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Mononuclear, Polynuclear, and Cluster Complexes of Molybdenum and Their Reactions as Models of Biochemical Systems and Processes

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Abstract—Data on the composition, structure, and properties (electronic and geometric structure, optical properties, thermodynamic functions) of mononuclear, polynuclear, and cluster complexes of bi-, tri-, tetra-, penta-, and hexavalent molybdenum are summarized and correlated. The thermodynamics, kinetics, and mechanisms of the ligand exchange, protonation–deprotonation, redox reactions, and formation–decomposition of cluster cores of molybdenum complexes in aqueous solutions are characterized.

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1. INTRODUCTION

Since the middle of the XX century, polynuclear molybdenum complexes attract enduring researchers' interest, primarily due to functions of these complexes in biological systems. Many enzymes (nitrogenases, oxidases, hydrogenases of various nature [1]) have metal-containing fragments in active groups. These metal-containing fragments have been examined in numerous studies [2]; their results show that active centers of many enzymes (such as xanthine oxidase, aldehyde oxidase, various dehydrogenases, etc.) contain several M atoms in different oxidation states, and the enzymatic process is a reversible electron transfer in the enzyme–substrate system. The thermodynamics of these processes are still poorly understood, because transformations of molybdenum compounds in solutions are complicated and diverse. In particular, the formal oxidation state of molybdenum can range from –2 to +6, and in aqueous solutions, from +2 to +6 [3]. Furthermore, molybdenum complexes in aqueous solutions readily enter into protonation and polymerization reactions, giving rise to plenty of coexisting species. A unique property of molybdenum is formation of stable aqua or aqua/oxo complexes in aqueous acid solutions (pH < 2) in all the five stable oxidation states.

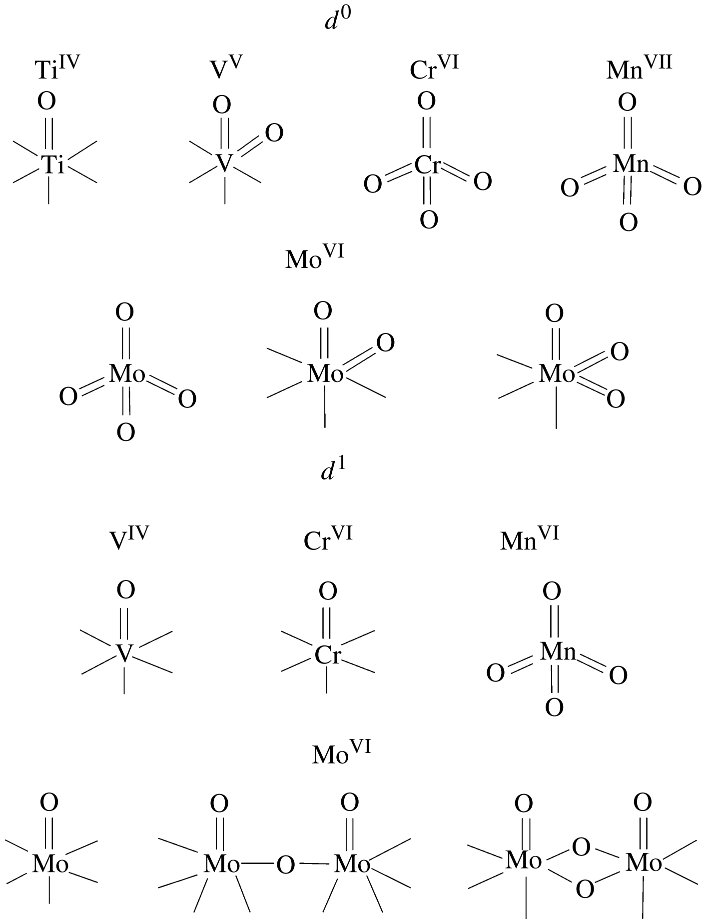
Even in the most complicated biochemical cycles, the key reactions are relatively simple (from the viewpoint of coordination chemistry) transformations involving mononuclear, polynuclear, and cluster complexes of molybdenum (ligand exchange, formation–decomposition of the cluster core, redox reactions) in aqueous solution as the most common medium for biological objects.

For detailed description of such complicated processes, it is necessary not only to study the reaction mechanisms but also to describe the thermodynamics of particular steps of multistep transformations, with the aim to determine the activation barriers and reaction energies, and also to reveal factors governing the possibility, direction, and mechanism of catalytic processes. It is also necessary to consider various redox properties of complexes and differences in the metal–metal bond strength (multiplicity) depending on the metal oxidation state.

The order we choose in this review, from hexavalent to lower oxidation states of Mo, is opposite to that commonly accepted in reviews of this kind, but it follows the logic from simpler to more complicated objects. It should also be noted that published papers rarely deal with comparative analysis of the behavior of molybdenum complexes in different oxidation states, even structurally related, and, the more so, with comparative analysis of related chemical reactions of these complexes.

2. MOLYBDENUM(VI) COMPLEXES

The overwhelming majority of Mo(VI) coordination compounds are oxo complexes [1]. Therefore, when considering the properties of mixed-ligand complexes containing, along with oxygen or its protonated forms, other ligands (e.g., organic), we should take into account the properties of the oxo complexes themselves. It is well known that transition metals in the oxidation states 4+ and higher, including Mo(VI), show pronounced affinity for the oxygen atom and tend to form “oxometallic ions” or oxo complexes [4]. The metal–oxygen bonds in such complexes are multiple and very strong; they are formed by σ and π interactions [1, 5]. In going to higher oxidation states, a transition metal tends to form a larger number of M–O bonds. Among cations having the d^0 electronic configuration, Ti(VI) and V(V) form octahedral species $TiO(H_2O)_5^{2+}$ and *cis*-$VO_2(H_2O)_4^+$; Cr(VI) and Mn(VII) form tetrahedral anions CrO_4^{2-} and MnO_4^-; and Mo(VI) forms both tetrahedra MoO_4^{2-} and octahedra MoO_6. Transition metal atoms in higher oxidation states very frequently form bi- and polynuclear species with bridging oxygen atoms. Characteristic structures of oxo complexes of some transition metals are given below.



The majority of the oxo complexes being discussed have the coordination number 4 or 6. However, the structure of these species is noticeably distorted because of very high strength of the metal–oxygen bonds. Therefore, these species often do not have regular tetrahedral or octahedral geometry (except MO_4^{m-} ions). X-ray diffraction studies showed that, in monooxo complexes of transition metals, the bonds in the *trans* position to the M–O bond are longer than those in the *cis* positions, and the central metal atom is noticeably displaced from the basal ligand plane [6].

2.1. Complexes of Molybdenum(VI) with Oxygen Donor Atoms

The structure and reactivity of Mo(VI) complexes are determined [7] by the number and type of coordinated oxygen atoms or their protonated forms.

Terminal oxygen atoms are arranged in the *cis* position relative to each other. This structure allows maximal utilization of the d_π orbitals (d_{xz}, d_{yz}, d_{xy} with ligands along x, y, and z axes) of the acceptor by strong π-donor oxo groups [1]. Many authors note [1, 3, 8, 9] structural fragments characteristic of Mo(VI) complexes: *cis*-MoO_2^{2+} and *fac*-MoO_3 for mononuclear complexes and $Mo_2O_3^{6+}$ and $Mo_2O_5^{2+}$ for binuclear complexes.

Four terminal oxygen atoms (O_t) bound to Mo(VI) by multiple bonds prevent bonding of Mo(VI) with other ligands. However, with a smaller number of terminal oxygen atoms, molybdenum coordinates other ligands; in so doing, the Mo–O_t multiple bonds become stronger. For example, the mean Mo–O_t bond length decreases in the order $MoO_4 > MoO_3L_3 > MoO_2L_4 > MoOL_5$.

Molybdenum(VI) complexes in most cases have an octahedral configuration. Other configurations can be realized in the following cases:

a complex contains four strong π-donor groups;

the size of the chelate rings and steric hindrance make occupation of octahedral positions unfavorable;

interligand steric repulsion and interactions between coordinated atoms of a polydentate ligand prevent normal arrangement of the ligands.

Molybdenum(VI) complexes exhibit a pronounced *trans* effect consisting in weakening and lengthening of the bond in the *trans* position to a ligand forming a strong bond with the central atom. Based on the bond length data, the ligands can be arranged in the following order with respect to the *trans* effect: CO, N_2 < NO < RN^{2-} < O^{2-} < N^{3-}.

Detailed studies showed that ligands having strong orbital overlap with the metal atom and forming strong covalent bonds destabilize the bond in the *trans* position and simultaneously enhance the *cis* bond with the central atom.

Oxo ligands undergo protonation and act as bridges in the formation of μ-oxo complexes. The molybdate ion MoO_4^{2-} containing four terminal oxo ligands prevails in solutions at pH > 7 and has a tetrahedral configuration. With a decrease in pH, the coordination number increases from 4 to 6, and octahedral Mo(VI) complexes start to prevail in the solution [1]. Analysis of the thermodynamic characteristics of reactions of successive protonation of the molybdate ion showed [10] that the coordination number changes in going from the monoprotonated molybdate ion $HMoO_4^-$ having the tetrahedral structure to the diprotonate octahedral species $[MoO_2(OH)_2(H_2O)_2]$.

An increase in the Mo(VI) concentration in acid solutions leads to condensation of the complexes and formation of a series of bi- and polynuclear complexes [11–13]. Dimerization of the Mo(VI) oxo complexes in 3 M $Na(H)ClO_4$ was studied in [12] in the Mo concentration range 3×10^{-5}–1.5×10^{-2} M. The following dimeric species were detected in the solutions: $[Mo_2O(OH)_9(H_2O)]^+$, $[Mo_2O(OH)_8(H_2O)_2]^{2+}$, and $[Mo_2O(OH)_7(H_2O)_3]^{3+}$. The equilibrium constant of the dimerization of $[Mo(OH)_5(H_2O)]^+$ with the formation of $[Mo_2O(OH)_8(H_2O)_2]^{2+}$ is 97 ± 15 l mol^{-1} at 25°C. In 2 M CF_3SO_3H at 25°C, the dimerization constant of the Mo(VI) complexes is 13.4×10^2 l mol^{-1}; correspondingly, at $C_{Mo(VI)} \le 1 \times 10^{-4}$ M, only mononuclear cations $[MoO_2(OH)(H_2O)_3]^+$ exist in the solution under these conditions.

Tytko et al. [14] summarized published data on mononuclear and polynuclear oxo complexes of Mo(VI) and on their protolytic equilibria in solutions with different supporting electrolytes and found that, at 25°C in 1 M NaCl, the following species exist in aqueous solutions of Mo(VI) of not-too-low concentrations [denoted as (*p,q*), where *p* and *q* are stoichiometric coefficients in the formula $H_p(MoO_4)_q^{(2q-p)-}$]: (1,1), (2,1), (2,2), (3,2), (4,3), (5,4), (6,4), (8,7), (9,7), (10,7), (11,7), (12,8), and (13,8). In 3 M $NaClO_4$ at 25°C, in addition to the above complexes, species of higher nuclearity were detected: (14,12), (15,12), (16,12), (32,18), and (64,36).

In 1 M $NaClO_4$ at pH 1.0 and 2.0, Cruywagen and Draaijer [15] detected the anions $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ and $[Mo_{18}O_{56}]^{4-}$, respectively. The speciation diagram similar to the diagrams [16] of the distribution of protonated species of Mo(VI) oxo complexes is shown in Fig. 1.

At the same time, the tendency toward formation of polynuclear compounds becomes considerably weaker with decreasing pH. The speciation diagram shows that, at pH < 1, the number of the coexisting mono- and polynuclear oxo complexes is minimal, and the monomer whose structure can be adequately [5] expressed by the formula $[MoO_2(OH)_2(H_2O)_2]$ is virtually the only species. At the same time, as the acid concentration is increased, the $[MoO_2(OH)(H_2O)_3]^+$ ion is formed by reaction (1):

$$[MoO_2(OH)_2(H_2O)_2] + H^+ \rightleftarrows [MoO_2(OH)(H_2O)_3]^+. \quad (1)$$

However, in less acidic solutions, even at low Mo(VI) concentrations, bi- and trinuclear complexes cannot be fully excluded from consideration.

