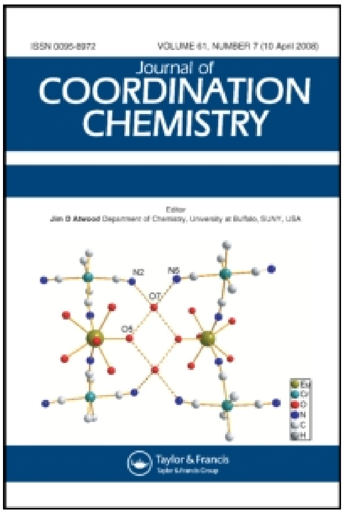

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SHORT COMMUNICATION
The Electronic Structures of the Tetra(μ-Sulfato) Dimolybdenum Ions

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An approximate but nonparameterized Hartree-Fock-Roothaan type MO calculation has been made for the ground state of each of the species $Mo_2(SO_4)_4^{4-}$ and $Mo_2(SO_4)_4^{3-}$ and the results are compared with available experimental data bearing on the electronic structures of these ions.

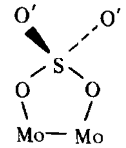
In order that the qualitative picture of quadruple bonds, originally given in 1965,[1] be developed into a more detailed and comprehensive description of the electronic structures of species containing such bonds, and closely related ones, two things are necessary. One is experimental data, especially spectroscopic data, with which to anchor all quantitative calculations to reality. The second is a body of theoretical techniques capable of providing quantitative descriptions of the electronic structures of such complex systems. The ideal way to proceed is to carry out both the experimental and computational studies in such a manner that they interact synergically. We have been engaged in such a program for several years and this paper is one of several reports we are now prepared to make on our progress.

Theoretical techniques capable of dealing with the electronic structures and spectra of polyatomic species containing metal atoms from the second and third transition series have only become available within recent years. It is important to note that when species with two (or more) tightly bonded metal atoms at the center are concerned, the various parameterized variations of crystal or ligand field theories are entirely inapplicable. It was first demonstrated[2,3] that calculations by the SCF-Xα-SW procedure are feasible. More recently, Veillard and coworkers[4] have carried out *ab initio* Hartree-Fock calculations on several species containing metal atoms (Mo,Tc) from the second transition series and it has been found[5] that these results and those obtained by the SCF-Xα-SW procedure on $Mo_2Cl_8^{4-}$,[2] $Mo_2(O_2CH)_4$[6] and $Tc_2Cl_8^{3-}$,[7] agree well as to the ordering and atomic provenance of the MO's. A third practical possibility for obtaining meaningful bonding descriptions of the species under discussion is the approximate Hartree–Fock method developed by Fenske,[8] particularly in the form in which it was given, and programmed, in 1972 by Hall and Fenske.[9] This method employs some approximate (but *not* empirical or parametric) procedures for evaluating multicenter integrals. Its advantage over the SCF-Xα-SW and, a fortiori, the full Hartree-Fock method is that it is very much faster and very much cheaper. Its advantage in these respects is so great that for many purposes it could well be the method of choice, certainly for an initial examination of a given problem.

In this communication we describe some calculations done several years ago on $Mo_2(SO_4)_4^{4-}$ and $Mo_2(SO_4)_4^{3-}$. Since these calculations were completed, experimental work[10-14] bearing on the electronic structures of these compounds has been conducted so that there now exists a significant body of data to allow a meaningful evaluation of the computational results.

The atomic coordinates of $Mo_2(SO_4)_4^{4-}$ and $Mo(SO_4)_4^{3-}$ for the calculations were taken from the available crystal structures of these ions.[10] The essential geometric features are summarized in *Figure 1*. The same atomic coordinates were used for both the $Mo_2(SO_4)_4^{4-}$ and $Mo_2(SO_4)_4^{3-}$ calculations. It is not anticipated that bond distance changes of ≃0.05 Å will seriously alter the results. Furthermore, any differences between the two calculations may then be entirely attributed to electronic effects. Basis functions were selected in the usual manner.[9] The sulfur and oxygen functions were taken from Clementi.[15] The molybdenum functions were provided by Richardson.[16] The outer valence atomic basis functions were represented by double zeta expansions, and the inner functions were reduced to single zeta form. The exponents for the molybdenum 5s and 5p functions were selected for maximum overlap with the bonded oxygen atoms (2.0 and 1.8, respectively). Outer functions are orthonormal by the Gram–Schmidt criterion with inner functions. The atomic functions were chosen to be consistent with the net atomic charges for the atoms, excluding the 5s and 5p populations on molybdenum. Thus the S(+3), O(−1) and Mo(+2) functions were used.

