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Fe–Mo–S complexes in the light of the molecular orbital theory

Ludmiła Szterenberg * and Bogusława Jeżowska-Trzebiatowska
Institute of Chemistry, University of Wrocław, 50-383 Wrocław, F. Joliot-Curie 14 (Poland)

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Abstract

The electronic structure of a series of Fe-Mo-S compounds has been calculated by use of Fenske–Hall and Extended Hückel methods. The applicability of both methods to the systems studied has been evaluated. The electronic structure of MoS_4^{2-} as a bidentate or as a tetradentate bridge ligand is discussed. On the basis of the two-center overlap population, the roles and the strengths of the metal–metal and metal–ligand bonds have been determined. The redox and other physicochemical properties of the Fe–Mo–S clusters are discussed.

Introduction

The burgeoning interest in iron–molybdenum–sulfur complexes and their tungsten counterparts arises in large measure from recent spectroscopic studies of the Fe–Mo nitrogenase proteins and their associated Fe–Mo cofactor. The results of these investigations point to the existence of an Fe–Mo–S cluster as yet in completely defined in terms of composition and structure and not encountered in any other biological system or as product of chemical synthesis. The complexes with $[MoS_4]^{2-}$ group as ligand [1–5], show some resemblance to biological clusters (as deduced from the published experimental data [4,6–12]). Thus an examination of the electronic structure and the bonding properties of Mo–Fe–S complexes have theoretical significance. The electronic structures of some of the systems have already been calculated by use of quantum chemistry methods [1,13–32].

We have studied the theoretical aspects of the iron–molybdenum–sulphur complexes obtained by chemical synthesis. The systems of our interest can be classed into two groups: the $[L_2FeMoS_4]^{2-}$ complexes (where L = NO, Cl, PhS) and the trinuclear $[(PhS)_2FeS_2FeMoS_4]^{3-}$, in which the $[MoS_4]^{2-}$ ion plays the role of bidentate ligand, and the complexes such as $[Cl_2FeMoS_4FeCl_2]^{2-}$) in which the $[MoS_4]^{2-}$ anion plays the role of tetradentate ligand. To investigate the electronic structure of these complexes we applied two different methods: the Extended

Hückel method (EH) [33–34] and the parameter-free semiquantitative Fenske–Hall method [35].

Computational details

The electronic structure of the iron–molybdenum–sulfur complexes was studied by use of Fenske–Hall LCAO MO and EH methods. A number of approximations were applied: Throughout the EH Clementi wave functions were used. The diagonal matrix elements of the effective Hamiltonian were approximated by valence orbital ionization potentials, and the off-diagonal matrix elements were approximated by the Wolfsberg–Helmholz expression. Parameters for the metal atom and for the ligand were taken from the literature [36–38]. An approximation to the Hartree–Fock–Roothaan technique, the Fenske–Hall method has been described [35]. The method is devoid of adjustable or empirical parameters, so that the results of a calculation (eigenvalues and eigenvectors) have been determined completely from the molecular geometry and from the basis functions. The basis functions applied were the Hartree–Fock–Roothaan atomic functions for free atoms or ions. They were chosen so as to make them consistent with the Mülliken charge and the electronic configuration of each atom under study. The basic set contained nd, $(n+1)s$, $(n+1)p$ AO's as valence orbitals for M^{1+}; all inner AO's were treated as frozen core orbitals [35,39]. The same procedure was applied to ligand atom. Analytical expressions for the functions were taken from ref. 40.

The geometry of the complexes was based on their structural determinations ($[NO)_2FeMoS_4]^{2-}$ [41], $[(SPh)_2FeMoS_4]^{2-}$ [42], $[Cl_2FeMoS_4]^{2-}$ [43], $[(Cl_2Fe)_2MoS_4]^{2-}$ [44]). For $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$ the structure proposed by Averill [45] was assumed, with separations equal to those in the $[(PhS)_2FeMoS_4]^{2-}$ complex [42]. The Fe–Fe bond lengths were assumed to be 2.69 Å. The basis and the local coordinate systems, assumed for calculations by the Fenske–Hall method are shown in Fig. 1. For the EH calculations the direction of the local coordinates is consistent with the direction of the fundamental system of coordinates and corresponds to the system assumed in the Fenske–Hall method (Fig. 1).

