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A Definitive Answer to a Bonding Quandary? The Role of One-Electron Resonance Structures in the Bonding of a $\{Cu_3S_2\}^{3+}$ Core

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Recently, this journal published a lively debate[1] between Santiago Alvarez, Roald Hoffmann, and Carlo Mealli about the electronic structure of a trigonally symmetric complex with a $\{Cu_3S_2\}^{3+}$ core (**1**) shown in Figure 1, which was first synthesized by the Tolman group.[2] This complex is not only an interesting model for biologically important copper–sulfur clusters, but also poses inherent problems in its electronic structure and its relationship to the salient structural and magnetic features of the compound. Of primary concern to the Alvarez–Hoffmann–Mealli (AHM) argument is the question of whether or not a transmolecular S–S bond exists in **1**, a question that has not yet received a definitive answer.[1,3,4] This stirred my enthusiasm, because the gray area between what is to be considered a chemical bond and what is not is one of great interest to me.[5] As discussed further below, Alvarez and the Hoffmann–Mealli team take opposing viewpoints on the electronic structure, although both camps seem to agree that the true electronic structure lies somewhere between their two extremes. Presented here is a re-reinterpretation of the electronic structure of **1** that advances a viewpoint in-between yet conceptually distinct from the extreme cases presented by Alvarez and Hoffmann–Mealli.

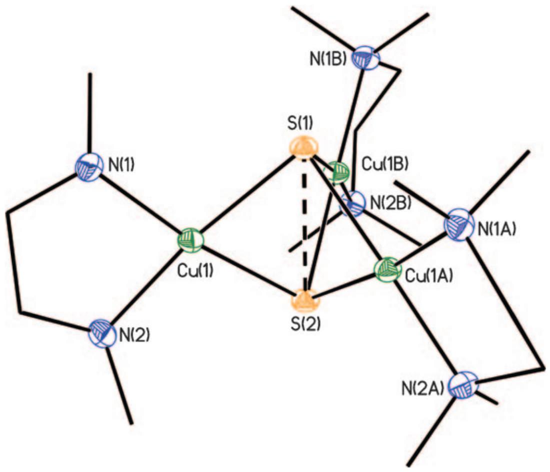

Figure 1. Molecular structure of the $[(tmedaCu)_3S_2]^{3+}$ trication (**1**). Ellipsoids for the carbon atoms are not shown, and hydrogen atoms have been removed for clarity.

Compound **1** adopts a trigonal-bipyramidal core geometry (Figure 1) in which the three Cu atoms occupy equatorial sites and the two S atoms occupy apical sites.[2] Each Cu atom adopts a square-planar geometry, having bonds to each of the two S atoms and ligation from a chelating tetramethylethylenediamine (tmeda) ligand. The Cu–S distances are 2.25 Å and the S···S distance is 2.73 Å. It is important to note that a crystallographic threefold axis passes through both S atoms and that an $S=1$ ground state was determined for the molecule by a solution magnetic-susceptibility measurement and a room-temperature EPR measurement. In agreement with the threefold symmetry of the molecule, the EPR spectrum showed hyperfine coupling to three equivalent Cu nuclei.

It should be mentioned here that a related $\{Cu_3O_2\}^{3+}$ compound (**2**) is also known,[6,7] which displays properties somewhat different from those seen in **1**. In the oxo system, one of the three Cu atoms is different from the other two, having Cu–O distances of 1.84 Å when the other two Cu atoms have Cu–O distances of 1.95 Å. The O···O distance, 2.37 Å, is too long to be considered an O–O bond. Compound **2** has a triplet ground state that arises from ferromagnetic coupling of two unpaired electrons ($J=+14\,cm^{-1}$, in which J is defined by the spin Hamiltonian $H=-2JS_AS_B$).[7] These properties of **2** are consistent with the view that the oxygen atoms may be considered as oxo ligands (O^{2-}), and that a mixed-valence $Cu^{II}/Cu^{II}/Cu^{III}$ set can be assigned, with the Cu^{III} ion being the one with the shorter Cu–O distances. The unpaired electrons on each Cu^{II} ion will ferromagneti-

