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A Molecular Orbital Study of Trimetallic $[M(MoS_4)_2]^{-n}$ Ions (M = Fe, Co)

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Intensive studies in transition metal complexes with $[MoS_4]^{-2}$ and $[WS_4]^{-2}$ thioanions acting as bidentate chelating ligands in the trimetallic $[M(MoS_4)_2]^{-n}$ type complexes were initiated by Müller *et al.* [1]. One can observe an increasing interest in these compounds. Their investigation has been stimulated by two factors: i) the discovery that some redox-proteins contain transition metal ions and the 'labile' sulfur in their active sites, and ii) the confirmation that there exist multimetal complexes of this type with a variety of electron populations.

We report here the results of our theoretical investigations of Fe and Co complexes with tetrathiomolybdate ions for various formal oxidation states of a central atom.

The approximate, but parameter-free Fenske–Hall LCAO MO method [2] was applied for the molecular orbital calculations. The interatomic distances and angles used for the $[Fe(MoS_4)_2]^{-3}$ complexes were based upon their structural determination [3]. Atomic coordinates assumed for $[Co(MoS_4)_2]^{-n}$ (n = 2, 3, 4) were the same as for the $[Co(WS_4)_2]^{-3}$ ion [4].

The basis functions applied were the Hartree–Fock–Roothaan atomic functions for free atoms or ions. They were chosen in such a manner as to make them consistent with Mulliken's charge and the electronic configuration of each atom under study. The basic set contained the nd, (n + 1)s, (n +1)p and (n + 1)d AO's as valence orbitals for M^{+1}; all inner AO's were treated as frozen core orbitals [2, 5]. The same procedure was applied to sulfur atoms. The 3s, 3p AO's for S^0 were used as valence orbitals, and all inner orbitals were frozen in their atomic form. The analytic expressions for the functions were taken from ref. 6.

In order to show how the molybdenum levels are ordered in the absence of another metal center, we also performed calculations for the free $[MoS_4]^{-2}$ ligand. The local systems of coordinates used for the calculations are shown in Fig. 1.

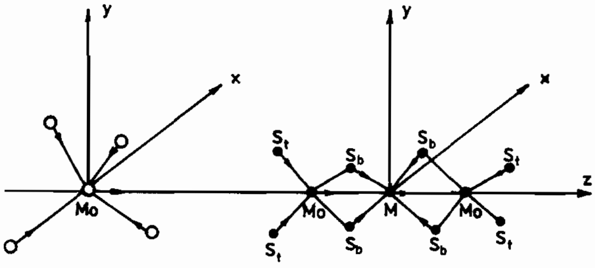

Fig. 1. The geometry and the coordinate system of $[MoS_4]^{-2}$ ion, T_d symmetry, and $[M(MoS_4)_2]^{-n}$ complexes, D_{2d} symmetry.

TABLE I. Percent Character and Energy of the Selected Molecular Orbitals of the $[M(MoS_4)_2]^{-3}$ Anions.

Energy [eV]	Orbital	Percent orbital character
$[Fe(MoS_4)_2]^{-3}$		
1.27	$7a_1$	67.0 d_{z^2}Fe
2.63	$3b_1$	82.2 $d_{x^2-y^2}$Fe
2.69	$7b_2$	57.3 d_{xy}Fe; 17.9 d_{z^2}Mo
4.13	9e*	64.9 $d_{xz,yz}$Fe; 16.0 p_zS_b
6.42	$4b_1$	59.9 $d_{x^2-y^2}$Mo; 13.8 p_xS_b
6.46	$3a_2$	61.0 $d_{x^2-y^2}$Mo; 14.6 p_xS_b
7.49	$8b_2$	42.4 d_{z^2}Mo; 16.2 d_{xy}Fe
7.49	$8a_1$	53.3 d_{z^2}Mo; 16.5 d_{z^2}Fe
8.57	10e	44.3 $d_{xz,yz}$Mo; 19.2 $p_{x,y}$Mo
8.75	11e	42.4 $d_{xz,yz}$Mo; 18.8 $p_{x,y}$Mo
8.88	$9b_2$	45.7 d_{xy}Mo; 17.8 p_zMo
8.90	$9a_1$	47.0 d_{xy}Mo; 18.4 p_zMo
$[Co(MoS_4)_2]^{-3}$		
0.66	$7a_1$	72.3 d_{z^2}Co
1.69	$3b_1$	77.2 $d_{x^2-y^2}$Co
1.94	$7b_2$	60.4 d_{xy}Co; 12.6 d_{z^2}Mo
3.16	9e*	61.2 $d_{xz,yz}$Co; 19.4 p_zS_b
6.10	$4b_1$	60.8 $d_{x^2-y^2}$Mo; 23.9 p_xS_t
6.19	$3a_2$	61.0 $d_{x^2-y^2}$Mo; 23.4 p_xS_t
6.91	$8a_1$	57.0 d_{z^2}Mo; 19.0 p_yS_t
7.06	$8b_2$	47.7 d_{z^2}Mo; 21.4 p_zS_t
8.47	10e	46.6 $d_{xz,yz}$Mo; 19.8 $p_{x,y}$Mo
8.51	$9a_1$	48.4 d_{xy}Mo; 19.6 p_zMo
8.54	$9b_2$	46.7 d_{xy}Mo; 18.2 p_zMo
8.56	11e	45.8 $d_{xz,yz}$Mo; 21.8 $p_{x,y}$Mo

