Electronic Structure

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S_4^{2-} Rings, Disulfides, and Sulfides in Transition-Metal Complexes: The Subtle Interplay of Oxidation and Structure**

Carlo Mealli, Andrea Ienco, Anne Poduska, and Roald Hoffmann**

A sulfur atom, with its six valence electrons, may reach an octet by association into S_n rings. Two-electron reduction of the rings usually leads to polysulfide chains S_n^{2-}. Small, neutral S_n rings are rare; witness S_4, for which there is scant evidence[1] and continuing theoretical uncertainty about its structure.[2] As is the case for S_3, the S_4 ring's instability is presumably due to lone-pair repulsion. On the other hand, coordinated S_4^{2-} most certainly exists, and as we will see, not only as a simple chain (of which Na_2S_4 is an example[3]). This paper moves toward an understanding of the variety of complexed S_4^{2-} structural types and in the process shows that some compounds which hitherto have been considered as disulfide complexes may be profitably seen as containing D_{2h}-distorted S_4^{2-} rings. Their formation is attributable to a coupling redox process induced by either an external oxidant or inner oxidation of coordinated metal centers. The analysis leads us to the problem of tuning the $S_2^{2-}/2S^{2-}$ interconversion as well. The electronic structure of some compounds in the literature is reinterpreted, and, we believe, there emerges the outline of a consistent way of thinking about redox coupling of sulfides and disulfides.

Our analysis was stimulated by the Isobe group's dications $[\{Cp^*{}_2M_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{2+}$, M = Ir, **1**; Rh, **2** (Figure 1, Cp* = η^5-C_5Me_5).[4] In these chair-like complexes, the S_4 rectangle has rather different S···S sides (e.g., 2.049(3) vs. 2.894(3) Å in **1**), the shorter ones being either along (in **1**) or across (in **2**) the M–M bonds. Compound **1** is obtained upon 2-e⁻ oxidation of the binuclear precursor $[Cp^*Ir(\mu\text{-}CH_2)_2(\mu\text{-}S_2)IrCp^*]$ (**3**),[4] in which the d^7 metal centers reach saturation with a formal Ir–Ir bond (whose actual length is 2.642(1) Å). The local geometry of the binuclear metal components is virtually unchanged in **1**. Our theoretical analysis[5] shows that the most dramatic effect of coupling (if there were no oxidation) is the destabilization of the σ* combinations formed, in the S_4 plane, by the $\pi_{\parallel}^*$ and $\pi_{\parallel}$ S_2 populated levels (σ_2^* and σ_1^* in Figure 2a,b). These are already in antibonding relationships (therefore destabilized) with the populated δ*–δ* and δ–δ metal combinations: σ_2^* starts from a particularly high energy, and it is from this orbital that 2e⁻ are easily removed on oxidation. Is the alignment of two dimers necessary for the latter to occur? The answer is probably no, since the DFT-optimized cation $\mathbf{3}^+$, with an isolated $\pi_{\parallel}^*$ singly occupied molecular orbital (SOMO), is a minimum from which a diradical coupling mechanism may be triggered.

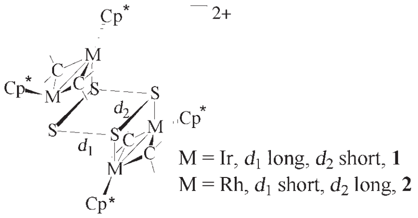

Figure 1. μ-S_4 Tetranuclear compounds of Group 9 metals.

