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Enthalpies of Reactions of Binuclear Molybdenum(III), (V), and (VI) Ethylenediaminetetracetate, Oxo, and Hydroxo Complexes in Aqueous Solutions

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Abstract — Enthalpies of consecutive stages of multistage transformations of binuclear molybdenum(III), (V), and (VI) ethylenediaminetetracetate, oxo, and hydroxo complexes in aqueous solutions were determined. Stabilization energies of cluster cores (energies of metal–metal bonds) were estimated for binuclear molybdenum complexes with acido ligands.

The role of polynuclear molybdenum complexes in biological systems, such as nitrogenase, oxidases, and hydrogenases of various nature, including metal fragments in their active centers, is the main reason for the interest in their studying. A number of works was dedicated to the composition of such metal fragments. At the same time, biochemical cycles themselves and their constituent reactions are still poorly known, especially from the structural thermodynamic viewpoint, because of the complexity and diversity of molecular transformations of molybdenum complexes. This results from the fact that the oxidation state of molybdenum varies in a wide range (from –2 up to +6), five oxidation states (from +2 up to +6) existing in aqueous solutions. Moreover, molybdenum complexes in aqueous solutions readily undergo protonation and polymerization, yielding a variety of coexisting species. Another unique property of molybdenum is the presence of aqua and aqua/oxo complexes for all five oxidation states in acidic aqueous solutions ($pH < 2$).

The key processes in most complex biochemical cycles are reactions traditional for coordination chemistry: ligand-exchange, cluster core formation/decomposition, and redox reactions that occur in water, a common medium for biological objects. Studying these types of reactions with mono- and polynuclear molybdenum complexes allows determination of their most important parameters (first of all, enthalpy characteristics and probable mechanisms) required for subsequent estimations of activation barriers and rates of reactions involving transition metal complexes in biological systems.

Below we present the results of a research into the mechanism and enthalpy characteristics of multistage ligand exchange, redox, and cluster core decomposition reactions for three binuclear ethylenediaminetetraacetate (edta), oxo, and hydroxo complexes $[Mo_2^{VI}O_6(edta)]^{4-}$, $[Mo_2^{V}O_4(edta)]$, and $[Mo_2^{III}(\mu_2\text{-}OH)_2\cdot(ac)(edta)]$ in aqueous solutions of hydrochloric and perchloric acids. These processes were studied by means of calorimetric titration with continuous titrant addition, which allows us to follow heat effects attendant in the titration in real time. This method provides precise heat effects of consecutive stages, which makes it very useful in studying intricate equilibria in aqueous solutions. Consecutive stages of transformations of all the three molybdenum complexes were established by a systematic and detailed analysis of the electronic absorption spectra of the complexes (band positions and intensities). Details of calorimetric and spectroscopic measurements and methods of synthesis and identification of the complexes were described earlier [1, 2].

Molybdenum(VI) binuclear complex $Na_4[Mo_2O_6\cdot(edta)]$. The heat effects (per 1 mol of complex) attendant in transformations of $[Mo_2O_6(edta)]^{4-}$ anion in $HClO_4$ and HCl solutions are shown in Fig. 1. As the concentration of perchloric acid is increased, one exothermic effect is observed up to ca. 3.0 M $HClO_4$. The complex anion $[Mo_2O_6(edta)]^{4-}$, which is extremely sensitive to pH, decomposes in the first stage immediately after acid addition, and then edta is protonated [3]. When three water molecules substitute for carboxyl oxygen and nitrogen atoms of edta, $MoO_3\cdot 3H_2O$ and then molybdic acid $[Mo(OH)_6]$ are formed. Upon further increase in perchloric acid concentration molybdic acid itself is also protonated to form $[Mo(OH)_5(H_2O)]$ [1, 2]. Thus the significant enthalpy effect in the differential curve (Fig. 1, curve *1*) is associated with reaction (1).

$$[Mo_2O_6(edta)]^{4-} + 6H^+ + 6H_2O$$
$$= 2[Mo(OH)_5(H_2O)]^+ + H_4edta, \quad (1)$$
$$\Delta H^0_{298}(1)\ -14 \pm 1\ \text{kJ mol}^{-1}\ \text{dimer.}$$

