

1987) where the corresponding Co—O bond distances, of 2.103 (3), 2.109 (2), 2.099 (1) and 2.133 (3) Å, respectively, follow the trend of increasing wavelengths of the absorption bands in the visible spectra (Zangrando *et al.*, 1987).

The observed geometrical distortions of CH<sub>2</sub>CF<sub>3</sub> [F—C—F angles in the range 104.5 (4)–106.0 (6)°] and the opening of the Co—C12—C13 bond angle [121.4 (3)°] may be rationalized, as for cobaloxime derivatives (Bresciani-Pahor, Calligaris, Randaccio, Marzilli, Summers, Toscano, Grossman & Liotta, 1985), in terms of changes of *s* and *p* character in the hybrid orbitals of C12 and C13.

We thank Professor L. G. Marzilli, Emory University, Atlanta, USA, for kindly supplying the crystals and MURST, Rome, for financial support.

*Acta Cryst.* (1992). **C48**, 1116–1117

## Structure of 2,2-Bis(chloromercurio)propionic Acid Dimethyl Sulfoxide Solvate

BY DUBRAVKA MATKOVIĆ-ČALOGVIĆ, ZORA POPOVIĆ AND BRANKA KORPAR-ČOLIG

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, POB 153, 41001 Zagreb, Croatia

(Received 4 November 1991; accepted 14 November 1991)

**Abstract.**  $\mu$ -[(1-Carboxy)-1,1-ethanediy]-bis(chloromercury)-dimethyl sulfoxide (1/1), [Hg<sub>2</sub>(C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>)-Cl<sub>2</sub>].C<sub>2</sub>H<sub>6</sub>OS,  $M_r = 622.3$ , monoclinic,  $P2_1/c$ ,  $a = 10.249$  (9),  $b = 11.184$  (2),  $c = 11.377$  (7) Å,  $\beta = 110.68$  (2)°,  $V = 1220$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.388$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 257.2$  cm<sup>-1</sup>,  $F(000) = 1096$ , room temperature,  $R = 0.037$  for 1394 unique reflections [ $I > 5\sigma(I)$ ]. The molecules of 2,2-bis(chloromercurio)propionic acid are connected to dimethyl sulfoxide molecules by O—H...O hydrogen bonds of 2.66 (2) Å. One Hg atom is approached by two O atoms [Hg...O, 2.92 (2) and 2.90 (1) Å] and the other by a Cl atom [Hg...Cl, 3.133 (6) Å] at distances shorter than the sum of the van der Waals radii.

**Experimental.** Dimercurated propionic acid is obtained as a minor product (up to 20%) of direct mercuration of propionic acid with mercuric propionate. Colourless crystals of its chloromercurio derivative, CH<sub>3</sub>C(HgCl)<sub>2</sub>COOH, crystallize from the dimethyl sulfoxide solution as a 1/1 solvate (Popović, 1988). Data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Intensities were measured using

### References

- BRESCIANI-PAHOR, N., CALLIGARIS, M., RANDACCIO, L., MARZILLI, L. G., SUMMERS, M. F., TOSCANO, P. J., GROSSMAN, J. & LIOTTA, D. (1985). *Organometallics*, **4**, 630–636.  
 COSTA, G., MESTRONI, G. & DE SAVORGNANI, E. (1969). *Inorg. Chim. Acta*, **3**, 323–328.  
 FRENZ, B. A. (1981). *Enraf-Nonius Structure Determination Package*. Version 18. Enraf-Nonius, Delft, The Netherlands.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 MARZILLI, L. G., BRESCIANI-PAHOR, N., RANDACCIO, L., ZANGRANDO, E., FINKE, R. G. & MYERS, S. A. (1985). *Inorg. Chim. Acta*, **107**, 139–145.  
 PARKER, W. O. JR., BRESCIANI-PAHOR, N., ZANGRANDO, E., RANDACCIO, L. & MARZILLI, L. G. (1985). *Inorg. Chem.* **24**, 3908–3913.  
 RANDACCIO, L., BRESCIANI-PAHOR, N., ZANGRANDO, E. & MARZILLI, L. G. (1989). *Chem. Soc. Rev.* **18**, 225–250.  
 ZANGRANDO, E., PARKER, W. O. JR., BRESCIANI-PAHOR, N., THOMAS, L. B., MARZILLI, L. G. & RANDACCIO, L. (1987). *Gazz. Chim. Ital.* **117**, 307–316.

