Russian Chemical Bulletin, International Edition, Vol. 52, No. 12, pp. 2555—2562, December, 2003 2555

Catalytic reduction of molecular nitrogen in solutions*

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Reports on nitrogen fixation in solution are reviewed. The optimum catalyst is the polynuclear complex. The reaction proceeds as a multielectron process, and the limiting step involves the electron transfer from a reducing agent.

Key words: molecular nitrogen, reduction, reducing agents, protic media, FeMo cofactor.

As far back as in 1964 M. E. Vol´pin and V. B. Shur have shown[1] that transition metal complexes, such as $CrCl_3$, $MoCl_5$, WCl_6, $FeCl_3$, and $TiCl_4$, in the presence of strong reducing agents ($LiAlH_4$, EtMgBr, and $Bu^i{}_3Al$) reduce molecular nitrogen to products that yield ammonia when decomposed with acid. Nitrides were subsequently recognized as the products in aprotic media. This work commemorated the discovery of a new area: reduction of molecular nitrogen in solutions. Later it has been found that Cp_2TiCl_2, $Ti(OR)_4$, $VO(acac)_2$, $ZrCl_4$, Cp_2Yb, and Cp_2Sm also react with dinitrogen, and the MgI_2—Mg, LiR, and $NaC_{10}H_8$ systems can act as reducing agents. The catalytic reduction of nitrogen to aluminum nitride was observed in the systems similar to $TiCl_4$—Al—$AlBr_3$. The first complex of molecular nitrogen with the $[RuN_2(NH_3)_5]I_2$ ruthenium compound was synthesized almost simultaneously.[2] Although attempts to reduce dinitrogen in a complex were unsuccessful, it was clear that complexes of molecular nitrogen should exist in the Vol´pin—Shur systems. In fact, soon we have synthesized the $[Cp_2TiR]_2N_2$ complex in which dinitrogen can be reduced to hydrazine and ammonia.[3] Later dinitrogen was reduced in the $W(N_2)_2(PR_3)_4$ and $Mo(N_2)_2(PR_3)_4$ complexes.[4]

The reduction of N_2 in protic media (MeOH, H_2O)[5] resulting in the formation of N_2H_4 and NH_3 was described in 1970. The process is similar to the process of biological nitrogen fixation.

Stoichiometry of biological nitrogen fixation obeys the equation

$$N_2 + 8\,H^+ + 8\,e + 16\,\mathrm{MgATP} \xrightarrow{\text{Nitrogenase}}$$

$$\longrightarrow 2\,NH_3 + H_2 + 16\,\mathrm{MgADP} + 16\,P_i.$$

The structure of MoFe protein of nitrogenase,[6] which reduces dinitrogen, has been determined soon by the X-ray diffraction method. We were able to synthesize[7] the Mo_8 complexes capable of catalytic dinitrogen reduction in the presence of Ti^{III} hydroxide or Na amalgam. The FeMo cofactor, which in the absence of protein can form a complex with N_2 and reduce acetylene, was isolated from the MoFe protein.

In the present work, we considered reasons for intertness of the N_2 molecule and methods of molecular nitrogen activation. To compare results on biological nitrogen fixation with model polynuclear systems of catalytic nitrogen fixation, recent data are also presented.

Specific features of the N_2 molecule

Inertness of the N_2 molecule is well known and manifested in its properties. Some physicochemical characteristics of the N_2 molecule are presented below.

Interatomic distance	1.095 Å
Ionization potential	15.58 eV
Dissociation energy	941 kJ mol^{-1}
Frequency of vibrations (in gas phase)	2231 cm^{-1}
Electron affinity	−1.8 eV
Proton affinity	5.12 eV
Energy of singlet-triplet transition	6.17 eV
Solubility in water	$1.7 \cdot 10^{-3}$ cm^3 per 1 cm^3
Solubility in benzene	$1.11 \cdot 10^{-1}$ cm^3 per 1 cm^3

The N_2 molecule is characterized by a very high bond energy $D(N\equiv N)$, a high ionization potential, and the negative electron affinity. Although the proton affinity is positive, it is comparatively low, *i.e.*, lower than that for methane (5.3±0.3 eV). The N_2 molecule is a very weak base and does not react even with strong acids. However, the bond energy itself does not explain dinitrogen inertness.

