Superclusters: A Host–Guest Complex with a Cyclic Array of Three Bridged $MoFe_3S_4$ Clusters**

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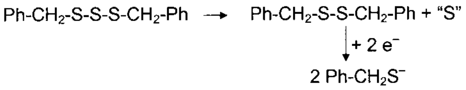
Ongoing research in our laboratory has been directed towards the design and synthesis of high nuclearity Mo/Fe/S clusters as structural analogues of the FeMo cofactor of the nitrogenase protein. Even though recent X-ray structure determinations of the FeMo protein of nitrogenase[1,2] have revealed in detail the structure of the FeMo cofactor, believed to be the site of nitrogen activation and reduction, the synthesis of exact analogues has not yet been accomplished.[3] Nevertheless, partial analogues exist among the plethora of Fe/Mo/S clusters.[4–6] Especially important among these are the $[(Cl_4\text{-cat})_2Mo_2Fe_6(PR_3)_6]$ (**1**; Cl_4-cat = Cl_4-catecholate; R = Et, *n*Pr, *n*Bu) double cubane clusters containing the simple $[MoFe_3S_4]^{2+}$ cores bridged in an edge-fused fashion.[7] These are very useful starting reagents for the synthesis of novel Mo/Fe/S clusters and have enabled us to further investigate new approaches for the rational synthesis of large-core structures. Here we report the synthesis of the new cyclic tricubane cluster $(Et_4N)_3[\{(Cl_4\text{-cat})(PPr_3)MoFe_3S_4Cl\}_3(\mu\text{-}SCH_2Ph)_3]$ (**2**). This cluster is a potential three-electron reducing agent with interesting host–guest characteristics.

Cluster **2** is synthesized by the reaction of $[(Cl_4\text{-cat})_2Mo_2Fe_6(P\textit{n}Pr_3)_6]$ with dibenzyltrisulfide (Bz_2S_3)[8] and Et_4NCl at ambient conditions in THF (details are provided in the Supporting Information). The role of Bz_2S_3 in this reaction is dual [Eq. (1)]. It provides elemental “S”, which causes the oxidative removal of the trialkylphosphanes bound to the four Fe atoms and provides Bz_2S_3. The latter facilitates the oxidation of each $[MoFe_3S_4]^{2+}$ subunit by one electron and promotes the breaking of the edge-shared fused arrangement, providing the bridging benzylthiolate ligands. The oxidation level of the subunits is supported by Mössbauer spectra consistent with the formulation $[Mo^{3+}Fe_2^{3+}Fe^{2+}S_4]^{3+}$ for each of the cubane units in the trimer.[9]



$$\begin{array}{c} \text{Ph-CH}_2\text{-S-S-S-CH}_2\text{-Ph} \longrightarrow \text{Ph-CH}_2\text{-S-S-CH}_2\text{-Ph} + \text{“S”} \\ \downarrow +\,2\,e^- \\ 2\ \text{Ph-CH}_2\text{S}^- \end{array} \qquad (1)$$

Black crystals of **2** suitable for single crystal X-ray structure determination[10] can be obtained upon recrystallization from THF/hexanes at room temperature. The molecular structure shows three $[MoFe_3S_4]^{3+}$ cuboidal units linked by three μ_2-BzS^- ligands (Figure 1). Each thiolate sulfur atom bridges two Fe atoms from two different cubane clusters. The three bridging thiolate μ_2-sulfur atoms and the six Fe atoms that participate in bridging lie in the same plane. The coordination of the third Fe atom in each cubane core is completed by a Cl^- ligand, whereas the Mo atom retains its original coordination environment (phosphane and Cl_4-cat). The Mo–Fe and Fe–Fe intracubane distances of the $[MoFe_3S_4]^{3+}$ cores are not significantly different than those in the known single cubane clusters with the same core. The three Fe–Fe intercubane distances (3.515, 3.561, and 3.624 Å) show the deviation of **2** from an ideal three-fold symmetry and are too long to account for any direct metal–metal intercubane interactions.

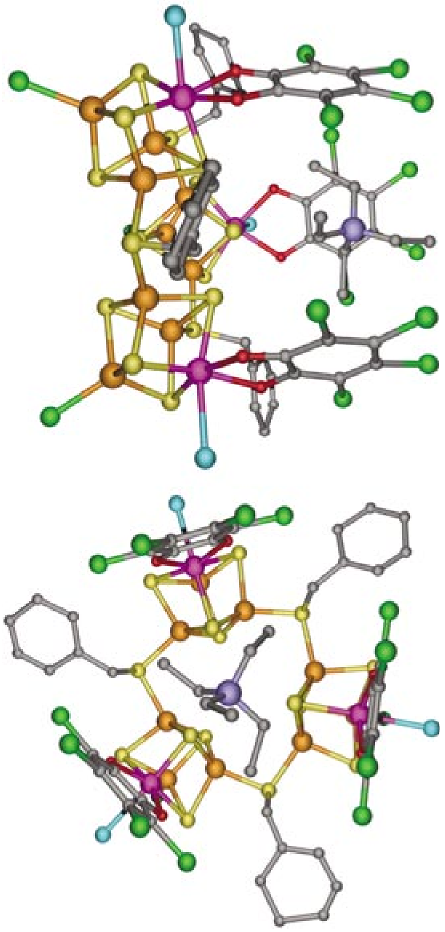


Figure 1. Two views of **2** showing the encapsulated Et_4N^+ counterion. The two Et_4N^+ ions outside the cavity and the alkyl groups of the phosphane ligands have been omitted for clarity.

