Inorg. Chem. **1981**, *20*, 849–853

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Crystal Structure and Molecular Geometry of $[(\eta^5\text{-}C_5H_5)_2Fe]_2As_4Cl_{10}O_2$, the Ferrocenium Salt of a Complex Oxychloroarsenate(III) Counterion

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Received May 27, 1980

The title compound crystallizes in the centrosymmetric monoclinic space group $C2/c$ with a a = 23.005 (3) Å, b = 7.410 (1) Å, c = 22.574 (4) Å, and β = 120.966 (12)°. Four formula units are contained in each unit cell. Diffraction data were collected with a Syntex P2$_1$ diffractometer (Mo Kα, 2θ = 3–45°), and the structure was refined to discrepancy indices of R_F = 2.8% and R_{wF} = 2.8% for those 1744 independent data with $I > 3\sigma(I)$. The ionic compound is composed of ferrocenium cations (in which the η^5-cyclopentadienyl systems are eclipsed) and a complicated oxychloroarsenate(III) dianion. The latter has the formulation $As_4Cl_{10}O_2^{2-}$ and contains two $Cl_2As–O–AsCl_2$ moieties which are held together by two chloride ions, each of which bridges three arsenic(III) atoms.

Introduction

Confirmed examples of halogen bridging between nonmetallic elements are extremely rare and are mainly confined either to unusual situations, e.g., $(Xe_2F_3^+)(AsF_6^-)$[4] and polyhalogen cations and anions,[5] or to halides of the heaviest nonmetals, e.g., TeF_4 and $TeCl_4$.[6]

We have shown previously that the aerobic oxidation of ferrocene in the presence of a group 5 trihalide can produce ferrocenium ion salts containing complex halo- and oxyhalopnictide anions. Two of these salts have been structurally characterized: $Cp_2FeBiCl_4$ (Cp = η^5-C_5H_5) contains an extended array of edge-sharing, irregular $BiCl_6^{3-}$ octahedra,[7] and $[(Cp_2Fe)_2(Sb_4Cl_{12}O)]_2 \cdot 2C_6H_6$ contains a novel octameric antimony cluster with doubly and quadruply bridging chlorine atoms.[8] We now wish to report the crystallographically determined structure of the product obtained from the combination of ferrocene and arsenic trichloride, i.e., $(Cp_2Fe)_2(As_4Cl_{10}O_2)$. The structure appears to be the first example of a halogen triply bridging two nonmetal atoms. (A possible alterative description of the structure is offered in the Discussion Section.)

Experimental Section

A. Preparation of $(Cp_2Fe)_2As_4Cl_{10}O_2$. To 100 mL of Spectrograde benzene containing 0.372 g (2.0 mmol) of ferrocene was added 0.362 g (2.0 mmol) of freshly distilled $AsCl_3$. The resulting solution was swirled in a 250-mL flask for a few minutes to saturate with air, stoppered, and allowed to remain undisturbed in a sunny window. Within 1 h, the flask's walls were dotted with forming crystals which were allowed to grow for 3–5 days to achieve a crystallographically useful size. The blue-black crystals were removed by filtration, washed with benzene, and air-dried. The yield was 15% (on the basis of ferrocene). The product was soluble with slow decomposition in water ($FeCl_3$ and $Cp_2FeFeCl_4$ were identified as products of decomposition) and was insoluble in a wide variety of organic solvents.

Table I. Experimental Data for the X-ray Diffraction Study on Crystalline $(Cp_2Fe)_2As_4Cl_{10}O_2$

(A) Crystal Parameters at 24 °C[a]

cryst system: monoclinic
space group: $C2/c$ [C_{2h}^6; No. 15]
a = 23.005 (3) Å
b = 7.4099 (8) Å
c = 22.574 (4) Å
β = 120.966 (12)°
V = 3299.6 (5) Å^3
Z = 4 (formula units)
ρ(calcd) = 2.13 g cm^{-3}
ρ(exptl) = 2.10 g cm^{-3}
mol wt: 1058.27

(B) Measurement of Intensity Data

diffractometer: Syntex P2$_1$
radiation: Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)
monochromator: highly oriented graphite
reflcns measd: $\pm h,+k,\pm l$
2θ range: 3–45°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 3.0°/min
scan width: $[2\theta(\text{Mo K}\alpha_1) - 0.7]° - [2\theta(\text{Mo K}\alpha_2) + 0.7]°$
std reflcns: $14,2,\bar{2}$; $4,0,\overline{12}$; 150; these were measured after every 97 reflections; no significant changes in intensity were observed
reflcns collected: 4183 total, yielding 2095 symmetry-independent data
abs coeff: μ = 59.2 cm^{-1}
ignorance factor: p = 0.015

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections of the forms $\{12,2,\overline{10}\}$, $\{9,1,\overline{10}\}$, $\{352\}$, $\{152\}$, $\{14,2,\bar{2}\}$, and $\{11,1,\overline{11}\}$.