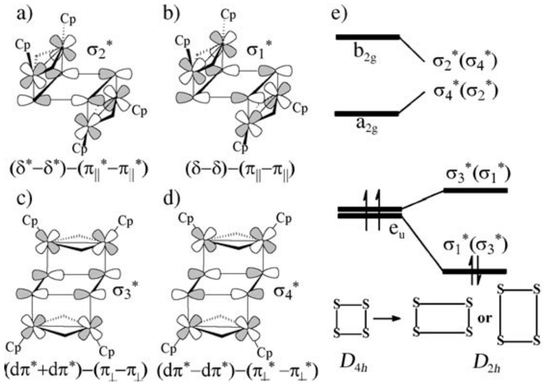

Figure 2. a–d) The four S_4^{2-} σ* levels in **1**. e) Jahn–Teller effect causing the rectangular distortion of the S_4^{2-} unit.

With reference to the new S–S bonding, the S_4^{2-} ring in **1** has the $(\sigma_1^2)(\sigma_2^2)(\sigma_1^{*2})$ configuration, which implies a formal 0.5 S–S bond order with a distance at least 0.7 Å larger than the single S–S bond (ca. 2.05 Å).[6] The alternative arrangements of the S_4^{2-} unit in **1** and **2** (Figure 1a) have an intuitive justification.[5] In an isolated S_4^{2-} *square*, the two lowest σ* levels are degenerate, that is, the $\pi_{\parallel}-\pi_{\parallel}$ and $\pi_{\perp}-\pi_{\perp}$ combinations corresponding to the drawings of σ_1^* and σ_3^* in Figure 2b,c. Since the whole S_4^{2-} σ* pattern (Figure 2e) hosts two electrons, a classic Jahn–Teller (JT) system results, with pairwise elongation and shortening of the S–S distances.

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[*] Dr. C. Mealli, Dr. A. Ienco
Istituto di Chimica dei Composti Organometallici, ICCOM-CNR
Via Madonna del Piano 10, 50019 Sesto Fiorentino, Firenze (Italy)
Fax:(+39) 055-5225203
E-mail: carlo.mealli@iccom.cnr.it

Dr. A. Poduska, Prof. R. Hoffmann
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, NY 14853-1301 (USA)
Fax: (+1) 607-255-5707
E-mail: rh34@cornell.edu

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The distortions shown by complexes **1** and **2** correspond to the stabilization of either the populated σ_1* or σ_3* level. In fact, calculations on **1** in the S_4 ring geometry of **2**, and vice versa, also yield minima (**1′** and **2′**), as yet unobserved experimentally. JT distortion to D_{2h} geometry is a reasonable alternative to the cleavage of a single S–S bond.

The removal of two electrons from the e_u level should support an uncharged S_4 bridge as a square. A second 2-e$^-$ chemical oxidation along the coupling pathway from **3** to **1** seems possible, because σ_1* is destabilized and becomes, at some point, the isolated highest occupied molecular orbital (HOMO) of the system. In fact, tetracation $[\{Cp_2Ir_2(\mu\text{-}CH_2)_2\}_2(\mu\text{-}S_4)]^{4+}$ (**4**) is computed to be a minimum. While the bond lengths are somewhat equalized, S_4 in **4** is far from being a square, since the S–S linkages parallel to the Ir–Ir bonds are still shorter than the others (2.18 vs. 2.65 Å). This result may be traced to unbalanced metal back-donations into the four σ_1*–σ_4* levels (Figure 2 a–d).

The experimental and theoretical evidence for the S_4^{2-} ring in suitable metal environments has prompted us to search for other, perhaps unrecognized, examples of this unit. At least two complexes in the Cambridge Structural Database,[7] reported as $[Cp^*Fe(\mu\text{-}S_2)_2FeCp^*]^{2+}$ (**5**, Cp* = η^5-C_5Me_5)[8] and $[L_2Cu(\mu\text{-}S_2)_2CuL_2](OTf)_2$ (**6**, $L_2 = Me_2NCH_2CH_2NMe_2$, OTf = weakly coordinated trifluoromethanesulfonate (triflate) anion),[9] feature a planar S_4 assembly similar to that of **1** and **2**. As shown in Figure 3, **5** is a triple-decker complex with the S_4 rectangle bicapped by Cp*Fe fragments, and **6** has a chairlike conformation. For neither of these molecules was the presence of a S_4^{2-} unit explicitly formulated.

