.467 (2) Å, *V* = 926.5 (8) Å<sup>3</sup>, *Z* = 4, *D*<sub>m</sub> (pycnometrically) = 2.98, *D*<sub>x</sub> = 3.00 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.7107 Å, μ = 17.11 mm<sup>-1</sup>, *F*(000) = 760, room temperature, final *R* = 0.028 for 818 independent observed reflections. The structure is built up of the discrete molecules. Mercury has digonal characteristic

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coordination being bonded to the saccharinate N atom and Cl atom at 2.021 (8) and 2.263 (3) Å, respectively. The Cl—Hg—N angle is 177.6 (3)°. The Hg atom has three additional Hg...O contacts of 2.793 (8), 2.811 (9) and 2.750 (10) Å with the saccharinate O atoms from neighbouring molecules so that it is effectively five-coordinated.

**Introduction.** This work is the continuation of our research on the crystal structure of different metal saccharinates (Jovanovski & Kamenar, 1982; Kamenar & Jovanovski, 1982). In an attempt to prepare mercury saccharinate by the reaction of HgCl<sub>2</sub> with sodium saccharinate from aqueous solution crystals of chloromercury(II) saccharinate appeared. However, mercury saccharinate was successfully prepared when HgCl<sub>2</sub> was substituted by mercury(II) acetate (Kamenar, Jovanovski & Grdenić, 1982). In the present paper we describe the structure determination of the title compound and its structural characteristics compared with those of other saccharinates.

**Experimental.** The compound was prepared for the first time by warming aqueous solutions of sodium saccharinate and mercury(II) chloride. Colorless thin prismatic crystals were grown from water solution. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range  $12 < \theta < 18^\circ$ . Crystal dimensions  $0.23 \times 0.10 \times 0.05$  mm; intensities of reflections with indices  $h0$  to 26,  $k0$  to 6,  $l0$  to 12;  $2 < 2\theta < 54^\circ$ ,  $\omega$ - $2\theta$  scans;  $\omega$ -scan width  $(0.6 + 0.35 \tan \theta)^\circ$ , graphite-monochromatized Mo K $\alpha$  radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 1283 reflections measured, 1066 unique, 818 with  $I > 3\sigma(I)$  labelled observed and used in structure solution and refinement. Data corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0.434, 0.199), Gaussian integration. Space groups  $Pca2_1$  or  $Pbcm$  from systematic absences  $Ok1$ ,  $l = 2n+1$ ;  $h0l$ ,  $h = 2n+1$ ;  $Pca2_1$  was assumed and confirmed by structure determination. The coordinates of the Hg atom were determined from a detailed analysis of the three-dimensional Patterson function and the coordinates of the remaining non-hydrogen atoms found *via* the heavy-atom method. Refinement on  $F$  by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final rounds of calculations the H atoms were positioned on geometrical grounds (C—H 0.95 Å) and included (as riding atoms) in the structure-factor calculations with an overall  $B(\text{iso})$  of 4.0 Å<sup>2</sup>. The final cycle of refinement included 127 variable parameters,

Table 1. *Positional parameters and equivalent isotropic thermal parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Hg	0.29334 (2)	-0.01542 (8)	0.00	2.399 (7)
Cl	0.3814 (2)	-0.2993 (7)	-0.0146 (4)	3.28 (6)
S	0.1839 (2)	0.4010 (7)	0.1409 (4)	2.12 (5)
O(1)	0.1611 (4)	0.213 (2)	0.2469 (9)	2.5 (2)
O(2)	0.2297 (4)	0.611 (2)	0.184 (1)	2.8 (2)
O(3)	0.1794 (5)	0.113 (2)	-0.223 (1)	3.3 (2)
N	0.2126 (4)	0.226 (2)	0.008 (2)	2.2 (2)
C(1)	0.1170 (6)	0.543 (2)	0.051 (1)	1.7 (2)
C(2)	0.0700 (7)	0.731 (3)	0.100 (2)	3.2 (3)
C(3)	0.0214 (7)	0.804 (3)	0.010 (2)	4.1 (3)
C(4)	0.0181 (7)	0.699 (3)	-0.125 (2)	3.8 (3)
C(5)	0.0656 (9)	0.506 (3)	-0.174 (2)	3.2 (3)
C(6)	0.1155 (7)	0.432 (3)	-0.088 (1)	2.5 (3)
C(7)	0.1693 (7)	0.243 (3)	-0.113 (1)	2.6 (3)
H(2)	0.0720	0.8050	0.1935	
H(3)	-0.0113	0.9307	0.0411	
H(4)	-0.0161	0.7563	-0.1861	
H(5)	0.0625	0.4302	-0.2667	

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as

$$\frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$$

$R = 0.028$ ,  $wR = 0.035$ , goodness-of-fit 1.34,  $w = 1/[\sigma^2(F_o) + 0.04(F_o)^2]$ . Max. shift/e.s.d. = 0.21; density in final difference map  $\pm 1.58 \text{ e } \text{Å}^{-3}$  in the vicinity of Hg. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed in Guelph on a PDP11/73 computer using *SDP-Plus* (B. A. Frenz & Associates Inc., 1982).

**Discussion.** Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.\* A view of the molecule prepared using *ORTEPII* (Johnson, 1976) and atom labelling are shown in Fig. 1. Fig. 2 shows the packing of the molecules in the unit cell. Interatomic distances and angles are given in Table 2.

