Published in final edited form as:

Polyhedron. 2013 July 13; 58: 206–217. doi:10.1016/j.poly.2013.02.031.

Structural Analysis of Cubane-Type Iron Clusters

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Abstract

The generalized cluster type $[M_4(\mu_3-Q)_4L_n]^x$ contains the cubane-type $[M_4Q_4]^z$ core unit that can approach, but typically deviates from, perfect T_d symmetry. The geometric properties of this structure have been analyzed with reference to T_d symmetry by a new protocol. Using coordinates of M and Q atoms, expressions have been derived for interatomic separations, bond angles, and volumes of tetrahedral core units (M_4 , Q_4) and the total $[M_4Q_4]$ core (as a tetracapped M_4 tetrahedron). Values for structural parameters have been calculated from observed average values for a given cluster type. Comparison of calculated and observed values measures the extent of deviation of a given parameter from that required in an exact tetrahedral structure. The procedure has been applied to the structures of over 130 clusters containing $[Fe_4Q_4]$ ($Q = S^{2-}$, Se^{2-} , Te^{2-} , $[NPR_3]^-$, $[NR]^{2-}$) units, of which synthetic and biological sulfide-bridged clusters constitute the largest subset. General structural features and trends in structural parameters are identified and summarized. An extensive database of structural properties (distances, angles, volumes) has been compiled in Supporting Information.

Keywords

cubane-type clusters; structural analysis; idealized T_d symmetry; molecular volumes

1. Introduction

Molecular structures are defined by shapes, chirality, and symmetry. Metric features conveying these properties are conventionally described in terms of bond distances and other interatomic separations, angles between bonded atoms, positional deviations from least-squares planes, and dihedral angles involving four or more bonded atoms (torsional angles) and/or non-bonded molecular fragments, usually planes. Overall shapes are described where possible by real or idealized point group symmetries. Among the many generic types of molecular metal-containing clusters is that incorporating the cubane-type core unit $[M_4(\mu_3-Q)_4]^z$ to which are usually appended four or more ligands L, leading to the generalized formulation $[M_4(\mu_3-Q)_4L_n]^x$ for a cluster of net charge x . A generalized cluster with $n = 4$, the most common type, is depicted in Figure 1. Hundreds of such clusters have been structurally defined by X-ray diffraction. The huge size of this cluster family arises

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because of the variability in M (both main group and transition series), bridging ligand Q (frequently chalcogenides), and the number and type of terminal ligands L (usually monodentate but also bi- and tridentate). Further, not all M atoms or Q or L ligands need be the same in a given cluster. In describing the family, the term “cubane-type” is advised because very few clusters present $[M_4Q_4]^z$ cores of rigorous cubic T_d symmetry.

Of all cubane-type cluster types, none has attracted experimental and theoretical scrutiny comparable to that directed to the $[Fe_4S_4]$ clusters. In the period 1972-75, the existence of cubane-type units $[Fe_4S_4(SCys)_4]$ in bacterial proteins was crystallographically demonstrated and the first analogue clusters $[Fe_4S_4(SR)_4]^{2-}$ were chemically synthesized.⁷⁻⁹ Since that time, in excess of 100 synthetic clusters have been prepared and structurally defined¹⁰ and over 50 structures of protein-bound clusters, some at or near atomic resolution, have been described. These results are compiled in the Cambridge Structural Database (CSD) and the Protein Data Bank (PDB). As will be seen, synthetic $[Fe_4S_4]^z$ clusters encompass the $z = 6-$ to $6+$ formal core oxidation states and other $[Fe_4Q_4]^z$ species contain bridging atoms or groups such as $Q = Se^{2-}$, Te^{2-} , $[NPR_3]^-$, and $[NR]^{2-}$. Because of the current interest in and significance of these cubane-type clusters in inorganic chemistry and biology and the extensive structural databases available, we have investigated core geometric parameters to discern intrinsic structural features. Among these are the infrequently considered *volumes* of $[Fe_4Q_4]^z$ cluster cores.

2. Cluster Shapes

Before proceeding to volumes and other features, we note certain considerations of cluster shapes. An $[M_4Q_4]$ cluster composed of two concentric interlocking M_4 and Q_4 regular tetrahedra of the same size has O_h symmetry when $M = Q$ and T_d symmetry when the tetrahedra are of different size and/or $M \neq Q$. Superimposed upon these high symmetries may be a myriad of distortions which lower the symmetry of the original tetrahedra and thus of the overall cluster. To accommodate the range of geometries, the descriptors “cubane-type”, “cubane-like” or “distorted cubane” are conventionally applied to an $[M_4Q_4]$ core entity built of recognizable tetrahedra. The M atoms may be closer or further from the center than the Q atoms, although for $[Fe_4S_4]$ clusters, the closer M_4 arrangement is almost always found.

The first $[Fe_4S_4(SR)_4]^{2-}$ clusters prepared closely approached idealized D_{2d} symmetry in which four Fe-S bonds roughly parallel to the core -4 axis are shorter than the eight Fe-S bonds perpendicular to that axis, leading to a compressed tetragonal shape.^{8,11-13} (Note: the Hermann-Mauguin -4 rotoinversion notation is used for the improper rotational axis to avoid confusion with the S_4 designation for the tetrasulfide core tetrahedron.) Subsequently, the opposite (elongated) distortion was observed together with numerous less symmetrical displacements from T_d symmetry, especially in the $[Fe_4S_4]^{1+}$ oxidation state. For the purpose of structural description, the issues of shape, distortion, and symmetry reside in the $[Fe_4S_4]^z$ core of a cluster. The ligand set L_n modulates electronic properties, changes in which are largely confined to the core, and may transmit intercluster solid state interactions that influence core structure. The early X-ray structures initiated development of procedures to assess distortions from idealized T_d symmetry, confirm point group symmetries, and identify orientations of individual clusters most closely approaching congruence.^{8,13,14} Subsequently, shape analysis has become more incisive and sophisticated with the application of continuous symmetry measures,¹⁵⁻¹⁷ which treats shape and symmetry as continuous properties such as might be encountered in a range of distortions from a reference symmetry. The method has been applied to Et_4N^+ salts of various $[Fe_4S_4L_4]^{3-}$ clusters ($L = Cl, SH$) at different temperatures, some of which very closely approach T_d symmetry.¹⁸ Another approach is based on the circumsphere (a sphere that contains a solid

and touches all vertices) and a T_d reference structure for $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-19}$. Circumspheres are defined by four Fe, four S, and four thiolate sulfur atoms. The structure is then analyzed in terms of positional deviations of the sphere centers and coordinates of these atoms from the reference. Although discussion of these approaches is beyond the purview of this article,²⁰ these methods provide analytical means for identification of point group symmetries and deviations therefrom.

3. Cluster Nomenclature

Clusters that are the subject of this study are designated generally as $[\text{Fe}_4\text{Q}_4\text{L}_4]^x$ where core ligands $\text{Q} = \text{S}^{2-}$, Se^{2-} , Te^{2-} , $[\text{NPR}_3]^-$, or $[\text{NR}]^{2-}$ and terminal ligands L are neutral, uninegative, unipositive, or dinegative, and mono-, bi-, or tridentate. The only exceptions are the clusters $[\text{Fe}_4\text{Q}_4(\text{CO})_{12}]$ (Figure 1), which contain six-coordinate iron sites. Ligand abbreviations are given in the Appendix. The few examples of clusters with mixed terminal ligands are not included here for their structural features are unexceptional compared to the closest homoligated examples. For simplicity, at constant Q clusters are symbolized as $[\text{L}]^y/z$ where z refers to core charge $[\text{Fe}_4\text{Q}_4]^z$ and y to the formal ligand charge such that cluster charge $x = 4y + z$. For example, $\text{Br}^-/2+$ refers to $[\text{Fe}_4\text{S}_4\text{Br}_4]^{2-}$ and $\text{Cp}^-/6+$ to $[\text{Cp}_4\text{Fe}_4\text{S}_4]^{2+}$. For the few cases with more than one ligand L at each Fe site, as with $\text{CO}/0$ for $[\text{Fe}_4\text{S}_4(\text{CO})_{12}]$, the correct formula is assumed. When $\text{Q} = \text{S}^{2-}$, the cluster designation is $\text{Q}/[\text{L}]^y/z$. Iron formal oxidation states are obtained from z . Clusters with constant L (where L is a general ligand class) and variable z constitute a *redox set*. Identical clusters with constant L class and z when isolated in more than one compound and/or crystalline state form a *group*. This nomenclature appears in the figures and throughout the text. The designation of Fe_4 , Q_4 , Fe_3Q , and FeQ_3 units as “tetrahedral” conveys general shape but does not imply strict T_d symmetry. As will be seen, the predominant cluster family contains $\text{Q} = \text{S}^{2-}$, with ligands $\text{L} = \text{halide}$, RS^- ($\text{R} = \text{alkyl}$, aryl), $[\text{N}(\text{SiMe}_3)_2]^-$, Cp^- , and NO^+ defining the main cluster redox sets. The NO^+ formalism is based on nearly linear Fe-N-O coordination.

