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New Synthesis and Structure of Diferrocenylmercury Monohydrate

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Abstract. $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\}_2Hg].H_2O$, $M_r = 588{\cdot}67$, monoclinic, $P2_1/c$, $a = 7{\cdot}705\,(5)$, $b = 10{\cdot}200\,(2)$, $c = 10{\cdot}618\,(2)$ Å, $\beta = 103{\cdot}11\,(3)°$, $V = 812{\cdot}7\,(9)$ Å^3, $Z = 2$, $D_x = 2{\cdot}405$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 111{\cdot}9$ cm^{-1}, $F(000) = 560$, $T = 295\,(1)$ K, $R = 0{\cdot}0388$, $wR = 0{\cdot}0507$, 1050 unique reflections, 673 reflections with $I > 3\sigma(I)$. Diferrocenylmercury is made by reaction of chloromercuryferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4HgCl)$, with cysteine. The coplanar cyclopentadienyl rings of the two antiparallel ferrocenyl moieties are linked linearly through an Hg atom; the C—Hg distance is 2·06 (2) Å; the mean Fe—C and C—C distances are 2·04 (2) and 1·41 (3) Å, respectively; the cyclopentadienyl rings are eclipsed.

Introduction. Diferrocenyl compounds $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_2X$, abbreviated Fc_2X, containing various bridging atoms or groups X are known (*Dictionary of Organometallic Compounds*, 1984), but only the compound in which X is CH_2CH_2 has been analyzed crystallographically (Doyle, Baenziger & Davis, 1974). Diferrocenylmercury has been prepared before by reaction of chloromercuryferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4HgCl)$ or FcHgCl, with several agents (Nesmeyanov, Perevalova, Golovnya & Nesmeyanova, 1954; Rausch, Vogel & Rosenberg, 1957; Rausch, 1963; Roling, Roling & Rausch, 1971). This report of the reaction with cysteine contributes to the study of reactions between mercurials and biological thiols (Taylor & Carty, 1977; Rabenstein, 1978). This crystallographic analysis complements the previous synthetic and spectroscopic studies of diferrocenylmercury, and it may contribute to the study of other diferrocenyl and diferricenium compounds.

Experimental. Chemicals were obtained from Aldrich Chemical Co. Chloromercuryferrocene (36·4 mg, 86 μmol) was dissolved, with stirring, in a mixture of 100 mL of DMF and 900 mL of 85 m*M* phosphate buffer at pH 7·0 and the solution was filtered. L-Cysteine, CysSH (5·2 mg, 43 μmol), was dissolved, with stirring, in the clear filtrate. The yellow precipitate, formed overnight at 277 K, was filtered, dried in air, and dissolved in 2 mL of benzene. Slow evaporation of benzene over ten days gave needle-like yellow crystals.

A crystal, 0·04 × 0·03 × 0·25 mm, was mounted on a glass fiber on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were measured from 25 reflections ($14 \le 2\theta \le 30°$); because of macroscopic twinning, the orientation of the *c* axis was confirmed with photographs. An empirical correction for absorption was based on ψ scans; after the structure was solved, a numerical correction was applied (Walker & Stuart, 1983); transmission coefficients were 0·765 to 1·236. 2192 reflections in the $+h$ hemisphere were collected by the ω–2θ scan method; $0 \le 2\theta \le 45°$; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}5384$ Å^{-1}. The intensities of the standard reflections $\bar{1}0\bar{4}$, $\bar{1}3\bar{5}$, $2\bar{2}\bar{6}$ varied by 0·30%. $R_{\text{int}} = 0{\cdot}0440$ for the 673 unique observed reflections with $I > 3\sigma(I)$.

The Fe, C and Hg atoms were located directly by the program *SHELXS*86 (Sheldrick, 1986) and refined anisotropically on the basis of F^2 magnitudes. The O atom was located from a difference Fourier synthesis and refined isotropically. The H atoms in calculated positions [C—H = 0·95 Å, $B_{\text{H}} = 1{\cdot}3 \times B(\text{iso})_{\text{C}}$] were used only for the calculation of F. 110 parameters were refined. The final R and wR values were 0·0388 and 0·0507; $w = 1/\sigma^2(|F_o|)$. The largest shift in the final cycle was 0·01 e.s.d.; the largest peak was 1·63 e Å^{-3}; $S = 1{\cdot}22$. Scattering factors and anomalous-scattering