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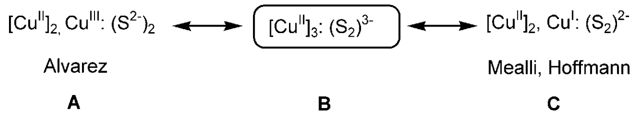
cally couple with each other because of the near-orthogonal Cu^{II}-O-Cu^{II} angle of 85° in the structure, which gives rise to the observed magnetic properties. This view of the electronic structure of **2** is supported by computational results by Solomon[7] and Alvarez.[2]

For **2**, assignment of the electronic structure as noted above is clear. For **1**, this is not so simple. The crystallographic equivalence of the three Cu atoms conflicts with a valence-trapped Cu^{II}/Cu^{II}/Cu^{III} model as found for **2**. Crystallographic disorder of the Cu positions could account for apparent equivalence of the Cu sites despite mixed valency, but the thermal ellipsoids of all of the atoms in the structure are normal and do not indicate any disorder. The crystal structure of **1** contains well-separated $[(\text{tmedaCu})_3S_2]^{3+}$ cations and SbF_6^- anions. Intermolecular S···S distances of more than 11 Å discount the possibility that intermolecular interactions can cause the unusual features of the trication. In analogy to **2**, Alvarez and co-workers have postulated a Cu^{II}/Cu^{II}/Cu^{III} mixed-valence system for **1** with two non-bonded sulfido (S^{2-}) ligands (**A** in Scheme 1).[2] Hoffmann and Mealli and their co-workers propose that an S–S-bonded disulfido ligand (S_2^{2-}) is bound to a mixed-valence set of Cu^{II}/Cu^{II}/Cu^{I} ions (**C** in Scheme 1).[3] The merits and shortcomings of each of these two limiting electronic structures, **A** and **C**, are amply detailed in the AHM article[1] and will not be recapitulated here. Instead, it should be noted that Alvarez, Hoffmann, and Mealli all presume full delocalization among the three Cu centers and that this delocalization is mediated by the covalency of the Cu–S bonds. From a more localized view, however, the mixed-valence assignments are difficult to rationalize: the highly oxidizing Cu^{III} ion would be expected to be chemically incompatible with fully reduced S^{2-} ligands, and square-planar coordination is an unlikely geometry for the d^{10} Cu^{I} ion.



Scheme 1. Possible electronic structures for **1**.

I present here another view of the electronic structure of **1** that was developed to deal expressly with the discrepancies noted above for either **A** or **C**. Specifically, proposed here is a situation in which a non-innocent S_2^{3-} ligand binds to three equivalent Cu^{II} centers (**B** in Scheme 1). If we consider electronic structures **A** and **C** to denote standard two-electron resonance structures of each other, then **B** arises from considering a one-electron resonance structure on the way from **A** to **C**. Nevertheless, **B** does represent a distinct electronic state of the molecule that does well to explain the above issues that are not addressed by either **A** or **C**. The equivalence of the three Cu centers in **B** is inherent because there is no mixed valency in the Cu atoms. The assignment of square-planar geometry for all three Cu^{II} centers makes sense from what one would expect based on ligand field theory. Furthermore, the triplet ground state in **1** that persists to room temperature is a result of strong antiferromagnetic coupling of the S_2^{3-} radical with the three odd electrons on the three Cu^{II} centers. The key difference between assignment **B** and the AHM structures (**A** and **C**) is that the molecule has strong antiferromagnetic coupling between the S_2^{3-} radical and the three Cu^{II} centers. This leads to four magnetic orbitals for the molecule and not just two. Therefore, DFT computations on an antiferromagnetically coupled triplet system may be made to test the validity of structure **B**.

