Redox transformations of polynuclear molybdenum alkoxides and their interaction with nitrogenase substrates: experimental and theoretical study

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The experimental and theoretical study of the electronic structure and IR spectra of the CO-containing molybdenum(0) alkoxide complexes of different nuclearity was carried out. The binding energy of the dinitrogen ligand was calculated for the tetranuclear $K_4[Mo(OR)(CO)_3]_4$ complexes catalyzing dinitrogen reduction. The theoretical study of structural changes for the 20-electron reduction of the catalytic cluster of the octanuclear $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}$ complex was performed. The interaction of the reduced cluster with the nitrogenase substrate was considered. Probable coordination modes of N_2, C_2H_2, and CO were analyzed, as well as the protonation reactions of the acetylene complexes, giving rise to two- and four-electron reduction products. The results of quantum chemical calculations are in good agreement with the experimental regularities observed for the catalytic reduction of the substrates in the presence of the Mo—Mg cluster.

Key words: quantum chemical calculations, DFT method, PBE functional, dinitrogen fixation, transition metal clusters, bond energy.

Reduction of molecular nitrogen to ammonia is one of the most complicated reactions in living nature. The reaction is catalyzed by enzyme nitrogenase, whose active center in terms of complexity includes a unique metal cluster: iron—molybdenum cofactor.[1] In spite of various experimental and theoretical studies, many aspects of the mechanism of dinitrogen fixation by the enzyme remain unclear.

The study of different model metallocomplex dinitrogen-fixing systems is among the most efficient approaches to investigation of the chemical mechanism of substrate transformation in the active center of nitrogenase. Many transition metal complexes containing molecular nitrogen as a ligand have been obtained so far, and only few homogeneous catalytic dinitrogen-fixing systems are known.[2—4] Among them, the Schrock system[4] is most studied in which a series of intermediates of the catalytic cycle was isolated and structurally characterized and the complete theoretical analysis of this cycle was carried out. However, this system has a low catalytic activity.

The protonic systems involving polynuclear compounds of low-valence molybdenum as catalysts form a unique class of non-biological dinitrogen-fixing systems that can reduce N_2 in aqueous-alcohol solutions under mild conditions with rates comparable with those of reduction with nitrogenase.[3] The chemical mechanism of activation and dinitrogen reduction in these systems, as well as the structure of their active centers and reaction intermediates, remain unknown. The number of structures of molybdenum-containing clusters (catalyst precursors forming active centers of dinitrogen fixation upon reduction) is small. In particular, the molecular structure of the oxomethoxide polynuclear mixed-valence molybdenum—magnesium complex $\{[Mg_2Mo^{VI}{}_4Mo^{V}{}_4O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{2+}\}\cdot 6MeOH$, which is formed upon the interaction of $MoCl_5$ with methanol in the presence of Mg^{2+} and NaOH, was described.[5] The reduction of the complex with sodium amalgam results in the polynuclear complex of low-valence molybdenum of an unknown structure, which catalyzes the reduction of dinitrogen to hydrazine.[6] In addition, the tetranuclear carbonyl complex of zero-valence molybdenum $K_4[Mo(OH)(CO)_3]_4$ was isolated from the titanium—molybdenum hydroxide dinitrogen-fixing system[7] and characterized by X-ray diffraction.[8] This complex is active in dinitrogen reduction in both the hydroxide systems with Ti^{III} or Cr^{II} hydroxides as reducing agents and in the amalgam systems.[9] The mechanism of catalysis of dinitrogen reduction involving this complex is also unknown.

The catalytic properties of the natural cluster FeMoco isolated from the enzyme and the molybdenum—magnesium cluster $\{[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{+2}\}\cdot 6MeOH$ in the reduced state in the reduction of C_2H_2 and inhibition of this process by CO and N_2 molecules have been studied earlier.[10] It was found

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that the kinetic regularities for natural and synthetic catalysts are fairly similar. This means that the catalytic Mo—Mg cluster resembles in all properties the isolated nitrogenase cofactor under the non-protein conditions, although this cluster can both coordinate and reduce the dinitrogen molecule. Therefore, the role of the protein matrix for the nitrogenase reaction can be obtained by revealing the mechanism of dinitrogen fixation in the considered model system, which shares many common features with the nitrogenase mechanism. However, the majority of theoretical works devoted to the quantum chemical study of the dinitrogen fixation mechanism involving FeMoco does not take into account its protein environment and this decreases the significance of the studies performed. At the same time, there is no theoretical analysis of the mechanism of nitrogenase substrates reaction in the presence of the Mo—Mg cluster, which is the most appropriate object for the elucidation of the regularities and mechanism of cluster catalysis of dinitrogen reduction.

The difficulties encountered in studying the Mo-containing dinitrogen-fixing systems are associated with restricted information on the structural chemistry of the Mo^{III} compounds and lability of the structures of the cluster compounds, especially the alkoxide clusters,[11] which are catalysts in these systems. The known structures of the low-valence Mo compounds were obtained, as a rule, under different conditions, and their interrelations remain unclear. We use the systematic approach to reveal the nature of chemical transformations of the Mo cluster compounds in the catalytic systems. This approach involves the consecutive study of the structure and mechanisms of formation of polynuclear molybdenum complexes at early stages of preparation of the dinitrogen-containing systems from molybdenum pentachloride in methanol in the presence of alkaline metal hydroxides and alkoxides followed by their reduction to the catalytic active state.

The DFT method is often chosen for the study of large transition metal clusters.[12—15] In the present work, the DFT method was used for the quantum chemical simulation of the structure of the unique synthetic catalysts of dinitrogen reduction, *viz.*, the magnesium-containing octanuclear molybdenum complex, and its ability to coordinate molecular nitrogen, acetylene, and carbon monoxide. The protonation of its complexes with acetylene resulting in the two- and four-electron reduction products was also studied by this method. The molecular and electronic structures of the $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}$ $[Mg(MeOH)_6]^{2+}$ cluster in the initial oxidized state were calculated.[16] In order to verify adequacy of the theoretical approach to the study of the low-valence Mo complexes, we calculated the structures and IR spectra of the carbonyl Mo^0 tetranuclear complexes synthesized in this work. The calculation results were compared with the experimental data.

Experimental

Since the carbonyl Mo^0 complexes are sensitive to air oxygen, the procedures on their synthesis and study were carried out under argon using the standard Schlenk techniques. Molybdenum pentachloride (Aldrich, 99.99%), potassium hydroxide (reagent grade, Chemapol), and argon (special purity grade) were used as received. Trivalent titanium chloride was obtained by the dissolution of titanium metal (special purity grade) in 9 *M* HCl. Methanol (pure grade, Reakhim) was absolutized by reflux with magnesium methoxide, distilled in an inert gas flow, and stored under argon.

Complex $K_4[Mo(OH)(CO)_3]_4$ was synthesized by alkaline alcoholysis of Mo^0 hexacarbonyl *via* the reaction $Mo(CO)_6$ + KOH in C_2H_5OH and isolated as a cesium salt.[17] Complex **1** was synthesized by the reduction of $MoCl_5$ with trivalent titanium hydroxide in the presence of CO according to an earlier described procedure.[8] The IR spectra of crystalline samples were recorded on a Perkin—Elmer Spectrum 100 IR spectrometer using a multiple attenuated total internal reflection (MATIR) attachment.

Calculation Procedure

The PRIRODA high-performance quantum chemical program package[18,19] with the application of the PBE nonempirical density functional[20] was used for calculations of the studied molybdenum-containing systems. The calculations were performed using the extended basis set for the SBK (Stevens—Bash—Krauss) effective core potential.[21,22] The SCRF PBE0PBE/LANL2DZ method in the framework of the Tomasi model (PCM) realized in the GAUSSIAN 03 program (version C.02) was used to take into account solvation.[23]

Calculations were performed without symmetry restraints. The character of the found stationary points was revealed by analysis of normal vibration frequencies with the analytical calculation of the second derivatives of the energy with respect to coordinates. The total energy was calculated with a correction to zero-point vibrations.

