solvents to which chloride has been added, the cluster undergoes an immediate reaction to afford $Fe_6S_6(PEt_3)_4Cl_2$, identified by its characteristic $^1H$ NMR spectrum,[13] and an unidentified black insoluble material. Aerial oxidation of $[Fe_6S_6(PEt_3)_6]^+$ or treatment with elemental sulfur in acetonitrile solution leads to the formation of $[Fe_6S_8(PEt)_6]^{2+}$ or $[Fe_6S_8(PEt_3)_6]^+$ (**5**), respectively. These clusters were identified by their $^1H$ NMR spectra.[27] The two oxidation reactions are further examples of core conversion reactions[12,13] in which the prismane- (**3**) and cubane-type $Fe_4S_4$ clusters may be recovered from the basket cluster $Fe_6S_6(PEt_3)_4Cl_2$, which itself is obtainable by a core conversion reaction of $Fe_7S_6(PEt_3)_4Cl_3$. In the present case, the conversion products are the stellated octahedral clusters **5** of established structure.[20,21]

**Summary.** This work has demonstrated that an Fe–S assembly system with triethylphosphine as the only terminal ligand affords $[Fe_6S_6(PEt_3)_6]^+$. This cluster also possesses the $Fe(\mu_2\text{-}S)(\mu_3\text{-}S)_4(\mu_4\text{-}S)$ basket core topology first observed in **1** and **2**, which are more oxidized by one electron. Tetrahedral stereochemistry at the sites Fe(1,3), also found in the preceding two clusters, appears to be an intrinsic feature of the stable basket cores $[Fe_6S_6]^{2+,+}$. In both oxidation levels, the other four Fe sites exhibit distorted trigonal-pyramidal coordination. $[Fe_6S_6(PEt_3)_6]^+$ has an electronically delocalized core structure, with only small dimensional differences relative to **1** and **2**. It undergoes oxidative core conversion reactions, affording the known clusters $[Fe_6S_8(PEt)_6]^{2+,+}$. Because of the absence of necessary compounds, it is not yet known whether the relative stabilities of basket and prismane (**3**) stereochemistries are dependent on core oxidation level or terminal ligand, or both.

Known Fe–S clusters of nuclearity 6 now include the set $[Fe_6S_6L_6]^{2-,3-}$ (**3**), $Fe_6S_6(PR_3)_4L_2$ (**1**, **2**), $[Fe_6S_6(PEt_3)_6]^+$ (**4**), $[Fe_6S_8(PEt)_6]^{2+,+}$ (**5**), and $[Fe_6S_9(SR)_2]^{4-}$.[2-4] None of the core units of these clusters have as yet been found to occur in proteins, but at least one 6-Fe cluster with a different stoichiometry may exist in certain hydrogenases.[28,29] A future report[14] will describe the electronic properties of **1**, **2**, and **4**. Further reactivity properties of $[Fe_6S_6(PEt_3)_6]^+$ are under examination.

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**Supplementary Material Available:** Tables of crystallographic data for $[Fe_6S_6(PEt_3)_6](BF_4)$, including a summary of data collection parameters, thermal parameters, calculated hydrogen atom positional parameters, and interatomic distances and angles (7 pages); a listing of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

(27) $^1H$ NMR ($CD_3CN$, 298 K): $[Fe_6S_8(PEt_3)_6]^+$, $\delta$ −11.4 ($CH_3$); $[Fe_6S_8(PEt_3)_6]^{2+}$, $\delta$ −44.9 ($CH_2$), −6.9 ($CH_3$).

(28) George, G. N.; Prince, R. C.; Stockley, K. E.; Adams, M. W. W. *Biochem. J.* **1989**, *259*, 597.

(29) Adams, M. W. W.; Eccleston, E.; Howard, J. B. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 4932.

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301

# Coupling of Thionitrosyls and Nitrosyls on Rhenium Fragments: A Molecular Orbital Analysis

Meinolf Kersting and Roald Hoffmann*

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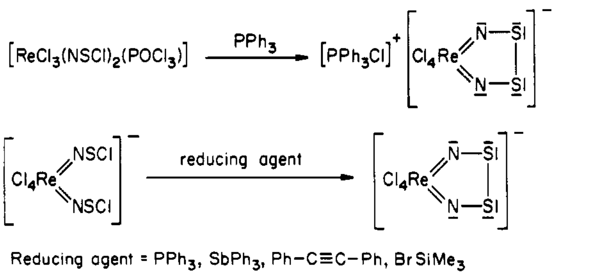
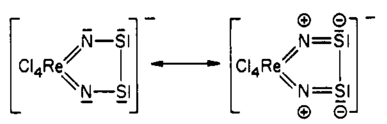
The electronic structure and bonding in complexes of the $[ReCl_4(N_2S_2)]^-$ type have been studied by using extended Hückel calculations. The reaction path and the electronic requirements for the possible coupling of two NS ligands, bonded to the same framework, were studied. The results are then compared with the hypothetical coupling of NO ligands and analyzed for two different types of coupling, involving either (a) the formation of a S–S (O–O) bond or (b) the formation of a N–N-bonded species.

## Introduction

Thionitrosyl complexes of transition metals were first discovered in 1974.[1] Compared to the vast number of nitrosyl complexes, only a small number of thionitrosyl complexes have been investigated. The reactivity pattern of NO compounds are complex,[2] and one might anticipate the same for NS compounds. However, the scarcity of complexes containing two or more NS ligands[3] has limited reactivity studies. Interestingly, a few complexes have been recently isolated and characterized,[4] in which apparently two NS ligands have been coupled on a transition-metal center forming a sulfur–sulfur bond, an observation previously unprecedented for NS complexes.