The reaction of $[Mo_2O_6(edta)]^{4-}$ complex with hydrochloric acid is more intricate. There are two exothermic effects in the concentration ranges 0–4 and 4–8.5 M HCl in the calorimetric titration curve (Fig. 1, curve *2*). Initially HCl reacts with a solution of the complex following scheme (1). As the concentration of HCl is increased to 4 M (first maximum in the differential curve; Fig. 1, curve *2*), the role of appearing acido ligand Cl^- becomes significant. The ligand replaces a water molecule to give a neutral complex [4] [scheme (2)].

$$[Mo(OH)_5(H_2O)]^+ + Cl^- \longrightarrow [Mo(OH)_5Cl] + H_2O, \quad (2)$$
$$\Delta H^0_{298}(2)\ -15 \pm 1\ \text{kJ mol}^{-1}.$$

At HCl concentrations of above 4 M (second maximum in the differential curve; Fig. 1, curve *2*), the neutral complex takes up a proton and one more Cl^- anion to give molybdenum(VI) oxochloride [schemes (3) and (4)].

$$[Mo(OH)_5Cl] + H^+ \longrightarrow [Mo(OH)_4Cl(H_2O)]^+, \quad (3)$$
$$[Mo(OH)_4Cl(H_2O)]^+ + Cl^- \longrightarrow [MoO_2Cl_2] + 3H_2O, \quad (4)$$
$$\Delta H^0_{298}(3) + \Delta H^0_{298}(4)\ -151 \pm 11\ \text{kJ mol}^{-1}.$$

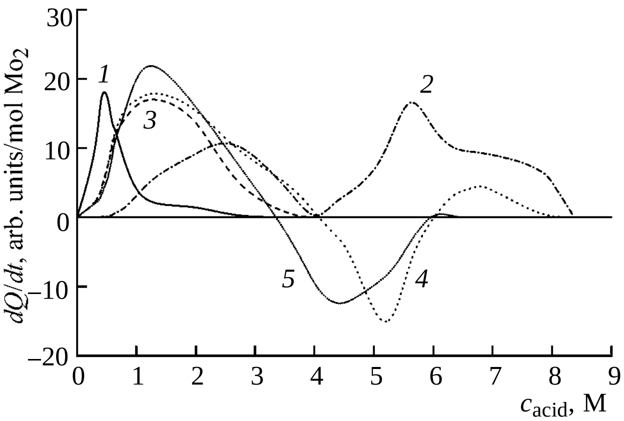

Fig. 1. Differential curves of calorimetric titration of aqueous solutions of molybdenum complexes (c_{comp} 3 × 10^{-2} M) $HClO_4$ and HCl. Titrant $HClO_4$. Complex: (*1*) $Na_4[Mo_2^{VI}O_6edta]$ and (*2*) $Na_2[Mo_2^V(\mu\text{-}O)_2O_2edta]$. Titrant HCl, complex: (*3*) $Na_4[Mo_2^{VI}O_6edta]$, (*4*) $Na_2 \cdot [Mo_2^5(\mu\text{-}O)_2O_2edta]$, and (*5*) $K[Mo_2^{III}(\mu\text{-}OH)_2(ac)edta]$.

We suppose that stage (4) is much faster than stage (3). The first reason for this supposition is that stage (4) involves two unlikely charged particles and second, a significant entropy increase produced by elimination of three water molecules and entering of a further large chlorine anion into the inner sphere of the complex with the resulting reduction of the coordination number from six to four [5]. When the concentration of hydrochloric acid is about 6 M, almost 90% of Mo(VI) have been incorporated into $[MoO_2Cl_2]$. At higher acid concentrations, one more chloride ion adds to the latter complex [scheme (5)], but this is a minor process [6].

$$[MoO_2Cl_2] + Cl^- \longrightarrow [MoO_2Cl_3]^-. \quad (5)$$

Molybdenum(V) binuclear complex $Na_2[Mo_2(\mu\text{-}O)_2 \cdot O_2(edta)$. The reaction between the binuclear complex $Na_2[Mo_2(\mu\text{-}O)_2O_2(edta)]$ containing the cluster core $[Mo_2(\mu\text{-}O)_2O_2]^{2+}$ with two bridging and two terminal oxygen atoms, with perchloric acid solution (Fig. 1, curve *3*) is accompanied, as with the molybdenum(VI) complex, by one exothermic effect at $HClO_4$ concentrations ranging from 0 to 3.5 M. In the first stage, too, edta is eliminated to give a binuclear hexaaqua complex (i.e. the cluster core is preserved) [7] [reaction (6)].