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An indication of intercubane electronic communication is apparent in the reduction properties as well as the EPR spectrum of **2**. The cyclic voltammogram (see the Supporting Information) reveals three reversible reduction waves at −0.47, −0.63, and 0.74 V, which correspond to the 3−/4−, 4−/5−, and 5−/6− couples, respectively. The single cubane clusters (with the $[MoFe_3S_4]^{3+}$ core) show a single reversible reduction wave with a potential that varies from 0.83 to 1.31 V.[12] The EPR spectrum of **2** is rather complex and does not resemble the $S = {}^3/_2$ signal of the single $MoFe_3S_4$ cubane clusters. This is probably due to intercubane coupling interactions.

In the solid state the three Et_4N^+ counterions of **2** are located in two sites. Two are found in general positions, whereas the third occupies a cavity formed by the three Cl_4-cat ligands. The latter are bound to the Mo atoms of each cubane core and have a *syn* orientation, thus creating a large electron-rich "pocket" which is evident in the space-filling model (Figure 2).

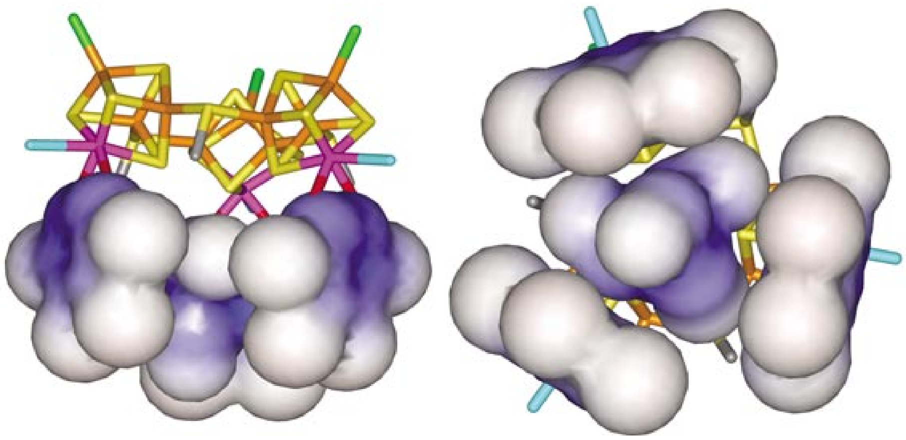

Figure 2. Space-filling model of the three Cl_4-cat ligands (left) and the Et_4N^+ counterion inside the cavity (right).

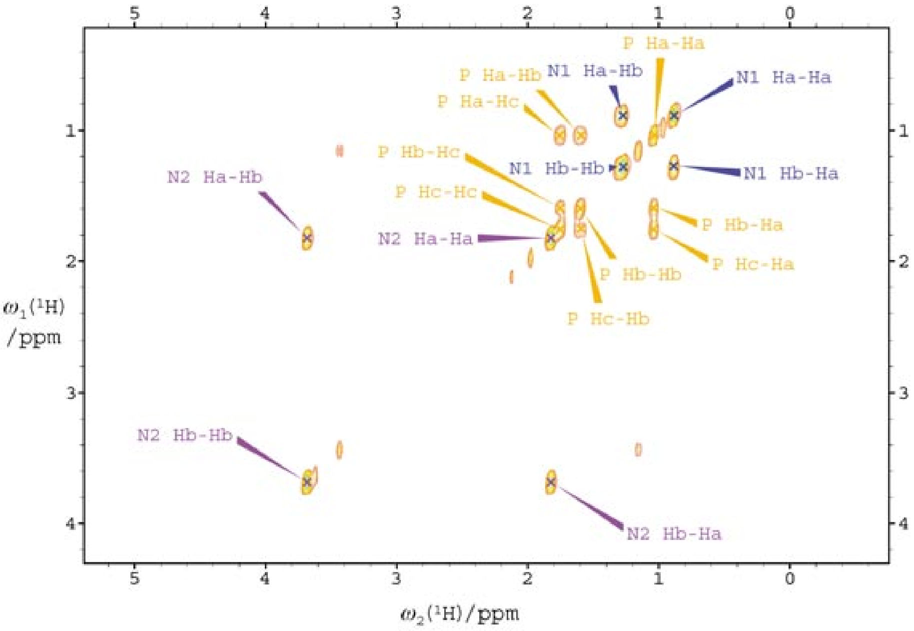

Figure 3. 2D-TOCSY ^{1}H NMR spectrum of **2**. The three sets of resonances and their crosspeaks have been depicted with different colors.

