# Construction of a Cyclic Tricubane Cluster [Cp*2Mo2Fe2S4]3(μ-S4)3 from the Mo2Fe2S4 Single Cubane Component
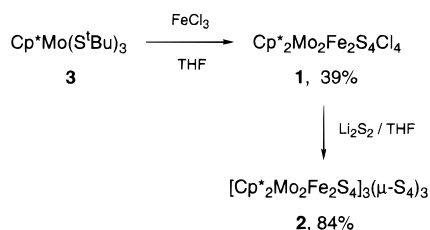
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Over the past two decades, extensive efforts have been made to synthesize mixed-metal sulfido clusters of high nuclearity, and exploitation of new cluster components continues to be an imperative step for accomplishing unprecedented arrangements of large core structures.[1] In particular, construction of clusters containing iron and/or molybdenum is one of the major objectives in this field. Although spontaneous self-assembly has been a dominant strategy for the synthesis of such clusters,[2] more rational approaches to aggregation of cluster units have also emerged.[3] For instance, dicubane clusters [(Fe$_4$S$_4$Cl$_3$)$_2$(μ-S)]$^{4-}$, [{MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)}$_2$(μ-S)$_2$]$^{6-}$, and [{MoFe$_3$S$_4$Cl$_2$(Cl$_4$-cat)}$_2$(μ-S)(μ-L)]$^{n-}$ (L = N$_2$H$_4$, $n$ = 4; L = CN, OH, $n$ = 5) were prepared by treating the corresponding single cubane complexes with Na$_2$S, (Et$_4$N)$_2$S, and NEt$_4$OH/L$_2$S.[4,5] Recently, it was reported that reaction of [Fe$_4$S$_4$Cl$_4$]$^{2-}$ with PR$_3$ and subsequent reduction resulted in fusion of two and four cubane cores.[6,7] In this paper, we report the synthesis of a new class of Mo$_2$Fe$_2$S$_4$ cubane complex, Cp*$_2$Mo$_2$Fe$_2$S$_4$Cl$_2$ (**1**; Cp* = η$^5$-C$_5$Me$_5$), and the formation of a novel cyclic tricubane cluster [Cp*$_2$Mo$_2$Fe$_2$S$_4$]$_3$(μ-S$_4$)$_3$ (**2**), from the reaction of **1** with Li$_2$S$_2$.

$$Cp*Mo(S^tBu)_3 \xrightarrow[\text{THF}]{FeCl_3} Cp*_2Mo_2Fe_2S_4Cl_4$$

$$\textbf{3} \qquad\qquad \textbf{1}, 39\%$$

$$\Big\downarrow Li_2S_2 \,/\, THF$$

$$[Cp*_2Mo_2Fe_2S_4]_3(\mu\text{-}S_4)_3$$

$$\textbf{2}, 84\%$$

We previously reported a C−S bond cleaving reaction of Cp*Mo(S$^t$Bu)$_3$ (**3**) leading to a Mo(VI) thio/thiolate complex,
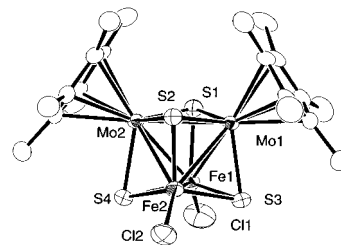


**Figure 1.** The structure of Cp*$_2$Mo$_2$Fe$_2$S$_4$Cl$_2$ (**1**) showing 50% thermal ellipsoids. Selected bond distances (Å): Mo1−Mo2 2.8219(7), Mo1−Fe1 2.760(1), Mo1−Fe2 2.761(1), Mo2−Fe1 2.753(1), Mo2−Fe2 2.754(1), Fe1−Fe2 2.791(1), Fe1−Cl1 2.180(3), Fe2−Cl2 2.197(2), Mo−S av 2.332, Fe−S av 2.263.