The equilibrium constant of reaction (1), K_{eq} 11.4 in 2 M $HClO_4$ [17], suggests that, without complexing agents, the $[MoO_2(OH)(H_2O)_3]^+$ ion will be the major (>90%) species at pH 0; this ion contains the stable structural fragment *cis*-MoO_2^{2+} characteristic [9] of

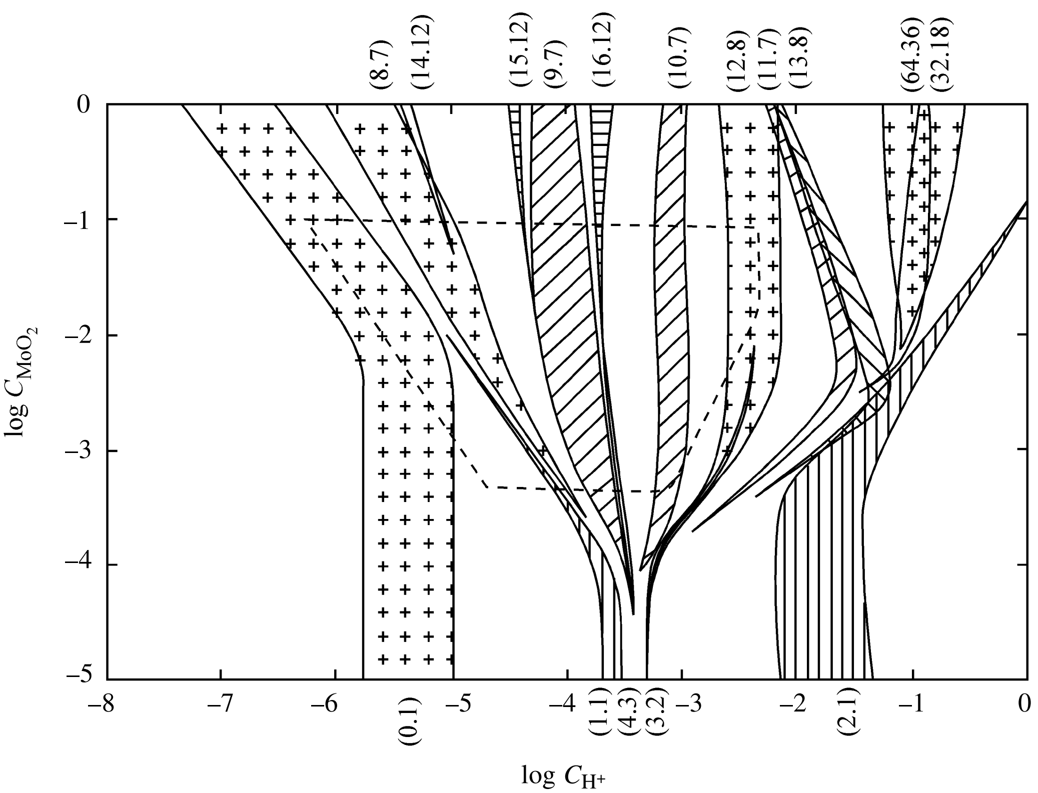


Fig. 1. Speciation diagram of Mo(VI) complexes in aqueous solutions [14]; the middle of each cross-hatched area corresponds to the conditions under which the concentration of the corresponding species is maximal, and the width denotes the relative content of this species.

mononuclear Mo(VI) complexes. Irrespective of the nature of other ligands, these complexes contain two short Mo=O bonds in the *cis* position. The Mo=O distance is 1.67±0.05 Å with rare exceptions, and the OMoO bond angle varies from 102° to 114°. The strong deviation from the nominal value of 90° is due to mutual repulsion of the Mo–O multiple bonds.

In particular, an increase in the HCl concentration in a solution containing Mo(VI) complexes leads to the formation of chloro complexes in which the MoO_2^{2+} fragment is preserved throughout the acid concentration range [reactions (2)–(4)]:

$$[MoO_2(OH)(H_2O)_3]^+ + Cl^- = [MoO_2(OH)Cl(H_2O)_2], \quad (2)$$

$$[MoO_2(OH)Cl(H_2O)_2] + Cl^- + H^+ = [MoO_2Cl_2] + 3H_2O, \quad (3)$$

$$[MoO_2Cl_2] + Cl^- = [MoO_2Cl_3]^-. \quad (4)$$

Calculation [18] of the equilibrium constants of reactions (2)–(4) gives $\log K_2$ $-0.89-0.04$, $\log K_3$ -1.42 ± 0.02, and $\log K_4$ -2.64 ± 0.09. These values suggest that the prevailing mononuclear Mo(VI) species in HCl solutions are $[MoO_2(OH)(H_2O)_3]^+$ (1–3.5 M HCl) and $[MoO_2Cl_2]$ (3.5–10 M HCl) (Fig. 2).

2.2. Complexes of Molybdenum(VI) with Polydentate Organic Ligands

Structural data are available [19] for numerous six-coordinate Mo(VI) complexes containing a MoO_2^{2+} group. One of characteristic features of such com-

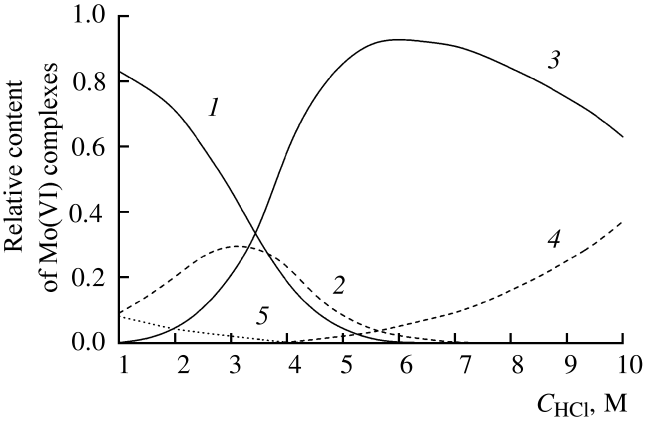


Fig. 2. Ratio of various Mo(VI) complex species in HCl solutions: (*1*) $[MoO_2(OH)(H_2O)]^{3+}$, (*2*) $[MoO_2(OH)\cdot Cl(H_2O)_2]$, (*3*) $[MoO_2Cl_2]$, (*4*) $[MoO_2Cl_3]^-$, and (*5*) $[MoO_2(OH)_2(H_2O)_2]$.

Table 1. Equilibrium constants of reactions of Mo(VI) oxo complexes with *edta*

Reaction		log *k*
MoO_4^{2-} + $H\textit{edta}^{3-}$ + H^+ $\longrightarrow$ $[MoO_3\textit{edta}]^{4-}$ + H_2O	(5)	8.8
MoO_4^{2-} + $\textit{edta}^{4-}$ + $2H^+$ $\longrightarrow$ $[MoO3\textit{edta}]^{4-}$ + H_2O	(6)	18.5
$[MoO_3\textit{edta}]^{4-}$ + H^+ $\longrightarrow$ $[MoO_3(H\textit{edta})]^{3-}$	(7)	7.5
$2MoO_4^{2-}$ + $\textit{edta}^{4-}$ + $4H^+$ $\longrightarrow$ $[Mo_2O_6\textit{edta}]^{4-}$ + $2H_2O$	(8)	35.1
MoO_4^{2-} + $[MoO_3\textit{edta}]^{4-}$ + $2H^+$ $\longrightarrow$ $[Mo_2O_6\textit{edta}]^{4-}$ + H_2O	(9)	17.2
MoO_3 + $\textit{edta}^{4-}$ $\longrightarrow$ $[MoO_3\textit{edta}]^{4-}$	(10)	10.7
$2MoO_3$ + $\textit{edta}^{4-}$ $\longrightarrow$ $[Mo_2O_6\textit{edta}]^{4-}$	(11)	19.5
MoO_3 + $[MoO_3\textit{edta}]^{4-}$ $\longrightarrow$ $[Mo_2O_6\textit{edta}]^{4-}$	(12)	8.8
$[Mo_2O_6\textit{edta}]^{4-}$ + $H_2\textit{edta}^{2-}$ $\longrightarrow$ $2[MoO_3(H\textit{edta})]^{3-}$	(13)	0.26

plexes is the occurrence of a strong *trans* effect. It is appropriate to consider this effect using as example complexes MoO_2L_2 with two symmetrical bidentate ligands. For example, in $MoO_2(PhCOCHCOPh)_2$, the length of the Mo–O bonds in the *trans* position to the $Mo–O_t$ bond is 2.17 Å, whereas the bonds in the *cis* position to the $Mo–O_t$ bond (and in the *trans* position to each other) are appreciably shorter: 1.99 Å. The complex of Mo(VI) with an unsymmetrical bidentate ligand 8-quinolinol, MoO_2Ox_2, has the C_2 symmetry with the nitrogen atoms in the *trans* positions to the $Mo–O_t$ bonds. The bond lengths in this complex are as follows [20]: $Mo–O_t$ 1.71, Mo–N 2.32, and $Mo–O_{(L)}$ 1.98 Å.

Cervilla et al. [21] suggested a general scheme of the formation and transformations of Mo(VI) complexes with hydroxy and polybasic carboxylic acids (tartaric, malic, malonic, lactic, oxalic, citric) and with polyhydric alcohols (mannitol, sorbitol, adonitol). They found that only mono- and binuclear complexes were formed in aqueous solutions; pH of the solution is the major factor responsible for the formation of particular complex species and for their mutual transformations in solutions.

The equilibrium constants of the interaction of molybdenum oxo complexes with ethylenediaminetetraacetate (*edta*) were determined by potentiometric titration and temperature-jump relaxation [22, 23]; the results (~10^{-2} M Mo, ~10^{-3} M *edta*) are given in Table 1. Among these data, the equilibrium constants of reactions (6) and (9) are actually the stability constants of the mono- and binuclear complexes with *edta* ($10^{18.5}$ and $10^{17.2}$, respectively). The first molybdate ion coordinates with *edta* more strongly than the second ion [24], which may be due both to steric hindrance and to the inductive effect of the MoO_3 group in the $[MoO_3\textit{edta}]^{4-}$ anion. The complexation step constants given in these papers are in good agreement with other published data [25].

The structure of the binuclear complex $[Mo_2O_6 \cdot \textit{edta}]^{4-}$ was determined [22, 26]; the Mo atoms are in the *trans* positions with respect to the bridging ligand. Also, from the similarity of the IR spectra of the crystalline complex in KBr and of its solution in D_2O [27], it was concluded [28] that the complex is kinetically inert.

Molybdenum(VI) in its complexes enters into redox reactions leading to its reduction. In dilute acids, Mo(VI) can be reduced both with typical chemical reductants (Hg [29], Sn, Zn/Hg, $N_2H_4 \cdot H_2O$ [30]) and electrochemically [31]; the reduction product is a Mo(V) complex. A detailed kinetic study of the electrochemical reduction of solutions of Mo(VI) complexes in trifluoromethanesulfonic acid showed [17] that the reduction involved mononuclear Mo(VI) complexes and yielded a mononuclear Mo(V) complex; its structure, however, could not be determined, because in the absence of complexing agents this complex rapidly transformed into the binuclear Mo(V) complex $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$. At the same time, when the reaction was performed in relatively concentrated (>6 M) solutions, when the formation of the binuclear complex was excluded, the reaction yielded the mononuclear complex $[MoOCl_5]^{2-}$ which was further reduced to $[MoCl_6]^{3-}$.

3. MOLYBDENUM(V) COMPLEXES

In solutions of noncomplexing acids, the most stable Mo(V) species is the extensively studied complex cation $[Mo_2O_4]^{2+}$. Under these conditions, even if monomeric species exist, they can only be intermediates. Nevertheless, both mono- and binuclear complexes of other structures do exist in the presence of any ligands. The characteristic structures of such complexes are shown above (d^1 configuration).

3.1. Mononuclear Molybdenum(V) Complexes

Apparently, the best studied among mononuclear Mo(V) complexes is the $[MoOCl_5]^{2-}$ anion which can be isolated as a solid in the form of various salts; in solutions it exists only at HCl concentrations exceeding 8 M, and only at HCl concentrations close to 9 M this species becomes prevalent. At lower acid concentrations, the $[MoOCl_5]^{2-}$ anion undergoes hydrolysis

Table 2. Electronic absorption spectra of molybdenum complexes in different oxidation states

Complex	Oxidation state	$\bar{\nu}_{exp}$, cm^{-1}	ε, l mol^{-1} cm^{-1}	λ_{exp}, nm	References
$[MoOCl_5]^{2-}$	V	41700	11100	240	[34]
		32200	5780	311	
		28200	475	355	
		22500	13.7	444	
		14050	19.0	712	
$[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$	V	39216	4320	255	[35]
		33898	3546	295	
		26042	103	384	
$[Mo_2(\mu\text{-}O)_2O_2\mathit{edta}]^{2-}$	V	33670	8980	297	[35, 36]
		25641	336	390	
$[Mo(H_2O)_6]^{3+}$	III	31250	19	320	[37]
		25907	13.3	386	
$[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$	III	27778	306	360	[38]
		17483	39	572	
		16026	43	624	
$[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(H_2O)_{10}]^{5+}$	III	23810	300	420 sh	[39]
		15748	240	635	
		12121	135	825	
$[Mo_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(H_2O)_9]^{5+}$	III, IV	25126	690	398	[39, 40]
		20202	345	495 sh	
		9524	300	1050	
$[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$	IV	32258	1200	310	[39, 40]
		20202	210	520	
$[Mo_2(\mu\text{-}OH)_2(Cl)_n(H_2O)_{8-2n}]^{(4-n)^+}$ (n = 1–2)	III	27626	626	362	[38]
		16981	72	589	
		15846	84	631	
$[Mo_2(\mu\text{-}OH)_2(SO_4)(H_2O)_6]^{2+}$	III	28090	303	356	[38]
		15361	43	651	

to form other mononuclear complexes, e.g., the related oxo species $[MoOCl_4]^-$ and $[MoOCl_4(H_2O)]^-$, with their subsequent polymerization [32, 33].

