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# A monoclinic polymorph of 1-(chloridomercurio)ferrocene

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**Key indicators**

Single-crystal X-ray study
$T$ = 100 K
Mean $\sigma$(C–C) = 0.018 Å
$R$ factor = 0.047
$wR$ factor = 0.108
Data-to-parameter ratio = 18.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.



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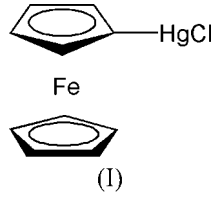
A monoclinic modification of chloridomercurioferrocene, [FeHgCl($C_5H_4$)($C_5H_5$)], was found on its crystallization from acetonitrile. A triclinic form of the title compound [Sunkel & Kiessling (2001). *J. Organomet. Chem.* **637**, 796–799] was crystallized from chloroform. Both forms have two molecules per asymmetric unit. In the monoclinic form, both molecules have an eclipsed conformation, while in the triclinic form one of them has an eclipsed and the other a staggered conformation. In the monoclinic crystals, molecules form infinite ribbons due to intermolecular secondary coordination between Hg and Cl atoms, while in the triclinic form molecules are arranged in tetramers.

## Comment

In general, polymorphism of organometallic compounds is as common as it is for all molecular crystals. For instance, polymorphism was described for ferrocene (Dunitz *et al.*, 1956; Takusagawa & Koetzle, 1979; Brock & Fu, 1997) and for several monosubstituted ferrocene derivatives such as (4-nitrophenyl)ferrocene (Roberts *et al.*, 1988; Gallagher *et al.*, 1997; Chang, 2006), 1,4-diferrocenyl-1,3-butadiyne (Maharaj *et al.*, 2003) and 1-phenyl-1-ferrocenylethanol (Ferguson *et al.*, 1993; Routaboul *et al.*, 2001). Halidomercurioferrocenes are frequent starting materials for the preparation of haloferrocenes, which in turn, are precursors for the synthesis of monosubstituted ferrocenes.




(I)

In the course of preparation of chloridomercurioferrocene, (I), upon its crystallization from acetonitrile a new monoclinic polymorph (space group $P2_1/c$, $Z$ = 8) was obtained (Fig. 1, Table 1). Previously, a triclinic form of (I), (space group $P\bar{1}$, $Z$ = 4), which was recrystallized from chloroform, was described by Sunkel & Kiessling (2001). Both forms contain two symmetry-independent molecules **A** and **B**. Even though the bond lengths and bond angles in both polymorphs are very similar, the molecular conformations in the two polymorphs are different: both molecules in the monoclinic form have almost eclipsed conformations, while in the triclinic form one molecule has an eclipsed and the other a staggered conformation. Pseudotorsion angles C—*Cg*—*Cg*—C(HgCl), where *Cg* is the centroid of the Cp ring, are equal to 11.1 (12) and

