A Bonding Quandary—or—A Demonstration of the Fact That Scientists Are Not Born With Logic

Santiago Alvarez,[a] Roald Hoffmann,[b] and Carlo Mealli[c]

Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday

Abstract: We document here a spirited debate among three colleagues and friends who have strong opinions on a specific bonding problem, the presence or absence of a cross-ring sulfur–sulfur bond in a trinuclear Cu_3S_2 cluster. The example may seem esoteric, but through their struggles with this specific bond (and with each other) the authors approach the more general problematic of chemistry, the chemical bond. The discussion focuses on bond lengths and the population of bonding and antibonding orbitals, and on oxidation states, electron counting, and associated geometries. It expands to encompass other bonding criteria, and introduces examples ranging far across organic and inorganic chemistry. The authors suggest molecules that might test their ideas. An Appendix to the paper discusses a matter rarely broached in the chemical literature—should one review for publication a paper which criticizes one of your own contributions.

Keywords: bond lengths · chemical bonding · cluster compounds · S—S bonding · sulfides

[a] Prof. S. Alvarez
Departament de Química Inorgànica and
Institut de Química Teòrica i Computacional (IQTC-UB)
Universitat de Barcelona
Martí i Franquès 1-11, 08028 Barcelona (Spain)
Fax: (+34)93-4907725

[b] Prof. R. Hoffmann
Department of Chemistry and Chemical Biology
Cornell University
Ithaca, NY 14853-1301 (USA)
Fax: (+1)6072555707

[c] Dr. C. Mealli
Istituto di Chimica dei Composti Organometallici
ICCOM-CNR
Via Madonna del Piano 10,
50019 Sesto Fiorentino, Firenze (Italy)
Fax: (+39)055225203

Introduction

The chemical bond is at the heart of our enterprise, yet its nature continues to be debated. Into the idea of a chemical bond enter experimental measures—distances, energies, force constants, spectroscopic and magnetic criteria—and theoretical ones: bond orders, overlap populations, quantum theory of atoms in molecules (QTAIM) bond paths, electron localization function (ELF) plots, and energy decompositions. If one allows oneself to use a multiplicity of criteria, bonds may exist by one measure, not by another. This is not a reason to wring our hands, nor complain how unscientific chemistry is (or how obstinate chemists are). Chemistry has done more than well in creating a universe of structure and function on the molecular level with just this "imperfectly defined" concept of a chemical bond. Or maybe it has done so well precisely because the concept is flexible and fuzzy.

We want to share with the community how a discussion on bonding played out around a specific group of compounds: small, sulfur-containing clusters of copper with associated ligands. It's a real story, with some fierce debate among friends, who questioned each others' bonding assignment both in print and in private conversations. We believe our discussion has something of value to other chemists, for several reasons:

1) There is in our exchange an underlying question of the existence or absence of a chemical bond (in this case, an S—S bond), a matter, as we have said, debated across the community and not just for these compounds.
2) The reaction in question—making or breaking a bond—is formally an oxidative addition or reductive elimination, a fundamental and widely useful organometallic reaction. So are redox reactions in general.
3) Polynuclear metal complexes of oxygen and sulfur are used by nature in a wide variety of biological redox reactions.

4) Much of what transpired in our exchange finds no place in the scientific literature, or is dealt out of it. And yet it is an essential part of the way science is done.

The participants in the debate are *Santiago* Alvarez (University of Barcelona), *Roald* Hoffmann (Cornell University), and *Carlo* Mealli (Istituto di Chimica dei Composti Organometallici, Firenze). They will use their first names throughout the debate. Each had important collaborators: Anne Poduska for Roald, Gabriel Aullón and Rosa Carrasco for Santiago, Andrea Ienco for Carlo. And the discussion centers on a compound made by William Tolman and co-workers (University of Minnesota). The text of the correspondence, as it evolved in real time, is available from the authors.[1] What we have here is a mutually agreed-on reconstruction of the debate's essential features.

How the Troubles Began

Roald: In 2007 in Ithaca, Anne Poduska was wending her way toward her Ph.D. One of her projects involved a theoretical analysis of the Isobe and Nishioka compounds:[1]

$$\left[\quad\right]^{2+}$$

M = Ir, d_1 long, d_2 short
M = Rh, d_1 short, d_2 long
(short <2.1Å, long >2.7Å)
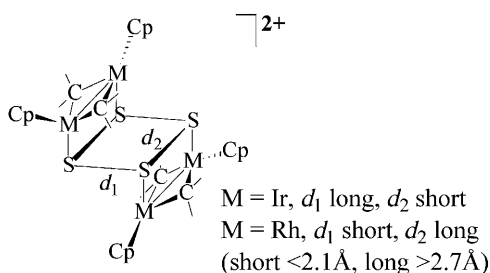
In these molecules, two S_2^{2-} complexes are reductively linked, forming two single S–S bonds and two "half" S–S bonds; we analyzed the composite system as a complex of a Jahn–Teller distorted S_4^{2-} ring. With my failing memory, I remembered vaguely that both Santiago and Carlo had done work on S···S bond formation across a metal-containing ring. So I wrote to both, asking for references.

Santiago: I replied to Roald's June 2007 E-mail, mentioning a number of cases where we had studied the "trading off" of M–M for S–S bonding. Among the papers I listed, there was one emerging from my collaboration with Tolman's group on a trigonal-bipyramidal Cu_3 complex without an S–S bond: $[(L_2Cu)_3(\mu_3\text{-}S)_2]^{3+}$, $L_2 = Me_2NCH_2CH_2NMe_2$ (called **A** throughout this paper).[2] Its structure, shown below, is also found in similar compounds with $L_2 =$ cyclohexyldiamine.[2,3] Little did I know what mentioning this work would get me into.
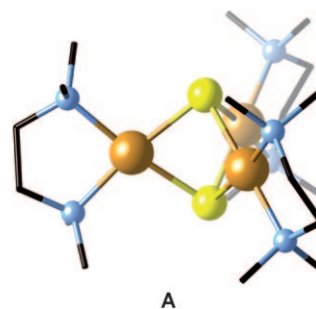
A

Carlo: I also supplied Roald and Anne with some references, for our interest in main group element–main group element (X–X) and M–M bonds is one of long standing.[4] I was fascinated by the Isobe and Nishioka compounds, and in the attempt of gaining a clearer picture of the bonding in these compounds, I carried out with Andrea additional calculations and qualitative molecular orbital (MO) analyses. We wondered whether there could be other structures thought to possess parallel S_2^{2-} units that in fact are being reductively coupled. And we found some.

I started to see more generally some analogy between the coupling of two disulfide bridges and the coupling of simpler sulfide ligands, S^{2-}, which can potentially undergo reductive coupling to S_2^{2-}. Excitedly, we corresponded with Roald about this.

Roald: Building off Carlo's and Andrea's enthusiasm, an Ithaca–Firenze collaboration took shape, examining the presence and absence of S–S coupling in a variety of organometallic systems. I brought up the Tolman/Alvarez article on the trinuclear cluster **A**, and upon reading it, Carlo started wondering whether such a compound might actually have an S–S bond, especially since the S–S separation of about 2.7 Å is similar (or even shorter) than those in the S_4 systems for which I and Anne proposed S–S coupling.

I could sense a good debate on the horizon.

Roald and Carlo: Eventually, we wrote a paper about S–S coupling—including a discussion about **A**—which we submitted to *Angewandte Chemie* on November 18, 2007. Through a MO and Mulliken population analysis, we reassigned the bonding in the molecule, saying that it was best seen as possessing a $Cu^{II}_2Cu^I$ configuration of the metals, with a coupled S_2^{2-} central unit. Being aware that our viewpoint was opposite to that of Santiago, who envisaged discrete sulfido ligands and $Cu^{II}_2Cu^{III}$ oxidation states in **A**, we sent him the manuscript we submitted for publication, saying, "We would appreciate your comments, of course. But you may want to save them for the review!"

Roald, Carlo, and Santiago: Indeed, shortly after receiving Roald's E-mail, Santiago got the manuscript for review. And he decided not to review it, writing to Roald and Carlo: "I hope you understand that I might tell Peter Gölitz

that there is a conflict of interest because of your opposing view to our description of Bill Tolman's compound **A**".

Roald found this interesting: Santiago's decision here, he thought, was not necessarily one that everyone in the community would make when faced with a similar problem. So Roald asked Santiago why he took this action, and he also asked Carlo what he would have done in a similar situation. Their opinions, as well as Roald's, we think are of interest to the community. They provide a glimpse, a small one, of the decisions people make in the reviewing process, a human dimension of our microsociety that generally remains obscure both to outsiders and to our own students when they begin. We present the three opinions as Appendix A to this paper.[2]
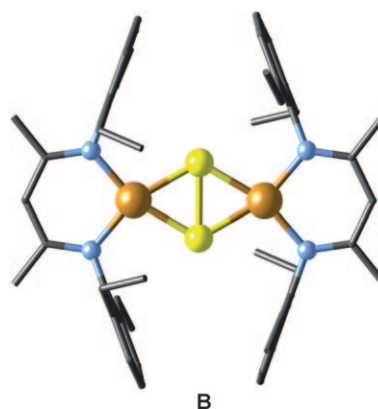
Our Differences, On the Record

That Santiago did not review our paper did not mean he agreed with it. Far from it. A spirited debate followed, both before the Mealli, Ienco, Poduska, and Hoffmann paper was published in early 2008 and after, up to the day this paper is written. To orient the reader, we begin by summarizing the different interpretations of the electronic structure of **A**. The viewpoint of Santiago, expressed in his original JACS paper,[2] is outlined first. Then, the related part of the manuscript produced by Roald, Carlo, and co-workers is faithfully reported as it eventually appeared in *Angewandte Chemie*.[5]

Santiago: The molecular ion **A** has interesting similarities with the Cu$_z$ catalytic site of nitrous oxide reductase, a tetracopper cluster with a tetrahedral μ_4-sulfido bridge.[6] The Cu$_3$S portion of Cu$_z$ resembles half of **A**, with almost identical Cu—S and Cu—N bond lengths. It is precisely what we perceived as two uncoupled sulfide ions that made Tolman propose it as a model for the Cu$_z$ site.

Another aspect that seemed to us consistent with the absence of an S—S bond in **A** and the resulting assignment of the Cu$^{II}_2$Cu^{III} oxidation states was the apparent "switching off" of S—S bonding on going from a related dinuclear Cu$_2$S$_2$ compound to the trinuclear **A**. When a parent mononuclear complex [L$_2$Cu(NCMe)] is allowed to react with sulfur, two different products are obtained, depending on the charge and steric bulk of L. With neutral and less bulky ligands, **A** is produced, having a long S—S distance of 2.70 Å. However, if an anionic and relatively sterically congested bidentate ligand is present, a dinuclear compound **B** forms by the same reaction, giving an S—S bond (1.97–2.30 Å). Thus, it seems that trimerization triggers an internal electron transfer to the S$_2^{2-}$ unit of the dimer **B** (which is assumed to form first), reducing it to two S^{2-} ions.