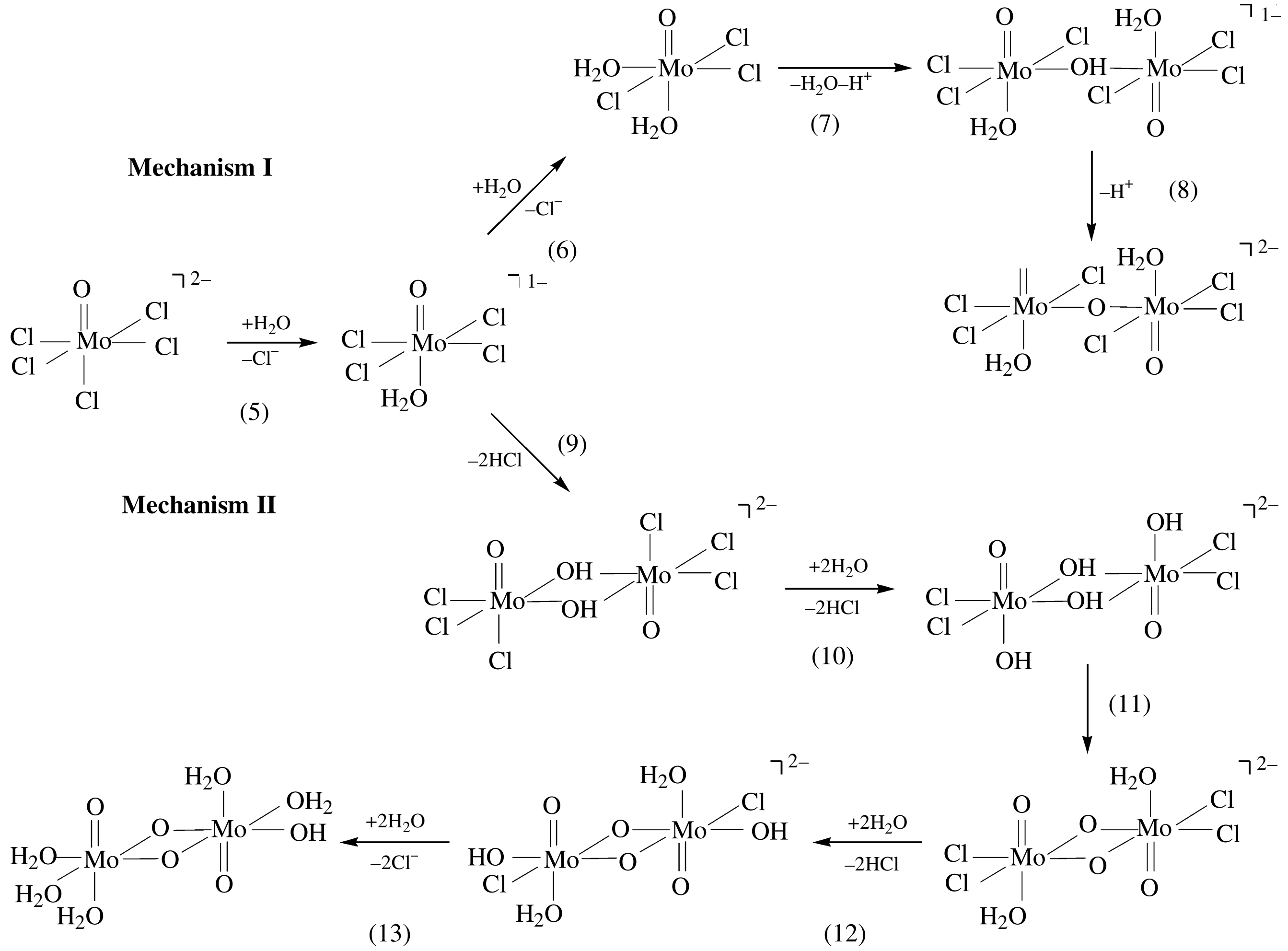
The existence of a five-coordinate anion $[MoOCl_4]^-$ along with the octahedral complexes is due to the strong *trans* effect of the terminal oxo ligand. For example, in the structure of $K_2[MoOCl_5]$, the lengths of the four equatorial Mo–Cl bonds are 2.40 Å, whereas the axial Mo–Cl bond (*trans* to the O atom) is appreciably longer: 2.59 Å. In the five-coordinate complex, the Mo–O bond is shorter (~1.60 Å) than in the octahedral complex (~1.67 Å).

The electronic absorption spectrum [34] of the $[MoOCl_6]^{2-}$ anion [34] contains five absorption bands indicated in Table 2. The hydrolysis of the complex is accompanied by an increase in the intensity of the bands at 444 [$^2B_2 \to {}^2B_1$ (I)] and 712 nm [$^2B_2 \to {}^2E$ (I)] in the range of HCl concentrations from 10 to 6 M, which was attributed in [41] to a decrease in the number of chlorine atoms in the inner coordination sphere and, as a result, to strengthening of the Mo–O bond.

3.2. Binuclear Molybdenum(V) Complexes

Aqua hydroxo complexes of Mo(V). The binuclear Mo(V) complex with one bridging oxygen atom (see above) $[Mo_2O_3]^{3+}$ is known [42] only as a fragment of complexes with organic ligands containing simultaneously two heteroatoms: N and S (e.g., *o*-thiopyridine). Therefore, in aqueous solutions species containing the $[Mo_2O_3]^{4+}$ fragment were not reported.

As shown for the first time by cryoscopic measurements [43] and experiments on ion exchange in solutions of noncomplexing acids, the main Mo(V) species in such media is the binuclear oxo aqua cation $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$, which is also, apparently, the final product of hydrolysis of mononuclear com-



plexes, including $[MoOCl_5]^{2-}$. This species is stable in a wide range of acid concentrations. In particular, according to data of electronic spectroscopy [35, 44], in $HClO_4$ solutions this species exists in the $HClO_4$ concentration range from 0.01 to 6 M.

The spectral characteristics of this cation are given in Table 2. These data are in good agreement with the spectra described in other papers [43, 45, 46].

In acid solutions, the binuclear complex is formed by hydrolysis of the monomeric species. The general scheme of hydrolysis [32, 47–49] includes Eqs. (5)–(13) and mechanisms I and II.

Mechanism I includes the following reactions [32]:

$$[MoOCl_5]^{2-} + H_2O \longrightarrow [MoOCl_4(H_2O)]^- + Cl^-, \quad (5)$$

$$[MoOCl_4(H_2O)]^- + H_2O \longrightarrow [MoOCl_3(H_2O)_2] + Cl^-, \quad (6)$$

$$2[MoOCl_3(H_2O)_2] \longrightarrow [Mo_2(\mu\text{-}OH)O_2Cl_6(H_2O)_2]^- + H_2O + H^+, \quad (7)$$

$$[Mo_2(\mu\text{-}OH)O_2Cl_6(H_2O)_2]^- \longrightarrow [Mo_2(\mu\text{-}O)O_2Cl_6(H_2O)_2]^{2-} + H^+. \quad (8)$$

As the acid concentration is decreased to 5 M, a dimer containing one bridging oxygen atom is formed. However, this seems improbable, because with a further decrease in the acid concentration in solution the amount of binuclear compounds should increase. Furthermore, at lower C_{HCl} the spectral pattern changes essentially [50], suggesting that another transformation mechanism (mechanism II), whose first step is also described by Eq. (5), is operative:

$$2[MoOCl_4(H_2O)]^- \longrightarrow [Mo_2(\mu\text{-}OH)_2O_2Cl_6]^{2-} + 2H^+ + 2Cl^-, \quad (9)$$

$$[Mo_2(\mu\text{-}OH)_2O_2Cl_6]^{2-} + 2H_2O \longrightarrow [Mo_2(\mu\text{-}OH)_2O_2Cl_4(OH)_2]^{2-} + 2H^+ + 2Cl^-, \quad (10)$$

$$[Mo_2(\mu\text{-}OH)_2O_2Cl_4(OH)_2]^{2-} \longrightarrow [Mo_2(\mu\text{-}O)_2O_2Cl_4(H_2O)_2]^{2-}, \quad (11)$$

$$[Mo_2(\mu\text{-}O)_2O_2Cl_4(H_2O)_2]^{2-} + 2H_2O \longrightarrow [Mo_2(\mu\text{-}O)_2O_2(OH)_2Cl_2(H_2O)_2]^{2-} + 2H^+ + 2Cl^-, \quad (12)$$

$$[Mo_2(\mu\text{-}O)_2O_2(OH)_2Cl_2(H_2O)_2]^{2-} + 2H_2O \longrightarrow [Mo_2(\mu\text{-}O)_2O_2(OH)_2(H_2O)_4] + 2Cl^-. \quad (13)$$

In this case, the dimer is formed already in an early step [step (9)], after which the chloride ions in the inner sphere are gradually replaced by hydroxy groups or water molecules [steps (10), (12), (13)] and inner-sphere proton migration occurs [step (11)]. The equilibrium constants of formation of the binuclear complex $[Mo_2(\mu\text{-}O)_2O_2Cl_4(H_2O)_2]^{2-}$ are as follows [48]: 4.01 (20°C), 3.82 (30°C), 3.65 (40°C); $\Delta H^0(14 + 18 + 19 + 20) = -31.4$ kJ (mol dimer)$^{-1}$; $\Delta S^0(14 + 18 + 19 + 20) = -31.4$ J (mol dimer)$^{-1}$ K^{-1}. Later it was shown [51] that the formation of the binuclear complex $[Mo_2(\mu\text{-}OH)_2O_2Cl_4(OH)_2]^{2-}$ [reaction (10)] occurs in the acid concentration range from 6 to 4.5 M and is accompanied by heat release, $\Delta H^0(14 + 18 + 19 + 20 + 21 + 22) = -44$ kJ (mol dimer)$^{-1}$. At an acid concentration less than 4.5 M, Mo(V) in solution exists in the form of binuclear complexes with chloride ions; the content of chloride ions in the inner sphere decreases in proportion with the acid concentration in the solution.

Particular attention should be given to the electronic structure of the binuclear complexes. As a rule, oxygen bridges are relatively short; therefore, the distances between the Mo atoms are also short, and metal–metal bonding may be possible. Indeed, the diamagnetism [49, 52] of the complexes containing the $[Mo_2(\mu\text{-}O)_2O_2]^{2+}$ group, short internuclear distances Mo–Mo (2.51–2.64 Å), and results of SCF MO LCAO calculations [1, 54] of isolated $[Mo_2(\mu\text{-}O)_2O_2]^{2+}$ groups indicate that a single two-electron σ bond Mo–Mo is realized in these complexes.

The well-known problem in experiments with Mo(V) oxo hydroxo complexes is their sensitivity to oxidation (including oxidation with atmospheric oxygen). In solutions with low acid concentrations (less than 3 M), Mo(V) compounds are readily oxidized with the formation of "molybdenum blues" [30, 55]. Molybdenum can be stabilized in oxidation state +5 by introducing strong N- or P-containing ligands into the inner sphere.