A 2D-TOCSY ^{1}H NMR experiment[13,14] was undertaken to determine whether the trapped Et_4N^+ ion is released in solution. The spectra revealed two sets of peaks that corresponded to Et_4N^+ ions in different environments (Figure 3). The resonances at $\delta =$ 3.683 ($CH_3\mathit{CH_2}N$) and 1.822 ppm ($\mathit{CH_3}CH_2N$) and their crosspeaks correspond to one set of Et_4N^+ ions; the resonances at $\delta = 1.753$ ($CH_3CH_2\mathit{CH_2}P$), 1.603 ($CH_3\mathit{CH_2}CH_2P$), and 1.036 ppm ($\mathit{CH_3}CH_2CH_2P$) and their crosspeaks correspond to the phosphane ligands of the Mo atoms; and the resonances at $\delta = 1.822$ ($CH_3\mathit{CH_2}N$) and 0.886 ppm ($CH_3\mathit{CH_2}N$) and their crosspeaks correspond to a unique Et_4N^+ ion. If only one type of counterion was present, one set of peaks (at $\delta = 3.683$ and 1.822 ppm) would be observed for Et_4N^+. The observation of two sets of resonances and the upfield shift of the second set provide direct evidence that, in solution, the trapped Et_4N^+ ion stays in the electron-rich cavity, and its protons experience the observed shielding.

The same motif of tricyclic arrangement of single cubane clusters exists in only one other example in the literature.[15] In that case three $Mo_2Fe_2S_4$ cores are linked by three $\mu_2,\eta^2\text{-}S_4^{2-}$ ligands "η" that give rise to a neutral polycubane cluster. The role of Et_4N^+ as a possible templating agent remains to be determined. It is unclear whether its presence is needed for an organization of the cubane cores prior to coupling. However, in experiments conducted with counterions other than Et_4N^+, different products are obtained that do not exhibit this characteristic cyclic arrangement of cubane units.[16] It should be emphasized that in the synthesis of the metastable Fe_6S_6 prismanes the role of Et_4N^+ is critical, as other counterions (Bu_4N^+ or Ph_4P^+) lead to the thermodynamically stable single cubane clusters.[17]

In **2**, the trigonal arrangement of three μ_3-S ligands, from the three different cubane cores facing the interior of the cavity, defines a site that is well suited for coordination to metal ions such as Fe^{2+} or Cu^+. At present, attempts are being made to replace the encapsulated Et_4N^+ ion in **2** with a transition metal ion and generate a coordinatively unsaturated site that is potentially useful for the activation and multielectron reduction of small molecules.

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Keywords: cluster compounds · host–guest chemistry · nitrogenase · reduction · S ligands

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[9] The Mössbauer spectrum is provided in the Supporting Information. Measurements in the presence of external magnetic fields in combination with EPR spectroscopy and magnetic susceptibility measurements are in progress to further characterize the magnetic and electronic properties of the complex.

[10] Crystal structure determination of **2**: Crystal dimensions $0.08 \times 0.40 \times 0.028$ mm, triclinic space group $P\bar{1}$, $a = 17.622$, $b = 17.933$, $c = 26.2359$ Å, $\alpha = 104.664$, $\beta = 91.324$, $\chi = 113.794°$, $V = 7265.38$ Å^3. $\rho_{\mathrm{calcd}} = 1.507$ mg m^{-3}. The full-matrix least-squares refinement based on F^2 converged to $R1$ $(I > 2\sigma) = 0.0838$ and $wR2 = 0.2126$, GooF $= 0.936$. The data were collected on a Bruker SMART CCD-based X-ray diffractometer, equipped with an LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 158 K, at the University of Michigan X-Ray facility ($2\theta_{\mathrm{max}} = 44.24$). The space group was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated using the software package SHELXTL v.6.1[11a] that revealed the locations of most non-hydrogen atoms. Several full-matrix least squares refinements followed by difference Fourier calculations were performed using SHELXTL, which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic thermal displacement parameters. From 43589 collected reflections, 17914 were independent; number of parameters 1324. The data were processed with SADABS for absorption correction.[11b] CCDC-234743 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] A homonuclear two-dimensional spectrum was collected in CD_2Cl_2 (no TMS) on a Bruker AMX 500 instrument (25 °C). An optimized high power 90° pulse of 7.55 µs was used. Spinlock time for the TOCSY experiment was 75 ms with a 13 dB low-energy pulse. The data were processed with the software package nmrPipe, where they were zero filled, and after Fourier transformation and manual phasing baseline correction was applied using the built-in automated function. The processed FIDs were converted into the UCSF format and were analyzed and assigned using the software package SPARKY.

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