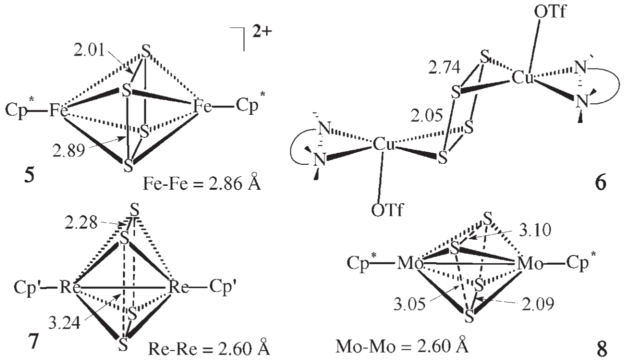

Figure 3. Schematic structures of complexes **5**–**8** with significant experimental parameters.

From a more complete interaction diagram for **5** (see the Supporting Information), we count eight S_4/Fe_2 bonding interactions which involve both the S_4^{2-} π and σ systems. By highlighting the role of the lower t_{2g}-like orbitals, Figure 4 a helps to define the metal oxidation state. Thus δ_2* (empty for the d^5–d^5 configuration) acts as an acceptor, while the corresponding δ_2 level back-donates into the S_4 σ*–σ* one, which lies empty at relatively high energy. Only much larger S···S separations would stabilize the σ*–σ* level in a manner that the electron flow is inverted, that is, S_4^{2-} is transformed into $2S_2^{2-}$ and the Fe^{III} into Fe^{IV} ions.

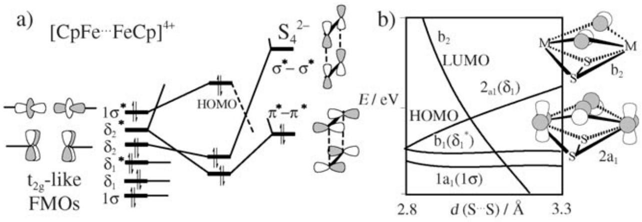

Figure 4. a) Selected fragment molecular orbital (FMO) interactions in **5**. b) HOMO–LUMO crossing for the scission of one S_2^{2-} unit in **8**.

The other systems in Figure 3, $[Cp'Re(\mu\text{-}S_2)_2ReCp']^{2+}$ (**7**, Cp′ = η^5-C_5EtMe_4)[10] and $[Cp^*Mo(\mu\text{-}S_2)(\mu\text{-}S)_2MoCp^*]$ (**8**)[11] contain two electrons less than **5**. In **7**, two sides of the S_4 rectangle are clearly nonbonding (3.24 Å), while the Re–Re separation is as short as 2.60 Å. In **8**, S_4 has a trapezoidal shape with three sides that are essentially nonbonding. According to Figure 4 a, the HOMO of **5** (and the similar Re and Mo conformers) is a well-isolated M–M σ* level; vacating it promotes direct M–M bonding. The structural flattening accompanies the evident uncoupling of the S_2^{2-} units, which stabilizes S–S σ*–σ* and sweeps away δ_2 from the frontier region. The emptying of the latter MO implies a further inner oxidation of the metals (from Re^{III} to Re^{IV}, that is, d^3–d^3 configuration).

The isoelectronic Mo_2 system **8** additionally features the scission of one S_2^{2-} unit into two S^{2-} ions, with a further change of the metal configuration to d^2–d^2. As shown in Figure 4 b, a high-lying S_2^{2-} σ* level (b_2, that is, one of those not involved in Mo_2/S_4 bonding), drops sharply in energy and crosses the filled MOs δ_1 ($2a_1$), δ_1* (b_1), and 1σ ($1a_1$). In the experimental geometry (right side), b_2 is populated in place of $2a_1(\delta_1)$, which becomes the new lowest unoccupied molecular orbital (LUMO). Given the d_δ–p_π antibonding character of the latter, the proposed Mo–Mo double bond in **8**[11] (2.599 Å) seems questionable, and multiple M–S bonding character can be instead assumed.