The reaction of (chlorothio)nitrene complexes $[ReCl_3(NSCl)_2(POCl_3)]$ or $[ReCl_4(NSCl)_2]^-$ with reducing agents such as $PPh_3$, $SbPh_3$, diphenylacetylene, or $BrSiMe_3$ gives the complexes $[ReCl_4(N_2S_2)]^-$. These have been crystallographically characterized in three examples by Dehnicke et al.[4] (**1**). In this reaction a reductive dehalogenation is likely to occur prior to the formation of a new sulfur–sulfur bond.




**1**

Thus, it may be suggested that during this reaction step a complex with two separate NS ligands cis to each other is formed

(1) (a) Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, New York, 1987; Vol. 2, Chapter 13.3.3, p 118. (b) Roesky, H. W.; Pandey, K. K. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 337. (c) Herberhold, M. *Nachr. Chem., Tech. Lab.* **1981**, *29*, 365.

(2) (a) Reference 1a, Vol. 2, Chapter 13.3.2, p 101. (b) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53. (c) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339. (d) Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

(3) (a) Weber, R.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1983**, *504*, 13. (b) Demant, U.; Willing, W.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *532*, 175.

(4) (a) Hiller, W.; Mohyla, J.; Strähle, J.; Hauck, H. G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 72. (b) Conradi, E.; Hauck, H. G.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *539*, 39.

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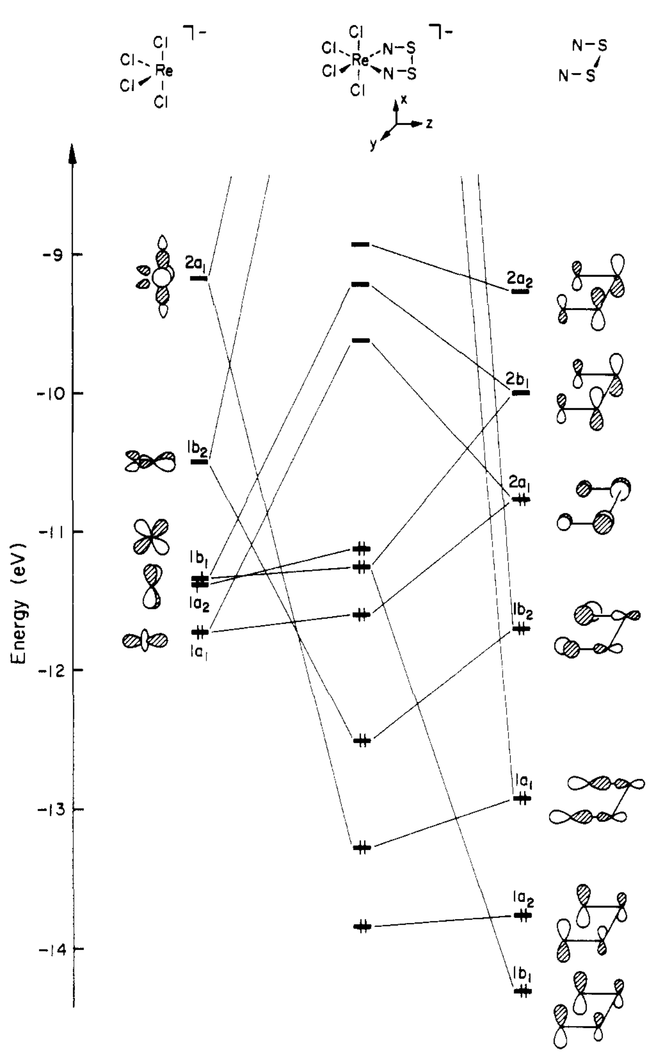



**Figure 1.** Schematic interaction diagram for the formation of $[ReCl_4(N_2S_2)]^-$ from $ReCl_4^-$ and $N_2S_2$ fragments. The $d^4$ $ML_4$ fragment orbitals are shown at left, and those of $N_2S_2$, at right.

as an intermediate. Unlike dinitrosyl complexes, complexes having two or more thionitrosyls on one metal center are rare and have only been characterized in but two examples.[3]

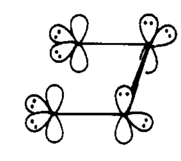
Metalladithiadiazines represent only a small fraction of transition-metal complexes bearing $N_xS_y$ ligands, and the coordination chemistry of $N_xS_y$ species is still a burgeoning field of inorganic chemistry.[5] Alternate dianionic $N_2S_2$ ligands involving a head-to-tail arrangement of two NS ligands have also been reported in a few examples.[6] The neutral species $N_2S_2$ exists as a ligand in a variety of transition-metal complexes and has been extensively reviewed.[5,7]

In this paper, we will look at the electronic requirements for the coupling of two NS ligands on a transition-metal fragment and compare it with the hypothetical formation of a $N_2O_2$ ligand. All molecular orbital calculations are performed by using the extended Hückel method.[8] This paper is also related to earlier work studying the coupling of carbonyls,[9] carbenes,[10] carbynes,[10] and ethylenes[11] on transition-metal centers.

## Electronic Structure of $[ReCl_4(N_2S_2)]^-$

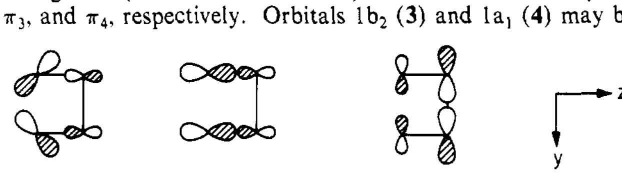
A suitable starting point for this analysis is the construction of the valence molecular orbitals (MO's) of $[ReCl_4(N_2S_2)]^-$ by an interaction of the MO's of the two fragments $ReCl_4^-$ and $N_2S_2$. Figure 1 shows the interaction diagram for that molecule; on the left-hand side are the fragment orbitals of the $d^4$ $ReCl_4^-$ unit.