The {Cu$_3$S$_2$}$^{3+}$ group in **A** presents two unpaired electrons and is highly symmetric (D_{3h}), with the three copper atoms appearing as equivalent both in the crystal structure and

B

from the hyperfine coupling with the copper nuclear spin seen in the EPR spectrum. Consistently, our calculations showed the two unpaired electrons to occupy two degenerate molecular orbitals composed of the three x^2–y^2 type orbitals with admixture of the π^* orbitals of the S$_2$ unit delocalized over the three copper atoms (2e'' in Figure 1). A related {Cu$_3$O$_2$}$^{3+}$ core[7] shown in **C**,[3] also with a triplet ground state, is asymmetric with localized Cu^{II}Cu^{III} oxidation states. We could explain such a difference as due to a reversal of the 2e'' and 3a$_2$'' orbitals and the ensuing Jahn–Teller effect (Figure 1). Therefore, to us both **A** and **C**

A   C
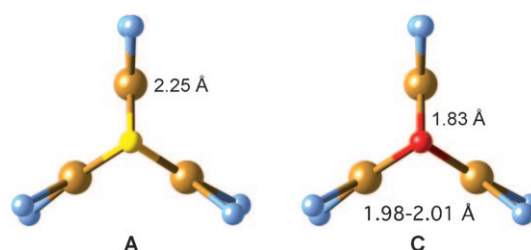
should be ascribed the formal oxidation state Cu$^{II}_2$Cu^{III}, and they differ in the localized or delocalized character of the mixed valence Cu$_3$ core, as well as in the presence or absence of a Jahn–Teller effect, both associated with the difference in electronic structures shown in Figure 1. It must be stressed that for the oxygen derivative **C**, with O—O at 2.36 Å, no one would claim a bond.

Carlo and Roald: We think there is S—S bonding in **A**. Here is the reasoning in our paper as published. Nothing is linear in the real world, and it must be admitted that the original version of the paper, sent to both the journal and Santiago, has been somewhat modified in this final product, following the intervening exchange of ideas that we had with Santiago:

*It has been proposed that the trigonal-bipyramidal Cu$_3$S$_2$ core of **A** contains uncoupled S^{2-} ions and consequently a Cu$^{II}_2$Cu^{III} configuration of the metals. Our previous consider-*

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[2] The reader less interested in chemistry than in struggles among chemists and ethical questions in the refereeing process might at this point just skip to the two Appendices of this paper.

[3] Interestingly, the deformation manifests itself in the Cu—O distances, given in **C**; this view emphasizes how similar the structures are otherwise.
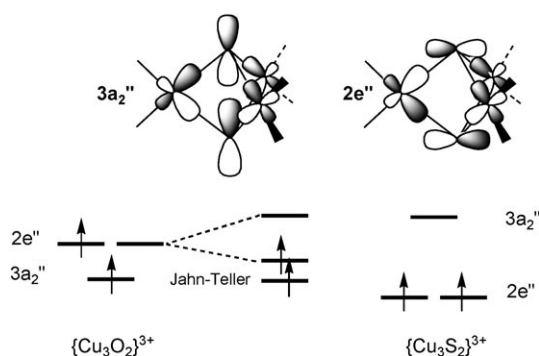
Figure 1. Comparison of the energy ordering and occupation of the molecular orbitals built up from x^2-y^2 copper atomic orbitals in the $\{Cu_3O_2\}^{3+}$ (**C**, left) and $\{Cu_3S_2\}^{3+}$ (**A**, right) clusters.

ations [earlier in this paper] on the $S_2^{2-}/2S^{2-}$ dichotomy lead us to reexamine this assignment, and suggest that, on balance, the sulfur atoms are coupled in **A**.

The diagram in Figure 2 shows that the levels $2a_2''$ (populated) and $3a_2''$ (empty) are the bonding and antibonding combinations between in-phase metal d_π orbitals and the S_2 σ^* level, respectively. The e'' set in-between with two unpaired electrons is Cu—S antibonding, as reflected by the weakened Cu—S bonds.
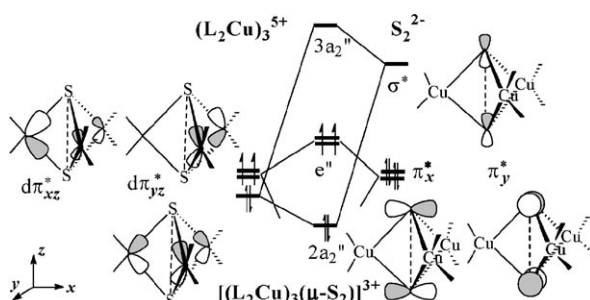

Figure 2. Frontier MOs in complex **A** with a D_{3h} Cu_3S_2 core.

We think there is S—S bonding in this molecule. To establish this point, we focus on the population of the σ^* FMO (fragment molecular orbital) of the diatomic fragment (see Figure 2). As a calibration, we looked at dimers of the type $[(PR_3)_2Pt(\mu\text{-}S)_2Pt(PR_3)_2]$, which unequivocally combine single sulfide bridges, not bonded to each other, and d^8 ions. In these compounds, the σ^* population is large (about 65 %) even when the S—S distance is fixed as short as 2.7 Å. Similar trends were found for selected trinuclear clusters such as $[\{(PR_3)_2Co\}_3(\mu_3\text{-}S)_2(\mu_2\text{-}SH)_2(\mu_2\text{-}PR_2)]^{2+}$ which clearly contains uncoupled sulfide-capping ligands.

In **A**, at the equilibrium S···S separation of 2.7 Å, the population of σ^* is 33 % and the value drops to < 10 % for S···S $\leq$ 2.3 Å. Only for S···S > 3.0 Å does the population of σ^* reach 60 %, a level at which reduction of S_2^{2-} to $2S^{2-}$ makes sense as an idealized interpretation. Further support for S_2 coupling comes from the computational result that for simpler ligands on each Cu center (two ammonia molecules), the S—S distance falls to 2.2 Å.[5]

Terms for Making It a Fair Fight

Roald, Santiago, Carlo: Dozens of e-mails wended their way between Firenze, Barcelona, Ithaca, and the many places the protagonists found themselves traveling to, both before and after the paper was published. We do not give the actual historical account of the debate, which was fraught, as any human action is, with many digressions. Instead we proceed as follows: we describe the essential points that we agree upon, and then argue out our disagreements (and oh, do they still remain!). And no, not immediately in the heat of the exchanges did we identify our common ground: this only occurred after much correspondence and also when we literally met on common ground in Barcelona.

Here are the things that we agree on: First, and most importantly, we concur that nobody can win this debate simply by performing the most powerful, state-of-the-art density functional theory (DFT) calculation possible for this specific system. Even as we do rely heavily on this useful quantum-mechanical computational method. We want more than numbers; we want understanding of chemically meaningful trends, which is essential for suggesting geometries and electronic states of as-yet-unmade molecules.

To get this qualitative understanding, we see the following factors as important in this Cu_3S_2 system (and for many organometallic molecules as well):

a) The nature of the metal M, the ligands L, and the capping atoms X.
b) The symmetry of the system (D_{3h} or distorted).
c) The geometries at L_2MX_2—locally "square planar" or "tetrahedral" are the possible extremes (implying torsion of the L_2M rotor with respect to MX_2). Also, the L-M-L angle turns out to be important.
d) The X···X and M—X separations. With only two geometrical parameters free in the trigonal-bipyramid geometry of the Cu_3S_2 core, there are implicit relationships between M—X, X···X or M···M separations and X-M-X or M-X-M angles.
e) The total charge on the system, or the electron count. An oxidation state or d-electron count assignment at each metal may follow, subject to assumptions on how ligand electrons are counted (a matter on which reasonable people differ).

We can also play with these factors computationally, testing the "limits" of the simplistic categories of bond/no-bond, as well as to propose new molecules that could further support or deny our hypotheses about the presence or absence of an S—S bond.

Out of the factors specified above, we agree that one is particularly important in our discussion: oxidation states. One group views the copper cluster **A** as having no bond between two formal S^{2-}, which indicates a $Cu^{II}_2Cu^{III}$ oxidation state of the metals. The other group views the very same molecule as having an S—S bond (i.e. $2S^{2-}$ have been

oxidized to S_2^{2-}) and having a $Cu^{II}_2Cu^{I}$ oxidation state of the metals.

Although we may disagree about the copper oxidation states, we do agree that oxidation states are a convenient way to keep track of electrons in a chemistry that is often tunable and tuned by redox processes. We concur that oxidation states certainly do not describe real charges on a metal/ion, however those "real" charges are measured or theoretically estimated.[8] Moreover, we also think that the oxidation state formalism is an extreme which could serve as a valence-bond starting point for a good calculation. So the best description of the ground state of **A** is no doubt a mixture of the two configurations cited. We are really arguing about which is the dominant configuration, realizing the truth will fall in-between.

Another point of agreement is about a general orbital diagram, given in Figure 3, which summarizes much information that we need for our discussion on $[(ML_2)_3(\mu\text{-}X)_2]$ mole-
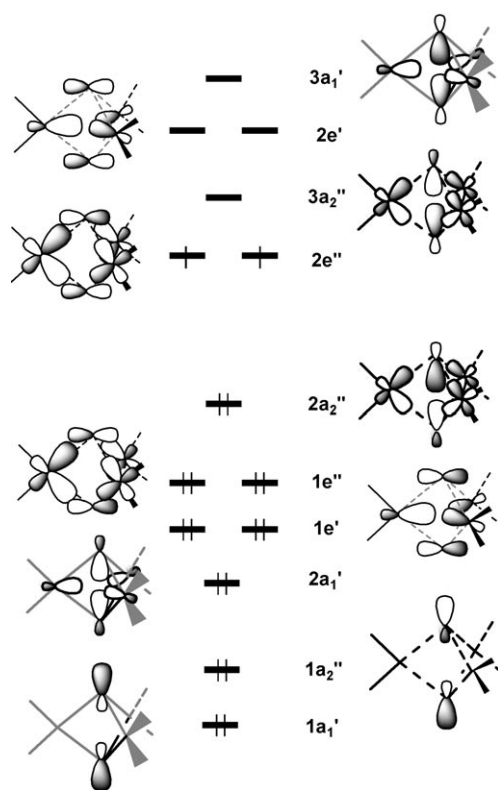

Figure 3. Qualitative diagram for the MOs in a M_3X_2 complex that enter the discussion. The occupation shown corresponds to compound **A**.

cules. It draws out schematically the six molecular orbitals that carry M—X bonding character, together with their antibonding counterparts, and the occupation shown corresponds to the case of the Tolman complex $[(CuL_2)_3(\mu\text{-}S)_2]^{3+}$. We show only one of the two e-type orbitals in the interest of conserving space: the combinations not shown involve the sulfur p orbitals perpendicular to the plane of the page.