$$[Mo_2(\mu\text{-}O)_2O_2(edta)]^{2-} + 4H^+ + 6H_2O$$
$$\longrightarrow [Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + H_4edta. \quad (6)$$

Evidence for this mechanism comes from the visible absorption spectrum (Fig. 2, curve *1*). As the $HClO_4$ concentration is increased from 0.4 to 2.0 M, a sharp decrease in the molar extinction (ε) at 420 nm (more than 4 times, from 330 to 80) is observed, which is caused by replacement of edta by H_2O molecules [5]. This reaction is observed up $HClO_4$ concentration of 3.5 M, which is much longer with the Mo(VI) complex. Moreover, this effect is almost three times stronger, in spite of the fact that in the case of $[Mo_2O_6(edta)]^{4-}$ the edta ligand is eliminated from two formally neutral $[MoO_3]$ particles, whereas in the case of $[Mo(\mu\text{-}O)_2O_2(edta)]^{2-}$ the edta ligand is eliminated from the positively charged unit $[Mo_2(\mu\text{-}O)_2O_2]^{2+}$. Apparently, the excess of perchloric acid favors protonation of bridging oxygen atoms [scheme (7)].

$$[Mo_2(\mu\text{-}O)_2O_2(H_2O)_6]^{2+} + 2H^+$$
$$\longrightarrow [Mo_2(\mu\text{-}OH)_2O_2(H_2O)_6]^{4,} \quad (7)$$
$$\Delta H^0_{298}(6) + \Delta H^0_{298}(7)\ -39 \pm 2\ \text{kJ mol}^{-1}.$$

Further increase in $HClO_4$ concentration produces neither spectral nor calorimetric changes in the system in question (Fig. 1, curve *3*). Hence, the cluster core of the complex is stable toward changes in the perchloric acid concentration from 0 to 6 M, and the preservation of the metal–metal bond is attributable to the absence of a competitive ligand.

The reaction of $[Mo_2(\mu\text{-}O)_2O_2(edta)]^{2-}$ with hydrochloric acid is fundamentally different (Fig. 1, curve *4*). There are two exothermic effects in the 0–4.0 and 6.0–8.5 M HCl sections of the titration curve and an endothermic effect in the 4.0–6.0 M HCl section. To elucidate the scheme of transformations in hydrochloric acid and to assign correctly the heat effects, we studied the electronic absorption spectra in detail. Figure 2 depicts changes in the spectrum of $[Mo_2(\mu\text{-}O)_2O_2(edta)]^{2-}$ solution at acid concentrations from 0 to 6.5 M. As the concentration of HCl is increased from 0 to 2.0 M, the intensity of the band at 450 nm assigned to a *d–d* transition (Fig. 2, curve *2*) decreases because of changed coordination of the $[Mo_2(\mu\text{-}O)_2O_2]^{2+}$ group, namely replacement of edta by water molecules [8]. At higher HCl concentrations, this band shifts red and enhances, attaining a maximum at c_{HCl} 5.0 M, which corresponds to the maximum endothermic deviation in the calorimetric curve. Further increase in acid concentration results in a sharp decrease in the intensities of spectral bands. This means that the reaction between $[Mo_2(\mu O)_2O_2 \cdot (edta)]^{2-}$ and HCl involves initial elimination of edta from the $[Mo_2(\mu O)_2O_2]^{2+}$ cluster, after which edta is protonated, and water molecules occupy the coordination vacancies previously occupied by edta carboxylic and amino groups [reaction (6)]. Further increase in HCl concentration (up to ~3.5 M) results not only in protonation of terminal oxygen atoms [reaction (7)], but also in replacement of water molecules in the inner coordination sphere by chloride ions [reaction (8)].

$$[Mo_2(\mu\text{-}OH)_2O_2(H_2O)_6]^{4+} + 2H^+ + 6Cl^- \longrightarrow [Mo_2(\mu\text{-}OH)_2(OH)_2Cl_6] + 6H_2O. \quad (8)$$

Reactions (6)–(8) lead to the first exothermic effect in the titration curve (Fig. 1, curve *4*).

$$\Delta H^0_{298}(6) + \Delta H^0_{298}(7) + \Delta H^0_{298}(8) = -46 \pm 3 \text{ kJ mol}^{-1}.$$

Further (compared with reactions in perchloric acid) replacement of water molecules by chloride ions [reaction (8)] predetermines a slightly stronger exothermic effect.