An analysis of the frontier orbitals shows a lower group of three levels, $1b_1$, $1a_2$, and $1a_1$, the nearly unperturbed remnants of the octahedral $t_{2g}$ set. The $2a_1$ and $1b_2$ orbitals are characteristic of a $ML_4$ fragment.[12] Depicted on the right-hand side in Figure 1 are the frontier orbitals of $N_2S_2$. Taken as neutral, the $N_2S_2$ moiety might be described as a bidentate ligand with a four-$\pi$-electron system (**2**).



**2**

The butadienoid $\pi$ orbitals are seen as $1b_1$, $1a_2$, $2b_1$, and $2a_2$ in Figure 1 (two of these are filled). We will call these $\pi_1$, $\pi_2$, $\pi_3$, and $\pi_4$, respectively. Orbitals $1b_2$ (**3**) and $1a_1$ (**4**) may be

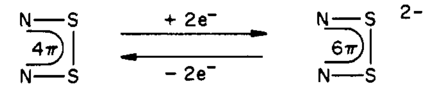



**3** **4** **5**

identified as the in-phase and out-of-phase combinations of N lone pairs directed away from the sulfur atoms. This makes them especially suitable for interacting with the $1b_2$ and $2a_1$ orbitals on the $ReCl_4^-$ side, from both an energy and an overlap point of view. These interactions are in fact the ones that contribute strongly to the $\sigma$ bonding between the two fragments.

Another orbital that plays a significant role is $2a_1$ (**5**), which interacts with $1a_1$ of $ReCl_4^-$ to a lesser extent than the interactions mentioned above. Interactions of $\pi$ type are weaker. They can be analyzed separately from $\sigma$-type interactions, since in this molecule a $\sigma$–$\pi$ separation is retained. The $1b_1$ orbital of $ReCl_4^-$ interacts with both $1b_1$ and $2b_1$ on $N_2S_2$. The resulting three-orbital pattern leaves an essentially nonbonding orbital behind, slightly below the highest occupied molecular orbital (HOMO), which itself is a nonbonding orbital, metal $d_{xy}$ in character. The fairly large gap between the HOMO and the LUMO, about 2 eV, indicates a stable molecule. The summation over all $\sigma$- and $\pi$-type interactions mentioned above gives a total overlap population of 0.658. Among these interactions, the dominant one is of $\sigma$ type, which contributes 0.554, to which the weaker $\pi$ type adds 0.104 to the overlap population.

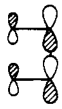
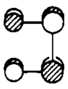
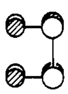
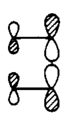
At this point we must focus on to the ambiguities of electron counting and oxidation states and establish a convention for counting electrons. We treated the $ReCl_4$ fragment as negatively charged and the $N_2S_2$ ligand **6a** as neutral. An alternative, perfectly reasonable, might be to let the $N_2S_2$ ligand have a charge of 2–. Then six $\pi$ electrons are distributed over four atoms (**6b**).




**6a** **6b**

(5) Gmelin Handbook of Inorganic Chemistry; Sulfur-Nitrogen Compounds, Part 2; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1985.
(6) (a) Hornemann, K.; Weiss, J. *Angew. Chem.* **1982**, *94*, 645; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 633. (b) Chivers, T.; Fait, J.; Schmidt, K. J. *Inorg. Chem.* **1989**, *28*, 3018.
(7) Dehnicke, K.; Müller, U. *Transition Met. Chem. (Weinheim, Ger.)* **1985**, *10*, 361.
(8) (a) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872. (b) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.
(9) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.
(10) (a) Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632. (b) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535.
(11) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952.
(12) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Albright, T. A. *Tetrahedron* **1982**, *38*, 1339. (c) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley: New York, 1984; Chapter 19. The unfilled $2a_1$ orbital, which has the shape drawn in this reference, lies at still higher energy for our compound.

**Table I.** Overlap Population between Sulfur Atoms and Fragment Molecular Orbital (FMO) Occupations for Specified Orbitals of $N_2S_2$[a]

| orbital | | overlap pop. | FMO occupation before interaction | FMO occupation after interaction |
|---|---|---|---|---|
|  | $2b_2$ | −0.516 | 0 | 0.001 |
|  | $2a_2$ ($\pi_4$) | −0.090 | 0 | 0.238 |
|  | $2b_1$ ($\pi_3$) | +0.081 | 0 | 0.627 |
|  | $2a_1$ | +0.241 | 2 | 1.110 |

[a] Orbitals are drawn in the $yz$ plane.

The reader might be reminded immediately of the dithiolene ligand ambiguity, which is related to this problem.[13]

However, our calculations give a charge of +1.32 to the $N_2S_2$ unit and a −2.32 charge to the $ReCl_4^-$ fragment, concentrated mostly on its Cl ligands. This would seem to argue against the dianionic resonance structure. Another approach, however, might be to focus on the population of fragment MO's. The numbers we obtain are as follows: $\pi_1$, 1.92; $\pi_2$, 1.98; $\pi_3$, 0.63; $\pi_4$, 0.23. These figures put some five $\pi$ electrons into the $\pi$ system, pointing to a situation intermediate between **6a** and **6b**. We have to live with an inherent ambiguity in assigning formal electron counts to the fragments in these molecules. The apparent discrepancy between the two approaches is due to depopulation of the high-lying $\sigma$ type orbitals $2a_1$ and $1b_2$. We will return later to this point, when we discuss some of its implications on the nature of the S–S bond.

