Synthesis and Structure of $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](BF_4)\cdot Me_2CO$: Implication of the Flexible Fe_4S_5 Framework

Shinji Inomata, Keiichi Hitomi, and Hiroshi Ogino*
Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77

(Received August 21, 1997; CL-970652)

A mixed ligand cluster, $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](BF_4)\cdot Me_2CO$, was synthesized and its X-ray crystal structure was determined. From the comparison of this structure with those of $Cp^*_3(Ph_2C_2S_2)Fe_4S_5\cdot THF$, $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](PF_6)\cdot 2Me_2CO$, and $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](PF_6)_2\cdot Me_2CO$ which have been reported previously, it is concluded that the Fe_4S_5 core of the clusters is flexible and easily undergoes deformation.

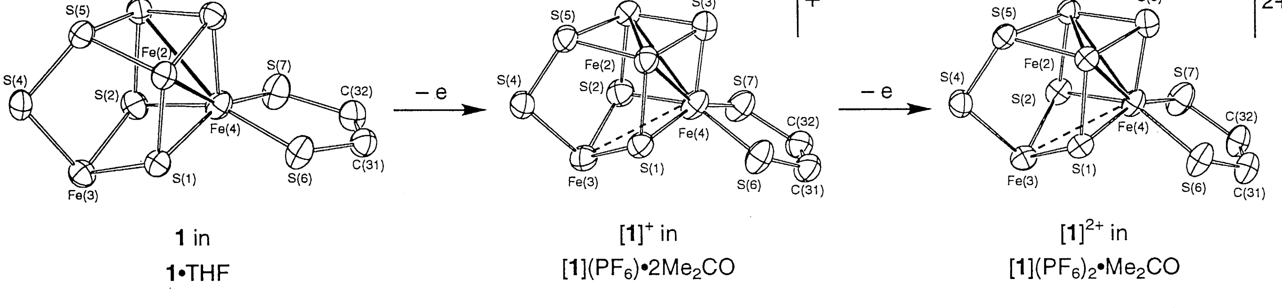
Recently we synthesized a mixed ligand tetrairon-sulfur cluster, $Cp^*_3(Ph_2C_2S_2)Fe_4S_5\cdot THF$ (**1**•THF), and its one- and two-electron oxidized clusters, [**1**]$(PF_6)\cdot 2Me_2CO$ and [**1**]$(PF_6)_2\cdot Me_2CO$. All clusters have been structurally characterized by X-ray crystallography (Figure 1).[1-4] Although structural change of cluster **1** accompanying its oxidation is not simple, the cluster shrinks as **1** is oxidized. This is due to the stepwise removal of antibonding electrons from cluster **1**. The Fe_4S_5 core of **1** has two Fe-Fe bonds with a V-shaped configuration. In the one-electron oxidized cluster [**1**]$(PF_6)\cdot 2Me_2CO$, there are three distinct Fe-Fe bonds. The distances Fe(1)-Fe(2), Fe(1)-Fe(4), and Fe(2)-Fe(4) are short (2.736(2) - 2.783(1) Å). The distances Fe(1)-Fe(3) and Fe(2)-Fe(3) are very long, indicating the absence of Fe-Fe bonds. In addition to this, the distance Fe(3)-Fe(4) (3.047(2) Å) is much shorter than the distances Fe(1)-Fe(3) and Fe(2)-Fe(3) in the same Fe_4S_5 core, indicating the presence of some weak Fe-Fe interaction between Fe(3) and Fe(4) atoms. The structure of cluster $[\mathbf{1}]^{2+}$ is similar to $[\mathbf{1}]^{+}$ and the Fe_4S_5 core of $[\mathbf{1}]^{2+}$ also contains three distinct Fe-Fe bonds. Weak interaction is again observed between Fe(3) and Fe(4) atoms (2.969(1) Å).

This paper describes synthesis of [**1**]$(BF_4)\cdot Me_2CO$ and its structural determination by X-ray crystallography. This cluster is isoelectronic with [**1**]$(PF_6)\cdot 2Me_2CO$ and hence [**1**]$(BF_4)\cdot Me_2CO$ is expected to be isostructural with [**1**]$(PF_6)\cdot 2Me_2CO$. Interestingly, however, there is significant difference in structure between [**1**]$(BF_4)\cdot Me_2CO$ and [**1**]$(PF_6)\cdot 2Me_2CO$. The comparison of the structures of these clusters is useful to understand how the Fe_4S_5 core is flexible.