Table II. Intensity Distribution for Diffraction Data from $(Cp_2Fe)_2As_4Cl_{10}O_2$

		theoretical[a]	
	obsd	centric	acentric
$\langle \lvert E \rvert \rangle$	0.821	0.798	0.886
$\langle \lvert E^2 \rvert \rangle$	1.000	1.000	1.000
$\langle \lvert E^2 - 1 \rvert \rangle$	0.909	0.968	0.736
$\lvert E \rvert > 1.0$	33.32%	31.73%	36.78%
$\lvert E \rvert > 2.0$	3.68%	4.55%	1.89%
$\lvert E \rvert > 3.0$	0.00%	0.27%	0.01%

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Anal. Calcd: C, 22.70; H, 1.91; Fe, 10.55; As, 28.32; Cl, 33.50. Found: C, 23.18; H, 2.12; Fe, 11.03; As, 27.99; Cl, 32.84.

In the absence of light, a blue-grey microcrystalline product was obtained which provided an elemental analysis similar to the product formed in the presence of light. In rigorously degassed and dried systems, no crystalline products were obtained after a 2-month exposure to sunlight.

B. Collection of Diffraction Data. The salt forms purple-black parallelepipeds which in thin sections appear wine-red by transmitted light. The crystal selected for study was of approximate dimensions

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Table III. Final Positional Parameters for $(Cp_2Fe)_2As_4Cl_{10}O_2$[a]

atom	*x*	*y*	*z*
As1	0.06531 (3)	0.59591 (7)	0.44265 (3)
As2	0.03304 (3)	0.22008 (7)	0.48021 (3)
Fe	0.18369 (4)	0.02119 (10)	0.31713 (4)
Cl1	0.02941 (8)	0.58809 (25)	0.33163 (8)
Cl2	0.17358 (7)	0.64431 (21)	0.47387 (8)
Cl3	0.07068 (7)	0.50950 (23)	0.59102 (9)
Cl4	0.12348 (8)	0.03919 (20)	0.54353 (8)
Cl5	−0.00706 (8)	0.04587 (22)	0.38596 (9)
O	0.08023 (17)	0.3615 (4)	0.45739 (20)
C1	0.1980 (5)	−0.2561 (9)	0.3265 (5)
C2	0.2566 (3)	−0.1724 (10)	0.3396 (3)
C3	0.2464 (3)	−0.0768 (9)	0.2843 (4)
C4	0.1804 (4)	−0.0973 (10)	0.2333 (3)
C5	0.1488 (3)	−0.2080 (10)	0.2567 (5)
C6	0.2164 (4)	0.2003 (9)	0.3991 (4)
C7	0.2031 (4)	0.2927 (8)	0.3400 (4)
C8	0.1361 (5)	0.2693 (10)	0.2913 (4)
C9	0.1069 (4)	0.1601 (12)	0.3192 (6)
C10	0.1567 (6)	0.1182 (11)	0.3863 (5)
H1	0.19145 (0)	−0.32972 (0)	0.35707 (0)
H2	0.29875 (0)	−0.18073 (0)	0.38187 (0)
H3	0.27945 (0)	−0.00715 (0)	0.28130 (0)
H4	0.15964 (0)	−0.04369 (0)	0.18876 (0)
H5	0.10278 (0)	−0.24580 (0)	0.23145 (0)
H6	0.25892 (0)	0.19411 (0)	0.44101 (0)
H7	0.23492 (0)	0.36051 (0)	0.33434 (0)
H8	0.11335 (0)	0.31915 (0)	0.24611 (0)
H9	0.06106 (0)	0.12120 (0)	0.29626 (0)
H10	0.15107 (0)	0.04634 (0)	0.41784 (0)

[a] The $As_4Cl_{10}O_2^{2-}$ system lies on a crystallographic center of symmetry at 0, $^1/_2$, $^1/_2$. The positions of atoms in the basic asymmetric unit are given; those in the other half of the system are labeled with a prime and are related to those in the basic asymmetric unit by the transformation $(x', y', z') = (-x, 1-y, 1-z)$.

