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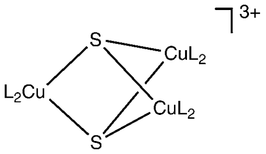
Antiferromagnetism or Delocalized Spin in a Cu_3S_2 Core?

Santiago Alvarez* and Eliseo Ruiz[a]

In a communication published in this journal, J. F. Berry proposes a Solomonic solution[1] to the debate held by Hoffmann and Mealli with one of us recently,[2] regarding the existence or not of sulfur–sulfur bonding in Tolman's complex **A**. Although Alvarez proposed that the triplet state found in **A** could be described by formal oxidation states $Cu^{II}Cu^{II}Cu^{III}$ and $(S^{2-})_2$, while Hoffmann and Mealli supported the alternative description $Cu^{II}Cu^{II}Cu^{I}/S_2^{2-}$, they agreed on a delocalization of the two unpaired electrons throughout the Cu_3S_2 skeleton. The conclusion drawn by Berry from DFT calculations is that the system is better described by three Cu^{II} ions the unpaired electrons of which are antiferromagnetically coupled with the electron of a radical anion S_2^{3-}.



A

We wish to call the attention to three main points regarding the work of Berry:

1) There are no essential differences between the calculations reported by us earlier and those performed by Berry regarding the delocalized triplet state, labelled **1T** by Berry. Some quantitative differences, though, will be commented upon below.
2) There are no essential differences between the two triplet states reported by Berry, a delocalized triplet **1T** and a supposedly localized ("broken symmetry") antiferromagnetic triplet **1T(AF)**.
3) No clear computational evidence is given by Berry to support the proposal of the open shell antiferromagnetically coupled state.

The assertion made by Berry that our early report of the "electronic structure, however, does not take into account spin polarization", is unjustified. All our discussion is based on unrestricted-DFT calculations reported in the original paper.[3] Although in a recent wider study[4] we represented the α and β occupied $2a_2''$ spin orbitals by a single schematic orbital for simplicity, it should not be interpreted as implying that they have the same energy and composition, since it is known that the α and β versions of a molecular orbital differ in open shell systems calculated with an unrestricted approach[5] due to spin polarization. There are only minute differences between the spin up and spin down orbitals from our calculations (Figure 1) and those reported by Berry in Figure 3 of his paper.

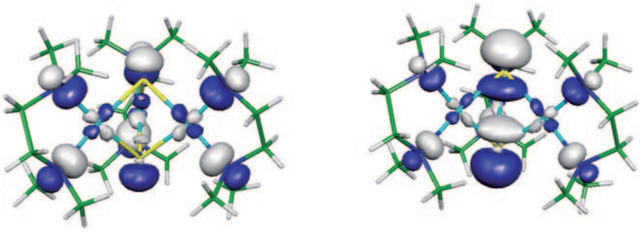


Figure 1. Isodensity surfaces (cutoff value 0.05) for the occupied $2a_2''$ Kohn–Sham orbitals of the $Cu_3S_2^{3+}$ complex for the α (left) and β (right) electrons.

The delocalized triplet state calculated by us is characterized by positive spin densities at the three copper (+0.31 each) and two sulfur (+0.16 each) atoms. The strong mixing of metal d and sulfur p orbitals in the singly occupied molecular orbitals is consistent with a spin delocalization mechanism.[5]

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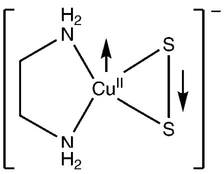
[a] S. Alvarez, E. Ruiz
Departament de Química Inorgànica and
Institut de Química Teòrica i Computacional
Universitat de Barcelona, Martí i Franquès 1–11
08028 Barcelona (Spain)
Fax: (+34) 93-4907725
E-mail: santiago.alvarez@qi.ub.es

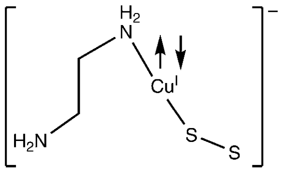
Berry's calculation identified as **1T(AF)** is not a "broken-symmetry" calculation, because localization of unpaired electrons on the Cu_3 or S_2 groups would preserve the full D_{3h} molecular symmetry. That the symmetry is not broken can be appreciated in the shape of the MO's shown in Figure 3, and in the equivalence of the Cu–S and Cu–N distances given in Table 1 of his paper.[1] Moreover, we do not think that it corresponds to an open shell triplet resulting from an antiferromagnetic coupling of three unpaired electrons at the copper and one unpaired electron at the sulfur atoms. Such a localized tetraradical state would result in spin densities of opposite spins at the copper and sulfur atoms, while the spin densities in **A** have the same sign throughout. As an example of the spin densities found in antiferromagnetically coupled systems,[6] we may recall a Mn^{II}–Cu^{II} dinuclear complex prepared by Kahn and co-workers, for which we obtain B3LYP spin densities at the Mn and Cu atoms of +4.82 and −0.56, respectively.