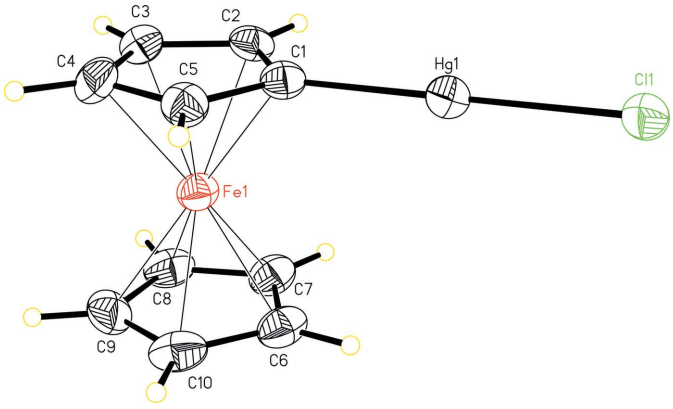



**Figure 1**
The molecular structure of (I), molecule **B** (100 K), showing 50% probability displacement ellipsoids.

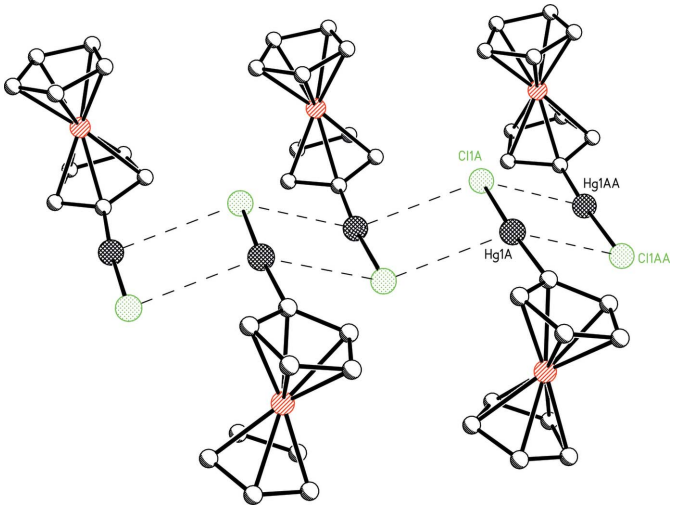



**Figure 2**
Ribbons of molecules **A** in the monoclinic modification of (I). H atoms have been omitted. Symmetry codes: (AA) $-x,y+\frac{1}{2},\frac{1}{2}-z$.

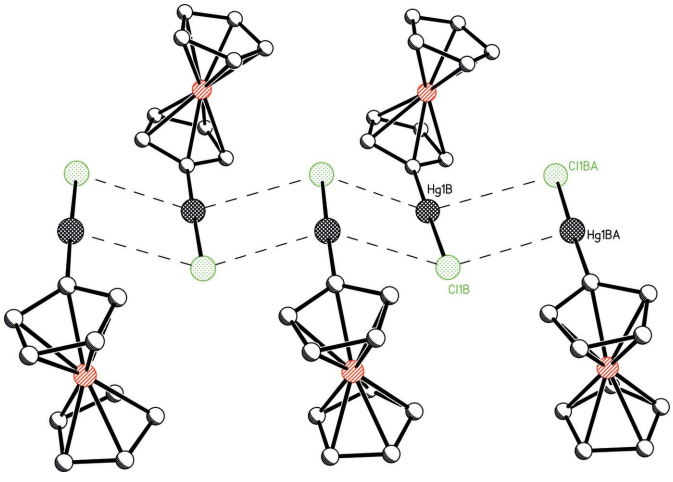



**Figure 3**
Ribbons of molecules **B** in the monoclinic modification of (I). H atoms have been omitted. Symmetry code: (BA) $1-x,y+\frac{1}{2},\frac{3}{2}-z$.

−8.8 (12)° in the monoclinic and to 40.9 and −1.7° in the triclinic form.