To determine the charge state of the reduced polynuclear Mo complex $Mo^{III}{}_8Mg_2$, the stability boundaries were calculated in an aqueous medium with allowance for possible protolytic equilibria. For this purpose, the values of pK of the protonation reaction of the complex were determined

$$pK = \Delta G_{298,H_2O}/(2.303RT),$$

the standard Gibbs energy in an aqueous solution ($\Delta G_{298,H_2O}$) was calculated from the equation

$$\Delta G_{298,H_2O} = \Delta G_{298}([Compl]^n) - \Delta G_{298}([Compl]^{n-1}) - \Delta G_{298}(H_{aq}{}^+) + \Delta G^{0\to *},$$

where $\Delta G_{298}([Compl]^n)$ is the standard free energy of the complex taking into account the contribution of the solvation energy, n is the charge of the complex, and $\Delta G^{0\to *}$ is the change in the free energy related to the transition of the system from the gaseous to the liquid state[24] determined from the equation

$$\Delta G^{0\to *} = RT\ln(24.46).$$

At T = 298 K $\Delta G^{0\to *}$ = 1.89 kcal mol^{-1}.

The free energy of a proton in the gas phase ($\Delta G_{298}(H_g^+)$) was determined from the equation

$$\Delta G_{298}(H_g^+) = H_{298}^\circ(H_g^+) - TS_{298}^\circ(H_g^+).$$

The free Gibbs energy of proton hydration was[25] $\Delta_h G_{298}^\circ(H^+) = -263.98$ kcal mol^{-1}, and the total energy of the proton in water was $\Delta G_{298}(H_{aq}^+) = -270.25$ kcal mol^{-1}.

The coordinates of the initial complex $[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{2+}$ were taken from the Cambridge Structural Database (CSD). The name of the complex in the CSD is KAWWIO.

Results and Discussion

Carbonyl molybdenum(0) complexes. We have previously shown[9] that the carbonyl complexes of low-valence molybdenum formed by the reduction of $MoCl_5$ in methanol with trivalent titanium hydroxide in the presence of CO are active in dinitrogen reduction. The molecular structure of complex **1** precipitated from solution as a bright yellow crystalline substance is unknown. The molecular structure of the $K_4[Mo(OH)(CO)_3]_4$ complex formed by the dissolution in water of carbonyl molybdenum complex **1** has earlier been determined. We proposed that complex **1** can either be a methoxide analog $K_4[Mo(OMe)(CO)_3]_4$, or one of the binuclear complexes $[Mo_2(CO)_8(OMe)_2]^{2-}$, $[Mo_2(CO)_6(OMe)_2]^{2-}$, and $[Mo_2(CO)_6(OMe)_3]^{3-}$ with the μ_2-OMe bridges differed in the number of CO ligands. The formation of these dimers can be assumed from the structure of the binuclear molybdenum complexes, as has been shown earlier,[26] which are formed under these reaction conditions but without CO.

The calculated structures of the proposed dimeric and tetrameric complexes are presented in Fig. 1. The theoretical IR spectra of these compounds along with the experimental IR spectra of the studied complexes are shown in Fig. 2.

The calculated structure of the $[Mo(OH)(CO)_3]_4^{4-}$ complex (see Fig. 1, *a*) is consistent with the X-ray diffraction data. The Mo—O and Mo—C distances are 0.07 and 0.06 Å shorter than the experimental[8] values respectively, whereas the C—O distances are 0.04 Å longer. The IR spectrum of the complex (see Fig. 2, curve *2*) exhibits two very intense bands at 1837 and 1734 cm^{-1}. In the experiment[8] these are the bands at 1863 and 1670 cm^{-1}

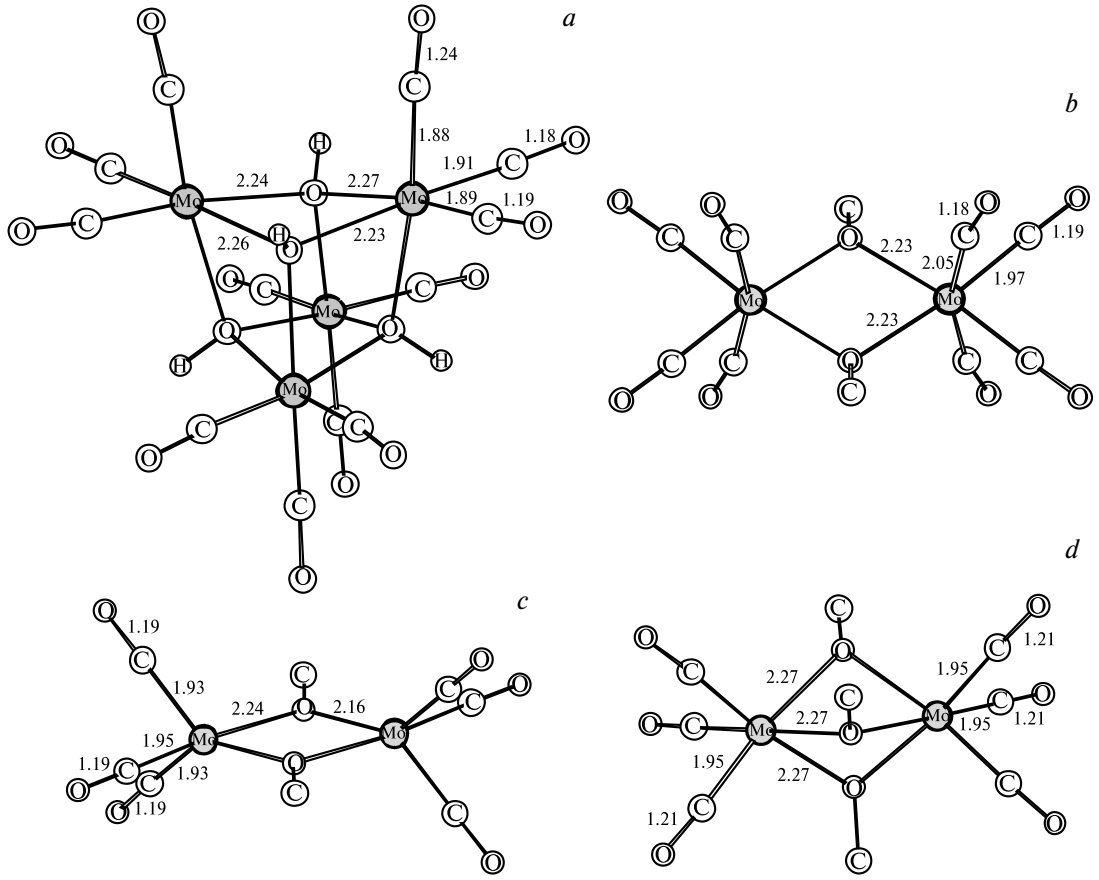


Fig. 1. Structures of the complexes calculated by the PBE/SBK method: $[Mo^0(OH)(CO)_3]_4^{4-}$ (*a*), $[Mo_2(CO)_8(OMe)_2]^{2-}$ (*b*), and $[Mo_2(CO)_6(OMe)_2]^{2-}$ (*c*), $[Mo_2(CO)_6(OMe)_3]^{3-}$ (*d*). Here and in Figs 3, 4, 6, and 7 bond lengths are given in Å.