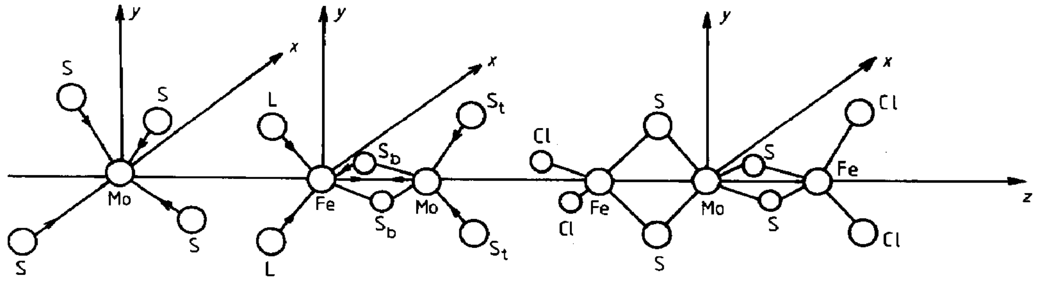


Fig. 1. The geometry and the coordination system of $[MoS_4]^{2-}$ ion and $[L_2FeMoS_4]^{2-}$, $[(Cl_2Fe)_2MoS_4]^{2-}$ complexes.

Discussion

Our studies were focused on:

(1) Comparing the electronic structure and the character of the $[MoS_4]^{2-}$ ion as the tetradentate bridge ligand and as the bidentate ligand.

(2) Determining the electronic structure of the Fe–S–Mo group in the various complexes.

(3) The effect of the terminal ligands on the structure, character and stability of the Fe–S–Mo group.

(4) The role of metal–metal bonding in the systems studied.

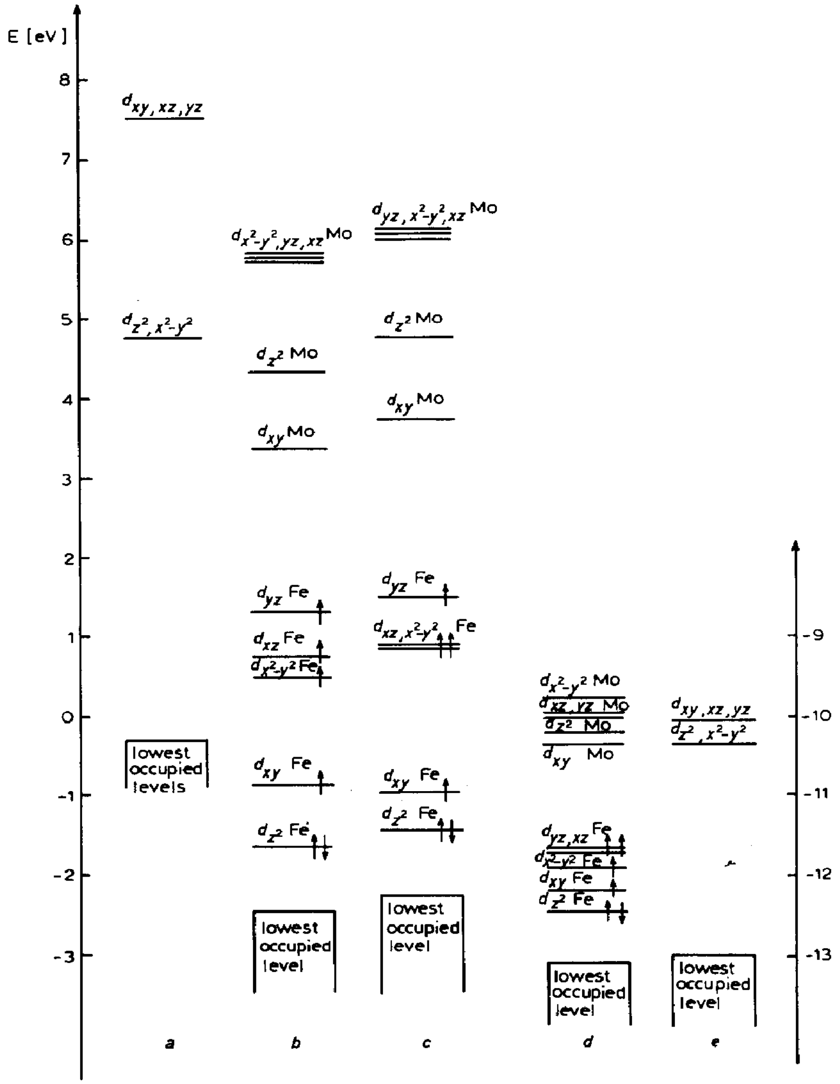


Fig. 2. Molecular orbital diagrams. The energy scale for Fenske–Hall calculations: *a*, $[MoS_4]^{2-}$; *b*, $[Cl_2FeMoS_4]^{2-}$; *c*, $[(HS)_2FeMoS_4]^{2-}$ (left) and the scale for EH calculations: *e*, $[MoS_4]^{2-}$; *d*, $[Cl_2FeMoS_4]^{2-}$ (right).