4. Geometric Considerations

4.1. A First Approach: Tetragonal Distortions

Given that the majority of the clusters $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$,³⁻ prepared in the early phase of $[\text{Fe}_4\text{S}_4]$ cluster chemistry exhibit tetragonally distorted core structures, initial attempts required inclusion of such distortions in the analysis. It was in this period (1972-82) that cluster volumes were first calculated. A generalized $[\text{M}_4\text{Q}_4]$ cluster with idealized D_{2d} symmetry and concentric M_4 and Q_4 tetrahedra can be described by the shape parameters identified in Figure 1c: distances from the center to the M and Q atoms (r_M and r_Q) and two polar angles formed by the -4 axis and the distance vectors r_M and r_Q ($\theta = 54.74^\circ$ for a perfect tetrahedron). The procedure, which utilizes atomic coordinates and is described elsewhere,²¹ affords the volume of the M_4 tetrahedron as eq 1; the Q_4 volume is obtained by an equivalent expression. The entire cluster volume $V(\text{M}_4\text{Q}_4)$ can be defined as the sum of the volumes of the M_4 tetrahedron and the four capping M_3Q tetrahedra, as will be discussed in detail in Section 4.2. The treatment, while restrictive, provided the first calculated volumes of Fe_4 (2.3-2.4 $\text{\AA}^3$) and S_4 (5.4-5.8 $\text{\AA}^3$) tetrahedra and of the complete core (9.5-9.9 $\text{\AA}^3$). It further showed that S_4 included *ca.* 2.3 times the volume of Fe_4 and that core volumes tend to increase upon reduction. A more efficient and general means of volume calculations for T_d symmetry and distortions therefrom is described next.

$$V(\text{M}_4) = 4(r_M^3 \cos \beta_M \sin^2 \beta_M) / 3 \quad (1)$$

4.2. Data Analysis

To discern intrinsic structural properties and dependencies, we consider only cubane clusters $[\text{Fe}_4(\mu_3\text{-Q})_4\text{L}_{(4,12)}]^x$ possessing core homoligation Q and non-face-bridging (terminal) homoligation L. A comprehensive collection of published small molecule structures was compiled from the CSD²² and direct literature sources. The number of synthetic clusters analyzed is extensive and nearly exhaustive. For protein-bound clusters, high-resolution (<1.5 Å) structures of simple electron transfer ferredoxin and high-potential iron-sulfur proteins were selected from the PDB²³ as representative examples. In cases where multiple determinations of the same crystal structure exist, the structure with the lowest residual index (R-factor) was analyzed. Three structures possess alkali metal counteranions that interact with either the Q or L ligands;²⁴ these interactions do not appear to affect the cluster cores, and these structures were therefore included in our analysis. The complete list of structural references is provided as Supporting Information, Table S0.

Cluster core distances and angles were extracted from the CSD via ConQuest²⁵ or, in other cases, from published or PDB coordinates via XP of the SHELXTL crystallographic analysis package.²⁶ For clusters with crystallographically imposed symmetry, unique metrics were weighted by the total number of symmetry-related observations when calculating mean values. Cluster volumes were obtained using the general volume (V) formula for a tetrahedron given by the scalar triple product eq 2,²⁷ where $\{\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}\}$ are its four vertices. Equation 2 allows direct calculation of Fe_4 , Q_4 , and Fe_3Q tetrahedral volumes from orthogonal (Cartesian) coordinates.

$$V = (1/6) |(\mathbf{a} - \mathbf{d}) \cdot ((\mathbf{b} - \mathbf{d}) \times (\mathbf{c} - \mathbf{d}))| \quad (2)$$

Absent specified straight edges and flat faces, an $[\text{M}_4\text{Q}_4]$ cubane structure is simply a set of coordinates that by themselves do not constitute an obvious, well-defined polyhedron. The total enclosed volume of the $[\text{M}_4\text{Q}_4]$ core is therefore undefined. We can construct a polyhedron with $[\text{M}_4\text{Q}_4]$ coordinates as vertices by choosing the M_4 tetrahedron and capping each of its faces with a Q vertex to create four M_3Q triangular pyramids. In formal geometric terms, this process of cumulation²⁷ yields a triakis tetrahedron²⁷ as a polyhedral description of the $[\text{M}_4\text{Q}_4]$ structure. We will adopt the chemically intuitive designation of tetracapped tetrahedron for this figure, specifically a tetracapped M_4 tetrahedron for the case just defined. The total enclosed polyhedral volume $V(\text{M}_4\text{Q}_4)$ is then the sum of the M_4 volume and the volumes of the four M_3Q tetrahedra, assuming that all M_3Q pyramids are external to the M_4 tetrahedron (true for all $[\text{Fe}_4\text{Q}_4]$ systems, see Section 4.5). This is the visualization and volume definition used throughout our analysis. A polyhedral description of the $[\text{M}_4\text{Q}_4]$ structure can also be achieved in an inverted fashion, i.e., as a cumulation of the Q_4 tetrahedron by MQ_3 pyramids (a tetracapped Q_4 tetrahedron), which leads to a different formulation of total enclosed volume ($V^*(\text{M}_4\text{Q}_4)$ in Section 4.4). To our knowledge, this alternate construction does not occur in the literature. Note finally that while tetracapped tetrahedra based on the M_4 or Q_4 subunits are obvious choices to describe the $[\text{M}_4\text{Q}_4]$ structure, other, less-symmetric polyhedra can also be defined from the same vertices.

4.3. T_d -Symmetric Cubanes

As the highest achievable symmetry for $[\text{M}_4\text{Q}_4]$ cubanes, the T_d symmetric core provides a useful *reference geometry* for comparison against observed structures. In Cartesian coordinates (Figure 1b), the T_d $[\text{M}_4\text{Q}_4]$ core can be completely described by two independent parameters $m > 0$ and $q > 0$ with M atoms at vertices $\{(m, m, m), (-m, -m, m),$

$(m, -m, -m), (-m, m, -m)\}$ and Q atoms at $\{(-q, -q, -q), (q, q, -q), (-q, q, q), (q, -q, q)\}$. Fundamental structural parameters can then be related according to eqs 3-7.

$$\text{M-Q bond length: } d_{\text{MQ}} = (3m^2 - 2mq + 3q^2)^{1/2} \quad (3)$$

$$\text{M} \cdots \text{M separation: } d_{\text{M}} = \sqrt{2}m \quad (4)$$

$$\text{Q} \cdots \text{Q separation: } d_{\text{Q}} = 2\sqrt{2}q \quad (5)$$

$$\text{Q-M-Q angle, } 0^\circ \leq \theta_{\text{M}} \leq 120^\circ: \cos \theta_{\text{M}} = (d_{\text{MQ}}^2 - 4q^2) / d_{\text{MQ}}^2 \quad (6)$$

$$\text{M-Q-M angle, } 0^\circ \leq \theta_{\text{Q}} \leq 120^\circ: \cos \theta_{\text{Q}} = (d_{\text{MQ}}^2 - 4m^2) / d_{\text{MQ}}^2 \quad (7)$$

