Cluster compounds containing *d*- and *p*-block metals: Molecular structure of μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$

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Abstract

μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ crystallizes in the orthorhombic space group *Pnma* with *a* 18.289(1), *b* 13.687(1), *c* 7.055(1) Å, and four molecules in the unit cell. On the basis of 1532 unique observed reflections the structure was refined to $R_w = 0.030$ for 136 refined parameters. μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ forms a *closo* tetrahedral cluster in which an almost isosceles triangle of Fe centers is capped by the bismuth atom. Each iron atom is complexed by a Cp-ring, and the iron–iron bonds are bridged by the carbonyl groups (Bi–Fe 2.573(1) and 2.574(1), Fe–Fe 2.606(1) and 2.578(1) Å).

Introduction

Mixed metal clusters containing metals from both the *d*-block and *p*-block elements have recently attracted considerable interest [1,2,3]. The characteristic electronic differences between main group and transition metals, as well as the special phenomena encountered at the borderline between the two ("closed-shell systems") can be expected to cause changes with reactivities of the transition metal fragments. For transition metal derivatives of main group elements novel coordination geometries and bonding modes have recently been observed in a variety of cases [4].

We report the crystal and molecular structure of μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$, a BiFe$_3$ *closo* cluster obtainable from the open BiFe$_3$ species Bi[Fe(C$_5$H$_5$)(CO)$_2$]$_3$ by photochemically-induced loss of three CO groups (Scheme 1). Its synthesis and properties were described previously [1].

Results

As Fig. 1 shows, μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ forms a tetrahedral *closo* cluster with the three iron atoms forming the basal plane of the tetrahedron and the bismuth atom

166
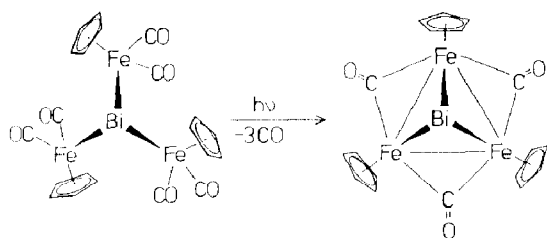
Scheme 1.

at the apex. The iron–iron bonds are bridged symmetrically by carbonyl groups, and each iron centre carries an additional Cp ring. The molecule has crystallographic m (C_s) symmetry. The mirror plane contains the atoms Bi, Fe1, Cp1, C2, O2 and bisects one Fe–Fe bond (between Fe2 and Fe2′). Although there are some minor structural differences, especially in the Fe–Fe bond lengths (Fe1–Fe2 2.606(1), Fe2–Fe2′ 2.578(1) Å), the overall molecular symmetry when the conformations of the Cp rings are included approaches $3m$ (C_{3v}). The Cp rings are inclined by 98.3/98.8° with respect to the Fe_3 plane, the Fe_2CO planes of the bridging CO groups form angles of 55.6/63.7° with the basal plane.

The Bi–Fe and the Fe–Fe bonds in μ_3-Bi[Fe(C_5H_5)(CO)]$_3$ (Tab. 1) are of comparable lengths. Remarkably, they are substantially shorter than those in the doubly Bi-capped Fe_3 cluster (μ_3-Bi)$_2$[Fe(CO)$_3$]$_3$ (Bi–Fe(av) 2.628(14), Fe–Fe(av) 2.745(11) Å) [5]. They are also shorter than those in the anionic tetrahedral species [(μ_3-Bi)Fe$_3$(CO)$_9$(μ_3-CO)]$^-$ (Bi–Fe(av) 2.650(2), Fe–Fe(av) 2.642(7) Å) [6]. This could be attributed in part to the fact that in the latter species the Fe–Fe bonds, while bridged by μ_3-Bi and μ_3-CO groups, are not bridged by further CO ligands. In
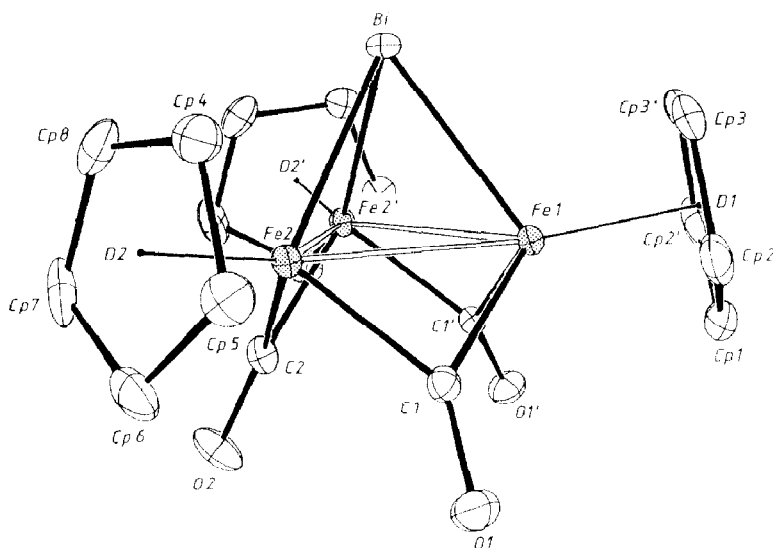