Synthesis of [**1**]$(BF_4)\cdot Me_2CO$ was carried out as follows: To a CH_2Cl_2 solution (20 cm^3) of **1**•THF (117 mg, 1.06×10^{-4} mol), was added $[(MeCp)_2Fe](BF_4)$ (42 mg, 1.4×10^{-4} mol) and the mixture was stirred for 20 min under a nitrogen atmosphere. After the solvent was evaporated, the residue was washed with water (50 cm^3) to remove excess $[(MeCp)_2Fe](BF_4)$. The resulting solid was dried in vacuo and then washed with hexane (25 cm^3) to remove $(MeCp)_2Fe$. The resulting powder was dissolved in acetonitrile (50 cm^3) and the solution was filtered and evaporated to dryness. Recrystallization was carried out by layering an acetone solution (5 cm^3) of the residue with hexane (20 cm^3).[5]

ORTEP drawing of [**1**]$(BF_4)\cdot Me_2CO$ is shown in Figure 2.[6] This cluster consists of four iron atoms, three μ_3-S ligands, and one μ_3-S_2 ligand. As a whole, its structure is quite similar to that of [**1**]$(PF_6)\cdot 2Me_2CO$. However, the Fe-Fe interatomic distances of [**1**]$(BF_4)\cdot Me_2CO$ are significantly different from those of [**1**]$(PF_6)\cdot 2Me_2CO$. Table 1 summarizes the Fe-Fe interatomic distances and some related data of **1**•THF, [**1**]$(BF_4)\cdot Me_2CO$, [**1**]$(PF_6)\cdot 2Me_2CO$, and [**1**]$(PF_6)_2\cdot Me_2CO$. The most striking point of the structural difference between [**1**]$(BF_4)\cdot Me_2CO$ and [**1**]$(PF_6)\cdot 2Me_2CO$ is the interatomic distance between Fe(3) and Fe(4) atoms. The Fe(3)-Fe(4) distance of [**1**]$(BF_4)\cdot Me_2CO$ (2.866(2) Å) is much shorter (by 0.18 Å) than that of [**1**]$(PF_6)\cdot 2Me_2CO$. On the contrary, the Fe(1)-Fe(4) distance of [**1**]$(BF_4)\cdot Me_2CO$ is longer by 0.10 Å than that of [**1**]$(PF_6)\cdot 2Me_2CO$. The structural difference would be caused by the packing effect. The averaged value of the six Fe-Fe distances of [**1**]$(BF_4)\cdot Me_2CO$ (3.12 Å) is close to that of [**1**]$(PF_6)\cdot 2Me_2CO$ (3.14 Å).

According to the metal fragment orbital model[7] and Dahl's MO bonding scheme,[8] total Fe-Fe bond order of $[\mathbf{1}]^{+}$ with 18 cluster electrons is three (Table 1). In fact, three Fe-Fe distances among Fe(1), Fe(2), and Fe(4) atoms are short. As mentioned above, however, the Fe(3)-Fe(4) distance in [**1**]$(BF_4)\cdot Me_2CO$ is also short. Therefore, there are four Fe-Fe bonding interaction as indicated by solid lines in Figure 2. It should be noted that the bond order of each of the four Fe-Fe



1 in
1•THF

$[\mathbf{1}]^{+}$ in
$[\mathbf{1}](PF_6)\cdot 2Me_2CO$

$[\mathbf{1}]^{2+}$ in
$[\mathbf{1}](PF_6)_2\cdot Me_2CO$

Figure 1. Structural change of **1** accompanying one- and two-electron oxidation. Cp* and Ph groups are omitted for simplicity.

Table 1. Fe-Fe and Fe-S distances (Å), number of cluster electrons, and total Fe-Fe bond order in cluster **1** and its oxidized species

Cluster	$\mathbf{1}\cdot$THF	$[\mathbf{1}](BF_4)\cdot Me_2CO$	$[\mathbf{1}](PF_6)\cdot 2Me_2CO$	$[\mathbf{1}](PF_6)_2\cdot Me_2CO$
Fe(1)-Fe(2)	3.300(1)	2.732(2)	2.736(2)	2.710(1)
Fe(1)-Fe(4)	2.716(1)	2.887(2)	2.783(1)	2.701(1)
Fe(2)-Fe(4)	2.725(1)	2.780(2)	2.767(2)	2.705(1)
Fe(3)-Fe(4)	3.307(2)	2.866(2)	3.047(2)	2.969(1)
Fe(1)-Fe(3)	3.769(1)	3.745(2)	3.760(2)	3.728(1)
Fe(2)-Fe(3)	3.760(2)	3.728(2)	3.765(2)	3.713(1)
Fe-Fe (av)[a]	3.26	3.12	3.14	3.09
Fe-S (av)	2.21	2.21	2.21	2.21
number of cluster electrons	19	18	18	17
total Fe-Fe bond order[b]	2.5	3	3	3.5

[a] The averaged value of the six Fe-Fe interatomic distances.

