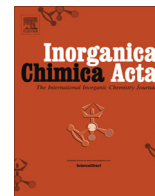




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Research paper

# Tetracapped tetrahedral ruthenium-sulfur clusters related to iron-sulfur structural units in metalloenzymes <sup>☆</sup>

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## ABSTRACT

The tetracapped tetrahedral  $\text{Ru}_4\text{S}_4\text{X}_4^z$  structures ( $\text{X} = \text{Cl}, \text{CN}, \text{SCH}_3$ ;  $z = 0$  to  $-4$ ) are proposed as cubanoid low-spin models for the  $\text{Fe}_4\text{S}_4$  structural units in metalloenzymes. Density functional theory indicates the  $\text{Ru}_4\text{S}_4\text{X}_4^{2-}$  dianions to have closed shell configurations. A bonding model with 4 external Ru–X bonds, 12 Ru–S bonds along the edges of an  $\text{Ru}_4\text{S}_4$  cube, 6 Ru–Ru bonds along the edges of a central  $\text{Ru}_4$  tetrahedron, and a four-center two-electron core bond is proposed for these systems.

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## 1. Introduction

Cubane-type  $\text{Fe}_4\text{S}_4$  centers, as one of the main types among the pervasive iron-sulfur clusters in biology, have been described structurally both in proteins and in model compounds, using structural, spectroscopic and theoretical methods [1–15]. Despite the generally accepted cubane-type representations, many of these metal-sulfur clusters feature metal-metal distances clearly shorter than the sum of the van der Waals radii [1,4,7]. The underlying topology of these  $\text{M}_4\text{S}_4$  units thus has 12 M–S bonds and 6 M–M bonds corresponding to tetracapped tetrahedra with the metal atoms at degree 6 vertices and the sulfur atoms at degree 3 vertices (Fig. 1). However, if the ratio of the six equivalent M–M distances to the 12 equivalent M–S distances is  $\sqrt{2} = 1.4142\dots$ , the spatial geometries of these  $\text{M}_4\text{S}_4$  units correspond to cubes with 12 equivalent M–S edges. Indeed, electronic structure analyses have in certain instances resorted to  $T_d$  symmetry elements in describing the central  $\text{Fe}_4$  unit [16].

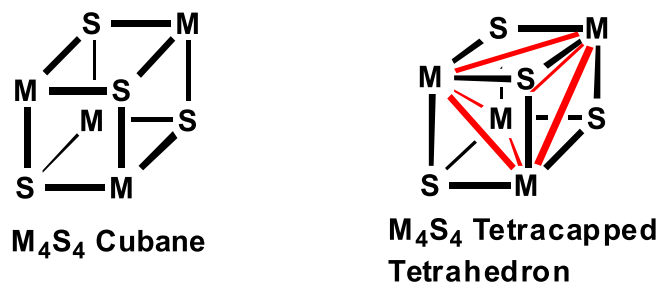
The electron count has been shown to play a key role in deciding between a symmetrical tetrahedral structure and a distorted one for  $\text{M}_4\text{S}_4\text{X}_4$  clusters. Thus, within the framework of the Dahl model, clusters such as  $(\text{C}_5\text{H}_4\text{Pr})_4\text{Mo}_4\text{S}_4$  feature full occupancy of the six bonding orbitals along the M–M edges, with empty antibonding orbitals; as such, the Mo–Mo distances are relatively short and the cluster remains symmetrically tetrahedral. At the other end of the spectrum, the cobalt counterpart  $(\text{C}_5\text{H}_5)_4\text{Co}_4\text{S}_4$  has the antibonding orbitals occupied, and hence features a geometry without any net metal-metal bonding. Iron clusters, depending on oxidation state, find themselves in between these two limiting situations [17].