Fig. 1. Perspective view of the molecular structure of μ_3-Bi[Fe(C_5H_5)(CO)]$_3$ in the crystal (ORTEP, displacement parameters at the 50% probability level; without hydrogen atoms). Primed atoms are related to unprimed ones by a crystallographic mirror plane which bisects the molecule and contains the atoms Bi, Fe1, Cp1, C2, and O2. The Fe–Fe interactions are indicated by open lines.

Table 1

Important bond distances (Å) and angles (°) for μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$. (Estimated standard deviations in units of the last significant figure are given in parentheses; see Fig. 1 for numbering scheme)

Bi–Fe1	2.573(1)	Bi–Fe2	2.574(1)
Fe1–Fe2	2.606(1)	Fe2–Fe2′	2.578(1)
Fe1–C1	1.923(5)	Fe2–C1	1.903(5)
Fe2–C2	1.923(6)		
C1–O1	1.196(6)	C2–O2	1.18(1)
Fe1–Cp1	2.06(1)	Fe1–Cp2	2.101(6)
Fe1–Cp3	2.166(5)	Fe2–Cp4	2.138(6)
Fe2–Cp5	2.085(5)	Fe2–Cp6	2.075(6)
Fe2–Cp7	2.092(6)	Fe2–Cp8	2.134(6)
Fe1–D1 ^{a}	1.75	Fe2–D2 ^{a}	1.74
Fe1–Bi–Fe2	60.85(2)	Fe2–Bi–Fe2′	60.11(3)
Fe2–Fe1–Fe2′	59.29(4)	Fe1–Fe2–Fe2′	60.36(2)
Bi–Fe1–D1 ^{a}	113.8	Bi–Fe2–D2 ^{a}	114.6
Fe2–Fe1–D1 ^{a}	148.3	Fe1–Fe2–D2 ^{a}	149.1
Fe2′–Fe2–D2 ^{a}	146.3		
Fe1–C1–O1	137.6(4)	Fe2–C1–O1	136.3(4)
Fe1–C1–Fe2	85.9(2)		
Fe2–C2–O2	137.9(2)	Fe2–C2–Fe2′	84.2(3)

^{a} D = Centroid of the Cp-rings.

[Bi{Fe(CO)$_4$}$_4$]$^{3-}$, with tetrahedrally four-coordinated Bi atoms and no Fe–Fe bonds, the Bi–Fe distances average 2.750(2) Å [7].

From these comparisons it is evident that μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ forms a particularly compact *closo* cluster. The short interatomic distances possible in μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ may also account for its ready formation from an open species by loss of CO groups. As a consequence of the incorporation into the tetrahedral cluster, the Bi atoms in μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$ are strongly pyramidalized. It should be mentioned, however, that the Bi also has a pyramidal coordination geometry in the open BiMn$_3$ cluster Bi[Mn(CO)$_5$]$_3$, (Mn–Bi–Mn 110.3(1)/106.9(1)/107.5(1)°) [2].

