The Crystal and Molecular Structure of Ferrocenium μ-Oxo-bis[trichloroferrate(III)]: a Product of Reaction of Ferrocene with Iron(III) Chloride *

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The product of reaction of ferrocene with iron(III) chloride, previously formulated as ferrocenium trichloroferrate(II), $[Fe^{III}(\eta-C_5H_5)_2][Fe^{II}Cl_3]$, is shown to be the μ-oxo compound $[Fe^{III}(\eta-C_5H_5)_2]_2[(Fe^{III}Cl_3)_2O]$.

The reaction of ferrocene with solutions of iron(III) chloride yields different products depending upon the reaction conditions. The best known[1] of these is the simple tetrachloroferrate(III) $[Fe^{III}(\eta-C_5H_5)_2][Fe^{III}Cl_4]$, but a different compound is obtained if excess ferrocene is used. This has been investigated by two groups[2,3] of workers: both adopted the formulation $[Fe(\eta-C_5H_5)_2][Fe^{II}Cl_3]$. Aharoni and Litt[2] were the first to propose that the compound contained an iron(II) anion: they based this on the results of an oxidation titration using aqueous Ce^{4+}. Stukan *et al.*[3] carried out a study utilising Mössbauer spectroscopy. Having prepared the compound twice, using reagents alternately enriched in iron-57, they were able to show that the cation and anion originated respectively in ferrocene and iron(III) chloride. They also noted that a frozen solution of ferrocene and iron(III) chloride enriched in iron-57 gave a clear iron(II) doublet in its Mössbauer spectrum. However, the parameters they assigned to the spectrum of the solid compound together with the uncommon stoicheiometry given to the iron(II) anion prompted us to investigate this compound further. Having recorded the Mössbauer spectrum of the compound as prepared using the published methods, we noted that there was no resonance which could be assigned to an iron(II) species. Accordingly, we carried out a full investigation. This has revealed that the salt contains the μ-oxo-chloroiron(III) complex anion $[(FeCl_3)_2O]^{2-}$: the ferrocenium analogue of the pyridinium salt reported by Nelson and co-workers.[4] After the completion of our study, we found that another group[5] had worked on this problem and had come to similar conclusions.

Results and Discussion

Crystal and Molecular Structure.—The unit cell is shown in Figure 1 with the atom numbering and bond parameters for the ferrocenium part are shown in Figure 2. It contains two crystallographically-independent ferrocenium cation sets and one set of $[(FeCl_3)_2O]^{2-}$ anions. These consist of two corner-sharing $FeCl_3O$ tetrahedra with parameters strikingly similar to those reported for the pyridinium salt[4] except for the larger Fe–O–Fe angle observed here (Figure 3). The Fe–Cl bond lengths are longer than in the $[FeCl_4]^-$ tetrahedron[6] indicating strong Fe–O π bonding. The chlorines are eclipsed in this anion as in the pyridinium salt. Inspection of Figure 3 reveals that the Fe–O bond length [1.757(2) Å] is among the shortest known, again indicating strong π bonding.

Two points of interest emerge if the structure reported here is compared with that of the pyridinium analogue[4] and then with $[Fe^{III}(\eta-C_5H_5)_2][Fe^{III}Cl_4]$.[6]

In the first pair, the ferrocenium and pyridinium cations occupy similar locations. One pyridinium is hydrogen bonded to a solvate pyridine, the other is free. Of the two ferroceniums, ferrocenium(3), that which is spatially analogous to the hydrogen-bonded pyridinium, occupies a smaller hole in the lattice and its atomic positions were easier to refine than those of ferrocenium(4). The latter showed greater disorder. The anion sub-lattices are remarkably similar.

The second pair of compounds are also very similar: here the μ-oxo anion is equivalent in size and location to two $FeCl_4$ units. The Fe–C and C–C distances show a similar spread of values and there is the characteristic ambiguity regarding the conformation of the cyclopentadienyl rings with respect to one another in ferrocenium(4). Ferrocenium(3) has staggered η-C_5H_5 rings.

Vibrational Spectrum.—The i.r. spectrum is dominated by a strong absorption at 853 cm^{-1} as has been recorded for the other salts and is assigned to an asymmetric Fe–O stretching mode. It has already been noted that this wavenumber is higher than is usual for M–O–M species and is consistent with strong π bonding. Absorption due to Fe–Cl stretching modes is observed at 363 and 318 cm^{-1} which agrees well with those of 360 and 311 cm^{-1} found in the pyridinium salt.[4]

Magnetic Properties.—The magnetic moment of this compound varies with temperature ($\mu_{eff.}$, Table 1) and if it is assumed that the ferrocenium cation has a magnetic moment of 2.4 B.M., independent of temperature, the anion moment ($\mu_{calc.}$) varies with temperature as indicated. This is qualitatively similar to that reported for the pyridinium salt[4] and is as expected for a moderately strongly-coupled antiferromagnet. An exchange integral has not been calculated because the cation moment would be expected to exhibit a small but unknown variation with temperature.