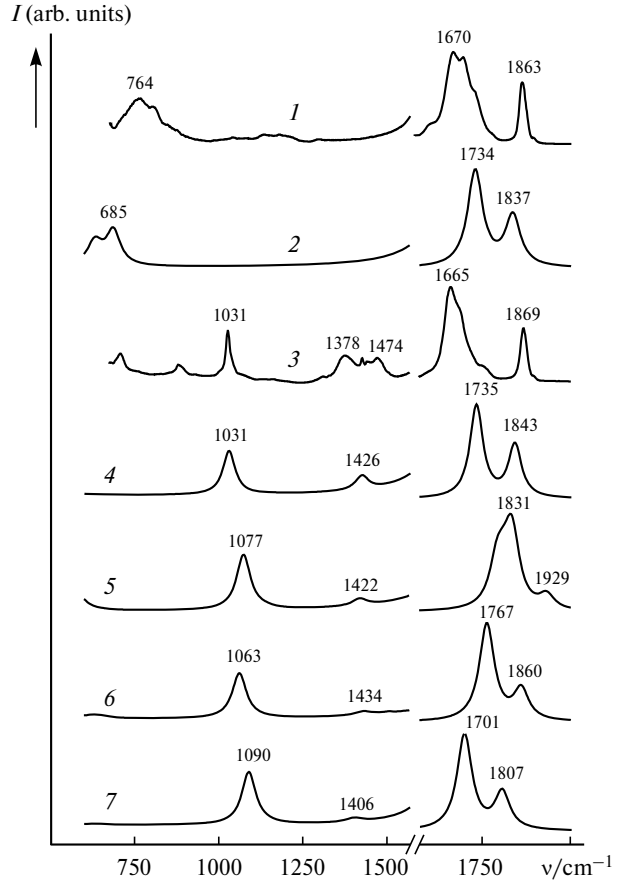


Fig. 2. IR spectra: experimental (*1*) and obtained by the PBE/SBK calculation for the $[Mo^0(OH)(CO)_3]_4^{4-}$ complex (*2*), experimental for complex **1** (*3*) and calculated by the PBE/SBK method for the $[Mo(OMe)(CO)_3]_4^{4-}$ (*4*), $[Mo_2(CO)_8(OMe)_2]^{2-}$ (*5*), $[Mo_2(CO)_6(OMe)_2]^{2-}$ (*6*), and $[Mo_2(CO)_6(OMe)_3]^{3-}$ (*7*) complexes. In the region from 500 to 1500 cm^{-1} the relative intensities of the experimental spectra have a scaling factor of 4; the factor is 8 for spectra *2*, *4*, and *5*; and the factor is 4 for spectra *6* and *7*.

split into several components (see Fig. 2, curve *1*) corresponding to the symmetric and antisymmetric stretching CO vibrations of the carbonyl groups. The split absorption band at 685 (764) cm^{-1} corresponds to the bending vibrations (Mo—C—O). The calculated structure and IR spectra of the $[Mo(OH)(CO)_3]_4^{4-}$ complex reproduce fairly well the experimental structure and spectra.

A comparison of the theoretical IR spectra of the carbonyl Mo complexes of different structure with the experimental complexes suggests the structure of complex **1**.

The structures of the $[Mo(OMe)(CO)_3]_4^{4-}$ and $[Mo(OH)(CO)_3]_4^{4-}$ complexes are similar. The Mo—O and Mo—CO bond lengths are 2.33 and 1.94 Å, respectively. The spectrum of the first complex (see Fig. 2, curve *4*) contains the absorption bands corresponding to the CO stretching vibrations (1843 and 1735 cm^{-1}) and also the absorption bands of the bending vibrations of the methyl group and the stretching vibrations of the O—Me group at 1426 and 1031 cm^{-1}, respectively.

The length of all Mo—O bonds in the $[Mo_2(CO)_8(OMe)_2]^{2-}$ complex (see Fig. 1, *b*) is 2.23 Å, which is 0.1 Å shorter than that corresponding values for the $[Mo(OMe)(CO)_3]_4^{4-}$ tetranuclear complex. The carbonyl ligands are more weakly bound to Mo. The Mo—CO bond lengths range from 1.97 to 2.05 Å. The relative intensity of the bands of the symmetric stretching vibrations of the C—O bonds in the IR spectrum of this complex (see Fig. 2, curve *5*) is much lower than that in the spectra of the tetranuclear complexes (curves *2* and *4*). This spectrum also exhibits a weak absorption band at 1422 cm^{-1} corresponding to the O—C stretching vibrations of two bridging methoxy groups. The $[Mo_2(CO)_6(OMe)_2]^{2-}$ (see Fig. 1, *c*) and $[Mo_2(CO)_6(OMe)_3]^{3-}$ complexes (see Fig. 1, *d*) have the more strongly bound terminal CO ligands (the bond lengths are 1.93, 1.95, and 1.95 Å, respectively). The first of them manifests the nonsymmetric coordination of the bridging OMe groups. The IR spectra of two latter complexes (see Fig. 2, curves *6* and *7*), as well as spectrum *5*, contain weak absorption bands corresponding to the stretching symmetric vibrations of the carbonyl group and the bending vibrations of the Me group. The O—C vibration bands of the bridging methoxy groups are shifted to the region of higher wave numbers.

An analysis of experimental spectra *1* and *3* of complexes $[Mo(OH)(CO)_3]_4^{4-}$ and **1** shows that the absorption bands caused by stretching vibrations of the terminal carbonyl groups have similar wave numbers. Theoretical spectra *2* and *4* of the $[Mo(OH)(CO)_3]_4^{4-}$ and $[Mo(OMe)(CO)_3]_4^{4-}$ complexes also contain absorption bands with similar values of wave numbers. However, the spectra of the methoxide complexes exhibit absorption bands corresponding to the bending vibrations of the Me groups and stretching vibrations of the O—C groups.

Thus, theoretical spectrum *4* (see Fig. 2) of the $K_4[Mo(OMe)(CO)_3]_4$ tetramer best of all corresponds to the experimental obtained spectrum (see Fig. 2, curve *3*). Therefore, it can be assumed that the methoxide tetranuclear molybdenum(0) complex is formed in methanol.

The calculated bond energy of the CO ligand for the $[Mo(OMe)(CO)_3]_4^{4-}$ complex is significant: 75.2 kcal mol^{-1}. The Mo—N_2 bond energy in the corresponding dinitrogen complex $[Mo_4(OMe)_4(CO)_{11}(N_2)]^{4-}$ is considerably lower: 48.2 kcal mol^{-1}. Therefore, the replacement of the CO ligand by the dinitrogen ligand in this system requires a high energy consumption (27 kcal mol^{-1}) and is thermally unattainable under mild conditions. Based on this, we may assume that the coordination of molecular nitrogen to the molybdenum center occurs only in the presence of the coordination vacancy or by the replacement of the more weakly bound ligand. For example, the Mo—O (MeOH) bond energy in the $[Mo_4(OMe)_4(CO)_{11}(MeOH)]^{4-}$ complex is 18.0 kcal mol^{-1}.

The vacancy can be formed due to the reduction of some CO ligands under the conditions of catalysis of dinitrogen reduction, which was experimentally observed.[8]

Structure of the $[Mg_2(MeOH)_4Mo^V_4Mo^{VI}_4O_{22}(OMe)_6]^{2-}$ complex in the reduced state. Several approaches were used for the simulation of the structure of the Mo—Mg complex in the active (towards N_2) state. The most part of the protonic catalytic systems of dinitrogen reduction[27,28] contain transition metal ions with the optimum configuration of the complexation metal d^2 and d^3. There are no direct experimental data on the structure and charge of the $[Mg_2(MeOH)_4Mo^V_4Mo^{VI}_4O_{22}(OMe)_6]^{2-}$ complex (hereinafter $Mg_2Mo^V_4Mo^{VI}_4$) in the state active towards N_2, but the results of gel chromatography[29] show that the number of metal centers is retained upon reduction.

It is assumed that the reduced complex is an octanuclear complex with the oxidation state of Mo +3 or lower. Let us assume as the first approximation that the charge −2 of the complex remains unchanged during reduction. Based on this structure of the $[Mg_2Mo^{III}_8]^{2-}$ complex, we can consider the reactions of its protonation and deprotonation with allowance for solvation effects. The structure of the reduced complex was determined using the model complex $[Mo_8Mg_2O_{22}(HOH)_4(OH)_6]^{2-}$ in which all OMe ligands are replaced by OH groups. It has earlier been shown[16] that the framework of this model complex slightly differs in geometry from that of the starting complex.

To reduce the $Mg_2Mo^{VI}_4Mo^V_4$ complex in which all Mo atoms gain the electronic configuration d^3, it is necessary to introduce 20 electrons and 20 protons into the system to retain the initial charge of the complex −2. There are many variants to protonate the terminal and bridging oxo groups and four bridging OH groups already present in the structure.