Another interesting aspect is the amount of delocalization within the metallacycle. A qualitative indication of delocalization is provided by the occupation of $\pi^*$ orbitals. From the figures given in Table I, it is quite obvious that both $\pi^*$ orbitals $\pi_3$ and $\pi_4$ show significant populations. This in turn can be traced back to back-bonding from metal d orbitals into the $\pi^*$ orbitals of the $N_2S_2$ moiety. The orbital of interest on the $ReCl_4^-$ side is $1b_1$: In our calculations, it lies above $1a_2$, but extremely close to it. With two electrons, both orbitals are half-filled and $1b_1$ donates some 0.63 electrons (see Table I) back to the $N_2S_2$ fragment. The same trend also applies to back-donation from the $ReCl_4^-$'s $1a_2$ orbital into $\pi_4$. Although this interaction is rather weak by comparison and we have not discussed it before, it is still capable of back-donating 0.24 electron. In some manner, this observation resembles the situation encountered in metallacyclopentadienes.[14]

An interesting experimental observation is the rather long S–S bond in these $[ReCl_4(N_2S_2)]^-$ complexes. Although S–S bonds may vary over a broad range[15] and "unusual" long sulfur–sulfur distances have been found in several complexes[16] and assigned as bonding interactions, the observed mean bond length of 2.59 Å is about 0.56 Å longer than in $S_8$ and significantly shorter than the van der Waals contact of 3.5–3.6 Å.[17] Can it still be considered as a "real" bond? We think the answer is yes. The important orbitals that let us argue this point are $\pi_4$ ($2a_2$), $\pi_3$ ($2b_1$), and $2a_1$. Table I shows the overlap population between the sulfur atoms for these orbitals and the fragment molecular orbital (FMO) occupation before and after interaction with the $ReCl_4^-$ fragment. The total S–S overlap population is 0.288 before interaction ($N_2S_2$) and 0.234 after. Both $\pi_4$ and $\pi_3$ are only slightly antibonding and bonding, respectively. They do not contribute much to bonding, no matter whether they are populated or depopulated. However, $2a_1$, which is clearly S–S bonding as indicated by its contribution to the total overlap population, is depopulated by about 0.9 electron. This is a lot, but the orbital must still be regarded as bonding. This observation is supported by magnetic measurements that do not indicate an "open" structure with diradical character on both sulfur atoms.[4b]

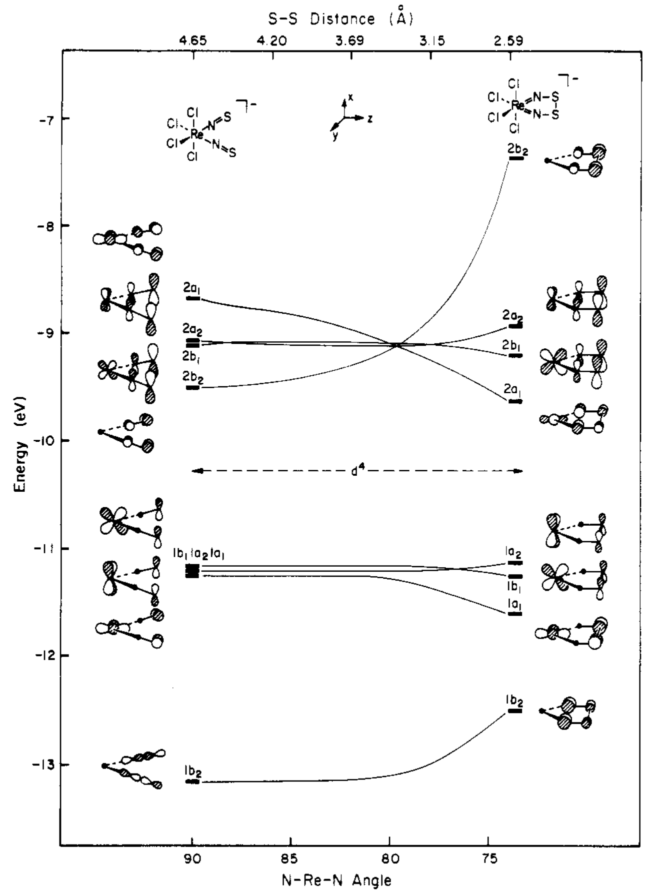
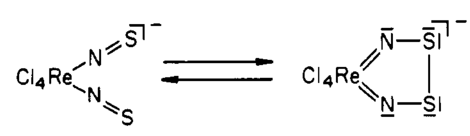



**Figure 2.** Evolution of energy levels of $[ReCl_4(NS)_2]^-$ along an idealized reaction coordinate, forming a S–S bond. Note the N–Re–N angle scale at the bottom and the nonlinear S–S distance scale at the top.

## Coupling of Two NS Ligands

Let us examine the electronic requirements and the evolution of frontier orbitals when two NS ligands in $[ReCl_4(NS)_2]^-$ (**7**)



**7** **1**

are coupled to form a $N_2S_2$ chelating unit (**1**) or the reverse reaction, the dismantling of a coordinated $N_2S_2$ fragment.

(13) (a) Reference 1a, Vol. 2, Chapter 16.5, p 595. (b) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253. (c) Burns, R. P.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303. (d) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.

(14) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(15) (a) Steudel, R. *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655.

(16) See, for instance: (a) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, *102*, 3624. (b) Davies, C. G.; Gillespie, R. J.; Park, J. J.; Passmore, J. *Inorg. Chem.* **1971**, *10*, 2781. (c) Chivers, T.; Proctor, J. *J. Chem. Soc., Chem. Commun.* **1978**, 642.