In acidic aqueous solutions, the complex $[Mo_2O_4 \cdot (H_2O)_6]^{2+}$ is readily oxidized with various oxidants (O_2, Fe^{3+}, $Cr_2O_7^{2-}$) with the formation [30, 55] of molybdic acid $[Mo(OH)_6]$. The standard electrode potential [56] of the Mo(VI)/Mo(V) couple in 1 M H_2SO_4 is 0.53 V. The kinetics of the reaction of the binuclear Mo(V) complex with the $[Fe(H_2O)_6]^{3+}$ ion in $HClO_4$ solutions [reaction (14)] is described [57] by Eq. (15):

$$[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 2Fe^{3+} + 2H_2O = 2[Mo(OH)_6] + 2Fe^{2+} + 4H^+, \quad (14)$$

$$-\frac{d[Mo_2O_4^{2+}]}{dt} = k[Mo_2O_4^{2+}]Fe^{3+}], \quad (15)$$

$$k = k_a + k_b/[H^+];\ k_a = 0.2\ \text{l mol s}^{-1};\ k_b = 1.27\ \text{s}^{-1};\ [H^+] = 0.6\text{–}1.5\ \text{M}.$$

Apparently, the rate-determining step is the abstraction of the first electron. Based on the inverse negative relationship of the rate constant of reaction (14) on the acid concentration, it was suggested that the limiting step of the oxidation of the binuclear Mo(V) complex is the reaction of the initial complex with the hydrolyzed Fe(III) cation $[Fe(OH)]^{2+}$ whose concentration in the solution decreases with an increase in the acid concentration; therefore, the reaction decelerates with increasing acid concentration.

Complexes of Mo(V) with ethylenediaminetetraacetate. When the complex $Na_2[Mo_2(\mu\text{-}O)_2O_2$*edta*] was characterized for the first time as a binuclear complex [22], it was shown by polarography and spectroscopy that there is one *edta* ligand per two Mo atoms in the complex and that this ligand coordinates in the bis-tridentate fashion to form a basket configuration. This molybdenum complex is unique in that the metal atoms to which *edta* coordinates are already linked with each other not only by two other bridges (O atoms) but also directly, by a metal–metal bond.

The complexation constant for $H_2[Mo_2(\mu\text{-}O)_2O_2 \cdot$ *edta*] is $(1.75 \pm 0.52) \times 10^{11}$ [58]. Owing to the chelate effect and donor power of the ligand heteroatoms, the complex is stable in solutions in a wide pH range (2–9), which is confirmed by the fact that the electronic absorption spectrum of the $[Mo_2(\mu\text{-}O)_2O_2$*edta*$]^{2-}$ anion (Table 2) remains unchanged for several days [35, 36].

Nevertheless, with an increase in the acidity *edta* is eliminated; the process is complete in 2 M $HClO_4$. The rate of *edta* elimination also depends on particular acid. For example, in 2 M HCl the dissociation is approximately twice as fast as in 2 M $HClO_4$ [35]. Another feature of the dissociation, revealed [35] by kinetic studies, is an unusual mechanism: first the bonds with carboxy groups are broken, with the subsequent protonation of the carboxy groups, and only then the Mo–N bonds are cleaved. This mechanism is apparently due to the considerably stronger *trans* effect of the terminal oxo groups, compared to the bridging oxo groups [59].

The chelate complex is considerably less susceptible to oxidation than the aqua ion. Even at pH > 1, a solution of $[Mo_2(\mu\text{-}O)_2O_2$*edta*$]^{2-}$ is insensitive to the presence of oxygen and stable for several days.

Table 3. Electronic absorption spectra of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ in acid solution (molar extinction coefficients are given per mole of Mo)

Acid	$\bar{\nu}_{exp}$, cm^{-1}	ε, $l\,mol^{-1}\,cm^{-1}$	λ_{exp}, nm
2 M HCl	32260, 19232	400, 71	310, 520
1 M H_2SO_4	32363, 19305	390, 69	309, 518
1 M HPTS,[a] 1 M $HClO_4$	33005, 19802	265, 63	303, 505

[a] HPTS is *p*-toluenesulfonic acid.

4. COMPLEXES OF MOLYBDENUM(IV)

Only one aqua complex containing molybdenum in oxidation state +4 is known [60]. Its structure is usually represented by the formula $[Mo_3(\mu_3O)(\mu\text{-}O)_3 \cdot (H_2O)_9]^{4+}$ (sometimes a brief formula, $[Mo_3O_4]^{4+}$, is used); it contains a bridging oxygen atom linked to three Mo atoms simultaneously. The complex is formed by coproportionation [61, 62] of Mo(III) with Mo(V) or of Mo(III) with Mo(VI) in 2 M HCl. The electronic absorption spectrum of the complex contains two bands [60, 62, 63] whose position is independent of particular acid (provided that the acid is noncomplexing) (Table 3). In the presence of chloride and sulfate ions, a slight bathochromic shift caused by formation of chloride and sulfate complexes is observed [63].

Participation of the trinuclear complex in redox reactions is largely determined by the strength of the cluster core $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3]^{4+}$. In acid solutions, electrochemical reduction of the trinuclear cluster $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ leads to the formation of a Mo(III) complex, $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(H_2O)_{10}]^{5+}$ ($E_{1/2}$ −0.25 V) whose structure is similar to that of the Mo(IV) complex [64], which determines the possibility of their reversible mutual transformation. At the same time, oxidation of the complex $[Mo_3(\mu_3\text{-}O) \cdot (\mu\text{-}O)_3(H_2O)_9]^{4+}$ is accompanied by breakdown of the stable polynuclear fragment; therefore, the rate constants of oxidation with various oxidants are low [65]. In particular, the complex does not noticeably react in $HClO_4$ solutions with $[Co(C_2O_4)_3]^{3-}$, and in the presence of stronger oxidants ($[Fe(phen)_3]^{3+}$, $[IrCl_6]^{2-}$) the oxidation is slow ($t_{1/2} > 1$ min). The primary oxidation product is apparently the binuclear Mo(V) complex $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$ [65]. However, its further oxidation to Mo(VI) with $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ is faster [57]; therefore, the final products of oxidation of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ in aqueous acid solutions are Mo(VI) compounds.

5. MOLYBDENUM(III) COMPLEXES

5.1. Mononuclear Complexes of Molybdenum(III) in Aqueous Solutions

After several unsuccessful attempts to prepare monomeric species containing the Mo(III) ion, the yellow triple-charged hexaaqua complex $[Mo(H_2O)_6]^{3+}$ was obtained [66–68] as a product of aquation of the hexachloromolybdate ion $[MoCl_6]^{3-}$ in noncomplexing acids (*p*-toluenesulfonic, HPTS; trifluoromethanesulfonic, HTFMS). In this case, the monomeric structure of the complex $[Mo(H_2O)_6]^{3+}$ was proved by its effective magnetic moment, 3.69 BM (34.2 $J\,T^{-1}$) [67], corresponding to three unpaired electrons.

The electronic absorption spectrum of $[Mo(H_2O)_6]^{3+}$ contains two weak absorption bands assigned [37] to *d–d* transitions (Table 2). One more very weak band at 560–600 nm ($\varepsilon < 0.5\ l\,mol^{-1}\,cm^{-1}$) is also mentioned [37]; it can be assigned to the spin-forbidden ${}^4A_{2g} \to {}^2T_{2g}$ transition.

Apparently, $[Mo(H_2O)_6]^{3+}$ is the only monomeric Mo(III) species in aqueous solutions at low acid concentrations. The existence of hydroxo complexes $[Mo(OH)_n(H_2O)_{6-n}]^{(3-n)+}$ at pH < 4 was reported by Mit'kina et al. [69]. They also stated that two hydroxo complexes $[Mo(OH)(H_2O)_5]^{2+}$ and $[Mo(OH)_2(H_2O)_4]^{+}$ with total stability constants of 10^{12} and 10^{23}, respectively, were formed at a molybdenum concentration of 10^{-4} M. However, the existence of such complexes in solutions with a high acid concentration was not confirmed in any other paper.

Solutions of the mononuclear molybdenum(III) aqua complex are unstable, and on standing for several days the solution color changes from yellow to green because of condensation of the complexes [31, 70] by reaction (16):

$$2[Mo(H_2O)_6]^{3+} = [Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 2H_2O + 2H^+. \quad (16)$$

At the same time, at high HCl concentrations (from 2 to 12 M) and Mo(III) concentration of 10^{-3} to

10^{-1} M, the complexes do not polymerize [71], as follows from the independence of the coefficients of the spin–lattice and spin–spin relaxation efficiency from the Mo(III) concentration.

5.2. Polynuclear Molybdenum(III) Complexes

The binuclear species $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ are formed by electrolytic reduction or reduction in a Jones reducer (Zn/Hg) in HPTS of Mo(VI) solutions [36], or by electrochemical reduction of binuclear species $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$ in HTFMS.

Solutions containing the $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ cations are stable in the absence of oxidants. They have a blue-green color and show three absorption bands in the electronic spectrum (Table 2) [70].

The band appearing at 360 nm, which was absent in the spectrum of $[Mo(H_2O)_6]^{3+}$, apparently characterizes the hydroxo-bridged structure $[Mo_2(\mu\text{-}OH)_2 \cdot (H_2O)_8]$. Analysis of the EXAFS spectra showed [72] that the distance between the Mo atoms in this dimer is 2.54 Å, which, along with the diamagnetism of the complex [38], suggests the presence of a multiple molybdenum–molybdenum bond.

In the presence of HCl in high concentrations, water molecules can be replaced with the formation of chloro complexes $[Mo_2(\mu\text{-}OH)_2Cl_n(H_2O)_{8-n}]^{(4-n)+}$, where $n = 1$ or 2 [32, 38]. This replacement causes a bathochromic shift of the long-wave bands in the electronic absorption spectrum of the complex [589 and 631 nm instead of 572 and 624 nm (Table 2)] but does not affect the position of the band at 360 nm, which is well consistent with the above assumption that this band is characteristic of the bridged fragment $[Mo_2(\mu\text{-}OH)_2]^{4+}$.

In contrast to its higher valence analogs, Mo(III) tends to form aqua complexes with more than two metal atoms. The most stable trinuclear species is the $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(H_2O)_{10}]^{5+}$ cation, also briefly designated as $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3]^{5+}$. According to structural data, this complex can be considered as a product of addition of a Mo atom via two hydroxo bridges to the stable core $[Mo_2(\mu\text{-}OH)_2]^{4+}$. In the process, the bridging O atoms remain protonated, which is confirmed by ion-exchange studies [40, 73].

The electronic absorption spectrum of $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(H_2O)_{10}]^{5+}$ differs essentially from that of the binuclear Mo(III) complex (Table 2) [39]. The absorption all bands are appreciably red-shifted (i.e., the electronic transition energy decreases), which is naturally associated with a decrease in the splitting of the *d* orbitals with an increase in the number of metal atoms in the core of the complex.

The chemical properties of the trinuclear complex only slightly differ from those of the binuclear complex: It enters into all the reactions characteristic of Mo(III), including the redox processes caused by the low [38, 56] reduction potential of the Mo(V)/Mo(III) couple, E −0.25 V. Therefore, experiments with such compounds require thorough precautions; if possible, the low oxidation state of molybdenum should be additionally stabilized by choosing appropriate ligands. The oxidation most probably does not result in the breakdown of the cluster core; the reaction product in this case is the trinuclear Mo(IV) complex $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$.

5.3. Complexes of Molybdenum(III) with Ethylenediaminetetraacetate

Mononuclear complexes of Mo(III) with *edta* are unknown. At the same time, two binuclear structures are formed by reduction of the corresponding Mo(V) complex $[Mo_2(\mu\text{-}O)_2O_2\mathit{edta}]^{2-}$ with zinc metal. When performed in acetate buffer [74] at pH 5, the reduction yields $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)\mathit{edta}]^{-}$. This complex contains four bridging ligands (i.e., all the ligands in the complex are bridging). When performed at a lower pH (3–4) in the absence of acetate ions [75], the reduction yields uncharged $[Mo_2(\mu\text{-}OH)_2(H_2O)_2\mathit{edta}]$. In both cases, ethylenediaminetetraacetate acts as a bis-tridentate ligand forming a characteristic basket configuration.

The Mo–Mo distance in the first compound, 2.43 Å, is even shorter than in the aqua complex, apparently, owing to formation of an additional acetate bridge. Diamagnetism of these complexes suggests that the metal–metal bond is triple ($\sigma + 2\pi$) [76].

Out of these two complexes, the $[Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)\mathit{edta}]^{-}$ anion appeared to be more resistant to oxidation owing to its "closed" structure, although in aqueous solution this complex also, similarly to its acetate-free analog, slowly takes up oxygen to form the initial species, $[Mo_2(\mu\text{-}O)_2O_2\mathit{edta}]^{2-}$.