Likewise, any two of these structural parameters can establish m , q , and the remaining structural metrics. In our analysis, we use the M-Q bond lengths d_{MQ} and Q-M-Q bond angles θ_{M} as independent, chemically significant parameters to establish the remaining relationships via eqs 8 and 9. The additive and subtractive solutions in eq 9 apply when Q is external and internal to the M_4 tetrahedron, respectively; only the former is relevant to known clusters. Volumes are obtained from eqs 10-13. Note that substitution of eqs 4 or 5 into the expression for the volume of a regular tetrahedron with edge length a , $V = (\sqrt{2}/12)a^3$,²⁷ affords eq 10 or 11. This approach allows comparison of actual metric parameters with those calculated for T_d symmetry based on mean values of M-Q bond lengths and Q-M-Q angles.

$$q = d_{\text{MQ}} \sin(\theta_{\text{M}}/2) / \sqrt{2} \quad (8)$$

$$m = 1/3 \left[q \pm d_{\text{MQ}} (1 + 2 \cos(\theta_{\text{M}}))^{1/2} \right] \quad (9)$$

$$V(\text{M}_4) = 8m^3/3 \quad (10)$$

$$V(\text{Q}_4) = 8q^3/3 \quad (11)$$

$$V(\text{M}_3\text{Q}) = (2m^2/3)(3q - m) \quad (12)$$

$$V(\text{M}_4\text{Q}_4) = V(\text{M}_4) + 4V(\text{M}_3\text{Q}) = 8qm^2 \quad (13)$$

4.4. Sample Volumes

The idea of molecular volumes is introduced by Table 1, which contains values for five well-known carbon and boron closed polyhedra. The volumes of interest here are those enclosed by polyhedra defined using specified atoms as vertices and bonds as edges, termed

“nuclear volumes” elsewhere.²⁸ Beyond the nuclear volume of a polyhedral structure, e.g., 162.4 Å³ for C₆₀, it is also possible to calculate an inner cavity volume (43.8 Å³) based on the van der Waals radius (1.47 Å) of an individual carbon atom.²⁸ The volumes in Table 1 assume the highest idealized symmetries as indicated and depend only on averaged edge lengths obtained from experimental observations, appropriately weighted for imposed symmetry when present. Standard equations for relevant polyhedral volumes are also provided in the table.

For further comparison, Table 1 includes data for eight metallocubanes. Volumes of the M₄ and Q₄ portions and [M₄Q₄] cores are obtained from eq 2. These reflect differences in bonding radii of bridging and metal atoms. For example, volume ratios for the pairs [Al₄Se₄]/[Al₄S₄] (1.16:1) and [Ga₄Te₄]/[Ga₄Se₄] (1.26:1) are anticipated by the covalent radius order Te (1.38 Å) > Se (1.20 Å) > S (1.05 Å).²⁹ The volume ratio [Ga₄Se₄]/[Al₄Se₄] = 1.02:1 is consistent with nearly equal covalent radius values of Ga (1.22 Å) and Al (1.21 Å).²⁹ For these closed shell centers, M–M interactions are negligible. A conspicuous feature of the thallium cluster is that the Tl₄ volume is substantially larger than the O₄ volume. In general, V(M₄) > V(Q₄) is aprecedented but infrequent property of cubane clusters (see below).

All volumes in this work are nuclear volumes of Fe₄ and Q₄ tetrahedra and [Fe₄Q₄] cores calculated by the generalized approach specified in sections 4.2-4.3. We illustrate the use of eq 13 for volume calculations for the two [Fe₄S₄] clusters in Table 1. The Me₄N⁺ salt/ ^tBuSH solvate form of [S^tBu][−]/2+ crystallizes with imposed D_{2d} cluster symmetry and therefore has only one unique Fe₃S volume. The cluster [Cp[−]/4+] has imposed 2-fold rotational symmetry, which gives two independent Fe₃S volumes. This cluster core deviates considerably from T_d symmetry, instead exhibiting a pronounced idealized D_{2d} geometry. Cluster volumes are calculated by eqs 14 and 15 using crystallographic coordinates.

$$V\left(\left[\text{S}^t\text{Bu}\right]^{-}/2+\right)=2.428+(4)(1.798)=9.62\text{\AA}^3 \quad (14)$$

$$V(\text{Cp}^{-}/4+)=3.265+(2)(1.715)+(2)(1.730)=10.16\text{\AA}^3 \quad (15)$$

Sample calculations 14 and 15 are based on the description of the [Fe₄S₄] core as a tetracapped Fe₄ tetrahedron (Section 4.2). For comparison, the volumes of corresponding tetracapped S₄ tetrahedra, V*[Fe₄S₄] (eq 16), are provide in eqs 17 and 18. V*[Fe₄S₄] is readily obtained from eqs 12 and 13 by exchange of labels M and Q and parameters *m* and *q*.

$$V^*(\text{M}_4\text{Q}_4)=V(\text{Q}_4)+4V(\text{MQ}_3) \quad (16)$$

$$V^*\left(\left[\text{S}^t\text{Bu}\right]^{-}/2+\right)=5.589+(4)(1.778)=12.70\text{\AA}^3 \quad (17)$$

$$V^*(\text{Cp}^{-}/4+)=3.068+(2)(1.739)+(2)(1.751)=10.05\text{\AA}^3 \quad (18)$$

The results of these [Fe₄S₄] calculations demonstrate that, exact values notwithstanding, even the relative ordering of total enclosed volumes depends on the choice of polyhedral description. Moreover, irrespective of precise formulation, total volume is necessarily a

complicated function of all physical factors that influence core geometry. As a consequence, the analysis of total $[M_4Q_4]$ core volumes is troublesome at the level of physical origins and trends, as will become evident in Section 5.3. We emphasize again that the tetracapped Fe_4 tetrahedron is the polyhedral model used in earlier work, and we employ it exclusively in our analysis here to enable consistent comparisons within the present survey and with prior reports.

4.5. Fe_4 and Q_4 Volumes; Convex and Concave FeQ_3 and QFe_3 Tetrahedra

Using the T_d reference geometry, we can delineate some basic structural relationships bearing on the position of M vs. Q atoms relative to the concentric M_4 and Q_4 tetrahedra in $[M_4Q_4]$ cubanes. In $[Fe_4S_4]$ clusters, the volume relationship $V(S_4) > V(Fe_4)$ is the norm as already noted, but there are cases of $V(Fe_4)$ comparable to or larger than $V(S_4)$ (for examples, see Figure 4 and Table 3). We examine the general T_d situation as follows, beginning at the Q-M-Q angle of 90° where the $[M_4Q_4]$ framework (defined by M-Q edges) forms a perfect cube with the M-Q-M angle at 90° and equal M_4 and Q_4 volumes. As the Q-M-Q angle expands past 90° , the M-Q-M angle compresses below 90° , the Q-Q separation becomes greater than the M-M separation, and the Q_4 volume exceeds the M_4 volume. This situation prevails for nearly all $[Fe_4Q_4]$ clusters surveyed insofar as average Q-Fe-Q angles are almost always obtuse (Figures 2b and 7b). The Q-M-Q angle reaches its limit at 120° , at which point the M vertices become coplanar with the faces of the Q_4 tetrahedron and the M-Q-M angle is 33.557° . This forms the boundary between convex and concave MQ_3 tetrahedra relative to the Q_4 tetrahedron, i.e., with M outside or inside the Q_4 tetrahedron, respectively; Q-M-Q angles must be less than 120° in either case. T_d -symmetric $[M_4Q_4]$ structures with concave MQ_3 tetrahedra are geometrically acceptable but chemically implausible due to unphysically close M-M distances and unphysically acute M-Q-M angles ($<33.557^\circ$). Lower symmetry structures that combine convex and concave MQ_3 units also appear physically implausible, and we have found no examples of concave FeQ_3 polyhedra in any $[Fe_4Q_4]$ structure.

The foregoing arguments apply correspondingly with M and Q positions reversed. For example, in the cluster CO/0, the average Fe-S-Fe and S-Fe-S angles are 96.0° and 83.6° , respectively; the Fe-Fe separation is therefore greater than the S-S separation (Figure 3), leading to an exceptional case where the Fe_4 volume is larger than the S_4 volume (Figure 4). Like concave MQ_3 units, concave M_3Q units, with Q inside the M_4 tetrahedron, are physically implausible and are not found in any $[Fe_4Q_4]$ structure, thus mandating the additive solution in eq 9 for real $[M_4Q_4]$ cores and allowing the generality of eq 13 in the calculation of total enclosed $[M_4Q_4]$ volume.