No concerted $S_2^{2-}/2S^{2-}$ interconversion can be observed for any of the isoelectronic Re and Mo systems, in view of the symmetry-forbidden character of the reaction (a consequence of the illustrated HOMO–LUMO crossing). Importantly, however, each electronic extreme may be found experimentally, as shown by the structures of **7** and **8**. Similar symmetry-forbidden $2S^{2-}/S_2^{2-}$ coupling/uncoupling mechanisms were pointed out by one of us[12] in the context of other puckered M_2S_2 frameworks, for example, $[(CO)_3Fe(\mu\text{-}S_2)Fe(CO)_3]$.[13,14]

We return, because its biomimetic implications are important, to the oxygen and chalcogenide chemistry at Cu_2 frameworks reported by Tolman and co-workers,[15] of which complex **6** is an example. An interesting parallelism emerges between the $2S_2^{2-}/S_4^{2-}$ and $2S^{2-}/S_2^{2-}$ dichotomies. For two oxygen-bridged systems of the type $L_6Cu_2O_2$, both the μ-peroxo and bis(μ-oxo) conformers have been characterized,[15] but the comparable Cu_2S_2 species (with either L_3Cu[16] or L_2Cu terminal fragments[17]) all feature a trans-annular S–S bond as short as 2.25–2.30 Å. The alternative $Cu_2(\mu\text{-}S)_2$ conformer is not found, not even computationally, for [(dki)Cu_2(μ-S_2)Cu(dki)] (**9**, dki = anionic β-diketiminate bis-chelate).[18]

In contrast with the case of the puckered Mo_2S_2 unit (Figure 4b), no HOMO–LUMO crossing occurs in the Cu_2S_2 planar geometry of **9** on elongating the S–S separation. In fact, the drop in energy of the σ* level is buffered by interaction with the in-phase combination of $d\pi_{\parallel}$ metal hybrids. At the experimental S–S distance, the bonding MO b_{2g} (Figure 5a) has prevailing metal character, also because the metal lobes point into the nodes of the sulfur p orbitals. Essentially, there are only three dative $S_2 \rightarrow Cu_2$ bonds, by which the saturating 32-electron count is attained, in the overall planar coordination of **9** (or 36 if two apical ligands are also present). Reduced donor capabilities of the S_2^{2-} ligand have been proposed for a Ni_2(μ-S_2) planar framework.[19]

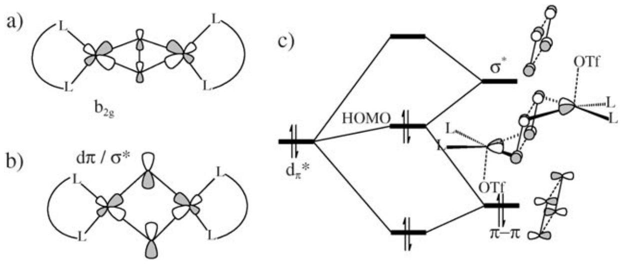

Figure 5. σ*/d_π Interactions in coupled (a) and uncoupled (b) Cu_2S_2 units. c) Critical three-orbital interaction in the Cu_2S_4 framework.

In the absence of major electronic obstacles, why is S_2^{2-} scission not observed for Cu_2S_2 frameworks? As shown in Figure 5b, the scission increases the overlap between metal and inner sulfur p lobes. The lowered energy of S_2 σ* also favors bonding and stabilization of the MO b_{2g}. The back-donation should increase to the point of promoting an inner redox process (σ* below d_π), but this seems inconsistent with the nature of the metal. In fact, Cu d orbitals lie low in energy, and oxidation to Cu^{III} requires drastic conditions, which may be met upon the uncoupling of the highly electronegative oxo ions in Cu_2O_2 systems[15] but not the equivalent S_2^{2-} unit. Interestingly, scission of the latter accompanies an externally forced 2-e^- reduction of **9** (as computationally tested[18]), but the Cu^{II} oxidation state is maintained (most likely in the state with single occupation of the x^2-y^2 magnetic orbitals).

