Reactions of Metal Carbonyl Derivatives. Part 22.[1] The Crystal and Molecular Structures of Dicarbonyl(η-cyclopentadienyl)(ethylthio)iron and μ-Ethylthio-bis[dicarbonyl(η-cyclopentadienyl)iron] Tetrafluoroborate, and a Comparison of their Molecular Parameters

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The solid-state structures of [Fe(cp)(CO)$_2$(SEt)] (1) and [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$] {[BF$_4$]$^-$ salt of (2)} (cp = η-C$_5$H$_5$) have been determined by single-crystal *X*-ray analyses. Compound (1) crystallises in the orthorhombic space group *Pnma* with cell parameters a = 14.118(5), b = 9.822(5), c = 7.443(5) Å, and Z = 4 while the [BF$_4$]$^-$ salt of (2) crystallises in the triclinic space group $P\bar{1}$ with a = 9.41(1), b = 11.36(1), c = 10.04(1) Å, α = 99.77(1), β = 104.40(1), γ = 67.83(1)°, and Z = 2. The structures have been solved by conventional Patterson and Fourier techniques and refined to R = 0.049 and 0.030 for 885 and 2 197 independent reflections respectively. Molecule (1) lies on a mirror plane of symmetry with the cyclopentadienyl group being disordered. The cation (2) has symmetry C_1 and contains the two cyclopentadienyl groups *cis* disposed with respect to the Fe(1)SFe(2) plane. The ct(cp)–Fe(1)–Fe(2)–ct(cp) [ct(cp) = centroid of the cyclopentadienyl group] torsional angle τ' is 58.2°. The Fe–S bond distance and the Fe–S–C bond angle remain essentially unaltered on co-ordination of (1) to [Fe(cp)(CO)$_2$]$^+$ to give (2). The n.m.r. data for the salt of (2) are interpreted in terms of fluxional behaviour in solution.

VERY few studies have been undertaken with the prime aim of establishing whether co-ordination of a particular ligand to a transition metal is accompanied by significant changes in the bond distances and the bond angles associated with the donor atom. Further, as far as we are aware, no investigations of this type have been reported which involve ligands containing donor atoms already bonded directly to a metal atom. Two ligands which have been analysed structurally before and after co-ordination are glyoxime[2] and the Schiff base *NN'*-*o*-phenylenebis(salicylideneimine).[3] Significant bond-distance and conformational changes were observed in both cases.

We have shown earlier that the metal-containing ligands MR(PPh$_2$) and MR(SEt) [MR = Fe(cp)(CO)$_2$ (cp = η-C$_5$H$_5$)] may be utilised in the synthesis of unusual polynuclear and metal cluster derivatives[4] and in particular that reaction of [Fe(cp)(CO)$_2$(SEt)] (1) with [Fe(cp)(CO)$_2$(solvent)]$^+$ [solvent = acetone or tetrahydrofuran (thf)] affords [{Fe(cp)(CO)$_2$}$_2$SEt]$^+$ (2).[5] Compounds (1) and (2) may be considered as being respectively the 1 : 1 and 1 : 2 adducts of [SEt]$^-$ and [Fe(cp)(CO)$_2$]$^+$. An *X*-ray crystallographic analysis of the two would thus provide a unique opportunity of establishing the effect of co-ordination of a donor ligand to an acceptor group identical to that to which the donor atom is already bonded on the molecular parameters associated with the latter atom.

EXPERIMENTAL

The compounds were prepared as described previously.[5,6] Infrared measurements were made on a Beckmann IR 12 spectrophotometer, while ^{1}H n.m.r. spectra were recorded on a Varian XL 100 instrument.

Crystal Data.—(*a*) C$_9$H$_{10}$FeO$_2$S, (1), M = 238.08, brown orthorhombic prisms, a = 14.118(5), b = 9.822(5), c = 7.443(4) Å, U = 1 032.10 Å^3, D_m = 1.51 g cm^{-3} (by flotation, ZnBr$_2$–NaCl solution), Z = 4, D_c = 1.53 g cm^{-3}, space group *Pnma*, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 15.43 cm^{-1}, F(000) = 488. (*b*) C$_{16}$H$_{15}$BF$_4$Fe$_2$O$_4$S, [BF$_4$]$^-$ salt of (2), M = 501.88, red-brown triclinic lozenges, a = 9.41(1), b = 11.36(1), c = 10.04(1) Å, α = 99.77(1), β = 104.40(1), γ = 67.83(1)°, U = 959.24 Å^3, D_m = 1.69 g cm^{-3} (by flotation, *m*-xylene–MeI), D_c = 1.69 g cm^{-3}, space group $P\bar{1}$, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 15.90 cm^{-1}, F(000) = 504.

