

Octanuclear Iron–Sulfur Clusters with Symmetrically Coupled Fe₄S₄ and Fe₄S₅ Cores

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Crystallographic investigations of the MoFe proteins of nitrogenase have recently led to detailed structural information on their P-cluster and FeMo-cofactor cluster constituents.¹ Both clusters are octanuclear, the former consisting of two Fe₄S₄ cubane cores linked via dual cysteinate bridges as well as by either an intercore S–S bond^{1a,b} or a commonly-shared core S atom,^{1c} and the latter of two cuboidal cores (one Fe₄S₃ and one MoFe₃S₃) joined by three bridging μ_2 -S atoms. In the interest of further understanding how these clusters are involved in the dinitrogen-fixing role of the enzymes, chemists are now presented with the task of preparing synthetic analogues, a formidable challenge in view of the unprecedented features inherent to the two bridged structures.² The direct coupling of two iron–sulfur cubane type clusters has previously been achieved primarily in three different structural variations: Fe₄S₄ cores connected by a single μ_2 -S atom,³ MoFe₃S₄ cores connected by one μ_2 -S atom linking Fe atoms and one μ_2 -X ligand (X = S²⁻, OH⁻, CN⁻, N₂H₄) linking octahedrally coordinated Mo atoms,⁴ and MFe₃S₄ cores (M = V, Nb, Mo, W, Re) connected by three μ_2 -(SR) groups linking octahedrally coordinated M atoms.^{5,6} Herein, we describe two octanuclear clusters, [Fe₈S₈(PCy₃)₆] (Cy = cyclohexyl) and [Fe₈S₁₂(CN⁻Bu)₁₂], each with a new mode of coupling between their respective tetranuclear core subunits, and each of potential utility as a precursor to the nitrogenase clusters.

A mixture of [Fe(PEt₃)₂Cl₂]⁷ (4.02 g, 11.0 mmol) and NaSPh (2.88 g, 22.0 mmol) was stirred in 50 mL of benzene for 2 h to give a deep red solution.⁸ Addition of benzyl trisulfide (4.60 g, 16.5 mmol), followed by PCy₃ (7.00 g, 25.1 mmol), to the filtered solution induced an immediate color change to brown accompanied by formation of a black precipitate. Upon benzene removal, the residue was extracted with 80 mL of toluene, producing a dark brown solution,⁹ which was filtered, reduced in volume to 40 mL, and allowed to stand for up to 6 days. Crystalline [Fe₈S₈(PCy₃)₆]·C₇H₈ (0.71 g, 21%) was recovered

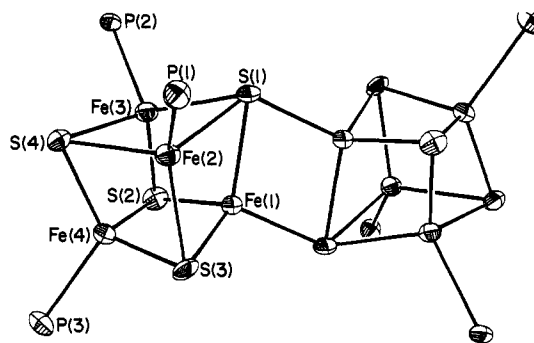


Figure 1. Core structure (50% probability ellipsoids) and atom-labeling scheme of the dicubane cluster [Fe₈S₈(PCy₃)₆]. The cluster resides on an inversion center located in the middle of the Fe₂S₂ rhomb linking its two cubane components. Selected intercube interatomic distances (Å) and angles (deg): Fe–Fe 2.681(8), Fe– μ_4 -S 2.309(7), μ_4 -S–Fe– μ_4 -S 110.7(2), mean μ_4 -S–Fe– μ_3 -S 113.1(3). Selected intracubane interatomic distances (Å): mean Fe(1)–Fe 2.64(3), Fe(2)–Fe(3) 2.523(6), mean Fe(4)–Fe 2.69(1), Fe(1)–S(1) 2.407(9), mean Fe(1)– μ_3 -S 2.305(2), Fe(2)–S(1) 2.388(10), Fe(2)–S(3) 2.267(10), Fe(2)–S(4) 2.306(7), Fe(3)–S(1) 2.351(7), Fe(3)–S(2) 2.287(7), Fe(3)–S(4) 2.320(9), mean Fe(4)– μ_3 -S 2.269(6), Fe(2)–P(1) 2.412(6), Fe(3)–P(2) 2.450(11), Fe(4)–P(3) 2.313(10).