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* Materials were presented at the Mark Vol´pin Memorial International Symposium "Modern Trends in Organometallic and Catalytic Chemistry" dedicated to his 80th anniversary.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2417—2424, December, 2003.

The energy of the triple bond in acetylene (962 kJ mol^{-1}) is approximately the same as that in the N_2 molecule and is even higher in carbon monoxide (1070 kJ mol^{-1}), whereas both C_2H_2 and CO are much more reactive than dinitrogen.

The electronic configuration of the N_2 molecule can be presented as $(1\sigma_g)^2(1\sigma_u{}^*)^2(2\sigma_g)^2(1\pi_u)^4(3\sigma_g)^2$. The highest occupied orbital $3\sigma_g$ is higher in energy than the $1\pi_u$ orbital due to the interaction of the s- and p-orbitals. Both occupied orbitals of N_2 ($3\sigma_g$ and $1\pi_u$) are strongly bonding: the energy of the $3\sigma_g$ orbital is −15.6 eV, and that of the $1\pi_u$ orbital is −17.1 eV. The lowest unoccupied energy ($1\pi_g{}^*$) is strongly antibonding: its energy is +7.3 eV.

Let us consider the energy of the successive triple bond cleavage of the N_2 molecule. The dissociation of the first of three bonds requires an energy higher than 410 kJ mol^{-1}, which is almost half an energy of the triple bond. The cleavage of the first bond of acetylene, on the contrary, demands a low energy (222 kJ mol^{-1}). This considerable difference is the main reason for different reactivities of acetylene and molecular nitrogen. The strength of the first bond in N_2 (compared to that in acetylene) is likely a consequence of the repulsion of two electron pairs and the π-bond of diazene: in acetylene the repulsion of two σ-bonds with hydrogen and the π-bond is much lower. At the same time, the energy of the triplet state of the N_2 molecule is much higher (6.17 eV) than the energy of the corresponding triplet level of acetylene (3.7 eV).

This difference gives rise to differences in the behavior of acetylene and dinitrogen in one- and two-electron reactions: these reactions are often permitted for acetylene but thermodynamically forbidden for N_2. For example, the hydrogenation of acetylene to ethylene is strongly exothermic: for the reaction

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

$\Delta H^\circ = -176$ kJ mol^{-1}. At the same time, the corresponding reaction of dinitrogen

$$N_2 + H_2 \rightarrow N_2H_2$$

is strongly endothermic: ΔH° is +213 and +234 kJ mol^{-1} for *trans*- and *cis*-diazene, respectively. Even the addition of the $H^\bullet$ atom, which is exothermic ($\Delta H^\circ = -171$ kJ mol^{-1} for acetylene), is endothermic for dinitrogen ($\Delta H^\circ = +37.6$ kJ mol^{-1}) in the reaction

$$N_2 + H^\bullet \rightarrow {}^\bullet N_2H.$$

Therefore, the chain radical reaction initiated by H atom addition is impossible, as well as catalytic hydrogenation through the step of formation of diazene as an intermediate. This is, most likely, the main reason for inertness of typical catalysts of hydrogenation with respect to dinitrogen.

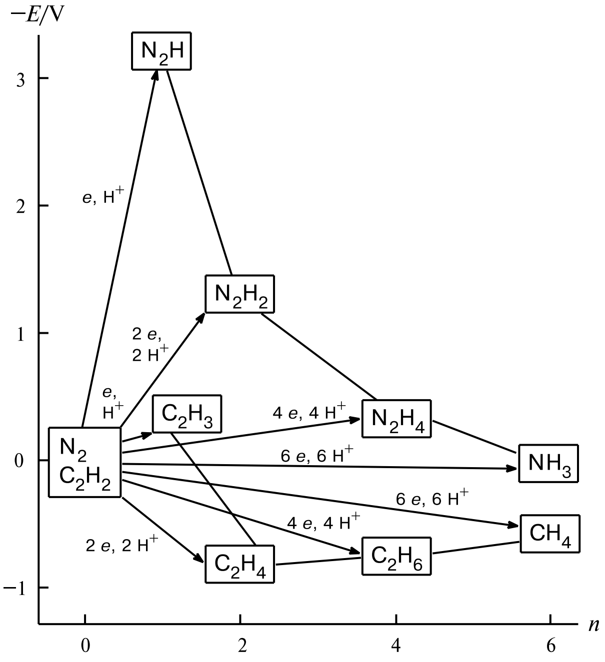


Fig. 1. Redox potentials (*E*) of one-, two-, four-, and six-electron transfer for dinitrogen and acetylene; *n* is the number of electrons.