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

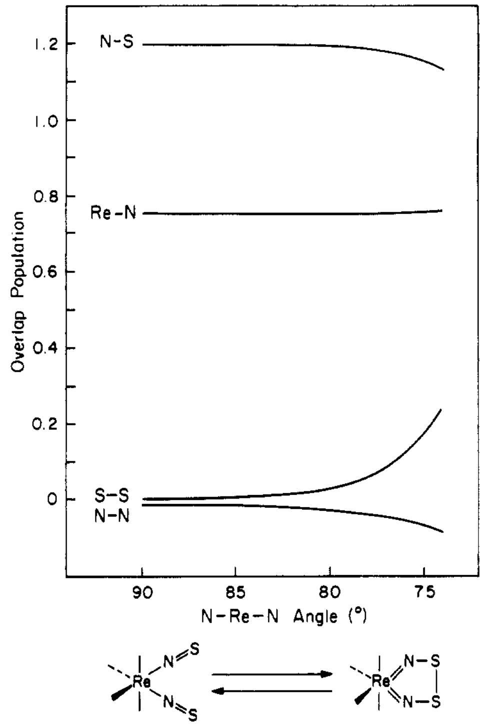



**Figure 3.** Overlap population between atoms along the $C_{2v}$ reaction coordinate, as described in the caption of Figure 2.

Figure 2 shows a correlation diagram of the energy levels of **7** to **1**, evolving along an idealized coupling coordinate (described in the Appendix).

On the dithionitrosyl side we have the $2a_1$ and $1a_1$ orbitals, which, when the reaction coordinate is followed, eventually become S–S $\sigma$ bonds. For a $d^4$ electron count, only $1a_1$ favors the coupled side. The critical orbital, however, is $1b_2$, which is locally S–S antibonding and which goes up in energy to a greater extent than $1a_1$ descends.

Along this reaction path, the overlap populations between atoms evolve as shown in Figure 3. The strong N–S bond is only slightly weakened, and the Re–N bond remains unaltered, as expected. The largest incremental change in overlap population occurs between the two sulfur atoms, which form the new bond.

Although the coupling is a nicely allowed reaction for a $d^4$ electron count, the coupled side is disfavored by 0.4 eV, primarily as a consequence of the destabilization of $1b_2$ along the reaction coordinate. This difference in energy can be further diminished to about 0 eV upon opening the equatorial Cl–Re–Cl angle from 90°. The motion reproduces qualitatively the way $[ReCl_4(N_2S_2)]^-$ deforms. Adding two more electrons, thereby reducing the system causes the reaction to encounter a level crossing and, hence, to become "forbidden".

A similar analysis may be made for the hypothetical coupling of two NS ligands forming a N–N bond instead. This reaction, as shown in Figure 4, emerges in our calculations as, albeit formally allowed, energetically very much uphill. The coupled side is destabilized by 6.1 eV. This is the result of the strong destabilization of $1b_2$, which in turn is due to strong repulsive interactions between the nitrogen atoms. The destabilization of the $1b_2$ orbital, with large coefficients on the atoms that will eventually form a bond, resembles the situation for the reductive elimination of two alkyl ligands from a cis four-coordinate complex.[18] In both cases the reaction is controlled by the evolution of a $b_2$ orbital along the reaction coordinate. A very small HOMO/LUMO gap is indicated for the coupled side, making it even more unstable. Moreover, the gap is sensitive to sulfur parameters, for the two orbitals involved are concentrated on S. A slight change in S

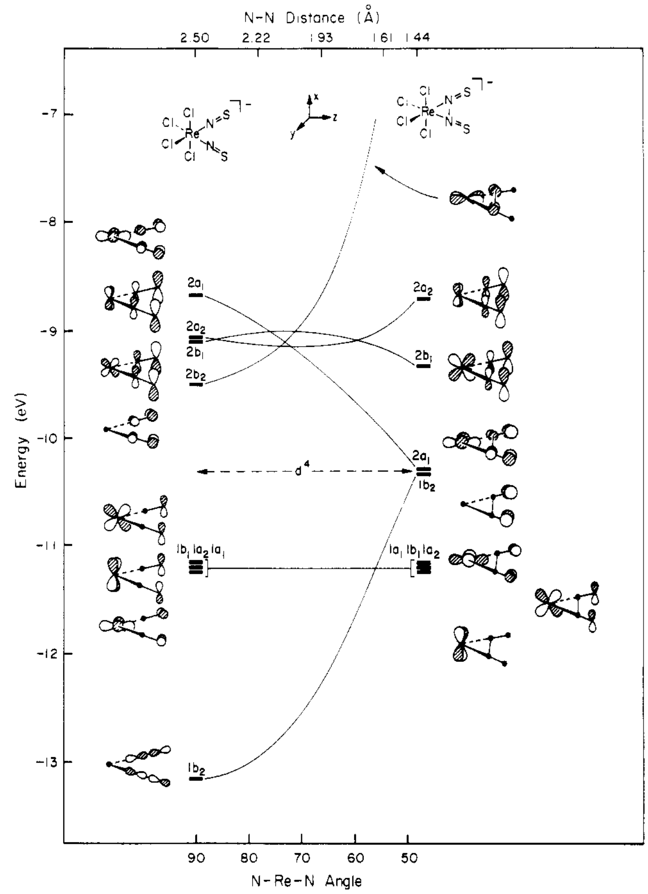


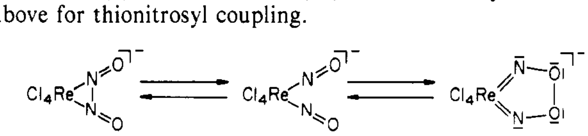

**Figure 4.** Evolution of energy levels of $[ReCl_4(NS)_2]^-$ along an idealized reaction coordinate, forming a N–N bond. Note the N–Re–N angle scale at the bottom and the nonlinear N–N distance scale at the top.

parameters actually leads to a level crossing, a formally forbidden reaction.

## NO/NO Coupling Reaction

With these observations in mind, do the same considerations also apply to the coupling of two nitrosyl ligands? NO/NO coupling reactions have been reported to occur on silica supported chromia. A *cis*-hyponitrite ligand ($N_2O_2$) bonded to the surface has been identified by IR spectroscopy.[19] Coupled $N_2O_2$ dimers were also proposed by Ibach et al.[20a] for interpretation of the spectra of NO adsorbed on Pt(111) and as intermediates in several transition-metal complexes.[20b] In another case, NO ligands combine to form a $N_2O_2$ ligand chelating a platinum atom in $[Pt(PPh_3)_2(N_2O_2)]$ via their oxygen atoms.[21]

We have analyzed the hypothetical pathway of the coupling of two NO ligands in $[ReCl_4(NO)_2]^-$ (**8**)[22] by forming either a N–N bond (**9**) or an O–O bond (**10**) in the same way as described above for thionitrosyl coupling.