The magnetic interactions in **1** may be modeled as shown in Figure 2, with one unpaired electron on each Cu center and one unpaired electron on the central S_2 unit. The spin coupling can be described with the spin Hamiltonian $H = -2JS_{S_2}(S_{Cu_1} + S_{Cu_2} + S_{Cu_3})$, in which $S_{S_2} = S_{Cu_1} = S_{Cu_2} = S_{Cu_3} = 1/2$, which was simplified to $H = -2JS_{S_2}S_{Cu}$, in which $S_{Cu} = 3/2$.[8] This spin Hamiltonian leads to an $S=1$ antiferromagnetically coupled state and an $S=2$ ferromagnetic state, which are separated in energy by $2J$. Because the $S=1$ state is the only state populated up to room temperature, J is assumed to be large and negative.

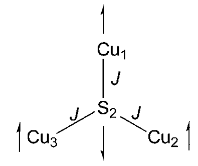


Figure 2. Spin coupling in **1**.

A proper wavefunction for the antiferromagnetic $S=1$ state (**1T(AF)**) is multideterminental and, therefore, cannot be treated by using DFT methods. The **1T(AF)** state can, however, be approximated by using a broken symmetry (3,1) formalism.[9] This method requires analysis of **1** in its $S=2$ state, **1Q**. The geometry of **1Q** was optimized and the results, shown in Table 1, are in good agreement with the crystal structure of **1**. This geometry was used as a starting point for the calculation of the electronic structure of **1T(AF)**. The magnetic orbitals of the **1T(AF)** state are shown in Figure 3. The three spin-up electrons occupy orbitals of a$_2''$ and e$''$ symmetry (in the D_{3h} point group). The a_2'' orbital has contributions from all three Cu $d_{x^2-y^2}$ orbitals, and the e$''$ set has contribution from these orbitals in an antibonding interaction with the p orbitals on the S atoms. Taken together, these three orbitals mainly derive from linear combinations of the three Cu $d_{x^2-y^2}$ orbitals. The spin-

Table 1. Experimental and calculated geometries for **1**.

	Experiment	**1T**	**1Q**
Cu–S [Å]	2.25	2.31	2.39
Cu–N [Å]	2.03	2.09	2.09
S···S [Å]	2.73	2.77	2.77

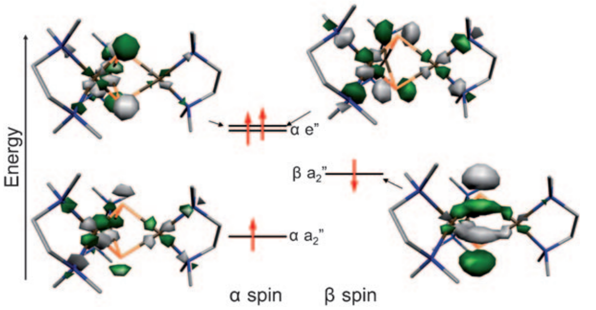


Figure 3. Partial molecular orbital diagram displaying the relative energies of the four magnetic orbitals in **1T**(**AF**). The spin-up (α) orbitals are shown on the left and the spin-down (β) orbital is shown on the right with isodensity cutoff 0.05. Hydrogen atoms have been removed from the structures for clarity.

down electron occupies an a_2'' orbital with a small contribution from the three Cu $d_{x^2-y^2}$ orbitals, but is mainly an S–S σ* orbital formed from p orbitals on the two S atoms. The α and β a_2'' orbitals have a calculated overlap, 0.85, that is notably less than one, and indicates strong antiferromagnetic coupling. The calculated value for J, $-2000\,\mathrm{cm}^{-1}$, supports this conclusion. From this point of view, **1** is a classical example of spin coupling between paramagnetic metal centers and a non-innocent ligand.[10]

