considerably larger for the sulfoxide system (0.58) than it is for the thioether (0.14). This is the largest value of α so far observed in the reactions of platinum(II) complexes with heterocyclic amines, now covering the range $\sim 0 < \alpha < 0.58$, and is surpassed only by the value of 0.89 observed[12] in the displacement of Cl^- from cationic $[Au(5\text{-}NO_2\text{-}1,10\text{-phen})Cl_2]^+$. It is clear now that the statement made many years ago[6] that the rate of nucleophilic substitution at platinum(II) is essentially independent of the basicity of the entering amine is no longer valid.

These results are consistent with the observation that the cis effect of a thioether is less than that of a sulfoxide and is characterized by a lower nucleophilic discrimination ability.[13]

The steric retardation effect is higher in the sulfoxide system, especially in the case of the racemic form of the ligand (Δ = 2.31, 1.8 as compared to 1.6 for the thioether complex), and it is worth noting that the retardation resulting from meta substitution is only apparent in the sulfoxide system. The higher discrimination (α) and larger Δ suggest strongly that bond making is more important in the sulfoxide system than in the thioether system.

In any comparison of the absolute reactivity of the bis(thioether) and bis(sulfoxide) complexes, we must take account of the difference in the leaving ability of the two types of donor. The most obvious difference between the displacement of the bis(sulfoxide) and the bis(thioether) is that in the former case ring opening is much faster than the subsequent loss of the monodentate ligand, whereas the loss of the monodentate thioether is fast compared to ring opening which becomes the rate-determining stage. On the basis that a second stage less than 5 times faster than ring opening could cause noticeable departure from a simple first-order kinetic rate law, it can be assumed that the k_2 for the loss of the monodentate thioether is greater than 5×10^{-2} M^{-1} s^{-1}. This is some 500 times faster than the observable displacement of the monodentate bis(sulfoxide) and therefore might be considered to be a measure of the *minimum* difference in the leaving-group effect of the two donor species.

The ring-opening rate constants, on the other hand, differ by a factor of 1 order of magnitude only, in spite of the fact that the cis effect of a single thioether is less than that of the corresponding sulfoxide. It is clear therefore that, in this case, leaving-group effects and electronic cis effects cannot alone account for the observed behavior. It is known, for example, from preparative chemistry, that one of the two sulfoxide ligands in *cis*-$[Pt(Me_2SO)_2Cl_2]$ is readily replaced by amines,[14] while a single Me_2SO cannot readily be replaced in aqueous solution. Wayland, in his study of the thermal isomerization of $Pt(R_2SO)_2Cl_2$ has shown[15] that the labilities of cis and trans pairs of sulfoxides are of similar magnitude in spite of the large difference in the trans effect of Cl and R_2SO. Furthermore, it has been shown that for a sterically hindered sulfoxide *i*-Pr_2SO the trans isomer is obtained in the preparative reaction ($PtCl_4^{2-} + R_2SO$), whereas the stable product of the analogous reaction with Me_2SO is the cis isomer,[14] the trans isomer appearing as an unstable intermediate that can be isolated only under certain conditions.[16] All of these observations indicate that mutual steric repulsion may play a very important part in promoting the unusual lability of a cis pair of sulfoxides and indeed may be as important as the mutual trans effect of sulfoxides. This problem is now being examined in depth and will be reported elsewhere.

Finally it is worth noting that in this aprotic, nonpolar solvent, the chloride which is under the moderate trans effect of the sulfoxide, and is generally considered to be a much more labile ligand, is retained in the product while the neutral ligand is lost (see note in Results and Discussion).

Preliminary experiments in methanol show that iodide and thiocyanate displace the chloride, and the ratio of the reactivity of the two isomers is as found here for their reactions with unhindered amines. On the other hand basic nucleophiles, e.g., N_3^-, CH_3O^-, and RNH_2, lead to a general decomposition of the substrate. This is another example of the way in which the ligand displaced from a complex can be determined by the solvent and the entering nucleophile.