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for diferrocenylmercury*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Hg	0·000	0·000	0·000	2·66 (2)
Fe	0·2496 (3)	0·0286 (2)	−0·2548 (2)	2·16 (4)
O	0·657 (5)	−0·006 (5)	0·002 (4)	4·6 (8)
C(11)	0·060 (2)	0·090 (1)	−0·159 (2)	3·0 (4)
C(12)	−0·021 (2)	0·056 (2)	−0·290 (2)	3·2 (4)
C(13)	0·055 (2)	0·140 (2)	−0·370 (2)	2·6 (4)
C(14)	0·181 (2)	0·219 (2)	−0·293 (2)	3·1 (4)
C(15)	0·183 (2)	0·188 (2)	−0·162 (2)	2·7 (4)
C(21)	0·494 (2)	0·005 (2)	−0·295 (2)	4·0 (4)
C(22)	0·367 (2)	−0·083 (2)	−0·373 (1)	3·5 (4)
C(23)	0·295 (2)	−0·164 (2)	−0·293 (2)	3·6 (4)
C(24)	0·380 (3)	−0·134 (2)	−0·163 (2)	4·5 (4)
C(25)	0·499 (2)	−0·028 (2)	−0·170 (2)	4·2 (5)

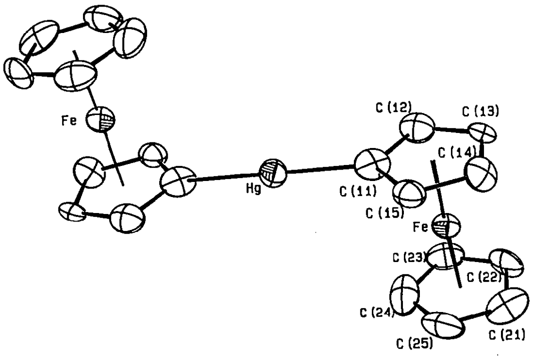

Fig. 1. Structure of diferrocenylmercury. Thermal ellipsoids for the C atoms enclose 50% of the probability density.

corrections were taken from *International Tables for X-ray Crystallography* (1974). The refinement was performed with the Enraf–Nonius (1979) *SDP* program on a DEC MicroVAX II computer.

Discussion. The atomic coordinates are listed in Table 1. The structure is shown in Fig. 1.* The molecule of diferrocenylmercury adopts the antiparallel (or *trans*) conformation, with the required center of symmetry at the Hg atom. The C—Hg distance, 2·06 (2) Å, is virtually identical to that in diphenylmercury (Grdenić, Kamenar & Nagl, 1977). The two cyclopentadienyl rings are planar, eclipsed, 3·31 Å apart, and virtually parallel (within 2·0°) to each other. The mean Fe—C and C—C distances, 2·04 (2) and 1·41 (3) Å, are equal to those in ferrocene (Seiler & Dunitz, 1979; Takusagawa & Koetzle, 1979), diferrocenyl (Macdonald & Trotter, 1964; Kaluski, Struchkov & Avoyan, 1964), and 1,2-bis(ferrocenyl)ethane (Doyle, Baenziger & Davis, 1974). This similarity of geometric structures explains the similarity of the electronic structures, manifest in the Mössbauer spectra (Wertheim & Herber, 1963).

Anionic ligands, such as cyanide and iodide, are commonly used for the preparation of R_2Hg from RHgX (Roling, Roling & Rausch, 1971; Coates, Green & Wade, 1967). Although thiolate is more nucleophilic than these other two anions, it does not seem to have been used for such preparations. Since the insoluble cystine (CysSSCys) and elemental mercury are not obtained, cysteine does not serve merely as a reducing agent. The reaction reported herein is a disproportionation, also known as symmetrization.

$$2\,\text{FcHgCl} + 2\,\text{CysS}^- \rightarrow \text{Fc}_2\text{Hg} + \text{Hg(CysS)}_2 + 2\,\text{Cl}^-.$$

The living cell contains many thiols (Jocelyn, 1972). The most abundant such compound is the cysteine-containing tripeptide glutathione, which serves as a versatile reducing agent. This study with cysteine shows that thiols (designed R'SH) and compounds RHgX *in vivo* can yield compounds R_2Hg as well as the thiolate adducts, RHgSR'. The disproportionation reactions may play a role in the toxicity of organomercurials.