Cp*Mo(S)$_2$(S$^t$Bu).[8] This reaction was facilitated by oxidants such as S$_8$ and grey selenium, and we anticipated that FeCl$_3$ would promote C−S bond cleavage as well. Thus, the complex **3** was treated with 1 equiv of FeCl$_3$ in THF to give immediately a dark red solution, and a further color change was noticed when the solution was stirred at room temperature for 12 h. Removal of the solvent and recrystallization of the resulting solid from CH$_2$Cl$_2$/hexane generated an unexpected tetranuclear cluster Cp*$_2$Mo$_2$Fe$_2$S$_4$Cl$_2$ (**1**) as black crystals in 39% yield.[9] The combustion analysis was in agreement with the formula, and the $^1$H NMR spectrum in CDCl$_3$ showed a broad singlet at 1.81 ppm (Cp*, the width at half-height $\nu_{1/2}$ = 33 Hz) indicating a weak paramagnetic nature of the compound. According to the cyclic voltammetric experiment, one reversible redox couple appears at −0.88 V ($E_{1/2}$ vs SCE) and one irreversible oxidation occurs at 1.14 V ($E_p$ vs SCE).[10] While there is uncertainty in defining oxidation states of the metal components, a plausible allotment may be Mo(IV) + Fe(II). Then reduction of iron from Fe(III) to Fe(II) is considered to occur during the cluster formation with the concomitant C−S bond breaking process.

As shown in Figure 1, the X-ray analysis revealed that complex **1** consists of a distorted Mo$_2$Fe$_2$S$_4$ cubane core. Two Cp* ligands and two Cl atoms further coordinate at the molybdenum and the iron sites, respectively.[11] Alternatively, the core structure can be viewed as a Mo$_2$Fe$_2$ tetrahedron face-capped by four sulfur atoms. While the main structural feature of **1** resembles closely that of Cp'$_2$Mo$_2$Fe$_2$S$_4$(NO)$_2$ (**4**; Cp' = η$^5$-C$_5$Me$_4$Et),[12a] their electron counts are different. The latter complex **4** is an electron-precise system with 60 cluster electrons,[13,14] and the four metal atoms are connected through direct metal−metal single bonds. On the other hand, the Mo$_2$-Fe$_2$ tetrahedral core of **1** carries 56 electrons, i.e., 4 electrons less than **4**, which is consistent with paramagnetism of the cluster. The electron-deficiency of **1** affects the Fe−Fe distance most significantly, being 0.087 Å longer than that of **4**. The

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(7) (a) The reaction of (NEt$_4$)$_2$[MoFe$_3$S$_4$Cl$_3$(Cl$_4$cat)(CH$_3$CN)] with NaBPh$_4$ (or NaPF$_6$) in the presence of PR$_3$ was reported to give the edge-linked double cubanes Mo$_2$Fe$_6$S$_8$(PR$_3$)$_6$(Cl$_4$cat)$_2$: Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 7832−7833. (b) It was reported that treatment of [Fe$_4$S$_4$I(ArNC)$_9$] with KBAr$_4$ afforded [{Fe$_4$S$_4$(ArNC)$_9$}$_2$][BAr$_4$]$_2$: Harmjanz, M.; Saak, W.; Haase, D.; Pohl, S. *J. Chem. Soc., Chem. Commun.* **1997**, 951−952.

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(9) For Cp*$_2$Mo$_2$Fe$_2$S$_4$Cl$_2$ (**1**): $^1$H NMR (CDCl$_3$) δ 1.81 (br, s, $\nu_{1/2}$ = 33 Hz). UV−vis (THF) $\lambda_{max}$ ($\epsilon$, M$^{-1}$ cm$^{-1}$) 299 (20 000), 459 (1600), 551 (760), 603 (530) nm. Anal. Calcd for C$_{20}$H$_{30}$S$_4$Mo$_2$Fe$_2$Cl$_2$: C, 31.07; H, 3.91; S, 16.59. Found: C, 30.92; H, 3.91; S, 16.28.
(10) The cyclic voltammograms of **1** and **2** were recorded in THF solution on a glassy carbon electrode with Bu$_4$NClO$_4$ as the supporting electrolyte. The potentials are reported vs saturated calomel electrode, SCE.
(11) Crystal data for Cp*$_2$Mo$_2$Fe$_2$S$_4$Cl$_2$ (**1**): monoclinic, *P*2$_1$/*n* (No. 14), $a$ = 9.526(2) Å, $b$ = 14.997(2) Å, $c$ = 18.917(3) Å, $\beta$ = 95.97(1)°, $V$ = 2688.8(8) Å$^3$, $Z$ = 8, $D_c$ = 1.910 g/cm$^3$, $2\theta_{max}$ = 50.0°, 5260 measured reflections of which 3755 with $I > 3.00\sigma(I)$ were used for the refinement to give $R$ = 0.036, $R_w$ = 0.049, and GOF = 1.92.
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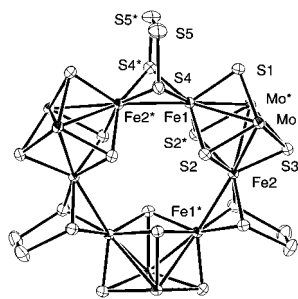(14) Harris, S. *Polyhedron* **1989**, *8*, 2843−2882.