It is useful to compare the electronic structure proposed here for **1** with that proposed by Alvarez, Hoffmann, and Mealli. The essentials of the AHM electronic structure are shown at the top of Figure 4. The key feature of this model is that the $2a_2''$ orbital is a two-electron orbital that has both Cu and S character, which directly leads to the argument of whether this orbital is mainly a Cu orbital, as suggested by Hoffmann and Mealli, or a S orbital, as noted by Alvarez. The degenerate $2e''$ orbitals are both singly occupied, which provides a reasonable explanation for the triplet ground state of the ion.[2] The AHM electronic structure, however, does not take into account spin polarization, which allows α- and β-spin electrons to have different energies and to occupy different regions of space. Thus, in the AHM model, the $2a_2''$ orbital is shown as a single two-electron orbital, whereas in **1T**(**AF**), the $2a_2''$ orbitals are an antiferromagnetically coupled pair of corresponding one-electron orbitals (Figure 4, bottom). The AHM $2a_2''$ orbital appears to be a linear combination of the $2a_2''$ orbitals in **1T**(**AF**).

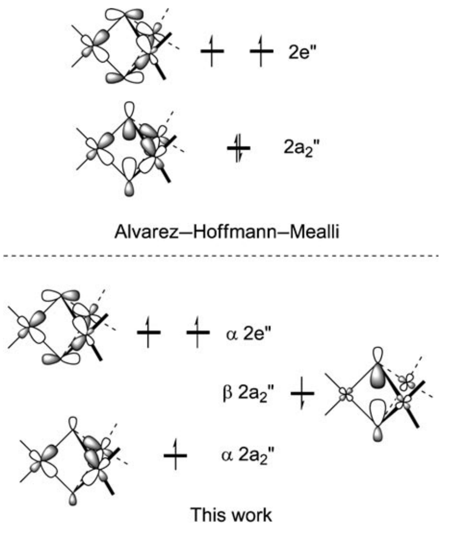


Figure 4. Partial schematic molecular orbital diagrams for **1** showing only the $2a_2''$ and $2e''$ levels (top: the AHM model, bottom: the model found in this study for **1T**(**AF**) and **1T**).

The major quantitative difference between a true two-electron orbital (or a set of one-electron orbitals that, despite spin polarization, may be represented as a single two-electron orbital) and a set of antiferromagnetically coupled one-electron orbitals is the overlap calculated between spin-up and spin-down electrons. This overlap, conveniently available through the use of the corresponding orbital transformation,[11] is exactly 1.00 for two electrons that have the same spatial occupancy, and in practice, values of 0.99 to 0.98 are observed for systems that have spin polarization.[12] A significantly lower overlap such as 0.85 in **1T**(**AF**) indicates that the two electrons may be described as an antiferromagnetically coupled pair.

I attempted to reproduce the AHM electronic structure for **1** by calculating **1** in an unrestricted triplet state, **1T** with $S=1$. The optimized geometric parameters of **1T** are given in Table 1. Notably, these agree with those seen from experiments, as well as those calculated by AHM. However, **1T** was found to be energetically equivalent to **1T**(**AF**) within $3\,\mathrm{kJ\,mol^{-1}}$. Additionally, upon inspection of the electronic structure of **1T**, the $2a_2''$ orbital was found to have spontaneously localized itself into an α- and β-spin corresponding orbital pair. The overlap calculated for these orbitals is 0.88, very similar to that seen in **1T**(**AF**). It may, therefore, be concluded that the **1T** state is identical to **1T**(**AF**) and that the electronic structure of **1** is best represented by the picture at the bottom of Figure 4.

The AHM argument emphasizes the view that delocalized bonding is, by its very nature, "fuzzy", and that models such as **A**, **B**, and **C** are always oversimplifications. My view is that the fuzzy electronic structure of **1** is more closely represented by **B** than by either **A** or **C**. Thus, **1** is to be considered as the first coordination compound synthesized that contains the unusual S_2^{3-} ion, a suggested name for which is the "subsulfide" ion. To the best of my knowledge this species has never before been described, although it shares close similarities with organic disulfide radical anions that have been studied in molecular systems as well as in proteins as reactive intermediates in S–S bond cleavage reactions.[13–17] These radical species contain a three-electron σ bond, which derives from population of the S–S σ bonding orbital by two electrons and population of the σ* orbital by one electron.[18] Thus, the formal S–S bond order would be 0.5. Recognition of the singly occupied S–S σ* orbital as the lone β-spin orbital in Figures 3 and 4 allows for a definitive answer to the question of S–S bonding in **1** that has beleaguered Alvarez, Hoffmann, and Mealli.[1] There is indeed an