Collection and Reduction of Data.—(*a*) [Fe(cp)(CO)$_2$(SEt)]. Preliminary cell dimensions and systematic absences were determined from oscillation, Weissenberg, and precession photographs. Accurate cell parameters were obtained from a least-squares analysis of the settings of 25 reflections measured on a Philips PW1100 four-circle diffractometer

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with graphite-monochromated Mo-K_α radiation. Three-dimensional intensity data were collected by the ω—2θ scan technique (scan width 1.2θ°, scan speed 0.04θ° s^{-1}) in the range $6 \leqslant 2\theta \leqslant 54°$ from a ground spherical crystal of diameter 0.45 mm. Three reference reflections monitored every 44 reflections measured had intensities which remained constant to within $\simeq 6\%$. A total of 1 178 reflections was collected, 229 of which were systematically absent or space-group equivalent. Of the remainder, 885 reflections had $I > 2.0\sigma(I)$ and were considered observed. No absorption corrections were made (for μR 0.69 the variation in A^* over the θ range employed is $< 5\%$) [7] but anomalous-dispersion corrections were applied to the iron-atom scattering curve.[8]

(*b*) $[\{Fe(cp)(CO)_2\}_2SEt][BF_4]$. Both preliminary and accurate cell parameters, and space-group symmetry, were determined as for (1). Three-dimensional intensity data were collected at a scan width of 1.4θ° and speed of 0.05θ° s^{-1} (ω—2θ scan technique) in the range $8 \leqslant 2\theta \leqslant 44°$ from a ground crystal of diameter 0.40 mm. The intensities of three reference reflections monitored after every 60 measured reflections remained constant to within 5%. 2 341 Reflections were collected of which 24 were rejected as being space-group equivalent and 120 had $I < 2.0\sigma(I)$. Lorentz-polarisation corrections were applied. No absorption corrections were made (for μR 0.64 the variation in A^* for the θ range employed was $< 5\%$) [7] but anomalous-dispersion corrections were applied to the heavy-atom scattering curves.[8]

Structure Determination and Refinement.—(*a*) $[Fe(cp)(CO)_2(SEt)]$. Analysis of a three-dimensional Patterson map [9] yielded the position of the iron atom. Since the systematic absences in the data, $hk0$, $h = 2n + 1$, and $0kl$, $k + l = 2n + 1$, indicated either the centrosymmetric space group *Pnma* or the non-centrosymmetric space group $Pn2_1a$ it was necessary to determine whether the structure was centrosymmetric or not. Normalised structure factors were calculated [10] and a statistical analysis indicated a centrosymmetric space group (average $|E^2 - 1| = 1.013$, average $|E| = 0.779$, $|E| > 1 = 33.1\%$, $|E| > 2 = 4.1\%$, $|E| > 3 = 0.01\%$). Successful refinement of the structure vindicated the choice of *Pnma*. An electron-density map phased on the iron atom revealed the positions of all of the non-hydrogen atoms in the asymmetric unit. Further refinement and a subsequent difference-Fourier map yielded the positions of the ethyl hydrogens. A final four cycles of refinement, including these hydrogen atoms, in which non-hydrogen atoms were assigned anisotropic temperature factors, resulted in an *R* value of 0.045. However, examination of the bond lengths and the anisotropic temperature factors associated with the cyclopentadienyl ring and an electron-density map thereof suggested that the ring was disordered. Refinement was therefore continued using a structure comprising two coplanar half-rings with isotropic temperature factors. Another four cycles of refinement were carried out allowing the site-occupancy factors of the carbon atoms in each half-ring to refine as two independent variables. After refinement their sum was 1.1 indicating that the model employed was a reasonable one. During the final four cycles of refinement, in which all the non-hydrogen atoms except the cyclopentadienyl carbon atoms had anisotropic temperature factors, the site-occupancy factors of the two half-cyclopentadienyl rings were allowed to vary with the restriction that their sum be equal to 1. The refinement converged to *R* 0.049.

(*b*) $[\{Fe(cp)(CO)_2\}_2SEt][BF_4]$. Analysis of a three-dimensional Patterson map yielded the positions of the two iron atoms.[9] A subsequent electron-density map based on the co-ordinates of these atoms followed by four cycles of accelerated least-squares refinement [9] revealed the positions of all the non-hydrogen atoms. Another four cycles of least-squares refinement in which all the atoms were assigned anisotropic temperature factors resulted in an *R* value of 0.046. In a final five cycles of refinement the hydrogen atoms were constrained to ride on their parent carbon atoms with C–H set at 1.08 Å, and with the geometry of their positions dictated by the types of carbon atoms involved. The isotropic temperature factors were refined as a single parameter for each type of hydrogen. The refinement converged to *R* 0.030.

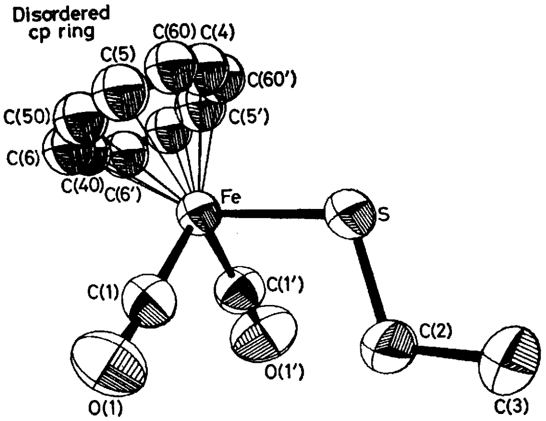

FIGURE 1 Molecular geometry of $[Fe(cp)(CO)_2(SEt)]$ showing the atomic nomenclature used in the analysis