Acknowledgment. We thank the Italian Council for Research, CNR, Rome, for financial assistance in a bilateral project of research and Mr. Giampaolo Silvestri for technical assistance.

Registry No. [*meso*-1,2-Bis(phenylsulfinyl)ethane]dichloroplatinum(II), 41233-57-2; [*rac*-1,2-bis(phenylsulfinyl)ethane]dichloroplatinum(II), 41276-66-8; py, 110-86-1; 4-Cl(py), 626-61-9; 4-Me(py), 108-89-4; 4-Et(py), 536-75-4; 3-Me(py), 108-99-6; 3,4-Me_2(py), 583-58-4; 3,5-Me_2(py), 591-22-0; 2-Me(py), 109-06-8; 2,4-Me_2(py), 108-47-4; *cis*-$[Pt(py)_2Cl_2]$, 15227-42-6; *trans*-$[Pt(py)_2Cl_2]$, 14024-97-6.

---

(12) L. Cattalini, A. Doni, and A. Orio, *Inorg. Chem.*, 6, 280 (1967).
(13) M. Bonivento, L. Cattalini, G. Marangoni, G. Michelon, A. P. Schwab, and M. L. Tobe, *Inorg. Chem.*, 19, 1743 (1980).
(14) P. D. Braddock, R. Romeo, and M. L. Tobe, *Inorg. Chem.*, **13**, 1170 (1974).
(15) J. H. Price, J. P. Birk, and B. B. Wayland, *Inorg. Chem.*, **17**, 2245 (1978).
(16) P. D. Braddock and M. L. Tobe, unpublished results.

Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Bonding in the Syn and Anti Isomers of Di-μ-sulfido-bis(sulfido(1,2-dimercaptoethanato)molybdate(V)) Anions

TRAVIS CHANDLER, DENNIS L. LICHTENBERGER,* and JOHN H. ENEMARK*

Received May 14, 1980

The electronic structure and bonding interactions in the syn, anti, and closed isomers of $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ are examined and compared through extended Hückel and Fenske–Hall molecular orbital calculations. A molybdenum–molybdenum bonding interaction is found to account for the diamagnetism of the complexes and to be important in determining the relative stability of the isomers. The predicted stabilities are syn > closed > anti.

Current interest in molybdenum enzymes and in molybdenum desulfurization catalysts has stimulated research on the coordination chemistry of sulfur-rich molybdenum complexes. One particularly stable class of compounds is di-μ-sulfido-

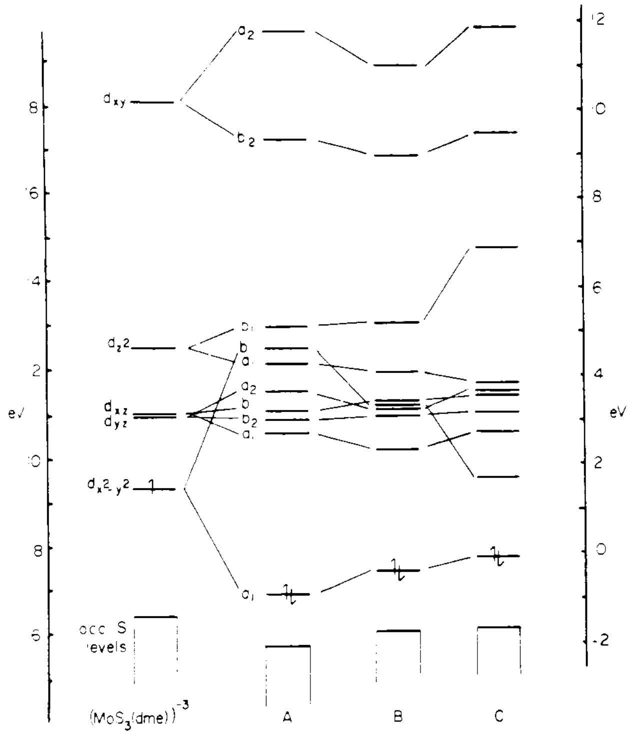
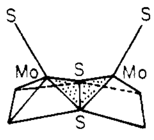
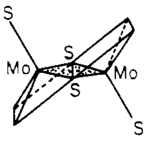