the  $\theta$ - $2\theta$  scan mode, scan width of 1.8° and scan speed of 0.06° s<sup>-1</sup>. Unit-cell parameters were determined by the least-squares procedure from 16 reflections, 11.7 <  $\theta$  < 12.7°. Three standard reflections (32 $\bar{3}$ , 263, 540) measured every 2 h showed a continuous drop in intensity amounting to 30% at the end of data collection. The crystal darkened under the influence of X-rays but after exposure it slowly (about one month) regained transparency. 2080 reflections were measured within the range  $2 \leq \theta \leq 30^\circ$  ( $0 \leq h \leq 13$ ,  $0 \leq k \leq 15$ ,  $-15 \leq l \leq 14$ ), 1908 unique ( $R_{\text{int}} = 0.036$ ), 1394 with  $I > 5\sigma(I)$ . Intensities were corrected for decay, Lorentz, polarization and absorption effects (maximum, minimum transmission coefficients 0.551, 0.242) (Harkema, 1979). Crystal dimensions (mm from centroid): (100,  $\bar{1}00$ ) 0.025, (010,  $0\bar{1}0$ ) 0.061, (001) 0.140, ( $00\bar{1}$ ) 0.152, ( $\bar{1}51$ ,  $\bar{1}5\bar{1}$ ) 0.070. Positions of the two Hg atoms were located by the Patterson method, other non-H-atom positions from a difference Fourier map. The structure was refined by the full-matrix least-squares procedure based on  $F$  with anisotropic temperature factors for all non-H atoms except the methyl carbon C5 of the DMSO solvate molecule. All atoms of the solvate molecule except O3, which is involved in

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
Hg1	0.0769 (1)	0.1297 (1)	0.4233 (1)	0.0408 (3)
Hg2	0.1226 (1)	0.4044 (1)	0.3488 (1)	0.0468 (4)
Cl1	0.1348 (7)	-0.0685 (4)	0.4006 (5)	0.056 (2)
Cl2	0.2402 (7)	0.5054 (6)	0.2394 (6)	0.068 (3)
S	0.4819 (11)	0.1876 (9)	0.4531 (8)	0.109 (5)
O1	0.225 (2)	0.325 (1)	0.632 (1)	0.062 (8)
O2	0.025 (2)	0.353 (1)	0.656 (1)	0.057 (7)
O3	0.332 (2)	0.197 (2)	0.381 (1)	0.071 (7)
C1	0.090 (3)	0.331 (2)	0.589 (2)	0.047 (9)
C2	0.021 (2)	0.308 (2)	0.450 (1)	0.033 (7)
C3	-0.131 (2)	0.327 (2)	0.400 (2)	0.039 (8)
C4	0.493 (4)	0.144 (4)	0.612 (2)	0.13 (2)
C5	0.543 (5)	0.332 (4)	0.496 (5)	0.16 (2)*

\* Atom C5 was refined isotropically.

hydrogen bonding, have high temperature factors. Position of the carboxyl H atom was located in the difference Fourier map (0.98 Å from O1), methyl H atoms from the mercurated propionic acid were included in calculated positions and refined with constrained bond lengths ( $U_{iso} = 0.05 \text{\AA}^2$ ). Refinement with unit weights (122 parameters) converged at  $R = 0.037$ ,  $wR = 0.041$ ,  $S = 4.70$ ,  $(\Delta/\sigma)_{max} = 0.01$ ,  $\Delta\rho = -1.33$  to  $3.34 \text{ e \AA}^{-3}$ . Atomic scattering factors and anomalous-dispersion coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No extinction correction was made. *SHELX76* (Sheldrick, 1976) and the *CRYSRULER* crystallographic package (Rizzoli, Sangermano, Calestani & Andreotti, 1987) were used. The atomic coordinates are given in Table 1 and interatomic distances and angles in Table 2. Packing of the  $\text{CH}_3\text{C}(\text{HgCl})_2\text{COOH}$  and DMSO molecules in the unit cell is shown in Fig. 1.\*

**Related literature.** The coordination of Hg is digonal with C—Hg—Cl angles of 177.6 (4) and 178.0 (6)°. The Hg—C distances are 2.10 (2) and 2.13 (2) Å, the Hg—Cl distances are 2.310 (8) and 2.333 (5) Å. These values are normal (Grdenić, 1981) and comparable to those in similar compounds, i.e.  $\text{C}_2\text{H}_5\text{C}(\text{HgCl})_2\text{COOH} \cdot \text{DMSO}$  (Korpar-Čolig, Popović, Sikirica & Grdenić, 1991),  $(\text{ClHg})_3\text{CCOOH} \cdot \text{DMSO}$  (Grdenić, Korpar-Čolig & Sikirica, 1984),  $\text{C}_2\text{H}_5\text{C}(\text{HgCl})_2\text{CHO}$  (Korpar-Čolig, Popović & Sikirica, 1984).