Table 1

Percent orbital character and energy of the molecular orbitals having substantial metal character (Fenske–Hall method)

Energy (eV)	Symmetry	Percent orbital character
$[(HS)_2FeMoS_4]^{2-}$		
−1.46	a_1	51.6% d_{z^2} Fe; 14.1% p_y S_l
−0.94	a_2	78.4% d_{xy} Fe; 11.4% p_x S_b
+0.78	b_1	61.4% d_{xz} Fe; 20.0% p_z S_b
+0.78	a_1	44.6% $\mathrm{d}_{x^2-y_2}$ Fe; 11.4% p_z S_l; 9.6% p_y S_l
+1.51[a]	b_2	56.0% d_{yz} Fe; 27.2% p_z S_t
+3.69	a_2	60.3% d_{xy} Mo; 23.8% p_x S_t
+4.76	a_1	49.2% d_{z^2} Mo; 19.8% p_y S_t
+6.05	b_2	46.3% d_{yz} Mo; 23.6% p_y Mo
+6.06	a_1	45.3% $d_{x^2-y^2}$ Mo; 17.6% p_z Mo
+6.08	b_1	44.6% d_{xz} Mo; 19.0% p_x Mo
$[Cl_2FeMoS_4]^{2-}$		
−1.64	a_1	59.6% d_{z^2} Fe; 10.0% p_y Cl; 5.7% d_{z^2} Mo
−0.87	a_2	73.8% d_{xy} Fe; 9.6% p_x Cl; 8.9% p_x S_b
+0.49	a_1	49.9% $d_{x^2-y^2}$ Fe; 10.2% p_z Cl; 5.7% d_{z^2} Mo
+0.77	b_1	58.3% d_{xz} Fe; 21.1% p_z S_b
+1.31[a]	b_2	62.5% d_{yz} Fe; 21.4% p_z Cl
+3.35	a_2	60.1% d_{xy} Mo; 23.9% p_x S_t; 15.0% p_x S_b
+4.41	a_1	50.5% d_{z^2} Mo; 18.5% p_y S_t; 12.6% p_z S_b
+5.70	a_1	46.4% $d_{x^2-y^2}$ Mo; 18.5% p_z Mo
+5.73	b_2	47.2% d_{yz} Mo
+5.79	b_1	45.0% d_{xz} Mo

[a] HOMO

(5) Examining the redox properties of Fe–S–Mo clusters.
(6) Comparing the applicability of the EH and the Fenske–Hall methods to studying the electronic structure.

The molecular orbital scheme of $[L_2FeMoS_4]^{n-}$ complexes obtained by use of the Fenske–Hall and EH methods indicates that there are four groups of occupied orbitals. The *s* orbitals of ligands that do not form effective M–L bonds are the lowest occupied. The next group of orbitals comprises mainly the *p* character of the sulfur atoms and the 4*d* character of molybdenum. This group is followed by the π nonbonding ligand orbitals. The highest occupied molecular orbitals are the strongly delocalized, multicenter orbitals having predominantly the character of the 3*d* orbitals of the iron and the *p* orbitals of the ligands (terminal, but mainly of the bridge). The lowest unoccupied molecular orbitals have predominantly the character of the 4*d* orbitals of molydenum. The sequence and energies of the most important fragments of orbital scheme for description of the electronic structure obtained for the $[Cl_2FeMoS_4]^{2-}$ and $[(HS)_2FeMoS_4]^{2-}$ ions by the Fenske–Hall and EH methods are shown in Fig. 2 together with molecular orbitals scheme for the $[MoS_4]^{2-}$

