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ARTICLE *in* INORGANIC CHEMISTRY · SEPTEMBER 1983

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An Unusual Disulfur-Bridged Nickel Dimer with a Ni_2S_2 Planar Framework. An Example of Binuclear Coupling Promoted by Transition Metals

Sir:

The compound $[(\text{triphos})\text{Ni}(\mu\text{-S}_2)\text{Ni}(\text{triphos})]\text{ClO}_4$ (**1**) (triphos = $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$) is a novel nickel dimer bridged by two sulfur atoms.¹ Figure 1 shows the two staggered L_3M type fragments held together by a disulfur moiety; the Ni_2S_2 bridging framework is crystallographically planar with a Ni-Ni distance of 3.865 (1) Å. Since the S-S distance of 2.208 (4) Å indicates a weakened bond (values in the range 1.98–2.15 Å have been found for coordinated disulfur ligands²), the structure represents a rare example of a η^2 binuclear ligand that is coplanar with the two metals. The known bridging groups in which the S-S vector is at right angles to the metal-metal vector have a puckered arrangement.²

Interesting, but not new,³ is that the coupling of the two sulfur atoms is achieved when nickel(II) perchlorate is reacted with hydrogen sulfide in the presence of triphos. Indeed, brown crystals of **1** are obtained on bubbling H_2S through a solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and triphos in dimethylformamide/1-butanol, at 40 °C for about 0.5 h. The reaction time is a crucial point. If H_2S is passed into the unwarmed solution for only a few minutes, the diamagnetic dimer $[(\text{triphos})\text{Ni}(\mu\text{-S})\text{Ni}(\text{triphos})]^{2+}$ is obtained as a major product. This compound, which contains a single linearly bridging sulfur atom, has been previously studied.⁴ Compound **1**, which slowly decomposes in air, is paramagnetic with a bulk magnetic moment of 2.04 μ_B at 22 °C per dimeric unit. The powder EPR spectrum,

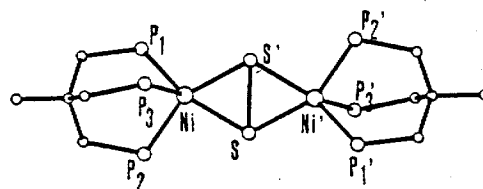


Figure 1. Inner skeleton of the complex cation $[(\text{triphos})\text{Ni}(\mu\text{-S}_2)\text{Ni}(\text{triphos})]^+$. Important bond distances (Å) and angles (deg): Ni-Ni', 3.865 (1); Ni-S, 2.234 (2); Ni-S', 2.217 (2); Ni-P(1), 2.228 (2); Ni-P(2), 2.232 (2); Ni-P(3), 2.255 (2); S-S', 2.208 (4); S-Ni-S', 59.5 (3); Ni-S-Ni', 120.5 (1); P(1)-Ni-P(2), 91.7 (1); P(1)-Ni-P(3), 92.6 (1); P(2)-Ni-P(3), 94.7 (1).

Table I. Summary of the In-Ring Bond Distances (Å) and Angles (deg)

	$[(\text{triphos})\text{NiS}]_2^+$ (1)	$[(\text{triphos})\text{CoS}]_2$ (3)	$[(\text{triphos})\text{CoS}]_2^+$ (2)
M-M	3.865 (1)	3.598 (2)	3.434 (8)
S-S	2.208 (4)	2.613 (8)	2.584 (21)
M-S (av)	2.225 (8)	2.23 (1)	2.15 (1)
M-S-M	120.5 (2)	108.0 (2)	106.0 (7)

recorded at 77 K, is characteristic of an $S = 1/2$ spin system with $g_{\perp} = 2.0$ and $g_{\parallel} = 2.18$.