Among the isomeric structures obtained at different variants of protonation of the complex, the structure in which all oxo ligands are protonated has the lowest energy (Fig. 3). The initial structure of the metal framework of the Mo—Mg complex[16] underwent changes due to the cleavage of one of the Mo—Mo bonds primarily present in the $Mg_2Mo^{VI}_4Mo^V_4$ complex and to the formation of six new bonds. Lengthening the Mo(2)—Mo(2′) distance to 3.55 Å is favorable for the formation of binuclear dinitrogen complexes from at least geometrical point of view. Another Mo(3)—Mo(3′) distance (2.51 Å)[24] is 0.15 Å shorter than that in the reduced complex (see Fig. 3). Also note the presence of the short hydrogen bond (1.86 Å) linking the hydroxo ligands of the Mo(3) and Mo(3′) centers.

The reduced model complex exhibits a substantial decrease (from 3.35 to 2.37 Å) in the Mg—μ_4-O distance in the $Mg_2Mo^{VI}_4Mo^V_4$ complex (see Ref. 16). The coordination sphere of the Mg atoms gains a new ligand due to this shift of the internal O atoms towards the Mg atoms. Simultaneously the Mo atoms at the periphery of the cluster lose the bond with the μ_4-O ligand. These Mo atoms become coordinatively unsaturated and, thus, manifest a higher affinity to substrates, including N_2. These structural rearrangements upon the formation of the active site are a consequence of the new Mo—Mo bonds in the reduced complex.

On the whole, the $[MgMo_4^{III}(\mu_4\text{-O})(\mu_3\text{-OH})_2(\mu_2\text{-OH})_7(OH)_4]_2^{2-}$ complex includes three double and four ordinary Mo—Mo bonds. The complex contains the Mo(3)—Mo(3′) binuclear fragment and two tri-

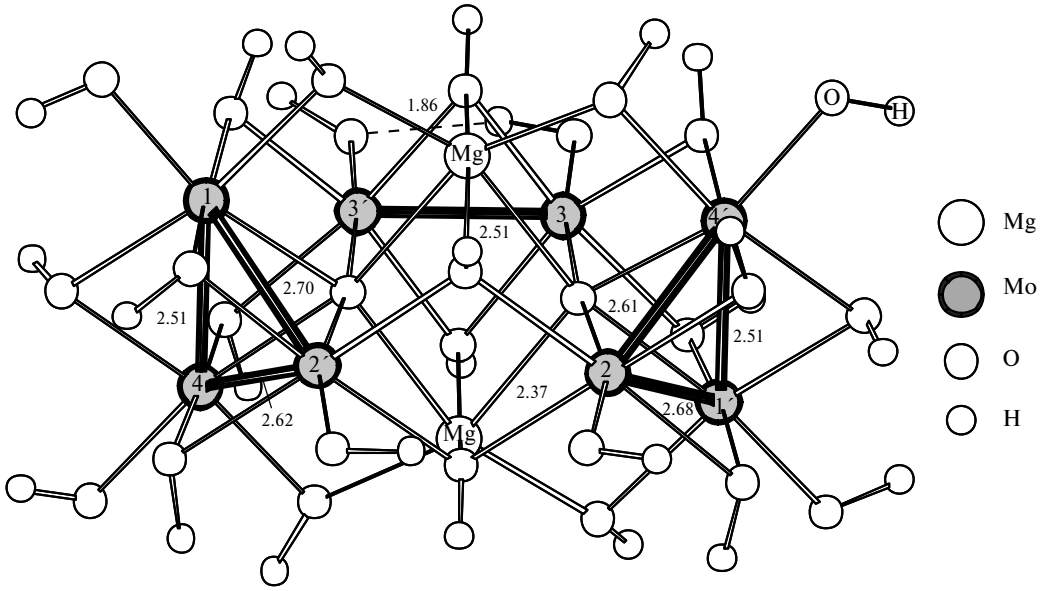


Fig. 3. Structure of the model reduced complex $[MgMo^{III}_4(\mu_4\text{-O})(\mu_3\text{-OH})_2(\mu_2\text{-OH})_7(OH)_4]_2^{2-}$.

Table 1. Spin density distribution and the relative energies ΔE of the $Mg_2Mo^{III}_8$ complex in various spin states (PBE/SBK data)*

Spin (S)	ΔE /kcal mol^{-1}	Total spin density of structural unit of complex /electron spin		
		Mo(3)—Mo(3′)	Mo(2)—Mo(4′)—Mo(1′)	Mo(1)—Mo(2′)—Mo(4)
1	0.3	1.89	1.06	−1.04
2	0	1.89	1.08	1.09
3	16.4	3.88	1.12	1.10
4	29.1	3.87	1.12	3.06

* All values correspond to adiabatic spin decoupling.

angular metallocycles: Mo(2)—Mo(4′)—Mo(1′) and Mo(1)—Mo(2′)—Mo(4) (see Fig. 3). The complex in the quintet state ($s = 2$) has the lowest energy. The transition to the state with the spin $s = 1$ is related to a slight (0.3 kcal mol^{-1}) increase in the energy of the complex (Table 1). The orientation of the total spins on the metallotriangles becomes antiparallel. On the transition to the septet state ($s = 3$) the Mo(3)—Mo(3′) distance of the binuclear fragment lengthens by 0.27 Å. The energy increase (16.4 kcal mol^{-1}) corresponds to this transition from the molybdenum—molybdenum double bond to the ordinary bond. The transition to the higher-lying excited state ($s = 4$) results in the double bond cleavage in the metallotriangle, which additionally demands 12.7 kcal mol^{-1}.

The structures of the complexes with different numbers of protons were calculated and their solvation energies in water were found to determine the charge of the $Mg_2Mo^{III}_8$ cluster. The initial $[Mg_2Mo^{III}_8]^-$ complex includes the aqua ligand at the Mo(3) atom. The addition of one more H^+ proton results in the appearance of the aqua ligand at the Mo(2) atom. The aqua ligands at the Mo(1) and Mo(1′) atoms are added in the $[Mg_2Mo^{III}_8]^{2+}$ complex. The energy characteristics of the main isomers of the $[Mg_2Mo^{III}_8]^n$ complexes with a change in the charge of the complex from −2 to +2 are given in Table 2.

Table 3 contains the values of the free energy and pK of the protonation of the reduced complex calculated by the data in Table 2. They change nonmonotonically, which is not physically justified and is caused by inaccuracies of the calculation. Taking into account that the values of pK change monotonically as the charge of the complex changes from −2 to +2, the obtained values of the free energy were corrected within a mean error of ±5 kcal mol^{-1} in the calculation of the energy for the PBE method. The values of the free energy of the corresponding protolytic equilibria obtained after the correction and the values of pK calculated from the free energy values are given in Table 3.

The range pK = 16.2—13.1 corresponds best of all to the experimental data on the conditions of substrate reduction.[10] According to the theoretical estimate, the complex with a charge of −1 should prevail under these conditions. It was shown for the hydroxide model molybdenum-containing dinitrogen-fixing systems by the electrodialysis method[30] that in acidic media the complexes mainly exist in the monocationic form, whereas in alkaline media the monoanionic form is a predominant species.

The replacement of the OH groups that are not involved in intramolecular hydrogen bonds by the OMe ligands was carried out for the main isomer of the model $[Mg_2Mo^{III}_8]^-$ complex. A similar replacement does not result in any noticeable distortion of the metal framework. The bond lengths in the metallotriangles remains unchanged compared to the model complex. Only the distances between the Mg and μ_4-O atoms are shortened to 2.29 Å. Thus, the Mg atoms cannot be coordination sites of the terminal methoxy ligands initially present in the semireduced structure of the $Mg_2Mo^{VI}_4Mo^{V}_4$ complex. The complex also includes the intramolecular hydrogen bond (1.56 Å) between the H atom of the MeOH ligand of the Mo(3) atom and the O atom of the OMe ligand of the Mo(3′) atom.