The successive electron transfer to the nitrogen molecule with simultaneous proton addition reflects these specific features (Fig. 1). The one- and two-electron transfers

$$N_2 + e + H^+ = {}^\bullet N_2H,$$

$$N_2 + 2\,e + 2\,H^+ = N_2H_2$$

correspond to the negative redox potential and require much stronger reducing agents than those used for the reduction of H^+.

On the contrary, the second and third bonds in the N_2 molecule are very weak. This results in the situation when the four- and six-electron reduction processes in an aqueous solution correspond to redox potentials of −0.36 and +0.55 V. In the presence of a metal cluster capable of withdrawing, for example, four electrons in turn and reacting simultaneously with dinitrogen to form hydrazine, the ${}^\bullet N_2H$ radical and N_2H_2 molecule become unnecessary (a comparatively weak reducing agent can effect the reduction). This cluster can exist in a protic medium.

The properties of dinitrogen and the systems reducing N_2 are considered in detail in the recent reviews and in the book.[8]

Intermediate dinitrogen complexes

Among nitrogen complexes containing molecular nitrogen, the first example was the synthesis of the

$[RuN_2(NH_3)_5]I_2$ complex.[2] It was obtained not from N_2 but by the reduction of $RuCl_3$ with hydrazine. Dinitrogen in the complex was assumed[2] to be reduced by $NaBH_4$ to ammonia (completely or partially). We pioneered in synthesizing[9] the $[RuN_2(NH_3)_5]I_2$ and $RuN_2Cl_2L_3$ mononuclear complexes using molecular nitrogen and proving unambiguously that N_2 in the complexes can be reduced by neither $NaBH_4$ nor other reducing agents, such as $CrCl_2$, EtMgBr, $Na_2S_2O_4$, and Zn + HCl. The reduction of dinitrogen in mononuclear complexes of the *cis*-$W(N_2)_2(PR_3)_4$ by acid has been studied[4] later

$$\textit{cis}\text{-}W(N_2)_2(PR_3)_4 + 4\,H_2SO_4 \longrightarrow$$
$$\longrightarrow N_2 + 2\,NH_3 + W^{VI}\text{-products} + 4\,[PR_3H]HSO_4.$$

This was a serious achievement but these complexes can hardly be intermediate compounds in nitrogen-reducing systems.

We were able to make the first observation of intermediate complexes in one of the Vol´pin—Shur systems for the interaction of Cp_2TiCl_2 with EtMgBr in ether.[3] When the temperature decreased to –100 °C, the solution turned blue and yielded the $[Cp_2TiR]_2N_2$ crystals. Upon the temperature increase to –60 °C, the complex was transformed in the $Cp_2Ti{=}N{-}N(MgCl){-}TiCp_2$ hydrazine derivative. Decomposition by sulfuric acid gave hydrazine in ~100% yield. Later several authors observed nitrogen reduction in other specially prepared complexes.[10—15] A complex with dinitrogen is first formed during this reduction, then N_2 is reduced in the complex, and the latter process cannot be considered as the reduction of free nitrogen.

Reduction of dinitrogen in protic media

Although in protic media N_2 can directly be reduced to hydrazine and ammonia, strong reducing agents are unstable in the protic environment, and dihydrogen is easily formed

$$2\,H^+ + 2\,e \longrightarrow H_2.$$

Therefore, the scope of systems active toward N_2 in protic solutions is more restricted than in aprotic media. Analysis of the M—N≡N—M binuclear complexes from the viewpoint of orbitals of the M atoms and N≡N fragments suggests that d^3 and sometimes d^2 and d^4 are the optimum electronic configurations of the complex-forming metal for dinitrogen reduction.