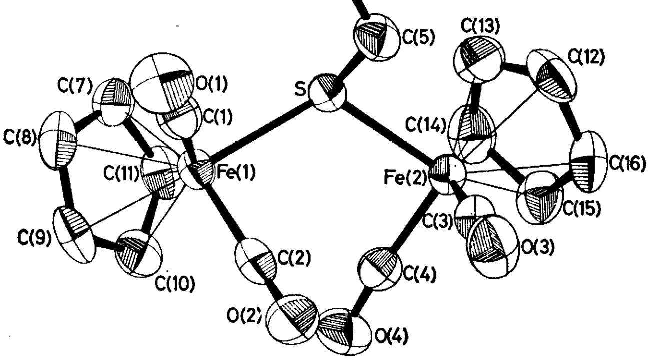

FIGURE 2 Molecular geometry of $[\{Fe(cp)(CO)_2\}_2SEt]^+$ showing the atomic nomenclature used in the analysis

Final atomic parameters for (1) and the $[BF_4]^-$ salt of (2) are in Table 1. Analyses of variance computed after the final cycles, observed and calculated structure factors, and thermal parameters for both compounds are listed in

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[7] 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1967, vol. 2, pp. 291—312.

[8] D. J. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] G. M. Sheldrick, Cambridge, 1975.

[10] Program NORMSF of the '*X*-Ray '72' library of crystallographic programs, Technical Report Tr-192, the Computer Science Centre, University of Maryland, version of July 1972.

TABLE 1

Fractional atomic co-ordinates (Å × 10^4) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
(*a*) [Fe(cp)(CO)$_2$(SEt)]			
Fe	2 272(1)	7 500	12 573(1)
S	1 970(1)	7 500	9 542(2)
C(1)	1 443(4)	8 802(6)	12 900(6)
O(1)	924(3)	9 686(5)	13 137(7)
C(1′)	1 443(4)	6 198(6)	12 900(6)
O(1′)	924(3)	5 314(5)	13 137(7)
C(2)	689(5)	7 500	9 276(10)
C(3)	436(7)	7 500	7 266(10)
C(4)	3 166(8)	7 500	14 869(17)
C(5)	3 349(7)	8 671(11)	13 832(15)
C(5′)	3 349(7)	6 329(11)	13 832(15)
C(6)	3 686(7)	8 191(12)	12 112(13)
C(6′)	3 686(7)	6 809(12)	12 112(13)
C(40)	3 704(13)	7 500	11 977(25)
C(50)	3 508(9)	8 597(15)	12 945(22)
C(50′)	3 508(9)	6 403(15)	12 945(22)
C(60)	3 145(9)	8 221(14)	14 633(19)
C(60′)	3 145(9)	6 779(14)	14 633(19)
(*b*) [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$]			
Fe(1)	7 075(6)	1 812(5)	1 731(5)
Fe(2)	4 010(6)	2 472(5)	4 057(5)
S(1)	4 848(11)	3 173(9)	2 473(10)
C(1)	6 352(46)	2 055(39)	−43(45)
O(1)	5 986(40)	2 168(33)	−1 197(31)
C(2)	6 575(43)	422(42)	1 549(39)
O(2)	6 271(35)	−478(30)	1 425(33)
C(3)	3 312(48)	1 441(42)	2 763(48)
O(3)	2 855(38)	775(32)	1 930(37)
C(4)	5 835(52)	1 270(42)	4 642(43)
O(4)	6 951(39)	485(33)	5 077(35)
C(5)	3 173(45)	3 516(41)	987(42)
C(6)	3 138(59)	4 563(45)	205(50)
C(7)	8 335(45)	3 045(41)	2 562(43)
C(8)	8 369(44)	2 340(41)	3 609(39)
C(9)	9 079(44)	1 042(43)	3 243(43)
C(10)	9 490(45)	915(46)	1 950(47)
C(11)	9 050(47)	2 168(47)	1 548(44)
C(12)	1 900(54)	3 978(47)	4 262(47)
C(13)	3 174(64)	4 395(42)	4 850(52)
C(14)	4 134(53)	3 638(45)	5 924(46)
C(15)	3 449(51)	2 741(44)	6 003(42)
C(16)	2 083(51)	2 954(48)	4 987(45)
B(1)	398(65)	7 255(52)	2 442(56)
F(1)	−434(35)	8 135(27)	3 357(28)
F(2)	91(44)	7 780(34)	1 250(30)
F(3)	−50(46)	6 220(34)	2 213(41)
F(4)	1 967(35)	6 862(35)	3 041(33)
H(51) *	209(4)	381(4)	135(4)
H(52)	328(4)	265(4)	29(4)
H(61)	212(5)	459(4)	−59(4)
H(62)	414(5)	436(4)	−23(4)
H(63)	291(5)	546(4)	81(4)
H(7)	784(4)	407(4)	254(4)
H(8)	792(4)	273(4)	454(3)
H(9)	927(4)	26(4)	384(4)
H(10)	1 003(4)	3(4)	137(4)
H(11)	923(4)	240(4)	62(4)
H(12)	95(5)	437(4)	341(4)
H(13)	337(6)	516(4)	452(5)
H(14)	520(5)	372(4)	657(4)
H(15)	390(5)	201(4)	672(4)
H(16)	129(5)	242(4)	478(4)

* Co-ordinates in Å × 10^3. *U* refined to 0.074, 0.113, and 0.078Å^2 for the CH$_2$, CH$_3$, and cyclopentadienyl hydrogens respectively.