The results of the calculations are most easily interpreted by first considering the orbital interactions within the $(SO_4)^{2-}$ units and the Mo_2 unit. Preliminary calculations were carried out on the $(SO_4)^{2-}$ ion at the geometry of this moiety in the complex. The highest occupied molecular orbitals (HOMOs) of $(SO_4)^{2-}$ are a closely grouped set of eight orbitals with 80–100% oxygen p_π character (π with respect to the oxygen-sulfur sigma bond). All other occupied valence orbitals represent the S–O sigma bonds, and are much lower in energy. The only unoccupied orbitals resulting from a minimal valence basis calculation of this ion are the anti-bonding sigma orbitals, which are very high in energy. The qualitative description of the d-orbital interactions in the Mo_2 unit is straightforward. The Mo 4d functions combine to form the σ, π, and δ types of two-center orbitals, and it may be expected that the magnitude of the interaction between the metal functions will decrease in the order $\sigma > \pi > \delta$.



Internuclear Distances		Angles	
Mo–Mo	2.11 Å	Mo-Mo–O	94.2°
Mo–O	2.136 Å	Mo–O–S	122.4°
S–O	1.51 Å	O–S–O	106.8°
S–O'	1.44 Å	O'–S–O'	112.5°

FIGURE 1 Geometry of the $Mo_2(SO_4)_4$ unit. The positions of the other sulfate ligands are generated by four-fold rotation about the Mo–Mo axis.

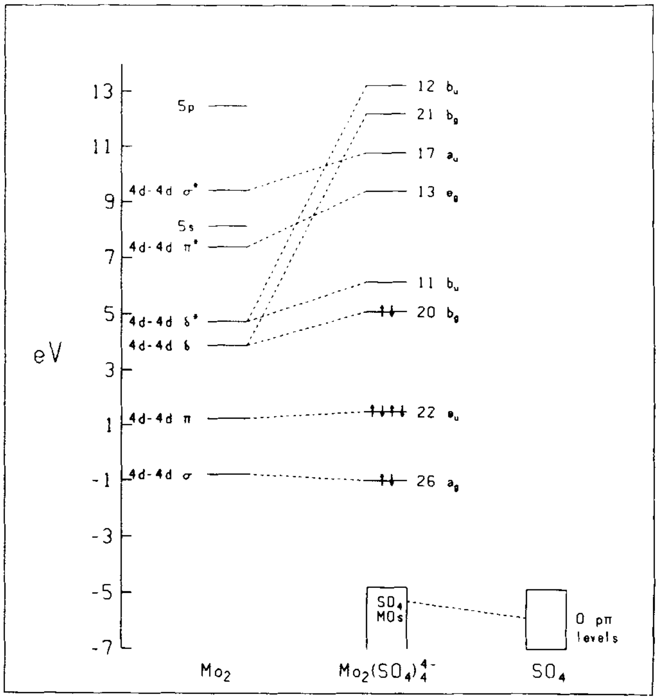


FIGURE 2 Correlation between the orbitals of Mo_2 and SO_4^{2-} in $Mo_2(SO_4)_4^{4-}$

A molecular orbital diagram of the interactions between Mo_2 and the four SO_4 ligands is shown in Figure 2 for the $Mo_2(SO_4)_4^{4-}$ complex. In this diagram, only the $21b_g$ and $12b_u$ molecular orbitals exhibit significant interaction between Mo_2 and $(SO_4)_4$. These orbitals are 82% Mo $4d_{x^2-y^2}$ (δ and δ^* between the molybdenum atoms) and are the virtual antibonding counterparts of the sigma bonds with the oxygen atoms of $(SO_4)_4$. All other orbitals are more than 90% pure metal or pure sulfate. All of the predominantly metal levels are slightly destabilized by interaction with the SO_4 groups, and the metal σ