5.4. Redox Reactions of Molybdenum(III) Complexes

Because of the extremely low reduction potential, $E(Mo^{V}/Mo^{III})$ −0.25 V, redox reactions are the most typical of Mo(III) compounds. Oxidation of binuclear complexes is often accompanied by cardinal changes in the structure of the cluster core; as a rule, the products and intermediates of such reactions are complexes containing three or more metal atoms. The characteristic products of oxidation of Mo(III) complexes are stable trinuclear clusters $[Mo_3^{IV}(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ or a mixed-valence cluster containing one Mo(IV) atom per two Mo(III) atoms [40, 77]. The occurrence of this process depends on the solution acidity and on the oxidant [73]. The structure $[Mo_3(\mu_3\text{-}O)(\mu\text{-}OH)_3 \cdot (H_2O)_9]^{5+}$ was suggested taking into account the formal oxidation state of Mo (+3.33) and changes in the electronic absorption spectra (Table 2). A specific feature of the spectrum of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(H_2O)_9]^{5+}$ is an absorption band appearing in the near-IR range (1050 nm); its intensity and half-width are comparable with those of the related intervalent bands in mixed-valence ruthenium complexes [78, 79].

In aqueous acid solutions in the presence of oxidants (O_2, Fe^{3+}, $[Co(C_2O_4)_3]^{3-}$, $IrCl_6^{2-}$), mononuclear $[Mo(H_2O)_6]^{3+}$ is readily oxidized [57, 80]. A detailed study of the reaction of Mo(III) hexaaqua cation with one-electron oxidants ($[Fe(H_2O)_6]^{3+}$, $[Co(C_2O_4)_3]^{3-}$, $IrCl_6^{2-}$) showed [80] that the oxidation kinetics is described by Eq. (17):

$$-\frac{d[\mathrm{Mo(V)}]}{dt} = -\frac{d[\mathrm{Fe(III)}]}{dt} = k[\mathrm{Mo(V)}][\mathrm{Fe(III)}]. \quad (17)$$

At a large excess of the Mo(III) complex, the final oxidation product is the binuclear Mo(V) complex $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$, which is further oxidized to Mo(VI) compounds in the presence of excess oxidant [56].

The binuclear Mo(III) complex $[Mo_2(\mu\text{-}OH)_2 \cdot (H_2O)_8]^{4+}$ is formed by electrolytic or chemical (with amalgamated zinc, Zn/Hg) reduction in HPTS of Mo(VI) solutions [38] or by electrochemical reduction of the binuclear Mo(V) complex $[Mo_2(\mu\text{-}O)_2O_2 \cdot (H_2O)_6]^{2+}$ in HPTS.

The reduction of $[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$ in HCl or H_2SO_4 solution also yields binuclear Mo(III) complexes $[Mo_2(\mu\text{-}OH)_2Cl_n(H_2O)_{8-n}]^{(4-n)-}$, where n = 1 or 2, and $[Mo_2(\mu\text{-}OH)_2(SO_4)(H_2O)_6]^{2+}$. In this case, long-wave bands in the electronic absorption spectrum undergo a bathochromic shifgt (Table 2), and the band at 360 nm remains unchanged, which also supports the assumption that this band is characteristic of the bridged structure [38].

Similarly to the mononuclear aqua cation, the complex $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ is readily oxidized with O_2, Fe^{3+}, and $[Co(C_2O_4)_3]^{3-}$; the oxidation product, Mo(V) complex, is also binuclear [70]: $[Mo_2(\mu\text{-}O)_2 \cdot O_2(H_2O)_6]^{2+}$. The binuclear complex $[Mo_2(\mu\text{-}OH)_2 \cdot (H_2O)_8]^{4+}$ is oxidized faster than the mononuclear complex $[Mo(H_2O)_6]^{3+}$ under the same conditions, which is due to structural similarity of the initial and final reaction components [3].

6. MOLYBDENUM(II) COMPLEXES

The first structurally characterized [81] Mo(II) compound was the binuclear complex $Mo_2(O_2CCH_3)_4$, virtually insoluble in water. Somewhat later [82], a molybdenum(II) chloride complex was prepared by the reaction of KCl with $Mo_2(O_2CCH_3)_4$ in cold hydrochloric acid. The compound was identified as $K_4Mo_2Cl_8 \cdot 2H_2O$ [82]; it was found that it contains the $[Mo_2Cl_8]^{4-}$ anion of the D_{4h} symmetry, in which the distance between the Mo atoms is 2.138 Å. In the subsequent period, the number of synthesized and identified binuclear Mo(II) complexes, some of which are water-soluble, grew very rapidly and still continues to grow [83]. The large interest in this class of compounds is due to a specific feature of binuclear Mo(II) complexes distinguishing them from other molybdenum coordination compounds: formation of a quaternary ($\sigma + 2\pi + \delta$) molybdenum–molybdenum bond. Qualitative description of this bond in terms of the MO theory was done for the first time by Cotton and Wilkinson [83]; they also substantiated experimentally and theoretically the possibility of describing the electronic structure of various Mo(II) complexes [including $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$] from the viewpoint of formation of a quaternary molybdenum–molybdenum bond.

6.1. Molybdenum(II) Complexes in Aqueous Solutions

The formation of a multiple metal–metal bond in Mo(II) complexes predetermines the possibility of their participation in reversible redox reactions, in view of the fact that the loss of one electron (and in some cases of several electrons) from the M–M bonding orbitals (or addition of electrons to M–M antibonding orbitals) does not fully break the metal–metal bond [83]. Thus, redox reactions involving clusters that contain multiple metal–metal bonds frequently occur without essential changes in the structure of the clusters and therefore are not hindered kinetically to a significant extent. This fact opens prospects for using clusters as catalysts in various industrial processes. In this connection, the modern studies concerning Mo(II) complexes primarily deal with redox properties of the complexes [84] and their possible catalytic activity [85], including reactions with complexes of other transition metals [86].

Chemical reactions involving these complexes can be subdivided into three main groups:

reactions involving no structural transformations of the central fragment of the binuclear complexes (adduct formation);

ligand substitution reactions (with or without oxidation of the Mo_2^{4+} fragment, depending on conditions);

complete breakdown of the dimer (redox reactions in which molybdenum is oxidized to molybdate ion or to other Mo species in higher oxidation states).

Ligand substitution reactions in molybdenum complexes $Mo_2(O_2CCH_3)_4$ and $K_4Mo_2Cl_8$ without breakdown of the cluster core Mo_2^{4+} occur in aqueous [87] and nonaqueous [88, 89] solutions relatively readily; however, the oxygen access should be excluded, because both starting complexes are rapidly oxidized in solutions.

Dissolution of $K_4[Mo_2Cl_8]$ in 1 M H_2SO_4 is accompanied by replacement of chloride ions in the coordination sphere of the complex by sulfate ions [87] with the formation of the complex $[Mo_2(SO_4)_4]^{4-}$:

$$[Mo_2Cl_8]^{4-} + 4SO_4^{2-} = [Mo_2(SO_4)_4]^{4-} + 8Cl^-. \quad (18)$$

In this complex, the Mo_2^{4+} fragment remains unchanged. The $[Mo_2(SO_4)_4]^{4-}$ anion exists in the eclipsed conformation (D_{4h} symmetry) with four bridging sulfate ions (Fig. 3).

The binuclear aqua cation $[Mo_2(H_2O)_8]^{4+}$ is formed on adding a small excess (1.1 : 1 relative to sulfate ions in the starting complex) of $Ba(CF_3SO_3)_2$ to a solution of the complex in CF_3SO_3H. After separation of the $BaSO_4$ precipitate, the solution contains the aqua complex $[Mo_2(H_2O)_8]^{4+}$, also having the eclipsed conformation [87].

The stability of the above-described complexes $[Mo_2Cl_8]^{4-}$, $[Mo_2(H_2O)_8]^{4+}$, and $[Mo_2(SO_4)_4]^{4-}$ in aqueous solutions is largely determined by their resistance to oxidation with atmospheric oxygen. The least stable is the Mo(II) aqua complex; its solutions are stable for only 3 h after the preparation [87]. Solutions of the complexes $[Mo_2Cl_8]^{4-}$ and $[Mo_2(SO_4)_4]^{4-}$ in hydrochloric and sulfuric acids, respectively, are stable for a long time in the absence of oxygen. At the same time, with an increase in the HCl concentration in solution, $[Mo_2Cl_8]^{4-}$ undergoes the following transformation:

$$[Mo_2Cl_8]^{4-} + H^+ = [Cl_3Mo(\mu\text{-}Cl)_2(\mu\text{-}H)MoCl_3]^{3-}. \quad (19)$$

This reaction occurs quantitatively if performed without oxygen access at 60°C or higher temperature [90]; it is the first reaction of oxidative addition involving a complex with a rigorously proved multiple metal–metal bond.

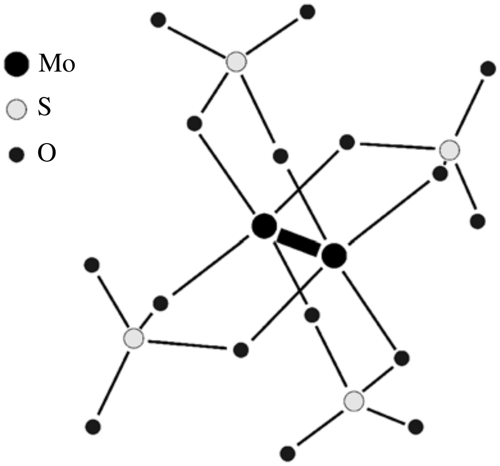


Fig. 3. Structure of the $[Mo_2(SO_4)_4]^{n-}$ anion (n = 3, 4).

A cyclovoltammetric study of hydrochloric acid solutions of $[Mo_2Cl_8]^{4-}$ showed that the oxidation occurred at approximately +0.5 V (vs. saturated calomel electrode) and the peak had a shape typical of a reversible process. Nevertheless, measurements in a wide range of HCl concentrations have not revealed the corresponding reduction peak [91]. Apparently, the $[Cl_3Mo(\mu\text{-}Cl)_2(\mu\text{-}H)MoCl_3]^{3-}$ ion is a product of irreversible electrochemical oxidation.

Similar studies of solutions of $[Mo_2(SO_4)_4]^{4-}$ in 0.2–9 M sulfuric acid showed that this complex underwent reversible oxidation at $E_{1/2}$ +0.22 V (vs. saturated calomel electrode) in accordance with reaction (20) [92]:

$$[Mo_2(SO_4)_4]^{4-} - e^- \rightleftarrows [Mo_2(SO_4)_4]^{3-}. \quad (20)$$

Oxidation of the complex $[Mo_2(SO_4)_4]^{4-}$ with oxygen [92] yields the $[Mo_2(SO_4)_4]^{3-}$ anion which can be precipitated with potassium sulfate in the form of the salt $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. The structure of the $[Mo_2(SO_4)_4]^{3-}$ anion is very similar to that of the $[Mo_2(SO_4)_4]^{4-}$ ion in $Mo_2(SO_4)_4 \cdot 2H_2O$ (Fig. 3) and differs only by the presence of axially bound water molecules instead of oxygen atoms of sulfate groups. A decrease in the multiplicity of the Mo–Mo bond from 4 to 3.5 ($\sigma^2\pi^4\delta^2 \rightarrow \sigma^2\pi^4\delta$) and an increase in the formal oxidation state of molybdenum in the complex from +2 to +2.5 lead to only a slight increase in the Mo–Mo bond length: from 2.111 to 2.164 Å [91].

6.2. Electronic Structure of Binuclear Molybdenum(II) Complexes

The electronic structure of binuclear Mo(II) complexes with bidentate-bridging ligands $[Mo_2(O_2CH)_4]$, $[Mo_2(O_2CCH_3)_4]$, $[Mo_2(O_2CCF_3)_4]$, $[Mo_2(O_2CC\cdot$

Table 4. Electronic structure parameters of neutral, cationic, and anionic forms of the [Mo_2L_4] clusters

Cluster	M–M intermolecular distance, Å	Order of two-center M–M bond	One-electron energy of M–M bonding molecular σ ordital, eV	One-electron energy of M–M bonding molecular π_1 ordital, eV	One-electron energy of M–M bonding molecular π_2 ordital, eV	One-electron energy of M–M bonding molecular δ ordital, eV	One-electron energy of M–M antibonding molecular δ* ordital, eV
[$Mo_2(O_2CCF_3)_4$]$^{1+}$	2.22	3.14	–13.96	–13.37	–13.37	–11.70	
[$Mo_2(O_2CCF_3)_4$]	2.17	3.37	–9.18	–8.89	–8.89	–7.57	
[$Mo_2(O_2CCF_3)_4$]$^{1-}$	2.12	3.12	–3.68	–3.40	–3.40	–1.74	0.56
[$Mo_2(O_2CCH_3)_4$]$^{1+}$	2.20	3.10	–11.67	–11.10	–11.10	–9.17	
[$Mo_2(O_2CCH_3)_4$]	2.15	3.40	–6.87	–6.62	–6.62	–5.04	
[$Mo_2(O_2CCH_3)_4$]$^{1-}$	2.18	3.06	–1.69	–1.38	–1.38	0.77	2.42
[$Mo_2(O_2CCOOH)_4$]$^{1+}$	2.21	3.15	–12.07	–11.93	–11.93	–10.37	
[$Mo_2(O_2CCOOH)_4$]	2.16	3.40	–8.08	–7.86	–7.86	–6.40	
[$Mo_2(O_2CCOOH)_4$]$^{1-}$	2.19	3.07	–2.99	–2.73	–2.73	–0.70	1.03

$FH_2)_4$], [$Mo_2(O_2CCOOH)_4$], and [$Mo_2(SO_4)_4$]$^{4-}$ was calculated by the DFT B3LYP method using SBK effective core potentials [93].