0.11 × 0.20 × 0.23 mm and was mounted in a 0.2-mm capillary, which was purged with argon, flame-sealed, fixed into an aluminum pin with beeswax, and mounted into a eucentric goniometer. The crystal was centered on the diffractometer, and the crystal class (monoclinic), orientation matrix, and accurate unit cell dimensions were determined as previously described;[9] details are presented in Table I.

All calculations were performed with use of the Syntex XTL in-house structure-solving package as modified by our research group at SUNY at Buffalo.[10,11] Data were corrected for absorption by an empirical method based upon a two-parameter (2θ and ϕ) interpolation between a series of normalized ψ scans of close-to-axial (i.e., $\chi = 90 \pm 10°$) reflections. These reflections used, their 2θ values, and their max:min intensity ratio variations around ψ were as follows: $22,0,\overline{10}$ [39.72°, 1.56]; $20,0,\overline{12}$ [36.15°, 1.57]; $12,0,\bar{8}$ [21.72°, 1.61]; $\overline{16},0,8$ [14.25°, 1.60].

The systematic absences (hkl for $h + k = 2n + 1$; $h0l$ for $l = 2n + 1$) indicated either the noncentrosymmetric space group *Cc* [C_s^4; No. 9] or the centrosymmetric space group $C2/c$ [C_{2h}^6; No. 15]. In view of the possible space group *Cc*, we collected one hemisphere of data ($\pm h, +k, \pm l$). This provides two equivalent forms for the centrosymmetric space group $C2/c$ [$I(hkl) = I(\bar{h}k\bar{l}) \neq I(hk\bar{l}) = I(\bar{h}kl)$] or a single form for the noncentrosymmetric space group *Cc*.

The resulting intensity distributions (Table II) marginally favor the centric case. The space group $C2/c$ was thus assumed and was confirmed by the successful solution and refinement of the crystal structure. The two equivalent forms of data were merged [$R(I)$ = 1.81% for 2088 pairs of averaged reflections] and were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflections with $I < 0$ were assigned a value of $|F_o| = 0$.

C. Solution and Refinement of the Structure. Data were placed on an approximately absolute scale via a Wilson plot which also provided the average overall thermal parameter ($\bar{B} = 2.95$ Å^2). The structure was solved by direct methods via the program MULTAN,[12] using 130 reflections with $|E| > 1.85$. The location of the arsenic and iron atoms were determined from the *E* map based on the phase solution of highest internal consistency.

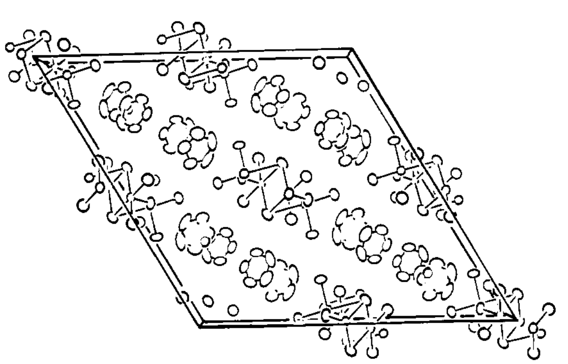

Figure 1. Packing of $(Cp_2Fe)_2As_4Cl_{10}O_2$ within the unit cell, viewed down *b*.

The remaining nonhydrogen atoms were located from a series of difference-Fourier syntheses, each being phased by an increasing number of atoms. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all 19 independent nonhydrogen atoms (172 parameters in all) led to convergence with $R_F = 3.2\%$ and $R_{wF} = 3.3\%$ for those 1744 reflections with $I > 3\sigma(I)$. Hydrogen atoms were now included in calculated positions, on the basis of d(C–H) = 0.95 Å,[13] and were assigned isotropic thermal parameters of $B = 7.0$ Å^2; these positions were updated as appropriate but were not refined.

Three further cycles of full-matrix least-squares refinement led to final convergence with $R_F = 2.8\%$, $R_{wF} = 2.8\%$, and GOF = 1.038. Final positional and thermal parameters are collected in Tables III and IV.

A final difference-Fourier synthesis showed no unexpected features, and the residual $\sum w(|F_o| - |F_c|)^2$ showed no major variations against $|F_o|$, $(\sin \theta)/\lambda$, identity or parity of index, sequence number, etc. The structure is thus complete and the weighting scheme satisfactory.