Mössbauer Spectra.—The Mössbauer spectra are shown in Figure 4 and numerical results are listed in Table 2. They reveal the presence of the two iron(III) species. One is a broad singlet with $\delta = 0.595$ mm s^{-1} which can be assigned to a ferrocenium cation. The second species has a quadrupole splitting, ΔE_Q 1.210 mm s^{-1}, centred at $\delta = 0.344$ mm s^{-1} at 78 K. The μ-oxo anion $[(FeCl_3)_2O]^{2-}$ can be assigned to this resonance. Apart from the pyridinium salt[4] mentioned above, ions of this formula have

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* *Supplementary data available* (No. SUP 56577, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

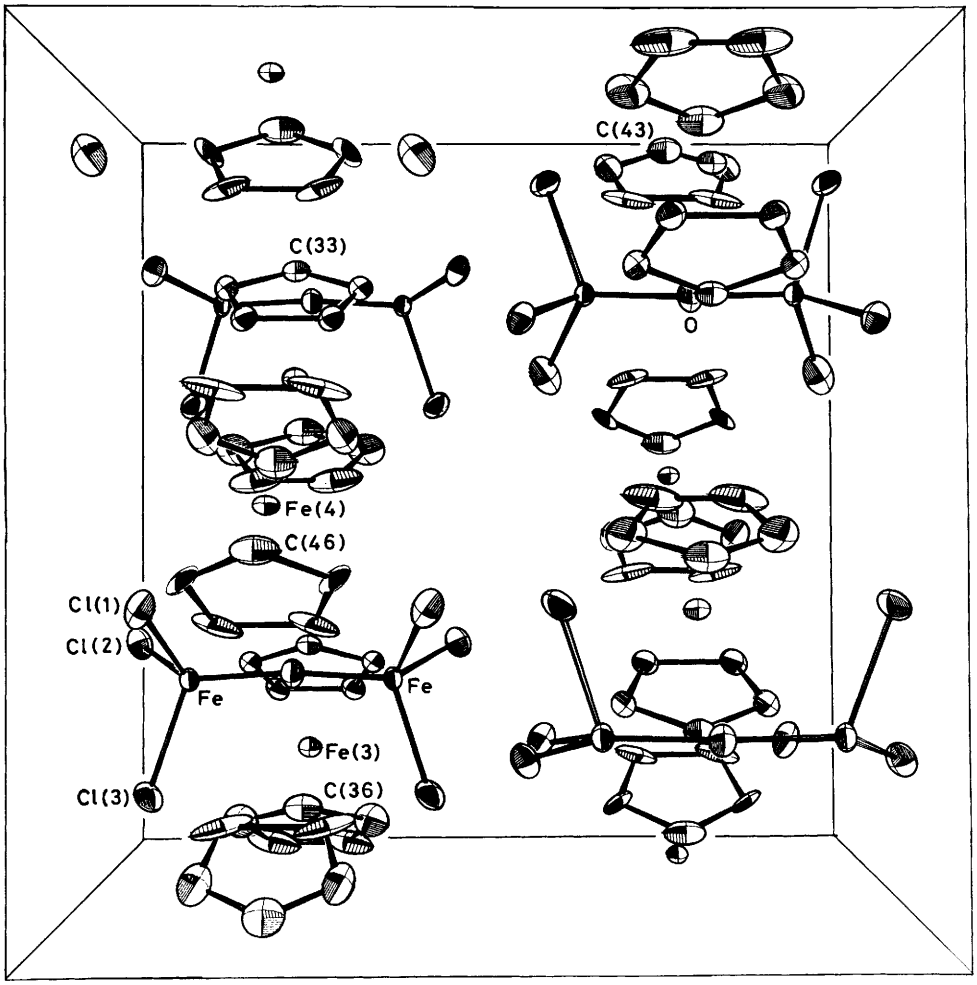
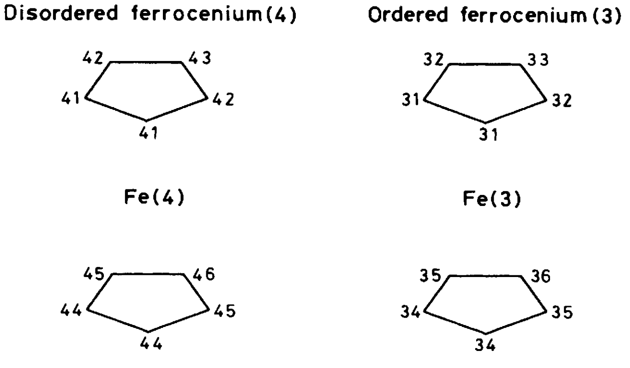