The main parameters of the electronic structure of [$Mo_2(O_2CH)_4$], [$Mo_2(O_2CCH_3)_4$], [$Mo_2(O_2CCF_3)_4$], [$Mo_2(O_2CCFH_2)_4$], [$Mo_2(O_2CCOOH)_4$], and [$Mo_2 \cdot (SO_4)_4$]$^{4-}$ are similar. In the electronic structure of all these clusters Mo_2L_4, the highest molecular orbitals occupied by electron pairs are the four MOs δ, π_1, π_2, and σ; the major contribution to them is made by the valence 4*d* orbitals of each of the two Mo atoms: D_{xy} in δ MO, d_{xz} in π_1 MO, d_{yz} in π_2 MO, and d_{z^2} in σ MO. These MOs are strongly bonding, as follows from their one-electron energies. These are the molecular orbitals of the M–M bonds in the Mo_2L_4 core; the corresponding antibonding orbitals δ*, π_1*, π_2*, and σ* are unoccupied. As a rule, the lowest bonding M–M molecular orbital is σ MO ($2e^-$); the two doubly degenerate molecular orbitals π_1 MO ($2e^-$) and π_2 MO ($2e^-$) lie somewhat higher, and δ MO ($2e^-$) lies considerably higher. The energies of all the M–M MOs decrease and the electrons located on them are stabilized with an increase in the electron-acceptor (decrease in the electron-donor) power of bindentate-bridging ligands L becauase of the decreased total electron density on M atoms and weakened interelectron repulsion in the region of M centers. The calculated orders of the two-center Mo–Mo bonds lie within a narrow range of large values, 3.4±0.1, and unambiguously indicate that these bonds in all the Mo_2L_4 clusters studied have high multiplicity (quaternary: δ + π_1 + π_2 + σ).

Calculations of the electronic structure were performed not only for neutral [Mo_2L_4] molecules but also for the cationic [Mo_2L_4]$^+$ and anionic [Mo_2L_4]$^-$ forms of all the six clusters (Table 4). These calculations show how the electronic and geometric structure of the clusters containing the same Mo_2^{4+} fragment varies depending on the electronic surrounding. Comparison of the electronic structure parameters of [Mo_2L_4] and [Mo_2L_4]$^+$ shows that removal of an electron from the bonding molecular δ orbital of the M–M bond leads to a decrease in the one-electron energies of all the other M–M MOs, to an increase in the M–M internuclear distance, and to a decrease in the order of the two-center M–M bond. However, these changes are minor, because only one of eight bonding electrons is removed from the Mo_2^{4+} core; furthermore, the interelectron repulsion decreases in the process. Comparison of the electronic structure parameters of [Mo_2L_4] and [Mod2L_4]$^-$ shows that addition of an electron to the antibonding molecular δ* orbital of the M–M bond also destabilizes the Mo_2^{4+} cluster core, as judged from an increase in the one-electron energies of all the MOs of the M–M bonds, from an increase in the M–M internuclear distance, and from a decrease in the order of the two-center M–M bond; the major causes of the destabilization are population with an electron of the previously vacant antibonding MO and increase in the interelectron repulsion.

Table 5. Total energies (hartree) of neutral, cationic, and anionic forms of $[Mo_2L_4]$ clusters

Cluster	$[Mo_2L_4]$	$[Mo_2L_4]^+$	$[Mo_2L_4]^-$
$[Mo_2(O_2CH)_4]$	–288.505355	–288.229515	–288.532945
$[Mo_2(O_2CCH_3)_4]$	–315.830184	–315.588527	–315.843778
$[Mo_2(O_2CCF_3)_4]$	–598.299354	–597.963635	–598.397617
$[Mo_2(O_2CCFH_2)_4]$	–409.964359	–409.681741	–410.006631
$[Mo_2(O_2CCOOH)_4]$	–438.422542	–438.132472	–438.476246
$[Mo_2(SO_4)_4]^{4-}$	–430.490150	–430.751048	–

On coordination of any (both σ-donor and σ-donor/π-acceptor) ligand Y (Y=H_2O, NH_3, CO, NO^+, NO, NO^-, O_2) in the axial position of the $[Mo_2L_4]$ cluster, with the formation of the complex $[Mo_2L_4Y]$, the strength and multiplicity of the two-center M–M bonds decrease, and the M_2^{4+} core as a whole is destabilized. The strongest destabilizing effect on the geometric and electronic structure of the $[Mo_2L_4]$ cluster with any chelate ligands L is exerted by the diatomic molecular cation NO^+ exhibiting a very high π-acceptor power. The destabilizing effects of coordination of a neutral O_2 molecule and especially of the molecular anion NO^- to $[Mo_2L_4]$ clusters are the least pronounced. On the whole, coordination of σ-donor/π-acceptor molecular ligands Y in axial positions of $[Mo_2L_4]$ clusters results in σ- and π-electron transfer between the $[Mo_2L_4]$ cluster and the coordinated ligand Y; this results in weakening (to various extents) of the M–M bond (increase in the internuclear distance $R_{M–M}$, decrease in the bond order $K_{M–M}$) in the structure of $[Mo_2L_4]$, primarily due to weakening or break of the M–M π bonds.

7. THERMODYNAMIC PARAMETERS OF REACTIONS OF MOLYBDENUM COMPLEXES IN AQUEOUS SOLUTIONS

A theoretical simulation of one-electron redox position of binuclear Mo(II) clusters was performed in [93] for the complexes with chelating ligands $[Mo_2(O_2CH)_4]$, $[Mo_2(O_2CCH_3)_4$, $[Mo_2(O_2CCF_3)_4]$, $[Mo_2(O_2CCFH_2)_4]$, $[Mo_2(O_2CCOOH)_4]$, and $[Mo_2 \cdot (SO_4)_4]^{4-}$.

Simulation of one-electron redox reactions. To simulate one-electron oxidation or reduction of Mo_2L_4 (electron loss or addition), the total energies were calculated for the neutral $[Mo_2L_4]$, cationic $[Mo_2L_4]^+$, and anionic $[Mo_2L_4]^-$ forms of all the six clusters (Table 5). The enthalpies of the one-electron oxidation reactions (electron loss) were estimated as the differences between the total energies of the cationic $[Mo_2L_4]^-$ and neutral $[Mo_2L_4]$ forms, and the enthalpies of reduction reactions (electron addition), as the corresponding differences for the anionic $[Mo_2L_4]^-$ and neutral $[Mo_2L_4]$ forms (Table 6).

The electron addition to a $[Mo_2L_4]$ cluster is exothermic, and the electron loss, endothermic, except the cluster $[Mo_2(SO_4)_4]^{4-}$ for which the electron loss is accompanied by a strong exo effect, apparently caused by stabilizing rearrangement of the electronic structure of this cluster because of a significant decrease in the total negative charge (naturally, with a decrease in the interelectron repulsion energy), at low energy consumption for the electron abstraction proper. With a decrease in the electron-donor power and, correspondingly, an increase in the electron-acceptor power of the chelating ligand L, the reduction of the cluster (electron addition) becomes more exothermic and the oxidation (electron abstraction), more endothermic.

Simulation of ligand addition reactions. Comparison of the calculated total energies of the clusters $[Mo_2L_4]$, $[Mo_2L_4Y]$ and ligands Y allows estimation of the enthalpy of addition of ligand Y to cluster $[Mo_2L_4]$ in the axial position:

$$\Delta H = E_{tot}(Mo_2L_4Y) - E_{tot}(Mo_2L_4) - E_{tot}(Y).$$

The results obtained show (Table 7) that the highest affinity (maximal negative enthalpy of coordination) for binuclear Mo(II) clusters of D_{4h} symmetry, $[Mo_2L_4]$, is exhibited by the nitrosyl cation NO^+,

Table 6. Enthalpies (kJ mol^{-1}) of one-electron redox reactions of $[Mo_2L_4]$

Cluster	Electron addition	Electron loss
$[Mo_2(O_2CCH_3)_4]$	–35	634
$[Mo_2(O_2CH)_4]$	–80	720
$[Mo_2(O_2CCFH_2)_4]$	–111	742
$[Mo_2(O_2CCOOH)_4]$	–141	761
$[Mo_2(O_2CCF_3)_4]$	–257	881
$[Mo_2(SO_4)_4]^{4-}$	–	–684

Table 7. Total energies (E_{tot}, hartree) of the clusters $[Mo_2L_4]$, $[Mo_2L_4Y]$ and ligand Y, and enthalpies of addition (kJ mol^{-1}) of ligand Y to cluster $[Mo_2L_4]$; cluster: (1) $[Mo_2(O_2CH)_4]$ and (2) $[Mo_2(O_2CCF_3)_4]$

E_{tot}				Enthalpy of reaction	Cluaster
Ligand	$[Mo_2L_4]$	$[Mo_2L_4Y]$	Y		
Y = H_2O	–288.5053	–305.6428	–17.1153	–58	1
Y = NH_3	–288.5053	–300.1846	–11.6494	–79	1
Y = CO	–288.5053	–310.0370	–21.5239	–20	1
Y = NO^-	–288.5053	–314.3017	–25.7230	–193	1
Y = NO	–288.5053	–314.2161	–25.7082	–7	1
Y = NO^+	–288.5053	–313.95587	–25.31326	–360	1
Y = O_2	–288.5053	–320.22549	–31.74950	+77	1
Y = NO^+	–598.2993	–623.6983	–25.3132	–225	2
Y = NO	–598.2993	–624.0140	–25.7082	–17	2
Y = CO	–598.2993	–619.8349	–21.5239	–30	2

apparently because of its very strong π-acceptor power and positive charge: The coordination of NO^+ with $[Mo_2L_4]$ causes energetically favorable (leading to a decrease in the total energy) redistribution of the electronic charge in the complex. Pronounced σ-donor properties are shown by ammonia and water molecules.

Binuclear Mo(II) complexes $[Mo_2^{II}(SO_4)_4]^{3-,4-}$. It is known [63] that binuclear molybdenum sulfate complexes undergo reversible one-electron transformation (21) in aqueous solutions:

$$[Mo_2(SO_4)_4]^{3-} + e \rightleftarrows [Mo_2(SO_4)_4]^{4-}. \qquad (21)$$

Taking into account axial coordination vacancies of both complexes, this reaction can be considered as a model for electron transfer in enzymatic processes involving substrate (*S*) oxidation proper with an oxidized form of an enzyme (E_{ox}) with the formation of the reduced form of an enzyme (E_{red}) and a product (P) [reaction (22)], followed by electron transfer to an acceptor (e.g., complex of transition metal M) after coordination of the reduced enzyme species on the coordinating center [94] [reaction (23)]:

$$\Phi_{ox} + C \longrightarrow \Phi_{red} + P, \qquad (22)$$

$$\Phi_{red} + M^{n+} \longrightarrow \Phi_{ox} + M^{(n-1)+}. \qquad (23)$$

Therefore, complete thermodynamic description of such a process is of indubitable interest from the viewpoint of elucidating the principal possibility of reversible electron transfer from/to the complex anion. In [95], we determined by differential calorimetric titration with continuous feeding of the titrant the enthalpy characteristics of the oxidation of the complexes $[Mo_2(SO_4)_4]^{4-}$ and $[Mo_2(SO_4)_4]^{3-}$ with Fe(III) in aqueous sulfuric acid solution:

$$[Mo_2(SO_4)_4]^{4-} + 8Fe^{3+} + 12H_2O$$
$$= 2Mo(OH)_6 + 8Fe^{2+} + 4HSO_4^- + 8H^+, \qquad (24)$$

$$[Mo_2(SO_4)_4]^{3-} + 7Fe^{3+} + 12H_2O$$
$$= 2\ Mo(OH)_6 + 7Fe^{2+} + 4HSO_4^- + 8H^+, \qquad (25)$$

$$\Delta H^0_{298}(24)\ -192 \pm 3\ \text{kJ mol}^{-1},$$
$$\Delta H^0_{298}(25)\ -167 \pm 3\ \text{kJ mol}^{-1}.$$

Hence, the enthalpy of redox reaction (26) in the same solution is $\Delta H^0_{298}(26) = \Delta H^0_{298}(24) - \Delta \mathrm{H}^0_{298}(25) = -25 \pm 6$ kJ mol^{-1}.

$$[Mo_2(SO_4)_4]^{4-} + Fe^{3+} \quad [Mo_2(SO_4)_4]^{3-} + Fe^{2+}. \qquad (26)$$

Knowing the enthalpy of the reaction $Fe_{aq}{}^{3+} + e = Fe_{aq}{}^{2+}$, ΔH^0_{298} –55 kJ mol^{-1}, we can readily determine the enthalpy of reaction (21): $\Delta H^0_{298}(21)$ +30 ± 6 kJ mol^{-1}.

