Crystal Structure of Tetraphenylarsonium *cis*-Tetracarbonyl(chloromercurio)(dichloromercurio)ferrate

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The crystal structure of the title compound has been determined by *X*-ray diffraction (heavy-atom) methods and refined by least squares to *R* 0.059 for 2 917 observed reflections. Crystals are triclinic $P\bar{1}$, a = 11.848(3), b = 13.524(4), c = 11.624(3) Å, α = 123.87(2), β = 94.01(2), γ = 90.91(2)°, Z = 2. Within the anion, the two mercury atoms are bonded *cis* in the co-ordination sphere of the six-co-ordinate iron atom [Fe–Hg 2.560(3) and 2.516(4) Å, Hg–Fe–Hg 80.3(1)°]. The anion lies close to a centre of symmetry and is linked to its inversion image by one of the chlorine atoms. The reduction in the Hg–Fe–Hg angle from the regular octahedral value is shown to be a consequence of the more extended Fe–Hg relative to the Fe–CO bonds, rather than to Hg · · · Hg interactions.

WHEN *cis*-[$Fe(CO)_4(HgCl)_2$] is treated with amines or halide ions addition reactions occur at the mercury atoms rather than substitution of carbonyl groups.[1] For example, pyridine readily adds to both of the chloromercurio-groups forming *cis*-[$Fe(CO)_4\{HgCl(py)\}_2$], the crystal structure of which has been determined.[2] Similarly, the reaction between [$AsPh_4$]Cl and *cis*-[$Fe(CO)_4(HgCl)_2$] in boiling methanol yields pale yellow prisms of [$AsPh_4$][$Fe(CO)_4(HgCl)(HgCl_2)$]. It was therefore considered of interest to determine the structure of this complex.

EXPERIMENTAL

The crystal used was a prism 0.08 × 0.10 × 0.20 mm. Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 30° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle

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[1] A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 1013.

[2] R. W. Baker and P. Pauling, *Chem. Comm.*, 1970, 573.

diffractometer. A unique data set in the range $2\theta < 100°$ was gathered by a conventional 2θ—θ scan, yielding 3 075 reflections of which 2 917 with $I > 2\sigma(I)$ were considered observed, and used in the structure determination and refinement.

Crystal Data.—$C_{28}H_{20}AsCl_3FeHg_2O_4$, M = 1 023, Triclinic, a = 11.848(3), b = 13.524(4), c = 11.624(3) Å, α = 123.87(2), β = 94.01(2), γ = 90.91(2)°, U = 1 540.1(6) Å^3, D_m = 2.18(2), Z = 2, D_c = 2.20 g cm^{-3}, $F(000)$ = 946, nickel-filtered Cu-K_α radiation, λ = 1.541 8 Å; μ(Cu-K_α) = 267 cm^{-1}. Space group $P\bar{1}$ (C_i^1, no. 2). Neutral atom scattering factors were used, those for Hg, As, Fe, and Cl being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[3,4]

TABLE 1

Atom fractional co-ordinates, with least-squares estimated standard deviations in parentheses (for Hg × 10^5; As, Fe, and Cl × 10^4; O and C × 10^3)

	x	*y*	*z*
(*a*) The cation			
As	8 856(2)	4 951(2)	2 399(2)
Ph ring (1)			
C(1)	982(1)	637(1)	326(2)
C(2)	961(2)	723(2)	301(2)
C(3)	1 031(2)	829(2)	377(3)
C(4)	1 115(2)	853(2)	482(3)
C(5)	1 139(2)	759(2)	503(3)
C(6)	1 074(2)	649(2)	423(2)
Ph ring (2)			
C(1)	975(1)	361(2)	167(2)
C(2)	947(2)	267(2)	180(2)
C(3)	1 008(2)	169(2)	120(2)
C(4)	1 099(2)	159(2)	041(2)
C(5)	1 126(2)	251(2)	026(2)
C(6)	1 063(2)	355(2)	089(2)
Ph ring (3)			
C(1)	792(1)	505(2)	374(2)
C(2)	818(2)	597(2)	513(2)
C(3)	748(2)	604(2)	609(2)
C(4)	656(2)	513(2)	563(2)
C(5)	635(2)	425(2)	426(3)
C(6)	705(2)	417(2)	328(2)
Ph ring (4)			
C(1)	792(2)	484(2)	092(2)
C(2)	703(2)	563(2)	132(2)
C(3)	635(2)	554(2)	023(3)
C(4)	654(2)	471(2)	−120(3)
C(5)	741(2)	395(2)	−149(2)
C(6)	813(2)	399(2)	−049(2)
(*b*) The anion			
Fe	3 593(2)	0 168(3)	2 844(3)
C(1)	222(2)	062(2)	319(2)
O(1)	129(2)	087(2)	338(2)
C(2)	372(2)	−060(2)	372(2)
O(2)	379(1)	−111(1)	422(1)
C(3)	317(2)	−123(2)	122(2)
O(3)	287(1)	−208(1)	013(1)
C(4)	424(2)	162(2)	427(2)
O(4)	464(2)	251(1)	513(2)
Hg(1)	56 093(7)	−04 661(8)	22 509(8)
Cl(1)	7 095(4)	−1 350(4)	2 896(5)
Hg(2)	39 381(7)	09 702(8)	13 899(9)
Cl(2)	4 376(4)	2 420(4)	0 829(4)
Cl(3)	6 843(4)	0 738(4)	1 518(4)

