

## Octanuclear Iron–Sulfur Clusters with Symmetrically Coupled Fe<sub>4</sub>S<sub>4</sub> and Fe<sub>4</sub>S<sub>5</sub> Cores

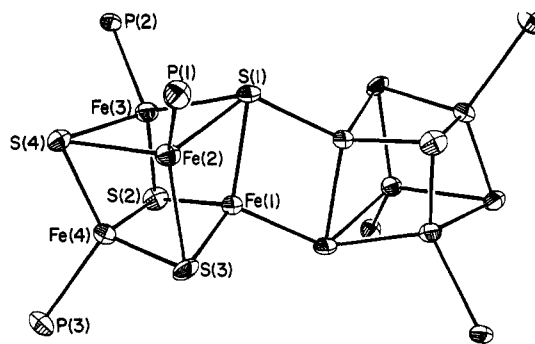
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Crystallographic investigations of the MoFe proteins of nitrogenase have recently led to detailed structural information on their P-cluster and FeMo-cofactor cluster constituents.<sup>1</sup> Both clusters are octanuclear, the former consisting of two Fe<sub>4</sub>S<sub>4</sub> cubane cores linked via dual cysteinate bridges as well as by either an intercore S–S bond<sup>1a,b</sup> or a commonly-shared core S atom,<sup>1c</sup> and the latter of two cuboidal cores (one Fe<sub>4</sub>S<sub>3</sub> and one MoFe<sub>3</sub>S<sub>3</sub>) joined by three bridging μ<sub>2</sub>-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.<sup>2</sup> The direct coupling of two iron–sulfur cubane type clusters has previously been achieved primarily in three different structural variations: Fe<sub>4</sub>S<sub>4</sub> cores connected by a single μ<sub>2</sub>-S atom,<sup>3</sup> MoFe<sub>3</sub>S<sub>4</sub> cores connected by one μ<sub>2</sub>-S atom linking Fe atoms and one μ<sub>2</sub>-X ligand (X = S<sup>2-</sup>, OH<sup>-</sup>, CN<sup>-</sup>, N<sub>2</sub>H<sub>4</sub>) linking octahedrally coordinated Mo atoms,<sup>4</sup> and MFe<sub>3</sub>S<sub>4</sub> cores (M = V, Nb, Mo, W, Re) connected by three μ<sub>2</sub>-(SR) groups linking octahedrally coordinated M atoms.<sup>5,6</sup> Herein, we describe two octanuclear clusters, [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] (Cy = cyclohexyl) and [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>-</sup>Bu)<sub>12</sub>], 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(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>7</sup> (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.<sup>8</sup> Addition of benzyl trisulfide (4.60 g, 16.5 mmol), followed by PCy<sub>3</sub> (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,<sup>9</sup> which was filtered, reduced in volume to 40 mL, and allowed to stand for up to 6 days. Crystalline [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>]·C<sub>7</sub>H<sub>8</sub> (0.71 g, 21%) was recovered



**Figure 1.** Core structure (50% probability ellipsoids) and atom-labeling scheme of the dicubane cluster [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>]. The cluster resides on an inversion center located in the middle of the Fe<sub>2</sub>S<sub>2</sub> rhomb linking its two cubane components. Selected intercube interatomic distances (Å) and angles (deg): Fe–Fe 2.681(8), Fe–μ<sub>4</sub>-S 2.309(7), μ<sub>4</sub>-S–Fe–μ<sub>4</sub>-S 110.7(2), mean μ<sub>4</sub>-S–Fe–μ<sub>3</sub>-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<sub>3</sub>-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<sub>3</sub>-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.<sup>10</sup> Single-crystal X-ray diffraction revealed the dicubane core structure illustrated in Figure 1.<sup>11a</sup> 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).<sup>12</sup> The isomer shifts (particularly those near 0.6 mm/s) fall into the range expected for tetrahedral Fe<sup>2+</sup>; however, no scale exists for comparison with other FeS<sub>3</sub>P coordinated species.