The model complex $Mg_2Mo^{III}_8$ with the charge +1 (hereinafter $[Compl]^+$) was used for the study of the interaction with the substrates, because this complex includes three types of aqua ligands bound to Mo atoms of different types: the terminal H_2O ligand of the Mo(1) atom in the

Table 2. Energies of the complexes ignoring (E) and taking into account zero-point vibration correction and the values of contributions to the standard free energy ΔG (calculated by the PBE/SBK method) and solvation energy for the model complexes E_{solv} (calculated by the LANL2DZ method)

Complex	$-E$	$-E_{ZPE}$	ΔG	$-E_{solv}$
	Hartree		kcal mol^{-1}	
$[Mg_2Mo^{III}_8]^{2-}$	1011.413856	1011.04053	183.11	193.76
$[Mg_2Mo^{III}_8]^-$	1012.01719	1011.63253	191.02	115.67
$[Mg_2Mo^{III}_8]^0$	1012.516144	1012.11922	198.49	96.80
$[Mg_2Mo^{III}_8]^+$	1012.922405	1012.51171	205.91	130.10
$[Mg_2Mo^{III}_8]^{2+}$	1013.242455	1012.81875	215.07	215.08

Table 3. Free energies ($\Delta G°_{298,H_2O}$/kcal mol^{-1}) and the values of pK for the protonation of the $[Mg_2Mo^{III}_8]$ complex with allowance for solvation obtained by the processing of the data of quantum chemical calculations (I) and after the approximation of thus calculated values of free energy (II)

Reaction	I		II	
	$\Delta G°_{298,H_2O}$	pK	$\Delta G°_{298,H_2O}$	pK
$[Mg_2Mo^{III}_8]^- \rightarrow [Mg_2Mo^{III}_8]^{2-} + H^+$	18.39	13.5	22.13	16.2
$[Mg_2Mo^{III}_8]^0 \rightarrow [Mg_2Mo^{III}_8]^- + H^+$	24.19	17.7	17.92	13.1
$[Mg_2Mo^{III}_8]^+ \rightarrow [Mg_2Mo^{III}_8]^0 + H^+$	12.49	9.1	13.71	10.1
$[Mg_2Mo^{III}_8]^{2+} \rightarrow [Mg_2Mo^{III}_8]^+ + H^+$	8.29	6.1	9.53	7.0

composition of the metallotriangle, the H_2O ligand of the Mo(2) atom in the metallotriangle involved in the hydrogen bond, and the H_2O ligand of the Mo(3) atom of the binuclear fragment (Fig. 4, complex $[Compl]^+$). This made it possible to compare the energy characteristics of the coordinated substrates on qualitatively different metal centers.

The $[Compl]^+$ complex in the ground state has the spin $s = 1$. The complex in the state with the spin $s = 2$ has a 2.7 kcal mol^{-1} higher energy that that in the ground state. In the quintet state $<S^2> = 6.53$, whereas after the annihilation of the spin component $S + 1$ it is 6.08, which is almost equal to an exact value of 6. The triplet state takes place for the parallel orientation of spins in the binuclear Mo(3)—Mo(3′) fragment and for the antiparallel orientation of spins of the Mo triangles. However, the values of $<S^2>$ before and after annihilation (5.26 and 11.99, respectively) indicate the presence of an admixture of the high-spin state. Accordingly, the interaction of C_2H_2, CO, and N_2 was studied for the model reduced $[Compl]^+$ complex at $s = 2$.

The bond energy of the aqua ligand with the Mo(1), Mo(2), and Mo(3) sites is 21.7, 31.2, and 33.0 kcal mol^{-1}, respectively (Table 4). The noticeable difference in the bond energies of the bond of the H_2O ligand with various centers is explained by the presence of the strong hydrogen

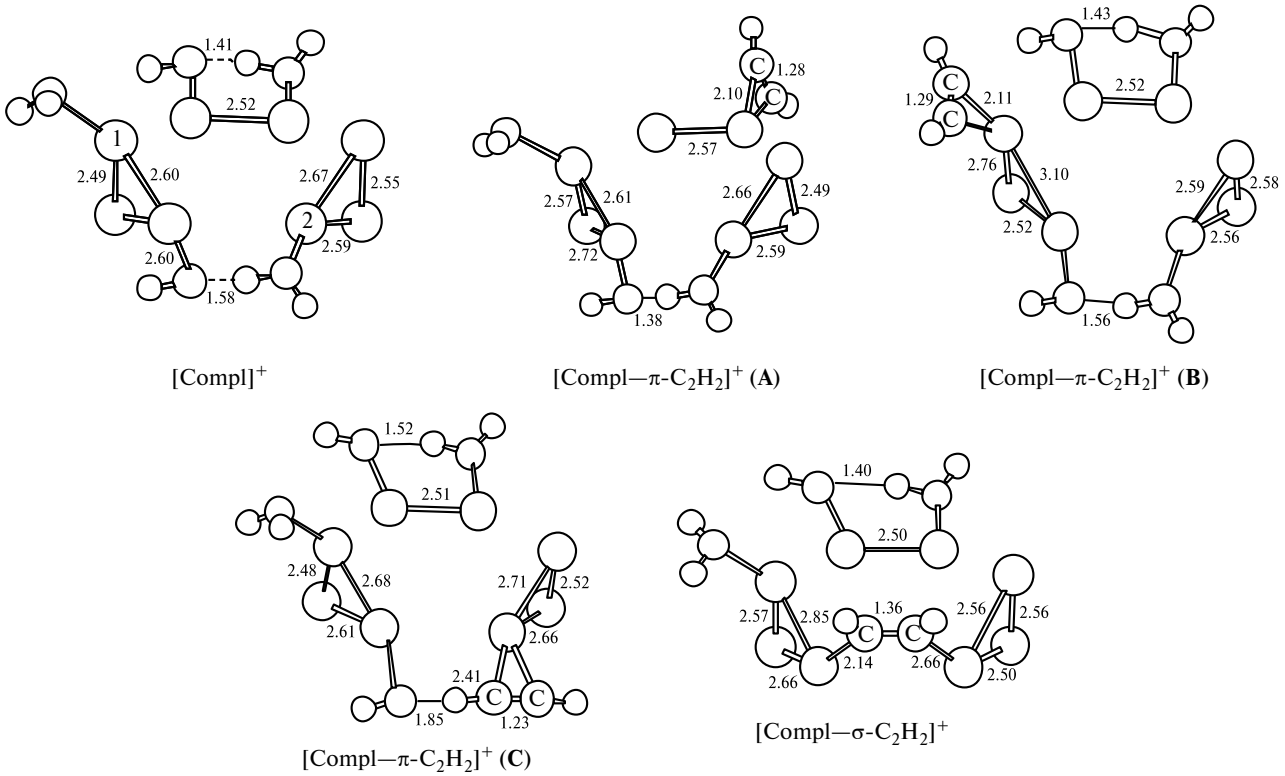


Fig. 4. Fragments of the structures of the $[Compl]^+$ complex and the isomeric acetylene $[Compl—C_2H_2]^+$ complexes containing the Mo and substrate atoms, aqua ligands, and OH ligands involved in intramolecular hydrogen bonds.

Table 4. Binding energies (E_b) of various substrates with coordination sites of the model reduced $Mg_2Mo^{III}_8$ complex, geometric characteristics of substrate binding on the Mo sites, and the energies of the complexes with allowance for zero-point vibration corrections (E_{ZPE})