S–S bond of order 0.5 in **1** that derives from an S–S $\sigma^2\sigma^{*1}$ electronic configuration. The S–S bond distance of 2.73 Å observed in this compound can now be reconciled with the data on S–S distances compiled by Alvarez from the Cambridge Structural Database.[1] These data show a bimodal distribution of S–S distances in M_2S_2 and M_3S_2 compounds, with maxima at approximately 2.00 Å for compounds containing the singly bonded S_2^{2-} ion, and at approximately 3.6 Å for compounds containing two non-bonded S^{2-} ions.[1] The S–S distance of 2.73 Å in **1** falls almost exactly between these two extremes, in accordance with the assignment of a half-bonded S_2^{3-} ion in **1**.

In their arguments, Alvarez, Hoffmann, and Mealli suggest[1] the need for further experimental work on **1**. Specifically, Cu K-edge X-ray absorption spectroscopy (XAS) is suggested so that the edge energy can be compared to known Cu^I, Cu^{II}, or Cu^{III} compounds. However, I suggest that a S K-edge XAS measurement would be more definitive in spectroscopically identifying the hole in the S 3p shell present in the electronic structure **B**. A sulfur 1s to 3p transition is fully allowed, and would undoubtedly be observable as a pre-edge feature in the spectrum. This technique has recently been tremendously successful in the identification of S radicals in metal dithiolene complexes.[10,19]

In summary, I suggest that configuration **B** is a better description of the electronic structure of compound **1** than either **A** or **C**. This assignment of configuration **B**, which assumes three identical Cu^{II} ions and an unprecedented S_2^{3-} ion in **1**, agrees well with the current experimental data. Specifically, the persistent triplet state that is observed at room temperature is well explained by **B** as the result of strong antiferromagnetic coupling between the three Cu^{II} ions and the S_2^{3-} radical. Furthermore, the observed S–S bond distance of 2.73 Å in **1** is halfway between what is expected for an S–S single bond and no S–S bond, in agreement with a formal S–S bond order of 0.5. The recognition of **B** as the correct electronic structure for **1** highlights the importance of considering one-electron resonance structures to describe transition-metal complexes, especially those that contain non-innocent ligands, which have been previously shown to exist in the coordination chemistry of dithiolate ligands.[10,19]

Appendix: Antiferromagnetic Coupling or Bonding?

In independent correspondence with Santiago Alvarez about this manuscript, the major difference between my approach and the AHM approach became clear: What I refer to here as antiferromagnetic coupling is simply considered to be bonding by AHM. Because the boundary between what should be called antiferromagnetic coupling and what should be considered a bond is not always entirely clear (and has also puzzled me before),[20] Alvarez and I explored our differences on this topic. Alvarez argued that the energy difference between **1Q** and **1T**(**AF**), approximately 8000 cm^{-1}, is too large to be considered as antiferromagnetic coupling, and should, therefore, indicate delocalized bonding. My view is that the energy difference between the high-spin and antiferromagnetic low-spin states is important, but that orbital overlap should also be taken into account. Bonding should be characterized by a large energy difference between the high- and low-spin states, as well as an overlap of 1.00 between the two electrons in the bonding orbital. There are many examples of compounds that are best described as singlet diradicals that are diamagnetic at room temperature owing to a very large negative value for *J*. Some of the best examples of these are the dithiolate complexes mentioned above. For another example, the hypothetical molecule H···He···H may be considered as the simplest model compound for studying antiferromagnetic coupling. The singlet–triplet gap in H···He···H with a fixed H···He distance of 1.25 Å is in the order of 5000 cm^{-1}.[21] The interaction between the two H atoms should be considered as antiferromagnetic coupling, however, and not bonding because of the overlap of 0.50 calculated between the magnetic orbitals. Similarly, strong antiferromagnetic coupling exists in **1**.