Figure 1. Molecular orbital diagrams of $[MoS_3(S_2C_2H_4)]^{3-}$ and the three isomers of $[Mo_2S_4(S_2C_2H_4)_2]^{2-}$. The energy scale of the monomer (left) and the scale of the three dimers (right) are aligned according to the diagonal Mo 4d orbital energies.

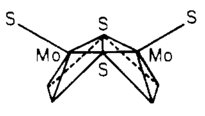
bridged binuclear molybdenum(V) compounds which have been observed in both syn (A) and anti (B) stereochemistries.[1,2]



A



B



C

Although molybdenum(V) has a $4d^1$ electron configuration, both types of dimers are diamagnetic. It has generally been assumed that the diamagnetism of $Mo_2(\mu\text{-}S)_2$ complexes results from a direct molybdenum–molybdenum bond.[3] However, it has been pointed out that the similarity of the Mo–S_b–Mo angles in the syn and anti isomers is also compatible with strong antiferromagnetic coupling through the bridging sulfido groups.[2]

Recently,[1,2] we determined the structures of both the syn and anti isomers of $Mo_2S_4(dme)_2^{2-}$, where dme is the dianion 1,2-dimercaptoethane. These structures are the first example of syn and anti isomers being isolated with the same set of ligands. The relative simplicity of the dme ligand enables the electronic structures of the two isomers to be investigated by molecular orbital calculations in order to assess the nature of the diamagnetism of these isomers and their relative stabilities. The electronic structure of another proposed conformation of the syn isomer, the "closed" conformation (C), has also been examined in this work. Conformation C has never been observed in a crystal structure.

The approximate but nonparametrized Fenske–Hall method was used for the molecular orbital calculations.[4] Atomic coordinates for the atoms for isomers A and B were obtained from the crystal structures.[2] The atomic coordinates for the hypothetical isomer C were obtained by rotating each half of isomer A by 32° about the axis through the bridging sulfido ligands. Each atom in C has the same bond distances and angles with adjacent atoms as in A. Basis functions for sulfur and carbon atoms were Clementi's double-ζ functions,[5] curve fit as described before.[4] Hydrogen 1s functions were single-ζ functions with an exponent of 1.2. Mo(2+) functions were used as before.[6] Comparison calculations were performed with the same atomic coordinates by the extended Hückel method[7] by using contracted 4d functions for Mo obtained from Hoffmann.[8] Contour maps of the molecular orbitals were generated by the program MOPLOT.[9]

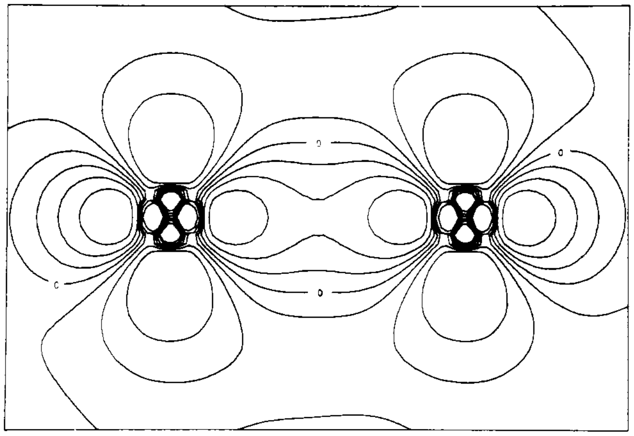


Figure 2. Plot of the HOMO of isomer A in the *xy* plane. The contour levels of ψ are 0.125, 0.070, 0.0313, 0.0, −0.0313, −0.070, and −0.125.