Beginning with c_{HCl} ~2.5 M, a new equilibrium is established in the system. As a result, a new absorption band appears in the electronic absorption spectrum at 680 nm (Fig. 2, curve *3*), which corresponds to formation of a mononuclear Mo(V) complex. Initially, its concentration in the solution is insignificant, and it increases significantly only at c_{HCl} > 4 M [scheme (9)].

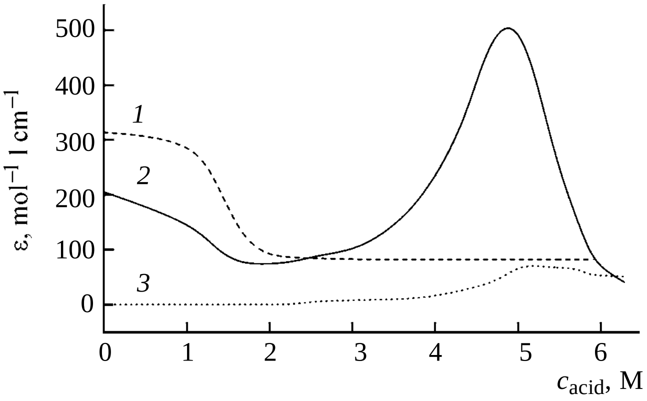

Fig. 2. Molar extinction coefficient (ε) of $[Mo^V_2(\mu\text{-}O)_2 \cdot O_2(edta)]^{2-}$ solution vs. concentration of (*1*) $HClO_4$ at 420 nm, (*2*) HCl at 450 nm, and (*3*) HCl at 680 nm.

$$[Mo_2(\mu\text{-}OH)_2(OH)_2Cl_6]^{4+} + 2H_2O \longrightarrow 2[MoOCl_3(H_2O)_2]. \quad (9)$$

The reaction produces an endothermic effect ($\Delta H^0_{298}(9)$ 44 × 3 kJ mol^{-1} dimer) which is observed up to $c_{HCl} \geq 6$ M (Fig. 1, curve *4*), i.e. until complete decomposition of the dimer.

At HCl concentrations of above 6 M, consecutive replacement of H_2O molecules by chloride ions occurs by reactions (10) and (11).

$$[MoOCl_3(H_2O)_2] + Cl^- \rightarrow [MoOCl_4(H_2O)]^- + H_2O, \quad (10)$$

$$[MoOCl_4(H_2O)]^- + Cl^- \longrightarrow [MoOCl_5]^{2-} + H_2O, \quad (11)$$

$$\Delta H^0_{298}(10) + \Delta H^0_{298}(11) = -35 \pm 6 \text{ kJ mol}^{-1}.$$

This is accompanied by a sharp decrease in the intensity of the absorption bands at 420 and 680 nm (Fig. 2). Finally, the mononuclear $[MoOCl_5]^{2-}$ anion is formed by reactions (10) and (11).

Molybdenum(III) binuclear complex $K[Mo_2 \cdot (\mu\text{-}OH)_2(ac)(edta)]$. Similarly to the Mo(V) complex, this compound contains the cluster core $[Mo_2(\mu\text{-}OH)_2]^{4+}$ with two bridging OH groups. In spite of fact that these Mo(V) and Mo(III) complexes

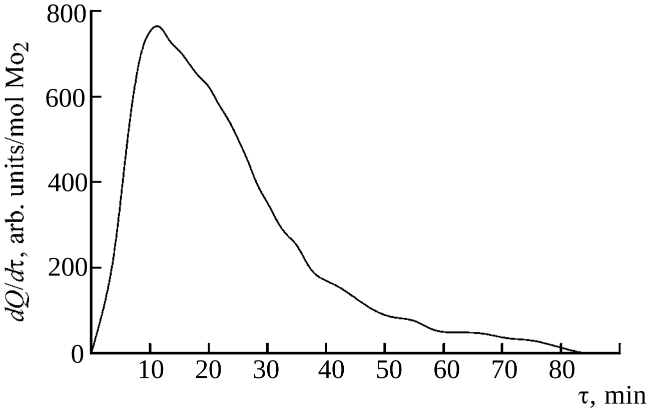

Fig. 3. Differential curve of portion calorimetric titration of aqueous $K[Mo_2(\mu\text{-}OH)_2(ac)(edta)]$ (c_{comp} 3×10^{-2} M) with 0.85 M perchloric acid.