Experimental Section

All computations were done with the ORCA program package by using DFT calculations.[22] The BP86[23,24] functional was used for geometry optimization by using initial atomic positions from the published crystal structure of **1**.[2] No geometry constraints were imposed in the optimization. Single-point and broken symmetry calculations were done by using the B3LYP[23,25] hybrid functional. The calculations employed the Ahlrichs basis sets[26] of triple-ζ quality (TZVP) for the Cu and S atoms, and smaller polarized SV(P) functions for the remaining non-hydrogen atoms. The electronic structure of **1T**(**AF**) was calculated by using the broken symmetry method,[9] and the corresponding orbital transformation[11] was used to evaluate overlap of the magnetic orbitals. The magnetic coupling J was calculated by using the method of Yamaguchi from [Eq. (1)].[27] Orbitals were visualized with the Molekel program.[28]

$$J = \frac{E_{HS} - E_{BS}}{\left\langle \hat{S}^2 \right\rangle_{HS} - \left\langle \hat{S}^2 \right\rangle_{BS}} \tag{1}$$

Note Added in Proof

These comments are a complete rebuttal of the correspondence to this article by Alvarez and Ruiz.[29] Four issues are raised in the review, which are shown here to be irrelevant to the main proposition of this paper, namely that **1** may be formally considered to contain an S_2^{3-} ligand corresponding to an S–S bond order of 0.5.

It is important to note that comparison of the orbitals shown here with those of Alvarez and Ruiz leads to the conclusion that both I and Alvarez and Ruiz have obtained a similar wavefunction, but that we differ in our interpretation of that wavefunction.

Alvarez and Ruiz discuss the extremely small energy difference between **1T** and **1T**(**AF**), 3 kJ mol^{-1}, which is well within the expected error in energies derived from DFT. As anticipated from their arguments, **1T** is indeed the lower energy state. The only reason for this, as mentioned by Alvarez and Ruiz, is that its energy was minimized in the correct equilibrium geometry. If the energy of **1T**(**AF**) were minimized in the same geometry as that of the **1T** state, the energies of the two would be identical, because they are essentially the same wavefunction. In fact, the results reported by Alvarez and Ruiz show this to be true. My interpretation of both **1T** and **1T**(**AF**) is that they represent a spin-coupled system with three Cu^{II} ions, while Alvarez and Ruiz argue that these wavefunctions are delocalized and correspond to a $Cu^{II}/Cu^{II}/Cu^{III}$ formulation.

As mentioned by Alvarez and Ruiz, I cite the overlap between the α- and β-spin $2a_2''$ orbitals as an important criterion for describing **1** as a spin-coupled system. The calculated overlap of ≈0.85 is significantly less than 1.00, but higher than that calculated for other examples of antiferromagnetically coupled systems.[12] Alvarez and Ruiz cite two examples with overlap integrals of 0.2 to 0.1, but these are for much more weakly coupled systems. The presence of a bridging atom between the two magnetic centers limits the possible overlap that can occur. Compound **1** is different in that the magnetic centers (the $\mathrm{Cu^{II}}$ ions and the sulfur atoms) are directly bonded to one another with no other atoms in between. This clearly leads to a higher overlap in **1**, not to mention the fact that the S atoms are bound not to just one, but to three magnetic $\mathrm{Cu^{II}}$ centers.