Complex	$-E_{ZPE}$/Hartree	Coordination site of substrate	E_b /kcal mol^{-1}	Bond length/Å
$[Compl]^+$	1012.511708	1	21.7	2.23 (Mo—H_2O)
		2	31.2	2.27 (Mo—H_2O)
		3	33.0	2.16 (Mo—H_2O)
$[Compl]^-$	1011.619364	3	30.6	2.13 (Mo—H_2O)
$[Compl—\pi\text{-}C_2H_2]^+$ **(A)**	1007.777242	3	51.2	1.28 (C—C), 2.10 (Mo—C_2H_2)
$[Compl—\pi\text{-}C_2H_2]^+$ **(B)**	1007.753876	1	25.3	1.29 (C—C), 2.11 (Mo—C_2H_2)
$[Compl—\pi\text{-}C_2H_2]^+$ **(C)**	1007.734167	2	22.4	1.23 (C—C), 2.41 (Mo—C_2H_2)
$[Compl—\sigma\text{-}C_2H_2]^+$ **(D)**	1007.720995	2, 2′	14.1	1.36 (C—C), 2.14, 2.14 (Mo—C_2H_2)
$[Compl—\pi\text{-}C_2H_2]^-$	1006.888991	3	51.4	1.29 (C—C), 2.11 (Mo—C_2H_2)
$[Compl—\pi\text{-}C_2H_4]^+$ **(A)**	1008.996517	3	46.3	1.44 (C—C), 2.17 (Mo—C_2H_4)
$[Compl—\pi\text{-}C_2H_4]^+$ **(B)**	1008.970631	1	18.8	1.43 (C—C), 2.20 (Mo—C_2H_4)
$[Compl—\sigma\text{-}CHMe]^+$ **(B)**	1008.960231	1	12.3	1.49 (C—C), 1.91 (Mo—C_2H_4)
$[Compl—CO]^+$ **(A)**	1017.014173	3	52.1	1.18 (C—O), 1.92 (Mo—CO)
$[Compl—CO]^+$ **(B)**	1016.987632	1	24.2	1.15 (C—O), 2.06 (Mo—CO)
$[Compl—CO]^+$ **(C)**	1016.972438	2	24.2	1.16 (C—O), 2.02 (Mo—CO)
$[Compl—CO]^-$	1016.136044	3	55.6	1.19 (C—O), 1.91 (Mo—CO)
$[Compl—N_2]^+$ **(A)**	1015.184893	1	10.4	1.11 (N—N), 2.16 (Mo—N_2)
$[Compl—N_2]^+$ **(B)**	1015.181192	2	17.6	1.12 (N—N), 2.06 (Mo—N_2)
$[Compl—N_2]^+$ **(C)**	1015.193887	3	27.3	1.14 (N—N), 1.96 (Mo—N_2)
$[Compl—N_2]^+$ **(D)**	1015.135615	2, 2′	−11.0	1.21 (N—N), 2.09, 2.14, 2.14 (Mo—N_2)
$[Compl—N_2]^-$	1014.314742	3	33.2	1.14 (N—N), 1.97 (Mo—N_2)

bond with H—O distances of 1.58 and 1.41 Å between the H_2O molecule coordinated on the Mo(2) or Mo(3) atom and between the OH ligands of the adjacent Mo atoms (see Fig. 4, complex $[Compl]^+$).

Coordination of acetylene on the Mo centers of the $Mg_2Mo^{III}_8$ model complex. The first step of the fixation of the substrate by the cluster catalytic system is its coordination on the Mo sites of the reduced Mg_2Mo_8 complex. Therefore, in this work we considered possible isomeric complexes $[Compl]^+$ with molecules C_2H_2, CO, and N_2, the binding energies (E_b) of the substrates with different Mo sites of the $[Compl]^+$ complex, and the energies of the substitution of the H_2O ligand by the substrate molecule (ΔE).

The fragments of structures of the isomeric acetylenic complexes $[Compl—C_2H_2]^+$ containing atoms of Mo and the substrate, as well as the aqua and OH ligands involved in intramolecular hydrogen bonds, are shown in Fig. 4. The π-coordination of acetylene on the Mo(3) site of $[Compl—\pi\text{-}C_2H_2]^+$ **(A)** is most favorable (see Fig. 4). The substitution of the aqua ligand of Mo(3) for acetylene is exothermic (−18.2 kcal mol^{-1}). The energy of the Mo(3)—C_2H_2 bond is twice that of the bond energy of the acetylene molecules with the Mo(1) and Mo(2) sites. Note that the energy of π-Mo(3)—C_2H_2 bond formation is high, because the formation of the complex is accompanied by the transformation of the Mo(3)—Mo(3′) double bond into the ordinary bond.

The isomeric complex with acetylene in π-coordination on the Mo(1) site, $[Compl—\pi\text{-}C_2H_2]^+$ **(B)**, is a high-energy species. The metal framework of the cluster is transformed: the Mo(1)—Mo(2′) double bond lengthens to 3.1 Å and is cleaved. The energy of the Mo(1)—C_2H_2 bond is 25.3 kcal mol^{-1}. The lengthening of the C=C bond compared to the free molecule in the complex is 0.08 Å. The substitution of the aqua ligand for acetylene is exothermic (−3.6 kcal mol^{-1}).

A similar substitution reaction on the Mo(2) site of the $[Compl—\pi\text{-}C_2H_2]^+$ complex **(C)** is endothermic (+8.8 kcal mol^{-1}). The Mo(2)—C_2H_2 bond energy is 22.4 kcal mol^{-1}. The coordination of acetylene on the Mo(2) site does not substantially change the metal framework of the complex (see Fig. 4). The Mo(2)—C_2H_2 bond lengths are 2.4 Å, which is by 0.3 Å longer than in the $[Compl—\pi\text{-}C_2H_2]^+$ complex **(A)**. A slight difference in bond energies of C_2H_2 with the Mo(2) and Mo(1) sites is explained by the presence in the $[Compl—\pi\text{-}C_2H_2]^+$ complex **(C)** of the short (1.85 Å) hydrogen bond between the OH ligand of Mo(2′) and the C_2H_2 group at the Mo(2) atom.

In the binuclear on the Mo(2) and Mo(2′) sites of $[Compl—\sigma\text{-}C_2H_2]^+$, acetylene has the longest C—C bond (1.36 Å). However, the formation of this complex is thermally unfavorable (see Table 4). In this case, the bond energy of acetylene is 14.1 kcal mol^{-1}.

Let us consider the intermediate complexes in the pathway of ethylene formation $[Compl—\pi\text{-}C_2H_4]^+$ **(A)**,

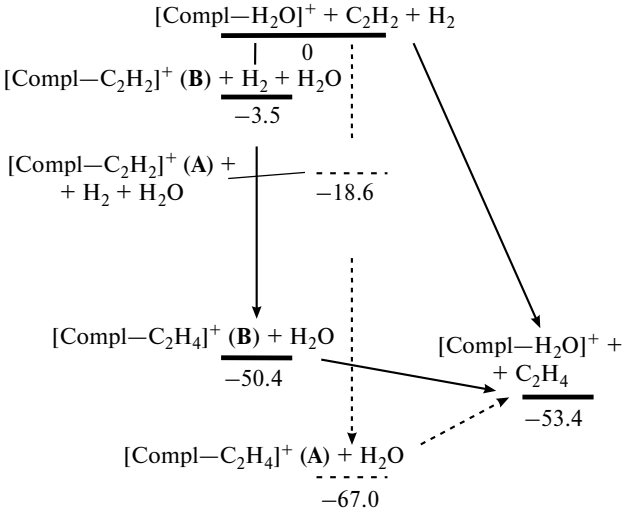


Fig. 5. Energy diagram of acetylene binding with the Mo(1) sites of the $[Compl—C_2H_2]^+$ complex (**B**) and the Mo(3) sites of the $[Compl—C_2H_2]^+$ complex (**A**) followed by its reduction. The energies are given in kcal mol^{-1}.

$[Compl—\pi\text{-}C_2H_4]^+$ (**B**) and ethane formation [Compl—π-CHMe]$^+$ (**A**), [Compl—π-CHMe]$^+$ (**B**) from the acetylene complexes (see Table 4). The main isomer of the $[Compl—\pi\text{-}C_2H_4]^+$ complex (**A**) is 16.2 kcal mol^{-1} lower in energy than $[Compl—\pi\text{-}C_2H_4]^+$ (**B**). We failed to localize the [Compl—σ-CHMe]$^+$ complex (**A**). The formation the $[Compl—\pi\text{-}C_2H_4]^+$ complex (**A**) has a 8.4 kcal mol^{-1} lower energy than the corresponding carbene complex with the CHMe ligand of the Mo(1) atom. The characteristics of the ethylene and ethane complexes are listed in Table 4.