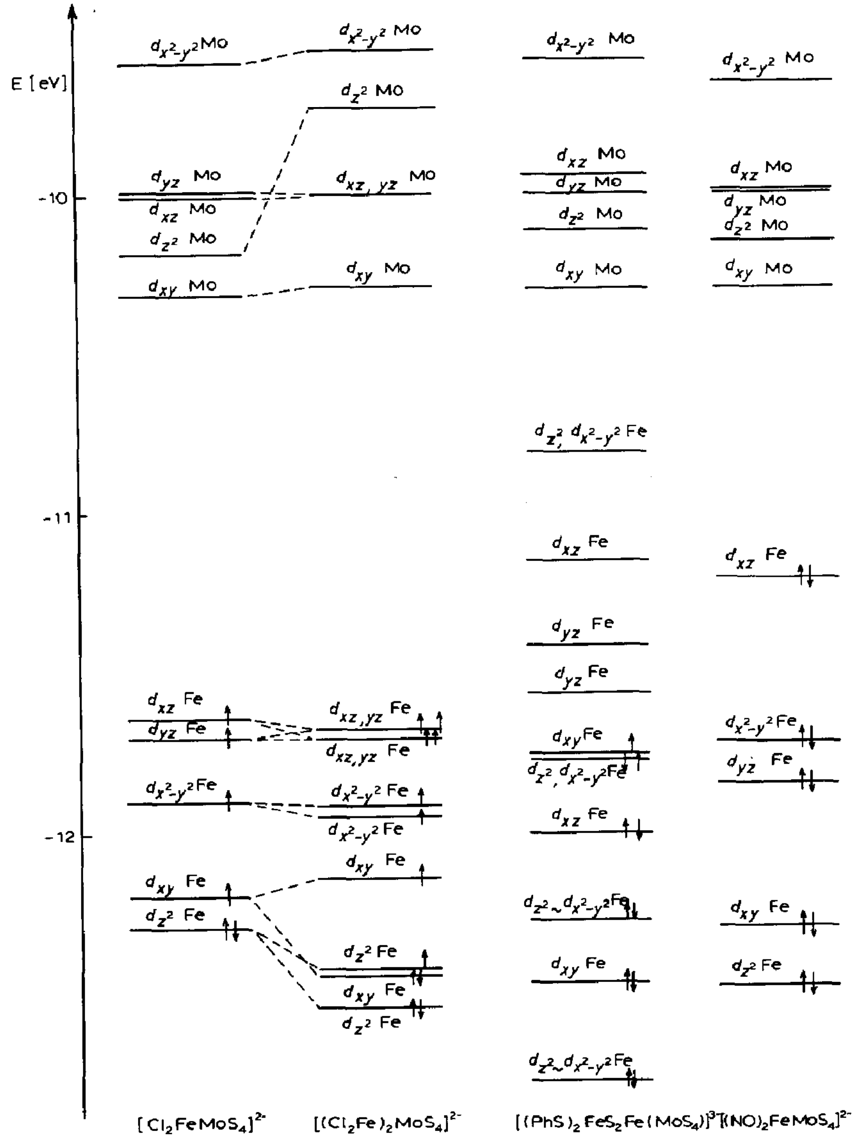


Fig. 3. MO diagrams, showing only the highest filled and lowest empty orbitals (EH calculations).

and as listed in Table 1. The molecular orbital scheme for the other ions under study is shown in Fig. 3. In contrast to $[Cl_2FeMoS_4]^{2-}$, no crossing over of the molecular orbital levels was observed for the occupied orbitals in $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$. Small changes in the sequence of the empty orbitals of ligands was observed (Fig. 3). Trends in the individual characteristics are analogous in both methods. However, two basic differences are observed, viz., (i) the Fenske–Hall energy levels are more spread out than the EH levels, and (ii) all the MO's in the EH calculations are downfield. The fact that the energies of higher filled molecular orbitals (as determined for the $[L_2FeMoS_4]^{2-}$ ions from Fenske–Hall calculations) are positive does not imply instability of the complexes or erroneous results. It should be noted

Table 2

Two-center total overlap populations from EH calculations.