5. Limits and Trends in Synthetic $[Fe_4S_4]^z$ Clusters

We seek here to discern limits, trends, and regularities of various metric parameters for cluster redox sets and groups. Relevant data for >100 $[Fe_4S_4]$ clusters encompassing Fe-S distances, S-Fe-S angles, and cluster volumes are provided in graphical format in Figures 2-5. Remaining metric information in graphical and tabular form is available as Supporting Information. In all plots of $[M_4Q_4]$ data, the symbol • (solid black circle) represents the mean experimental value of a given quantity (distance, angle, volume) and vertical bars mark the smallest and largest individual experimental values of a given quantity for all members in a group of clusters. The symbol

○ (hollow red circle) is the calculated value in T_d symmetry for that quantity based on mean M-Q and Q-M-Q values for a given cluster. The difference between • and

points for a structural parameter of a given cluster is an indication of the deviation of that parameter from the value in a T_d -averaged structure. The number of clusters observed for a given group is widely variable, and in some cases there is only one example. This number is listed in the figures on the right-hand axis. We use oxidation states as markers without necessary implication, especially in the non-innocent $[dt]^{2-}$ and NO^+ and highly covalent Cp^- cases, that they convey meaningful electron distributions. In identifying trends, mean values of all observations of a given parameter are the primary criteria regardless of the number of observations. The purpose is to disclose parameter trends, but it must be borne in mind that some of these trends are based on limited observations with small dispersions in values and may not hold when additional data are accumulated.

5.1. S-Fe-S Angles and Fe-S Distances

The terminal ligand environment on $[Fe_4S_4]$ clusters is diverse, spanning a range of coordination numbers, steric demands, and ligand field strengths. We therefore begin our analysis by examining general relationships between core structure and L environment. As the most obvious geometric parameters of physical significance, S-Fe-S bond angles, which probe the metal coordination environment, and Fe-S distances, which reflect bonding interaction between metal and core ligand, are taken as starting points for initial consideration. These values are visualized in Figure 2 and trends are summarized in Table 2.

The correlation of S-Fe-S bond angle with metal coordination number is obvious. As expected, this angle is largest at tetrahedral metal geometries, with average values in the range 100 - 107° . Bidentate L ligands, which increase the coordination number to five, lead to more acute angles of 95 - 101° , with the larger angles of *ca.* 100° in clusters coordinated by 1,3-chelates (dtc^- , pyt^-) with narrow bite angles. The smallest S-Fe-S angles belong to six-coordinate, or formally six-coordinate in the case of Cp^- , centers with values in the normal octahedral range of 84 - 92° . For the most part, the dispersion of observed angles for a given $[L]^y/z$ is less than 5° . Larger ranges indicate geometry distortions arising from ligand steric effects, bidentate chelation and the resulting asymmetric FeS_3 environment, and/or localized metal-metal bonding, especially in the case of $L = Cp^-$; ³⁰ the latter factors result in very pronounced (*ca.* 30°) dispersions.

Fe-S bond lengths depend on a more complicated interplay of factors, including oxidation state, spin state, and coordination number. The large majority of clusters are constructed of high-spin $Fe^{II,III}$ sites with bond lengths in the interval 2.27 - 2.33 Å. In accord with metal ion radii, ³¹ reduced cores ($[Fe_4S_4]^{1+,0}$) generally occur at the longer end of this range, with all-ferrous cubanes, including CO/0 which has octahedral metal sites (Figure 1), at the outer limit. The shortest bond lengths (2.20 - 2.24 Å) are in strong field systems in high oxidation states or with non-innocent ligands ($L = NO^+$). While general trends are discernible using mean values, individual observations must be interpreted with caution as the bond length variation within a given type can be quite large (>0.1 Å) even for simple monodentate ligands (e.g., $L = SAr^-$), exceeding, for example, differences arising from change in oxidation state. These large intervals suggest that other considerations (metal geometry in five-coordinate sites, cluster electronic structure, and lattice packing) significantly affect Fe-S bond length.

5.2. Mean Values and T_d Symmetry

The availability of mean Fe-S distances and S-Fe-S angles allows the calculation of all remaining geometric parameters for ideal T_d -symmetric cores. We find that T_d values

accurately predict mean observed values in the majority of cluster types, even for singular examples, indicating that most $[\text{Fe}_4\text{S}_4]^Z$ cores are well-described as averaging to T_d geometry. For the purpose of structural analysis, this implies that properties affecting Fe-S distance and S-Fe-S angle modify other geometric parameters in a systematic, interdependent manner. For example, the presence of tetrahedral iron centers and normal Fe-S bond lengths leads to characteristically acute Fe-S-Fe angles ($70-78^\circ$), whereas cores with higher coordinate metal geometries result in more expanded angles at μ_3 -S atoms. This does not mean that the Fe-S distance and S-Fe-S angle are always the parameters of primary structural significance; physical influences can manifest most plainly in other geometric parameters, and Fe-S and S-Fe-S metrics will adjust accordingly. The exceptions to T_d -symmetric cores are clusters with five-coordinate iron centers where distortions can be traced to square pyramidal metal geometries that distinguish local axial and basal Fe-S bonds, particularly for $L = \text{dt}^{2-}$, and clusters with $L = \text{Cp}^-$ where localized Fe-Fe bonding results in pronounced distortions to D_{2d} symmetry.³⁰ For the extreme $L = \text{dt}^{2-}$ and Cp^- cases, the presence of core distortions is also evident in the large dispersions associated with all core distance and angle types except the Fe-S bond length; the plasticity of the $[\text{Fe}_4\text{S}_4]^Z$ core does not appear to extend to Fe-S bonds.

5.3. Volumes

We conclude the discussion of general structural characteristics with a consideration of Fe-Fe and S-S core contacts (Figure 3) and core volumes (Figures 4 and 5). First we observe that Fe_4 and S_4 volumes are essentially cubic functions of mean Fe-Fe and S-S distances (eqs 9 and 10), respectively. These volumes are therefore sensitive probes of trends in the homoatomic core contacts. We focus on the former with knowledge that the latter relate analogously. Second, we postulate that increased steric repulsion between terminal ligands and core sulfides distorts metal geometry primarily by compression of the S-Fe-S angle; this, in turn, will increase the Fe-Fe separation and the Fe_4 volume, and decrease the S-S separation and the S_4 volume. Third, the relationship of the Fe_4 and S_4 volumes to the S-Fe-S angle (eqs 8-11) implies that trends in Fe_4 volumes will be mirrored by opposite trends in S_4 volumes, as evident overall in Figure 4. The Fe_4 volumes are considered below. Finally, while the total $[\text{Fe}_4\text{S}_4]$ core volumes (Figure 5) provide a global metric for cluster sizes, their physical interpretation is problematic. Difficulties arise both from the intrinsic nature of total volume, which reflects the complex, simultaneous interaction of all structural parameters, and the extrinsic definition of said volume. As previously shown in Section 4.4, total core volumes depend on, and order according to, the polyhedral description imposed.

The Fe_4 volumes of clusters with tetrahedral metal centers and common 1+ to 3+ core oxidation states are tightly grouped at $2.3-2.6 \text{ \AA}^3$. The exceptions belong to the $L = [\text{N}(\text{SiMe}_3)_2]^-$ redox set (including one member with a 4+ core oxidation state), which we attribute to interligand repulsion from tightly bound hindered amide ligands (Fe-N distance $1.86 - 1.98 \text{ \AA}$); indeed, the S-Fe-S angles in this redox set are the most acute for all $[\text{Fe}_4\text{S}_4]$ clusters containing tetrahedral metal centers. Core oxidation states below 1+ give Fe_4 volumes under $2.4 \text{ \AA}^3$. For the strong-field $L = \text{NO}^+$ set, metal-metal bonding³² provides one rationale for the diminished volumes. In weak-field clusters, we suggest that increasing metal ionic radii act to diminish interligand repulsion to give smaller Fe_4 volumes. Finally, higher coordinate metal centers produce the largest Fe_4 volumes ($>2.6 \text{ \AA}^3$) due to their compressed bond angles. In the case of $\text{CO}/0$, the maximal length of its Fe-S bonds ($2.33 \text{ \AA}$ ³³) in conjunction with its octahedral metal centers leads to an exceptionally large Fe_4 volume.

