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The Electronic Structure of Sulfido-Bridged Binuclear Molybdenum(V) Complexes Containing Mo–Mo Interaction

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The electronic structure was calculated by the parameter-free Fenske-Hall method for $[MoO(C_5H_5)]_2S_2$, $[MoS(C_5H_5)]_2S_2$ *and* $[Mo_2S_2(S_2C_2H_4)_2]^{-2}$ *in order to discuss the bonding, as well as the magnetic and electrochemical properties, of binuclear Mo(V) complexes with the* $[Mo_2S_2L_2]^{+2}$ *(L = S or O) unit with special consideration of the terminal ligands effect.*

Introduction

Molybdenum is an important transition metal in biological systems. It is an integral part of various redox enzymes such as xanthine oxidase, nitrogenase and nitrate reductase [1]. Its unique properties seem to be due to its ability to exist in a number of different oxidation states as well as to coordinate with a variety of ligands.

The Mo_2S_2 bonding system in which two sulfur atoms span two metal atoms is the most common one. Di-μ-sulfido-bridged binuclear Mo(V) complexes which undergo reversible oxidation-reduction reactions are regarded as especially interesting compounds [2, 3]. In these stable binuclear species each molybdenum atom is strongly bound to the terminal oxo- or sulfido-group.

In this paper we present the results of our theoretical investigations on representative complexes of $[MoO(C_5H_5)]_2S_2$, $[MoS(C_5H_5)]_2S_2$ and $[Mo_2S_4(S_2C_2H_4)_2]^{-2}$.

The purpose of our work was to resolve the specific nature of the metal–metal bond in this type of complexes and to determine the electrochemical properties of these dimeric cluster systems.

Computational Details

The semi-quantitative Fenske-Hall LCAO MO method was applied [4] in our study. The method is an approximate Hartree-Fock-Roothaan SCF LCAO molecular orbital approach which involves neither arbitrary nor adjustable parameters, depending only upon the choice of wave functions and atomic coordinates as input data. The operation is self-consistent.

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 the Mulliken's charge and the electronic configuration of each atom under study. The basic set contained 4d, 5s, 5p and 5d AOs as valence orbitals for Mo^{+1}; all inner AOs were treated as frozen core orbitals [4, 5]. The same procedure was applied to ligands. The 1s AO for H^0, the 2s, 2p AOs for C^0, O^0 and the 3s, 3p AOs for S^0 were used as valence orbitals, and all inner orbitals were frozen in their atomic form. Analytic expressions for the functions were taken from ref. [6].

The interatomic distances and angles used for the examined complexes were based upon their structural determinations (Table I). The related bond angles were averaged so that the atomic coordinates conformed to an idealized C_{2h} geometry.

TABLE I. Mean Geometrical Parameters Used for the MO Calculations.

Complex	Mo–Mo (A)	Mo–S_b (A)	S_b–S_b (A)	Mo–S_t(O_t) (A)	Ref.
$[MoS(C_5H_5)]_2S_2$	2.894	2.317	3.616	2.126	[7]
$[MoO(C_5H_5)]_2S_2$	2.894	2.317	3.616	1.679	[8]
$[Mo_2S_4(S_2C_2H_4)_2]^{-2}$	2.878	2.321	3.643	2.129	[9, 10]

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TABLE II. Percent Character and Energy of the Orbitals Containing Substantial Molybdenum Character.