In unraveling the bonding interactions within  $\text{M}_4\text{S}_4$  clusters, iron also presents a complication owing to the facile accessibility of several spin states as well as its redox activity [18]. Thus, each of the four iron centers may be found in the two main oxidation states Fe(II) and Fe(III), each with three different available spin states, as well as the more exotic Fe(I) and Fe(IV) oxidation states (described so far not in  $\text{Fe}_4\text{S}_4$  clusters, but rather in simpler biological metal centers such as hydrogenases, diiron enzymes, and others [18]). This then offers a range of overall charges on the cluster from  $[\text{Fe}_4\text{S}_4]^0$  to  $[\text{Fe}_4\text{S}_4]^{4+}$ , each with as many as 11 possible spin states. In addition, in the lower spin states, many further electronic structures are achievable by considering the possibility of antiferromagnetic coupling, in itself a source of detailed descriptions [9,14,18,19]. An added complexity arises from the accessibility of

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**Fig. 1.** Comparison of cubane and tetracapped tetrahedron structures for  $M_4S_4$  clusters ( $M = Fe, Ru$ ). The  $M-M$  bonds in the  $M_4$  subtetrahedron are depicted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

multiple local minima of varying symmetries [9,14]. In this latter respect, recent studies have examined as many as four such minima per oxidation state, with a general tendency towards global preferences for higher-spin states, at least in these isolated in vacuo models [9,14]. Furthermore, many-particle quantum mechanics has more recently been employed to show that the Heisenberg double exchange model generally used for describing iron-sulfur clusters may underestimate the number of low-lying excited states by as much as two orders of magnitude, with the difference being related to  $d \rightarrow d$  excitations and with vibrational fluctuations found on energy levels close to those of such low-lying same-spin excited states [20].

The above-quoted publications, as well as many other references therein, offer a comprehensive and clear view of the  $Fe_4S_4$  chemistry. However, yet another perspective may be provided by simplifying some of the inherent complexities in the  $Fe_4S_4$  systems using the analogous  $Ru_4S_4$  systems. The greater ligand field strengths of analogous complexes of the second row transition metal ruthenium relative to the first row transition metal iron necessarily make higher spin states also higher energy structures relative to a low-spin ground state. This simplifies the resulting energy surfaces thereby providing a basis of establishing a closed shell configuration. Perturbation of this closed shell configuration can lead to higher spin states that are energetically competitive in the corresponding iron systems. It has also been pointed out that  $Ru_4S_4$  clusters are less fluxional at room temperature, compared to  $Fe_4S_4$  clusters [17]. For this theoretical study we have chosen the following  $Ru_4S_4X_4^z$  systems ( $z = 0$  to  $-4$ ):

- (1)  $Ru_4S_4(CN)_4^z$ : The cyanide ligand is the prototypical strong field ligand which is expected to stabilize low spin states as much as possible.
- (2)  $Ru_4S_4Cl_4^z$ : The chloride ligand is a much weaker field ligand and is likely to be present in biological systems.
- (3)  $Ru_4S_4(SCH_3)_4^z$ : The methylthio ligand is chosen as a model for the type of organosulfur ligands present in biological systems of interest.

None of these  $Ru_4S_4X_4^z$  systems is known experimentally. However,  $Cp_4Ru_4S_4$  species ( $Cp = \eta^5-MeC_5H_4$  or  $\eta^5-Me_5C_5$ ) have been synthesized and characterized structurally by Rauchfuss and coworkers [21–25]. These structures are not good models for the  $M_4S_4X_4$  metalloenzymes since a neutral  $\eta^5-Cp$  ligand is a five-electron donor whereas the neutral SR ligands are one-electron donors. This leads to distorted structures for the central  $Ru_4S_4$  units with only two Ru–Ru bonds for neutral  $Cp_4Ru_4S_4$  and three Ru–Ru bonds for the  $[Cp_4Ru_4S_4]^{2+}$  dication. Therefore these  $Cp_4Ru_4S_4$  species are not included in this work.