in the form of black rhombic plates.¹⁰ Single-crystal X-ray diffraction revealed the dicubane core structure illustrated in Figure 1.^{11a} The compound proved insoluble in most common solvents with the exception of dichloromethane. Analysis of its Mössbauer spectrum indicates the presence of three types of iron atoms in an appropriate 1:1:2 ratio, consistent with the essentially equivalent environments of Fe(2) and Fe(3).¹² The isomer shifts (particularly those near 0.6 mm/s) fall into the range expected for tetrahedral Fe²⁺; however, no scale exists for comparison with other FeS₃P coordinated species.

The [Fe₈S₈(PCy₃)₆] cluster possesses idealized point group symmetry C_{2h} and exhibits a new structure type in which two Fe₄S₄ cubane cores are directly linked via two Fe–S bonds, with no intermediate bridging atoms (Figure 1). In congruence with the majority of iron–sulfur clusters, the structure is composed entirely of edge-sharing FeX₄ (X = S, L) tetrahedra where L is a monodentate terminal ligand such as PCy₃. On the basis of this principle, a complete database of structures has been generated for iron–sulfur clusters of nuclearity 8 or less.¹³ Of the 79 possible Fe₈S₈L₆ isomers generated, *only* the dicubane geometry (Figure 1) meets the empirically derived structural requirements that higher nuclearity iron–sulfur clusters be uniterminally ligated with S atom bridging modalities in the range μ_2 – μ_4 . Note that each edge shared between two tetrahedral Fe centers corresponds to an Fe₂S₂ rhomb, and that the central intercube rhomb in [Fe₈S₈(PCy₃)₆] is rigorously planar, whereas the intracubane rhombs are not planar by virtue of the folding necessary in establishing a cubane geometry. The cubane subunits themselves display a number of structural

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(6) Nonbridged octanuclear Fe–S clusters containing concentric Fe₈ cubes and S₆ octahedra have been reported previously in [Fe₈S₄S₆]^{2–3–4–}. (a) Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 907. (b) Pohl, S.; Opitz, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 863.

(7) [Fe(PEt₃)₂Cl₂] was prepared by stoichiometric reaction of FeCl₂ and PEt₃ in THF. ¹H NMR (C₆D₆): δ 75.8 (CH₂), 2.2 (CH₃).

(8) All reactions were performed under a pure dinitrogen atmosphere at room temperature.

(9) The FAB mass spectrum of this solution exhibits a parent peak at $m/z = 1473$ corresponding to an unprecedented [Fe₄S₄(PCy₃)₄] cluster. Presumably, loss of one PCy₃ upon standing facilitates dimerization and subsequent precipitation as the sparingly soluble dicubane product.

(10) Anal. Calcd for C₁₁₅H₂₀₆Fe₈P₆S₈: C, 55.74; H, 8.38; Fe, 18.03; P, 7.50; S, 10.35. Found: C, 55.93; H, 8.19; Fe, 18.16; P, 7.29; S, 10.50.