Figure 1. Unit-cell contents of ferrocenium μ-oxo-bis[trichloroferrate(III)]



C(41)–Fe(4)	2.045	C(44)–Fe(4)	2.061
C(42)–Fe(4)	2.063	C(45)–Fe(4)	2.066
C(43)–Fe(4)	2.012	C(46)–Fe(4)	2.020
C(42)–C(43)	1.297(17)	C(44)–C(45)	1.408(23)
C(42)–C(41)	1.349(19)	C(45)–C(46)	1.246(18)
C(41)–C(41)	1.397(32)	C(44)–C(44)	1.593(41)
C(42)–C(43)–C(42)	111.5(1.8)	C(45)–C(46)–C(45)	116.6(2.7)

Figure 2. Atomic-numbering scheme and bond distances (Å) and angles (°) for the ferrocenium cations

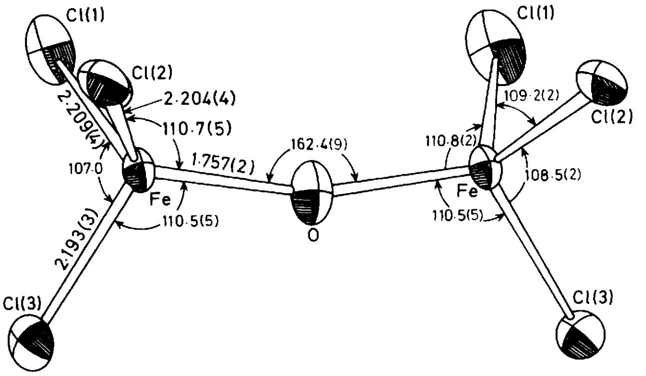


Figure 3. ORTEP drawing of the $[(FeCl_3)_2O]^{2-}$ molecule showing bond distances (Å) and angles (°)

been reported as the tetramethylammonium,[7] tetraethylammonium,[8] tetraphenylphosphonium,[9] tris(1,10-phenanthroline)iron(II),[10,11] and $[\{(Ph_3P)_2CSe\}_2]^{2+}$[11] salts. Mössbauer spectral data have been reported for three[4,9,10] of these derivatives: they agree well with our results. Including the present work, structural details are now available for five[4,9,10,11] examples. Of these, the anions fall into two classes:

Table 1. Variation with temperature of experimental ($\mu_{\text{eff.}}$) and calculated ($\mu_{\text{calc.}}$) magnetic moments for ferrocenium μ-oxo-bis[trichloroferrate(III)]

$\mu_{\text{eff.}}$/B.M.[a]	$\mu_{\text{calc.}}$/B.M.[b]	T/K
3.27	2.22	295
3.26	2.20	293
3.21	2.13	263
3.18	2.08	236
3.08	1.93	199
3.01	1.81	167
2.93	1.69	136
2.87	1.57	116
2.83	1.49	96.9
2.79	1.43	87.7

[a] Calculated using relative molecular mass = 356. [b] Magnetic moment per iron atom of anion calculated assuming $\mu_{\text{eff.}}$ for the ferrocenium cation is 2.4 B.M., independent of temperature.

Table 2. Mössbauer data for ferrocenium μ-oxo-bis[trichloroferrate(III)]*

T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	$\Gamma_{\frac{1}{2}}$/mm s^{-1}	Area (%)
300	0.238 ± 0.003	1.197 ± 0.003	0.250 ± 0.005	53 ± 2
	0.445 ± 0.004	0.0	0.417 ± 0.009	47 ± 3
150	0.317 ± 0.002	1.215 ± 0.002	0.260 ± 0.004	48 ± 2
	0.550 ± 0.005	0.0	0.571 ± 0.008	52 ± 2
78	0.344 ± 0.001	1.210 ± 0.001	0.285 ± 0.001	48 ± 2
	0.595 ± 0.004	0.0	0.701 ± 0.005	52 ± 2
4.2	0.355 ± 0.002	1.216 ± 0.002	0.313 ± 0.005	51 ± 3
	0.582 ± 0.008	0.0	0.680 ± 0.011	49 ± 3

* Chemical isomer shifts are with respect to 95% ^{57}Fe-enriched foil, errors to one standard deviation; δ, ΔE_Q, and $\Gamma_{\frac{1}{2}}$ are the chemical isomer shift, quadrupole splitting, and full-width at half-height respectively.