With more electropositive metals, inner oxidation and S_2^{2-} uncoupling are possible. For instance, the Co^{III} complex $[L_4Co(\mu\text{-}S)_2CoL_4]^{2+}$ (**10**, L_4 = cyclam),[20] obtained by reacting disulfide with Co^{II} ions, features a S···S separation which is about 0.6 Å larger than in **9**. Since the isolobal relationship of the d^7 L_4Co and d^9 L_2Cu fragments suggests similar chemistry, the difference derives from the relatively higher energy of the Co d orbitals and hence the stability of Co^{III} ions. Incidentally, when the reaction leading to **10** is performed with Ni^{II}, the product **11** shows an intact S_2^{2-} bridge and no oxidation to Ni^{III}.[20] The two extra electrons occupy, unpaired, z^2 Ni orbitals (Ni–N_{ax} antibonding), which are not involved in any major Ni_2S_2 bonding.

In the absence of bulky substituents at the dinitrogen L_2 chelate, the trinuclear product $[(L_2Cu)_3(\mu_3\text{-}S)_2]^{3+}$ (**12**) is formed, likely upon the addition of another L_2Cu^I unit to the preformed S–S coupled dimer **9**. It has been proposed that the trigonal-bipyramidal Cu_3S_2 core of **12** contains uncoupled S^{2-} ions and consequently a $Cu^{II}{}_2Cu^{III}$ configuration of the metals.[21] Our previous considerations 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 **12**. A fierce, but amicable (and we think enlightening) debate on this topic with S. Alvarez will be presented elsewhere.

The diagram in Figure 6 shows that the levels $1a_2''$ (populated) and $2a_2''$ (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.

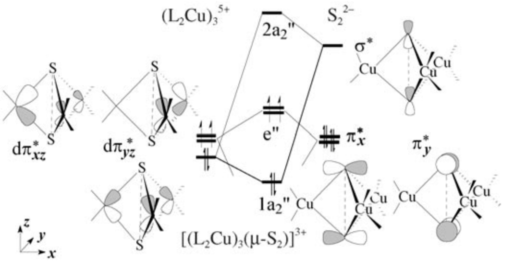

Figure 6. Frontier MOs in complex **12** with a D_{3h} Cu_3S_2 core.

We think there is S–S bonding in this molecule. To establish this point, we focus on the population of the σ* FMO of the diatomic fragment (see Figure 6). 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 $[\{(PR_3)_2Co\}_3(\mu_3\text{-}S)_2(\mu_2\text{-}SH)_2(\mu_2\text{-}PR_2)]^{2+}$,[22] which clearly contains uncoupled sulfide capping ligands.[23]

In **12**, at the equilibrium S···S separation of 2.7 Å, the population of σ* is 33 % and the value drops to less than 10 % for $d(S\cdots S) \leq 2.3$ Å. Only for $d(S\cdots S) > 3.0$ 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.

Because of the high electronegativity of oxygen, the metals are more effectively oxidized in the $[L_6Cu_3O_2]^{3+}$ analogue of **12**.[24] Here, an evident JT effect destroys the threefold symmetry and allows stronger coordination of the two oxo ligands to one single Cu^{III} ion ($\Delta d(Cu\text{–}O) \approx 0.2$ Å). In contrast, there is no evidence of such an effect in the Cu_3S_2 system, even when the $2a_2''$ and e″ levels, with two electrons available, become almost degenerate at S–S distances greater than 2.7–2.8 Å.

