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Structural determination of a trinuclear iron–cobalt mixed cluster complex bicapped with sulfur

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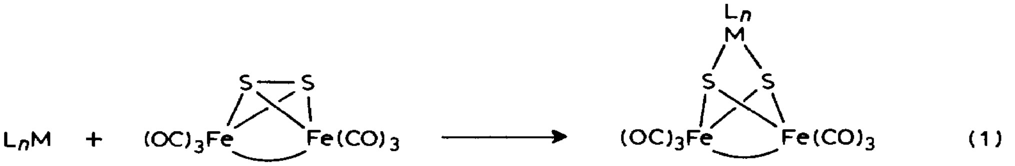
Abstract

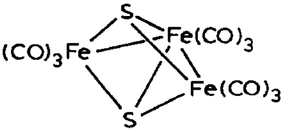
The cluster complex $[Fe_2(CO)_6(CoZCp)(S)_2]$ obtained from the reaction of $[Co(ZCp)(CO)_2]$ ($ZCp = \eta^5$-$C_5H_4CO_2Me$) with (μ-dithio)bis(tricarbonyliron) has been subjected to an X-ray diffraction study. Contrary to expectation, two Co–Fe bonds were newly formed while the Fe–Fe bond present in the starting complex was cleaved by the reaction. The weak $(CO)_3Fe$–$Fe(CO)_3$ bond compared to the CpCo–CoCp and CpCo–$Fe(CO)_3$ bonds ($Cp = \eta^5$-C_5H_5) in the metal triangle clusters have been verified by extended Hückel MO (EXH-MO) calculations.

The oxidative addition of the S–S linkage of (μ-dithio)bis(tricarbonyliron) to various low-valent transition metal species has been developed by Seyferth and co-workers [1]. It follows the general reaction scheme of eq. 1, where L_nM includes

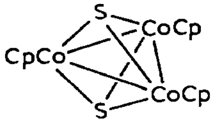


(1)

$(PPh_2CH_2CH_2PPh_2)Ni$, $(PPh_3)_2Pd$, $(PPh_3)_2Pt$, CpCo, ($Cp = \eta^5$-C_5H_5), and $(CH_3)_2Sn$. In the course of our study on cyclopentadienylcobalt-sulfur cluster complexes [2], we were interested in the structure of the trinuclear iron–cobalt–sulfur cluster formed according to reaction 1, $Fe(CO)_3$ and CoCp being isoelectronic. The known structure of $Fe_3(CO)_9S_2$ (1) has an open C_{2v} geometry with one Fe–Fe distance much longer than the other two [3]. The isoelectronic $(CoCp)_3S_2$ (**2**), on the other hand, possesses a closed D_{3h} structure [4].



(**1**)



(**2**)

Since our initial attempt to obtain single crystals of $[Fe_2(CO)_6(CoCp)S_2]$ was unsuccessful, we used $[Co(ZCp)(CO)_2]$ ($ZCp = \eta^5\text{-}C_5H_4CO_2Me$) in place of $(CoCp)(CO)_2$ in reaction 1. In this paper the X-ray analysis of the resulting single crystals of $[Fe_2(CO)_6(CoZCp)(S)_2]$ (**3**) is reported.

Results and discussion

The atomic coordinates are listed in Table 1 and important bond lengths and angles are listed in Table 2. Figure 1 depicts the perspective view and numbering scheme of complex **3**.