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* Lists of structure factors, calculated H-atom coordinates, bond angles, anisotropic temperature factors, least-squares planes, amplitudes of thermal vibrations, torsional angles, and bond distances and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51053 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetramethylammonium *catena*-Di-μ-chloro-argentate(I)

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Abstract. $[N(CH_3)_4][AgCl_2]$, $M_r = 252{\cdot}9$, orthorhombic, *Immm*, $a = 8{\cdot}825\,(3)$, $b = 14{\cdot}526\,(4)$, $c = 6{\cdot}570\,(2)$ Å, $V = 842{\cdot}2\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}99$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 2{\cdot}93$ mm^{-1}, $F(000) = 496$, $T = 170$ K, $R = 0{\cdot}032$ for 549 unique observed $[I \geq 3\sigma(I)]$ reflections and 43 parameters. The $[AgCl_2]^-$ anion is a one-dimensional infinite polymeric chain composed of edge-sharing $AgCl_4$ tetrahedra, in which the Ag—Cl distances are 2·599 (1) and 2·618 (1) Å and the Ag···Ag contacts are 3·137 (1) and 3·433 (1) Å.

Introduction. In halocuprates(I) crystallizing with symmetrically substituted tetraalkylammonium and related unipositive cations, the coordination number of copper(I) in the anion has been found to increase regularly with decreasing size of the cation (Andersson & Jagner, 1986, 1987). Previous crystallographic studies on haloargentates(I) containing tetraalkylammonium cations have been mainly concerned with iodoargentates(I), which have been shown to contain infinite polymeric species based on silver(I) iodide tetrahedra, *viz* $[N(C_4H_9)_4][Ag_3I_4]$(Gilmore, Tucker & Woodward, 1971), $[N(CH_3)_4]_2[Ag_{13}I_{15}]$ (Geller & Lind, 1970), $[N(CH_3)_4][Ag_2I_3]$ (Meyer, 1963; Kildea, Skelton & White, 1986) and $[N(CH_3)_4][AgI_2]$ (Peters, von Schnering, Ott & Seidenspinner, 1984). A double chain composed of edge-sharing silver(I) bromide tetrahedra, analogous to the $[Ag_2I_3]^-$ chain in $[N(CH_3)_4][Ag_2I_3]$ (Meyer, 1963; Kildea, Skelton & White, 1986), occurs in $[N(CH_3)_4][Ag_2Br_3]$ (Jagner, Olson & Stomberg, 1986). There would appear to be no previous crystallographic investigation of chloroargentates(I) crystallizing with tetraalkylammonium cations; far-IR spectroscopic studies on the tetraethylammonium and tetramethylammonium compounds, however, indicate the presence of infinite chain anions of stoichiometry $[Ag_2Cl_3]^-$ and $[AgCl_2]^-$, respectively (Bottger & Geddes, 1967). As part of an investigation of the dependency of the coordination of silver(I) in chloroargentates(I) on cation size, we have determined the structure of $[N(CH_3)_4][AgCl_2]$.

Experimental. The compound was prepared according to the method of Kuhn & Schretzmann (1955, 1957), using 0·10 g (0·7 mmol) AgCl [ICN Biomedicals, K & K], 0·076 g (0·7 mmol) tetramethylammonium chloride [Fluka] and 15 ml dimethylformamide; colourless elongated prisms, m.p. 566–568 K, being obtained after a few days. Preliminary unit-cell dimensions and space group from rotation and Weissenberg films, suggesting isostructurality with $[N(CH_3)_4][AgI_2]$ (Peters *et al.*, 1984); intensity data collected on a Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions (distance to faces from vertex chosen as origin for absorption correction): 0·000 $(001,0\bar{1}0,1\bar{1}0)$, 0·389 $(00\bar{1})$, 0·261 $(\bar{1}10)$, 0·164 (010), 0·109 (120), 0·129 $(\bar{1}\bar{2}0)$ mm. 15 reflections used to determine unit-cell parameters; $3{\cdot}5 \leq 2\theta \leq 55°$; $0 \leq h \leq 11$; $0 \leq k \leq 18$; $0 \leq l \leq 8$; ω–2θ scan mode, variable 2θ scan rate: 2·5–20·0 °min^{-1}; 96-step profiles; Lehmann & Larsen (1974) profile-analysis method used to calculate the intensities (Lindqvist & Ljungström, 1979); variation in intensity of 2 standard reflections, measured every 48 reflections, < 2%, 583 unique non-systematically absent reflections measured, of which 549 with $I \geq 3\sigma(I)$; absorption correction with *ABSORB* (DeTitta, 1985), transmission factors 0·481–0·652. The coordinates of $[N(CH_3)_4][AgI_2]$ (Peters *et al.*, 1984) were checked against the Patterson function and used as starting point for the refinement. H atoms located from difference map; non-H atoms refined with anisotropic and H atoms with isotropic thermal parameters. Full-matrix least-squares refinement based on F gave final $R = 0{\cdot}032$ (549 reflections; 43 parameters), $wR = 0{\cdot}043$, $w = [\sigma^2(F_o) + 0{\cdot}0002F_o^2]^{-1}$;

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