Throughout the analysis, the residual $\sum w(|F_o| - |F_c|)^2$ was minimized. The analytical scattering factors[14a] for neutral As, Fe, Cl, O, C, and H were used. Both $\Delta f'$ and $\Delta f''$ values[14b] were included for all nonhydrogen atoms.

Results and Discussion

Interatomic distances and their estimated standard deviations (esd's) are listed in Table V; interatomic angles, with eds's, are given in Table VI. A view of the packing of Cp_2Fe^+ and $As_4Cl_{10}O_2^{2-}$ moieties in the unit cell (as viewed down *b*) is shown in Figure 1, while a stereoscopic view of the $As_4Cl_{10}O_2^{2-}$ framework appears as Figure 2. The scheme used for labeling atoms is indicated in Figures 3 (anion) and 4 (ferrocenium ion).

The structure is composed of ferrocenium cations (Cp_2Fe^+) and anionic $As_4Cl_{10}O_2^{2-}$ units in the required 2:1 ratio. There are no abnormally short contacts between the individual ions.

It is difficult to arrive at a unique, unequivocal description of the $As_4Cl_{10}O_2^{2-}$ moiety. At one extreme a charge-separated model could be chosen to describe the anionic unit. Within the framework of this description, two neutral $Cl_2As–O–AsCl_2$ molecules[15] are present along with two chloride ions.

At the other extreme a more delocalized view of the entire $As_4Cl_{10}O_2^{2-}$ system can be invoked.

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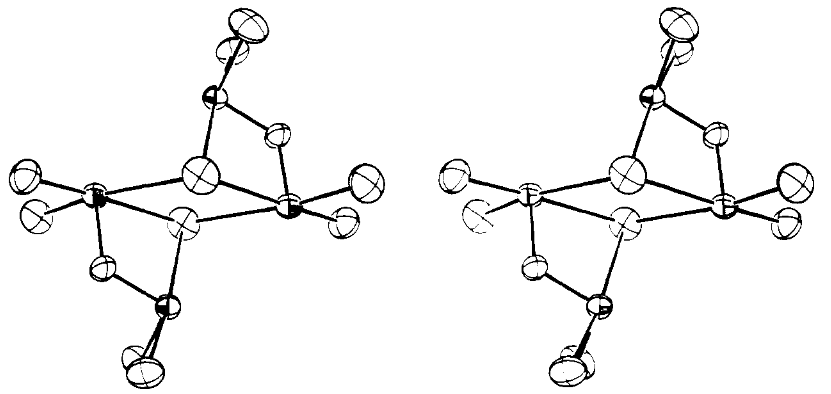

Figure 2. Stereoscopic view of the $As_4Cl_{10}O_2^{2-}$ system.

Table IV. Anisotropic Thermal Parameters[a] (in Å²) for the Nonhydrogen Atoms in $(Cp_2Fe)_2As_4Cl_{10}O_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As1	2.764 (25)	2.776 (26)	2.410 (26)	0.013 (20)	1.339 (21)	0.122 (21)
As2	2.849 (26)	3.01 (3)	3.50 (3)	−0.374 (21)	1.969 (23)	−0.020 (22)
Fe	3.21 (4)	2.67 (4)	3.37 (4)	0.20 (3)	1.93 (3)	0.00 (3)
Cl1	4.77 (8)	7.62 (11)	2.31 (7)	1.12 (7)	1.50 (6)	0.58 (7)
Cl2	3.02 (6)	4.71 (8)	4.50 (8)	−0.82 (6)	1.76 (6)	0.32 (6)
Cl3	2.99 (6)	5.83 (9)	4.22 (8)	−0.14 (6)	1.16 (6)	−0.13 (7)
Cl4	4.38 (8)	3.99 (7)	4.66 (9)	0.88 (6)	2.09 (7)	1.02 (6)
Cl5	4.56 (8)	5.30 (9)	4.56 (9)	−1.50 (7)	2.07 (7)	−1.68 (7)
O	3.44 (17)	2.61 (16)	5.04 (22)	−0.11 (13)	2.82 (17)	0.34 (15)
C1	10.0 (6)	2.4 (3)	9.0 (6)	1.2 (3)	7.2 (5)	0.7 (3)
C2	4.9 (4)	5.5 (4)	3.7 (4)	2.3 (3)	1.2 (3)	−1.0 (3)
C3	5.0 (4)	5.5 (4)	5.6 (4)	0.3 (3)	4.0 (3)	−0.4 (3)
C4	5.5 (4)	6.7 (4)	2.6 (3)	1.9 (3)	1.5 (3)	−0.6 (3)
C5	3.4 (3)	4.8 (4)	9.5 (6)	−1.9 (3)	3.0 (4)	−4.5 (4)
C6	7.1 (4)	4.1 (3)	4.4 (4)	0.7 (3)	3.0 (3)	−1.0 (3)
C7	7.6 (5)	3.0 (3)	6.2 (4)	0.2 (3)	4.3 (4)	0.1 (3)
C8	7.7 (5)	4.4 (4)	6.5 (5)	3.2 (4)	3.0 (4)	1.3 (3)
C9	5.0 (4)	6.5 (5)	12.5 (8)	0.5 (4)	5.7 (5)	−2.1 (5)
C10	10.9 (7)	5.6 (4)	9.6 (6)	0.1 (5)	8.9 (6)	−0.7 (4)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table V. Interatomic Distances (Å) with Esd's