*HOMO.

The energy level diagrams for the investigated complexes comprise three distinct regions. The s and p orbitals of sulfur which do not form effective M–L bondings are the lowest occupied ones. The next group of orbitals exhibit mainly the p character of the sulfur atoms, and the 4d character of molybdenum and 3d character of the metals (Fe, Co). Their energies and the greatest contribution (calculated) of the atomic orbitals are presented in Table I. The

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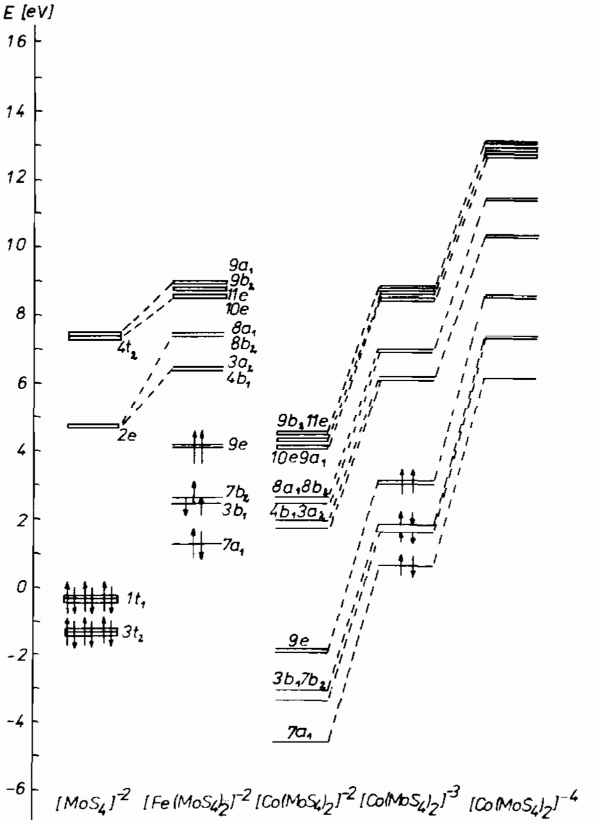

Fig. 2. MO diagrams, showing only the highest filled and lowest unfilled orbitals for $[MoS_4]^{-2}$ and $[M(MoS_4)_2]^{-n}$ anions.

highest unoccupied molecular orbitals exhibit a predominant character of the 4d and 5d orbitals of molybdenum and the 4d character of the metal (Fe, Co) atoms. In the obtained sequence of the molecular orbitals for the systems under study, the orbitals of $7A_1$, $3B_1$, $7B_2$, 9E symmetry have been identified as the highest occupied molecular orbitals, with the ($3d_{z^2}{}^2$, $3d_{x^2-y^2}{}^2$, $3d_{xy}{}^1$, $3d_{xz}{}^1$, $3d_{yz}{}^1$Fe) and ($3d_{z^2-y^2}{}^2$, $3d_{xy}{}^2$, $3d_{xz}{}^1$, $3d_{yz}{}^1$Co) configurations for $[Fe(MoS_4)_2]^{-3}$ and $[Co(MoS_4)_2]^{-3}$, respectively. The lowest empty orbital (LUMO) for these systems is essentially in the molybdenum localized molecular orbital of B_1 symmetry.