5.4 Redox Trends

Oxidation state variability is a hallmark of $[\text{Fe}_4\text{S}_4]$ clusters,^{10,34} and structurally characterized examples exist for $\text{L} = \{\text{NO}^+, \text{Cp}^-, [\text{N}(\text{SiMe}_3)_2]^-, \text{SAr}^-\}$ in three oxidation states and $\{\text{Cl}^-, \text{SH}^-, \text{SAlk}^-, \text{CN}^-, \text{dtc}^-, \text{dt}^{2-}\}$ in two. In Table 2, we identify the $[\text{Fe}_4\text{S}_4]^z$ redox series **A-D** and **E-I** containing three and two members, respectively, and summarize trends in selected mean structural parameters. We have excluded the dt^{2-} redox set from this analysis due to complicating non-innocent ligand behavior.³⁵ In the table, each series describes members of the same redox set. A plus sign indicates that the relevant metric increases with increasing core charge z , and a negative sign signifies the opposite, i.e., decreasing metric trend with increasing z . For many parameters, redox differences are small, and the deduced trends should therefore be viewed with caution, especially in cases where only two redox states are compared. For this reason, we treat only parameters with obvious redox dependencies in the following discussion. The detailed data in Supporting Information should be consulted for accurate analysis of situations involving more subtle redox effects.

Within each redox series, Fe-S distances decrease progressively with increasing oxidation state and decreasing ionic radii. The only exception is for $\text{L} = [\text{N}(\text{SiMe}_3)_2]^-$, where the progression reversed slightly in the most oxidized form (Figure 2a); the origin of this deviation is uncertain but may be related to steric limits reached by the hindered amide ligand. The S-Fe-S angles typically compress upon oxidation, which is attributable to the effect of increased interligand repulsion as metal radii decrease. The strong field $\text{L} = \text{NO}^+$ and Cp^- systems, however, display the opposite behavior. In these cases, oxidation appears to depopulate occupied antibonding Fe-Fe MO's, shortening Fe-Fe contacts and thereby expanding S-Fe-S angles.

In most cases, oxidation leads to a progressive decrease in the volume of the S_4 tetrahedron, but leaves the Fe_4 volumes largely unaffected or only slightly altered (Figure 4). Again, the strong field $\text{L} = \text{NO}^+$ and Cp^- systems are the exceptions, with the former showing volume decreases in the Fe_4 tetrahedron and little effect on the S_4 tetrahedron, and the latter showing decreasing volume for Fe_4 but increasing volume for S_4 . Volume trends, where apparent and significant, are entirely in accord with the redox-dependent behavior of the S-Fe-S angle.

The absence of consistent redox-dependent behavior in Fe_4 volumes and the S_4 volume in the $\text{L} = \text{NO}^+$ redox set is unexpected and merits consideration. In discussing volumes, we have focused on the impact of S-Fe-S angle on both Fe_4 and S_4 tetrahedra. The anomalous cases, however, illustrate the interaction of the S-Fe-S angle and Fe-S distance. Consider the usual situation where S-Fe-S and Fe-S metrics both decrease and oxidation state increases. From eq 11, these trends clearly give strictly decreasing coordinate q , and, hence, decreasing S_4 volume. The effect on coordinate m is more complex and can be non-monotonic depending on parameter values. This explains the odd behavior of the Fe_4 volume. It remains unknown if there is a physical rationale -- for example, the existence of an optimal Fe-Fe separation in weak-field $[\text{Fe}_4\text{S}_4]$ clusters -- that accounts for the curiously persistent combination of S-Fe-S and Fe-S parameters to yield redox-independent Fe_4 volumes. For $\text{L} = \text{NO}^+$ clusters, the S-Fe-S and Fe-S metrics trend in opposite directions such that their combination in eq 9 negates the obvious redox correlation in S_4 volume. Finally, we emphasize that m coordinates and redox differences therein are intrinsically smaller than equivalent q values in nearly all cases; this serves to further obscure redox-dependent patterns in Fe_4 volumes.

6. $[\text{Fe}_4\text{Q}_4]^z$ Clusters

Diversity in cubane clusters extends to variation in core ligand Q. To expand the range of structural effects, we examine cases where Q is a heavy element chalcogenide ($\text{Q} = \text{Se}^{2-}$,

Te²⁻) or a light atom nitrogen anion (Q = [NPR₃]⁻, [NR]²⁻). Ligand-, geometry-, and redox-dependent structural trends previously identified in sulfide clusters are reproduced in these other core ligand systems, and only distinctive features need be discussed explicitly.

6.1. Q = Se²⁻, Te²⁻

Leading metric features are summarized and compared with analogous sulfide clusters in Table 3. Total [Fe₄Q₄] core volumes are plotted for the 16 available cases in Figure 6; other structural information is available in Supporting Information. Data for these clusters include three two-membered redox series **J-L**, and redox trends in selected parameters for these heavy chalcogenide series are set out in Table 2.

Core metrics track largely as expected at parity of L and z: where Q-Fe-Q angles expand, Fe-Q-Fe angles become more acute, and Q-Q distances and Q₄ volumes increase dramatically due to the longer Fe-Q bond lengths. The Fe-Fe and Fe₄ volumes also increase, but only slightly (0.05 Å, 0.2 Å) relative to sulfide; the near invariance of the Fe₄ volume across chalcogenide cores with high-spin tetrahedral metal centers is striking.

Excluding the low-spin cases (Se²⁻/CO/0, Figure 1, and Se²⁻/Cp⁻/7+, the latter highly distorted from T_d symmetry), ranges of mean values of metric parameters for Q = Se²⁻/Te²⁻ at all available L and z combinations are summarized below. Volumes may be compared in Table 3. Overall, results at constant L and z disclose the expected periodic trend in Q of S < Se < Te for distances and volumes directly involving the chalcogen and Te < Se < S for Fe-Q-Fe angles. The largest volume known for any [Fe₄Q₄] cluster is found with Se²⁻/CO/0 (15.26 Å³), which is 16% larger than that of S²⁻/CO/0 (Table 3). The tellurium analogue of these clusters has not been prepared.

6.2. Q = [NPR₃]⁻, [NR]²⁻

At present, all [Fe₄Q₄] clusters with nitrogen anion Q are constructed from tetrahedral iron centers and formally monoanionic phosphinimide ([NPR₃]⁻; 2 examples) or dianionic organoimide ([NR]²⁻; 14 examples) core ligands. Data for Fe-N bond distances and N-Fe-N angles are plotted in Figure 7 and core volumes are available in Figure 8. Ranges of mean values for other structural features are summarized below for the [NR]²⁻ and [NPR₃]⁻ ligand classes. Clusters of this type currently comprise four cluster oxidation states, ranging from all-ferric to all-ferrous, and a single two-membered, redox set, designated **M** in Table 2. The [NR]²⁻-ligated redox series **M** faithfully follows the trends established previously in chalcogenide cubanes containing weak-field, tetrahedral metal centers.

Light atom nitrogen anion core ligation provides a distinct structural contrast to chalcogenide ligation. Being 2p donors, nitrogen anions give substantially shorter Fe-Q bond lengths relative to sulfide, with phosphinimides at longer separations than organoimides (2.06-2.07 Å vs. 1.95-1.99 Å) owing to the reduced nitrogen charge density and lower Fe^{II} oxidation state in systems containing the former. The N-Fe-N angles (94-97°) are substantially smaller than typical tetrahedral values, and Fe-N-Fe angles expand relative to Q = S²⁻ to compensate. Nitrogen anion cubanes therefore exhibit a recognizably “cube-like” geometry in comparison to chalcogenide clusters. One possibility is that the unusually compressed N-Fe-N angles in organoimide clusters (compare with Figure 2b) may arise from short Fe-Fe contacts. In this model, expansion of the angle would decrease Fe-Fe separation to destabilizing values.³⁶ However, the phosphinimide clusters show similar N-Fe-N angles yet have substantially longer Fe-Fe distances. An alternative explanation may lie in the acute bond angles at nitrogen, which are expected to be electronically disfavored, particularly for a four-coordinate 2p atom. Expansion of the N-Fe-

N angle would necessarily compress the Fe-N-Fe angle further, leading to additional destabilization.