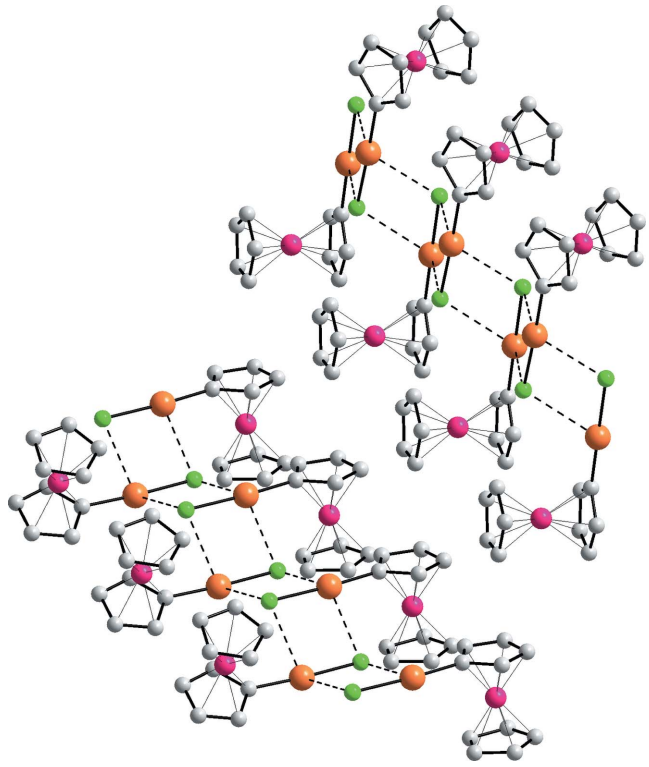


**Figure 4**
Relative orientation of ribbons in the monoclinic modification of (I). H atoms have been omitted.

In the monoclinic crystal structure, molecules **A** form ribbons (Fig. 2) where every Hg atom is coordinated by two Cl atoms of neighboring molecules with almost equal Hg···Cl distances [Hg1AA···Cl1A = 3.212 (3) Å and Hg1A···Cl1AA = 3.277 (3) Å; Hg1A—Cl1A = 2.343 (3) Å]. Molecules **B** form similar ribbons (Fig. 3) with slightly different distances between Hg and Cl atoms [Hg1BA···Cl1B = 3.158 (3) Å and Hg1B···Cl1BA = 3.379 (3) Å; Hg1B—Cl1B = 2.340 (3) Å]. Ribbons of molecules **A** and **B** extend along the *b* axis and their planes are almost perpendicular to each other [86.1 (9)°] (Fig. 4). In the triclinic modification, molecules **A** and **B** collectively form tetramers (Fig. 5) where the coordination of the Hg atom is different from that found in the monoclinic form. Every Cl atom forms one coordination bond with the Hg atom of a neighboring molecule. Thus, the Hg atom in the structure of the monoclinic form has a 'seesaw' coordination and in the triclinic form a T-coordination, both of which are quite common for the Hg atom. These data suggest that compound (I) is a good candidate for the formation of a variety of supramolecular aggregates.

## Experimental

Compound (I) was synthesized using the procedure described by Fish & Rosenblum (1965). Fast recrystallization of (I) from acetonitrile produced a pale-yellow flaky material. It was possible to crystallize a sample suitable for X-ray analysis from acetonitrile. The triclinic modification of (I) was crystallized from DMSO. To test that the bulk synthesized material contains only one polymorph, a powder sample

was analyzed *via* powder X-ray diffractometry. The patten was very similar to the calculated pattern for the monoclinic modification.

*Crystal data*

| | |
|---|---|
| $[FeHgCl(C_5H_4)(C_5H_5)]$ | $V$ = 2003.2 (16) Å$^3$ |
| $M_r$ = 421.06 | $Z$ = 8 |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a$ = 24.618 (11) Å | $\mu$ = 16.97 mm$^{-1}$ |
| $b$ = 5.997 (3) Å | $T$ = 100 (2) K |
| $c$ = 14.136 (7) Å | 0.60 × 0.50 × 0.03 mm |
| $\beta$ = 106.288 (6)° | |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII CCD area-detector diffractometer | 21721 measured reflections<br>4251 independent reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003) | 3739 reflections with $I > 2\sigma(I)$<br>$R_{int}$ = 0.056 |
| $T_{min}$ = 0.035, $T_{max}$ = 0.630 | |

*Refinement*

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.047 | 235 parameters |
| $wR(F^2)$ = 0.108 | H-atom parameters constrained |
| $S$ = 1.00 | $\Delta\rho_{max}$ = 1.86 e Å$^{-3}$ |
| 4251 reflections | $\Delta\rho_{min}$ = −1.16 e Å$^{-3}$ |

All H atoms were positioned geometrically (C—H = 1.00 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. There is highest residual density peak is 0.81 Å from Hg1A and the deepest hole is 1.28 Å from C1B; these are due to considerable absorption effects which could not be completely corrected.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL-NT* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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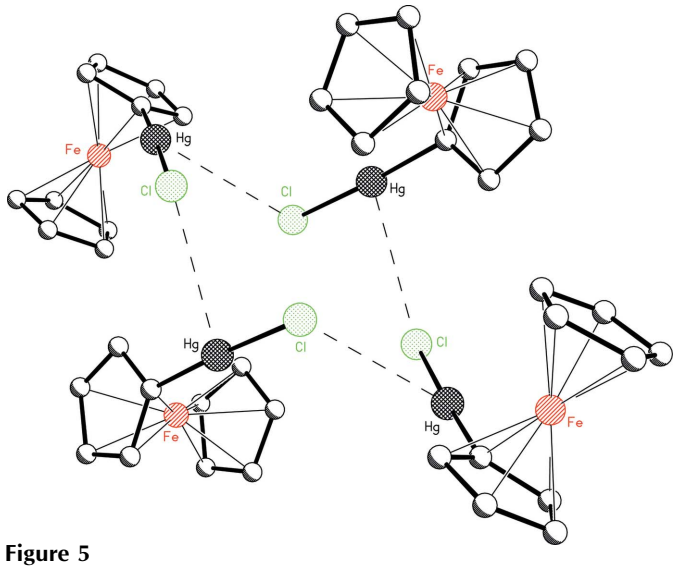


**Figure 5**
Tetramers in the triclinic modification of (I). H atoms have been omitted.

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