[b] Based on the direct application of the metal fragment orbital model[7] and Dahl's MO bonding scheme.[8]

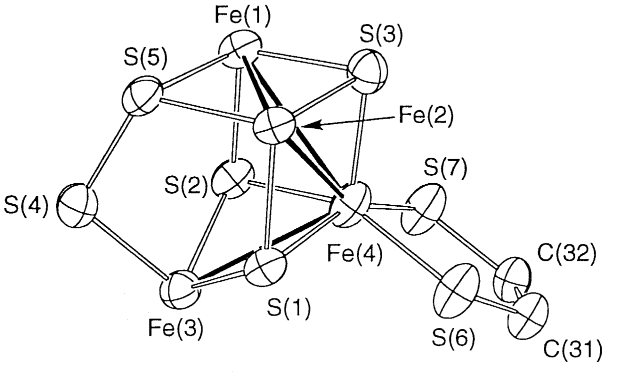


Figure 2. ORTEP drawing of the cationic moiety in $[\mathbf{1}](BF_4)\cdot Me_2CO$. Cp* and Ph groups are omitted for simplicity. Thermal ellipsoids are at 30% probability level.

bonds is less than unity. In fact, these distances are somewhat longer than the Fe-Fe single bond distances observed in $Cp_4Fe_4S_4$ (2.63 Å,[9] 2.65 Å[10]) and $(MeCp)_4Fe_4S_4$ (2.61 Å).[11]

The Fe(3)-Fe(4) distance of $[\mathbf{1}](BF_4)\cdot Me_2CO$ is even shorter than that of $[\mathbf{1}]^{2+}$ with total Fe-Fe bond order of 3.5. These findings indicate that the Fe_4S_5 framework is quite flexible. The averaged value of the six Fe-Fe interatomic distances of **1** decreases successively as it is oxidized to $[\mathbf{1}]^+$ and then $[\mathbf{1}]^{2+}$, which is consistent with the expectation from the MO bonding scheme.[7,8]

Although the Fe-Fe interatomic distances are quite sensitive toward oxidation, the Fe-S bond distances are insensitive. The averaged Fe-S bond distance of **1** (2.21 Å) is kept constant upon oxidation to $[\mathbf{1}]^+$ and $[\mathbf{1}]^{2+}$.

References and Notes

1 Abbreviations of ligands: Cp = C_5Me_5; MeCp = MeC_5H_4; Cp' = Cp derivative.

2 S. Inomata, H. Tobita, and H. Ogino, *J. Am. Chem. Soc.*, **112**, 6145 (1990).

3 S. Inomata, H. Tobita, and H. Ogino, *Inorg. Chem.*, **31**, 722 (1992).

4 S. Inomata, K. Hitomi, H. Tobita, and H. Ogino, *Inorg. Chim. Acta,* **225**, 229 (1994).

5 $[Cp^*_3(Ph_2C_2S_2)Fe_4S_5](BF_4)\cdot Me_2CO$ ($[\mathbf{1}](BF_4)\cdot Me_2CO$) Yield: 61 mg (49%). Data for $[\mathbf{1}](BF_4)\cdot Me_2CO$: ^1H NMR (300 MHz, $CDCl_3$) δ -1.8 (br, 15H, Me, $W_{1/2}$ = 100 Hz), 3.7 (br, 30H, Me, $W_{1/2}$ = 99 Hz), 7.0-7.1, 7.5-7.8 (m, 10 H, Ph). IR (KBr) 2972 (w), 1707 (m, Me_2CO), 1593 (w), 1489 (w), 1458 (w), 1427 (m), 1375 (m), 1219 (w), 1167 (w), 1084 (m), 1055 (vs, BF), 1036 (m), 1016 (m), 866 (w), 744 (m), 698 (m) cm^{-1}. MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m/z* 1030 (M^+-1, 100), 895 (M^+-Cp*-1, 14), 655 (M^+-Cp*-$Ph_2C_2S_2$+1, 13), 520 (M^+-2Cp*-$Ph_2C_2S_2$+1, 15). Anal. Found: C, 48.04; H, 5.11%. Calcd for $C_{47}H_{61}BF_4Fe_4OS_7$: C, 47.98; H, 5.23%.

6 Crystal data for $[\mathbf{1}](BF_4)\cdot Me_2CO$: $C_{47}H_{61}BF_4Fe_4OS_7$, *FW* = 1176.7, monoclinic, space group $P2_1/c$, a = 16.626(2) Å, b = 21.468(3) Å, c = 14.647(2) Å, β = 93.19(1)°, V = 5219.4(11) Å^3, Z = 4, D_c = 1.50, D_m = 1.49 g cm^{-3}, $\mu(MoK\alpha)$ = 14.4 cm^{-1}. Diffraction data were collected at 21°C on a Rigaku AFC-4A diffractometer with graphite-monochromated MoKα radiation. The structure was solved by the direct method (RANTAN81). All non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic thermal parameters to converge R = 0.086 and R_w = 0.092 for 5894 reflections ($|F_o| > 3\sigma(F_o)$).

7 S. Harris, *Polyhedron,* **8**, 2843 (1989).

8 Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Am. Chem. Soc.*, **99**, 408 (1977).

9 R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

10 C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966).

11 H. L. Blonk, J. G. M. van der Linden, J. J. Steggerda, R. P. Geleyn, J. M. M. Smits, G. Beurskens, P. T. Beurskens, and J. Jordanov, *Inorg. Chem.*, **31**, 957 (1992).