Supplementary Publication No. SUP 22247 (24 pp.).* All the calculations were carried out on a UNIVAC 1106 computer at the University of Cape Town.

RESULTS AND DISCUSSION

The molecular geometry of [Fe(cp)(CO)$_2$(SEt)] (1) and [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$], {[BF$_4$]$^-$ salt of (2)}, and the atomic nomenclature utilised in their description are shown in Figures 1 and 2 respectively. Selected bond lengths and bond angles are given in Tables 2 and 3 while least-squares planes and torsion angles are in Table 4.

TABLE 2

Selected bond lengths (Å) with estimated standard deviations in parentheses

(*a*) [Fe(cp)(CO)$_2$(SEt)]			
Fe(1)–S(1)	2.296(2)	Fe(1)–C(1)	1.751(5)
S(1)–C(2)	1.819(7)	C(2)–C(3)	1.539(9)
C(1)–O(1)	1.150(6)	Fe(1)–C(4)	2.12(1)
Fe(1)–C(5)	2.12(1)	Fe(1)–C(6)	2.14(1)
Fe(1)–C(40)	2.07(2)	Fe(1)–C(50)	2.07(1)
Fe(1)–C(60)	2.09(1)	C(4)–C(5)	1.41(1)
C(5)–C(6)	1.45(1)	C(6)–C(6′)	1.36(2)
C(40)–C(50)	1.33(2)	C(50)–C(60)	1.41(2)
C(60)–C(60′)	1.42(3)		
(*b*) [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$]			
Fe(1)–S(1)	2.297(2)	Fe(2)–S(1)	2.304(2)
Fe(1)–C(1)	1.770(6)	Fe(1)–C(2)	1.780(6)
Fe(2)–C(3)	1.770(6)	Fe(2)–C(4)	1.778(6)
S(1)–C(5)	1.851(5)	C(5)–C(6)	1.520(7)
C(1)–O(1)	1.139(5)	C(2)–O(2)	1.142(5)
C(3)–O(3)	1.144(6)	C(4)–O(4)	1.134(6)
Fe(1)–C(7)	2.104(6)	Fe(1)–C(8)	2.103(6)
Fe(1)–C(9)	2.100(6)	Fe(1)–C(10)	2.081(6)
Fe(1)–C(11)	2.101(6)	Fe(2)–C(12)	2.105(6)
Fe(2)–C(13)	2.109(6)	Fe(2)–C(14)	2.108(6)
Fe(2)–C(15)	2.093(6)	Fe(2)–C(16)	2.093(6)
C(7)–C(8)	1.413(7)	C(8)–C(9)	1.397(7)
C(9)–C(10)	1.414(7)	C(10)–C(11)	1.424(7)
C(7)–C(11)	1.405(7)	C(12)–C(13)	1.411(8)
C(13)–C(14)	1.400(8)	C(14)–C(15)	1.417(7)
C(15)–C(16)	1.397(7)	C(12)–C(16)	1.410(7)
B(1)–F(1)	1.383(7)	B(1)–F(2)	1.347(7)
B(1)–F(3)	1.360(8)	B(1)–F(4)	1.376(7)

TABLE 3

Selected bond angles (°) with estimated standard deviations in parentheses

(*a*) [Fe(cp)(CO)$_2$(SEt)]			
S(1)–Fe(1)–C(1)	90.7(2)	C(1)–Fe(1)–C(1′)	93.9(2)
Fe(1)–S(1)–C(2)	107.0(2)	Fe(1)–C(1)–O(1)	177.6(5)
C(5)–C(4)–C(5′)	109(2)	C(4)–C(5)–C(6)	106(2)
C(5)–C(6)–C(6′)	109(2)	C(50)–C(40)–C(50′)	109(2)
C(40)–C(50)–C(60)	110(2)	C(50)–C(60)–C(60′)	105(2)
(*b*) [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$]			
Fe(1)–S(1)–Fe(2)	117.4(2)	S(1)–Fe(1)–C(1)	96.4(2)
S(1)–Fe(1)–C(2)	95.3(2)	S(1)–Fe(2)–C(3)	91.1(2)
S(1)–Fe(2)–C(4)	96.2(2)	C(1)–Fe(1)–C(2)	92.6(2)
C(3)–Fe(2)–C(4)	94.4(2)	Fe(1)–S(1)–C(5)	109.5(2)
Fe(2)–S(1)–C(5)	104.4(2)	S(1)–C(5)–C(6)	110.0(4)
Fe(1)–C(1)–O(1)	175.3(2)	Fe(1)–C(2)–O(2)	179.1(4)
Fe(2)–C(3)–O(3)	179.7(2)	Fe(2)–C(4)–O(4)	175.3(4)
Mean internal angle of cp ring bound to Fe(1)	108.0(7)		
Mean internal angle of cp ring bound to Fe(2)	108.0(5)		
F–B–F (mean)	109.5(1.5)		

Compound (1) reveals no unusual features. The molecule is essentially octahedral with the cyclopentadienyl group occupying three co-ordination sites. It is bisected by a crystallographic mirror plane which contains the iron and sulphur atoms and the two carbons of the ethyl group. The cyclopentadienyl group is disordered with the two half-rings comprising it being essentially coplanar regular pentagons. The average

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

angle subtended at the centroid of the cyclopentadienyl group by a vertex of one of the half-rings and an adjacent vertex of the other ring is 36°. The bond lengths and bond angles in the compound do not deviate from values expected.