Energy (eV)	Orbital	Percent orbital character	
$[MoO(C_5H_5)]_2S_2$			
−11.27	A_g[a]	33 d_{z^2} (Mo + Mo');	33 $d_{x^2-y^2}$ (Mo + Mo');
		3 p_z (S + S');	2 p_z (O + O')
−5.72	B_u	50 d_{yz} (Mo + Mo');	18 p_y (O + O');
		14 p_y (S + S')	
−5.00	A_u	54 d_{xy} (Mo + Mo');	24 p_x (O–O')
−4.60	B_g	27 d_{xz} (Mo + Mo');	24 d_{xy} (Mo–Mo');
		19 p_x (O + O');	9 p_x (S + S')
−4.44	A_g	59 d_{yz} (Mo – Mo');	18 p_y (O – O')
−3.84	B_u	42 d_{z^2} (Mo – Mo');	24 p_x (S – S');
		16 $d_{x^2-y^2}$ (Mo – Mo')	
−3.05	B_g	29 d_{xy} (Mo – Mo');	22 d_{xz} (Mo + Mo');
		6 p_x (S + S');	5 p_y (S – S')
−1.28	B_u	28 $d_{x^2-y^2}$ (Mo – Mo');	16 d_{z^2} (Mo – Mo')
−1.22	A_u	37 d_{xz} (Mo – Mo');	15 p_z (S – S')
−0.51	A_g	25 $d_{x^2-y^2}$ (Mo + Mo');	15 d_{z^2} (Mo + Mo')
$[MoS(C_5H_5)]_2S_2$			
−10.75	A_g[a]	34 d_{z^2} (Mo + Mo');	31 $d_{x^2-y^2}$ (Mo + Mo');
		5 p_z ($S_t + S'_t$);	2 p_z ($S_b + S'_b$)
−6.36	B_u	43 d_{yz} (Mo + Mo');	23 p_y ($S_t + S'_t$);
		15 p_y ($S_b + S'_b$)	
−6.15	A_u	45 d_{xy} (Mo + Mo');	31 p_x ($S_t - S'_t$)
−5.59	B_g	32 d_{xy} (Mo – Mo');	25 p_x ($S_t + S'_t$)
−5.46	A_g	53 d_{yz} (Mo – Mo');	23 p_y ($S_t - S'_t$)
−3.80	B_u	43 d_{z^2} (Mo – Mo');	23 p_x ($S_b - S'_b$)
−2.98	B_g	33 d_{xz} (Mo + Mo');	20 d_{xy} (Mo – Mo')
−1.78	B_u	26 $d_{x^2-y^2}$ (Mo – Mo');	16 d_{z^2} (Mo – Mo')
−1.23	A_u	36 d_{xz} (Mo – Mo');	13 p_z ($S_b - S'_b$)
−1.08	A_g	23 $d_{x^2-y^2}$ (Mo + Mo');	14 d_{z^2} (Mo + Mo')
$[Mo_2S_4(S_2C_2H_4)_2]^{-2}$			
−0.46	A_g[a]	39 d_{z^2} (Mo + Mo');	18 p_y ($S_t - S'_t$);
		17 $d_{x^2-y^2}$ (Mo + Mo');	6 p_z ($S_b + S'_b$)
+4.30	B_u	33 d_{yz} (Mo + Mo');	23 d_{z^2} (Mo – Mo');
		13 p_y (Mo + Mo');	10 p_y ($S_b + S'_b$)
+4.90	B_u	39 d_{z^2} (Mo – Mo');	21 p_y ($S_t + S'_t$)
+5.03	A_u	46 d_{xy} (Mo + Mo');	20 p_x ($S_t - S'_t$)
+5.11	B_g	32 d_{xy} (Mo – Mo');	25 d_{xz} (Mo + Mo')
+5.66	A_g	35 d_{yz} (Mo – Mo');	16 p_y ($S_t - S'_t$)
+6.33	A_g	24 $d_{x^2-y^2}$ (Mo + Mo');	20 p_y (Mo – Mo')
+7.25	B_u	42 $d_{x^2-y^2}$ (Mo – Mo');	20 p_x ($S_b - S'_b$)
+9.50	B_g	28 d_{xz} (Mo + Mo');	20 d_{xy} (Mo – Mo')
+11.10	A_u	33 d_{xz} (Mo – Mo')	

[a] HOMO.

The local Cartesian coordinate systems for each dimer were chosen as follows: 1) the z axes of each molybdenum atom were oriented towards the midpoint of two bridging atoms, while the x axes were directed parallel to the S–S vector, 2) the z axes of each bridging S atom were pointed towards the mid-

TABLE III. Two-center Molybdenum–Molybdenum Overlap Populations.

Mo–Mo[a]	$[MoO(C_5H_5)]_2S_2$	$[MoS(C_5H_5)]_2S_2$	$[Mo_2S_4(S_2C_2H_4)_2]^{-2}$
$d_{z^2} - d_{z^2}$	0.04664	0.04741	0.06125
$d_{x^2-y^2} - d_{x^2-y^2}$	0.00257	0.00254	0.00167
$d_{yz} - d_{yz}$	0.00480	0.00527	0.00312
Total overlap population	0.05401	0.05522	0.06604

[a] 5d orbital contributions are not included.

point of two molybdenum atoms, and the x axes were directed parallel to the Mo–Mo vector, 3) the z axes of each ligand atom were directed towards the molybdenum atom, 4) the y axes of all atoms were determined by the right-hand rule.

Results and Discussion

The energy level diagrams for the investigated complexes comprise three distinct regions. The σ and π orbitals of ligand which do not form effective Mo–L bondings are the lowest occupied ones. The next group of orbitals exhibits mainly the p character of the bridge and the terminal sulphur (oxygen) atoms and the 4d character of molybdenum. Their energies and the greatest contribution (calculated) of the atomic orbitals are presented in Table II. The highest unoccupied molecular orbitals exhibit the predominant character of the 5d, 5p and 5s of molybdenum and the σ*, π* character of ligands.