The energies of these orbitals will vary with M and L in predictable ways; for instance the levels will be lower in energy for M=Cu than for M=Ni, two cases of interest to us, but also for a higher oxidation state of the same metal. The L-M-L angle and the X···X distance will affect especially the energy of the crucial a_2'' orbitals, as well as their composition. In particular, the relative weight of the metal d and bridging atom p_z orbitals in $2a_2''$ and $3a_2''$ varies in-between the two extremes shown in Figure 4, depending on the factors just commented on.
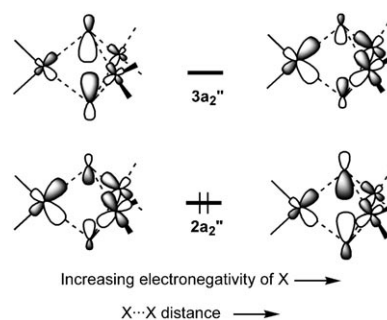

Figure 4. Factors that may favor localization or delocalization of the M_3X_2 MOs of a_2'' symmetry.

Let the Jousting Begin

In spite of the common ground that we eventually reached, there remain major conceptual differences among us. In this section, Santiago presents arguments in support of his case; a rebuttal from Carlo and Roald, speaking separately, ensues. There is always the question in any debate as to who gets the last word. But, since we're friends here, and Roald and Carlo are too verbose in stating their positions,[4] it seems fair to give Santiago the last (well, maybe) word.

Santiago: Here are the essential points of my disagreement with Roald and Carlo's conclusions.

During the discussion with Roald and Carlo on the submitted version of their paper, I admitted that the bonding in the Cu_3S_2 core is highly covalent and probably neither the $Cu^{II}_2Cu^{III}$ configuration proposed by us nor the $Cu^{II}_2Cu^{I}$ alternative is an accurate definition of its electronic structure. However, I pointed out two structural aspects that seemed to me inconsistent with their model with an S—S bond and the corresponding $Cu^{II}_2Cu^{I}$ formal oxidation states. I will number my points so as to make it easier for Carlo and Roald to respond:

[1] I did not think that the Cu^{I} formulation is in keeping with the square planar environment of the three copper atoms in Tolman's compound. We would expect a four-coordinate copper(I) atom to have a tetrahedral coordination sphere. My concern somehow permeated into the final version of their manuscript, reproduced as follows:

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[4] and Roald gets the last word too much anyway.

*As always, the metal oxidation state and configuration assignments are an idealization of the actual delocalized bonding situation. Our view, that the sulfurs in **A** are coupled and the Cu oxidation states are closer to $Cu^{II}_2Cu^I$ than to $Cu^{II}_2Cu^{III}$, does face an apparent problem—the square-planar coordination at the coppers is maintained, and that is certainly more typical of Cu^{III} than Cu^{II} or Cu^I. A suggestion of how this may be rationalized is given in the Supporting Information.*

*The real situation also may be less dichotomous. An extended Hückel Walsh diagram for **A** (see SI), constructed by varying the S···S separation from 2.2 to 3.1 Å, shows signs of an avoided crossing between the levels $3a_2''$ and $2a_2''$ at about 2.7–2.8 Å. The corresponding orbital mixing is likely the mechanism by which the electrons in $2a_2''$ are transferred from the metals to the sulfur atoms. That avoided crossing is also an indication that a multiconfigurational computation (which we have not yet attempted) might yield a description that melds both metal configurational assignments.*[5]

[2] The sulfur–sulfur distance was to me too long to be considered a bonding distance. I went to the Cambridge Structural Database (CSD)[9] for an overview and found that the distance between two sulfur atoms supported by two or three transition metals presented the bimodal distribution shown in Figure 5. To me, the experimental distribution of over one thousand sulfur–sulfur distances clearly distinguishes those compounds with S−S bond and distances shorter than 2.30 Å from those with non-bonded S···S distances larger than 2.58 Å. The distance in compound **A** (2.7 Å experimentally, 2.6 Å in our DFT calculations) clearly belongs to the second group. Such a bimodal distribution with a gap between the two maxima, I argued, is the signature of two distinct minima in the potential energy surface separated by an energy barrier, according to the *structural correlation principle* postulated by Dunitz and Bürgi.[10] A comparison of calculated potential energy surfaces and the stereochemistry of metal atoms in four-coordinate complexes recently carried out in our group[11] nicely shows the corre-

spondence between potential energy minima and structural distribution maxima.

At some point during our exchange of E-mails, my friends claimed that I was getting "into two positions which don't seem to be ultimately very *chemical*—one is not allowing the community partial bonding; the other is on focusing on bond lengths only". Their argument was that carbon–carbon bonds in π-bonded olefin complexes do present a wide variety of bond distances, even very long ones. Similarly, they said, the dihydrogen complexes show a continuous variation between bonds and non bonds. I provided them with more structural statistics, showing that in those two cases there is a single peak in the distribution of the distances (the histogram for dihydrido/dihydrogen complexes is shown in Figure 5), in contrast with the two distinct peaks found for sulfur–sulfur distances suported by metal atoms.

Besides the two points of disagreement associated with geometrical bonding parameters, I also had conceptual reasons for viewing their assignment of a formal sulfur–sulfur bond as objectionable.

[3] Considering the population of the σ* orbital of the S_2 fragment as a criterion for the existence or not of an X−X bond is a quantitative approach that establishes a sharp border between bond and non bond and will always be questionable: one can ask why a population of, say, 0.45 electrons means no bond and 0.35 means bond? Adopting such a criterion would leave us without arguments to predict beforehand the existence of a bond from qualitative criteria such as Lewis structures or electron counting. Moreover, what we admit as a criterion for the existence of a σ bond is the difference in population between the bonding and antibonding orbitals, not just the population of σ*.

[4] From my previous studies on the slightly simpler M_2X_2 cores I was convinced that for a particular M_3X_2 compound there are two neatly different geometries possible, one with a long and one with a short X···X distance, and that they can be switched by appropriate tuning of the electron count (i.e., by a redox reaction). To illustrate this concept, Rosa and Gabriel calculated two hypothetical nickel compounds analogous to the Tolman copper cluster, but with two and four less electrons, $[(L_2Ni)_3S_2]^{2+}$ and $[(L_2Ni)_3S_2]^{4+}$.[12]

According to our qualitative reasoning based on the orbital diagram of Figure 3, we predicted them to represent the long/short distance dichotomy, and calculations confirmed that the S_2 unit is stretched in the first case to 2.87 Å, but squeezed to a short 2.26 Å upon two-electron oxidation.

[5] The coordination geometry of the S atoms in **A** presents four bonds in the same
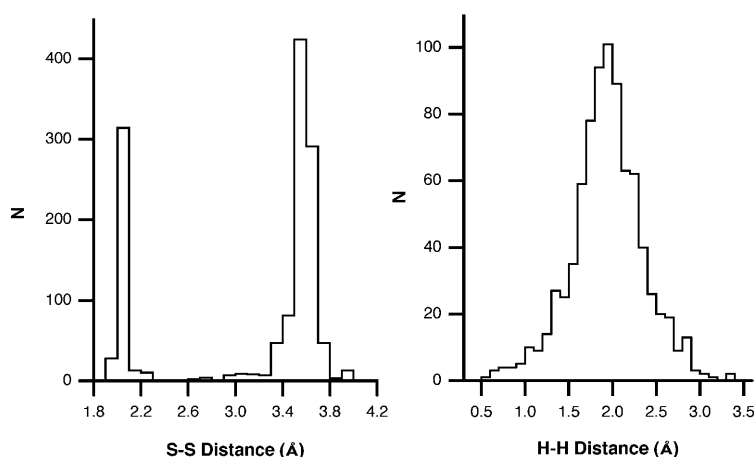

Figure 5. Distribution of the sulfur–sulfur distances in M_2S_2 and M_3S_2 cores (left) and of the hydrogen–hydrogen distances between two neighboring hydrogen atoms bonded to a transition metal (right), retrieved from the CSD

region of space and none in the opposite direction. I tend to think, maybe in a simple minded way, that sulfur makes use of sp³ hybrid orbitals for bonding and therefore there cannot be four two-electron bonds stemming from each S atom in **A**, but one should rather invoke delocalized bonding involving simultaneously the three metals *and* the opposing sulfur atom. During the discussion Roald pointed out that there is nothing wrong with having such a bonding pattern and referred to the topologically analogous [1.1.1]propellane, **D**.[13,14]

C-C = 1.55 - 1.60 Å

D
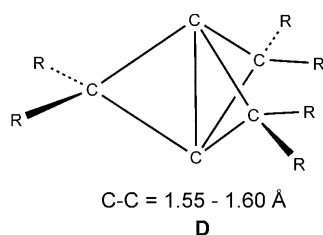
I argue that the four short carbon distances from an apical carbon are not two-electron bonds, but a delocalized description of the bonding in that molecule is required, that includes occupation of an outward-pointing lone pair at the apical atoms and only three sp³ hybrids of each bridgehead carbon atom can be used to form its four C−C "bonds". The presence of those lone pairs has been substantiated recently through an analysis of the electron localization function.[15]

Carlo: I respond here to points [1], [2], and [4] raised by Santiago and leave it to Roald to comment on the other objections.

[1] Your expectation of a tetrahedral geometry for a d^{10} ML_4 molecule makes sense in our usual way of thinking in inorganic chemistry. But there are situations (I believe the present $L_6Cu_3S_2^{3+}$ system is one such) where the metal–ligand bonding is different, allowing a square-planar, four-coordinate d^{10} complex.⁵ This situation occurs when the σ-donor function of a ligand lies much higher in energy than any d metal orbital. It then makes sense—in a bonding picture based on perturbation theory—to assign one bonding electron pair (a high-lying one, originally viewed as belonging to the ligand) to x^2-y^2. In this case, the ligand is such a strong base that it is better seen as an acid. The M→L donation does not change the coordination geometry, but the metal can be formulated as d^{10} rather than d^8.

This is an old question in organometallic chemistry—should one describe all ligands as Lewis bases, even if the obvious acidity of some ligand molecules such as BR_3 or

SnR_3 clearly disfavors the anionic formulation?[18] The relative energies and overlaps of the interacting M and L orbitals help to frame viewpoints bridging the "this ligand is a base" and "this ligand is an acid" dichotomy. This is what we attempted to do with the Tolman's compound **A**.

The proposal for such an "inverted" assignment of electrons is not novel, especially for copper. An admittedly controversial instance is Snyder's suggestion[19,20] that, in planar $[Cu(CF_3)_4]^-$, a Cu^I metal is bound to one CF_3^+ and three CF_3^- ions, in an averaged VB picture with four equivalent resonance structures. In MO terms (see **E**), in this molecule a ligand combination of four carbon σ hybrids (antibonding b_{1g}) lies about 35 kcal mol^{-1} higher than x^2-y^2 (in an extended Hückel (eH) calculation). Thus, the electron assignment depends both on the particular set of ligands and metal nature, copper being almost unique for combining low energy and highly contracted d orbitals.