The structure was solved by the heavy-atom method and refined by block-diagonal (9 × 9) least squares; in the final stages of refinement, a full-matrix procedure was approximated by refining the parameters of the anion and the phenyl rings as single blocks. All the atoms were refined anisotropically according to the form $\exp[-2\pi^2(U_{11}h^2a^{*2} \ldots + 2U_{23}klb^*c^*)]$. Hydrogen atoms were not located in difference maps and were not included in the refinement. At convergence all parameter shifts were $< 2\sigma$, R being 0.059 and R' [$= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$] being 0.071 with the parameter n = 2 being found appropriate in a weighting scheme of the form $w = [\sigma^2(F_o) + 10^{-4}n(F_o)^2]^{-1}$.

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) Cation geometry

(*i*) The phenyl rings

	(1)	(2)	(3)	(4)
As–C(1)	1.90(2)	1.90(2)	1.93(2)	1.91(2)
As–C(1)–C(2)	120.8(13)	121.0(14)	117.6(15)	116.6(15)
As–C(1)–C(6)	115.8(18)	117.6(19)	118.8(13)	119.4(17)

Mean C–C 1.40
Mean C–C–C 120

(*ii*) Arsenic angular geometry

C(11)–As–C(21)	109.7(7)	C(21)–As–C(31)	111.0(10)
C(11)–As–C(31)	109.3(7)	C(21)–As–C(41)	109.6(8)
C(11)–As–C(41)	108.1(10)	C(31)–As–C(41)	109.1(9)

(*b*) Anion geometry

Fe–C(1)	1.73(2)	C(2)–Fe–C(3)	93.4(9)
Fe–C(2)	1.81(3)	C(2)–Fe–C(4)	97.7(12)
Fe–C(3)	1.85(1)	C(2)–Fe–Hg(1)	83.4(6)
Fe–C(4)	1.83(2)	C(2)–Fe–Hg(2)	163.6(6)
Fe–Hg(1)	2.560(3)	C(3)–Fe–C(4)	165.1(13)
Fe–Hg(2)	2.516(4)	C(3)–Fe–Hg(1)	84.3(6)
C(1)–Fe–C(2)	99.2(12)	C(3)–Fe–Hg(2)	82.8(9)
C(1)–Fe–C(3)	95.0(9)	C(4)–Fe–Hg(1)	87.1(7)
C(1)–Fe–C(4)	93.0(9)	C(4)–Fe–Hg(2)	83.7(11)
C(1)–Fe–Hg(1)	177.3(11)	Hg(1)–Fe–Hg(2)	80.3(1)
C(1)–Fe–Hg(2)	97.1(11)		
C(1)–O(1)	1.16(3)	Fe–C(1)–O(1)	177(2)
C(2)–O(2)	1.13(4)	Fe–C(2)–O(2)	177(1)
C(3)–O(3)	1.11(2)	Fe–C(3)–O(3)	176(2)
C(4)–O(4)	1.11(2)	Fe–C(4)–O(4)	179(3)
Hg(1) · · · Hg(2)	3.272(6)	Fe–Hg(1)–Cl(1)	137.9(2)
Hg(1)–Cl(1)	2.443(6)	Fe–Hg(2)–Cl(2)	159.0(1)
Hg(2)–Cl(2)	2.446(6)	Fe–Hg(1)–Cl(3)	116.7(1)
Hg(1)–Cl(3)	2.676(6)	Fe–Hg(2)–Cl(3^{I})	95.1(1)
Hg(2^{I})–Cl(3)	2.899(4)	Cl(1)–Hg(1)–Cl(3)	101.0(2)
		Cl(2)–Hg(2)–Cl(3^{I})	88.6(2)
		Hg(1)–Cl(3)–Hg(2^{I})	90.8(1)

Roman numeral I denotes atom at $1 - x, \bar{y}, \bar{z}$.