**Figure 2.** The structure of [Cp*$_2$Mo$_2$Fe$_2$S$_4$]$_3$($\mu$-S$_4$)$_3$ (**2**) showing 50% thermal ellipsoids; Cp* groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo−Mo* 2.760(2), Mo−Fe1 2.802-(2), Mo−Fe2 2.800(2), Fe1−Fe2* 2.610(3), Mo−S1 2.325(3), Mo−S2 2.296(3), Mo−S3 2.325(2), Fe1−S1 2.197(4), Fe1−S2 2.267(3), Fe1−S4 2.213(3), Fe2−S2 2.163(3), Fe2−S3 2.193(4), Fe2−S4* 2.214-(3), Fe1−S4−Fe2* 72.2(1), S4−Fe1−S4* 83.4(1).

Mo−Mo distance of 2.8219(7) Å and the mean Mo−Fe bond length of 2.757 Å are both comparable to the corresponding distances of **4** (Mo−Mo, 2.8419(7) Å; Mo−Fe, 2.7654(7) Å). Although various M$_2$M'$_2$S$_4$ clusters having cyclopentadienyl auxiliaries are known,[12,14,15] most of them were procured with $\pi$-acceptor ligands such as CO and NO. Thus, a unique feature of **1** is chloride ligation to each iron atom, which has the advantage of serving as a potential building unit for the synthesis of polycubane cluster aggregate.

The aggregation of **1** was accomplished by treating it with dry Li$_2$S$_2$ in THF,[16] and an unprecedented tricubane cluster [Cp*$_2$Mo$_2$Fe$_2$S$_4$]$_3$($\mu$-S$_4$)$_3$ (**2**) was isolated as black crystals in 84% yield by recrystallization from toluene.[17] The Mo:Fe:S ratio of 1:1:4 was consistent with the X-ray fluorescence microanalysis, and the molecular structure was determined by the X-ray analysis, where the crystals were found to be solvated by toluene.[18] Three Mo$_2$Fe$_2$S$_4$ cubane skeletons are linked by three $\mu_2,\eta^2$-S$_4$(2−) ligands, as shown in Figure 2. Each S$_4$-(2−) ligand bridges two Fe atoms of different cubanes, which is situated perpendicular to the Fe−Fe vector. Being crystallized in the hexagonal $P6_3/m$ space group, the molecule has crystallographic $D_{3h}$ symmetry. A $C_3$ axis runs through the center of molecule, and all Fe atoms and six cubane S atoms, S1 and S3, lie in a mirror plane. Within each cubane core, the Mo−Mo distance is 0.06 Å shorter than that of **1**, and Mo−Fe distances are elongated by 0.04 Å. Most significant difference between the cubane geometries of **1** and **2** is that there is no direct Fe−Fe interaction for **2** and the iron atoms are separated by 3.235-(2) Å. Instead, a new intercubane Fe−Fe bond is formed with the distance of 2.610(3) Å. As this intercubane Fe−Fe bonding is taken into account, the tetrahedral Mo$_2$Fe$_2$ unit has 62 cluster electrons, and the consequence is the long Fe−Fe distance within the cubane simply because the extra two electrons must reside in an antibonding molecular orbital.[12,19,20] It is of interest to



**Figure 3.** Positive electrospray ionization mass spectrum of [Cp*$_2$-Mo$_2$Fe$_2$S$_4$]$_3$($\mu$-S$_4$)$_3$ (**2**). The inset shows (a) an expansion of the **2** + H$^+$ peaks and (b) the calculated isotopic distribution of the ion.