(11) Crystallographic data were collected at 223 K on a Nicolet R3/mV diffractometer employing Mo K α radiation and were empirically corrected (XEMP) for absorption effects with the aid of azimuthal Ψ -scans. The structures were solved by direct methods (XS) and refined against observed data ($F_o > 6\sigma F_o$) with successive full-matrix least-squares cycles (SHELXL-PLUS). (a) [Fe₈S₈(PCy₃)₆]·C₇H₈, P1, $a = 14.001(5)$ Å, $b = 14.588(4)$ Å, $c = 18.548(8)$ Å, $\alpha = 70.51(3)^\circ$, $\beta = 71.76(3)^\circ$, $\gamma = 61.61(2)^\circ$, $V = 3087(2)$ Å³, $Z = 1$, 7131 unique data, 2536 observed data, $R = 0.0810$, $R_w = 0.0766$. (b) [Fe₈S₁₂(CN⁻Bu)₁₂]·5C₆H₆, P2₁/c, $a = 15.132(6)$ Å, $b = 20.123(9)$ Å, $c = 21.278(11)$ Å, $\beta = 109.72(3)^\circ$, $V = 6099(5)$ Å³, $Z = 2$, 7994 unique data, 3803 observed data, $R = 0.0870$, $R_w = 0.0943$.

(12) Fit of Mössbauer data (δ , ΔE_Q (mm/s, 4.2 K)): 0.49, 2.20 (27%), 0.60, 1.14 (47%), 0.62, 0.73 (21%). Isomer shifts (δ) are referenced to Fe metal at room temperature.

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irregularities, the most obvious being an unusually short Fe(2)–Fe(3) distance of 2.523(6) Å, as compared with the other more typical Fe–Fe distances (mean 2.66(4) Å). Somewhat more subtle are the slightly elongated intracubane Fe–S(1) bond distances (mean 2.38(2) Å), as compared with the other intracubane Fe–S distances (mean 2.29(3) Å) and the intercubane Fe–S distance of 2.309(7) Å. Bulky PCy₃ ligands surround the cluster core, leaving only a single exposed S atom (S(4)) at each end, and it is most likely the closeness of their packing which gives rise to the considerable range of observed S–Fe–P bond angles (100.9(3)–122.9(3)°). The coupled metal–sulfur core connectivity of [Fe₈S₈(PCy₃)₆] has been observed in three other clusters, all of the type [M₂Mo₆S₈(H₂O)₁₈]⁸⁺ (M = Co, Cu, Pd) where the M atoms are tetrahedrally coordinated, occupying the Fe(1) positions, and the Mo atoms are octahedrally coordinated, each with three H₂O ligands.¹⁴ A similar type of coupling interaction joins two face-capped octahedral Co₆S₈ cores to form the cluster [Co₁₂S₁₆(PEt₃)₁₀]²⁺; here the intercore rhomb angles are less oblique due to the square pyramidal Co coordination.¹⁵ Analogous bridging arrangements are also commonly found linking hexanuclear cluster cores in extended solid frameworks,¹⁶ intimating the possibility of obtaining a two-dimensional framework of directly linked Fe₄S₄ cores from a similar reaction system with the exclusion of PCy₃. The intractable nature of such frameworks^{18b} might be construed to suggest that the core coupling in [Fe₈S₈(PCy₃)₆] is chemically irreversible; however, this remains to be tested.

An octanuclear cluster featuring cubane-like cores coupled in a less compact manner has also been obtained. Reaction of the [2:2] site-differentiated cubane [Fe₄S₄(SET)₂(CN^tBu)₆]¹⁹ (0.66 g, 0.68 mmol) with H₂S (4.1 mmol) in benzene produced black crystalline [Fe₈S₁₂(CN^tBu)₁₂] in low yield (ca. 0.03 g).²⁰ Single-crystal X-ray diffraction exposed a core structure approaching C_{2h} symmetry and consisting of two Fe₄S₅ subunits coupled through two bridging μ₂-S atoms (Figure 2).^{11b} Composed of two tetrahedral (Fe(1), Fe(2)) and two octahedral (Fe(3), Fe(4)) iron centers, the Fe₄S₅ components are related to the standard cubane core through formal replacement of one μ₃-S²⁻ atom with a μ₃-S₂²⁻ unit. Depending on whether the disulfide unit binds in a side-on or entirely end-on (as found in [Fe₈S₁₂(CN^tBu)₁₂]) fashion, two different Fe₄S₅ isomers are possible, both of which have been observed in the clusters [Fe₄S₅Cp₄]⁺²⁺ and [Fe₄S₅(MeCp)₄]⁺, respectively.²¹ The mode