The Fe_4 volumes exhibit Q-dependent variation, with $Q = [\text{NPR}_3]^-$ clusters in the range of sulfide clusters (Figure 4a) and $Q = [\text{NR}]^{2-}$ clusters at the lowest extreme. The N_4 volumes are of course much smaller than the lowest S_4 volumes. Accordingly, the $[\text{Fe}_4\text{N}_4]$ volumes are smaller than any $[\text{Fe}_4\text{S}_4]$ volumes, and reach a minimum with $[\text{NAlk}]^{2-}/\text{Cl}^-/4+$ ($6.93 \text{ \AA}^3$). We note finally that the R_3P - or R-substituent on the nitrogen atoms provides an adjustable structural parameter that does not exist in the chalcogenide clusters. In principle, these substituents could play electronic and/or steric roles in modulating core geometry. Small electronic effects are detectable in Fe-N distances, which tend to be shorter for arylimides relative to alkylimides, but clear steric effects have not yet been observed.

7. Protein-Bound $[\text{Fe}_4\text{S}_4]^z$ Clusters

We conclude our analysis of $[\text{Fe}_4\text{S}_4]$ clusters by comparing observations of biological clusters to the data compiled for synthetic species. For structural accuracy, we have restricted biological cases to the highest-available resolution ($<1.5 \text{ \AA}$) macromolecular structures of small soluble electron-transfer proteins. These are the ferredoxins (Fds, 14 clusters) and the high-potential proteins (HPs, 10 clusters) which occur in the cysteine-ligated form $[\text{Fe}_4\text{S}_4(\text{SCys})_4]$. These proteins contain either one or two $[\text{Fe}_4\text{S}_4]$ clusters as the sole redox-active cofactors. The physiologically relevant redox couples are $[\text{Fe}_4\text{S}_4]^{1+}/2+$ for Fds and $[\text{Fe}_4\text{S}_4]^{2+}/3+$ for HPs. In the following discussion, individual structures are identified by their PDB ID codes.

Selected structural parameters for protein-bound and thiolate-ligated synthetic clusters are summarized in Table 4. For each synthetic cluster type, minimum, maximum, and average values obtained from the all members of that type are specified. The tabulation of protein types is divided between Fds and HPs but with recognition that it is the external protein environment of the clusters rather than any intrinsic core property that differentiates the two. Overall, the structural metrics for the biological systems exhibit a high degree of consistency with values observed in small molecule cores, and no specific protein-derived structural influences on core dimensions are apparent.

The determination of cluster redox state is problematic in macromolecular crystallography and, in principle, it might be possible to make definitive assignments based on structural trends observed in synthetic species. To explore this possibility, we examine S_4 volumes which, unique among the structural metrics for synthetic clusters, present distinguishable, non-overlapping ranges that correlate to individual core oxidation states (see Figure 4b). For our chosen macromolecular structures, which have either no (most) or $z = 2+$ (some) core charge assignments, we find that most Fd and HP structures show S_4 volumes in the interval expected for $[\text{Fe}_4\text{S}_4]^{2+}$ (*ca.* $5.5 \text{ \AA}^3$), the core redox state usually obtained in standard preparation and purification procedures for synthetic and biological clusters. Only one outlier occurs for the HP structures (1HLQ, $5.85 \text{ \AA}^3$). This volume exceeds the largest value observed in reduced $z = 1+$ thiolate-ligated synthetic clusters, but such an oxidation state is unlikely for a HP cluster. Among Fds, two structure shows a distinctly small S_4 volumes (6FDR, $5.24 \text{ \AA}^3$; 6FDR, $5.30 \text{ \AA}^3$) in the $z = 3+$ range, which in turn is also an improbable state for this type of protein, and five Fd clusters (2FG0, 6FD1, 3EUN, 1IQZ, 1IRO; 5.62 - $5.67 \text{ \AA}^3$) fall between the synthetic cluster intervals for $z = 2+$ and $1+$. We conclude that while the high-resolution structures in Table 4 on average display S_4 volumes that agree with the typical core oxidation state $z = 2+$, specific examples can and do deviate outside of diagnostic ranges. Whether a specific volume reflects a discrete oxidation state, a mixture of

oxidation states (e.g., due to radiation damage), the influence of protein environment, and/or limitations in data quality is a matter that requires careful consideration.

Although the crystal structure of the fully reduced iron protein of *Azotobacter vinelandii* at 2.25 Å resolution³⁷ falls outside the resolution limit imposed on the biological structures in Table 4, we examine it briefly. The protein cluster, which is fully cysteine-ligated, is described as being in the all-ferrous $[\text{Fe}_4\text{S}_4]^0$ oxidation state. It is one of the very few synthetic or biological examples of this state; as such it is isoelectronic with the synthetic clusters $[\text{CN}]^-/0$ (6.21 Å³) and $\text{NHC}/0$ (6.14 Å³) having the indicated S_4 volumes. The S_4 volume in the protein is reported to be in the 5.9–6.2 Å³ range depending on the restraints used in the refinement. These values are substantially larger than those for reduced $z = 1+$ synthetic clusters or for the Fd and HP protein clusters considered above. Although the data are decidedly limited, the S_4 volume appears to be a parameter that may be useful in substantiating an all-ferrous core in addition to other physical properties, including ⁵⁷Fe Mössbauer isomer shifts.¹⁰ $[\text{Fe}_4\text{S}_4]$ volumes are of lesser value in this respect. The volume of the iron protein cluster is reported as 9.23 Å³, smaller than values for $z = 1+$ synthetic clusters and the surveyed protein clusters. As noted earlier, while the tendency of thiolate-ligated synthetic clusters is to increase in $[\text{Fe}_4\text{S}_4]$ volume upon reduction, the dispersion in values within a given core oxidation state exceeds the differences between mean volumes for the different redox states.

8. Summary and Conclusions

This work was undertaken to assess general structural characteristics of cubane-type $[\text{M}_4\text{Q}_4]$ cores, particularly in comparison with exact T_d symmetry. The central premise is that all T_d structural metrics (interatomic distances and angles, volumes of tetrahedra comprising the core) can be calculated from two independent parameters, coordinate m of atom M and coordinate q of atom Q. Expressions have been derived for distances, angles, and volumes in terms of these parameters. Equivalently, any two structural properties, taken here as distance M–Q and angle Q–M–Q, can be used to evaluate m , q , and the other structural features. Clusters analyzed include those with $\text{M} = \text{Fe}$ and $\text{Q} = \text{S}^{2-}$, Se^{2-} , Te^{2-} , $[\text{NPR}_3]^-$, and $[\text{NR}]^{2-}$. For $[\text{Fe}_4\text{S}_4]$ clusters, the most expansive subgroup of cubanes that includes both synthetic and biological clusters, tetrahedral metrics are calculated from experimental Fe–S and S–Fe–S values of a single cluster or mean values averaged over a group of clusters with constant terminal ligand L and core charge z . Comparison of observed and calculated values for a given structural parameter allows ready identification of the extent of deviation of that parameter from the value required in T_d symmetry. Overall, clusters with monodentate ligands (primarily $\text{L} = \text{RS}^-$, halide, CN^- , $[\text{N}(\text{SiMe}_3)_2]^-$, NO^+) average closely to tetrahedral structures, whereas higher-coordinate ligands, particularly Cp^- , tend to show larger deviations, especially in volumes. Structural trends in redox sets of clusters (constant Q and L, variable z) have been identified (Table 2).

For other chalcogenide clusters, structural parameters nearly always trend according to the periodic properties of selenium and tellurium, such that for the entire chalcogenide family of clusters the order $\text{Te} > \text{Se} > \text{S}$ applies to Fe–Q and Q–Q distances, Q–Fe–Q angles, and Q_4 and $[\text{Fe}_4\text{Q}_4]$ volumes and the reverse order to Fe–Q–Fe angles. For clusters with nitrogen anion bridges, distance and volume parameters in particular are smaller because of the relative radii of nitrogen and sulfur. In this last family of clusters, significant differences in bond distances and volumes are observed between $[\text{NPR}_3]^-$ and $[\text{NR}]^{2-}$ clusters, with longer distances and larger volumes for the former clusters owing to reduced nitrogen charge density and lower metal oxidation state.