Computation was carried out on the local CDC 6200 machine with a local variant of the '*X*-Ray '72 ' program system.[5] Structure amplitudes, anisotropic thermal parameters, and details of planes through phenyl rings are deposited as Supplementary Publication No. SUP 21753 (15 pp., 1 microfiche).† Phenyl carbon atoms are labelled C(*n*1—6), *n* = 1—4 being the ring number with C(*n*1) attached to the arsenic atom. The metal environments are labelled as shown in Figure 1. Results are given in Tables 1—3.

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† For details see Notices to Authors, No. 7, *J.C.S. Dalton*, Index issue, 1975.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[5] '*X*-Ray' program system, Technical Report TR 192, the University of Maryland Computer Science Centre, U.S.A., version of June 1972.

TABLE 3

Least-squares planes through the iron environment in the form $pX + qY + rZ = s$ where the orthogonal Å frame (X,Y,Z) is defined by X parallel to a,Z in the ac plane. Atom deviations (Å) are in square brackets; σ (Å) is the estimated standard deviation of the defining atoms

10^4p	10^4q	10^4r	s	σ	χ^2
Plane (*i*): Fe, C(1), C(3), C(4), Hg(1)					
0 626	4 085	−9 106	−2.459	0.09	99.8
[Fe −0.01, C(1) −0.05, C(3) 0.10, C(4) 0.10, Hg(1) −0.05]					
Plane (*ii*): Fe, C(2)—(4), Hg(2)					
9 603	−2 787	−0 161	3.928	0.13	191
[Fe −0.17, C(2) 0.14, C(3) −0.04, C(4) −0.04, Hg(2) 0.11]					
Plane (*iii*): Fe, C(1), C(2), Hg(1), Hg(2)					
2 829	8 733	4 180	2 606	0.02	7.78
[Fe 0.02, C(1) 0.01, C(2) −0.03, Hg(1) 0.01, Hg(2) −0.02, Cl(1) 0.24, Cl(2) 0.80, Cl(3) 0.86, Cl(2^{I}) −2.72]					

DISCUSSION

The unit-cell contents (Figure 1) comprise $[AsPh_4]^+$ cations, which adopt their usual configuration based on the AsC_4 tetrahedron and are unremarkable in their geometry, and the anionic organometallic species. Within the latter the co-ordination of the iron atom is pseudo-octahedral with the four carbonyl groups and the two mercury atoms mutually *cis* as is the case in the other derivatives of this type which have been studied.[2,6] The iron–carbonyl geometries are unremarkable. The iron–mercury distances differ significantly, but are nonetheless comparable to previous observations, and as in the other *cis*-$FeHg_2$ derivatives the Hg–Fe–Hg angle is significantly reduced from 90°. Although the structure determination confirms the previous assignment of the anion as $[Fe(CO)_4(HgCl)(HgCl_2)]^-$, the species lies close to an inversion centre and interacts with its $(1 - x, \bar{y}, \bar{z})$ image and is more correctly regarded as a dimer. Atoms Cl(1) and Cl(2) are primarily associated with Hg(1) and Hg(2) respectively, the Hg–Cl distances being equal [2.443(6) and 2.446(6) Å] although the Fe–Hg–Cl angles are considerably different [137.9(2) and 159.0(1)°] and there is a long interaction Cl(2) ··· Hg(1) at $1 - x, \bar{y}, \bar{z}$ of 3.044(4) Å. The two anions are bridged by Cl(3) [Cl(3)–Hg(1) 2.676(6), Cl(3)–Hg(2) at $1 - x, \bar{y}, \bar{z}$ 2.899(4) Å]. The Hg–Cl distances involving effectively non-bridging chlorine atoms are longer than those for $HgCl_2$ [2.25,[7] 2.23(2) (crystal),[8] and 2.34 Å (vapour) [9]], although both mercury geometries are considerably perturbed from linearity.