The fact that the energy of the highest occupied orbitals was close to zero (for $[Mo_2S_4(S_2C_2H_4)_2]^{-2}$) does not indicate that the dimer was unstable or that the results are misleading. It should be remembered that 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 situation in solution), it will bring a similar shift in all energy levels. Roughly, this will result in a decrease of each energy level by about 3 eV per unit charge [11] *i.e.* 6 eV for the anion $[Mo_2S_4(S_2C_2H_4)_2]^{-2}$.

The description of bonding in the studied systems is based on the following sequence of the metal–metal orbitals: $\sigma \ll \pi < \delta < \pi < \pi^* < \sigma^* < \delta^* < \pi^*$ for $[MoO(C_5H_5)]_2S_2$; $\sigma \ll \pi < \delta < \delta^* < \pi^* < \sigma^* < \pi < \pi^*$ for $[MoS(C_5H_5)]_2S_2$ and $\sigma \ll \pi < \sigma^* < \delta < \delta^* < \pi^* < \pi < \pi^*$ for $[Mo_2S_4(S_2C_2H_4)_2]^{-2}$ with a ground state configuration σ^2 (if z axes are assumed to be colinear to the metal–metal bond, the σ, π and δ orbitals denote the bonding combinations of the valence (d_{z^2}), ($d_{xz,yz}$) and (d_{xy}) orbitals while σ*, π* and δ* are the corresponding antibonding counterparts, respectively).

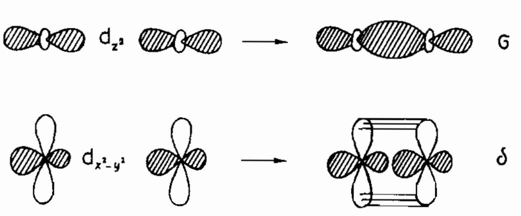

Fig. 1. The two d orbitals, components of HOMO.

As can be seen from the calculations presented in Table II, we deal here with a dominant σ, π or δ character of the appropriate molecular orbitals. The percent contributions of d-orbitals of the central molybdenum atoms in the molecular orbitals equal 40–60%. The relatively small contribution of the pure σ, π or δ molybdenum orbitals results from: 1) mixing of σ – δ, π – δ in the MOs of the complex, ii) strong delocalization of bondings within the $[Mo_2S_2L_2]^{+2}$ core. The two components σd and δd of the HOMO, for instance, are shown in Fig. 1. Both are bonding. Since the overlap of orbitals leading to σ bond is greater than that in δ bond (as indicated by the overlap population values (Table III)), the σ character is predominant. The geometry of the examined compounds allows the metal orbitals interaction with the p combinations of the bridge sulphur atoms and with the p combinations of terminal (sulphur or oxygen) ligands of the same symmetry, which results in the delocalization of bondings in the whole $[Mo_2S_2L_2]^{+2}$ system (see Fig. 2). It follows from Table II that in HOMO the metallic character is predominant. The contribution of the S_b and $S_t(O_t)$ p orbitals is minimal. They play a significant role in the LUMO, which will be discussed later.

The sequence and values of the splitting molecular orbitals revealed that the energy separation over the σ and σ* orbitals exceeds that between the π and π* or δ and δ* orbitals, which reflects the σ character of the metal–metal interaction. The energy

TABLE IV. Two-center Molybdenum[a]–Sulphur and Sulphur–Sulphur Overlap Populations.

Complex	Mo–S_b	Mo–S_l	Mo–S_l	S_b–S_b
$[MoO(C_5H_5)]_2S_2$	0.2858			0.0019
$[MoS(C_5H_5)]_2S_2$	0.2854	0.5217		0.0017
$[Mo_2S_4(S_2C_2H_4)_2]^{-2}$	0.2661	0.4684	0.2297	0.0015

[a] 5d orbital contributions are not included.

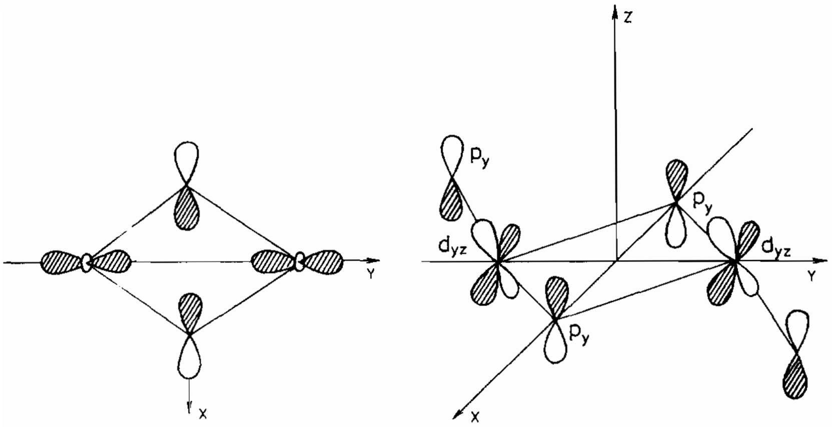

Fig. 2. Schematic representation of orbital interactions in the HOMO (left) and in the LUMO (right) of the investigated complexes.

difference between the σ and σ* MO is a direct measure of those interactions.