	$[MoS_4]^{2-}$	$[(NO)_2FeMoS_4]^{2-}$	$[Cl_2FeMoS_4]^{2-}$	$[(Cl_2Fe)_2MoS_4]^{2-}$	$[(PhS)_2FeMoS_4]^{2-}$	$[(PhS)_2FeS_2FeMoS_4]^{2-}$
Fe—Mo		0.0372	0.0641	0.0630	0.0682	0.0739
Fe—S_b(FeS_2Mo)		0.6897	0.6340	0.5470	0.6492	0.6331
Mo—S_t	0.9529	0.9771	0.9609		0.9878	0.9991
Fe—S_b(FeS_2Fe)						0.7200
Fe—Fe						0.0411
Fe—L_t		0.4885	0.5300	0.5240	0.6285	0.6408
Mo—S_b		0.8394	0.7885	0.8510	0.8010	0.8077

that the calculations do not allow for the potential resulting from the change on the cation. Such a potential is spherically symmetrical (good approximation for a solution) and it results in a shift in the energies for all electron levels. Approximate energies obtained for each level should be lowered by about 3 eV per cationic charge unit. In the Fenske–Hall calculations the energy separation between the HOMO's and the LUMO's is overestimated by a factor of roughly two. It was arrived at by comparing the $\Delta E_{\mathrm{HOMO-LUMO}}$ value in both methods for the $[\mathrm{MoS_4}]^{2-}$ ion ($\Delta E =$ 5.03 eV in Fenske–Hall and $\Delta E = 2.7$ eV in EH calculations) with the position of the first $1t_1 \rightarrow 2e$ band in the electronic absorption spectrum $\Delta E = 2.63$ eV [46–47].

Our calculations reveal that in each Mo–Fe–S compound studied, there exists a very weak metal–metal bond. Some consistencies concerning the strength of the chemical bonds have been obtained by analyzing the two-center Mulliken overlap populations [48]. The EH and Fenske–Hall calculations reveal the same general trend. The metal–metal bonding interaction is not large and is of the same order for all the compounds studied (see Table 2). Detailed studies involving the Fenske–Hall method for $[\mathrm{Cl_2FeMoS_4}]^{2-}$ and $[\mathrm{(HS)_2FeMoS_4}]^{2-}$ (Table 3) reveal that the predominant contribution to the metal–metal bond is mainly by its $d\sigma$ components. The other components are rather weak and do not contribute significantly to the total strength of the bond. Non-effective orbitals for the metal–metal overlap are involved by way of a metal–ligand bond.

In all cases under study, the two-center overlap population revealed some consistencies about the metal–ligand bond strength. The bonding interaction between metal and ligand falls in the order: $P(\mathrm{Mo{-}S})_{\mathrm{b}}) > P(\mathrm{Mo{-}S_t}) > P(\mathrm{Fe{-}S_b}) >$ $P(\mathrm{Fe{-}L})$ and $P(\mathrm{Mo{-}S_t})(\mathrm{complex}) \approx \mathrm{P(Mo\text{-}S)(MoS_4{}^{2-})}$.

The strong metal–bridge sulphur bonding is evidence for the stability of such systems; the stability is due to the extensive electron delocalization in the $\mathrm{Fe{-}MoS_4}$ arrangement. The large contribution of p electrons of the bridge sulphur and of the terminal ligands to the highest occupied molecular orbitals (Table 1) contributes significantly to the stabilization of the cluster systems. The large negative charge on the sulphur in the free $[\mathrm{MoS_4}]^{2-}$ ligand, as calculated from the Mülliken population analysis, was found to be practically unchanged for the terminal sulphur in all the compounds studied. However for the sulphur in the bridge it decreases drastically (Table 4). When $[\mathrm{MoS_4}]^{2-}$ is a tetradentate bridge ligand, the flow of charge to the chloride ligand, $\mathrm{S_b} \rightarrow \mathrm{Cl}$ and $\mathrm{Fe} \rightarrow \mathrm{Cl}$, is more effective, and results in a strengthening of the $\mathrm{Mo{-}S_b}$ bond and in a weakening of the $\mathrm{Fe{-}S_b}$ bond, so that the $\mathrm{Fe{-}MoS_4}$ complexes display great versatility in redox bonding and reactivity. This

Table 3

Two-centre molybdenum–iron overlap population for $[\mathrm{Cl_2FeMoS_4}]^{2-}$ and $[\mathrm{(PhS)_2FeMoS_4}]^{2-}$ from Fenske–Hall calculations

	$[\mathrm{Cl_2FeS_2MoS_2}]^{2-}$				$[\mathrm{(PhS)_2FeS_2MoS_2}]^{2-}$			
	Mo d_{z^2}	Mo $d_{x^2-y^2}$	Mo d_{yz}	Mo p_z	Mo d_{z^2}	Mo $d_{x^2-y^2}$	Mo d_{yz}	Mo p_z
Fe d_{z^2}	0.0277			0.0147	0.0255			0.0147
Fe $d_{x^2-y^2}$		0.0007				0.0006		
Fe d_{yz}			0.0018				0.0015	