We thank Professor D. Grdenić for his interest in this work and helpful discussions. The financial sup-

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54858 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Hg1—C11	2.333 (5)	Cl1—Hg1—C2	177.6 (4)
Hg1—C2	2.13 (2)	Cl2—Hg2—C2	178.0 (6)
Hg2—Cl2	2.310 (8)	C4—S—C5	95 (2)
Hg2—C2	2.10 (2)	O3—S—C5	107 (2)
S—O3	1.47 (2)	O3—S—C4	105 (1)
S—C4	1.84 (3)	O1—C1—C2	115 (2)
S—C5	1.74 (5)	O1—C1—O2	122 (2)
O1—C1	1.30 (3)	O2—C1—C2	123 (3)
O2—C1	1.20 (4)	Hg1—C2—C1	105 (1)
C1—C2	1.51 (2)	Hg1—C2—C3	112 (1)
C2—C3	1.47 (3)	Hg1—C2—Hg2	101 (1)
O1—H1	0.98	Hg2—C2—C1	110 (1)
Hg1...Hg2	3.265 (2)	Hg2—C2—C3	112 (1)
Hg1...O3	2.92 (2)	C1—C2—C3	115 (2)
Hg1...O2 <sup>ii</sup>	2.90 (1)		
Hg2...Cl1 <sup>ii</sup>	3.133 (6)		
O1...O3 <sup>iii</sup>	2.66 (2)	O1—H1...O3 <sup>iii</sup>	176
H1...O3 <sup>iii</sup>	1.69		

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

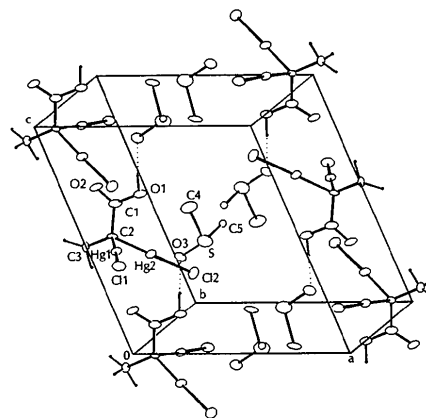


Fig. 1. Packing of  $\text{CH}_3\text{C}(\text{HgCl})_2\text{COOH}$  and  $(\text{CH}_3)_2\text{SO}$  molecules in the unit cell. Hydrogen bonds are shown by dotted lines.

port from the Foundation for Scientific Research of Croatia is gratefully acknowledged.

#### References

- GRDENIĆ, D. (1981). *Connections in the Crystal Structures of Mercury Compounds*. In *Structural Studies of Molecules of Biological Interest*, edited by G. DODSON, J. P. GLUSKER & D. SAYRE, pp. 207–221. Oxford: Clarendon Press.
- GRDENIĆ, D., KORPAR-ČOLIG, B. & SIKIRICA, M. (1984). *J. Organomet. Chem.* **276**, 1–8.
- HARKEMA, S. (1979). *ACXR*. Program for absorption correction. Department of Chemical Technology, Drienerlo, The Netherlands.
- KORPAR-ČOLIG, B., POPOVIĆ, Z. & SIKIRICA, M. (1984). *Croat. Chem. Acta*, **57**, 689–694.
- KORPAR-ČOLIG, B., POPOVIĆ, Z., SIKIRICA, M. & GRDENIĆ, D. (1991). *J. Organomet. Chem.* **405**, 59–65.
- POPOVIĆ, Z. (1988). PhD Thesis. Univ. of Zagreb, Croatia.
- RIZZOLI, C., SANGERMANO, V., CALESTANI, G. & ANDREOTTI, G. D. (1987). *J. Appl. Cryst.* **20**, 436–439.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.