Table 1

Atomic coordinates ($\times 10^4$) and equivalent temperature factors for **3** with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}
Co	763(0)	1064(1)	2121(0)	2.0(0.0)
Fe(1)	2042(0)	1335(1)	3025(0)	2.4(0.0)
Fe(2)	386(0)	2716(1)	3480(0)	2.6(0.0)
S(1)	1230(1)	3910(2)	2700(1)	2.5(0.0)
S(2)	1066(1)	−149(2)	3459(1)	2.6(0.0)
O(1)	2760(3)	2941(9)	4757(3)	6.6(0.2)
O(2)	2752(2)	−2754(7)	3023(3)	5.8(0.1)
O(3)	2997(2)	3067(8)	1832(3)	6.1(0.2)
O(4)	−781(3)	203(9)	4038(3)	6.6(0.2)
O(5)	983(3)	4574(8)	5207(3)	5.9(0.1)
O(6)	−679(2)	5900(8)	2748(3)	6.1(0.1)
O(7)	1669(2)	1711(6)	−34(2)	4.0(0.1)
O(8)	1026(3)	4564(6)	177(3)	5.3(0.1)
C(1)	2507(3)	2300(9)	4083(4)	3.7(0.1)
C(2)	2478(3)	−1173(9)	3019(4)	3.5(0.1)
C(3)	2622(3)	2408(9)	2301(4)	3.7(0.1)
C(4)	−337(3)	1176(9)	3817(3)	3.8(0.1)
C(5)	741(3)	3848(9)	4549(3)	3.7(0.1)
C(6)	−262(3)	4697(9)	3038(3)	3.6(0.1)
C(7)	2096(4)	2876(12)	−563(5)	6.1(0.2)
C(8)	1143(3)	2730(8)	287(3)	3.2(0.1)
C(9)	703(2)	1338(7)	757(3)	2.4(0.1)
C(10)	866(3)	−774(7)	1011(3)	2.6(0.1)
C(11)	282(3)	−1510(8)	1420(3)	3.1(0.1)
C(12)	−240(2)	84(9)	1429(3)	3.3(0.1)
C(13)	10(2)	1853(8)	1016(3)	2.9(0.1)

Table 2

Selected bond distances (Å) and angles (°) for **3** with standard deviations in parentheses

Distance (Å)			
Co–Fe(1)	2.541(1)	Co–Fe(2)	2.521(1)
Fe(1)–Fe(2)	3.369(1)		
Co–S(1)	2.156(1)	Co–S(2)	2.165(1)
Fe(1)–S(1)	2.243(1)	Fe(1)–S(2)	2.236(1)
Fe(2)–S(1)	2.244(1)	Fe(2)–S(2)	2.241(2)
S(1)–S(2)	2.899(2)		
Co–C(9)	2.065(4)	Co–C(10)	2.097(5)
Co–C(11)	2.093(5)	Co–C(12)	2.077(5)
Co–C(13)	2.064(4)		
C(9)–C(10)	1.434(6)	C(10)–C(11)	1.414(7)
C(11)–C(12)	1.413(7)	C(12)–C(13)	1.417(7)
C(13)–C(9)	1.440(7)	C(8)–C(9)	1.473(7)
Fe(1)–C(1)	1.806(5)	Fe(1)–C(2)	1.811(6)
Fe(1)–C(3)	1.797(6)	C(1)–O(1)	1.132(7)
C(2)–O(2)	1.139(7)	C(3)–O(3)	1.153(8)
Fe(2)–C(4)	1.808(6)	Fe(2)–C(5)	1.805(5)
Fe(2)–C(6)	1.807(5)	C(4)–O(4)	1.127(8)
C(5)–O(5)	1.127(7)	C(6)–O(6)	1.132(7)
Angle (°)			
Fe(1)–Co–Fe(2)	83.44(4)	S(1)–Co–S(2)	84.28(5)
S(1)–Fe(1)–S(2)	80.68(5)	S(1)–Fe(2)–S(2)	80.56(5)
Fe(1)–S(1)–Fe(2)	97.34(5)	Fe(1)–S(2)–Fe(2)	97.61(6)
Co–Fe(1)–C(1)	140.5(2)	Co–Fe(2)–C(5)	143.1(2)
Co–Fe(1)–C(2)	108.2(2)	Co–Fe(2)–C(4)	108.4(2)
Co–Fe(1)–C(3)	107.0(2)	Co–Fe(2)–C(6)	104.6(2)

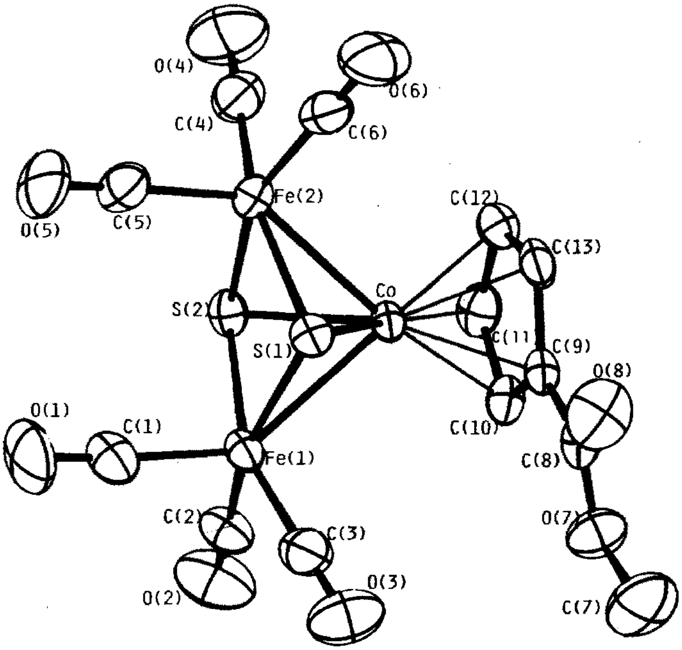


Fig. 1. The molecular structure of 3.