Experimental

Crystal structure determination of μ_3-Bi[Fe(C$_5$H$_5$)(CO)]$_3$

Enraf–Nonius CAD4 diffractometer, Mo-K_α radiation, λ 0.71069 Å, graphite monochromator, T 22°C. Crystal dimensions 0.10 × 0.23 × 0.50 mm^3, C$_{18}$H$_{15}$BiFe$_3$O$_3$, M_r = 655.84, orthorhombic, space group *Pnma* (No. 62), a 18.289(1), b 13.687(1), c 7.055(1) Å, V 1766.0 Å^3, Z = 4, d_{calcd} 2.466 g/cm^3, μ(Mo-K_α) 123.4 cm^{-1}, $F(000)$ = 1232. Of 4273 measured reflexions, 1989 were unique and 1532 observed with $F_o \geq 4.0$ $\sigma(F_o)$ ((sin θ/λ)$_{max}$ 0.638 Å^{-1}, *hkl* range: +23, +9, ±17, $\theta/2\theta$ scan, $\Delta\omega = 0.85 + 0.35$ tan θ°. Corrections for decay (−1.1%), Lp effects, and for absorption were applied. For the latter scans at intervals of 10° around the diffraction vectors of eight selected reflexions near χ 90° allowed evaluation of the relative transmission (0.37–1.00). The structure was solved by conventional Patterson techniques and refined by Fourier methods. Three out of a total of eight independent hydrogen atoms could be located in difference maps, and the re-

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters for μ_3-Bi[Fe(C$_5$H$_5$)-(CO)]$_3$. ($B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}]$).

Atom	x	y	z	B_{eq}
Bi	0.46743(2)	0.250	0.44619(3)	2.351(4)
Fe1	0.51042(5)	0.250	0.7935(1)	1.94(2)
Fe2	0.39252(3)	0.34418(5)	0.6952(1)	2.04(1)
O1	0.4521(2)	0.3919(3)	1.0628(5)	3.45(8)
O2	0.2934(3)	0.250	0.9599(9)	4.6(1)
C1	0.4509(3)	0.3462(4)	0.9185(7)	2.22(9)
C2	0.3382(4)	0.250	0.840(1)	2.7(1)
Cp1	0.5948(5)	0.250	0.988(1)	5.8(3)
Cp2	0.6021(3)	0.3339(4)	0.869(1)	4.3(1)
Cp3	0.6143(3)	0.3016(4)	0.6854(8)	3.1(1)
Cp4	0.3989(3)	0.4635(4)	0.5003(9)	3.4(1)
Cp5	0.3970(3)	0.4964(3)	0.6882(8)	3.4(1)
Cp6	0.3312(3)	0.4657(4)	0.7704(9)	4.2(1)
Cp7	0.2929(3)	0.4117(4)	0.631(1)	4.8(1)
Cp8	0.3352(4)	0.4109(4)	0.4655(9)	4.3(1)

mainder were placed at calculated positions. The H atoms were kept fixed in the refinement, while all other atoms were refined with anisotropic displacement parameters. Refinement converged at R (R_w) = 0.025 (0.030), GOF = 0.895 for 136 refined parameters and 1525 observables. Seven reflexions were suppressed in the final refinement cycles owing to abnormally large F_o/F_c differences, presumably caused by extinction. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2$ (F_o^2) and $\sigma^2(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]/Lp^2$. p was set to 0.05 to give a "flat" analysis of variance. The maximum ratio of shift to error in the final refinement cycle was 0.32. The final difference map had maxima of 1.15 e/Å^3 near Bi, but was otherwise featureless. Neutral isolated atom scattering factors for all non-hydrogen atoms were taken from ref. 8. Scattering factors for the H atoms, based on a bonded spherical atom model, were from ref. 9. Corrections for anomalous scattering were applied to all atoms [10]. All calculations were carried out by use of SDP-PLUS [11].

Table 1 lists the important bond distances and angles, and Table 2 the atomic coordinates. Complete tables of atomic parameters and lists of observed and calculated structure factor amplitudes have been deposited [12].

Acknowledgement

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