(A) Iron–Carbon Distances within the Ferrocenium Ion

Fe–C(1)	2.074 (7)	Fe–C(6)	2.078 (7)
Fe–C(2)	2.063 (8)	Fe–C(7)	2.068 (6)
Fe–C(3)	2.064 (9)	Fe–C(8)	2.064 (8)
Fe–C(4)	2.052 (7)	Fe–C(9)	2.065 (11)
Fe–C(5)	2.064 (8)	Fe–C(10)	2.082 (12)
		av Fe–C	2.067

(B) Carbon–Carbon Distances within the Ferrocenium Ion

C(1)–C(2)	1.372 (14)	C(6)–C(7)	1.386 (11)
C(2)–C(3)	1.346 (10)	C(7)–C(8)	1.367 (14)
C(3)–C(4)	1.362 (11)	C(8)–C(9)	1.391 (15)
C(4)–C(5)	1.370 (12)	C(9)–C(10)	1.385 (16)
C(5)–C(1)	1.434 (13)	C(10)–C(6)	1.389 (10)
		av C–C	1.380

(C) As–O and As–Cl Distances within the $As_4Cl_{10}O_2^{2-}$ System

As(1)–O	1.769 (3)	As(1)–Cl(3)	2.920 (2)
As(2)–O	1.766 (4)	As(2)–Cl(3)	2.889 (2)
As(1)–Cl(1)	2.199 (2)	As(2′)–Cl(3)	3.062 (2)
As(1)–Cl(2)	2.241 (2)	As(1)···As(2)	3.110 (1)
As(2)–Cl(4)	2.260 (2)	As(1)···Cl(3′)	3.349 (2)
As(2)–Cl(5)	2.242 (2)		

The $As_4Cl_{10}O_2^{2-}$ system lies about the crystallographic center of symmetry at (0, ¹/₂, ¹/₂). Bond lengths within the two equivalent $Cl_2As\text{–}O\text{–}AsCl_2$ fragments are As(1)–Cl(1) = 2.199 (2) Å, As(1)–Cl(2) = 2.241 (2)Å, As(2)–Cl(4) = 2.260 (2) Å, As(2)–Cl(5) = 2.242 (2) Å, As(1)–O = 1.769 (3) Å, and As(2)–O = 1.766 (4) Å. Atoms Cl(3) and Cl(3′) are clearly in the correct location to each bridge three arsenic atoms. The relevant distances about Cl(3) are As(1)–Cl(3) = 2.920 (2) Å, As(2)–Cl(3) = 2.889 (2) Å, and As(2′)–Cl(3) = 3.062 (2) Å. (The As(1′)···Cl(3) distance of 3.349 (2) Å is substantially longer and is clearly nonbonding.)