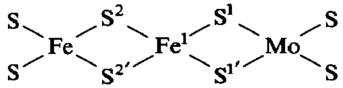
Table 4

Calculated charges on the metal and sulphur atoms

	$[MoS_4]^{2-}$	$[(NO)_2$-$FeMoS_4]^{2-}$	$[Cl_2FeMoS_4]^{2-}$	$[(PhS)_2$-$FeMoS_4]^{2-}$	$[Cl_2FeMoS_4$-$FeCl_2]^{2-}$	$[(PhS)_2FeS_2$-$FeMoS_4]^{3-}$
Mo	+2.222 +1.271 [a]	+2.158	+2.367 +1.418 [a]	+2.279 +1.417 [a]	+2.397	+2.243
Fe		−2.181	+0.784 0.649 [a]	+0.358	+0.805	+0.687 [b] +0.045
S_b		−2.292	−0.785 −0.708 [a]	−0.764 −0.710 [a]	−0.730	−0.772 [b] −0.609
S_t	−1.055 −0.818*	−1.062	−1.020 −0.784 [a]	−0.928 −0.777 [a]		−1.010

[a] Values calculated by the Fenske–Hall method

[b] Values apply to the Fe_1 and S_1 according to the figure:



versatility is due in part to the closeness of S and Mo energy levels, which in turn leads to enhanced redox and chemical reactivity. It is perhaps partly this type of reactivity that accounts for the presence of Fe–MoS_4 systems in enzymes and in industrial catalytic systems [7,49]. Of electrochemical importance are: the relative ease with which the compounds are oxidized or reduced, the number of electrons transfered during oxidation or reduction, and the reversibility of the electron-transfer process. The redox chemistry of the complexes determines the character and also the energy of the lowest virtual MO and the highest occupied MO. The energy difference between the HOMO and LUMO is approximately proportional to the redox potential [50]. For all the $[L_2FeMoS_4]^{2-}$ complexes the HOMO's are mainly determined by orbitals localized on the Fe–S_b moieties (50–60% Fe 3d and 20% S 3p) while the LUMO's are mainly determined by orbitals localized on the S_t–Mo–S_b moieties ($\simeq$ 50–60% Mo 4d, 10–20% 3p S_b, 10–20% 3p S_t). Previous electrochemical studies on $[(PhS)_2FeS_2MoS_2]^{2-}$ [51] and $[Cl_2FeS_2MoS_2]^{2-}$ [52] have shown that these complexes undergo an irreversible one-electron reduction. Fig. 2 indicates that such reduction of $[(PhS)_2FeS_2MoS_2]^{2-}$ and $[Cl_2FeS_2MoS_2]^{2-}$ would place on additional electron in the molecular orbitals involving the π interaction between orbitals, to result in an additional stabilization of the orbitals having E symmetry. Energy lowering of the MO with the predominant contribution of the d_{xy}Fe results in increase of the ΔE_{E-T_2} splitting and reversibility of such a process should not be expected. Irreversible one-electron oxidation and reduction processes have been observed for $[(PhS)_2FeS_2FeS_2MoS_2]^{3-}$ [53]. In this case an additional electron is thought to occupy the δ bonding combination of d_{xy} orbitals of the two Fe atoms, or the very close orbital being π^* combination of d_{yz} orbitals. Instead, in the one-electron oxidation process the system takes on the configuration as follows:

$$\sigma\left(\mathrm{d}_{z^2} \sim d_{x^2-y^2}\right)^2\ \delta^*\left(d_{xy}\right)^2\ \sigma\left(d_{z^2} \sim \mathrm{d}_{x^2-y^2}\right)^2\ \pi^*\left(d_{xz}\right)^2\ \sigma\left(d_{z^2} \sim \mathrm{d}_{x^2-y^2}\right)^2$$

The $[(NO)_2FeMoS_4]^{2-}$ complexes have the configuration $(d_{z^2}\mathrm{Fe})^2(d_{xy}\mathrm{Fe})^2(d_{yz}\mathrm{Fe})^2$-$(\mathrm{d}_{x^2-y^2}\mathrm{Fe})^2(d_{xz}\mathrm{Fe})^2 < (d_{xy}\mathrm{Mo})$. The observed magnetism of that system [1] and the energy difference between the HOMO and LUMO (which exceeds 7 eV) (Fig. 2) revealed that neither the temperature-dependendent paramagnetism nor the redox processes should be expected.

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