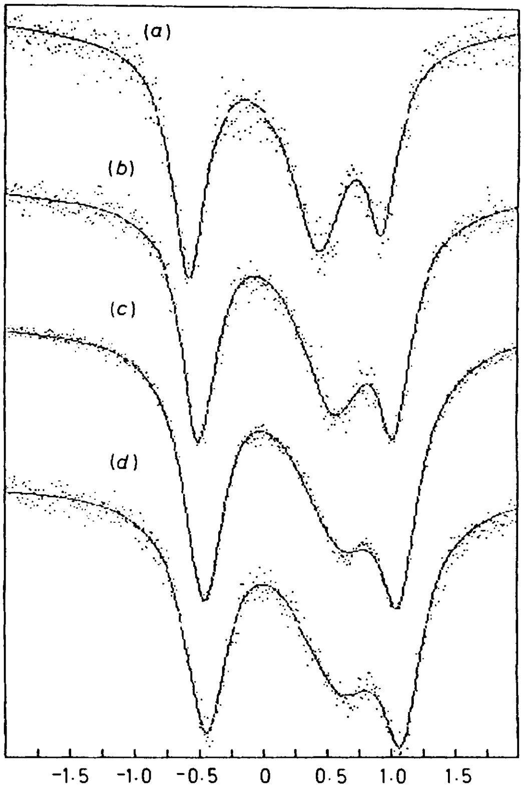


Figure 4. Mössbauer spectra of ferrocenium μ-oxo-bis[trichloroferrate(III)] at (*a*) 300, (*b*) 150, (*c*) 78, and (*d*) 4.2 K

those that have staggered chlorides[9–11] and those that are eclipsed (this work and ref. 4). The known bond lengths of these Fe–O–Fe fragments are similar suggesting that the positions of the Cl atoms do not affect the π bonding. Although the Fe–O–Fe bond angle has a marked effect on the magnetic moment of the anion with the linear examples[9,10] being diamagnetic, the small variations in structure among these examples are probably due to crystal-packing effects. A review of this system is available.[12]

Thus, ferrocenium μ-oxo-bis[trichloroferrate(III)] is a product of reaction of ferrocene with iron(III) chloride. The results of the labelling experiment[3] indicate that ferrocenium and an iron(II) species are primary products. We recorded the Mössbauer spectrum of a high-concentration frozen solution or iron(III) chloride and ferrocene, both containing natural abundance iron. As with the earlier work,[3] we also observed an iron(II) species. This is presumed to be the precursor of the oxy-anion and it would seem as if dioxygen is implicated. The formation of oxy-anions by reaction of ferrocene with Lewis acids is well established as a photochemical process with species such as $[As_4Cl_{10}O_2]^{2-}$ fully identified[13] as a product from this reaction with $AsCl_3$. But our reaction is carried out in an atmosphere of dinitrogen and without deliberate irradiation. The oxidative step remains obscure and we are forced to consider the involvement of solvent molecules as oxygen atoms. However, the origin of this compound has been considered in detail by Neuse *et al.*[5]

Experimental

Magnetic measurements were carried out over the temperature region 80—300 K using the Gouy method on a magnetic balance supplied by Newport Instruments, Newport Pagnell. The calibrant was $Hg[Co(NCS)_4]$. Mössbauer spectra were recorded on a microprocessor-based constant acceleration spectrometer supplied by Cryophysics (U.K.) Ltd. It was calibrated using iron foil and spectral results were fitted using a least-squares program.

Crystal Data for $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeCl_3)_2O]$.—$C_{20}H_{20}Cl_6Fe_4O$, M = 712.48, orthorhombic, a = 14.576(2), b = 13.380(3), c = 14.223(4) Å, U = 2 773.87 Å^3, D_c = 1.634 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 0.7107 Å, F(000) = 1.416, μ = 26.3 cm^{-1}, space group *Pnma* (no. 62).

The crystals were grown from ethyl methyl ketone, absolute ethanol, and diethyl ether solution using the method described.[2] Crystals separated as large dark violet square plates which showed a beet red colouration if observed with transmitted light. *X*-Ray intensities were recorded on a CAD-4 diffractometer using monochromatised Mo-K_α radiation. *X*-Ray intensities of the 17 layers 0—16 were recorded at 292—294 K. Reflections with sin θ/λ ⩽ 0.60 gave 2 866 recorded intensities of which 2 491 were statistically significant with $I > 2\sigma(I)$. The intensities were corrected for Lorentz and polarisation factors but not for absorption.