We have attempted a calculation of the purported antiferromagnetic open shell triplet (Figure 2 in reference [1]) by localizing positive spins at the copper atoms and negative spins at the sulfur bridges (Jaguar code), but the calculations converged to the delocalized triplet with only positive spins throughout. The two calculations gave exactly the same energy.

To test the possibility of an S_2^{3-} group bound to a Cu^{II} center, we also attempted the U-B3LYP optimization of a mononuclear complex **B** with an open shell singlet bearing two unpaired electrons, one at the copper atom and one at the S_2 unit. A localized singlet state could not be obtained, but rather the optimization led to a spinless diamagnetic complex **C** with a two-coordinated Cu^I ion and a monodentate disulfide ion (S_2^{2-}).



B



C

What do we know about the similar pair of calculations reported by Berry, **1T** and **1T(AF)**? Other than the different localization of the α and β $2a_2''$ spin orbitals commented above, the only datum given is that they are "energetically equivalent within 3 kJ mol^{-1}". We suspect that the small energy difference is associated to the different molecular geometry used for those two calculations. It must be recalled that Berry's **1T** corresponds to an optimized geometry, while his **1T(AF)** calculations were performed on the geometry optimized for the quintet state. The electron configuration of the quintet state differs from that of the triplet by the promotion of an electron in the framework bonding $2a_2''$ orbital to a framework antibonding orbital (probably $3a_2''$), resulting in significantly longer Cu–S bonds (Table 1 in ref. [1]). It is thus natural that the same delocalized triplet obtained in the two calculations **1T** and **1T(AF)** differ in energy only because of the different molecular structures employed.

The main criterion for Berry's interpretation of the electronic structure is the value of the overlap integral between the α and β magnetic orbitals (0.85). The deviation of that overlap integral from unity is not unexpected for spin-polarized molecular obitals. Furthermore, it is practically identical to the overlap integral found by Berry for the delocalized triplet **1T** (0.88) and does not seem therefore a good indication of localization of the α and β $2a_2''$ electrons at the Cu_3 and S_2 fragments of the molecule, respectively. In fact, in the H⋅⋅⋅He⋅⋅⋅H model mentioned by Berry, with two antiferromagnetically coupled hydrogen atoms, the overlap integral is much smaller (0.23).[7] In another example reported by Neese, the coupling of two fluoro-bridged Cu^{II} ions in $[Cu_2(\mu\text{-}F)(H_2O)_6]^{3+}$, the overlap integral between the α and β orbitals in the broken-symmetry state is still smaller (0.16).[8]

In summary, we think that the results of Berry's **1T(AF)** calculations are the same as his delocalized **1T** triplet, essentially coincident with our earlier results,[3] with only slight differences due to the different geometries used in each case. His attempt to perform a localization of the magnetic orbitals by means of "broken-symmetry calculations" most likely led to the same solution than for the delocalized system, and differences between **1T** and **1T(AF)** are only due to the different geometries used. He then reinterpreted the spin polarization seen in the occupied Kohn–Sham orbitals of A_2'' symmetry as an antiferromagnetic coupling between an $(S_2)^{3-}$ radical and a $(Cu^{II})_3$ cluster. Neither theoretical nor experimental evidence is given of the presence of an unpaired electron with negative spin at the S_2 group. The proposal of an unprecedented subsulfide species should therefore require clearer theoretical or experimental evidence.

Note Added in Proof

Some of the comments added in proof to the paper of Berry have already been already addressed by us above and only a few additions will be briefly commented here. The assertion that a true antiferromagnetic singlet state must have a zero spin density at all points in space does not apply to the present case, since the net spin of the molecule is non-zero. For molecules with non-zero spin, the two alternative spin configurations (leading to total spin up and spin down, respectively) become non-degenerate in the presence of a magnetic field. For that reason, spin density distributions such as the one depicted in Figure 2 of Berry's paper should represent a physical reality that has been established by polarized neutron diffraction experiments in cases in which antiferromagnetic coupling is out of question.[9]

The different sign of the spin density at the p atomic orbitals of the sulfur atoms can be straightforwardly explained by the interplay of spin delocalization (positive spin) and spin polarization (negative spin). Yet, the net positive spin at the sulfur atoms indicate a predominance of the delocalization of the unpaired electrons throughout the Cu_3S_2 skeleton, consistent with a class III mixed valence compound but incompatible with an antiferromagnetic state.

The claim that "the $Cu^{II}/Cu^{II}/Cu^{III}$ formulation of Alvarez and the $Cu^{II}/Cu^{II}/Cu^{I}$ formulation of Hoffmann and Mealli" is "even more unlikely, if not impossible", is at odds with experimental facts. Cu^{II}/Cu^{I} mixed valence compounds are quite common in complexes with varying degrees of nuclearity, while other delocalized $Cu^{II}/Cu^{II}/Cu^{III}$ compounds are well documented.[10]

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