From this consideration it follows that in the investigated systems the molybdenum–molybdenum bond is effectively single.

The highest occupied orbital A_g (d_{z^2}) is filled with two electrons. Therefore, the ground state of the complexes is the orbital singlet ^1A_g. Since the energy separation between the HOMO and LUMO exceeds 4 eV in all cases (Table II), the contribution of the excited triplet state to the ground state (responsible for the temperature dependent paramagnetism) should be excluded. This conclusion is in excellent agreement with experimental results [1, 8, 10].

More detailed characteristics of the bondings are given by Mulliken's overlap populations [12]. Nevertheless, although they are not significant in the absolute scale comparison, values for similar systems allows us to obtain the correct trend. Taking into account the above mentioned limitations the conclusions can be applied to the molybdenum–molybdenum, molybdenum–sulphur and sulphur–sulphur bondings only. The most important overlap populations of the examined complexes are presented in Tables III–IV. The data in Table III confirm the predominant contribution of the dσ orbitals to the metal–metal bonding. The contribution of the dπ and dδ orbitals is several times lower than that of the dσ orbitals. In all of these complexes the Mo–Mo overlap population value is of the same order. The overlap population between molybdenum and the bridge sulphur is almost twice as low as that between molybdenum and the terminal sulphur (Table IV). It should be noted that each bridge sulphur is involved in two Mo–S bondings. The calculated population values indicate the existence of a double bonding between molybdenum and the terminal sulphur, whereas the bonding between molybdenum and the bridge sulphur approximates to a double bonding. As follows from the overlap population calculations (Table IV), the S–S 'crossring' bonding is negligible.

One of the most important features of the Mo(V) complexes with double sulfido-bridges is their relative ability to a one-electron reduction. The presented calculations allow us to state that the lowest unoccupied molecular orbital LUMO, accessible for the electron in the reduction process of the complexes with the $[Mo_2S_2L_2]^{+2}$ core, is composed mainly from the d orbitals of molybdenum and the p orbitals of the bridge atoms and terminal ligands. The character of the LUMO suggests the dependence of reduction ability on the nature of terminal ligands L rather than on the other ligands. The results obtained for the model systems $[MoL(C_5H_5)]_2S_2$ allow us to expect an increase of the reduction ability of these complexes, by replacement of the oxygen ligand by sulphur ligand. The calculated energy difference between HOMO and LUMO proportional to the redox potential amounts to 5.55 eV and 4.39 eV for $[Mo_2S_2O_2]^{+2}$ and $[Mo_2S_4]^{+2}$, respectively. For the investigated $[Mo_2S_4(S_2C_2H_4)_2]^{-2}$ ion the value equals 4.76 eV (it should be remembered here that the reduction potentials are strongly dependent on the charge of the molecule, and if the last one is negatively charged the reduction potential must be corrected for the charge difference).

The calculations also revealed that the appearance of sulphur instead of terminal oxygen results in a higher electron delocalization within the binuclear unit. The contribution of the p orbitals of oxygen in the LUMO of the $[MoO(C_5H_5)]_2S_2$ complex amounts to about 18%, and the contribution of the d orbitals of molybdenum amounts to about 50% (see Table II). In the similar molecular orbital of $[MoS(C_5H_5)]_2S_2$ the contribution of p orbitals of the terminal sulphur and of d orbitals of molybdenum equals 23% and 43% respectively. A similar trend is observed in the other molecular orbitals. The delocalization causes the first free orbital LUMO for additional electrons in the case of $[MoS(C_5H_5)]_2$-S_2 to have a lower energy equal to –6.3 eV, while the orbital of $[MoO(C_5H_5)]_2S_2$ exhibits an energy equal to –5.72 eV (see Table II).

The results of our calculations confirmed the conclusion that there is a relative ease of reduction of $[Mo_2X_2Y_2]^{+2}$ center (where X, Y = S or O; n + M = 4) based on electrochemical studies [2, 3, 9, 13, 14].

Theoretical studies of some other aspects of electrochemical properties of complexes with the $Mo_2X_nY_m]^{+2}$ core, *i.e.* the number of electrons transferred in redox processes and the stability of such processes are the subject of further studies.

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