E
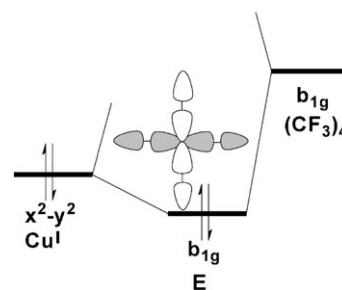
In contrast to Snyder's view, common chemical intuition favors Cu^{III} in square-planar $[Cu(CF_3)_4]^-$; in fact, the Cu^I proposal was fiercely criticized by Kaupp and von Schnering.[20] The direction of the Cu–C electron flow is to some degree a semantic problem, but to me a d^{10} (rather than d^8) metal seems reasonable as a starting point. Analogously, in compounds of type **A** there is a similar relationship between the a_2'' metal combination of the x^2-y^2-type orbitals and the S_2 σ* combination of the same symmetry (see Figure 4). Due to the diffuseness of the sulfur orbitals, σ* is very sensitive to the S−S distance and, for values of about 2.65–2.70 Å, it lies again (a coincidence) ca. 35 kcal mol^{-1} higher than the Cu orbital (eH). For this reason, the proposed assignment of the bonding electrons to copper has its own logic. Also, I saw an analogy with the M−η²H_2 interaction involving H_2 σ*; that in turn led to a disagreement between me and Roald (see Appendix B).

To help us understand the subtle role played by the a_2'' orbitals in **A** (see Figure 4), the eH Walsh diagram of Figure 6 shows the frontier orbital variations on elongating S−S, and suggests a mechanism for inner electron transfer. Irrespective of the intermediate energy of the singly populated e″ frontier orbitals (refer to Figure 2), there is evidence for an "avoided crossing" between the MOs $2a_2''$ and $3a_2''$, which both carry S−S antibonding but Cu−S bonding and antibonding characters, respectively. The bonding character is gradually switched between the two levels in question.

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⁵ There are some known examples of square-planar, 18-electron, d^{10}-metal complexes (e.g. the Ag^I complexes such as $[Ag(olefin)_4]^+$,[16] and the compounds referenced in a review.[17] In these the bonding and antibonding combinations of the metal x^2-y^2 and the b_{1g} ligand MO are likely to be both filled, a net repulsive interaction on top of three metal–ligand bonding ones. The metal p_z, an alternative place for the last electrons, is high in energy.
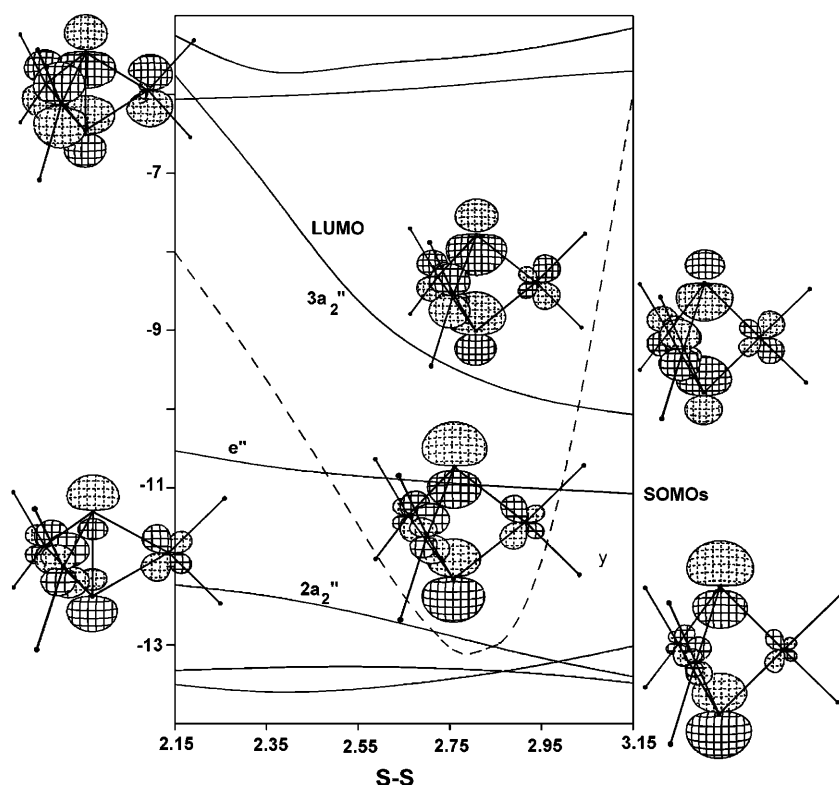
Figure 6. Walsh Diagram (constructed with the eH package Cacao[21]) for elongating the S−S distance while keeping fixed the Cu−S ones (2.23 Å). The eH total energy (dashed line) minimizes close to the experimental structure and its full scale range is 70 meV.

Around 2.7 Å, the metal and sulfur weights are similar, but over 3 Å the sulfide character prevails in $2a_2''$. At this point, the geometry is already far from any experimental and/or optimized one.

[2] Your CSD histogram of Figure 5 is illuminating, showing that no S−S bond of 2.30–2.58 Å has been experimentally found in the M_3X_2 and M_2X_2 families. I feel that the absence of such examples is not definitive proof of only two possibilities: S_2^{2-} or $2S^{2-}$. I would like to propose one way that this S−S distance gap could be closed: computationally, for now, and perhaps experimentally in the future. Andrea and I have noticed that differently tailored nitrogen ligands affect the opening of the N-M-N angles and in turn the S−S distance in $[L_6Cu_3S_2]^{3+}$ compounds. First, we carried out a series of full and partial DFT optimizations (all triplets) for the model compound $[(NH_3)_6Cu_3S_2]^{3+}$, with single amine donors. This fully optimized all ammonia model has a short S−S distance of 2.21 Å and larger N-Cu-N angles of 101°.

We had a hunch that the N-Cu-N angle might have a governing role in S−S coupling, so we systematically optimized the structures at different fixed N-Cu-N angles. The results are shown graphically in Figure 7. As the angle gradually changes, so does the S−S distance. Also, the PES is rather flat; the largest energy difference with respect to the fully optimized structure is at most 6.5 kcal mol^{-1} as the N-Cu-N angles vary between 85° and 110°. The corresponding σ* S$_2$

population ranges smoothly between 25% (at 85°) and 2% (at 110°).

We have actually designed other, more realistic chelates (the results to be fully reported elsewhere) that create, within the $[(L_2)_3Cu_3S_2]^{3+}$ system, compounds falling in both the shorter and larger S−S range but also in the "S−S empty zone" of the histogram in Figure 5. As an example, the structure of $[(NH=CH−CH_2−CH_2−CH=NH)_3Cu_3S_2]^{3+}$ (see Figure 8) optimizes as a minimum with the N-Cu-N angles of 97° and the "intermediate" S−S distance of 2.52 Å (σ* population = 19%).

If we believe the DFT calculations, the $2d^9d^{10}$ configuration and a disulfide ligand are appropriate for free ammonias (at large N-Cu-N angles), or other chelates allowing an even larger bite than that shown in Figure 8. Far from being tetrahedral, the reduced metal structure is most close to a trigonal planar one, as in d^{10} $[L_2M(\eta^2\text{-}H_2)]$ complexes. Also for this reason, I continue to imagine an S−S bond persisting up to distances around 2.7 Å as in **A**, while a major discontinuity would occur with an actual 2e$^-$ oxidation of the metals and the definite separation of the capping sulfide anions (this is never observed, either experimentally and/or computationally). Obviously, a planar d^{10} metal would be indefensible in presence of discrete sulfido capping ligands.

[4] I find thought-provoking your optimization of a stable $[L_6Ni_3(\mu\text{-}S_2)]^{4+}$ upon 2e$^-$ oxidation of its dicationic precur-
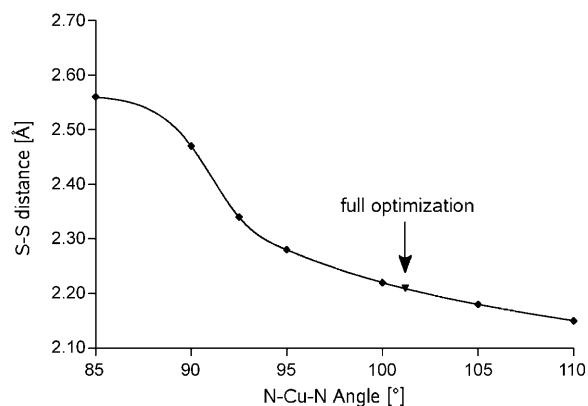

Figure 7. The S−S distance (optimized) as a function of N-Cu-N angle (fixed) in the model complex $[(NH_3)_6Cu_3S_2]^{3+}$.
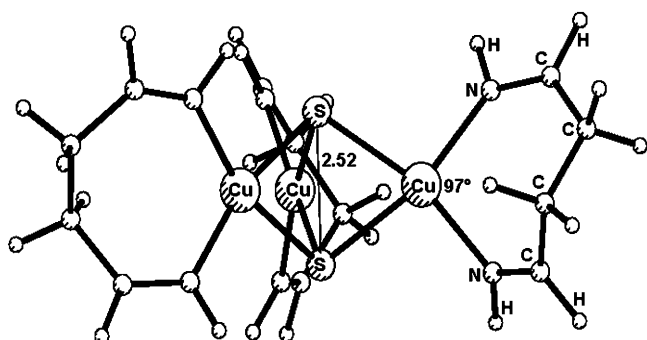
Figure 8. The optimized structure of the model trication [(NH=CH–CH₂–CH₂–CH=NH)₃Cu₃S₂]³⁺ with an S–S distance about 0.13–0.20 Å shorter than in the experimental analogues known to date.[2,3]

sor.[6] The dramatic shortening of the S-S distance to 2.26 Å confirms how prone these TBP frameworks are to various internal or external redox processes involving coupling (or decoupling) between all the vertices. We construct elsewhere a general relation between equatorial, apical and interaxial bonding in TBP compounds formed by main group elements alone, or containing three equatorial metals, over a wide range of skeletal electron counts.[22] Here, I only wish to remark how interaxial and skeletal bonding may correlate for a given electronic structure of the M₃X₂ skeleton. In the context of Figure 3 and 6, we see that in Ni₃S₂ compounds the 2e″ level is invariably depopulated. The S−S σ* 2a₂″ level is the HOMO of $[L_6Ni_3(\mu-S_2)]^{2+}$ but the LUMO of $[L_6Ni_3(\mu-S_2)]^{4+}$ (and there is a significantly large HOMO–LUMO gap also in this latter compound). The gap increases with the amount of S−S σ* character in 2a₂″ when S−S is shortened. At the same time, this 2a₂″ level is also M₃−S₂ bonding and its depopulation causes a generalized elongation of the Ni−S bonds.