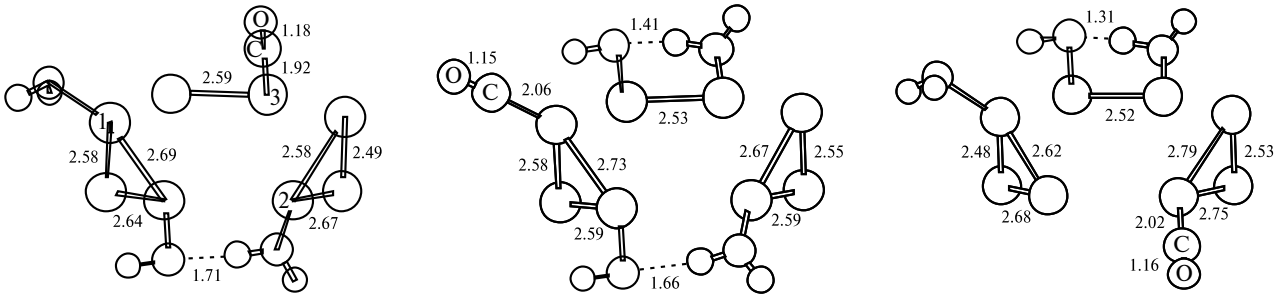
The replacement of the aqua ligand by acetylene is exothermic only on the Mo(1) and Mo(3) sites. The formation of the intermediate ethylene complex is possible on the Mo(1) site. That this possibility is unavailable for the Mo(3) site is related to the fact that the substitution of C_2H_4 in the intermediate ethylene complex for the water molecule is energetically unfavorable (Fig. 5). However, ethane can be formed in the case of binding on the Mo(3) site.

Several mutually replaceable sites coordinating the substrate were experimentally shown[10] to be on the catalytic Mg_2Mo_8 cluster. One of these sites predominantly gives ethylene, and another produces ethane. This agrees with the theoretical data on two sites favorable for acetylene coordination in the reduced $Mg_2Mo^{III}{}_8$ complex. Ethylene is formed on one of these sites, and ethane is formed on another site. Thus, the structure of the $Mg_2Mo^{III}{}_8$ complex determined by quantum chemical simulation of the reduction of the initial $Mg_2Mo^{IV}{}_4Mo^{V}{}_4$ complex adequately reflects specific features of the catalytically active site.

Coordination of carbon(II) oxide on the Mo sites of the $Mg_2Mo^{III}{}_8$ complex. The CO molecule is an efficient inhibitor of reduction of the substrates with the multiple bond and, hence, information on the binding sites of the active complex capable of forming bonds with CO is interesting. Let us consider regularities of CO coordination on the $[Mg_2Mo^{III}{}_8]^+$ complex.

The data obtained are presented in Fig. 6 and in Table 4. The $[Compl—CO]^+$ complex (**A**) in which the CO molecule is coordinated on the Mo(3) site has the highest energy. The lengthening of the C—O bond in this complex is the largest (0.04 Å) compared to that in the free molecule. The significant value of the energy of the Mo(3)—CO bond (52.1 kcal mol^{-1}) is summated from the cleavage energy of one of the Mo(3)—Mo(3′) bonds and the energies of formation of the Mo(3)—CO bond (see Fig. 5). For this coordination of the C—O bond, the hydrogen bond between the OH and H_2O ligands of the metallotriangles is noticeably strengthened. The replacement of the aqua ligand of Mo(3) by CO gives an energy gain of 19.1 kcal mol^{-1}.

The less stable complex $[Compl—CO]^+$ (**B**) is formed when the aqua ligand of the Mo(1) site is replaced by CO with an energy gain of 2.5 kcal mol^{-1}. The C—O bond length in this complex is nearly the same as in the free CO molecule: 1.14 Å (PBE/SBK). The energy of the Mo(1)—CO bond is lower than that for the Mo(3) site



$[Compl—CO]^+$ (**A**) $[Compl—CO]^+$ (**B**) $[Compl—CO]^+$ (**C**)

Fig. 6. Fragments of the structures of the isomeric carbonyl $[Compl—CO]^+$ complexes containing the Mo and substrate atoms, aqua ligands, and OH ligands involved in intramolecular hydrogen bonds.

(24.2 kcal mol^{-1}). The hydrogen bond between the OH and H_2O ligands of the framework metallotriangles is lengthened by 0.08 Å, whereas the hydrogen bond between the OH and H_2O ligands of the binuclear Mo fragment remains the same as in [Compl]$^+$.

A similar reaction for the Mo(2) site is endothermic (+7.0 kcal mol^{-1}). The energy of the Mo(2)—CO bond is the same as that for the Mo(1) site (24.2 kcal mol^{-1}). The hydrogen bond cleavage accompanying the removal of the aqua ligand at the Mo(2) atom and the enhancement of the hydrogen bond of the ligands of the binuclear Mo fragment, which accompanied the shortening of the O—H distance by 0.08 Å compared to [Compl]$^+$, contribute to the change in the energy of the system upon CO coordination.

Thus, the [Compl]$^+$ complex contains two sites of CO binding for which the replacement of the H_2O ligand by CO is exothermic: Mo(1) and Mo(3). The coordination of acetylene is possible on the same sites. Therefore, the conditions for the competitive inhibition of acetylene reduction with carbon(II) oxide appear in this case. The obtained information does not contradict the experimental data[10] on the mixed type of inhibition of acetylene reduction with carbon oxide. Competitive inhibition occurs at the stage of complex formation, whereas noncompetitive inhibition is observed at the stage of decomposition of the catalyst—substrate complex.

Interaction of molecular nitrogen with the model $Mg_2Mo^{III}_8$ complex. The highest bond energy is characteristic of the dinitrogen complex [Compl—N_2]$^+$ (**C**). The N—N bond is weakly activated (its length only 0.03 Å longer than that in the free N_2 molecule). The charge densities on the terminal and proximal N atoms almost coincide. The Mo(3)—N_2 bond is fairly short (1.96 Å), which corresponds to the significant energy of N_2 binding (27.3 kcal mol^{-1}), although the formation of this bond is accompanied by the shortening of the hydrogen bond between the OH and H_2O ligands of the metallotriangles by 0.12 Å compared to [Compl]$^+$ (Fig. 7, see Table 4). The replacement of the aqua ligand of the Mo(3) atom by the dinitrogen ligand is endothermic (+5.7 kcal mol^{-1}).

The formation of the isomeric [Compl—N_2]$^+$ complex (**A**) upon the replacement of the aqua ligand of Mo(1) by N_2 is the endothermic substitution reaction (+11.3 kcal mol^{-1}). This reaction does not result in any changes in the geometry and spin density distribution of the metal framework. The bond energy of N_2 in this complex is significant (10.4 kcal mol^{-1}).

The [Compl—N_2]$^+$ complex (**B**) with the terminal N_2 ligand of the Mo(2) site is 8.0 kcal mol^{-1} higher in energy that the main isomer. The Mo—N bonds are 0.1 Å longer than that for the terminal binding of N_2 with the Mo(3) site. This affects the energy of the Mo—N bond: 17.6 kcal mol^{-1}, which is noticeably lower than the corresponding energy for the [Compl—N_2]$^+$ complex (**C**), although the coordination of N_2 on the Mo(2) site is not accompanied by the Mo(3)—Mo(3′) bond cleavage and there is the short hydrogen bond between the ligands of the binuclear fragment. The replacement of the aqua ligand by the dinitrogen ligans requires 13.6 kcal mol^{-1}.