Volumes of Fe_4 and Q_4 tetrahedra and the $[\text{Fe}_4\text{Q}_4]$ core are significant molecular features in our analyses. Although they provide additional quantitative measures of molecular site, volumes are infrequently utilized as structural parameters. In particular, the Q_4 volume appears to be a sensitive structural marker of cluster oxidation state. The range of $[\text{M}_4\text{Q}_4]$ volumes (defined as the enclosed volume of the tetracapped M_4 tetrahedron per sections 4.2–4.3; 8.5–17 $\text{\AA}^3$, Table 1) encompasses the interior volumes of the familiar polyhedral species $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ (8.3, 12.4 $\text{\AA}^3$) but are much smaller than, e.g., dodecahedrane (28 $\text{\AA}^3$) and other well-known closed molecular polyhedra. In principle, M positions can lie inside or outside the Q_4 tetrahedron for a given $[\text{M}_4\text{Q}_4]$ cubane, and similarly for Q positions and the M_4 tetrahedron. An argument is presented that outside convex-polyhedral structures are highly favored, which is consistent with observations of all $[\text{Fe}_4\text{Q}_4]$ cubane-type clusters.

Lastly, this work provides an extensive repository of structural information not available elsewhere. For each cluster analysed, all Fe–Q, Fe–Fe, and Q–Q distances, Fe–Q–Fe, Q–Fe–Q, Fe–Fe–Fe, and Q–Q–Q angles, and Fe_4 , Q_4 , and $[\text{Fe}_4\text{Q}_4]$ volumes are provided as Supporting Information, with the complete data set summarized in tabular and graphical formats.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported at Harvard University by NIH Grant GM 28856 and at the University of Waterloo by NSERC, CFI, and ORF. LLT gratefully acknowledges the support of a University of Waterloo Undergraduate Research Internship and a Queen Elizabeth II Graduate Scholarship in Science and Technology.

Appendix

(a) Abbreviations

(b) Supporting Information

All structural identification codes and citations (Table S0), complete structural metrics (Fe–Q, Fe–Fe, Q–Q distances; Q–Fe–Q, Fe–Q–Fe, Fe–Fe–Fe, Q–Q–Q angles; Fe_4 , Q_4 , $[\text{Fe}_4\text{Q}_4]$ volumes: Tables S1–S52) and plots (Figures S1–S30), and the derivation of the general volume formula for the C_{60} framework (I_h truncated icosahedron).

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Figure 1.

(a) Generalized cubane-type $[M_4Q_4L_4]$ cluster with tetrahedrally coordinated atoms M, μ_3 -bridging ligands Q, terminal ligands L (listed in Figure 2), and overall charge x . (b) Schematic structure of $[Fe_4Q_4(CO)_{12}]$ containing octahedral iron sites and negligible direct metal-metal interactions. (c) Definition of parameters in the initial analysis of M_4Q_4 tetragonal distortions. (d) Coordinate system in the $T_d[M_4Q_4]$ geometrical model in which the M_4 and Q_4 tetrahedra are inscribed in concentric cubes with Q atoms external to the M_4 tetrahedron.

Figure 2.

(a) Fe-S distances (Å) and (b) S-Fe-S angles (deg) for [Fe₄S₄] clusters. The symbol • (solid black circle) represents the average of all observations for the indicated number of clusters in a specific group (right axis) and the vertical bars signify the limiting (largest and smallest) values within the group.

Figure 3.

(a) Fe-Fe distances (Å) and (b) S-S distances (Å) for [Fe₄S₄] clusters, with data presented as in Figure 2. The symbol

(hollow red circle) is the calculated parameter value in *T_d* symmetry using averaged Fe-S and S-Fe-S data.

Figure 4.
 (a) Fe_4 and (b) S_4 volumes ($\text{\AA}^3$) for $[\text{Fe}_4\text{S}_4]$ clusters, with data presented as in Figure 3.

Figure 5.
[Fe₄S₄] core volumes (Å³) for [Fe₄S₄] clusters, with data presented as in Figure 3.

Figure 6. $[\text{Fe}_4\text{Q}_4]$ core volumes ($\text{\AA}^3$) for $\text{Q} = \text{Se}^{2-}$ and Te^{2-} clusters, with data presented as in Figure 3.

Figure 7. (a) Fe-N distances (Å) and (b) N-Fe-N angles (deg) for $[\text{Fe}_4\text{Q}_4]$ clusters ($\text{Q} = [\text{NPR}_3]^+$, $[\text{NR}]^{2-}$), with data presented as in Figure 2.

Figure 8. $[\text{Fe}_4\text{Q}_4]$ core volumes ($\text{\AA}^3$) for $Q = [\text{NPR}_3]^-$ and $[\text{NR}]^{2-}$, with data presented as in Figure 3.

Fe-Te 2.59-2.63 Å > Fe-Se 2.40-2.44 Å

Te-Fe-Te 110-112° > Se-Fe-Se 105-107°

Fe-Te-Fe 61-65° < Fe-Se-Fe 69-72°

Fe Fe (Te) 2.65-2.82 Å ≈ Fe Fe (Se) 2.76-2.83 Å

Te Te 4.28-4.34 Å > Se Se 3.83-3.92 Å

		$[\text{NR}]^{2-}$	$[\text{NPR}_3]^-$
Fe	Fe	2.61-2.69 Å <	2.73-2.81 Å
N	N	2.89-2.94 Å <	3.04-3.07 Å
Fe-N-Fe		83.4-84.9° ≈	83.1-85.4°
Fe ₄		2.09-2.29 Å ³ <	2.39-2.61 Å ³
N ₄		2.83-3.01 Å ³ <	3.29-3.40 Å ³
Fe ₄ N ₄		6.93-7.49 Å ³ <	8.06-8.45 Å ³

Table 1

Volumes ($\text{\AA}^3$) of Miscellaneous Molecules^a

		V ($\text{\AA}^3$)	CSD refcode
C_8H_8	(O_h cubane)	3.73b	CUBANE
$\text{C}_{20}\text{H}_{20}$	(I_h dodecahedrane)	28.21 ^c	DOPSIK01
C_{60}	(buckminsterfullerene)	162.4 ^d	<i>d</i>
$[\text{B}_{10}\text{H}_{10}]^{2-}$	(D_{4d} bicapped square antiprism)	8.30e	WIYVEF
$[\text{B}_{12}\text{H}_{12}]^{2-}$	(I_h icosahedron)	12.37f	ETADCB

	$V(\text{M}_4)$	$V(\text{Q}_4)$	$V(\text{M}_4\text{Q}_4)$	($\text{\AA}^3$)
$[\text{Co}_4\text{S}_4(\text{P}^i\text{Pr}_3)_4]$	2.08	5.26	8.50	LUGJAZ
$[\text{Fe}_4\text{S}_4(\text{S}^t\text{Bu})_4]^{2-}$	2.43	5.59	9.62	KEYWAM
$[\text{Cp}_4\text{Fe}_4\text{S}_4]$	3.27	3.07	10.16	CPEFES01
$[\text{Al}_4\text{S}_4(\text{CMe}_2\text{Et})_4]$	3.32	4.93	11.36	REKYIP
$[[\text{Al}_4\text{Se}_4(\text{CMe}_2\text{Et})_4]$	3.73	6.14	13.22	REKYOV
$[\text{Ga}_4\text{Se}_4(\text{CMe}_2\text{Et})_4]$	3.83	6.21	13.50	REKZAI
$[\text{Ga}_4\text{Te}_4(\text{CMe}_2\text{Et})_4]$	4.73	8.10	16.99	REKZEM
$[\text{Ti}_4(\text{OCH}_2\text{CMe}_3)_4]$	6.25	3.78	15.85	MILBAK

^aVolume formulae are available in ref. 27 except for that of the C_{60} truncated icosahedron, which is derived in Supporting Information.^bEdge length $a = 1.551 \text{ \AA}$.^c I_h dodecahedron: $V = (1/4)[15 + 7\sqrt{5}]a^3$, $a = 1.540 \text{ \AA}$.^d I_h truncated icosahedron: $V = (5/12)(3 + \sqrt{5})(2a + b)^3 - (1/2)(5 + \sqrt{5})a^3$, $a = 1.455 \text{ \AA}$ (intrapentagon), $b = 1.391 \text{ \AA}$ (interpentagon); David, W. I. F.; Ibberson, R. M.; Mathewman, J. C.; Prassides, K.; Dennis, T. J. S.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1991**, *353*, 147-149.^e D_{4d} uniform square antiprism: $V = (1/3)[4 + 3\sqrt{2}]a^3$, $a = 1.828 \text{ \AA}$. Square pyramid: $V = (1/3)a^2(e^2 - a^2/2)^{1/2}$, $a = 1.828 \text{ \AA}$ (basal edge), $e = 1.697 \text{ \AA}$ (lateral edge).^f I_h icosahedron: $V = (5/12)(3 + \sqrt{5})a^3$, $a = 1.783 \text{ \AA}$.