TABLE 4

Least-squares planes and torsion angles. The equations of the planes are expressed in orthogonalised space as $PX + QY + RZ = S$, d is the perpendicular distance from each atom to the plane in Å, and atoms marked with an asterisk were not included in the calculation

(*a*) [Fe(cp)(CO)$_2$(SEt)]

Plane 1: C(4), C(5), C(6), C(5′), C(6′)

$$1.2755x + 0.0y + 2.5327z = 7.9579$$

	d		*d*		*d*
C(4)	0.011	C(5)	−0.009	C(6)	0.003
C(5′)	−0.009	C(6′)	0.003	C(40) *	0.007
C(50) *	−0.023	C(60) *	−0.076	C(50′) *	−0.023
C(60′)	−0.076	Fe *	−1.757		

(*b*) [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$]

Plane 1: C(7), C(8), C(9), C(10), C(11)

$$8.3339x + 3.8655y + 2.2834z = 5.7767$$

	d		*d*		*d*
C(7)	−0.004	C(8)	0.002	C(9)	−0.003
C(10)	−0.001	C(11)	−0.029	Fe(1) *	1.714

Plane 2: C(12), C(13), C(14), C(15), C(16)

$$-4.5978x + 4.0791y + 6.9935z = 2.7466$$

	d		*d*		*d*
C(12)	−0.001	C(13)	0.003	C(14)	0.002
C(15)	−0.003	C(16)	−0.005	Fe(2) *	1.726

Angle between planes 1 and 2: 97.4°

Torsion angles (°):

C(1)–Fe(1)–Fe(2)–C(3)	−52.0	C(1)–Fe(1)–Fe(2)–C(4)	−150.1
C(2)–Fe(1)–Fe(2)–C(3)	31.4	C(2)–Fe(1)–Fe(2)–C(4)	−66.7

The molecular packing in the unit cell is shown in Figure 3. No intermolecular close contacts are observed; the average volume occupied by a non-hydrogen atom is 19.9 Å^3.

Compound (2) consists of two Fe(cp)(CO)$_2$ moieties bridged symmetrically by an ethanethiolate group. The two cyclopentadienyl groups are *cis* disposed with respect to the Fe(1)S(1)Fe(2) plane but lie on either side of the plane orthogonal to the latter and containing the

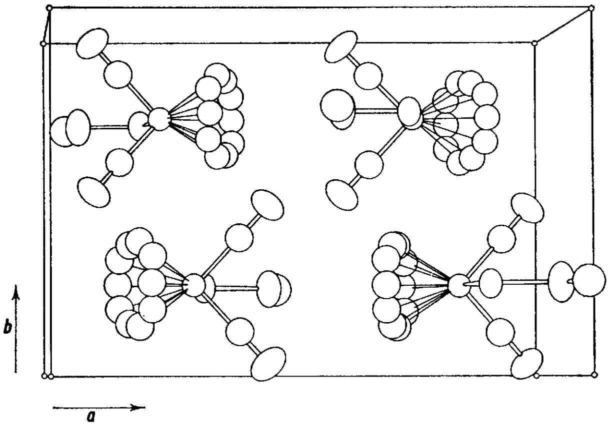


FIGURE 3 Molecular packing in the unit cell of [Fe(cp)(CO)$_2$(SEt)] as projected onto the (001) plane

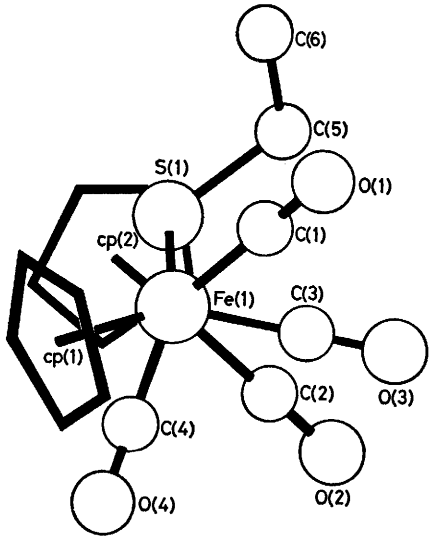


FIGURE 4 The ion [{Fe(cp)(CO)$_2$}$_2$SEt]$^+$ as viewed down the Fe–Fe vector

TABLE 5

Comparison of the molecular symmetry, the ct(cp)–M(1)–M(2)–ct(cp), τ′, and X–M(1)–M(2)–ct(cp), τ″, torsion angles, the M–M and M–X bond distances, and the M–X–M bond angles for some compounds of the type [{M(cp)(CO)$_2$}$_2$X] [a]