It was previously reported that when the above reaction is performed by using cobalt(II) in place of nickel(II), the paramagnetic (one unpaired electron per dimeric unit) cation $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]^+$ (**2**) is invariably obtained.⁵ The same primary geometry⁶ is found in both **1** and **2**, but the latter complex shows a conspicuously longer S-S distance of 2.584 (2) Å and a shorter M-M separation, i.e. 3.434 (8) Å. We recall at this point that **2**, which has a total of 2 electrons less than **1**, may be both oxidized to a double charged species or reduced to the uncharged complex $[(\text{triphos})\text{Co}(\mu\text{-S})_2\text{Co}(\text{triphos})]$ (**3**). The X-ray analysis of **3** has shown that the addition of 1 electron to **2** does not change the S-S distance significantly (2.61 (1) Å) but lengthens the Co-Co separation to 3.598 (2) Å. Table I summarizes important geometrical parameters for structures **1**–**3**. Notice that the S-S and M-S

(1) $[(\text{triphos})\text{Ni}(\mu\text{-S}_2)\text{Ni}(\text{triphos})]\text{ClO}_4$ (fw = 1530.4), parallelepiped-shaped deep brown crystals (dimensions of the selected crystal $0.12 \times 0.06 \times 0.07$ mm³): triclinic, $P\bar{1}$, a 14.419 (5) Å, b 12.677 (5) Å, c 12.676 (6) Å, α = 76.35 (9)°, β = 63.78 (8)°, γ = 70.58 (9)°, ρ_{calcd} = 1.30 g/cm³ for $Z = 1$. The crystallographic computing was carried out by using the SHELX76 system. The source of the scattering factors is the same as in ref 5. Transmission factors varied between 0.94 and 0.88. A total of 4622 reflections with $I \geq 3\sigma(I)$ ($\theta \leq 23^\circ$) were used in the refinement of 168 structural parameters. The complex dimer lies on a center of inversion. There is however a clear inconsistency between this symmetry and the presence of only one ClO_4 anion for dimeric cation. Attempts to refine the structure in $P\bar{1}$ failed due to the high correlations between the structural parameters of the centrosymmetric parts of the dimer. Our ultimate solution was the assignment of 0.5 population parameters to the ClO_4 site in the least-squares cycles. At the end of the refinement ($R(F) = 0.073$, highest peaks in ΔF maps ~ 1 e/Å³), some disorder still affects the ClO_4 region but the chemical information on the dimer is reliable.

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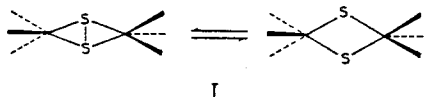
(4) (a) Mealli, C.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 2513. (b) Mealli, C.; Sacconi, L. *Ibid.* **1982**, *21*, 2870.

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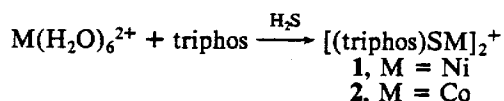
(6) The primary geometry is defined as that of the M_2S_2 plane having two sulfur atoms bridging two terminal (triphos)M groups irrespective of the relative orientation of the latter. A recent redetermination (to be published) of the structure of **2** having ClO_4 in place of BPh_4 as counterion shows that the conformation of the $\text{L}_3\text{M}-\text{ML}_3$ fragment is staggered whereas bond distances and angles are almost unchanged. Thus, the torsion of about 15° toward the eclipsed conformation previously reported for **2**⁵ is attributable to different packing forces. Torsional barriers are usually very low for sixfold rotors, and EHMO calculations confirm that this is indeed the case for these compounds.

distances themselves fully describe the geometry of the planar M_2S_2 ring.

The series of structures at hand represent a very favorable situation where we can follow the structural rearrangements in a system with constant primary geometry but varying total electron count. Hopefully this system may also offer an understanding of the electronic requirements for the transition-metal-assisted coupling or cleavage of two sulfur atoms, I.



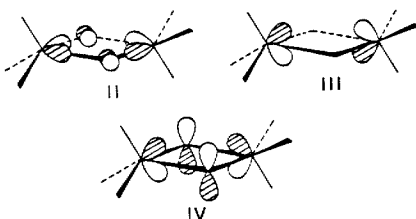
A formal counting of electrons in the complexes can be done by considering that the total charge of the S_2 grouping varies between 4- and 2-. These limits correspond either to no interaction between the sulfido anions or to a single bond between the sulfur species. Although a S-S distance of ca. 2.6 Å does not exclude some interaction between the sulfur atoms,⁷ compounds 2 and 3 are near the former limit. Conversely, the short S-S distance in 1 suggests approach to the latter limit. Accordingly, the metals may be regarded as having formal oxidation state II/III (d^7/d^6) in 2, II (d^7/d^7) in 3, and I/II (d^9/d^8) in 1. Therefore, the reactions leading to 1 and 2 are only stoichiometrically analogous since, in the