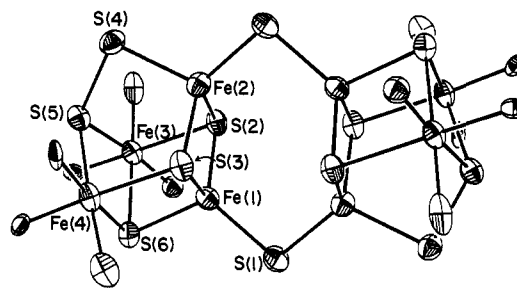


Figure 2. Core structure (50% probability ellipsoids) and atom-labeling scheme of [Fe₈S₁₂(CN^tBu)₁₂]. Unlabeled ellipsoids represent C atoms. The cluster resides on an inversion center. Selected interatomic distances (Å) and angles (deg) between Fe₄S₅ subunits: Fe··Fe 3.269(4), mean Fe–S(1) 2.185(2), μ₃-S··μ₃-S 3.428(6), Fe–S–Fe 96.9(2), mean μ₂-S–Fe–S(2,3) 115.9(8). Selected interatomic distances (Å) and angles (deg) within Fe₄S₅ subunits: Fe(1)–Fe(2) 2.798(4), mean Fe(1)–Fe(3,4) 2.980(7), Fe(3)··Fe(4) 3.479(4), mean Fe(2)··Fe(3,4) 3.646(6), mean Fe(1,2)–S 2.26(1), mean Fe(3,4)–S 2.36(2), mean Fe–C 1.85(3), S(4)–S(5) 2.102(6), Fe(2)–S(4)–S(5) 91.4(2), mean Fe(3,4)–S(5)–S(4) 112.4(2), mean S–Fe(1,2)–S 104(1), mean S(5)–Fe(3,4)–S(6) 83.2(1), mean of other S–Fe(3,4)–S 96.0(3).

of coupling in the [Fe₈S₁₂(CN^tBu)₁₂] cluster is related to that in one of the nitrogenase P-cluster models^{1a,b} in that it contains two μ₂-S atoms bridging tetrahedral Fe centers. Importantly, the incorporation of an extra S atom (S(4)) in the core subunits has a profound influence on the coupling arrangement. In effect, it forces the Fe(1)–S(2)–Fe(2)–S(3) rhomb into a much more planar configuration (the mean deviation of these atoms from a least squares fitted plane is 0.04 Å) than exists in the cubane precursor [Fe₄S₄(SET)₂(CN^tBu)₆],¹⁹ minimizing repulsive intercore interactions between lone pairs on opposing S atoms. The result is a long intercore μ₃-S··μ₃-S separation of 3.428(6) Å, and the absence of any intercore S–S bond such as the one found in the P-cluster model.

It is hoped that the new structural features disclosed by the octanuclear clusters [Fe₈S₈(PCy₃)₆] and [Fe₈S₁₂(CN^tBu)₁₂] introduced here will be of value in the continuing effort to produce synthetic analogues of the nitrogenase clusters. Future reports will describe solution and reactivity properties of these clusters.

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Supporting Information Available: X-ray structural information, including tables of crystal and intensity collection data, positional and thermal parameters, and interatomic distances and angles (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840 and references therein. Particularly noteworthy examples include the Chevrel phases¹⁷ and a series of extended frameworks with formulas [Re₆Se₈Cl_{2+n}]ⁿ⁻ (n = 0, 1, 2, 4) built up from [Re₆Se₈]²⁺ cluster cores.¹⁸

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(20) FAB-MS (DMF): *m/z* 1828. ¹H NMR (C₆D₆): δ 1.40 (br, CH₃).