The overall geometry of the molecule is essentially identical to that of **1** with only the Co(ZCp) group replacing the apical $Fe(CO)_3$ unit. The Fe–Fe distance is 3.369(1) Å which indicates that the Fe–Fe bond has been broken. The Co–Fe–Fe and Co–S–S planes have a dihedral angle of 90.0° and the two $Fe(CO)_3$ units are oriented almost symmetrically with respect to the Co–S–S plane. Thus with the exception of the ZCp unit, the rest of the molecule is in pseudo C_{2v} symmetry. The Fe(1)–S(1)–Fe(2)–S(2) atoms are located almost in the same plane, the deviations from best plane being Fe(1) −0.07, Fe(2) −0.08, S(1) 0.20, and S(2) 0.22 Å. The dihedral angle formed by the C(1)–C(2)–C(3) and C(4)–C(5)–C(6) planes is 126.5°.

While the Fe–Fe distance of the present complex is similar to that of the non-bonding Fe–Fe distance in **1**, the mean value of the Co–Fe distances, 2.531(1) Å, is significantly shorter than the mean value of the corresponding Fe–Fe bonds in **1**, 2.60(1) Å. Since the bonding radius of Co atom (1.24 Å) is similar to that of Fe(1.25 Å), the shorter metal–metal bonds in **3** compared with those in **1** may be attributed to the stronger interaction between the Co(ZCp) and $Fe(CO)_3$ units than to that between the two $Fe(CO)_3$ units.

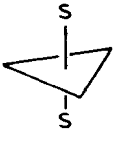
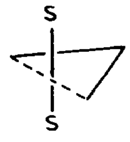
When a regular triangle framework, made of three CoCp or $Fe(CO)_3$ units, is bicapped with two sulfur atoms each of which donates 4 electrons, the total electron count is 50. Since the number of electrons expected for a normal triangle cluster complex is 48, the two excess electrons must occupy the metal–metal antibonding orbital(s) [2]. If the metal–metal bonds are sufficiently strong the complex keeps its triangular frame as in **2**, if not one of the metal–metal bonds is cleaved as in **1** or **3**. Comparison of the structures of **1**, **2**, and **3**, we suggest that the metal–metal bond weakens in the order CpCo–CoCp > CpCo–$Fe(CO)_3$ > $(CO)_3Fe–Fe(CO)_3$.

That the metal–metal σ-interaction with an $M(C_6H_6)$ or $M(C_5H_5)$ fragment is stronger than with an $M(CO)_3$ unit has been suggested by Hoffmann and co-workers, on the basis of EXH-MO calculations on binuclear complexes, $(C_6H_6)M–MnH_3$ and $(CO)_3M–MnH_3$ [5]. We used the EXH-MO calculations to check if this trend in metal–metal bonding arises from the difference between the Cp and $(CO)_3$ ligands or whether it is due to the metal itself.

The calculations were performed on two geometries, (i) a D_{3h} structure, i.e. a regular triangle with the metal–metal distance of 2.6 Å, and bicapped with sulfur

Table 3

Calculated total-energy difference between geometries **i** and **ii**

Complex	Relative energy (eV) [a]	
	 (i)	 (ii)
(a) $[Fe(CO)_3]_3(S)_2$	0.0	−1.65
(b) $[Fe'Cp]_3(S)_2$	0.0	−0.46
(c) $[CoCp]_3(S)_2$	0.0	1.77

[a] The negative relative energy means stabilization.