**Scheme 1**



● = Cp*Mo   ○ = Fe
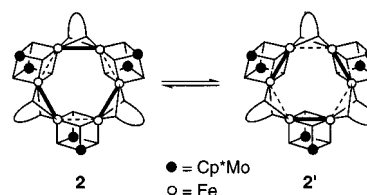
propose another Fe−Fe $\sigma$-bond alternation geometry **2'** as illustrated in Scheme 1. If the intercubane Fe−Fe bond is cleaved, then the Mo$_2$Fe$_2$ core becomes electron precise and the intracubane Fe−Fe bond would be formed. This bond isomer **2'** should electronically be feasible,[20,21] and a certain electronic perturbation may induce transformation from the observed structure **2** to **2'**.

As one would expect from the above electron count, the tricubane cluster **2** is diamagnetic, and the Cp* proton signal appears at 1.93 ppm as a sharp singlet in the $^1$H NMR spectrum. Interestingly, **2** is quite soluble in toluene and THF in spite of the large size of the cluster. The UV−vis spectrum in toluene exhibits a characteristic absorption at 412 nm, while the spectrum of **1** is featureless. The redox property of **2** also differs from **1**, and it is characterized by three reversible redox couples at 0.69, 0.26, and −0.11 V ($E_{1/2}$ vs SCE) and one irreversible reduction step at −0.85 V ($E_p$ vs SCE).[10] The electrospray ionization mass (ESI) spectrometry, carried out by adding a small amount of acetic acid to a THF solution of **2**, deserves comment.[22] The positive ion ESI spectrum, provided in Figure 3, clearly shows two sets of ion peaks associated with mono- and di-protonated species, [M + H]$^+$ and [M + 2H]$^{2+}$, with the correct isotope distributions. The tricubane structure is readily protonated under the mass condition, and such species might well be generated in a preparative scale. Further study of reactivity of **1** and **2** is currently underway.

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(17) For [Cp*$_2$Mo$_2$Fe$_2$S$_4$]$_3$($\mu$-S$_4$)$_3$ (**2**): $^1$H NMR (C$_6$D$_6$) δ 1.93 (s); UV−vis (THF) $\lambda_{max}$ ($\epsilon$, M$^{-1}$ cm$^{-1}$) 412 (30 000), 470 (5800), 645 (2900) nm. Anal. Calcd for C$_{67}$H$_{98}$S$_{24}$Mo$_6$Fe$_6$: C, 31.15; H, 3.82; S, 29.78. Found: C, 31.47; H, 4.19; S, 30.95.

(18) Crystal data for [Cp*$_2$Mo$_2$Fe$_2$S$_4$]$_3$($\mu$-S$_4$)$_3$·C$_7$H$_8$ (**2**): hexagonal, $P6_3/m$ (No. 176), $a = 16.264(8)$ Å, $c = 19.949(6)$ Å, $V = 4572(3)$ Å$^3$, $Z = 2$, $D_c$ = 1.877 g/cm$^3$, $2\theta_{max}$ = 55.0°, 2109 measured reflections of which 1305 with $I > 3.00\sigma(I)$ were used for the refinement to give $R = 0.043$, $R_w = 0.054$, and GOF = 1.87.
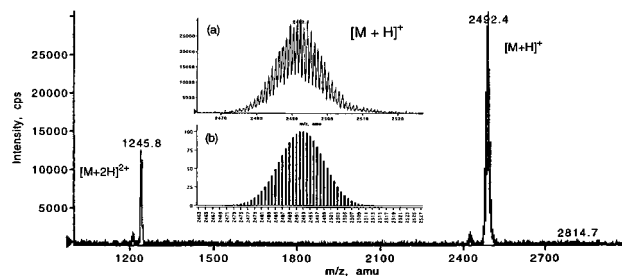
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