		Angle (°)		Distance/Å		Angle (°)
Compound	Molecular [b] symmetry	τ′	τ″	Fe–Fe or Mn–Mn	Fe–X (av.) or Mn–X (av.)	Fe–X–Fe or Mn–X–Mn
[{Fe(cp)(CO)$_2$}$_2$GeCl$_2$] [c]	C_2	75.8	142.1	4.24	2.36	128.4
[{Fe(cp)(CO)$_2$}$_2$SnCl$_2$] [d]	C_2	71.2	144.4	4.49	2.49	128.6
[{Fe(cp)(CO)$_2$}$_2$SnMe$_2$] [e]	near C_2	87.4	134.3	4.59	2.60	123
[{Fe(cp)(CO)$_2$}$_2$Sn(cp)$_2$] [f]	C_2	104.5	127.8	4.36	2.57	115.9
[{Fe(cp)(CO)$_2$}$_2$Sn(ONO)$_2$] [g]	C_2	44.7	157.7	4.57	2.56	126
[{Fe(cp)(CO)$_2$}$_2$SbCl$_2$][Sb$_2$Cl$_7$] [h]						
(cation 1)	near C_2	71.8	137.7	4.51	2.45	134.6
(cation 2)	near C_2	76.7	141.0	4.50	2.44	134.9
[{Fe(cp)(CO)$_2$}$_2$SO$_2$] [i]	near C_2	98.9	128.7	3.91	2.28	118.0
[{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$]	C_1	58.2	255.2	3.93	2.30	117.4
[{Fe(cp)(CO)$_2$}$_2$I][BF$_4$] [j]	near C_2	153.0	105.49	4.26	2.59	110.8
[{Mn(cp)(CO)$_2$}$_2$CCHPh] [k]				2.73	1.97	88.0
[{Mn(Mecp)(CO)$_2$}$_2$SEt][ClO$_4$] [l]	near C_2	156.3	98.4	2.93	2.26	81.0

[a] ct(cp) = Centroid of the cyclopentadienyl group; M = Fe or Mn, X = bridging group. [b] The groups attached to the bridging atom have not been taken into consideration in determining the molecular symmetry. For C_2 symmetry, $2\tau'' + \tau' = 360°$. [c] Ref. 11. [d] Ref. 12. [e] Ref. 13. [f] Ref. 14. [g] Ref. 15. [h] Ref. 16. [i] Ref. 17. [j] Ref. 18. [k] A. N. Nesmeyanov, G. G. Aleksandrov, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *J. Organometallic Chem.*, 1976, **110**, C36. [l] Ref. 28.

Fe(1)–Fe(2) vector. The ct(cp)–Fe(1)–Fe(2)–ct(cp) [ct(cp) = centroid of the cyclopentadienyl group] torsion angle τ' is 58.2°. Figure 4 illustrates the cation as viewed along the Fe(1)–Fe(2) vector. The conformation of (2) contrasts with those for other compounds or species of the type $[\{Fe(cp)(CO)_2\}_2X]$ (X = bridging ligand) whose structures have been accurately determined.[11-18] These all have C_2 or near-C_2 symmetry as illustrated in Figure 5; their ct(cp)–Fe(1)–Fe(2)–ct(cp), τ', and X–Fe(1)–Fe(2)–ct(cp), τ'', torsion angles are given in Table 5.* The difference in conformation between (2) and those compounds tabulated can no doubt be associated with the bridging groups in the latter having local C_{2v} symmetry unlike the bridging ethanethiolate ligand. Approximate conformational calculations using the device of empirical atom pair potentials[20] indicate two preferred conformations for (2), neither of which are C_2. The calculated torsion angles for the two are $\tau' = 55.7°$ and $\tau'' = 255.4°$ and $\tau' = 157.6°$ and $\tau'' = 30.8°$ respectively, the former conformation being, in fact, that adopted by (2) in the crystals under investigation (τ' 58.2 and τ'' 255.2°). Attempts to isolate crystals of the $[BF_4]^-$ salt of (2) having the latter conformation and suitable for crystallographic studies were unsuccessful, but significantly in early syntheses the uncrystallised salt gave only two C–O stretching peaks in the solid-state i.r. spectrum whereas the crystal batch employed for the *X*-ray analysis gives three, all of approximately equal intensity.

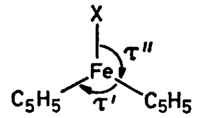
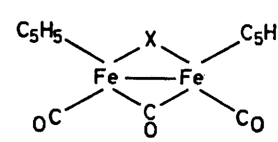


FIGURE 5 The normal conformation of molecules of the type $[\{Fe(cp)(CO)_2\}_2X]$ (X = bridging ligand) as viewed along the Fe–Fe vector. Carbonyl groups have been omitted for clarity

Similar to what is found for (1), the iron atoms in (2) are roughly octahedral while the sulphur environment is distorted tetrahedral. An ' electron count ' predicts the absence of a Fe–Fe bond and consistent with this is the Fe–S–Fe bond angle of 117.4° and the Fe–Fe distance of 3.93 Å. The latter is very similar to that found for $[\{Fe(cp)(CO)_2\}_2SO_2]$[17] but considerably less than the corresponding distances for the other compounds of the type $[\{Fe(cp)(CO)_2\}_2X]$ referred to in Table 5. The shorter Fe–Fe distances for the sulphur-bridged compounds are obviously associated with the shorter Fe–S distances as compared with the other Fe–X distances. Significantly, while the $[BF_4]^-$ salt of (2) and $[\{Fe(cp)(CO)_2\}_2SO_2]$ readily lose carbon monoxide to produce $[Fe_2(cp)_2(CO)_3(SEt)][BF_4]$ ($[BF_4]^-$ salt of 3; X = SEt), and $[Fe_2(cp)_2(CO)_3(SO_2)]$ (3; X = SO_2), respectively,[1,5,21,22] analogous reactions involving the other bridged compounds given in Table 5 (which possess longer Fe–Fe and Fe–X distances) have not been reported.†