The received schemes of the one-electron levels are somewhat different from the qualitative picture presented by Müller [1]. Contrary to the quoted literature [1] in our calculations all molecular orbitals with the predominant 3d character of metal (Fe, Co) were found between the occupied orbitals localized on the sulfur ligands and the free orbitals of the 4d character of molybdenum. A similar molecular orbital scheme was foreseen by Coucouvanis [7] on the basis of an analysis of the electronic spectra of the $M'S_4$-Fe complexes (where M' = Mo, W). From our studies on the $[M(M'S_4)_2]^{-n}$ systems it follows that the replacement of the $[MoS_4]^{-2}$ ligands by the $[WS_4]^{-2}$ ions did not cause qualitative changes in the molecular orbital sequence [8]. On the basis of the scheme presented in [1], it is impossible to explain the existence of a stable paramagnetic (S = 2) [Fe-$(WS_4)_2]^{-2}$ ion [7].

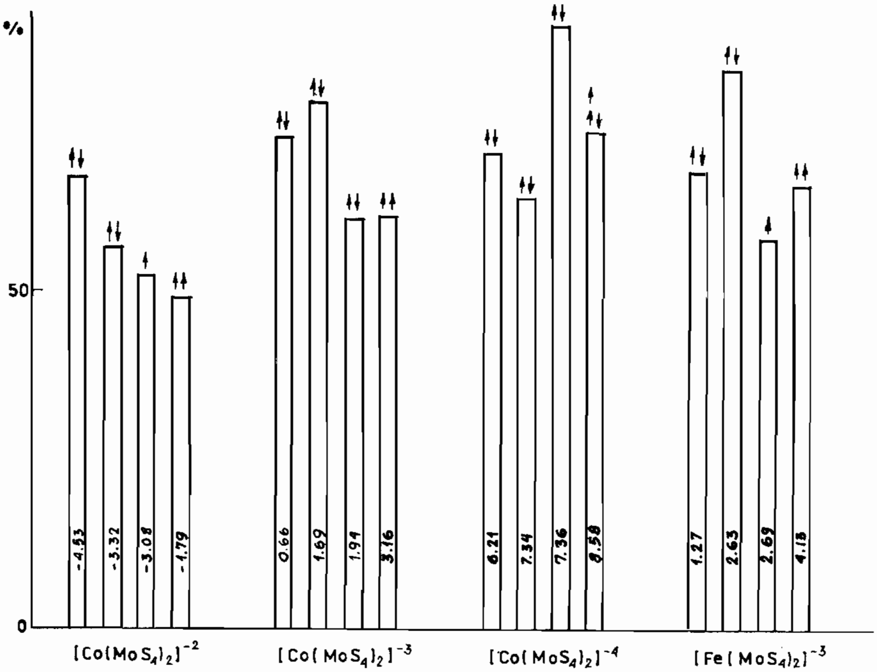

Fig. 3. The composition and the relative position of the MO of $[M(MoS_4)_2]^{-n}$ complexes containing substantial metal (Fe, Co) character.

TABLE II. Two-center Total Overlap Populations.

Complex	M–Mo	M–S_b	Mo–S_b	Mo–S_t
$[Fe(MoS_4)_2]^{-3}$	0.0698	0.1652	0.3493	0.4337
$[Co(MoS_4)_2]^{-2}$	0.0592	0.1787	0.3590	0.4388
$[Co(MoS_4)_2]^{-3}$	0.0691	0.1683	0.3630	0.4193
$[Co(MoS_4)_2]^{-4}$	0.0736	0.1507	0.3672	0.3915
$[MoS_4]^{-2}$				0.4326

The results obtained for different overall charges of the $[Co(MoS_4)_2]^{-n}$ ion indicate changes of the orbital energy and of the character of the particular orbitals. The shift of the molecular orbitals caused by the addition of one or two electrons into the $[Co(MoS_4)_2]^{-2}$ system is shown in Fig. 2. This result presented in Fig. 2 shows that with an increasing negative charge on the complex, all the energy levels are shifted to more positive values. The calculations do not take into account the potential caused by cations. If such a potential is spherically symmetric (which is a good approximation of the condition of the solution), it brings a similar shift in all the energy levels. Roughly, this will result in a decrease of each energy level of about 3 eV per unit charge [9].