Table 2Empirical Trends in Mean Structural Parameters for Members of Redox Series A–M^a

series	Q/ L/ z	Fe–Q ^b	Q–Fe–Q ^c	Fe	Feb	Q	Q ^b	Fe ₄ d	Q ₄ d	Fe ₄ Q ₄ d
A	S ²⁻ / NO ⁺ / 6–,5–,4–	–	+	–		(–)	–	*	–	
B	S ²⁻ / Cp ⁻ / 4+,5+,6+	–	+	–		+	–	+	–	
C	S ²⁻ / [N(SiMe ₃) ₂] ⁻ / 2+,3+,4+	*	–	+		–	+	–	*	
D	S ²⁻ / [SAr] ⁻ / 1+,2+,3+	–	–	*		–	*	–	(–)	
E	S ²⁻ / Cl ⁻ / 1+,2+	–	–	–		–	–	–	–	
F	S ²⁻ / [SH] ⁻ / 1+,2+	–	–	(+)		–	(+)	–	–	
G	S ²⁻ / [SAlk] ⁻ / 1+,2+	–	–	–		–	–	–	–	
H	S ²⁻ / [CN] ⁻ / 0,1+	–	–	+		–	+	–	–	
I	S ²⁻ / [dtc] ⁻ / 2+,3+	–	–	+		–	+	–	(+)	
J	Se ²⁻ / [SAlk] ⁻ / 1+,2+	–	–	–		–	–	–	–	
K	Se ²⁻ / [SAr] ⁻ / 1+,2+	–	–	+		–	+	–	–	
L	Te ²⁻ / PR ₃ / 0,1+	–	–	(–)		–	(–)	–	–	
M	[NtBu] ²⁻ / Cl ⁻ / 3+,4+	–	–	(–)		–	(–)	–	–	

^aPlus or minus signs: parameter increases or decreases, respectively, with increasing core charge *z*; parentheses: weak trends (changes of less than 0.005 Å in distance and 0.01 Å³ in volume); *: no clear trend.

^bDistance

^cAngle

^dVolume.

Table 3

Comparisons of Selected Interatomic Distances ($\text{\AA}$) and Volumes ($\text{\AA}^3$) of $[\text{M}_4\text{Q}_4]^{0,1+,2+}$ Clusters with $\text{Q} = \text{S}^{2-}$, Se^{2-} , Te^{2-} ^a

cluster	Fe-Q	Fe	Fe	Q	Q	M_4	Q_4	M_4Q_4
$\text{S}^{2-}/\text{Cl}^-/1+$	2.32	2.79		3.65		2.55	5.72	10.02
$\text{Se}^{2+}/\text{Cl}^-/2+$	2.41	2.83		3.83		2.66	6.60	10.82
$\text{S}^{2-}/\text{Cl}^-/2+$	2.29	2.77		3.59		2.51	5.46	9.75
$\text{S}^{2-}/[\text{SAIk}^-]/1+$	2.32	2.76		3.66		2.49	5.77	9.88
$\text{Se}^{2-}/[\text{SAIk}^-]/1+$	2.44	2.81		3.92		2.61	7.08	10.92
$\text{Te}^{2-}/[\text{SAIk}^-]/1+$	2.63	2.82		4.30		2.62	9.29	12.04
$\text{S}^{2-}/[\text{SAr}^-]/1+$	2.31	2.74		3.65		2.42	5.74	9.68
$\text{Se}^{2-}/[\text{SAr}^-]/1+$	2.44	2.76		3.92		2.48	7.06	10.57
$\text{Te}^{2-}/[\text{SAr}^-]/1+$	2.63	2.82		4.30		2.63	9.25	12.06
$\text{S}^{2-}/[\text{SAIk}^-]/2+$	2.29	2.75		3.61		2.44	5.52	9.61
$\text{Se}^{2-}/[\text{SAIk}^-]/2+$	2.42	2.80		3.87		2.57	6.79	10.67
$\text{S}^{2-}/[\text{SAr}^-]/2+$	2.28	2.73		3.60		2.41	5.51	9.52
$\text{Se}^{2-}/[\text{SAr}^-]/2+$	2.41	2.78		3.85		2.54	6.72	10.54
$\text{Te}^{2-}/\text{PR}_3/0$	2.61	2.65		4.34		2.20	9.66	10.80
$\text{S}^{2-}/\text{PR}_3/1+$	2.27	2.71		3.60		2.34	5.49	9.34
$\text{Te}^{2-}/\text{PR}_3/1+$	2.59	2.65		4.30		2.19	9.37	10.66
$\text{S}^{2-}/\text{CO}/0$	2.33	3.45		3.11		4.86	3.53	13.10
$\text{Se}^{2-}/\text{CO}/0$	2.45	3.63		3.27		5.65	4.13	15.26

^a Average values are used when multiple observations are available

Table 4Comparisons of Selected Structural Metrics for Synthetic and Protein-Bound [Fe₄S₄] Clusters

metric ^a		[L] ^p /z ^b					protein ^b	
		[SAIk] ⁻ /1+	[SAIk] ⁻ /2+	[SAr] ⁻ /1+	[SAr] ⁻ /2+	[SAr] ⁻ /3+	Fd	HP
Fe-S (Å)	min	2.27	2.23	2.24	2.22	2.22	2.18	2.18
	max	2.34	2.34	2.37	2.33	2.31	2.35	2.36
	avg	2.32	2.29	2.31	2.28	2.27	2.28	2.29
S-Fe-S (°)	min	102.5	100.6	102.5	101.8	100.6	99.2	101.6
	max	106.5	107.8	107.5	107.3	105.6	109.0	107.7
	avg	104.4	104.1	104.8	104.3	103.3	104.3	104.8
Fe ⁴ (Å ³)	min	2.45	2.37	2.38	2.38	2.42	2.34	2.34
	max	2.51	2.55	2.46	2.47	2.50	2.48	2.37
	avg	2.49	2.44	2.42	2.41	2.46	2.40	2.36
S ₄ (Å ³)	min	5.71	5.46	5.70	5.44	5.27	5.24	5.44
	max	5.81	5.59	5.76	5.61	5.28	5.67	5.85
	avg	5.77	5.52	5.74	5.51	5.28	5.52	5.60
Fe ₄ S ₄ (Å ³)	min	9.75	9.39	9.57	9.42	9.42	9.34	9.38
	max	9.97	9.88	9.76	9.69	9.61	9.72	9.52
	avg	9.88	9.61	9.68	9.52	9.52	9.51	9.44

^a min, max, and avg refer to the minimum, maximum, and average values of all observations for members of that type.^b Data and citations are available in Supporting Information.

Cp ⁻	C ₅ H ₅ ⁻ , MeC ₅ H ₄ ⁻
CSD	Cambridge Structural Database
dt ²⁻	dithiolene, <i>cis</i> -[R ₂ C ₂ S ₂] ²⁻ (R = CN, CF ₃)
dtc ⁻	<i>N,N'</i> -diethyldithiocarbamate(1-), Et ₂ NCS ₂ ⁻
Fd	ferredoxin
HP	high-potential protein (HiPIP)
L	generalized terminal ligand
M	generalized metal
[NC-M] ⁻	[CpMn(CO) ₂ CN] ⁻ , [W(CO) ₅ CN] ⁻
NHC	<i>N</i> -heterocyclic carbene
PDB	Protein Data Bank
[pyt] ⁻	pyridine-2-thiolate(1-)
Q	generalized μ ₃ -bridging ligand