(3)

A recent crystallographic study on a series of substituted derivatives of $[Fe_3(CO)_{12}]$ has indicated that the maximum distance by which two iron atoms in compounds of this type can be separated and remain bridged by a carbonyl group is *ca.* 2.7 Å.[25] If a maximum Fe–Fe distance of this order is imposed on compounds of type (3), those with the longer Fe–X bonds will have abnormally large X–Fe–C and small Fe–X–Fe bond angles. This will lead to increased steric strain which in turn will account for the inability to convert those $[\{Fe(cp)(CO)_2\}_2X]$ species having the larger Fe–X distances into derivatives of type (3). The inability[26] to produce $[Fe_2(cp)_2(CO)_3(PPh_2)]^+$ by irradiation of $[\{Fe(cp)(CO)_2\}_2(PPh_2)]^+$ can be explained along these lines.

In contrast to the examples mentioned earlier in the text,[2,3] co-ordination of (1) to $[Fe(cp)(CO)_2]^+$ to afford (2) is not accompanied by any significant change in the bond distances and angles associated with the donor

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* In making this comparison consideration has only been given to those compounds or species with simple bridging ligands, *e.g.* I, SO_2, SnR_2, *etc.* The compound $[\{Fe(cp)(CO)_2\}_3SbCl]^+$ (ref. 19) can of course also be regarded as a species of the type $[\{Fe(cp)(CO)_2\}_2X]$ with X = $[ClSbFe(cp)(CO)_2]^+$. Significantly, the relative orientation of two of the Fe(cp)(CO)$_2$ fragments (2) and (3) in this cation is that illustrated in Figure 5 [ct(cp)–Fe(2)–Fe(3)–ct(cp) 100.3, Sb–Fe(2)–Fe(3)–ct(cp) 130.1° (the numbering scheme is that adopted by Dahl *et al.*[19])]. On the other hand, the disposition of fragments (1) and (3) with respect to each other is similar to that found in compound (3) [ct(cp)–Fe(1)–Fe(3)–ct(cp) 8.0, Sb–Fe(1)–Fe(3)–ct(3) 113.3°].

† The compounds $[Fe_2(cp)_2(CO)_3(GeMe_2)]$[23] and $[Fe_2(cp)_2(CO)_3(MPh_2)]$ (M = Si, Ge, or Sn)[24] are known but Fe–Fe and Fe–X bond distances for the parent tetracarbonyl derivatives, $[\{Fe(cp)(CO)_2\}_2(GeMe_2)]$ and $[\{Fe(cp)(CO)_2\}_2(MPh_2)]$, are not available.

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atom. Thus the Fe–S distance and the Fe–S–C(ethyl) angle for (1) are essentially the same as the corresponding parameters for (2). However, a real, albeit small, increase in the average Fe–C(terminal carbonyl) bond distance of 0.025 Å (4σ) and a similar small decrease in the average C–O bond distance are observed on co-ordination. This respective increase and decrease is consistent with the i.r. data; the lowering of the C–O stretching frequencies from (2) to (1) [ν(C–O) at 2 053s, 2 042m (sh), and 2 007s cm^{-1} in CH_2Cl_2 for (2); at 2 029s and 1 981s cm^{-1} in CH_2Cl_2 for (1)] is explained in terms of increased back donation from the iron to the carbonyl groups and increased occupancy of the C–O antibonding orbitals. The apparent insensitivity of the Fe–S bond distance to decreased electron density on the iron atom, as revealed by the i.r. data, is somewhat surprising, particularly if the increase in the S–C bond distance from (1) to (2) [1.819(7) to 1.851(5) Å] is taken into account, and presumably reflects two opposing electronic effects. The increase in the Fe–S bond length that might result from the increased co-ordination about the sulphur atom is evidently counterbalanced by the increased positive charge on the iron atoms in moving from the neutral monomer to the cationic dimer.

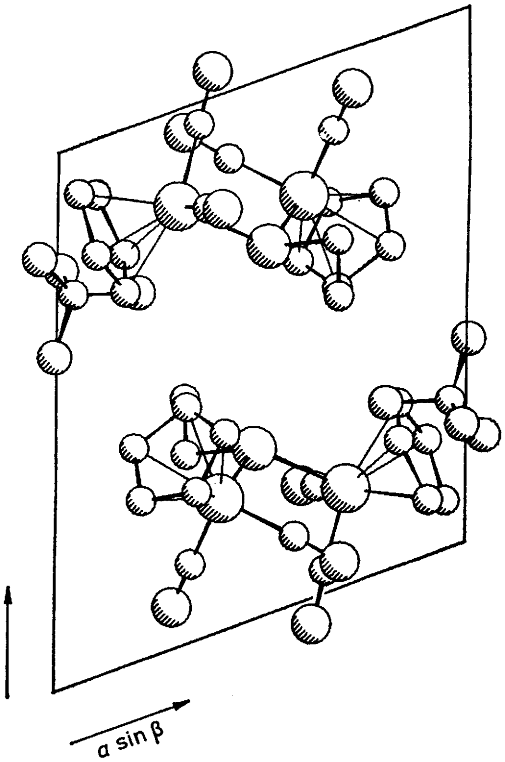

FIGURE 6 Molecular packing in the unit cell of [{Fe(cp)(CO)$_2$}$_2$SEt][BF$_4$] as projected on to the (001) plane

The average volume occupied by a non-hydrogen atom in the unit cell of the [BF$_4$]$^-$ salt of (2) is 17.1 Å^3. The packing is thus closer than in (1). A projection of the molecular packing in the unit cell on to the (001) plane is shown in Figure 6.