An essential aspect of the Ni tetracation (highlighted by an eH FMO analysis) is that, after the two-electron oxidation, the Ni−S bonding which arises from a₂″ symmetry interactions is not totally cancelled. In fact, the low lying S₂ lone pair (1a₂″ MO in Figure 4) does not remain inert but donates to the metals. Therefore, the donor capabilities of S₂²⁻ are not limited to only four lone pairs, as it might be assumed in a first approximation. A similar feature is also found in the C₅H₆ propellane[13] (already mentioned by you, **D**) with one axial and six peripheral C−C bonds. Here again, a low-lying a₂″ level, externally hybridized with the carbon 2s orbitals, must contribute to the six peripheral C−C bonds.

An additional point: I wish to make a final comment on one of your initial statements, Santiago, in which you proposed

very similar electronic structures for the known Cu₃O₂[7] and Cu₃S₂ compounds and their equal Cu$^{II}_2$Cu^{III} configuration. In the Cu₃O₂ complex **C**, with no three-fold symmetry as a consequence of a Jahn–Teller distortion, one metal is more strongly bound to the two apical atoms (the corresponding Cu−O distances are about 0.2 Å shorter than the others). Moreover, the O⋯O separation is only 0.34 Å shorter than the sum of the dianionic oxo radii. In contrast, the corresponding difference in Cu₃S₂ is as large as 1 Å, and, as discussed, the relatively stronger S⋯S interaction has implications for potentially different oxidation states of the elements. Also significantly, the sulfur system does not show any pair of stronger M−X bonds at a single metal atom that would mark its d⁸ square-planar coordination. The M−X and X−X distance are mutually dependent, so I infer that the electronic structure of Cu₃S₂ is rather different from the generalized 2X₂²⁻ and Cu$^{II}_2$Cu^{III} formulation. This is instead the only possibility for Cu₃O₂.

Roald: [1]: I personally think Santiago has a point when one looks at the totality of transition-metal chemistry. Molecule **A** is a special, high-symmetry situation, and I could do some hand-waving around that, but in the end, the absence of tetrahedral distortion or twisting toward it troubles me. Not that there aren't a number of square-planar d¹⁰ complexes, for instance of Ag^I, which Carlo mentioned. I think it would be fun to design some ligands that sterically allow, or even favor, tetrahedral geometries at Cu.

[2] Santiago's CSD-based histogram is impressive. My outlook is based on a nose for the unusual (looking too much for perversion?): I think the distances that are in-between—neither a full bond, nor no bond—are the interesting ones. I also believe deeply in a continuity of chemistry—S−S bonding is there (or is not there, or is partially there) whether one is looking at organic, main-group inorganic, or transition-metal or solid-state chemistry. I also have to confess to an antipathy to either-or attitudes or dichotomizations.

Early on I encountered partial S−S bonding in thiothiophthenes (trithiapentalenes), understandable as electron-rich three-center bonding systems. Compound **F**[23] is a representative structure of this class, showing asymmetric S−S bond distances of 2.18 and 2.52 Å, which differ from the typical S−S distances in the symmetrical thiothiophthenes (2.31–2.36 Å). The whole range of Santiago's gap is covered by a goodly number of these compounds traversing a classical Bürgi–Dunitz hyperbola.
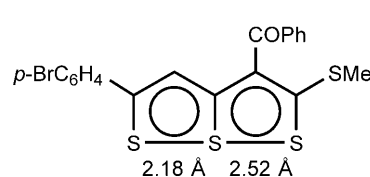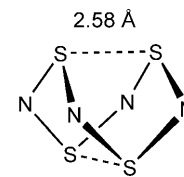
Another example of partial S−S bonding, falling on the border of that gap in Santiago's diagram, is found in S_4N_4 and related compounds, shown in **G**.[24]

Santiago looks at his histogram (Figure 5), sees a dearth of compounds with S···S contacts between 2.15 and 2.85 Å, and a real gap between 2.30 and 2.58 Å, a gap that he interprets as a region that separates bond from no-bond. I look at the overall picture and focus on the few structures in the 2.15–2.85 Å interval. I remember (vaguely at first, then led to the work by J. K. Bashkin) a discussion I had once with Ed Stiefel around two of these, 2.73–2.8 Å.[25] Stiefel noticed the anomalous distances, agonized over them, came to a conclusion of partial disulfide bond formation, I had and have no troubles conceiving of a partial S−S bond for two sulfurs separated by 2.6 Å.

Let me put it another way, as provocatively as I can. Had Santiago in hand that CSD histogram when he calculated the S···S separation in compound **A**, he might have sat up and said, "Hey, that's a very untypical S−S separation, right on the border of the gap in my histogram. Is the structure wrong? Can't the sulfurs get further apart, while remaining bonded to the coppers? Or, maybe, just maybe, the structure is giving us a big clue to something interesting going on?"

[3] I think to establish bonding between a pair of atoms one should look in principle at the population of all the orbitals of the underlying coordinated diatomic. This is because bonding can be weakened by depopulation of bonding orbitals or population of antibonding ones—and even the so-called lone pairs are weakly bonding or antibonding. But as we have learned for coordinated H_2 or C_2H_4 or CO, it appears that population of σ* (π* in the case of C_2H_4 and CO) does the most damage to bonding.

My experience, rooted in my respect for chemical tradition and the rudiments of political psychology (learned mainly by teaching introductory chemistry), is that if you propose something seemingly weird (an S_2 threading a Cu_3 ring?), tread gently. Try to validate your criterion (and so get people to accept it) by looking first at cases where there is general community agreement.

Here's something everyone will agree on: when two S^{2-} ions interact, there is no bond. When two neutral S atoms or two S^- ions interact, there will be a bond. That's for isolated atoms—when two S atoms/ions are incorporated into a molecule, the occupation numbers of σ and σ* FMOs will not be 2 or 0; there will be some donation out of σ and acceptance of electrons into σ*.

How much? Let's take a molecule where everyone agrees (because of the history of inorganic chemistry, and it's consistent with so much else) that there is *no* effective S···S bond. These would be the locally square-planar d^8–d^8 [L_2M-$(\mu_2$-S$)_2$ML$_2$] complexes. They are a major contributor to Santiago's CSD graph. Here's a typical one: [(PPh$_2$Pyr)$_2$Pt(μ-

S)]$_2$, with a S···S separation of 3.01 Å.[26] In an eH calculation with PH$_3$ ligands, σ* is populated at 75% (1.5 electrons).[7] We now have an operational definition of "large" population of σ* in a real molecule without an S−S bond.

Now let's take a simple amine (L=NH$_3$) model of compound **A**, whose DFT-optimized structure turns out to have S−S short, 2.21 Å. It's not (yet) a real molecule, but no one would question the S−S bond at that distance. Here σ* is only 7% occupied.

If we do a calculation on the Cu_3S_2 compound **A**, at its experimental distance of 2.72 Å, the S···S σ* occupation is 39%.[8] It's intermediate between 0 and 100%, but we think that this is closer to the bonded model cited above. The σ orbitals remain largely occupied.[9]

[5] Propellane is a strange molecule for sure—I continue to be amazed that it exists.

There are other examples of all four bonds to a main group element atom lying in one hemisphere: SF_4 is one, but it is hypervalent, and the deformation different from the one in **A**. There are square-pyramidal, four-coordinate bromide complexes, and pentagonal pyramidal iodides of Cu^I.[29] There is a horde of $CaAl_2Si_2$ structures[30] (**H**) these have Al$_2$Si$_2^{2-}$ two-dimensional layers, "electron-precise" in the sense of each atom in the layer having four electrons formally, and being four-coordinate. But one of the atoms is quasi-tetrahedral, while the other is umbrella-shaped.

H   I

Closer to **A** and {Ni$_3$S$_2$}$^{2+}$ compounds cited are the remarkable Huttner complexes, [E$_2${W(CO)$_5$}$_3$], E = As, Bi, Sb,[31] structure **I**. Each retains short multiple E−E bonds while having the E$_2$ dumbbell coordinated to three organometallic fragments.

Another point: Quantum theory of atoms in molecules (QTAIM) analyses of bonding are quite popular these days. Santiago carried out such an analysis on compound **A**, find-

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[7] In our published paper, reproduced above, we used a [(Ph$_3$P)$_4$Pt$_2$S$_2$] model,[27] and reported 65% for the σ* population. Subsequently, we realized that there are serious problems with the correctness of this reported structure[28] which is why we switched here to a different model.
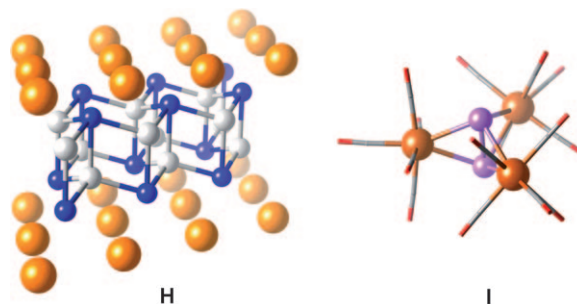
[8] In our published paper, we wrote 33%. This number came from an calculation on a [(NH$_3$)$_6$Cu$_3$S$_2$]$^{3+}$ model with an imposed S−S distance of 2.70 Å. A calculation on the **A** geometry as reported gives 39% occupation of σ*; a calculation on a theoretically optimized geometry (Cu−S and Cu−N both elongated about 4% relative to the crystal structure) gives 27% occupation of σ*.

[9] The "lone pairs" are not very well-developed at this separation—so the S−S σ bonding is distributed among 1σ$_g$, mainly S 3s, and 2σ$_g$, mainly S 3p. The population of 1σ$_g$ in **A** is 84%, of 2σ$_g$ 97%. The antibonding 1σ$_u$ combination is 94% occupied. These are all eH results.

ing a bond critical point between the sulfurs. It might seem that this would support Carlo's and my point of view, that there is an S−S bond. Carlo tries to believe it, but as far as I am concerned, "Thanks, but no, thanks." Bond critical points are a consequence of the topology of electron density—there is a bond critical point between two S atoms in S_2 for sure, but I bet there is also one between two S^{2-} ions approaching. There are 60 bond critical points[32] between He and the 60 carbons of $He@C_{60}$.[10] In my opinion, the existence of a bond critical point is not a criterion for bonding.

Santiago's Final Rebuttal: [1] Roald mentioned the possibility of designing ligands that would favor the tetrahedral geometries at Cu. Han et al.[34] had actually prepared one such compound with three tetrahedral copper(I) ions linked by peripheral bridging bis(diphenyl-phosphino)amine ligands with two triple bridging hydrosulfide ions at a very long S···S distance (3.48 Å). This compound, however, has four more valence electrons in the Cu_3S_2 skeleton than Tolman's complex **A**. But we have now two variables to play with, the electron count and the orientation of the ligands. I wouldn't be surprised if somebody comes up with a compound with tetrahedrally coordinated copper atoms and a short S-S distance. According to our framework electron counting rules[33] we would expect this to happen for a $Cu_3S_2^+$ core.