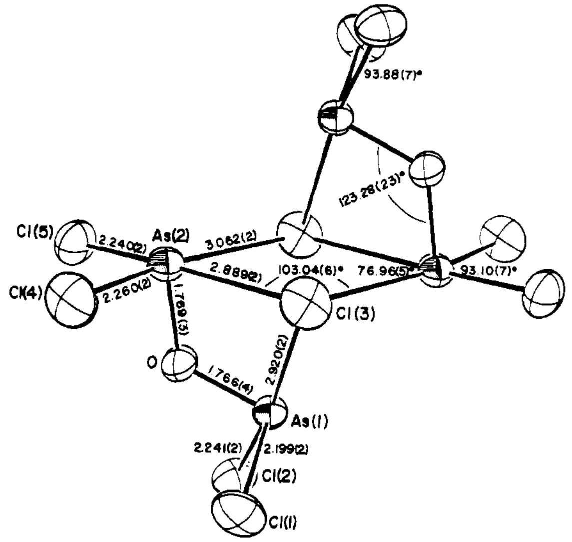

Figure 3. Atomic labeling with bond distances and angles for the $As_4Cl_{10}O_2^{2-}$ system. This system lies about a crystallographic inversion center.

If the fully charge-separated model were the correct description, then little or no effect should be seen in the terminal As–Cl distances. However, the As–Cl distances for the ter-

Table VI. Selected Interatomic Angles (Deg) with Esd's for $(Cp_2Fe)_2As_4Cl_{10}O_2$

(A) Angles for the Ferrocenium Ion

C(1)-Fe-C(2)	38.73 (35)	C(7)-Fe-C(8)	38.64 (35)	C(1)-C(2)-C(3)	110.79 (75)	C(7)-C(8)-C(9)	108.46 (85)
C(2)-Fe-C(3)	38.09 (31)	C(8)-Fe-C(9)	39.38 (40)	C(2)-C(3)-C(4)	108.19 (72)	C(8)-C(9)-C(10)	107.77 (95)
C(3)-Fe-C(4)	38.64 (31)	C(9)-Fe-C(10)	39.00 (43)	C(3)-C(4)-C(5)	108.83 (73)	C(9)-C(10)-C(6)	107.56 (93)
C(4)-Fe-C(5)	38.88 (33)	C(10)-Fe-C(6)	39.02 (37)	C(4)-C(5)-C(1)	107.29 (77)	C(10)-C(6)-C(7)	108.11 (78)
C(5)-Fe-C(1)	40.55 (37)	av C-Fe-C	39.00	C(5)-C(1)-C(2)	104.88 (80)	av C-C-C	108.00
C(6)-Fe-C(7)	39.06 (32)			C(6)-C(7)-C(8)	108.09 (76)		

(B) Angles for the $As_4Cl_{10}O_2^{2-}$ System

As(1)-O-As(2)	123.28 (23)	Cl(1)-As(1)-O	96.38 (10)	Cl(1)-As(1)-Cl(3)	88.42 (6)
Cl(1)-As(1)-Cl(2)	93.88 (7)	Cl(2)-As(1)-O	91.22 (14)	Cl(2)-As(1)-Cl(3)	173.25 (6)
Cl(4)-As(2)-Cl(5)	93.10 (7)	Cl(4)-As(2)-O	91.85 (14)	Cl(4)-As(2)-Cl(3)	172.43 (6)
As(1)-Cl(3)-As(2)	57.83 (3)	Cl(5)-As(2)-O	94.55 (14)	Cl(5)-As(2)-Cl(3)	93.01 (6)
As(1)-Cl(3)-As(2′)	73.50 (3)	Cl(3)-As(1)-O	73.77 (13)	Cl(4)-As(2)-Cl(3′)	96.74 (6)
As(2)···As(1)···As(2′)	85.03 (2)	Cl(3)-As(2)-O	83.22 (13)	Cl(5)-As(2)-Cl(3′)	169.73 (6)
As(1)···As(2)···As(1′)	94.97 (2)	Cl(3′)-As(2)-O	82.24 (13)		

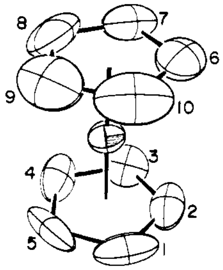

Figure 4. Atomic labeling for the Cp_2Fe^+ ion. Note the eclipsed conformation and the librational motions of the rings. Hydrogen atoms are omitted for the sake of clarity.