As always, the metal oxidation state and configuration assignments are an idealization of the actual delocalized

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bonding situation. Our view, that the sulfur atoms in **12** 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 copper centers 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 **12** (see the Supporting Information), constructed by varying the S···S separation from 2.2 to 3.1 Å, shows signs of an avoided crossing between the levels $2a_2''$ and $1a_2''$ at about 2.7–2.8 Å. The corresponding orbital mixing is likely the mechanism by which the electrons in $1a_2''$ are transferred from the metals to the sulfur atoms. That avoided crossing is also an indication that a multi-configurational computation (which we have not yet attempted) might yield a description that melds both metal configurational assignments.

The arguments adduced above with respect to the $2S^{2-}/S_2^{2-}$ dichotomy help us to clarify the $2S_2^{2-}/S_4^{2-}$ one. Returning to the latter, a full interaction diagram for **6** is presented in the Supporting Information; an evident feature is that the S_4^{2-} π system donates only three electron pairs to the metal centers. In fact, as shown in Figure 5c, the combination π–π interacts with d_π*, which is populated, and their four-electron repulsion is likely the cause for an about 15° skewing of the S_4^{2-} ring from orthogonality with the L_2Cu planes. However, the d_π* combination back-donates electrons into the S_4^{2-} σ* level. Similarly to **9**, such an interaction allows the system to be described as formed by two d^9 spins antiferromagnetically coupled through the S_4^{2-} bridge. Our attempts to optimize a conformer of **6** with much more separated S_2^{2-} ligands invariably lead to the experimental structure with two S···S distances of 2.81 Å (see the Supporting Information).[25] Conversely, more electropositive metal atoms, such as Ti, Ru, Mn, and Co, favor the inner S_4^{2-} scission,[26] as the S···S distances are from 0.4 to 0.8 Å larger than the 2.74 Å found in **6**. Amongst the latter species, there is a cyclam Co^{III} complex analogous to **10**,[26e] which confirms the parallel behavior of the S_2^{2-} and S_4^{2-} units on coupling/uncoupling.

The crucial role played by the metallic element emerges from the above comparisons. In fact, the stabilization of the S_4^{2-} ring as a bridge depends on the ability of the metal centers to accept electron density from the S_4^{2-} π system (four metal atoms do this better than two). The metals must be sufficiently electronegative to avoid significant charge transfer to the S_4^{2-} σ system, first through back-donation and eventually through oxidative addition. In this respect, metals such as Fe, Ni, and Cu (which dislike higher oxidation states such as +4, +3, and +3, respectively) seem most appropriate to stabilize the S_4^{2-} ring. Other chalcogenides may form similar yet not fully recognized ring structures.[27]

In conclusion, the disulfide anion is unique, prone to both scission and dimerization, both of which are tuned subtly by the coordinated metal fragment. These aspects are particularly relevant, since important biological processes are regulated by the inner electron transfer process between a metal and coordinated sulfide anions. As an example, we quote one of the known nitrogenases (the FeMoco active site[28]) in which two *cis* S^{2-} ligands coordinated to a Mo^{VI} ion couple together to give η^2-S_2^{2-}. Interestingly, the nature of the metal appears to be critically important also in these cases, since a W in place of a Mo atom inhibits the functionality of the enzyme.[28]

We believe we have constructed an electronic framework for understanding the geometrics of four contiguous sulfur atoms in a complex and pointed out the strategies for tuning this remarkable set of deformations of a ring. We also begin to see how the nature of the main-group element and of the metal influence $2S^{2-}/S_2^{2-}$ and $2S_2^{2-}/S_4^{2-}$ and related transformations.

Experimental Section

Computational details: All DFT calculations were carried out at the B3LYP level[29] of theory by using the Gaussian03 program.[30] The qualitative MO interpretation has been developed with the help of the extended Hückel molecular orbital based (EHMO-based) CACAO package. More details are given in the Supporting Information.[31]

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