## 2. Materials and methods

Full geometry optimizations were carried out on the  $Ru_4S_4X_4^z$  ( $X = Cl, CN, SMe; z = 0$  to  $-4$ ) systems at the BP86/6-31G(d,p) [26,27] level of theory for all atoms except ruthenium, for which the SDD (Stuttgart-Dresden ECP plus DZ) basis set [28] was used. Single point calculations with the B3LYP and OPBE functionals were then also performed on these geometries in order to compare the relative energies of each series of spin states, given the known tendency of BP86 to favor lower-spin states [29]. Nevertheless, it was found that all three functionals yield qualitatively the same results in terms of ordering of the spin state energies for any of the examined species; therefore, only the BP86 data are discussed in text. All calculations were performed with the Gaussian 09 package [30] using the fine grid (75,302) for numerically evaluating the integrals,  $10^{-8}$  hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, RMS force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and RMS displacement of 0.001200 bohr as default settings. The characters of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies to confirm that genuine minima were obtained. In this way all of the structures reported in this paper were found to be genuine minima. The results are listed in Tables 1–3 for the structures within 25 kcal/mol of the global minima. Extensive tables containing data for all of the optimized structures, including higher energy and higher spin state structures, are provided in the Supporting Information.

## 3. Results

A tetracapped tetrahedral  $Ru_4S_4X_4^z$  structure with ideal  $T_d$  symmetry would be expected to have equal lengths for the six Ru–Ru edges of the central  $Ru_4$  tetrahedron. Such equivalent edge lengths are only found in the singlet dianions  $Ru_4S_4X_4^{2-}$  ( $X = Cl$  and  $CN$ ) (Tables 1 and 2 and Fig. 2). In singlet  $Ru_4S_4(SCH_3)_4^{2-}$  the six Ru–Ru edges are not quite equal but differ in length by a maximum of only 0.03 Å, presumably owing to the effects of the pendant  $CH_3S$  groups (Table 3). The predicted Ru–Ru edge lengths of 2.81 Å in singlet  $Ru_4S_4Cl_4^{2-}$  and 2.79 Å in singlet  $Ru_4S_4(CN)_4^{2-}$  are close to the experimental value of 2.76 Å for the two Ru–Ru short bonding interactions in the central  $Ru_4$  cluster of  $(\eta^5-MeC_5H_4)_4Ru_4S_4$ , as determined by X-ray crystallography [21] and somewhat shorter on average than reported in previous DFT calculations of the dication  $(C_5H_5)_4Ru_4S_4^{2+}$  [17]. These Ru–Ru distances are also somewhat shorter than the experimental Ru–Ru single bond distances of 2.85 Å in  $Ru_3(CO)_{12}$  as determined by X-ray crystallography [31,32]. Similarly the predicted Ru–S edge lengths of 2.28 Å in singlet  $Ru_4S_4Cl_4^{2-}$  and 2.29 Å in singlet  $Ru_4S_4(CN)_4^{2-}$  can be compared with the experimental value of 2.34 Å for the Ru–S edges in  $(\eta^5-MeC_5H_4)_4Ru_4S_4$ . The ratio of the Ru–Ru bond lengths to the Ru–S bond lengths in  $Ru_4S_4X_4^z$  ( $X = Cl, CN$ ) of  $\sim 1.22$  is  $\sim 13\%$  less than the ideal  $\sqrt{2} = 1.414$  for an ideal  $Ru_4S_4$  cube, but significantly in line (Fig. 3) with structures previously described as essentially tetrahedral [17]. As a result of this discrepancy the sulfur atoms are further from the center than the ruthenium atoms in the distorted  $Ru_4S_4X_4^z$  ( $X = Cl, CN$ ) cubes. However, ideal  $T_d$  symmetry is maintained in these two systems unlike the other  $Ru_4S_4X_4^z$  derivatives ( $z = 0$  to  $-4$ ).

These singlet  $Ru_4S_4X_4^{2-}$  structures are the lowest energy structures by substantial margins ranging from 9.5, 12.6, and 21.6 kcal/mol for  $X = CH_3S, Cl$ , and  $CN$ , respectively. Note that the largest difference of 21.6 kcal/mol is for  $Ru_4S_4(CN)_4^{2-}$  where  $X$  is the very strong field  $CN$  ligand. All of these observations indicate that the dianions  $Ru_4S_4X_4^{2-}$  represent the closed shell electronic configurations for the  $Ru_4S_4X_4^z$  systems.

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