Table VII. Least-Squares Planes[a,b] for the Cp_2Fe^+ Ion

atoms	dev	atoms	dev
Plane I: $0.4944X - 0.8010Y - 0.3377Z + 0.2320 = 0^c$			
C(1)*	−0.006 (9)	C(6)	−3.396 (8)
C(2)*	0.004 (8)	C(7)	−3.371 (8)
C(3)*	−0.000 (8)	C(8)	−3.395 (9)
C(4)*	−0.004 (8)	C(9)	−3.421 (10)
C(5)*	0.006 (8)	C(10)	−3.430 (10)
Fe	−1.6987 (8)		
Plane II: $0.4741X - 0.8150Y - 0.3332Z + 3.6207 = 0^c$			
C(6)*	−0.000 (8)	C(1)	3.422 (9)
C(7)*	0.003 (8)	C(2)	3.401 (8)
C(8)*	−0.004 (9)	C(3)	3.373 (8)
C(9)*	0.004 (10)	C(4)	3.387 (8)
C(10)*	−0.002 (10)	C(5)	3.430 (8)
Fe	1.7045 (8)		

[a] Atoms marked with an asterisk were used in calculating the planes. [b] Dihedral angle (I/II) = 1.44°. [c] Orthonormal coordinates.

minal As–Cl bonds fall into the range 2.199 (2)–2.260 (2) Å and all are longer than the As–Cl distance of 2.17 Å found from a recent crystallographc study of $AsCl_3$[16] (and which agrees well with the value determined from earlier electron diffraction studies).[17]

The elongation in terminal As–Cl bonds in the present structure can be taken as an indication of some measure of covalent character in the bonding of $Cl_2As–O–AsCl_2$ units to Cl(3) and Cl(3′). In addition to this, the average of the terminal As–Cl bond distances on As(1) (which participates in only *one* bridging chloride bond) is 0.030 Å shorter than the average for As(2), which has *two* such bridging bonds.

The terminal Cl–As–Cl angles, Cl(1)–As(1)–Cl(2) = 93.88 (7)° and Cl(4)–As(2)–Cl(5) = 93.10 (7)°, are substantially smaller than the corresponding angles in $AsCl_3$ (97.7°).[16]

It is relevant to note that a crystallographic study of $Cs_3As_2Cl_9$ has been interpreted in terms of ionized Cs^+Cl^- and intact $AsCl_3$ molecules stacked in pairs along their threefold axes with an inter-$AsCl_3$ As···Cl distance of 2.76 Å.[18]

The $As_4Cl_{10}O_2^{2-}$ system has precise (crystallographically-required) C_i symmetry and approximates to an idealized C_{2h} symmetry.

The Ferrocenium Ion. The η^5-cyclopentadienyl ligands are each planar within the limits of experimental error (see Table VII). The iron atom lies symmetrically between the five-membered rings and is −1.6987 (8) Å from the plane defined by atoms C(1)–C(5) and +1.7045 (8) Å from the plane defined by atoms C(6)–C(10). The dihedral angle between these planes is 1.44°. The iron–carbon distances range from Fe–C(4) = 2.052 (7) Å to Fe–C(10) = 2.082 (12) Å, averaging 2.067 Å. The carbon–carbon distances range from C(2)–C(3) = 1.346 (10) Å to C(5)–C(1) = 1.434 (13) Å, averaging 1.380 Å—a value substantially below the accepted C–C (η^5-cyclopentadienyl) bond length of ~1.43 Å and in keeping with the large amplitude of librational motion found for the Cp rings (see Table IV and Figure 4).

It is pertinent, at this time, to make some brief observations on differences observed between ferrocene derivatives and ferrocenium ion complexes.

(1) All determined ferrocenium ion structures show an *eclipsed* configuration for the two η^5-C_5H_5 systems: $(Cp_2Fe^+)(picrate^-)$,[19] $(Cp_2Fe^+)(3CCl_3CO_2H^-)$,[20] $(Cp_2Fe^+)(I_3^-)$,[21] $[(\eta^5\text{-}C_5H_4Me)_2Fe^+](I_3^-)$,[22] $(Cp_2Fe^+)(BiCl_4^-)$,[7] and $[(Cp_2Fe^+)_2(Sb_4Cl_{12}O^{2-})]_2 \cdot 2C_6H_6$.[8] In contrast to this, *neutral* ferrocene derivatives (*in the solid state*) are normally found in the staggered conformation unless sterically forced away from this arrangement. This has been summarized by Churchill and Wormald.[23] The reasons for this are not at all clear. In fact, electron diffractions measurements on ferrocene indicate that (*in the gas phase at 140 °C*) ferrocene has an eclipsed equilibrium conformation with a barrier to rotation of only 0.9 ± 0.3 kcal/mol.[24]

(2) The average Fe–C distance determined for the present molecule [2.067 Å; σ(ext) = 0.009 Å, σ(av) = 0.003 Å][25] and