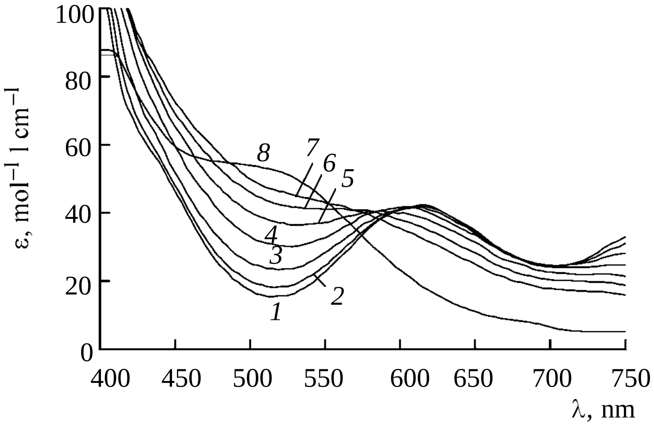

Fig. 4. Changes in the electronic absorption spectrum of $[Mo_2(\mu\text{-}OH)_2(ac)(edta)]^-$ solution on its reaction with 0.85 M perchloric acid. Reaction duration, min: (*1*) 0, (*2*) 10, (*3*) 20, (*4*) 30, (*5*) 40, (*6*) 50, (*7*) 60, and (*8*) 90.

with edta are similar in structures, their behavior in perchloric acid differ significantly.

Reaction of $[Mo_2(\mu\text{-}OH)_2(ac)(edta)]^-$ with perchloric acid begins immediately after the acid has been added and is almost complete after 70–80 min. The total enthalpy effect of the reaction is -310 ± 11 kJ mol^{-1} (Fig. 3). The fact that this value is much larger than the enthalpies of ligand-exchange reactions, we determined earlier or found in the literature [9], suggests that this reaction is redox in nature. This conclusion is proved by changes in the electronic absorption spectrum of the solution (Fig. 4). In the first stage, instead the band at 610 nm, two close absorption bands appear at 624 and 527 nm (Fig. 4, curves *1*–*3*), thus broadening the initial spectrum. It is sensible to assume that, similarly to all the previous cases, addition of a strong acid results in elimination of the weak acids Hac and H_4edta and subsequent replacement of their anions by solvent molecules to form an aqua complex [scheme (12)].

$$[Mo_2(\mu\text{-}OH)_2(ac)(edta)]^- + 5H^+ + 8H_2O$$
$$\longrightarrow [Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + H_4\text{edta} + \text{Hac}, \quad (12)$$
$$\Delta H^0_{298}(12)\ -36 \times 2\ \text{kJ mol}^{-1}.$$

This stage gives rise to an extremely reactive complex $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ capable of reducing even such an inert oxidant as perchloric acid. This sharply attenuates the band at 624 nm and shifts it blue to 572 nm (Fig. 4, curves *3*–*8*). Furthermore, absorption in the UV range (< 400 nm) also attenuates. The final spectrum of the solution contains a broad absorption band with its maximum at 400 nm and a shoulder near 500 nm. Note that such a blue-shifted spectrum is characteristic of the trinuclear cation $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ whose cluster core consists of molybdenum(IV) atoms only [10]. Thus, the redox process in the solution under study can be described by scheme (13).

$$3[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} - 6e$$
$$\longrightarrow 2[Mo_3^{IV}(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+} + 4H_2O + 10H^+, \quad (13)$$
$$\Delta H^0_{298}(13)\ -310 \pm 11\ \text{kJ mol}^{-1}\ \text{dimer}.$$

Using the redox potential $E^0(Mo^{IV}/Mo^{III})$ [11] and assuming that the perchlorate anion is reduced to the chloride ion, we estimated the Gibbs energy ΔG^0_{298} of this redox reaction at –314 kJ mol^{-1} dimer. Assuming entropy effects in these solutions to be insignificant, we can contend that this value nicely fits the experimental enthalpy of reaction (13).