Least-squares refinement was carried out at the University of Essex PDP-10 computer using the program SHELX.[14] Scattering factors were taken from Cromer and Waber.[15] Atomic co-ordinates are given in Table 3.

Table 3. Positional parameters with estimated standard deviations in parentheses for $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeCl_3)_2O]$

Atom	*x*	*y*	*z*
Anion			
Fe	0.237 92(8)	0.120 62(8)	0.045 85(8)
Cl(1)	0.378 72(21)	0.074 80(27)	0.009 34(31)
Cl(2)	0.144 08(31)	0.076 18(29)	0.932 26(26)
Cl(3)	0.199 61(22)	0.040 93(21)	0.174 69(20)
O	0.232 61(74)	0.25*	0.066 18(78)
Cations			
Fe(3)	0.143 38(11)	0.75*	0.862 63(13)
Fe(4)	0.482 85(11)	0.75*	0.204 72(13)
C(31)	0.489 20(81)	0.197 79(184)	0.366 25(102)
C(32)	0.448 17(107)	0.167 48(139)	0.286 10(110)
C(33)	0.424 77(136)	0.25*	0.232 31(121)
C(34)	0.286 24(64)	0.197 62(72)	0.479 03(69)
C(35)	0.241 88(65)	0.166 09(70)	0.396 96(79)
C(36)	0.214 55(89)	0.25*	0.344 38(106)
C(41)	0.147 59(76)	0.197 80(129)	0.684 75(98)
C(42)	0.095 84(88)	0.169 89(92)	0.610 64(138)
C(43)	0.063 50(119)	0.25*	0.571 47(126)
C(44)	0.388 08(78)	0.190 48(166)	0.776 41(116)
C(45)	0.442 52(121)	0.170 74(105)	0.696 81(144)
C(46)	0.471 14(157)	0.25*	0.661 31(152)

* Parameter fixed.

Determination of Structure.—At the beginning of the structure determination, the position of only one iron atom could be found from the Patterson synthesis. A Fourier synthesis using this iron gave an *R* value of 0.85 and gave the positions of two further iron atoms. Subsequently, these positions were found to be compatible with the Patterson synthesis. Further Fourier synthesis with the additional iron atoms inserted gave an *R* value of 0.79 and allowed the location of the chlorine atoms and, subsequently, the carbon and oxygen atoms. An unsuccessful attempt was made to refine the structure in the non-centrosymmetric space groups: this gave an inferior *R* value and was abandoned.

On insertion of the carbon and oxygen atoms, an *R* value of 0.15 was achieved. There was no difficulty in locating the carbon atoms of ferrocenium(3) and this has staggered cyclopentadienyl rings. The carbon atoms of ferrocenium(4) were refined in an eclipsed conformation but from the state of the difference map, a staggered conformation could equally have been chosen. Hydrogen atoms were located by a difference Fourier map but were not refined. Full-matrix least-squares refinement with the atomic co-ordinates and anisotropic thermal parameters as variables gave an *R* value of 0.12. A further two cycles of least-squares refinement gave an *R* value of 0.108.

The weighted R' $\{= [(\Sigma w\Delta^2/\Sigma w)|F_o|]\}$ was 0.0990 and a distribution of reflections based on $\sin\theta/\lambda$ gave an even distribution of $w\Delta^2$.

Preparation of $[Fe(\eta\text{-}C_5H_5)_2]_2[(FeCl_3)_2O]$.—The compound was prepared following the procedure given[2] for the preparation of ferrocenium trichloroferrate(II).

Anhydrous $FeCl_3$ (0.030 mol, 4.86 g) in diethyl ether (250 cm^3) was added to ferrocene (0.040 mol, 7.44 g) in ethyl methyl ketone (200 cm^3) and ethanol (100 cm^3) under nitrogen over a period of a few minutes. The resulting deep green solution was rotatory evaporated at 70 °C to reduce the solvent to *ca.* 50 cm^3. The pressure was then allowed to rise to atmospheric and the flask cooled to ambient temperature. After 48 h, dark violet crystals had formed and the solvent was orange-brown. The crystals were washed twice with ether, acetone, ethyl methyl ketone, ethanol, and carbon tetrachloride and dried in a vacuum desiccator over $CaCl_2$ (Found: C, 33.6; H, 2.6; Cl, 30.0; Fe, 31.6. $C_{20}H_{20}Cl_6Fe_4O$ requires C, 33.70; H, 2.85; Cl, 29.85; Fe, 31.35%).

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