atoms at 1.45 Å above and below the metal plane and (ii) a C_{2v} geometry, i.e. the D_{3h} structure is deformed so that one of the metal–metal distances is elongated to 3.4 Å and the sulfur atoms are shifted to above and below of this elongated edge. For the metal units which occupy the vertices of the triangle, we checked (**a**) the $Fe(CO)_3$ unit, (**b**) a hypothetical Fe′Cp unit in which the geometry and the electron count (8*d*-electrons) were taken from the CoCp unit, but the parameters for the metal were those for Fe, and (**c**) the CoCp unit. The calculated relative energies between the two geometries, **i** and **ii** for each metal unit, are listed in Table 3. Although absolute energy values by EXH-MO calculations are unreliable, the large differences in the relative energies calculated are of importance. On going from geometry **i** to geometry **ii**, the cluster complex containing the $Fe(CO)_3$ triangle is stabilized while that containing the CoCp unit is destabilized. It is noteworthy that the complex with the Fe′Cp vertices does not significantly change its energy when its geometry is changed. We suggest that the preference for one of the two geometries strongly depends on the nature of the ligand and that of the metal, both of which are equally important.

Experimental

Preparation of [$Fe_2(CO)_6(CoZCp)(S)_2$] (3)

Complex **3** was prepared by a modification of the procedure for the synthesis of unsubstituted cyclopentadienylcobalt analog of **3** described by Seyferth et al. [1]. A solution of [$Co(ZCp)(CO)_2$] (0.67 g, 2.8 mmol) and [$Fe_2S_2(CO)_6$] (0.48 g, 1.4 mmol) in THF (50 ml) was irradiated by a high pressure mercury lamp for 7 h, during which CO gas was evolved (ca. 100 ml). The resulting dark solution was evaporated and the residue was redissolved in a minimum amount of benzene. Column chromatography on silicagel gave a dark band which was eluted with benzene. Concentration and addition of hexane yielded black crystals of **3** (0.3 g, 41% based on Fe); m.p. 114–115 °C. ^1H NMR (C_6D_6): δ 3.38 (s, 3H, CO_3Me); 4.88 (broad t, 2H, Cp); 5.73 (broad t, 2H, Cp) ppm. Analysis. Found: C, 29.86; H, 1.38; S, 12.10. $C_{13}H_7CoFe_2O_8S_2$ calcd.: C, 29.69; H, 1.34; S, 12.19%.

Crystal structure determination

The crystal and refinement data are summarized in Table 4. The structure was solved by a direct method which revealed the position of the two Fe and Co atoms. The remaining atoms were located from subsequent difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with isotropic thermal parameters, by block-diagonal least squares. Anomalous dispersion effects for Co and Fe were included in the calculation using the $\Delta f'$ and $\Delta f''$ values taken from ref. 6. Atomic scattering factors were from International Tables [7]. Tables of anisotropic temperature factors, hydrogen atom coordinates, and structure factors are available from the authors.

EXH-MO calculations

The computational parameters for the extended Hückel calculations were taken from ref. 8. A modified Wolfsberg–Helmholz formula [9] was used. The following idealized bond distances and angles were used: Co–$(C)_{Cp}$, 2.1146; C–C, 1.41; C–H, 1.05; Fe–C, 1.80; C–O, 1.135 Å; C–Fe–C 97.18; C–Fe–Fe 115.66; dihedral angle

Table 4

Crystal and refinement data of **3**

Formula	$C_{13}H_7CoFe_2O_8S_2$
M	525.9
Crystal size, mm	0.37×0.24×0.16
Space group	monoclinic, $P2_1/a$
a, Å	18.504(3)
b, Å	6.459(2)
c, Å	15.193(3)
β,	99.38(1)
V, Å^3	1791.5(7)
Z	4
ρ(calcd), g·cm^{-3}	1.95
μ, cm^{-2}	27.7
Radiation	graphite-monochromated Mo-K_α
Diffractometer	Rigaku
Scan speed, ° min^{-1}	constant, 3.6
2θ scan limits, deg	$2 < 2\theta < 55$
Scan method	$\omega - 2\theta$
Data collection	$\pm h, +k, +l$
Standard reflections	3 std/150 rflns (var. <1%)
Unique data	4636
Unique data, $F_0 \geq 3\sigma F_0$	2994
R, %	3.24
R_w, (w = 1.0), %	3.79
Number of parameters	264
GOF	3.1
$\Delta(\rho)_{max}$, eÅ^{-3}	0.64

$(C\text{-}C\text{-}C)_{CO,Fe(1)}/(C\text{-}C\text{-}C)_{CO,Fe(2)} = 120.0°$. For geometry (i): all M–M 2.60, M–S 2.087 Å. For geometry ii: M–M = 2.60, 2.60 and 3.40, M–S = 2.234, 2.234, and 2.444 Å.

Acknowledgment

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