**9** **8** **10**

(18) (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Hoffmann, R. In *Frontiers of Chemistry*; Laidler, K. J., Ed.; Pergamon Press: New York, 1982; p 247.

(19) (a) Kugler, E. L.; Kokes, R. J.; Gryder, J. W. *J. Catal.* **1975**, *36*, 142. (b) Kugler, E. L.; Gryder, J. W. *J. Catal.* **1975**, *36*, 152. (c) Kugler, E. L.; Kadet, A. B.; Gryder, J. W. *J. Catal.* **1976**, *41*, 72.

(20) (a) Ibach, H.; Lehwald, S. *Surf. Sci.* **1978**, *76*, 1. (b) Bhaduri, S.; Johnson, B. F. G. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 156. (c) Meyer, C. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1976**, *98*, 1364. (d) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 3325.

(21) Bhaduri, S.; Johnson, B. F. G.; Pickard, A.; Raithby, P. R.; Sheldrick, G. M.; Zuccaro, C. I. *J. Chem. Soc., Chem. Commun.* **1977**, 354.

(22) (a) Mronga, N.; Müller, U.; Dehnicke, K. *Z. Allorg. Allg. Chem.* **1981**, *482*, 95. (b) Miki, E.; Mizumachi, K.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3068.

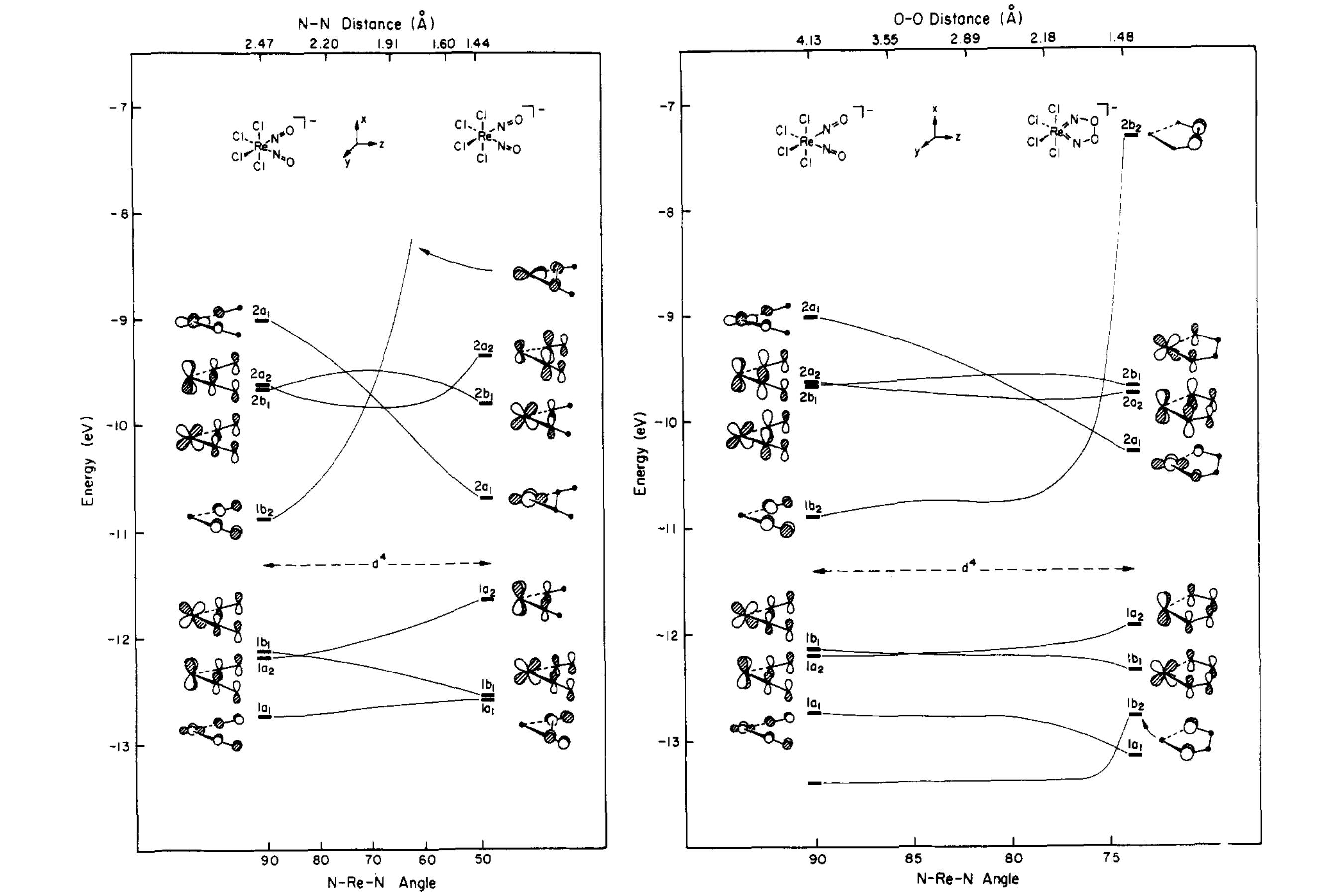



**Figure 5.** Walsh diagram for the coupling of two NO ligands in $[ReCl_4(NO)_2]^-$: (a) involving the formation of a N–N bond; (b) involving the formation of an O–O bond.