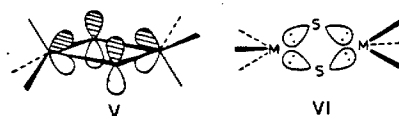
former case, a reduction of the nickel ions occurs with the formation of S-S bonding. That is to say that the formation of 1 may also be regarded as the first step toward reductive elimination of an S_2 unit from two sulfido ligands.

The bonding capabilities of the S_2 grouping are dramatically changed within the series. If the 18-electron rule is used for qualitative evaluation, S_2^{4-} must be taken as a 10-electron donor in the cobalt complexes, while S_2^{2-} serves as a 6-electron donor in the nickel compound. In a loose manner, total counts of 17.5 and 18 electrons can be formally calculated at each metal center in 1, 2, and 3 respectively.

The above considerations find some support from a preliminary analysis⁸ of the orbital interactions of $L_6M_2^{4b}$ and S_2 fragments. Frontier MOs of increasing energy are schematically shown in II-IV. III is a metal-centered MO since



no combination of sulfur p orbitals can overlap positively with it. A different population of III (HOMO in 2 and 3) cannot affect the S-S distance. The LUMO (in 2 and 3) is IV, a metal-sulfur π^* orbital. Its low-lying bonding counterpart, V, can be regarded as a donation of an S_2 π lone pair into appropriate metal orbitals. Besides, the other four σ lone pairs are donated to the metals, VI. II is a delocalized description of one of those, that involving the p_z combination of two sulfido anions. When IV becomes populated, as is the case



in 1, most of the sulfur to metal π donation is obviously lost; at the same time, the S-S π -bonding nature of IV may trigger a shortening of the S-S distance. The fact itself is not sufficient to fully rationalize the observed S-S coupling. On the other hand, a shortening of the S-S distance rapidly destabilizes the S_2 σ^* orbital that participates in the formation of II. Thus, on account of the progressively larger energy gap between the interacting fragment orbitals, the S_2 contribution almost disappears in II where the populating electrons acquire more and more metallic character. At a S-S distance of 2.2 Å, the empty S_2 σ^* combination lies unmixed at high energy. Accordingly, the following points may be rationalized: (i) a formal reduction of the metals, (ii) the formation of an S-S bond order, and (iii) the diminishing of the donor capabilities of the S_2 unit. The EPR data are supportive of the assignment of the HOMO (IV) in 1. This and other points will be described in detail in a forthcoming paper.

Acknowledgment. Thanks are due to Professor Roald Hoffmann for stimulating discussions and encouragement.

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Supplementary Material Available: Listings of positional and thermal parameters for 1 (3 pages). Ordering information is given on any current masthead page.

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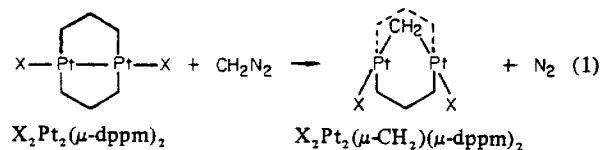
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Stefano Midollini

Received April 20, 1983

Mechanism of "Molecular A-Frame" Formation by Methylene Insertion into a Platinum-Platinum Bond

Sir:

The literature contains no reports of the rates and mechanisms of μ -methylene complex formation by insertion reactions of diazomethane. We thus undertook studies of this general reaction type, utilizing the dinuclear haloplatinum(I) complexes $X_2Pt_2(\mu\text{-dppm})_2$, where dppm = bis(diphenylphosphino)methane, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$. The reaction in which a μ -methylene group is inserted into the Pt-Pt bond of the parent complex, shown in eq 1, yields the well-characterized "molecular A-frame" product.¹



Binuclear and polynuclear metal complexes may serve as models for intermediates formed during reactions catalyzed by metal surfaces.²⁻⁵ Relatively new groups of such complexes

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