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that determined for $(Cp_2Fe^+)(BiCl_4^-)$[7] (average ≈ 2.076 Å)[26] appear to be marginally longer than that reported for ferrocene (2.058 Å from electron diffraction[24b] or 2.045 Å from X-ray diffraction)[27] and for most ferrocene derivatives.[23]

(3) The Fe–ring distances of 1.6987 (8) and 1.7045 (8) Å (average = 1.7016 Å) in the present structure agree with those determined in *ordered* ferrocenium structures—viz, 1.70 Å in $(Cp_2Fe^+)(BiCl_4^-)$[7b] and 1.69 and 1.70 Å in $[(\eta^5\text{-}C_5H_4Me)_2Fe^+](I_3^-)$.[22] These values are, again, slightly larger than those found in ferrocene (1.66 Å).[27]

The preferential "eclipsed" configuration for Cp_2Fe^+ seems reasonable in light of the increases (over the Cp_2Fe derivatives) in the Fe–C and Fe–ring distances. The greatest remaining puzzle with respect to conformation is why ferrocene derivatives are *staggered* in the solid state while ferrocene is *eclipsed* (and close to freely rotating) in the gas phase.

The longer Fe–C and Fe–ring distances in Cp_2Fe^+ suggest that the oxidation step ($Cp_2Fe \rightarrow Cp_2Fe^+$) removes an electron which is just slightly bonding with respect to iron–ring interactions. This is consistent with theoretical treatments of the molecular orbitals for ferrocene.[28-30]

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. $(Cp_2Fe)_2As_4Cl_{10}O_2$, 75880-92-1; $AsCl_3$, 7784-34-1; Cp_2Fe, 102-54-5.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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[25] σ(ext) is an external estimate of the error on an individual bond distance obtained by the "scatter" of measurements of N equivalent bonds, viz., $\sigma(\text{ext}) = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$. σ(av) is the esd on the average value calculated by $\sigma(\text{av}) = [\sum(d_i - \bar{d})^2/(N^2 - N)]^{1/2}$.

[26] Reference 7b gives Fe–C distances to only two decimal places. This value is the average of the 10 reported values and may well suffer from rounding errors.

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Crystal and Molecular Structure of a Macrocyclic Complex of Gold(III)

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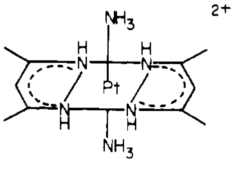
Received June 26, 1980

(5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) chloride dihydrate, prepared by condensation of $[Au(en)_2]Cl_3$ with 2,4-pentanedione, crystallizes in the monoclinic space group $C2/c$ with a = 23.002 (19) Å, b = 6.931 (3) Å, c = 12.828 (16) Å, β = 108.66 (9)°, and Z = 4. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations to a conventional R value of 0.037 for 2500 reflections. The gold atom is located at a crystallographic center of symmetry, and the macrocyclic cation is very nearly planar. Bond lengths within the β-diiminate rings indicate extensive π delocalization. The β-diiminate ring parameters are compared with those reported for related complexes.

Previous publications from this laboratory[1,2] and others[3,4] have shown that complexes containing β-diiminate chelate rings are formed when amine complexes of Pt(IV) and Au(III) react with β-diketones in aqueous base. The crystal structure of one of the Pt(IV) complexes, I, was reported earlier.[1] The six-membered β-diiminate rings were found to be planar, and the pattern of bond distances around the rings indicates complete delocalization of π electrons as shown in I.

The gold(III) β-diiminate complexes examined thus far have been prepared by condensation of $[Au(en)_2]Cl_3$ with a variety of β-diketones.[2] These are 14-membered, tetraaza ring, 12π macrocyclic species exemplified by the cation (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) hereafter referred to as II, which may be regarded as the parent member of the series.



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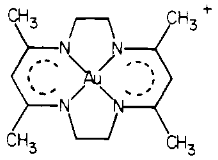

II

Although a few complexes of the above macrocyclic ligand are known for first-row transition-metal ions,[5,6] no structural details have been reported. In this paper we present the results of an X-ray crystallographic study of the chloride salt of II. Structural details of II are compared with those of related macrocyclic complexes.

Experimental Section

The macrocyclic cation II was prepared by the general method reported earlier,[2] and its chloride salt was precipitated by adding excess LiCl to the filtered reaction mixture. The product was recrystallized with use of acetone and diethyl ether. Slow evaporation of a 1-butanol

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