The fact that hydrochloric acid has no oxidizing properties and the structural similarity of molybdenum(V) and (III) binuclear edta complexes make similar the calorimetric patterns of their reactions with HCl. There are two effects in the curve of calorimetric titration of $[Mo_2(\mu\text{-}OH)_2(ac)(edta)]^-$ with HCl (Fig. 1, curve *5*): an exothermic effect at c_{HCl} 0–3.5 M and an endothermic effect at c_{HCl} 3.5–6 M. The spectral changes in the solution are shown in Fig. 5. No remarkable changes are observed in the visible spectral region up to acid concentrations of about 3.5 M, while the intensity of UV absorption (Fig. 5, curves *1*–*4*) increases significantly. A similar effect was observed in the first two stages in the previous ex-

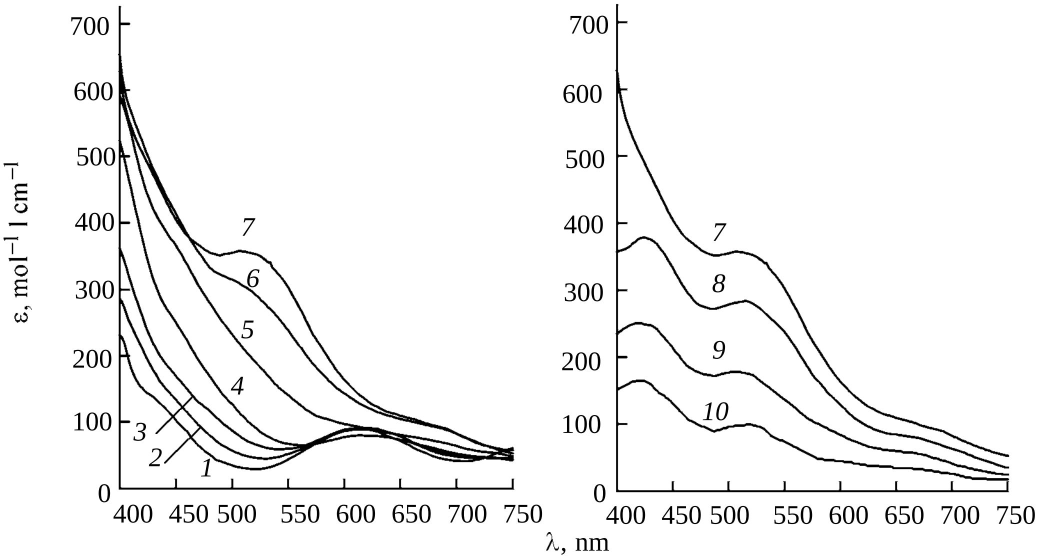

Fig. 5. Changes in the electronic absorption spectrum of $[Mo_2^{III}(\mu\text{-}OH)_2(ac)(edta)]^-$ solution on its reaction with hydrochloric acid. c_{HClO_4}, M: (*1*) 0, (*2*) 1.08, (*3*) 1.98, (*4*) 3.40, (*5*) 4.46, (*6*) 5.29, (*7*) 5.95, (*8*) 7.14, (*9*) 7.94, and (*10*) 8.93.

periments, and it was also assigned to elimination of bridging acido ligands and the formation of the $[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ aqua complex by reaction (12). The enthalpy of this reaction is –36 ± 2 kJ mol^{-1}, which is close to the enthalpy of the formation of molybdenum (V) aqua complex by reaction (6), namely –39 ± 2 kJ mol^{-1}. This fact provides supportive evidence for our concept of the behavior of these binuclear molybdenum complexes in acidic aqueous solutions. Further increase of the acid concentration from 3.5 to 6 M (Fig. 5, curves *4*–*7*) gives rise to a rapid appearance of strong absorption bands at 425 and 520 nm. Such intensity enhancement is typical of formation of mononuclear complexes from binuclear. However, the aqua complex is stable in aqueous solutions, and its decomposition should be preceded by replacement of solvent molecules in the inner coordination sphere by chloride ions whose concentration in the solution continuously increases. Therefore, the behavior of the complex in this region of HCl concentrations can be described by schemes (14) and (15).

$$[Mo_2(\mu\text{-}OH)_2(H_2O)_8]^{4+} + 4Cl^- \longrightarrow [Mo_2(\mu\text{-}OH)_2Cl_4(H_2O)_4] + 4H_2O, \quad (14)$$

$$[Mo_2(\mu\text{-}OH)_2Cl_4(H_2O)_4] + 2H^+ + 2Cl^- \longrightarrow 2[MoCl_3(H_2O)_3], \quad (15)$$

$$\Delta H^0_{298}(14) + \Delta H^0_{298}(15) = -38 \pm 3 \text{ kJ mol}^{-1} \text{ dimer.}$$

The final section of the titration curve (c_{HCl} > 6 M) shows almost no heat effects. However, the visible region of the absorption spectrum changes drastically (Fig. 5, curves *7*–*10*). The intensity of absorption at 425 and 520 nm decreases, whereas band positions remain unchanged. The decrease in ε results from gradual substitution of chloride ions for water molecules in the inner coordination sphere of the complex [schemes (16)–(18)].