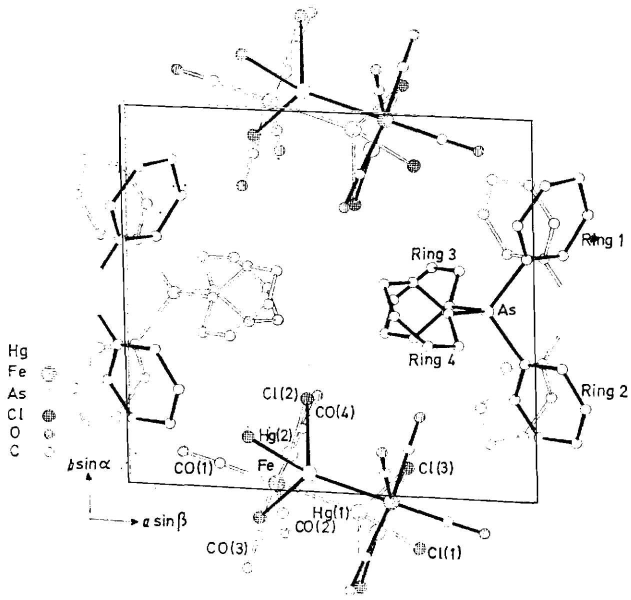

FIGURE 1 Unit-cell contents projected down c, showing the atom-labelling system

The stereochemical arrangement of any number of ligands about a metal atom can be calculated by minimizing the total repulsion energy between all donor atoms, or alternatively between all metal–ligand bonds.[10] The stereochemistry for compounds in which two unidentate ligands are different from the other four is shown in Figure 2. The M–A, M–B, M–C, and M–D bond lengths are defined as unity, and the M–E and M–F bond lengths defined as R. Points where M–E and M–F intersect the sphere of unit radius are denoted by E′ and F′ respectively. The location of A, B, C, D, E′, and F′ are given by the spherical co-ordinates ϕ_i and θ_i, the axes being defined so that $\phi_{E'} = \phi_{F'}$, $\theta_{E'} = 90$, and $\theta_{F'} = 270°$. The distance between any two points on the surface of the sphere is given by $d_{ij} = [2 - 2\cos\phi_i\cos\phi_j - 2\sin\phi_i\sin\phi_j\cos(\theta_i - \theta_j)]^{\frac{1}{2}}$. Distances between atoms E and F and other donor atoms are given by expressions of the type $d_{AE}{}^2 = (1 - R)^2 + Rd_{AE'}{}^2$ and $d_{EF} = Rd_{E'F'}$. As usual it is assumed that the repulsion

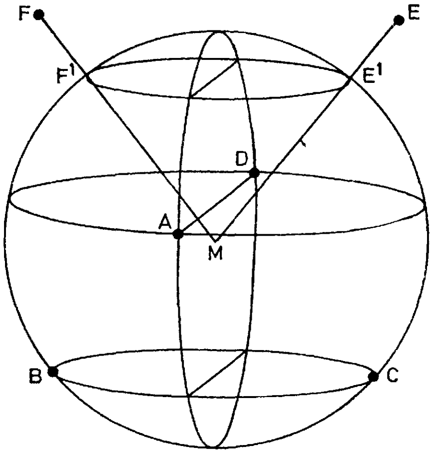

FIGURE 2 General stereochemistry of MX_4Y_2

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[6] H. W. Baird and L. F. Dahl, *J. Organometallic Chem.*, 1967, **7**, 503.

[7] D. Grdenić, *Arkiv. Kemi*, 1950, **2**, 14.

[8] P. D. Brotherton and A. H. White, *J.C.S. Dalton*, 1973, 2698.

[9] A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.

[10] J. C. Dewan and D. L. Kepert, *J.C.S. Dalton*, 1975, 959 and refs. therein.

energy u_{ij} between any two donor atoms is proportional to some inverse power n of the distance between them. The value of n is not known, but the best agreement with experiment appears to be with values in the range 6—10. The total repulsion energy U is then as in (1)

$$U = \sum_{ij} u_{ij} = \sum_{ij} a d_{ij}^{-n} = aX \quad (i < j) \qquad (1)$$

where a is a proportionality constant and X is the repulsion-energy coefficient calculated from the value of n and the geometry of the co-ordination polyhedron.

