Octanuclear Iron–Sulfur Clusters with Symmetrically Coupled Fe₄S₄ and Fe₄S₄ 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 cysteinyl bridges as well as by either an intercore S–S bond1–5 or a commonly-shared core S atom,6 and the latter of two cuboidal cores (one Fe₄S₄ and one MoFe₃S₃) joined by three bridging µ₃-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.7 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 µ₂-S atom,8 MoFe₃S₃ cores connected by one µ₂-S atom linking Fe atoms and one µ₁-X ligand (X = S²⁻, OH⁻, CN⁻, N₂),9 linking octahedrally coordinated Mo atoms,10 and MoFe₃S₄ cores (M = V, Nb, Mo, W, Re) connected by three µ₂-(SR) groups linking octahedrally coordinated M atoms.11 Herein, we describe two octanuclear clusters, [Fe₄S₄(PCy₃)₆] (Cy = cyclohexyl) and [Fe₄S₄(CN-η-C₅H₄)₄], 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)₃Cl]³⁺ (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.10 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, which was filtered, reduced in volume to 40 mL, and allowed to stand for up to 6 days. Crystalline [Fe₄S₄(PCy₃)₆]Cl·H₂O (0.71 g, 21% yield) was recovered in the form of black rhombic plates.11 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 approximate 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 Fe₄S₄P coordinated species.

The [Fe₄S₄(PCy₃)₆] cluster possesses idealized point group symmetry Cs 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 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 Fe₄S₄L₆ isomers generated, only the dicubane geometry (Figure 1) meets the empirically derived structural requirements that higher nuclearity iron–sulfur clusters be unterminally ligated with S atom bridging modalities in the range µ₂–₄. Note that each edge shared between two tetrahedral Fe centers corresponds to an Fe₄S₄ rhomb, and that the central dicubane rhomb in [Fe₄S₄(PCy₃)₆] is rigorously planar, whereas the intracubane discriminations are not planar by virtue of the folding necessary in establishing a cubane geometry. The cubane subunits themselves display a number of structural features.

(8) Anal. Calcd for Cd₉H₇O₂Fe₂P₇S₇: C, 55.74; H, 8.38; Fe, 18.03; P, 13.86. Found: C, 55.93; H, 8.19; Fe, 18.16; P, 13.27. (9) Crystallographic data were collected at 223 K on a Nicolet R3/mV single-crystal X-ray diffractometer employing Mo Kα 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 (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77). The structures were solved by direct methods (XS) and refined against observed data (R = 0.77).
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 [M₆O₆S₈
(H₂O)₁₆]⁺ (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. A similar type of coupling interaction joins two face-
capped octahedral Co₆S₈ cores to form the cluster [Co₂S₄₆
(PCy₃)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 hexa-
nuclear cluster cores in extended solid frameworks, 16 intimating
the possibility of obtaining a two-dimensional framework of
directly linked Fe₈S₈ cores from a similar reaction system with
the exclusion of PCy₃. The intractable nature of such frameworks 18
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 [Fe₈S₈(SEt)₄(CNBu)] 19 (0.66
g, 0.68 mmol) with H₂S (4.1 mmol) in benzene produced black
crystalline [Fe₈S₈(CNBu)] 20 in low yield (ca. 0.03 g). 20 Single-
crystal X-ray diffraction exposed a core structure approaching
C₃₆h symmetry and consisting of two Fe₈S₈ subunits coupled
through two bridging µ₂-S atoms (Figure 2). 11,15 Composed of
two tetrahedral (Fe(1), Fe(2)) and two octahedral (Fe(3), Fe-
(4)) iron centers, the Fe₈S₈ components are related to the
standard cubane core through formal replacement of one µ₂-
S²⁻ atom with a µ₃-S²⁻ unit. Depending on whether the
disulfide unit binds in a side-on or entirely end-on (as found in
[Fe₈S₈(CNBu)] 20 ) fashion, two different Fe₈S₈ isomers are
possible, both of which have been observed in the clusters
[Fe₈S₈(CP₃)₄] 2+ 22 and [Fe₈S₈(MeCP₃)₄] 2+ , respectively. 23 The mode

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**Figure 2.** Core structure (50% probability ellipsoids) and atom-labeling scheme of [Fe₈S₈(CNBu)] 20. Unlabeled ellipsoids represent C atoms. The cluster resides on an inversion center. Selected interatomic distances (Å) and angles (deg) between Fe₈S₈ subunits: Fe–Fe 2.369-
(4), mean Fe–S(1) 2.185(2), µ₃-S••µ₁-S 3.428(6), Fe–S–Fe 96.2(2), mean µ₂-S–Fe–S(2,3) 115.9(8). Selected interatomic distances (Å) and angles (deg) within Fe₈S₈ subunits: Fe(1)–Fe(2) 2.798(4), mean Fe(1)–Fe(3,4) 2.980(7), Fe(2)–Fe(4) 3.479(4), mean Fe(2)–Fe(3,4) 3.606(4), mean Fe(1,2,3)–S(5,6) 2.26(1), mean Fe(3,4)–S(6) 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(4)–S(5) 112.4(2), mean S–Fe(1,2)–S(1041), mean S(5)–Fe(3,4)–S(6) 83.2(1), mean of other S–Fe(3,4)–S 96.0(3).

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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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