$$[MoCl_3(H_2O)_3] + Cl^- \longrightarrow [MoCl_4(H_2O)_2]^- + H_2O, \quad (16)$$

$$[MoCl_4(H_2O)_2]^- + Cl^- \longrightarrow [MoCl_5(H_2O)]^{2-} + H_2O, \quad (17)$$

$$[MoCl_5(H_2O)]^{2-} + Cl^- \longrightarrow [MoCl_6]^{3-}. \quad (18)$$

The heat effects of ligand-exchange reactions are close to zero, because in this region of acid concentrations their equilibrium constants are close to 1 [9]. Under our experimental conditions, reaction (17) is most probably the final stage, because for the hexachloro complex to be formed the concentration of HCl should be no lower than 10 M. Published ε values for $[MoCl_6]^{3-}$ (60 at 425 nm and 45 at 520 nm) [12], too, are lower than experimental (Fig. 5).

Metal–metal bond energy. The low enthalpies of reactions of binuclear edta, oxo, and hydroxo complexes of molybdenum in various oxidation states in aqueous media point to a principal possibility for such processes to occur in biological objects under very mild conditions.

On the other hand, the resulting data allow us to estimate such an important stability and reactivity characteristic of binuclear complexes as the energy of the Mo–Mo bonds in the binuclear cluster. Thus,