I don't think the $[Ag(olefin)_4]^+$ complex you mention[16] makes a good case for a d^{10} square planar stereochemistry in general, because there the four olefin groups are rigidly held in the same plane by four cyclohexyl bridges, making the tetrahedral geometry impossible.[11] If that constraint is removed, as in $[Ag(cod)_2]^+$, the coordination around the silver atom is tetrahedral.[35] But yes, one can find several square planar structures of Cu^I and Ag^I complexes in the Cambridge database. Many of those are special in several respects: some have tetradentate ligands with a planar topology, some others are in fact two coordinate with two donor atoms held at longer distances in multidentate ligands, while nearly half of them could be considered as six-coordinated because of the presence of short metal-counterion distances. Nevertheless, there are still some whose square-planar geometry is not easy to explain and may be worthy of a deeper theoretical study.

We have intensely debated in private conversations Snyder's proposal of a Cu^I oxidation state in $[Cu(CF_3)_4]^-$, but I will not reproduce my arguments here because it represents a different problem. In this mononuclear complex, what Snyder proposed and Carlo supports is that it should be formulated as composed of a Cu^I ion and a $\{(CF_3)_4\}^{2-}$ set of ligands, at difference with the "classical" formulation as Cu^{III} and $\{(CF_3)_4\}^{4-}$. But no matter how you look at it, the total number of valence electrons for the central ion is sixteen. What we generally predict is that a four-coordinate, sixteen-electron complex should be square planar, while an eighteen-electron one should be tetrahedral. As a sequel of this debate, we have considered $[Cu(CF_3)_4]^-$ in the wider context of families of complexes with different oxidation states and donor atoms of varying electronegativities, and published a more detailed discussion elsewhere.[36]

The case of **A** is quite different in two respects. First, we cannot apply electron counting rules to each individual copper atom because of the strong delocalization of the $x^2−y^2$ electrons (1e″ and $2a_2″$ MO's in Figure 3), except for the two extreme oxidation states, $Cu_3S_2^-$ with all Cu^I and two sulfido bridges (equivalent to Han's compound), and $Cu_3S_2^{7+}$ with all Cu^{III} and a disulfido bridge (isoelectronic with the $Ni_3S_2^{4+}$ complex calculated by us[33]). Between these two extremes, one can conceive eight one-electron oxidation steps, in most of which the formal occupation of the copper d orbitals would be fractional. What stereochemistry should we expect when the three copper atoms have an average electron configuration such as $d^{9.33}$ or $d^{8.66}$, as would correspond to your and my proposals for compound **A**? Honestly, I do not think we have a clear answer to this question. The second peculiarity of **A**, as compared with $[Cu(CF_3)_4]^-$, is that the S_2 group in the former acts as a non-innocent ligand, and therefore alternative assignments of oxidation states and consequent d^n configurations ensue, a problem that is at the basis of the present debate.

[2] The effect of external bond angles on the S···S distance found by Carlo does not surprise me, since we had previously done similar calculations for dinuclear M_2X_2 cores.[37] For those, we found a correlation between the peripheral L-M-L bond angle and the X−X distance: "other things being equal, a larger L-M-L bond angle should appear for the molecule with an X−X bond than for that with isolated S^{2-} ions".[38]

I agree that your Figure 7 shows a continuous variation in the S−S distance with the L-Cu-L angles. However, when I look at this plot, I see three regions with different slopes: two plateaus corresponding to long and short distances, respectively, separated by a transition zone in which the distance changes sharply with the bond angle. That graph has then two alternative interpretations, depending on what you focus on, continuity or dichotomy in S−S bonding. But you may agree that the N-Cu-N bond angles in **A**, mostly imposed by the chelating nature of the external ligands (88°, both experimentally and computationally), clearly correspond to the region of long distances in Figure 7.

[4] One of my research goals in the past years has been to provide a delocalized version of bonding in rhombic $[(ML_n)_2(XR_y)_2]$ systems, because in those systems the same orbitals of the ML_n and XR_y fragments ($n = 2–4$ and $y = 0–3$) participate simultaneously in M−X, M−M, and X−X bonding. It is therefore sensible to discuss the structural details of the M_2X_2 core as a whole, based on the occupation and

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[10] One can move beyond the existence or absence of a bond critical point. Santiago finds that the electron density at the S−S and M−S bond critical points changes with the number of electrons. To quote him:[33] "This, combined with the changes in the corresponding bond distance in $Cu_3S_2^{3+}$, $Ni_3S_2^{2+}$ and $Ni_3S_2^{4+}$, clearly shows that the S−S bond is weakest and M−S strongest for $Ni_3S_2^{2+}$, while S−S is strongest and M−S weakest for $Ni_3S_2^{4+}$, with the values for $Cu_3S_2^{3+}$ being intermediate."

[11] The atomic coordinates of that structure were not published.

bonding characteristics of its framework molecular orbitals. Taking into account their bonding characteristics with respect to those three types of interatomic interactions as well as their occupations, we came out with simple rules that allow us to predict the existence or not of short through-ring M−M or X−X interactions.[38]

In the process of writing a report of Rosa's results on **A**, the present debate prompted us to extend our framework electron counting scheme to the M_3X_2 cages.[33] Accepting, at least in part, your view point that there is some residual S−S bonding in **A**, I would stress that this is a quantitative issue, different from what occurs when one removes four electrons, as in the $\{Ni_3S_2\}^{4+}$ complex that we have calculated. In that case there is a qualitative change in the bonding situation that results in a really short S−S distance.

Some concluding thoughts: While Roald declares having an antipathy to either-or attitudes, I believe that there are times for dichotomy and times for continuity. I find interesting, for instance, that the negative charge at the S_2 group in mono-, di-, and trinuclear complexes shows a monotonous increase with the number of Cu−S bonds, whereas the S−S distance changes only—in an abrupt way—upon formation of the second and sixth Cu−S bonds.[33] I think also on spin crossover complexes. Sometimes they change their magnetic behavior and associated properties (such as color or metal–ligand bond lengths) gradually as the temperature is decreased, but some complexes undergo an abrupt change from high spin to low spin, within a temperature interval of only a few degrees.

Then, why have we taken so much pains to discuss whether there is or not a sulfur–sulfur bond, to use metal oxidation states that correspond to particular ways of localizing the electrons, or to debate on the population of S_2^{x-} units as if they were independent entities? I think this is the result of our psychological need for simple naming conventions to address complex realities, such as the bonding in the Cu_3X_2 molecule **A**. We distinguish night from day, even if there is no discontinuity in the intensity of the light that we receive from the sun. That does not prevent us from enjoying the beautiful atmosphere and nuances of dawn or dusk, no matter how hard it may be to tell day from night.

In the end, maybe this is what we are debating here. At the sunset of the sulfur–sulfur bonding, you are pointing to the sky, where we can still see the precise colors and shapes of the clouds on a dark blue background. On my side, I am looking at the valley and the western face of the mountains,[12] where only black silhouettes remind us of the trees and small towns in front of us. I hope that with this debate I made you look also at the shaded zones as much as I had to raise my eyes to the open sky. May we all enjoy the full palette of differently illuminated areas at twilight.

Carlo, Roald, Santiago: *Basta*! As the reader can see, this spirited debate is not over. OK, what have learned?

1. The obvious—that reasonable human beings, even people from "the same school" can differ on such a seemingly simple question as "Is there a bond between the two sulfurs in **A**?" Perhaps the lesson is not that people disagree (for it is in our nature to do so, and that is how science progresses) but that the concept of the chemical bond is not simple. This would have been nothing new to Robert Mulliken, who has a well-known quote to that effect.[13] As we said at the outset, the presence or absence of a bond may be judged by several experimental and theoretical criteria. What was interesting in our discussion is how we moved from simple distance criteria to other gauges of bonding.

2. As inorganic chemists (OK, theoreticians, we're smiling) we always knew that oxidation states and d-electron configurations were a convenient fiction, even as they are of tremendous utility in chemistry. Our initial stances in this debate made us (all) somehow stiffen, pushing us to the categorical "It's $Cu^{III}(Cu^{II})_2$"; or "No, it's $Cu^{I}(Cu^{II})_2$." That's not where we would normally like to be, so to speak. With time, we relaxed and saw these were extremes—and still remained insistent that the situation was closer to one or the other!

3. The special strength of molecular orbital thinking—composed in our day in doses of reliable DFT and correlated Hartree–Fock computations, in part of qualitative orbital pictures and arguments vouched in the friendly language of perturbation theory—is that it can bridge extremes and allow people to talk to each other.[14] This is why the Walsh diagram of Figure 6 is important: it allows one to see in a single graphic a continuous transition between having almost no S−S bonding and having much of it. The challenge to today's DFT-inclined quantum chemistry community is to devise a language of Walsh and interaction diagrams that is as easy and as chemical as the eH FMO way of thinking, but still retains the reliable aspects of DFT.

4. The debate was *productive* in many ways. It made us think through and rethink the distance criterion for bonding. It brought together organic and inorganic chemistry. It made us comb the literature for examples in support of our views. It made us think about the tetrahedral–square-planar distinction for d^{10} complexes in more detail than any of us had ever done before. We thought, we *learned*.

Most productive are the real, tangible, chemical suggestions arising from this work. Some are conceptual advan-

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[13] "I believe the chemical bond is not so simple as some people seem to think."

[14] A reviewer remarked "I could not avoid feeling that the question could have been resolved nicely by valence bond theory." We're not sure about "resolved," but certainly VB theory can also provide the bridging function between two extreme descriptions.

[12] I wrote this paragraph in Prullans, on June 7, 2008, facing the valley of La Cerdanya and the impressive walls of the Cadí mountains, after a three-day meeting on "Not Strictly Inorganic Chemistry".

ces—we think we understand much better now the factors that influence internal oxidative and reductive processes, such as what one needs in ligands, metals, and geometries to effect oxidative coupling. The work was productive in suggesting molecules that illustrate the bonding considerations, from $[(L_2Ni)_3S_2]^{4+}$ to the ligands designed by Carlo and Andrea to hold a certain L-Cu-L angle. Still other experiments that come to mind are of probing the metal oxidation state in **A** by comparing its X-ray absorption spectra with those of the non-controversial mono- and dinuclear complexes having copper in +1 and +2 oxidation states. And it would be interesting to test the endurance of the M_3X_2 skeleton to the attack of the sulfur lone pairs by a Lewis acid.

Fundamental disagreements are frustrating. But in the end, even as each of us seemed occasionally bereft of logic to the other(s) (in all permutations!), the underlying feeling was that it was important to keep arguing, because at stake was nothing less than our understanding. That the discussion, frustrating as it sometimes was, would teach us something about chemical bonding (and collectively we have been at it for decades!): this kept us writing.

We think there is something in this story for you too. And don't miss the Appendices; you will be amused.