The last issue raised by Alvarez and Ruiz pertains to "spin densities". These are numbers that derive from Mulliken population analysis of a wavefunction, for which reason I prefer to use the term "spin populations". Before invalidating the arguments made by Alvarez and Ruiz concerning these little numbers, I ask a simple rhetorical question: Are these numbers physically meaningful? I argue that they are not for broken-symmetry wavefunctions, or wavefunctions like those in **1** that have broken spin symmetry. A simple example of this may be given by an examination of the spin populations for the hypothetical linear H···He···H molecule in its broken-symmetry antiferromagnetic singlet state. Here the spin population on the helium atom is zero, and the spin populations in the two hydrogen 1s orbitals are + and −0.86. A three-dimensional plot of the spin density of the molecule would show negative spin density around one hydrogen atom and positive spin density around the other. This situation, however, evidently defies the Pauli exclusion principle requiring wavefunctions to be antisymmetric with respect to exchange of electrons. A true wavefunction for the antiferromagnetic singlet state must have a spin density of exactly zero at all points in space. Thus, the spin populations that appear in broken-symmetry wavefunctions are artifacts of the use of the broken-symmetry formalism. However, this fact has not stopped these spin populations from being interpreted in the manner that Alvarez and Ruiz present.

As stated by Alvarez and Ruiz, the spin populations on the Cu and S atoms are indeed all positive, with values of 0.35 and 0.08, respectively. However, this is not the whole story. Analysis of the spin populations of the S atoms shows that these spin populations vary widely depending on which p orbital is considered. The S p_x and p_y orbitals have positive spin populations of 0.16 each, but the S p_z orbitals have *negative* spin populations of −0.25. The overall positive spin population for the S atoms is due to the fact that the negative spin populations of the p_z orbitals are nullified by the positive spin populations of the p_x and p_y orbitals. The p_x and p_y orbitals have significant positive spin population because of their involvement in the two α-spin $2e''$ orbitals. Thus, the spin populations of opposite sign that Alvarez and Ruiz have searched for in **1** are indeed present, but were not detected in their analysis because of the two unpaired electrons in the $2e''$ orbitals.

I conclude by noting that the arguments used by Alvarez and Ruiz to defend their original interpretation of **1** do not look at the $\mathrm{Cu_3S_2}$ problem from a big picture point of view. The big question is that of the S−S bond order, for which I suggest a formulation of three identical $\mathrm{Cu^{2+}}$ ions with an S−S bond of 0.5 in an $\mathrm{S_2^{3-}}$ unit. None of the arguments of Alvarez and Ruiz discredit this proposal. Alvarez and Ruiz suggest delocalized $\mathrm{Cu^{II}/Cu^{II}/Cu^{III}}$ ions bound to two $\mathrm{S^{2-}}$ ligands. However, they have provided no reasonable explanation for why two sulfide ions would approach each other at a distance of 2.7 Å, and have not given any rationale for the coexistence of copper in its highest oxidation state with sulfur in its most reduced form.

The suggestion of a formal subsulfide ion ($\mathrm{S_2^{3-}}$) in **1** is admittedly improbable, because of the fact that this ion has never been observed before. However, I find the $\mathrm{Cu^{II}/Cu^{II}/Cu^{III}}$ formulation of Alvarez and the $\mathrm{Cu^{II}/Cu^{II}/Cu^{I}}$ formulation of Hoffmann and Mealli to be even more unlikely, if not impossible. To quote Sherlock Holmes: "When you have eliminated the impossible, whatever remains, however improbable, must be the truth."[30] It is in this deductive vein that I propose the subsulfide ion in **1**, to avoid the unrealistic oxidation states proposed by Alvarez, Hoffmann, and Mealli. I will agree with Alvarez and Ruiz, though, that experimental verification of the subsulfide ion is necessary, and I have mentioned in this paper that S K-edge X-ray absorption spectroscopy will be a key experiment to test this hypothesis. Alvarez and Ruiz also note a lack of "computational evidence" for the subsulfide ion, though my opinion is that nothing in chemistry may be proven by computations alone. One must always keep in mind that computations produce bonding models, frequently complicated and intricate ones to be sure, but models nonetheless. Computational results are either supported by experiments, in which case they are usually accepted, or they are found to be inconsistent with experiments, and may be discarded, and a new model formulated. Naturally, the operational test of my theoretical model is whether it is compatible with experiment, and I have already detailed how this model is in agreement with the currently available data as well as the need for further experiments.

Keywords: bond theory · cluster compounds · copper · density functional calculations · sulfur

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