**Table II.** Parameters Used in the Extended Hückel Calculations

| atom | orbital | $H_{ii}$, eV | $\zeta_1$ | $\zeta_2$ | $C_1^a$ | $C_2^a$ |
|---|---|---|---|---|---|---|
| Re | 5d | −12.66 | 5.343 | 2.277 | 0.6662 | 0.5910 |
| | 6s | −9.36 | 2.398 | | | |
| | 6p | −5.96 | 2.372 | | | |
| Cl | 3s | −26.3 | 2.183 | | | |
| | 3p | −14.2 | 1.733 | | | |
| N | 2s | −26.0 | 1.950 | | | |
| | 2p | −13.4 | 1.950 | | | |
| O | 2s | −32.3 | 2.275 | | | |
| | 2p | −14.8 | 2.275 | | | |
| S | 3s | −20.0 | 2.122 | | | |
| | 3p | −11.0 | 1.827 | | | |

[a] Coefficients used in the double-$\zeta$ expansion of the d orbitals.

The results are shown in Figure 5. Our calculations reveal that in both modes the coupled sides are much disfavored, **9** by 2.4 eV and **10** by 4.3 eV.

The coupling of nitrosyls thus seems unlikely. What is interesting is that were it possible to remove some of the destabilization, it should be easier to form a N–N bond rather than one between two oxygen atoms. This observation, which is opposite to thionitrosyl coupling described earlier, where a S–S bond is more likely to be formed, is due to the reversal of electronegativity for N/O vs N/S. In this case, the orbital of interest, $2b_2$, as it evolves along the reaction coordinate, is more concentrated on the more electronegative atom. It thus ascends more rapidly in energy.

## Summary

We have analyzed the electronic structure of $[ReCl_4(N_2S_2)]^-$ complexes, in which two thionitrosyl ligands have been coupled to form a five-membered metallacycle. Two possible pathways for thionitrosyl coupling have been investigated. From a Walsh diagram analysis and calculations of the total energy, it appears that coupling of two NS ligands so as to form a S–S bond is more probable than coupling via nitrogen atoms. In an analogous manner, similar pathways for the hypothetical coupling of nitrosyl ligands in $[ReCl_4(NO)_2]^-$ complexes have been examined, leading to the conclusion that coupling of NO ligands is disfavored in general, but might occur via N–N bonding.

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## Appendix

All calculations were performed by using the extended Hückel method[5] with weighted $H_{ij}$'s.[23] The atomic parameters for Re, Cl, N, S, O, C, and H atoms are given in Table II.

For all model compounds, simplified geometries were assumed based on those geometries given in ref 4.

(1) $[ReCl_4(N_2S_2)]^-$: Re–Cl = 2.38 Å; Re–N = 1.77 Å; N–S = 1.52 Å; S–S = 2.59 Å; $Cl_{eq}$–Re–$Cl_{eq}$ = 90°; $Cl_{ax}$–Re–$Cl_{ax}$ = 180°; N–Re–N = 74°; Re–N–S = 151.7°.

(2) Reaction coordinate from $[ReCl_4(NS)_2]^-$ to $[ReCl_4(N_2S_2)]^-$ (S–S bond): N–S, 1.52 Å; N–Re–N, 90 to 74°; Re–N–S, 180 to 151.7°; final S–S bond length, 2.59 Å.

(3) Reaction coordinate from $[ReCl_4(NS)_2]^-$ to $[ReCl_4(N_2S_2)]^-$ (N–N bond): N–S, 1.52 Å; N–Re–N, 90 to 48°; Re–N–S, 180 to 174.86°; final N–N bond length, 1.44 Å.

(4) Reaction coordinate from $[ReCl_4(NO)_2]^-$ to $[ReCl_4(N_2O_2)]^-$ (O–O bond): N–O, 1.17 Å; N–Re–N, 90 to 74°; Re–N–O, 180 to 127.47°; final O–O bond lengths, 1.48 Å.

(5) Reaction coordinate from $[ReCl_4(NO)_2]^-$ to $[ReCl_4(N_2O_2)]^-$ (N–N bond): N–O, 1.17 Å; N–Re–N, 90 to 48.6°; Re–

(23) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

N-O, 180° to 174.29°; final N-N bond length, 1.44 Å.

All angles were varied linearly along the reaction coordinate; bond lengths remained constant.

**Note Added in Proof.** Recently, another coordination compound, $[PPh_4][ReF_2Cl_2(N_2S_2)]$, bearing the $N_2S_2$ ligand has been prepared and its crystal structure has been established.[24] The S-S bond length in this compound (2.429 Å) is slightly shorter than those published previously.[4] It indicates that the potential energy surface for S-S bond length variations is quite shallow.

(24) Dehnicke, K. Personal communication.

Contribution from the Division of Chemical and Physical Sciences, Deakin University, Geelong, Victoria 3217, Australia

# Exchange and Other Reactions Associated with Zinc(II) Dithiocarbamate Oxidation and Reduction Processes Observed at Mercury and Platinum Electrodes in Dichloromethane