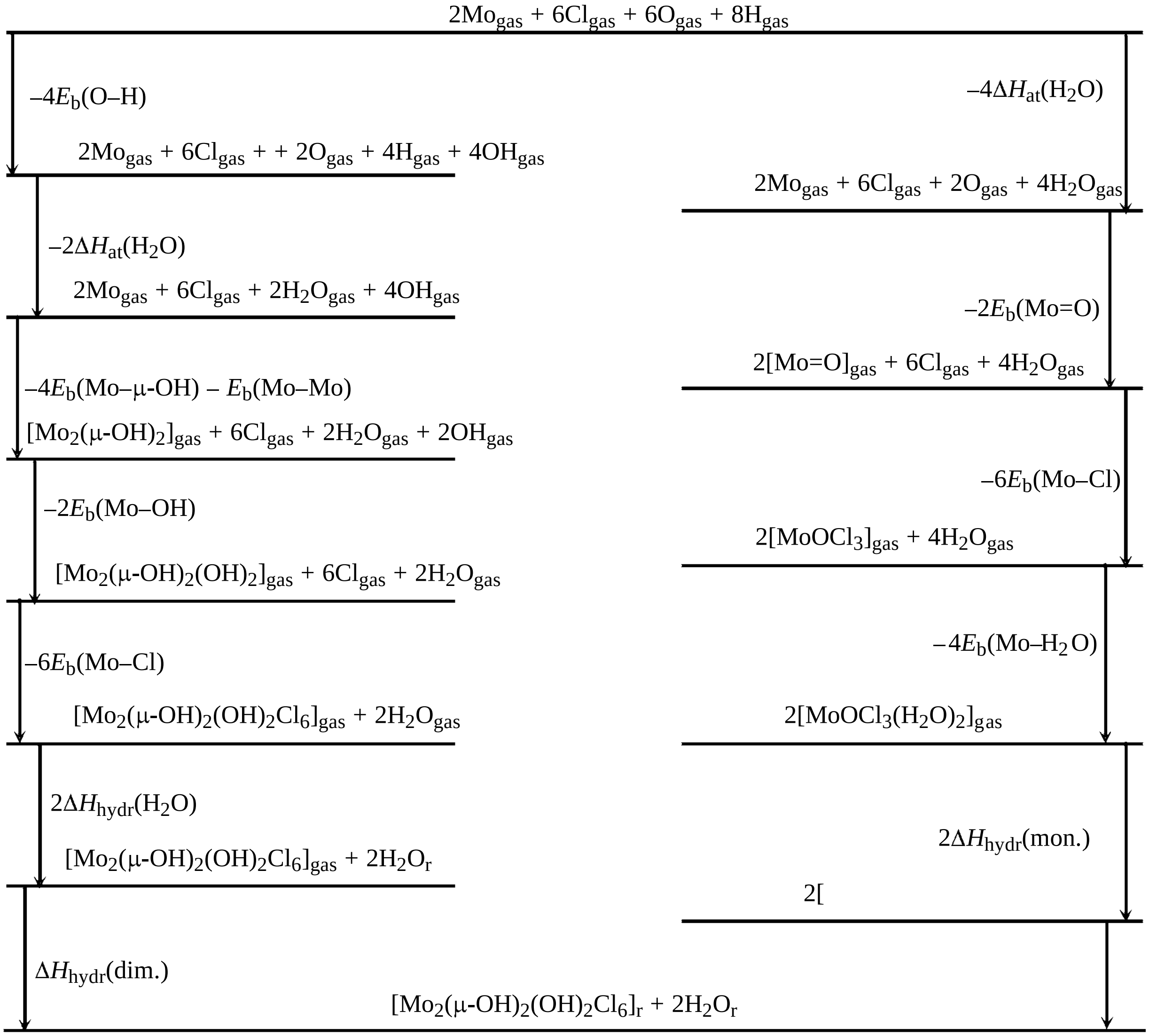

Fig. 6. Thermochemical cycle based on the dimerization enthalpy.

using the enthalpy of the formation of the molybdenum(V) binuclear complex from two corresponding mononuclear fragments by reaction (19), we can construct a thermochemical cycle (Fig. 6), where the enthalpy of this reaction (which formally is a dimerization reaction) is equal to the experimental enthalpy of reaction (9) with opposite sign.

$$2[MoOCl_3(H_2O)_2] \longrightarrow [Mo_2(\mu\text{-}OH)_2(OH)_2Cl_6] + 2H_2O, \qquad (19)$$

$$\Delta H^0_{298}(19) = -\Delta H^0_{298}(9) = -44 \pm 3 \text{ kJ mol}^{-1}.$$

This thermochemical cycle involves consecutive association of free atoms into group and molecules (i.e. formation of interatomic bonds), followed by hydration of the resulting two mononuclear fragments [ΔH_{hydr}(mon.)], one binuclear complex [ΔH_{hydr}(dim.)], and two water molecules in the aqueous solution.

$$\begin{aligned}&-4E_b(O–H) - 2\Delta H_{at}(H_2O) - 4E_b(Mo–\mu\text{-}OH)\\&- E_b(Mo–Mo) - E_b(Mo–OH) - 6E_b(Mo–Cl)\\&+ 2\Delta H_{hydr}(H_2O) + \Delta H_{hydr}(dim.)\\&= -4\Delta H_{at}(H_2O) - 2E_b(Mo{=}O) - 6E_b(Mo–Cl)\\&- 4E_b(Mo–H_2O) + 2\Delta H_{hydr}(mon.) - \Delta Hr. \qquad (20)\end{aligned}$$

The summands $6E_b$(Mo–Cl) are the same in the left- and right-hand sides of this equation. Then, using known bond energies (kJ mol^{-1}): E_b(O–H) 487.0, $\Delta H_{at}(H_2O)$ 921.5, E_b(Mo–μ-OH) 225.0, E_b(Mo–OH)

300.0, E_b(Mo=O) 700.0, and E_b(Mo–H_2O) 66.0, and taking into account that the enthalpy of water hydration is equal to the enthalpy of its condensation (–42 kJ mol^{-1}), we obtain Eq. (21).

$$E_b(\text{Mo–Mo}) = 19\ \text{kJ} + [\Delta H_{hydr}(\text{dim.}) - 2\Delta H_{hydr}(\text{mon.})]. \quad (21)$$

As the size of the binuclear complex and the total size of two mononuclear complexes are almost the same, the difference in the enthalpies of hydration [ΔH_{hydr}(dim.)] – 2ΔH_{hydr}(mon.)] can be expressed through the energies of the corresponding number of the hydrogen bonds (E_{hb}) formed by the hydrogen and oxygen atoms of the =O, OH, and OH_2 fragments of the ligands in their molecular structures. Thus we obtain Eq. (22).

$$[\Delta H_{hydr}(\text{dim.}) - 2\Delta H_{hydr}(\text{mon.})] = -(4E_{hb}) - (-12E_{hb}) = 8E_{hb} = 200\ \text{kJ}. \quad (22)$$

Finally, we obtain E_b(Mo–Mo) = 220 ± 30 kJ mol^{-1}. This value, which is close to the metal–metal bond energies in clusters with weak-field ligands, calculated by quantum-chemical methods [13], points to a high energetic stabilization of the binuclear complex by electronic interactions in its M_2 cluster group.

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