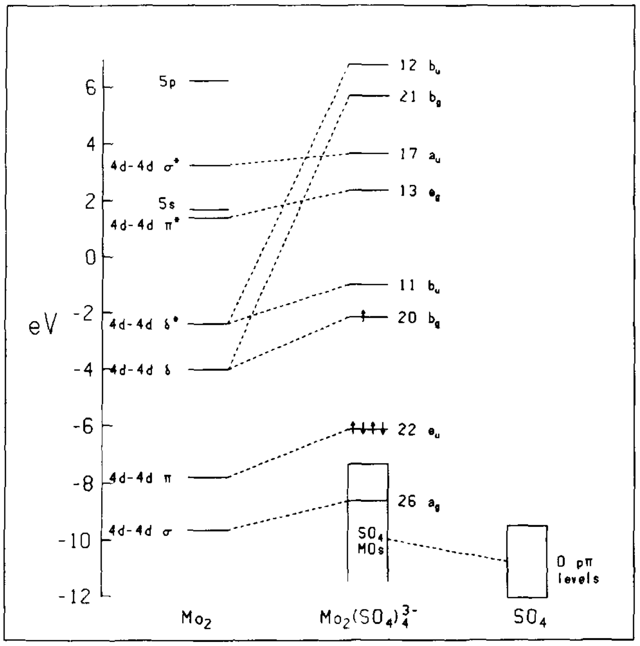


FIGURE 3 Correlation between the orbitals of Mo_2 and SO_4^{2-} in $Mo_2(SO_4)_4^{3-}$

and σ* orbitals are slightly stabilized by inclusion of the 5s and 5p basis functions, but the qualitative order of these levels is not altered. The highest occupied orbitals are the $26a_g$, $22e_u$ and $20b_g$. These represent the metal σ, π, and δ bonds, and hence the calculations indicate a quadruple metal–metal bond.

The δ interaction is not large. The energy separation between the $20b_g$ (δ) and $11b_u$ (δ*) levels is only 1.06 eV. This bond contributes 0.08 e^- to a total metal–metal overlap population of 0.85 e^-.

The effects of removing one electron from the $20b_g$ (δ) orbital are shown in the molecular orbital diagram of $[Mo_2(SO_4)_4]^{3-}$ in Figure 3. All of the metal levels are stabilized with respect to the sulfate levels, and, as a consequence, the interactions between between the metal levels and the sulfate levels are increased. The stabilization of the metal is such that the metal–metal sigma bond is now lower in energy than some of the sulfate orbitals. Nonetheless, the orbital description of the complex is not changed. The metal–metal d bond overlap population is reduced to 0.81 e^-, entirely by the loss of a single electron from the δ bond.

The effects of certain approximations in the calculational procedure on these molecular orbital diagrams require comment. For instance, the orbital energies will be somewhat different with full treatment of the two-center interactions, and with a treatment of one-center terms that does not require degeneracy of the metal d functions. However, because of the small degree of mixing between the metals and the sulfate ligands, and because the metal d functions which contribute to the occupied valence orbitals have very similar populations (1.00 ± .05 e^-), it is not anticipated that our qualitative description will change significantly. It is also worth mentioning that since the Fenske–Hall procedure is simply an approximate Hartree–Fock–Roothaan method, it may well be expected to have the same limitations, namely that without CI an incorrect ground state may result for a 1st transition series system, as happened for dichromium tetraacetate.[4, 17–19] The effects of counter-ions, weakly bound waters of hydration, etc., also have not been included in these calculations. Such interactions with the $[Mo_2(SO_4)_4]^{n-}$ ions may be expected to stabilize some orbitals with respect to others. However, as the calculations on the (4–) and (3–) ions have shown, only a severe alteration of the molecular potential will significantly change the orbital description for these complexes.

The results of the present calculations are consistent with the known properties of these complexes. In particular, the lowest energy electronic transition for $Mo_2(SO_4)_4^{4-}$ is δ → δ*[12] and the unpaired electron in $Mo(SO_4)_4^{3-}$ is known to have axial symmetry and is evenly distributed between the molybdenum nuclei.[10] The 0.05 Å greater Mo–Mo distance in the (3–) ion compared to the (4–) ion is completely consistent with the decrease in Mo–Mo 3d overlap population from 0.85 e^- to 0.81 e^- resulting from removal of a single δ-bonding electron.

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