Compounds of the type [{Fe(cp)(CO)$_2$}$_2$X] can adopt a number of distinct conformations in which the molecular symmetry is higher than C_1.* These are illustrated in Figure 7. The two cyclopentadienyl rings are magnetically equivalent for conformations (A)—(D), (F), and (G) but non-equivalent for (E); for X = SEt, however, conformations (C) and (D) contain non-equivalent cyclopentadienyl groups. The ^{1}H n.m.r. spectrum of the [BF$_4$]$^-$ salt of (2) contains a single cyclopentadienyl resonance down to a temperature of −60 °C [in $(D_3C)_2CO$]. Although this is consistent with conformations (A), (B), (F), and (G), these are eliminated as possible structures for (2) in solution on the basis of steric considerations. Conformation (D) is that adopted by the majority of compounds of the type [{Fe(cp)(CO)$_2$}$_2$X] in the solid state.[11—18,†] and although the n.m.r. evidence is not consistent with (2) having a rigid structure of this conformation in solution it can readily be reconciled in terms of the presence of two rapidly interconverting enantiomers of this stereochemistry.

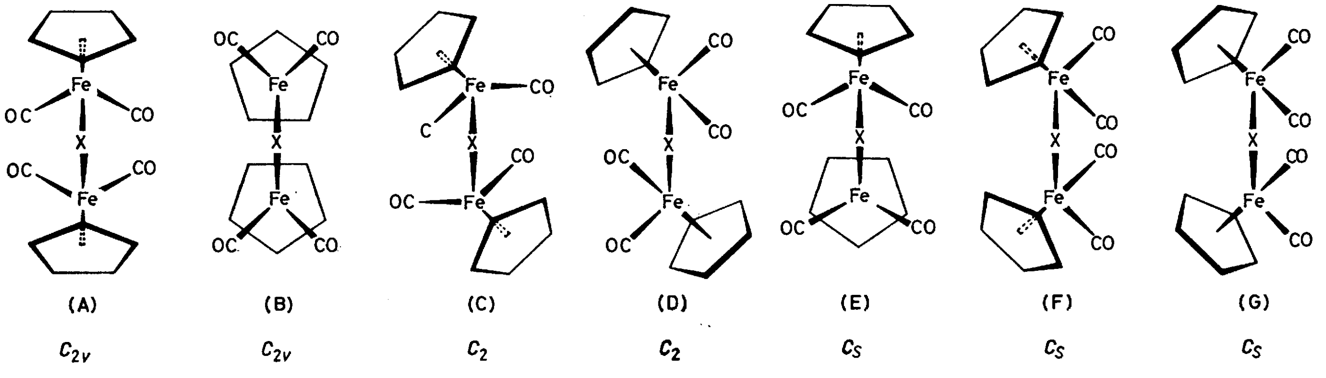

FIGURE 7 Possible conformations of compounds of the type [{Fe(cp)(CO)$_2$}$_2$X] (X = bridging group) with symmetry higher than C_1 as viewed directly above the bridging atom. Groups attached to the bridging atom have not been taken into consideration in determining the molecular symmetry

* In establishing the symmetry of the molecule, groups attached to the bridging atom have not been taken into consideration.

† It has previously been proposed [27] that [{Fe(cp)(CO)$_2$}$_2$X] (X = GeMe$_2$, SnMe$_2$, or SnEt$_2$) adopt conformation (E) in solution whereas [{Fe(cp)(CO)$_2$}$_2$X′] (X′ = GeCl$_2$, GeI$_2$, SnCl$_2$, or SnI$_2$) adopt a conformation of symmetry C_1 in this phase. However, this proposal was based primarily on i.r. intensity data and needs to be confirmed by more substantial evidence.

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Fluxional behaviour of this nature has been observed previously for [{Mn(Mecp)(CO)$_2$}$_2$SEt][ClO$_4$] in solution.[28] This species, which has near-C_2 symmetry in the solid state (not taking into consideration the ethyl group), contrasts with (2) in that it contains a metal–metal bond; the latter will undoubtedly lead to a higher barrier to rotation about the Mn–S bonds and to less ready interconversion of the two enantiomers of this cation compared with (2). The solid-state i.r. spectrum of the [BF$_4$]$^-$ salt of (2) contains three C–O stretching modes, all of comparable intensity (2 050, 2 035, and 1 996 cm^{-1}). The solution spectrum reveals a similar pattern except that one of the peaks is present as a shoulder [2 053s, 2 042m (sh), and 2 007s cm^{-1} in CH$_2$Cl$_2$]. Although this might be interpreted in terms of the salt adopting different stereochemistries in solution and the solid state, the conformational calculations described earlier in the text indicate that this will not be the case. However, irrespective of whether (2) adopts C_1 or C_2 symmetry in solution it is apparent that it must exhibit fluxional behaviour.

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