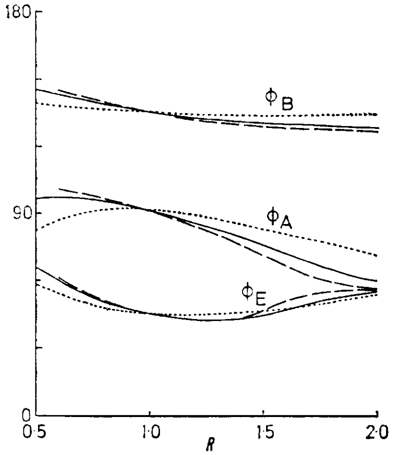

FIGURE 3 Variation of angular co-ordinates (°) for *cis*-MX_4Y_2 as a function of bond-length ratio *R*. $n = 1$ (···), 6 (– – –), and 12 (—)

Two minima are found on each potential-energy surface. The first is the conventional *cis*-octahedral structure with $\phi_{E'} = \phi_{F'}$ *ca.* 45, $\phi_A = \phi_D$ *ca.* 90, $\phi_B = \phi_C$ *ca.* 135, $\theta_A = 0$, $\theta_B = 270$, $\theta_C = 90$, and $\theta_D = 180°$. The variation of ϕ_A, ϕ_B, and $\phi_{E'}$ with the bond-length ratio R is shown in Figure 3. Of particular relevance to the present work is the observation that as R increases above unity, ϕ_E initially decreases from 45°, reaching values of 41—42° for R 1.2—1.4. As the M–E and M–F bond lengths further increase the angular parameters approach the tetrahedral values, $\phi_A = \phi_{E'} = 54.7$ and $\phi_B = 125.3°$. The observation that the Hg–Fe–Hg angle ($2\phi_{E'}$) is reduced from the regular octahedral value of 90 to 80.3° is therefore not a consequence of direct Hg–Hg bonding but simply a consequence of the more extended Fe–Hg bonds compared with the Fe–CO bonds. The angles which the Fe–CO bonds make with the two-fold axis, ϕ_A 82.6 and ϕ_B 130.4°, are also in good agreement with these calculations for R 1.3.

The second minimum on the potential-energy surfaces corresponds to the conventional *trans*-octahedral structure, $\phi_{E'} = \phi_{F'} = 90$, $\phi_A = \phi_D = (180 - \phi_B) = (180 - \phi_C)$ *ca.* 45, and $\theta_A = -\theta_B = (180 - \theta_C) = (\theta_D - 180)°$. At high values of R ($n = 1$, $R > 1.9$; $n = 6$, $R > 1.4$; $n = 12$, $R > 1.3$), $\theta_A \neq 0$ corresponding to a puckering of the ABCD plane, until the tetrahedron is again approached. For purposes of comparison the stability of the planar *trans*-octahedral structure defined by θ zero was also calculated. The stability of the *cis*- and *trans*-octahedral structures relative to the planar *trans*-octahedral structure is shown in Figure 4 for $n = 6$. It can be seen that for $R <$ *ca.* 0.8, the planar *trans* structure is the most stable, for R *ca.* 0.8—1.2 the planar *trans* and *cis* structures are of comparable stability, and for $R >$ *ca.* 1.2 the *cis* structure is the most stable. Similar relations are obtained for $n = 3$—12. For $n = 1$, the planar *trans* structure remains slightly more stable even for $R > 1.2$.

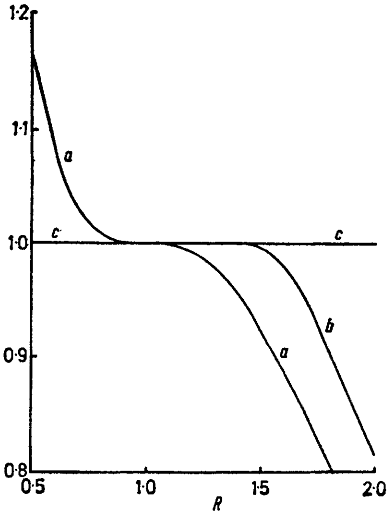

FIGURE 4 Energy (arbitrary units) of *cis*-(*a*) and *trans*-octahedral (*b*) forms of MX_4Y_2 relative to the planar octahedral form (*c*) as a function of the bond-length ratio, *R*

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