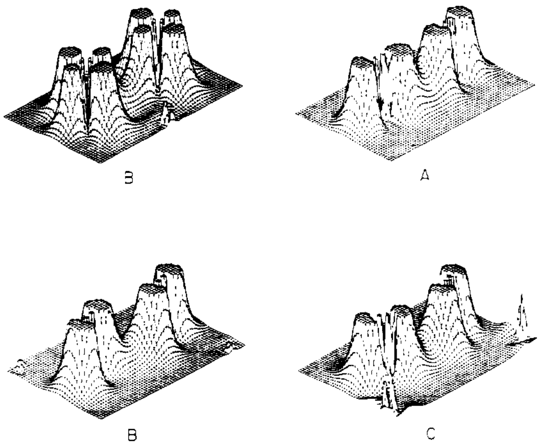


Figure 3. Electron density maps of the HOMO's of isomer B in the plane of the molybdenum and bridging sulfur atoms (top left) and isomers A, B, and C in the plane of the molybdenum and terminal sulfur atoms.

In order to show how the metal levels are ordered in the absence of another metal center, we also performed calculations on the $[MoS_3(dme)]^{3-}$ fragment. The local coordinates for the Mo atom have the *z* axis pointed toward the terminal sulfur and the *x* and *y* axes lying between the basal sulfur atoms. The resultant levels have the expected splitting for approximate C_{4v} symmetry (see first column, Figure 1), with

---

(1) G. Bunzey, J. H. Enemark, J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, **99**, 4168 (1977).

(2) G. Bunzey and J. H. Enemark, *Inorg. Chem.*, **17**, 682 (1978).

(3) See, for example, D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3721 (1967).

(4) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).

(5) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

(6) T. F. Block, R. F. Fenske, D. L. Lichtenberger, and F. A. Cotton, *J. Coord. Chem.*, **8**, 109 (1978).

(7) J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann, *QCPE*, **10**, 344 (1977).

(8) B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979).

(9) D. L. Lichtenberger, R. F. Fenske, *QCPE*, **10**, 284 (1975).

Table I. Calculated Mulliken Charge Analysis of the Isomers by the Fenske-Hall Method

	A	B	C
Mo–Mo 4d overlap population in HOMO	0.048	0.028	0.030
Mo–Mo 4d total overlap population	0.087	0.061	0.078
bridging sulfur charge	0.572–	0.595–	0.586–
terminal sulfur charge	0.580–	0.612–	0.612–

d_{xy} most destabilized and d_{z^2} also substantially destabilized. The d_{xz} and d_{yz} orbitals are essentially degenerate, and $d_{x^2-y^2}$ lies lowest.

The same local coordinate system for the molybdenum atoms was maintained in the calculations on the binuclear isomers so that the $d_{x^2-y^2}$ orbitals are directed for σ overlap between the metals. The relative stability and interaction of the metal levels follow qualitative expectations. The highest occupied molecular orbital (HOMO) for all three isomers is primarily the σ-bonding combination of the metal $d_{x^2-y^2}$ orbitals. The orbital contours for isomer A are shown in Figure 2. Comparison of the molecular orbitals of the three isomers shows that isomer A has maximum overlap of the $d_{x^2-y^2}$ orbitals with one another. This is reflected in the splitting of the $d_{x^2-y^2}$ levels in the molecular orbital diagram (Figure 1). It is also observed in the buildup of electron density between the Mo centers in the electron density diagrams in Figure 3.

The extended Hückel and Fenske–Hall calculations predict the same general character for the HOMO in the three isomers. The high negative charges on the bridging and terminal sulfur atoms (Table I) destabilize the sulfur basis levels so that the resulting metal–sulfur antibonding levels are too high in energy to be the HOMO. Inclusion of sulfur 3d levels had very little influence on the results. The total calculated metal–metal overlap populations for A, B, and C are about the same as found[6] for the δ bond in $Mo_2(SO_4)_4{}^{2-}$. This metal–metal bonding interaction is not large but is sufficient to explain the diamagnetic behavior without invoking a strong antiferromagnetic coupling mechanism.