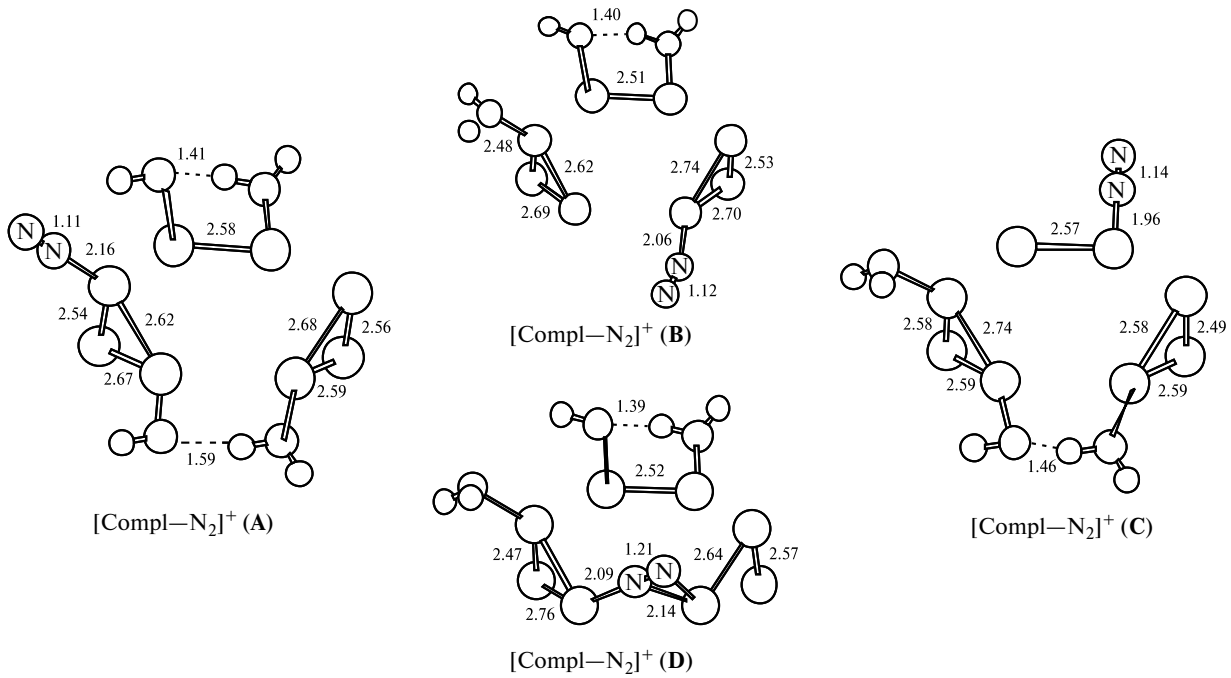


Fig. 7. Fragments of the structures of the isomeric carbonyl [Compl—N_2]$^+$ complexes containing the Mo and substrate atoms, aqua ligands, and OH ligands involved in intramolecular hydrogen bonds.

In the energy scale the complex with the bidentate coordination of N_2, $[Compl—N_2]^+$ (**D**), has a 36.6 kcal mol^{-1} higher energy that the main isomer. This complex was obtained by the substitution of the H_2O ligand of Mo(1) for N_2 and the displacement of the μ_3-OH ligand of Mo(2′) to the terminal position, which is accompanied by considerable expenditure of energy (42.3 kcal mol^{-1}). The N—N bond is significantly activated and close to the double bond (1.21 Å). The geometry of molecular nitrogen binding in this complex is shown in Fig. 7. The complexes with a similar coordination of N_2, *viz.*, $[\{(NPN)Ta\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}N_2)]$ (NPN = $(PhNSiMe_2CH_2)_2PPh$),[31] and $\{2\text{-}[2,6\text{-}(Pr^i)_2PhN{=}C(Me)]6\text{-}[2,6\text{-}(Pr^i)_2PhNC{=}CH_2]\text{-}(C_5H_3N)\}Fe(\mu,\eta^2\text{-}N_2)Na(THF)$,[32] have been synthesized previously. In spite of the binuclear character of binding and a considerable activation of the bond, the total energy of N—N binding is negative (−11.0 kcal mol^{-1}), because this energy is summated from the energy of formation of the Mo—N bond and the energy consumed by the Mo(2)—Mo(1′) bond cleavage.

The $[Compl—N_2]^+$ complexes with the monodentate coordination of N_2 have a lower energy (see Fig. 7). The replacement of the H_2O ligand of the Mo site upon the formation of the binuclear complex of N_2 is energetically less favorable. The substitution reaction requires too high energy for the coordination of N_2 on the Mo(3) site even for the main isomer. This assumes that the coordination of molecular nitrogen on the $Mg_2Mo^{III}{}_8$ clusters and its subsequent reduction require molybdenum to be in a more reduced state.

This assumption explains the experimental observation, according to which acetylene competitively inhibits the reduction of N_2, whereas acetylene reduction is not inhibited by dinitrogen.[10] Evidently, the formation of the coordination bond and reduction of C_2H_2 occur if the Mo sites are reduced to the oxidation state +3.

For the further reduction of the $Mg_2Mo^{III}{}_8$ complex, the Mo atoms (Mo^0) gain the electronic configuration d^6. In this case, twice as much electrons are observed on each Mo site than needed for filling the metal—metal bonding orbitals. For this reason, no metal—metal bonds are observed in the tetranuclear Mo^0 complex with a longer Mo—Mo spacing (see Fig. 1). The high binding energy of the dinitrogen molecule (up to 50.0 kcal mol^{-1}) was found for the $[Mo_4(OH)_4(CO)_{11}N_2]^{4-}$ complex.

Thus, it can be expected that the further reduction of the Mo_2Mg_8 cluster would result in the additional rearrangement of the metal framework and its affinity to the dinitrogen molecule would increase. However, the theoretical simulation of this reduction step is difficult because of the absence of the reference experimental information, since of the structures of the polynuclear Mo^{III} complexes and, the more so, the mixed-valence Mo^{III}—Mo^{II} complexes are not determined so far.

The study of the interaction with the substrates was also carried out for the anionic $[Mg_2Mo^{III}{}_8]^-$ cluster with one aqua group on the Mo(3) site. The calculation of the bond energies of N_2, CO, and C_2H_2 with the Mo(3) site and the corresponding reactions of substitution of the aqua ligand of the Mo(3) site for the substrate molecules showed that the energy characteristics for the model $[Mg_2Mo^{III}{}_8]^-$ complex are consistent with the data for the similar cationic complex (see Table 4). The binding energy of the H_2O ligand of the Mo(3) site is 30.6 kcal mol^{-1}. The energies of the Mo—CO (55.6 kcal mol^{-1}) and Mo—C_2H_2 (51.4 kcal mol^{-1}) bonds are comparable with similar values for the cationic complex considered earlier. The value of N_2 binding with the Mo(3) site for the anionic complex (33.2 kcal mol^{-1}) exceeds a similar value determined for the cationic complex by 5.9 kcal mol^{-1}. The substitution of the H_2O ligand for N_2 becomes exothermic (−3.2 kcal mol^{-1}). However, to compensate the contribution to the free energy related to the high translational entropy of gaseous dinitrogen, it is necessary that the heat effect of this reaction would be ~10 kcal mol^{-1}. Only then the equilibrium constant of the reaction of water substitution for N_2 in the coordination sphere of the cluster would be higher than 1.

Thus, the theoretical study of the electronic structure, IR spectra, and energy of binding of the N_2 ligands by the tetranuclear molybdenum(0) complexes, as well as the structure of the $[Mg_2(MeOH)_4Mo_8O_{22}(OMe)_6]^{2-}$ complex for its 2-electron reduction, was performed. The relationship between the structure and the value of spin of the Mo_8Mg_2 cluster in the reduced state was studied. The possibility of rearrangement of the metal framework upon reduction was shown, and the Mo—Mo interactions was classified. The spin and charge states of the complex were determined. A considerable decrease in the binding energies of the aqua ligands in the reduced complexes was found, which favors their substitution for the substrate molecule. The possible coordination modes of molecular nitrogen, acetylene, and carbon monoxide to the $Mo^{III}{}_8Mg_2$ complex were studied. The primary reactions of protonation of the acetylene complexes resulting in its two- and four-electron reduction products were also studied.

The quantum chemical simulation performed suggests a probable oxidation state of the Mo centers in the catalytically active polynuclear Mo complexes.

The calculated values of energies of substitution of the aqua ligands for the substrate molecules on various Mo sites of the reduced $Mo^{III}{}_8Mg_2$ complex are well consistent with the experimental data that illustrate the regularities of the catalytic behavior of this cluster. This indicates that the structure of the reduced $Mo^{III}{}_8Mg_2$ complex determined by quantum chemical modeling correctly reflects the specific features of the catalytic center.

The calculations were performed at the Calculation Complex MVS-100K of the Interdepartmental Supercomputer Center of the Russian Academy of Sciences and were financially supported in part by the Ministry of Education and Science of the Russian Federation in the framework of the Federal Target Program "Scientific and Scientific—Pedagogical Personnel of Innovative Russia" for 2009—2013.

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