Reaction (21) is characterized by a relatively low half-wave potential: $E_{1/2}$ +0.22 V vs. saturated calomel electrode [63]; from this potential, the Gibbs energy of the process can be determined: ΔG^0_{298} +44 kJ mol^{-1}.

From the set of the experimental data, the thermodynamic characteristics (enthalpy, entropy, Gibbs energy) of the reversible one-electron reduction–oxidation of binuclear sulfate complexes $[Mo_2(SO_4)_4]^{3-}$ and $[Mo_2(SO_4)_4]^{4-}$ were determined:

$$\Delta H^0_{298}\ +30\ \text{kJ mol}^{-1},\ \Delta S^0_{298}\ -47\ \text{J mol}^{-1}\ \text{K}^{-1},$$
$$\Delta G^0_{298}\ +44\ \text{kJ mol}^{-1}.$$

From the consistent results [96–98] of simultaneous measurements of the enthalpies (by calorimetric titration with continuous feeding of the titrant) of multistep exchange and redox (with the breakdown of the cluster core) reactions in aqueous acid solutions and of the electronic (UV–visible) absorption spectra of these solutions, the schemes of consecutive transformations of molybdenum species were elucidated. These scheme involve mono- and binuclear {$[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^-$, $[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_6(SO_4)]^{2+}$, $[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+}$, $[Mo_2^V(\mu\text{-}O)_2O_2(edta)]^{2-}$, $[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$} complexes of hexa-, penta-, and trivalent molybdenum with acido ligands (*edta*, oxo, and hydroxo complexes).

Binuclear molybdenum(V) complex $[Mo_2^V(\mu\text{-}O)_2 \cdot O_2(H_2O)_6]^{2+}$. The binuclear Mo(V) complex $[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$ with two bridging and two terminal oxygen atoms in the binuclear cluster moiety $[Mo_2^V(\mu\text{-}O)_2O_2]$ enters into a fast equilibrium reaction of *edta* elimination with the formation of the corresponding binuclear Mo(V) aqua cation:

$$\begin{aligned}&[Mo_2^V(\mu\text{-}O)_2O_2(edta)]^{2-} + 4H^+ + 6H_2O\\ &= [Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + H_4edta. \qquad (27)\end{aligned}$$

The enthalpy of this exchange reaction is $\Delta H^0_{298}(27)$ -39 ± 1 kJ mol^{-1}.

The same binuclear complex enters into the oxidation reaction:

$$\begin{aligned}&[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 2Fe^{3+} + 2H_2O\\ &= 2[Mo^{VI}(OH)_6] + 2Fe^{2+} + 4H^+. \qquad (28)\end{aligned}$$

The enthalpy of this oxidation reaction is $\Delta H^0_{298}(28)$ $+44 \pm 2$ kJ (mol electrons)$^{-1}$.

The binuclear Mo(V) aqua cation formed by reaction (27) undergoes protonation of first bridging [reaction (29)] and then terminal [reaction (30)] oxygen atoms, with simultaneous dehydration:

$$\begin{aligned}&[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 2H^+\\ &\longrightarrow [Mo_2^V(\mu\text{-}OH)_2O_2(H_2O)_6]^{4-}, \qquad (29)\end{aligned}$$

$$\begin{aligned}&[Mo_2^V(\mu\text{-}OH)_2O_2(H_2O)_6]^{4+} + 2H^+ + 6Cl^-\\ &\longrightarrow [Mo_2^V(\mu\text{-}OH)_2(OH)_2Cl_6] + 6H_2O, \qquad (30)\\ &\Delta H^0_{298}(29) + \Delta H^0_{298}(30) = -7 \pm 3 \text{ kJ}.\end{aligned}$$

Then reaction (31) occurs:

$$\begin{aligned}&[Mo_2^V(\mu\text{-}OH)_2(OH)_2Cl_6] + 2H_2O\\ &\longrightarrow 2[Mo^VOCl_3(H_2O)_2], \qquad (31)\\ &\Delta H^0_{298}(31)\ +44 \pm 3 \text{ kJ}.\end{aligned}$$

Finally, reactions (32) and (33) result in exothermic formation of the final mononuclear complex:

$$[Mo^VOCl_3(H_2O)_2] + Cl^- \longrightarrow [Mo^VOCl_4(H_2O)]^-, \qquad (32)$$

$$[Mo^VOCl_4(H_2O)]^- + Cl^- \longrightarrow [Mo^VOCl_5]^{2-}, \qquad (33)$$

$$\Delta H^0_{298}(32) + \Delta H^0_{298}(33) = -35 \pm 6 \text{ kJ}.$$

Mononuclear molybdenum(III) complex $[Mo^{III} \cdot (H_2O)_6]^{3+}$. The mononuclear Mo(III) complex $[Mo^{III} \cdot (H_2O)_6]^{3+}$ enters into redox reaction (34):

$$\begin{aligned}&2[Mo^{III}(H_2O)_6]^{3+} + 4Fe^{3+}\\ &= [Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 4Fe^{2+} + 2H_2O + 8H^+, \qquad (34)\\ &\Delta H^0_{298}(34)\ -144 \pm 4 \text{ kJ}.\end{aligned}$$

Binuclear molybdenum(III) complex $[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^-$. The binuclear Mo(III) complex $[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^-$ with two bridging OH groups in the binuclear cluster group $[Mo_2^{III}(\mu\text{-}OH)_2]$ enters into exchange reaction (44) with the formation of the fully substituted binuclear Mo(III) complex $[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+}$:

$$\begin{aligned}&[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^{1-} + 5H^{1+} + 8H_2O\\ &= [Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} + Hac + H_4edta. \qquad (35)\end{aligned}$$

The enthalpy of this exchange reaction is $\Delta H^0_{298}(35)$ -34 ± 1 kJ.

In the same solution, this complex is oxidized with iron(III) sulfate to a Mo(VI) compound [reaction (36)]:

$$\begin{aligned}&[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^{1-} + 6Fe^{3+} + 10H_2O\\ &= 2[Mo^{VI}(OH)_6] + 6Fe^{2+} + 5H^{1+} + Hac + H_4edta. \qquad (36)\end{aligned}$$

The enthalpy of this oxidation reaction is $\Delta H^0_{298}(36)$ -60 ± 1 kJ.

In the above-mentioned acid solutions, Fe(III) oxidizes the completely substituted binuclear Mo(III) complex $[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ to the binuclear Mo(V) complex $[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}$ [98] [reaction (37)]:

$$\begin{aligned}&[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 4Fe^{3+}\\ &= [Mo^V{}_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 4Fe^{2+} + 6H^+. \qquad (37)\end{aligned}$$

The enthalpy of this redox reaction is $\Delta H^0_{298}(37)$ -92 ± 4 kJ.

In aqueous acid solutions, the binuclear Mo(III) and Mo(V) complexes react with each other to form an "intermediate" Mo(IV) aqua complex $[Mo_2^{IV}(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ containing, along with two μ-O atoms, also a μ_3-O atom [reaction (38)]:

$$\begin{aligned}&3[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 3[Mo_2^V(\mu\text{-}O)_2O_2(H_2O)_6]^{2+}\\ &= 4[Mo_3^{IV}(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_9]^{4+} + 2H^+ + 8H_2O. \qquad (38)\end{aligned}$$

The binuclear Mo(III) oxo hydroxo complex also enters into oxidation reactions that alter (but do not destroy) the cluster core [reaction (39) or (40)]:

$$3[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} - 2e^- \longrightarrow 2\ [Mo_2^{III}MoIV(\mu_3\text{-}O)(\mu\text{-}OH)_3(H_2O)_9]^{5+} + 4H_2O + 4H^+, \quad (39)$$

$$3[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} - 6e^- \longrightarrow [Mo_3^{IV}(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+} + 4H_2O + 10\ H^+. \quad (40)$$

Calculation of the free energy of redox reaction (40) by the Nernst equation using the reduction potential $E^0(Mo^{IV}/Mo^{III})$ −0.17 V gives ΔG_{298}^0 −294 kJ, which is well consistent with the experimental enthalpy of reaction (40): $\Delta H_{298}^0(40)$ -310 ± 11 kJ.

The bridging acido ligands can be eliminated with the formation of the binuclear aqua complex $[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ [reaction (41)]:

$$[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^- + 5H^+ + 8H_2O \longrightarrow [Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} + H_4edta + Hac, \quad (41)$$
$$\Delta H_{298}^0(41)\ -36\pm2\ \text{kJ}.$$

The behavior of the binuclear aqua complex in the region of high HCl concentrations can be represented by schemes (42) and (43), with the subsequent gradual replacement of the water molecules remaining in the inner sphere by the chloride anion [reactions (44)–(46)]:

$$[Mo_2^{III}(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 4Cl^- \longrightarrow [Mo_2^{III}(\mu\text{-}OH)_2Cl_4(H_2O)_4] + 4H_2O, \quad (42)$$

$$[Mo_2^{III}(\mu\text{-}OH)_2Cl_4(H_2O)_4] + 2H^+ + 2Cl^- \longrightarrow 2[Mo^{III}Cl_3(H_2O)_3], \quad (43)$$
$$\Delta H_{298}^0(42) + \Delta H_{298}^0(43) = -38\pm3\ \text{kJ},$$

$$[Mo^{III}Cl_3(H_2O)_3] + Cl^- \longrightarrow [Mo^{III}Cl_4(H_2O)_2]^- + H_2O, \quad (44)$$

$$[Mo^{III}Cl_4(H_2O)_2]^- + Cl^- \longrightarrow [Mo^{III}Cl_5(H_2O)]^{2-} + H_2O, \quad (45)$$

$$[Mo^{III}Cl_5(H_2O)]^{2-} + Cl^- \longrightarrow [Mo^{III}Cl_6]^{3-} + H_2O. \quad (46)$$

The enthalpies of reactions (44)–(46) are close to zero.

Binuclear molybdenum(VI) complex $[Mo_2^{VI}O_6\cdot(edta)]^{4+}$. In aqueous acid solutions, the binuclear complex $[Mo_2^{VI}O_6(edta)]^{4+}$ is exothermally hydrated with the protonation of *edta* [reaction (47)]:

$$[Mo_2^{VI}O_6(edta)]^{4-} + 6H^+ + 6H_2O \longrightarrow 2[Mo^{VI}(OH)_5(H_2O)]^{1+} + H_4edta, \quad (47)$$
$$\Delta H_{298}^0(47)\ -14\times1\ \text{kJ}.$$

This is followed by reactions (48)–(50):

$$[M^{VI}(OH)_5(H_2O)]^{1+} + Cl^- \rightarrow [Mo^{VI}(OH)_5Cl] + H_2O, \quad (48)$$
$$\Delta H_{298}^0(48)\ -15\pm1\ \text{kJ},$$

$$[Mo^{VI}(OH)_5Cl] + H^+ \longrightarrow [Mo^{VI}(OH)_4Cl(H_2O)]^+, \quad (49)$$

$$[Mo^{VI}(OH)_4Cl(H_2O)]^+ + Cl^- \longrightarrow [Mo^{VI}O_2Cl_2] + 3H_2O, \quad (50)$$
$$\Delta H_{298}^0(49) + \Delta H_{298}^0(50) = -151\pm+11\ \text{kJ}.$$

On the whole, several consecutive–parallel processes occur simultaneously in the solutions under consideration; these processes can be reflected by the following scheme:

$$\begin{tikzcd} Mo_2^{III} \arrow[r, "Fe^{3+}"] & Mo_2^{V} \arrow[r, "Fe^{3+}"] \arrow[d, "Mo_2^{III}"] & Mo^{VI} \\ & Mo_3^{IV} & \end{tikzcd}$$

It should be emphasized that the measured enthalpies of the reactions under consideration, involving binuclear *edta*, oxo, and hydroxo complexes of Mo in different oxidation states in aqueous solutions, are low, suggesting the principal possibility of the occurrence of similar reactions in biological objects under very mild conditions, taking into account also the obvious requirement that biochemical processes should not have high thermal effects.