Appendix A: On Reviewing or Not Reviewing Papers Where You Have a Vital Interest

As we mentioned, when Carlo and Roald's work essentially reassigning the formal oxidation states in the paper of Santiago and Bill Tolman was submitted for publication, it was quite naturally (from the editor's perspective) sent to Santiago for review. He recused him, to use a legal term. But not everyone would have done that. Thinking that the reasons for reviewing or not reviewing a paper might be of interest, Roald wrote the following to both:

"Santiago, there is something interesting here, and it may be a question that some people, young and old, would ask: "Why not review the paper, and criticize it as strongly as you can?" If there is a strong difference of opinion, some would fight to prevent it being published. Others (few, I think) would do what you did. Did you do it because it is a general conviction of yours in such cases? Or because of some perceived respect and an accompanying desire to avoid conflict with me? Or something else?

What would you have done in a similar situation, Carlo?"

Here are the responses:

Santiago: *Why did I have doubts about making a negative report?*

One reason is that I try to avoid being dogmatic (probably because I have a natural tendency to dogmatize) and admit that another colleague may have an opposing view that is just as respectable as mine.

Second, given the special relationship I have with Roald and the friendship with Carlo, I found it more appropriate to give my point of view in a friendly way and leave it up to them to decide whether to take it into account or not.

Third, it seemed to me that the discussion on the Cu_3S_2 system was lateral to the main topic of your paper, which dealt with Isobe's compounds. Therefore, I felt that making a negative report would in part have been unfair, because the Isobe story was elegantly explained.

Fourth, I felt really uncomfortable in the double role of holding a friendly, yet uncompromising, discussion with both Roald and Carlo and trying to make an objective report.

Finally, from my readings on the history of science, I have come to the conclusion that important issues are sooner or later dealt with by other researchers, and debates, such as the one we were having, are rarely settled once and forever. So, why should I prevent someone from publishing a view that differs from mine, when we are dealing more with concepts than with facts (the facts supporting my ideas were structural data, those supporting your opposing view were some computational results)?

Is it a general conviction of mine in such cases?

It is hard to tell, this was a very special case. Trying not to be too indulgent with myself, maybe the best thing to do is to recall the closest case in which I was involved. It was also an interesting story. We (Gabriel and myself) had been studying a complex—a polynuclear palladium molecule reported by Chen, Shimada and Tanaka—which they proposed as showcasing the unusual Pd^{VI} oxidation state,[39] because several aspects of its molecular structure and physical properties seemed to us inconsistent with that oxidation state. We had concluded that the authors had overlooked the presence of Si−Si σ-bonded ligands, which would take the formal oxidation state to Pd^{II}.

We were at the stage of starting to write an article with our results when I received from Peter Gölitz a paper on the same compound by Chris Cramer and co-workers in Minnesota,[15] so I explained the situation to Gölitz, telling him that there was a potential conflict of interest and that I better refuse to make a report on Cramer's paper. But he replied asking me to submit my paper to *Angewandte Chemie* and still make the report; in correspondence, our paper would go to Minnesota for review. Although I knew Chris (he had been on sabbatical in Barcelona), I did not have a close relationship with him, and I did not feel like I could not make a negative report if I felt it appropriate.

The story ended with both papers being accepted, with positive reports from each other and from additional referees, and they were published side by side.[40] In those papers, we disproved the existence of a Pd^{VI} oxidation state, but demonstrated that the Japanese group had discovered instead the first example of a Si_2 group σ-bonded to a transition metal!

Was there some perceived respect and an accompanying desire to avoid conflict with Roald?

Certainly, there is respect for someone who has been so influential in my scientific and intellectual endeavors. But there is also a long-standing friendship and the perception

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[15] Notice the coincidences with the present case: Gabriel, Peter Gölitz, a Japanese compound, a colleague from Minnesota.

that I could argue with Roald without eroding our relationship. How could I forget the topic Roald chose for his honorary degree at our University, "The Disputation at Barcelona"? I was sure that Roald would not feel angry if I tried to refute some of his assertions.[41]

Carlo: I think that I would have behaved very similarly to Santiago.

It is true that by accepting a paper to referee one should behave as a priest in the confessional and keep the secret. This is professional deontology and one is left alone with his own responsibilities. But we are all humans and cannot ignore the identity of the person(s) we are supposed to judge. In this case, Roald must be for Santiago as he is for me: namely the one who has greatly influenced my way of thinking and my scientific career. Why confront the person who is most respectful in my eyes, especially if there is an unexpected disagreement? Maybe I am the one who is wrong.

At that time, I felt a little unhappy with Santiago because he seemed to reject our viewpoint. Also, I realized how unhappy he might have been. Nobody likes contradiction of an analysis already considered as properly done. I imagine that these were Santiago's feelings and for this, I found Santiago's behavior even more worthy of appreciation. While he could feel safe as a secret referee, he proposed giving up any judgment and let other people do it.

Another point to consider is that, in this case, the decision to be made by Santiago was not directly harmful to a third party. The matter is more serious in a committee that decides on who is hired or promoted. Or in the allocation of research funds. The judgment at hand only concerned the quality of science to be published. The more discussed, the better it is. Usually, when I referee papers I am critical. I write down my viewpoint but also I explicitly leave to the authors the option of taking my perspective into account in their revision or not. Obviously, this applies only if something appears controversial but not definitely wrong.

In conclusion, it has been good that eventually we have had the possibility of publishing the ideas which later have stimulated the present debate. After all, I am convinced that our viewpoints are not so much divergent. There is a great range in-between bond formation and bond breaking (especially for a soft element as sulfur) and this is the message that we have all learned and want to transmit.

Roald: As my initial question revealed, I was aware of the special factor that might affect a decision on reviewing or recusal in this case—the relationship that emerged from working with both Santiago and Carlo, of initial mentorship that grew into friendship with the years. In that situation, to deal with scientific disagreements is difficult. To have the human bond and my teaching reaffirmed by you in the way you did is…deeply touching.

I am torn in responding to my own question. Both Santiago and Carlo have brought up the important issue of letting into the literature contrary views. I very much agree. Parenthetically, for this reason I never question the decision of an editor to publish a paper for which I have given a negative review. I may mumble (in Russian, so few understand) "*idioty*", that's about it. The world will sort things out. This is also why sometimes I wonder about refereeing in general, all that effort by the community to keep out indifferent work (not a little of that) and crank papers (a smattering), when we are teaching our students anyway to distinguish junk from routine from good science.

To get back to the "review or not review" quandary, one could argue that no one can make a stronger argument against a paper than the person whose work is in some way being questioned in that paper. The reviewer's critical intelligence is at its sharpest then. There may also be factors in the original thinking that were omitted or not verbalized—here is a chance for them to surface. Having the original author's admittedly partisan argument is good for science. And an editor needs all the help he or she can get to form an informed judgment.

A counterargument is that in a balance of judgments, when some reports on a paper are likely to be critical anyway, a fault-finding review may easily tip the balance against acceptance. Especially if the editor is not expert in the field. Responding to that in turn is Carlo's good point that a negative publication review is hardly as critical as one on funding or promotion—the work will get published somewhere.

The refereeing process often raises significant questions, not on facts (mute as they are) but on interpretations. Conceptual issues bother the community, but are rarely the subject of public discussion. Sometimes I wish reviews were published. Not all, but some. Or be accessible on-line to all. The ideal editor, a perceptive and reflective person, might keep a list of the conceptual issues that arise in the course of spirited yet reasoned (rather than merely vituperative) reviews. I bet certain questions have a way of rearing their head again and again. Our ideal editor (I know one) might collect such issues, cull the list from time to time, maybe proactively solicit an essay, or organize a conference on the ideas that bother the community.

Let me not evade answering my own question. Agonizing about voicing a disagreement with a respected mentor, I would have reviewed the paper. In a note to the editor I would have said, "You should know that I have a special interest here, my work is being questioned. I will tell you what I think, but I'm prejudiced; you might get a balanced opinion from x, y, or z." I would have written a review and identified myself as a reviewer.

There are no easy choices here, for human and scientific considerations cannot be separated. And not only in this refereeing process.

Appendix B: A Christmas Exchange

The reader should not get the idea that it just came naturally for Roald and Carlo to sing a duetto in unison. To give a flavor of their interaction, some exchanges in the period around Christmas 2007 are shown here:

Carlo: Christmas was approaching, I was about to go on a long-awaited vacation (in Spain!) with my wife and friends. But the revision had to be done. I spent many hours working with Andrea Ienco on further calculations and on drawings, in support of ideas I had had around the special bonding situation of the S_2^{2-} unit.

I saw a relationship between the present bonding situation and the d^{10} L_2M (μ^2-H_2) complexes (or olefin analogues). In all of these systems, the oxidative addition of the metal seems to adapt to a continuum of situations, subtly governed by the nature of the metals and the coligands.[42] Also, in the Cu_3S_2 case, metal-backdonation controls the extent of S−S coupling. I wrote to Roald:

"I hope that my arguments are convincing enough and close the debate over the $Cu_2^{II}Cu^I$ or $Cu^{II}_2Cu^{III}$ configuration problem…It is Christmas Eve, I have worked too much and Elisabetta is getting nervous."

Roald: I answered:

"This doesn't make sense, Carlo. It's time to stop deluding yourself that S_2^{2-} is like H_2 or ethylene."

I also said to myself, sotto voce,

"Maybe those guys are thinking—this Jewish slavedriver in Ithaca has no respect for Christmas. Nor the great Italian and Catalan traditions of taking off for the holidays. And he doesn't have a life (like a wife…), he just works all the time."

But I didn't think too hard. They were friends, and they were just as addicted to the science as I was.

Carlo: I didn't give up. I sent some further cogent arguments on Christmas day, ending:

Again, I wish to make my point clear. The idea was not to compare d^{10} $[L_2M(\eta^2$-$H_2)]$ or $[L_2M(\eta^2$-$C_2H_4)]$ complexes with mononuclear d^{10} $[L_2M(\eta^2$-$S_2)]$ compounds (if any) in general. The relation that I propose is limited to the key a_2'' interaction in the D_{3h} symmetry. The two electrons involved (those which make the difference between $Cu_2^{II}Cu^I$ and $Cu_2^{II}Cu^{III}$ configurations) are delocalized over three d_π metal orbitals. Together the latter have cylindrical symmetry and act as a single metal d_π orbital does in $[L_2M(\eta^2$-$H_2)]$ species.

To be more convincing, I drew for Roald Scheme **J**, adding:

M-d_π + σ* **M$_3$-d_π + σ***

J
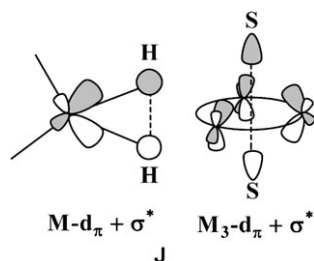
The interaction M_3–d_π + σ* is analogous to the M–d_π + σ* one in the classic dihapto coordination and its associated dichotomy (i.e., hydrogen vs. dihydride or olefin addition vs.

metallocyclopropane). As far as the M_3–S_2 interaction of a_2'' type remains a back-donation, I don't see anything wrong with the local planar geometry of the metals and an indicative $2d^9d^{10}$ configuration for them.