A. M. Bond* and A. F. Hollenkamp

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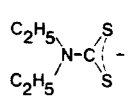
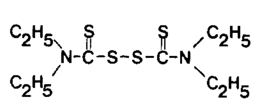
The electrochemical behavior of zinc(II) dithiocarbamate complexes ($Zn(RR'dtc)_2$) has been investigated at both platinum and mercury electrodes and compared with that of the analogous cadmium complexes ($Cd(RR'dtc)_2$). Oxidation at mercury electrodes in the presence of $M(RR'dtc)_2$ (M = Zn, Cd) consists of three reversible processes. The first of these involves an exchange reaction between metal(II) dithiocarbamate and electrode mercury: $M(RR'dtc)_2 + Hg \rightarrow Hg(RR'dtc)_2 + M^{2+} + 2e^-$ (M = Zn, Cd). This reaction is mediated by formation of a bimetallic cation $[MHg(RR'dtc)_2]^{2+}$, small amounts of which were detected on the synthetic time scale associated with bulk electrolysis experiments at a mercury-pool electrode. The remaining two oxidation processes arise from formation of $Hg(RR'dtc)_2$, which is in equilibrium with the bimetallic complex at the electrode surface. At platinum electrodes, oxidation processes are observed at much more positive potentials than at mercury electrodes and yield the thiuram disulfide complexes $[MR_2R'_2tds]^{2+}$. However, for $Zn(RR'dtc)_2$, the more positive oxidation potential ($E_p(Zn)$ = 1.6 V vs $E_p(Cd)$ = 1.3 V vs Ag/AgCl) leads to further oxidation to give an unidentified product. The oxidation products formed at platinum electrodes in bulk electrolysis experiments interact strongly with electrode mercury to give polarographic responses that are similar to those for the oxidation products formed at mercury electrodes, demonstrating the considerable lability of the zinc- (and cadmium-) mercury dithiocarbamate interactions. Reduction processes for $Zn(RR'dtc)_2$ are less affected by the choice of electrode material than are the oxidation processes. At both platinum and mercury electrodes, the major reduction process occurs at very negative potentials (approximately -2 V vs Ag/AgCl) and yields elemental zinc or zinc amalgam, respectively, and free dithiocarbamate. At mercury electrodes, a minor additional reduction pathway involving exchange between $Zn(RR'dtc)_2$ and electrode mercury was noted. The analogous process for $Cd(RR'dtc)_2$ provides the major route for reduction of the cadmium complexes at mercury electrodes. Surprisingly, no reduction of $Cd(RR'dtc)_2$ is observed at platinum electrodes.

The electrochemical behavior of $Hg(RR'dtc)_2$ (RR'dtc = dialkyldithiocarbamate; see structure I)[1,2] and $Cd(RR'dtc)_2$[3] complexes has been described in some detail, particularly at mercury electrodes. In contrast, while the chemically related $Zn(RR'dtc)_2$



$Et_2dtc^-$

I



$Et_4tds$

II

compounds are used widely in the chemical industry[4,5] and a great deal is known about their general chemical reactivity and physical chemistry, little is known of their redox properties. Electrochemical oxidation of $Zn(Et_2dtc)_2$ in acetone (0.1 M $Et_4NClO_4$) at a platinum electrode has been shown to give a poorly defined, chemically irreversible response at a very positive potential.[6] The product(s) was (were) not isolated, but one was postulated to be a thiuram disulfide ($Et_4tds$, structure II) complex of zinc(II), $[Zn(Et_4tds)]^{2+}$, on the basis of extrapolation from the observation that related species are formed via chemical (halogen) oxidation of zinc(II) dithiocarbamates.[7] That is, oxidation at solid electrodes has been assumed to be ligand based. The only other report on electrochemical oxidation processes concerns the polarographic behavior of $Zn(pyrrdtc)_2$ at positive potentials in methyl isobutyl ketone (0.1 M $Bu_4NClO_4$).[8] A single oxidation wave at -0.05 V vs the saturated calomel reference electrode was shown to be a chemically reversible two-electron step. The proposed mechanism involved an exchange reaction between the zinc complex and electrode mercury to form $Hg(pyrrdtc)_2$ and zinc(II) ions. This is analogous to the mechanism reported for $Cd(RR'dtc)_2$.[3]

The reduction of $Zn(RR'dtc)_2$ complexes at mercury electrodes has been addressed briefly.[8,9] In methyl isobutyl ketone[8] and dimethylformamide[9] a reduction process occurs at very negative potentials, which has been proposed as a two-electron step leading to the formation of zinc amalgam and free dithiocarbamate ion. However, as in the oxidation studies cited above, controlled-potential electrolysis experiments were not undertaken so that conclusive evidence regarding the products (and intermediates) of redox processes is not available.

The purpose of this study is to present a more complex view of the electrochemical behavior of $Zn(RR'dtc)_2$ complexes at both mercury and platinum electrodes and to compare results with known and new information now available on electrochemical processes for the corresponding cadmium(II) dithiocarbamate complexes. The detailed investigations reveal hitherto unknown complexities and the formation of a new class of bimetallic complexes.

(1) Bond, A. M.; Colton, R.; Dillon, M. L.; Moir, J. E. *Inorg. Chem.* **1984**, *23*, 2883.
(2) Bond, A. M.; Colton, R.; Hollenkamp, A. F.; Hoskins, B. F.; McGregor, K. *J. Am. Chem. Soc.* **1987**, *109*, 1969.
(3) Bond, A. M.; Colton, R.; Dillon, M. L.; Hollenkamp, A. F.; Moir, J. E. *Inorg. Chem.* **1985**, *24*, 1591.
(4) Hassall, K. A. *The Chemistry of Pesticides. Their Metabolism, Mode of Action and Uses in Crop Protection*; Macmillan: London, 1982; p 197.
(5) Morrell, S. H. In *Rubber Technology and Manufacture*, 2nd ed.; Blow, C. M., Hepburn, C., Eds.; Butterworth Scientific: London, 1982; p 171.
(6) Nieuwpoort, A.; Dix, A. H.; Porskamp, P. A. T. W.; Van der Linden, J. G. M. *Inorg. Chim. Acta* **1979**, *35*, 221.
(7) Brinkhoff, H. C.; Grotens, A. M.; Steggerda, J. J. *Rec. Trav. Chim Pays-Bas* **1970**, *89*, 11.
(8) Ichimura, A.; Kitagawa, T.; Kitamura, H.; Morimoto, Y. *Bunseki Kagaku* **1984**, *33*, E503.
(9) Budnikov, G. K.; Ulakhovich, N. A.; Toropova, V. F. *Talanta* **1978**, *25*, 263.

0020-1669/90/1329-0284$02.50/0 