8. ENERGIES OF M–M BONDS IN MOLYBDENUM CLUSTERS

One of the main factors generating the interest in thermodynamic parameters of compounds with metal–metal bonds is accumulation of data for estimating the energies of these bonds in cluster complexes of transition metals [99–102].

The enthalpies of formation of complex cluster chlorides $A_pM_nCl_q$ (where A is alkali metal; M = Nb, Mo, W, Re; *p* 1–4, *n* 2–6, *q* 8–14) were determined from the calorimetrically measured enthalpies of their solution (in hydrogen peroxide or potassium hexacyanoferrate solutions) and combustion, and also from the enthalpies of reaction of the corresponding binary chlorides ACl and M_nCl_m [99]. From these data, the energy of the M–M interaction (per electron participating in the M–M bonding) in these cluster chlorides was calculated. It was found that this quantity varies within a relatively narrow range, 100–140 kJ, despite the fact that the group under consideration includes clusters of different d elements with different formal valences of M atoms and different stoichiometries.

Cavell et al. [100–102] reported on thermodynamic studies of redox reactions in aqueous solutions, involving cluster complexes of Cr(II), Mo(II), and W(II) with the binuclear cores Cr_2^{4+}, Mo_2^{4+}, and W_2^{4+} and organic ligands like $N(CH_3)_2^-$ and CH_3COO^-. These reactions lead to partial or complete oxidation of the metal with the formation of Cr(VI), Mo(VI), or W(VI) compounds (oxidants: O_2, $Cr_2O_7^{2-}$, Fe^{3+}) and complete breakdown of the M_2^{4+} fragments. From the thermodynamic data obtained, the metal–metal bond energies in the binuclear fragments Cr_2^{4+}, Mo_2^{4+}, and W_2^{4+} were calculated: E_b(Cr–Cr) 205 ± 20, E_b(Mo–Mo) 334 ± 20, and E_b(W–W) 340 ± 20 kJ mol^{-1}.

Enthalpy of dimerization of the complex $[Mo^{III} \cdot (H_2O)_6]^{3+}$. Comparison of the experimentally determined [96, 97] enthalpies of the analogous reactions (43) and (46) of oxidation of the mononuclear $[Mo \cdot (H_2O)_6]^{3+}$ and binuclear $[Mo_2^{III}(\mu\text{-OH})_2(H_2O)_8]^{4+}$ Mo(III) complexes, respectively, with iron(III) sulfate in acid solutions to the same binuclear complex of Mo(V), $[Mo_2^{V}(\mu\text{-O})_2O_2(H_2O)_6]^{2+}$ (ΔH^0_{298}(43) –144 ± 4, ΔH^0_{298}(46) –92 ± 4 kJ) allows estimation [96, 98] of the enthalpy of dimerization (60) of the mononuclear complex $[Mo^{III}(H_2O)_6]^{3+}$ to the corresponding binuclear complex:

$$2[Mo^{III}(H_2O)_6]^{3+}$$
$$= [Mo_2^{III}(\mu\text{-OH})_2(H_2O)_8]^{4+} + 2H_2O + 2H^{1+}, \qquad (51)$$
$$\Delta H^0_{298}(51)\ -52 \pm 8\ \text{kJ}.$$

Thus, the formation of the Mo(III) dimer from two monomeric species is accompanied by a large exo effect. This is primarily due to the formation of a multiple M–M bond in the binuclear (cluster) complex $[Mo_2^{III}(\mu\text{-OH})_2(H_2O)_8]^{4+}$. Of course, this exo effect should not be identified solely with the energy of the M–M bond in the binuclear cluster $[Mo_2^{III}(\mu\text{-OH})_2]$ or, more specifically, in the binuclear cluster core $[Mo_2^{III}]$, because transformation (51) involves not only formation of M–M bonds, but also rearrangements of other bonds formed by the central atoms with their terminal and bridging ligands, namely: Twelve terminal bonds between the Mo atoms and H_2O molecules in the two monomeric species disappear, and in the arising binuclear cluster eight similar bonds and four bonds of each Mo atom with two bridging OH groups are formed instead; two equivalent octahedrally coordinated mononuclear oxo complexes MoO_6 transform into one binuclear complex $O_4Mo(\mu_2\text{-O})_2MoO_4$ with two μ-O atoms (see Section 2). Nevertheless, it can be assumed that the energy of the M–M bond in this binuclear cluster is close to the value of the above exo effect. Thus, the energetic stabilization of the binuclear Mo(III) complex by formation of M–M bonds is confirmed by direct experimental data.

Energy of the M–M bond in the M_2 *group.* The energy of the M–M bond in the binuclear M_2 group is an important quantity for interpreting the stability and reactivity of the binuclear complex. From the experimental enthalpies of successive steps of multistep transformations of binuclear *edta*, oxo, and hydroxo complexes of molybdenum in aqueous solutions [97], we estimated the energy effects of stabilization of cluster "cores" M_2 (energies of formation of M–M bonds) in some binuclear molybdenum complexes with acido ligands. For example, using the enthalpy of formation of a binuclear Mo(V) complex from two monomeric fragments [reaction (52)], we can construct a thermochemical cycle shown in Fig. 4.

$$2[Mo^{V}OCl_3(H_2O)_2]$$
$$\longrightarrow [Mo_2^{V}(\mu\text{-OH})_2(OH)_2Cl_6] + 2H_2O. \qquad (52)$$

In this cycle, the enthalpy of reaction (52) (formally, of dimerization) is equal to the experimentally determined enthalpy of reaction (31) with the minus sign: $\Delta H^0_{298}(52) = -\Delta H^0_{298}(31) = -44 \pm 3$ kJ. This thermochemical cycle reflects the successive combination of free atoms into groups and then into molecules (i.e., formation of bonds between atoms), followed by hydration of two monomeric fragments, one binuclear complex, and two water molecules in aqueous solution.

$$-4E_b(\text{O–H}) - 2\Delta H_{at}(H_2O) - 4E_b(\text{Mo–}\mu\text{-OH}) - E_b(\text{Mo–Mo})$$
$$- 2E_b(\text{Mo–OH}) - 6E_b(\text{Mo–Cl}) + 2\Delta H_{hydr}(H_2O)$$
$$+ \Delta H_{hydr}(\text{dim}) = - 4\Delta H_{at}(H_2O) - 2E_b(\text{Mo–O})$$
$$- 6E_b(\text{Mo–Cl}) - 4E_b(\text{Mo–H2O}) + 2\Delta H_{hydr}(\text{mon}) - \Delta H_{soln}.$$

In this expression, the summands $-6E_b$(Mo–Cl) in the left and right sides of the equality are equal. Then, using the known bond energies (kJ mol^{-1}) E_b(O–H) 487, $\Delta H_{at}(H_2O)$ 921, E_b(Mo–μ-OH) 225, E_b(Mo–OH) 300, E_b(Mo=O) 700, and E_b(Mo–H_2O) 66 and taking into account that the enthalpy of hydration of water is equal to the enthalpy of its condensation, –42 kJ mol^{-1}, we obtain the following expression:

$$E_b(\text{Mo–Mo}) = 19\ \text{kJ} + [\Delta H_{hydr}(\text{dim}) - 2\ \Delta H_{hydr}(\text{mon})].$$

Inasmuch as the sign of the binuclear complex and the total size of two mononuclear fragments are approximately equal, the difference between the enthalpies of hydration, ΔH_{hydr}(dim) – $2\Delta H_{hydr}$(mon), can be expressed through the energies (E_{HB}) of the corresponding number of hydrogen bonds formed by the

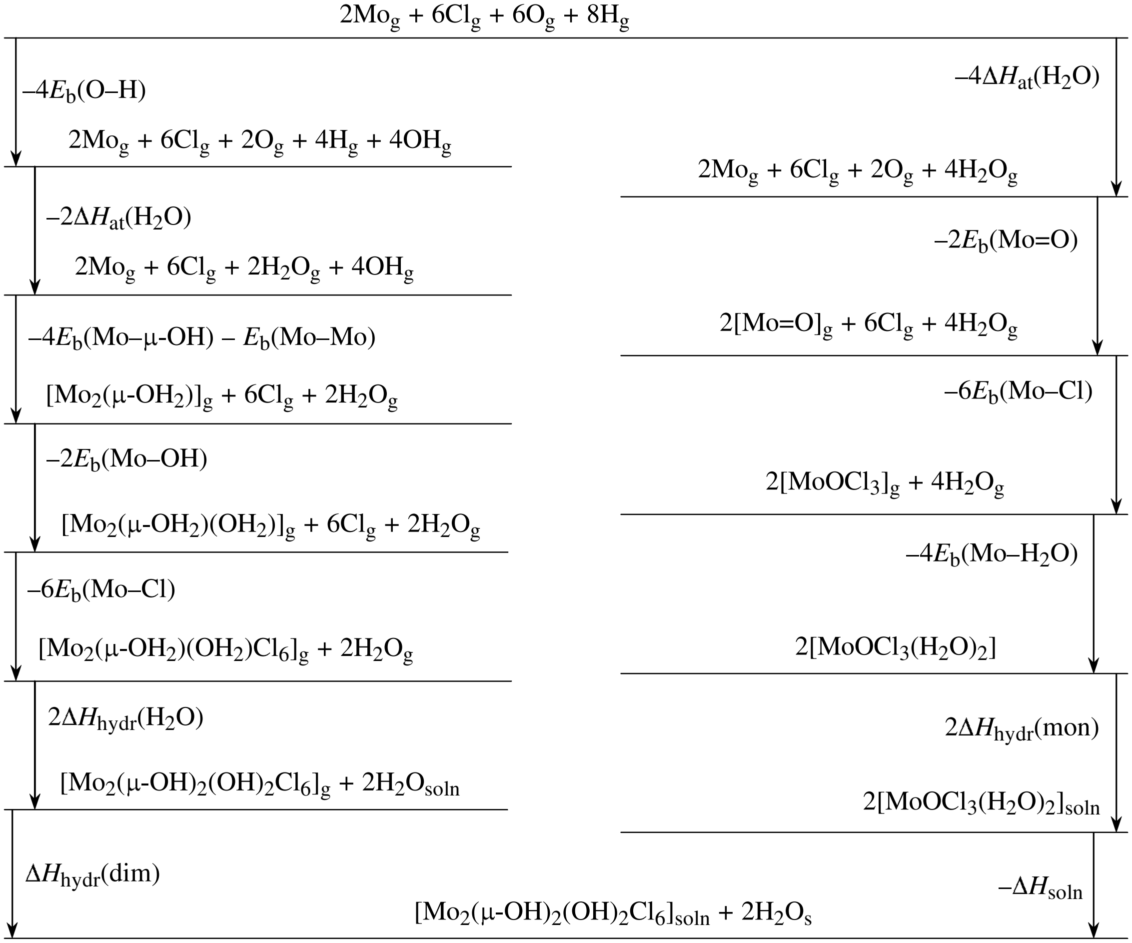


Fig. 4. Thermochemical cycle for estimating the bond energy in the M_2 group.

hydrogen and oxygen atoms in the ligands =O, –OH, and $–OH_2$ in the molecular structures of the complexes:

$$[\Delta H_{hydr}(dim) - 2\Delta H_{hydr}(mon)] = -(4E_{HB}) - (-12E_{HB}) = 8E_{HB} = 200 \text{ kJ}.$$

Finally, $E_b(Mo–Mo) = 220 \pm 30$ kJ; this quantity is close, according to quantum-chemical calculations, to the M–M bond energies in clusters with weak-field ligands [103] and indicates that the binuclear complex is strongly stabilized by the M–M electronic interactions in the M_2 cluster group.

In all the cases, it is clear that the M–M bond energy depends on the nature of the transition metal and formal valence of its atoms in the cluster, and also on the nature and number of coordinated ligands. The accuracy of estimations of the metal–metal bond energies is in some cases low because of significant assumptions made in estimations of the metal–ligand bond energies; since the number of metal–ligand bonds in the cluster complexes under consideration is always larger than the number of metal–metal bonds, the reliable estimation of the M–L bond energies becomes the key problem in calculations of the M–M bond energies.

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