Along the redox series $[Co(MoS_4)_2]^{-n}$, the sequence of molecular orbitals is preserved independently of n. Some changes in the MO sequence appear due to the replacement of the Fe central ion by Co (Fig. 2). By the successive transition passing from $[Co(MoS_4)_2]^{-2}$ to $[Co(MoS_4)_2]^{-4}$, the gap between the HOMO and the LUMO decreases and all empty orbitals are shifted downward into the region of occupied orbitals (Fig. 2). Figure 3 illustrates variations in the composition of the predominantly (Fe, Co) localized orbital on going from $[Co(MoS_4)_2]^{-2}$ to $[Co(MoS_4)_2]^{-4}$ and $[Fe(MoS_4)_2]^{-3}$. For the $[Fe(MoS_4)_2]^{-3}$ ion the contribution of the central atom to the HOMO orbitals increases as compared with the isoelectronic $[Co(MoS_4)_2]^{-2}$ ion. This contribution increases with the increase in formal oxidation state of the central ion (Fig. 3). We have performed the Mülliken population analysis in order to determine the strength of the particular bondings in the system under study, as well as of their changes caused by different charges on the complexes. Although the overlap populations are not significant in the absolute scale comparison, values obtained for similar systems allow us to obtain the correct trend. The most important overlap populations of the examined complexes are presented in Table II. The data in Table II confirm that the total metal–metal overlap population is not large, and the dσ orbitals contribute predominantly to the interactions of that type. The contribution of dπ and dδ orbitals is almost zero. The overlap population between the metal (Co, Fe) and bridge sulfur is almost twice as low as that between molybdenum and the bridge sulfur. Further analysis of the data presented in Table II revealed that an increase in the formal oxidation state of the central atom is accompanied by an increase in the metal–metal bonding strength. The Mo–S_b population values remain practically unchanged, while the values for the Co–S_b and Mo–S_t bonds decrease. The obtained values for the two-center overlap populations allow us to calculate the changes in the geometric structure of a complex in dependence on the formal oxidation state of the central atom. For the $[Co(MoS_4)_2]^{-n}$ complex anion, the increase of the n value should be accompanied with some shortening of the Co–Mo bond and an elongation of the Co–S_b and Mo–S_t bonds. On the other hand, as follows from the calculations, the Mo–S_b bond was not sensitive to the charge changes and its length should not vary. Müller *et al.* [10] examined the analogous tungsten complexes and have discovered in $[Co(WS_4)_2]^{-3}$ a longer W–S_t bond than in $[Co(WS_4)_2]^{-2}$. This statement was confirmed by i.r. spectra. The ν_{as} W–S_t was shifted from 467 cm^{-1} for $[Co(WS_4)_2]^{-3}$ to 491 cm^{-1} for $[Co(WS_4)_2]^{-2}$.

The charges on the particular centres, calculated from the population analysis, could be evidence of their reactivity (Table III). Reduction of the complexes is accompanied by a lowering of the positive charge on the central atoms and a slight increase in the charge on molybdenum atoms. Electron

TABLE III. Calculated Charges on the Metals and Sulfur Centers of the $[M(MoS_4)_2]^{-n}$ Ions.

Complex	Molybdenum	Metal (Fe, Co)	Bridging sulfur	Terminal sulfur
$[Fe(MoS_4)_2]^{-3}$	+1.450	+0.628	−0.802	−0.830
$[Co(MoS_4)_2]^{-2}$	+1.418	+0.557	−0.644	−0.703
$[Co(MoS_4)_2]^{-3}$	+1.459	+0.526	−0.762	−0.841
$[Co(MoS_4)_2]^{-4}$	+1.494	+0.518	−0.894	−0.981
$[MoS_4]^{-2}$	+1.271			−0.818

density grows significantly on sulfur atoms. Localization of the additional electron density on the ligand atoms, but not on a central atom, is consistent with conclusions based on the Mössbauer investigation [3]. This statement reveals that only sulfur atoms are responsible for the ability of such complexes to transfer electrons or to gather them under appropriate conditions. By the investigations of the $[M(WS_4)_2]^{-n}$ complexes, Müller *et al.* [10, 11] arrive at a similar conclusion.

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