The structure is built up of individual C<sub>7</sub>H<sub>4</sub>ClHgNO<sub>3</sub>S molecules. The Hg atom has digonal characteristic coordination being bonded to the saccharinate N atom and Cl atom with Hg—Cl and Hg—N bond lengths 2.263 (3) and 2.021 (8) Å, respectively. The Hg—Cl distance is close to the mean value [2.291 (9) Å] of the corresponding distances in the structure of HgCl<sub>2</sub> (Subramanian & Seff, 1980). The Hg—N distance falls close to the range of 2.03–2.06 Å found in mercury(II) saccharinate (Kamenar, Jovanovski & Grdenić, 1982) as well as in other structures with an Hg—N covalent bond (*e.g.* Breiting & Brodersen, 1970; Oppolzer & Weber, 1972; Brauer, 1979).

\* Lists of structure factors, thermal parameters, mean-plane data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44561 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Cl—Hg—N angle [177.6 (3)°] deviates only slightly from linearity.

There are three O atoms from three different saccharinate ligands approaching an Hg atom at Hg...O distances of 2.793 (8), 2.811 (9) and 2.750 (10) Å (see Fig. 2 and Table 2). Since the O...Hg...O angles range from 69.2 to 159.0°, the coordination polyhedron of the effectively five-coordinated Hg atom (Grdenić, 1965) can be described as an irregular trigonal bipyramid.

The saccharinate ligand is planar within experimental error. The maximum deviation from the least-squares plane defined by N, S, C(1), C(2), C(3), C(4), C(5), C(6) and C(7) is 0.046 (9) Å for the N atom, while the distance of Hg and Cl atoms from the same plane is 0.088 (1) and 0.080 (3) Å, respectively.

Bond lengths and angles within the saccharinate ligand are close to the values found in Hg<sup>II</sup> saccharinate (Kamenar, Jovanovski & Grdenić, 1982) as well as in Na and Mg saccharinates (Jovanovski & Kamenar, 1982) and in mixed K<sub>2</sub>Na saccharinate (Malik, Haider, Hossain & Hursthouse, 1984), Mn<sup>II</sup> saccharinate (Kamenar & Jovanovski, 1982) and in the corresponding isomorphous saccharinates of Fe<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Cu<sup>II</sup>, Cd<sup>II</sup> and Cr<sup>II</sup> (Haider, Malik, Ahmed, Hess, Riffel & Hursthouse, 1983; Haider, Malik, Das & Hursthouse, 1984; Cotton, Lewis, Murillo, Schwotzer & Valle, 1984) and Sn<sup>IV</sup> saccharinate (Chuprunov, Gromilov, Stolyarova, Tarkhova & Belov, 1982).

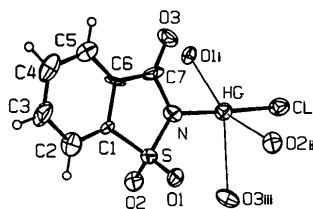


Fig. 1. Perspective view of the molecule showing the atom numbering scheme and vibrational ellipsoids at the 50% level. The labels (i), (ii) and (iii) refer to the equivalent positions given in Table 2.

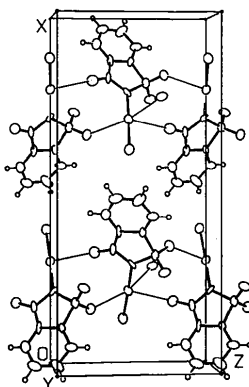


Fig. 2. Molecular packing of the title compound in the unit cell.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Hg—Cl	2.263 (3)	O(3)—C(7)	1.23 (2)
Hg—N	2.021 (8)	N—C(7)	1.45 (2)
Hg...O(1 <sup>i</sup> )	2.793 (8)	C(1)—C(2)	1.39 (2)
Hg...O(2 <sup>ii</sup> )	2.811 (9)	C(1)—C(6)	1.43 (2)
Hg...O(3 <sup>iii</sup> )	2.750 (10)	C(2)—C(3)	1.36 (2)
S—O(1)	1.426 (9)	C(3)—C(4)	1.38 (3)
S—O(2)	1.433 (10)	C(4)—C(5)	1.42 (2)
S—N	1.622 (13)	C(5)—C(6)	1.35 (2)
S—C(1)	1.750 (12)	C(6)—C(7)	1.44 (2)
Cl—Hg—N	177.6 (3)	C(2)—C(1)—C(6)	122. (1)
O(1)—S—O(2)	117.2 (6)	C(1)—C(2)—C(3)	118. (1)
O(1)—S—N	110.1 (5)	C(2)—C(3)—C(4)	122. (1)
O(1)—S—C(1)	109.1 (5)	C(3)—C(4)—C(5)	120. (1)
O(2)—S—N	109.8 (5)	C(4)—C(5)—C(6)	120. (1)
O(2)—S—C(1)	112.4 (5)	C(1)—C(6)—C(5)	118. (1)
N—S—C(1)	96.2 (5)	C(1)—C(6)—C(7)	112. (1)
Hg—N—S	128.2 (7)	C(5)—C(6)—C(7)	130. (1)
Hg—N—C(7)	120.4 (9)	O(3)—C(7)—N	122. (1)
S—N—C(7)	111.2 (7)	O(3)—C(7)—C(6)	126. (1)
S—C(1)—C(2)	129. (1)	N—C(7)—C(6)	112. (1)
S—C(1)—C(6)	108.8 (9)		

Roman numerals refer to the following equivalent positions which should be applied to the second atom: (i)  $\frac{1}{2}-x, y, z-\frac{1}{2}$ ; (ii)  $x, y-1, z$ ; (iii)  $\frac{1}{2}-x, y, \frac{1}{2}+z$ .

This work was supported by NSERC Canada (GF and B. Kaitner), by the Foundation for Scientific Research of S. R. Croatia, Zagreb (B. Kamenar), and the Foundation for Scientific Research of S. R. Macedonia, Skopje (GJ).

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