Probably you are realizing now how stubborn I am.

Roald: How could I disagree?

After reading Carlo's "reasonable" response, I found myself flushed, pulse racing, measured my blood pressure, and found it over 200. Answering Carlo, with clearly superior arguments, brought it down.

Now I had two stubborn guys on my hands.

Carlo: As the messages flew back and forth on Christmas, we thought to assign a comparable solemnity to our responses in the following days by writing in the e-mail subject line the corresponding Saint's Name. So Roald's letter to me of December 26th had as its subject line "St. Stephan". On December 27, I headed my message, "Saints Roald and Carlo, Martyres."

Roald: On December 28, I tried to get us out of the combat zone:

"I feel good that we can talk and argue, but also for the things behind it, that these questions of understanding still matter to both of us. And, facing realities of aging, especially that I retain the desire to learn what and why those little molecules are up to."

Acknowledgement

[1] K. Isobe, Y. Ozawa, A. Vázquez de Miguel, T. W. Zhu, K. M. Zhao, T. Nishioka, T. Ogura, T. Kitagawa, *Angew. Chem.* **1994**, *106*, 1934; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1882; T. Nishioka, H. Kitayama, B. K. Breedlove, K. Shiomi, I. Kinoshita, K. Isobe, *Inorg. Chem.* **2004**, *43*, 5688.

[2] E. C. Brown, T. J. York, W. E. Antholine, E. Ruiz, S. Alvarez, W. B. Tolman, *J. Am. Chem. Soc.* **2005**, *127*, 13752.

[3] J. T. York, I. Bar-Nahum, W. B. Tolman, *Inorg. Chem.* **2007**, *46*, 8105.

[4] C. Mealli, S. Midollini, *Inorg. Chem.* **1983**, *22*, 2785; C. Mealli, A. Orlandini in *Metal Clusters in Chemistry, Vol. 1* (Eds.: P. Braunstein, L. A. Oro, P. Raithby), Wiley-VCH, Weinheim, **1999**.

[5] C. Mealli, A. Ienco, A. Poduska, R. Hoffmann, *Angew. Chem.* **2008**, *120*, 2906; *Angew. Chem. Int. Ed.* **2008**, *47*, 2864; see some extensions of this work in: A. Poduska, R. Hoffmann, A. Ienco, C. Mealli, *Chem. Asian J.* **2009**, *4*, 302; C. Mealli, A. Ienco, A. Messaoudi, A. Poduska, R. Hoffmann, *Inorg. Chim. Acta* **2008**, *361*, 3631.

[6] K. Brown, K. Dijnovic-Carugo, T. Haltia, I. Cabrito, M. Saraste, J. J. G. Moura, I. Moura, M. Tegoni, C. Cambillau, *J. Biol. Chem.* **2000**, *275*, 41133.

[7] A. D. Cole, D. E. Root, P. Mukherjee, E. I. Solomon, T. D. P. Stack, *Science* **1996**, *273*, 1848.

[8] R. Hoffmann, *Am. Sci.* **2001**, *89*, 311. See also M. Jansen, U. Wedig, *Angew. Chem.* **2008**, *120*, 10176; *Angew. Chem. Int. Ed.* **2008**, *47*, 10 026 ; H. Raebiger, S. Lany, A. Zunger, *Nature* **2008**, *453*, 763; S. Riedel, M. Kaupp, *Coord. Chem. Rev.* **2009**, *253*, 606.

[9] F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380.

[10] H.-B. Bürgi, in *Perspectives in Coordination Chemistry* (Eds.: A. F. Williams, C. Floriani, A. E. Meerbach), Helvetica Chimica Acta, Basel, **1992**; H.-B. Bürgi, *Acta Crystallogr. Sect. A* **1998**, *54*, 873; H.-B. Bürgi, J. D. Dunitz, *Structure Correlations*, VCH, Weinheim, **1994**; P. Murray-Rust, H.-B. Bürgi, J. D. Dunitz, *J. Am. Chem. Soc.* **1975**, *97*, 921.

[11] J. Cirera, E. Ruiz, S. Alvarez, *Inorg. Chem.* **2008**, *47*, 2871.

[12] The tetracation is not known, but there are a number of dicationic examples of this molecular type, with S−S = 2.67–2.95 Å: F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, *Z. Naturforsch. B* **1991**, *46*, 1161; F. Cecconi, C. A. Ghilardi, S. Midollini, A. Orlandini, A. Vacca, J. A. Ramírez, *J. Chem. Soc. Dalton Trans.* **1990**, 773; D. Fenske, H. Fleischer, H. Krautscheid, *Z. Naturforsch. B* **1990**, *45*, 127; C. A. Ghilardi, S. Midollini, A. Orlandini, G. Scapacci, *J. Chem. Soc. Dalton Trans.* **1992**, 2909; I. Haiduc, R. F. Semeniuc, M. Campian, V. C. Kravtsov, Y. A. Simonov, *Polyhedron* **2003**, *22*, 2895; K. Matsumoto, N. Saiga, S. Tanaka, S. Ooi, *J. Chem. Soc. Dalton Trans.* **1991**, 1265; D. A. Vicic, W. D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 7606.

[13] K. B. Wiberg, F. H. Walker, *J. Am. Chem. Soc.* **1982**, *104*, 5239.

[14] A recent paper, W. Wu, J. Gu, J. Song, S. Shaik, P. C. Hiberty, *Angew. Chem.* **2009**, *121*, 1435; *Angew. Chem. Int. Ed.* **2009**, *48*, 1407, carries references to the extensive theoretical literature on propellane, and characterizes the bonding within as of the charge-shift type.

[15] V. Polo, J. Andrés, B. Silvi, *J. Comput. Chem.* **2007**, *28*, 857.

[16] J. E. McMurry, G. J. Haley, J. R. Matz, J. C. Clardy, J. Mitchell, *J. Am. Chem. Soc.* **1986**, *108*, 515.

[17] A. G. Young, L. R. Hanton, *Coord. Chem. Rev.* **2008**, *252*, 1346.

[18] G. Parkin, *Organometallics* **2006**, *25*, 4744.

[19] J. P. Snyder, *Angew. Chem.* **1995**, *107*, 112; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 80; J. P. Snyder, *Angew. Chem.* **1995**, *107*, 1076; *Angew. Chem. Int. Ed.* **1995**, *34*, 986.

[20] M. Kaupp, H. G. v. Schnering, *Angew. Chem.* **1995**, *107*, 1076; *Angew. Chem. Int. Ed.* **1995**, *34*, 986.

[21] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399; C. Mealli, A. Ienco, D. M. Proserpio in *Book of Abstracts of the XXXIII ICCC*, ICCC, Florence, **1998**, p. 510.

[22] C. Mealli, A. Messaoudi, A. Ienco, *Theor. Chem. Acc.* **2009**, *123*, 365.

[23] T. Blorholm, J. P. Jacobsen, C. T. Pedersen, *J. Mol. Struct.* **1981**, *70*, 444; R. Gleiter, R. Gygax, *Top. Curr. Chem.* **1976**, *63*, 49; L. K. Hansen, A. Hordvik, *Acta Chem. Scand.* **1973**, *27*, 411; N. Lozac′h, *Adv. Heterocycl. Chem.* **1971**, *13*, 161.

[24] R. Gleiter, *Angew. Chem.* **1981**, *93*, 442; *Angew. Chem. Int. Ed.* **1981**, *20*, 444; H. W. Roesky, *Adv. Inorg. Chem. Radiochem.* **1979**, *21*, 239, and references therein.

[25] J. M. Berg, D. J. Spira, K. O. Hodgson, A. E. Bruce, K. F. Miller, J. L. Corbin, E. I. Stiefel, *Inorg. Chem.* **1984**, *23*, 3412.

[26] V. W.-W. Yam, P. K.-Y. Yeung, K.-K. Cheung, *Chem. Commun.* **1995**, 267.

[27] H. Li, G. B. Carpenter, D. A. Sweigart, *Organometallics* **2000**, *19*, 1823.

[28] A. Ienco, M. Caporali, F. Zanobini, C. Mealli, *Inorg. Chem.* **2009**, *48*, 3840.

[29] The relevant experimental papers of the Jagner and Hartl groups are cited in our theoretical analysis of these compounds: L. Subramanian, R. Hoffmann, *Inorg. Chem.* **1992**, *31*, 1021.

[30] C. Zheng, R. Hoffmann, *J. Solid State Chem.* **1988**, *72*, 58; C. Zheng, R. Hoffmann, R. Nesper, H. G. v. Schnering, *J. Am. Chem. Soc.* **1986**, *108*, 1876, and references therein.

[31] G. Huttner, U. Weber, L. Zsolnai, *Z. Naturforsch.* **1982**, *37*, 707; K. Plößl, G. Huttner, L. Zsolnai, *Angew. Chem.* **1989**, *101*, 482; *Angew. Chem. Int. Ed.* **1989**, *28*, 446; B. Sigwarth, L. Zsolnai, H. Berke, G. Huttner, *J. Organomet. Chem.* **1982**, *226*, C5.

[32] E. Cerpa, A. Krapp, A. Vela, G. Merino, *Chem. Eur. J.* **2008**, *14*, 10232.

[33] R. Carrasco, G. Aullón, S. Alvarez, *Chem. Eur. J.* **2009**, *15*, 536.

[34] L. Han, L.-X. Shi, L.-Y. Zhang, Z.-N. Chen, M.-C. Hong, *Chem. Commun.* **2003**, 281.

[35] A. Albinati, S. V. Meille, G. Carturan, *J. Organomet. Chem.* **1979**, *182*, 269.

[36] G. Aullón, S. Alvarez, *Theor. Chem. Acc.* **2009**, *123*, 67.

[37] G. Aullón, M. Hamidi, A. Lledós, S. Alvarez, *Inorg. Chem.* **2004**, *43*, 3702.

[38] S. Alvarez, A. A. Palacios, G. Aullón, *Coord. Chem. Rev.* **1999**, *185/186*, 431.

[39] W. Chen, S. Shimada, M. Tanaka, *Science* **2002**, *295*, 308.

[40] G. Aullón, A. Lledós, S. Alvarez, *Angew. Chem.* **2002**, *114*, 2036; *Angew. Chem. Int. Ed.* **2002**, *41*, 1956; E. C. Sherer, C. R. Kinsinger, B. L. Kormos, J. D. Thompson, C. J. Cramer, *Angew. Chem.* **2002**, *114*, 2033; *Angew. Chem. Int. Ed.* **2002**, *41*, 1953.

[41] R. Hoffmann, *Chemistry, Democracy and the Disputation at Barcelona*, Universitat de Barcelona, Barcelona, **1992**; R. Hoffmann, *Butll. Soc. Catalana Cienc. Fis. Quim. Mat.* **1993**, *14*, 13.

[42] G. J. Kubas, *Chem. Rev.* **2007**, *107*, 4152.