The [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] cluster possesses idealized point group symmetry C<sub>2h</sub> and exhibits a new structure type in which two Fe<sub>4</sub>S<sub>4</sub> 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 FeX<sub>4</sub> (X = S, L) tetrahedra where L is a monodentate terminal ligand such as PCy<sub>3</sub>. On the basis of this principle, a complete database of structures has been generated for iron–sulfur clusters of nuclearity 8 or less.<sup>13</sup> Of the 79 possible Fe<sub>8</sub>S<sub>8</sub>L<sub>6</sub> isomers generated, only the dicubane geometry (Figure 1) meets the empirically derived structural requirements that higher nuclearity iron–sulfur clusters be unitermally ligated with S atom bridging modalities in the range μ<sub>2</sub>–4. Note that each edge shared between two tetrahedral Fe centers corresponds to an Fe<sub>2</sub>S<sub>2</sub> rhomb, and that the central intercube rhomb in [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] 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 Fe<sub>8</sub> cubes and S<sub>6</sub> octahedra have been reported previously in [Fe<sub>8</sub>S<sub>8</sub>I<sub>8</sub>]<sup>2–3–4–</sup>. (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(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] was prepared by stoichiometric reaction of FeCl<sub>2</sub> and PEt<sub>3</sub> in THF. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 75.8 (CH<sub>2</sub>), 2.2 (CH<sub>3</sub>).

(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 [Fe<sub>4</sub>S<sub>4</sub>(PCy<sub>3</sub>)<sub>4</sub>] cluster. Presumably, loss of one PCy<sub>3</sub> upon standing facilitates dimerization and subsequent precipitation as the sparingly soluble dicubane product.

(10) Anal. Calcd for C<sub>115</sub>H<sub>206</sub>Fe<sub>8</sub>P<sub>6</sub>S<sub>8</sub>: 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.

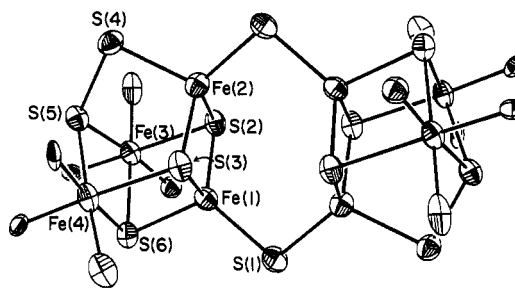
(11) Crystallographic data were collected at 223 K on a Nicolet R3/mV diffractometer employing Mo Kα radiation and were empirically corrected (XEMP) for absorption effects with the aid of azimuthal Ψ-scans. The structures were solved by direct methods (XS) and refined against observed data (F<sub>o</sub> > 6σF<sub>o</sub>) with successive full-matrix least-squares cycles (SHELX-TL PLUS). (a) [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>]·C<sub>7</sub>H<sub>8</sub>, P1, a = 14.001(5) Å, b = 14.588(4) Å, c = 18.548(8) Å, α = 70.51(3)°, β = 71.76(3)°, γ = 61.61(2)°, V = 3087(2) Å<sup>3</sup>, Z = 1, 7131 unique data, 2536 observed data, R = 0.0810, R<sub>w</sub> = 0.0766. (b) [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>-</sup>Bu)<sub>12</sub>]·5C<sub>6</sub>H<sub>6</sub>, P2<sub>1</sub>/c, a = 15.132(6) Å, b = 20.123(9) Å, c = 21.278(11) Å, β = 109.72(3)°, V = 6099(5) Å<sup>3</sup>, Z = 2, 7994 unique data, 3803 observed data, R = 0.0870, R<sub>w</sub> = 0.0943.