The calculations indicate that the metal–metal interaction is also significant in determining the relative stability of the isomers as based on total energy analysis. Although it must be remembered that total energy analysis at this level of calculation is extremely approximate, it is worth noting that both the extended Hückel and Fenske–Hall[10] approaches indicate that isomer A is the most stable and that isomer C is more stable than isomer B. This is the same order as the *total* Mo–Mo 4d overlap populations given in Table I.

It is interesting that the order of isomer stabilities and Mo–Mo overlap populations for B and C does not follow the order of $d_{x^2-y^2}$ interactions and HOMO stabilities as shown in Figure 1. This is because the structure of isomer C is such that the reduction in Mo–Mo $d_{x^2-y^2}$ interaction is partly compensated by an improved d_{z^2} (and d_{xz}) interaction. The interaction of the empty d_{z^2} orbital with the HOMO and the filled orbitals involving bridging S atoms is complex but is evidenced by the destabilization of the empty d_{z^2} (b_1) orbital in Figure 1 and the overlap populations in Table I. The Mo–Mo 4d overlap populations in the HOMO's of B and C are nearly the same, but the Mo–Mo overlap population in the lower filled orbitals is greater for C than for B. These lower orbitals account for a substantial portion of the Mo–Mo interaction in all isomers.

Previous electrochemical studies on $[Mo_2S_4(dme)_2]^{2-}$ have shown that isomers A and B both undergo irreversible two-electron oxidations.[1] Figure 1 indicates that such an oxidation would destroy the metal–metal bonding in the HOMO. Reversible one-electron reductions have been found[1] for isomers A and B of $[Mo_2S_4(dme)_2]^{2-}$ and for other related syn complexes containing the $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ fragment.[11] Figure 1 suggests that reduction of A and B would place an additional electron into molecular orbitals involving weak π or δ interactions between the d_{xz} (or d_{yz}) orbitals. For C an additional electron is predicted to occupy the σ-antibonding combination of the $d_{x^2-y^2}$ orbitals of the two Mo atoms.

At present no experimental data are available on the relative stabilities of isomers A, B, and C, and there are no experimental studies of the interconversion of these isomers. This lack of experimental data is due in part to the absence of good synthetic routes to $[Mo_2S_4(dme)_2]^{2-}$ and related complexes containing the $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ fragment. However, the recent development of efficient routes to such compounds[12] should make it possible to experimentally probe the nature of the bonding in the complexes and the relative stabilities which have been predicted here for isomers A, B, and C.

Acknowledgment. We wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Institutes of Environmental Health Sciences (Grant ES-00966), and the University of Arizona Computer Center for partial support of this research. Dennis L. Lichtenberger is an Alfred P. Sloan Foundation Fellow, 1979–1981.

Registry No. *syn*-$[Mo_2S_4(dme)_2]^{2-}$, 65137-00-0; *anti*-$[Mo_2S_4(dme)_2]^{2-}$, 65045-65-0; $[MoS_3(dme)]^{3-}$, 75311-42-1.

---

(10) D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 366 (1978).

(11) F. A. Schultz, V. R. Ott, D. S. Rolison, D. C. Bravard, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **17**, 1758 (1978).

(12) K. F. Miller, A. E. Bruce, K. Joyce, J. L. Corbin, and E. I. Stiefel, Abstracts, 178th National Meeting of the American Chemical Society, Washington, D.C., Sept 1979, No. INOR 240; K. F. Miller, A. E. Bruce, J. L. Corbin, S. Wherland, and E. I. Stiefel, *J. Am. Chem. Soc.*, **102**, 5102 (1980).