(12) Fit of Mössbauer data (δ, ΔE<sub>q</sub> (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 PCy<sub>3</sub> 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 [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] has been observed in three other clusters, all of the type [M<sub>8</sub>Mo<sub>6</sub>S<sub>8</sub>(H<sub>2</sub>O)<sub>18</sub>]<sup>8+</sup> (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 H<sub>2</sub>O ligands.<sup>14</sup> A similar type of coupling interaction joins two face-capped octahedral Co<sub>6</sub>S<sub>8</sub> cores to form the cluster [Co<sub>12</sub>S<sub>16</sub>(PEt<sub>3</sub>)<sub>10</sub>]<sup>2+</sup>; here the intercore rhomb angles are less oblique due to the square pyramidal Co coordination.<sup>15</sup> Analogous bridging arrangements are also commonly found linking hexanuclear cluster cores in extended solid frameworks,<sup>16</sup> intimating the possibility of obtaining a two-dimensional framework of directly linked Fe<sub>4</sub>S<sub>4</sub> cores from a similar reaction system with the exclusion of PCy<sub>3</sub>. The intractable nature of such frameworks<sup>18b</sup> might be construed to suggest that the core coupling in [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] 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 [Fe<sub>4</sub>S<sub>4</sub>(SEt)<sub>2</sub>(CN<sup>t</sup>Bu)<sub>6</sub>]<sup>19</sup> (0.66 g, 0.68 mmol) with H<sub>2</sub>S (4.1 mmol) in benzene produced black crystalline [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>t</sup>Bu)<sub>12</sub>] in low yield (*ca.* 0.03 g).<sup>20</sup> Single-crystal X-ray diffraction exposed a core structure approaching C<sub>2h</sub> symmetry and consisting of two Fe<sub>4</sub>S<sub>5</sub> subunits coupled through two bridging μ<sub>2</sub>-S atoms (Figure 2).<sup>11b</sup> Composed of two tetrahedral (Fe(1), Fe(2)) and two octahedral (Fe(3), Fe(4)) iron centers, the Fe<sub>4</sub>S<sub>5</sub> components are related to the standard cubane core through formal replacement of one μ<sub>3</sub>-S<sup>2-</sup> atom with a μ<sub>3</sub>-S<sub>2</sub><sup>2-</sup> unit. Depending on whether the disulfide unit binds in a side-on or entirely end-on (as found in [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>t</sup>Bu)<sub>12</sub>]) fashion, two different Fe<sub>4</sub>S<sub>5</sub> isomers are possible, both of which have been observed in the clusters [Fe<sub>4</sub>S<sub>5</sub>Cp<sub>4</sub>]<sup>+2+</sup> and [Fe<sub>4</sub>S<sub>5</sub>(MeCp)<sub>4</sub>]<sup>+</sup>, respectively.<sup>21</sup> The mode



**Figure 2.** Core structure (50% probability ellipsoids) and atom-labeling scheme of [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>t</sup>Bu)<sub>12</sub>]. Unlabeled ellipsoids represent C atoms. The cluster resides on an inversion center. Selected interatomic distances (Å) and angles (deg) between Fe<sub>4</sub>S<sub>5</sub> subunits: Fe••Fe 3.269(4), mean Fe–S(1) 2.185(2), μ<sub>3</sub>-S••μ<sub>3</sub>-S 3.428(6), Fe–S–Fe 96.9(2), mean μ<sub>2</sub>-S–Fe–S(2,3) 115.9(8). Selected interatomic distances (Å) and angles (deg) within Fe<sub>4</sub>S<sub>5</sub> 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 [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>t</sup>Bu)<sub>12</sub>] cluster is related to that in one of the nitrogenase P-cluster models<sup>1a,b</sup> in that it contains two μ<sub>2</sub>-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 [Fe<sub>4</sub>S<sub>4</sub>(SEt)<sub>2</sub>(CN<sup>t</sup>Bu)<sub>6</sub>],<sup>19</sup> minimizing repulsive intercore interactions between lone pairs on opposing S atoms. The result is a long intercore μ<sub>3</sub>-S••μ<sub>3</sub>-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 [Fe<sub>8</sub>S<sub>8</sub>(PCy<sub>3</sub>)<sub>6</sub>] and [Fe<sub>8</sub>S<sub>12</sub>(CN<sup>t</sup>Bu)<sub>12</sub>] 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 phases<sup>17</sup> and a series of extended frameworks with formulas [Re<sub>6</sub>Se<sub>8</sub>Cl<sub>2+n</sub>]<sup>n-</sup> (n = 0, 1, 2, 4) built up from [Re<sub>6</sub>Se<sub>8</sub>]<sup>2+</sup> cluster cores.<sup>18</sup>

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(20) FAB-MS (DMF): *m/z* 1828. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.40 (br, CH<sub>3</sub>).