In 1970 Shilov *et al.*[5] reported the first reproducible results demonstrating efficient nitrogen reduction involving protons. The systems reducing dinitrogen in water or methanol are presented in Table 1. They are mainly based on V^{II}, Mo^{III}, Nb^{III}, Ta^{III}, and Ti^{II}, *i.e.*, on ions with the d^2 and d^3 electronic configurations. The systems are active in alkaline media and predominantly include hydroxides, *i.e.*, heterogeneous systems are mainly considered. In addition, a unique family of homogeneous systems based on the V^{II} complexes with catechols, which reduce dinitrogen under mild conditions, is described.[16]

One of the simplest and most efficient heterogeneous systems includes the V^{II}—Mg^{II} mixed hydroxides. The reduction of N_2 occurs in aqueous or alcoholic suspensions of freshly prepared hydroxides formed by the addition of alkali excess to a mixture of VCl_2 and $MgCl_2$. Hydrazine and ammonia are formed with high rates in the reaction at room and lower temperatures and under the atmospheric pressure of N_2.

Hydrazine is mainly formed at high alkali concentrations (pH 13—14) and under high N_2 pressures

$$4\,V(OH)_2 + N_2 + 4\,H_2O \longrightarrow 4\,V(OH)_3 + N_2H_4.$$

Table 1. Systems reducing dinitrogen in protic media ($p_{N_2} \approx 100$ atm)

M*	Reducing agent	T/°C	Products	Yield /mole per 1 mole of M
Ti^{II} (d^2)	Na/Hg	20	N_2H_4, NH_3	0.01
V^{II} (d^3)	$V(OH)_2 + Mg(OH)_2$ (pH 14.3)	20	N_2H_4, NH_3	0.65
	$V(OH)_2 + Mg(OH)_2$ (pH 12)	20	NH_3	0.35
	V^{II} + catechol (pH 10.5)	20	NH_3	0.75
Mo^{III} (d^3)	$Ti(OH)_3$	60	N_2H_4, NH_3	1
	$Ti(OH)_3 + Mg(OH)_2$	110	N_2H_4, NH_3	170
	$Cr(OH)_2$	90 (90)**	N_2H_4, NH_3	0.80 (0.015)**
	Na/Hg (p = 1 atm)	20	N_2H_4, NH_3	1700
	Eu/Hg (p = 1 atm)	20	N_2H_4, NH_3	26
Nb^{III} (d^2)	$Nb(OH)_3$	35	N_2H_4, NH_3	0.09
Ta^{III} (d^2)	$Ta(OH)_3$	35	N_2H_4	0.02

* The electronic configuration is given in parentheses.

** Without Mo.

At low alkali concentrations (pH 8—12), ammonia is formed directly from dinitrogen without intermediate formation of free hydrazine

$$6\,V(OH)_2 + N_2 + 6\,H_2O \longrightarrow 6\,V(OH)_3 + 2\,NH_3.$$

Freshly prepared mixed hydroxide contains the vanadium(II) clusters reactive toward dinitrogen. Some indirect data indicate that the number of vanadium ions in the nitrogen-activating clusters is equal to four or six. The kinetic analysis of reduction shows that the reaction can be considered as pseudo-homogeneous, and the Michaelis—Menten correlation is fulfilled for the nitrogen pressure. This makes it possible to determine the enthalpy of formation of a complex with dinitrogen ($\Delta H = -16.7$ kJ mol^{-1}) and calculate the activation energy ($E = 35.1$ kJ mol^{-1}).[17]

Thus, the intermediate complexes are very unstable and highly reactive. The behavior of dinitrogen in the presence of the V^{II}—Mg^{II} hydroxide system throws doubt upon the concept that the N_2 molecule is inert. In fact, molecular nitrogen can be active in the system that is neither a strong acid (or a base) nor a very strong reducing agent (or an oxidant). An important condition for a high reactivity of dinitrogen is the possibility to form a complex containing at least four electron-donating atoms.

Soluble vanadium(II) complexes[16]

The exact structure of the intermediate vanadium(II) cluster in the mixed V^{II} and Mg^{II} hydroxide is difficult to determine and, hence, we directed our efforts to search for a homogeneous system that reduces N_2 in a protic medium. We succeeded in finding the V^{II} complexes with catechol or substituted aromatic diols (triols), which can efficiently reduce N_2 in homogeneous aqueous or alcoholic media.[16]

The reaction with unsubstituted catechol complexes in water occurs at pH 8.5—13.5, and the maximum yield was achieved at pH 10.5. Later the number of catechol complexes active toward dinitrogen has been increased but the family of the vanadium(II) complexes with aromatic diols remains unique. No other complexes capable of dinitrogen reduction in protic homogeneous media are found so far.

The reaction of N_2 with the catechol complexes in methanol occurs at room temperature and under the atmospheric pressure of N_2. The yield of ammonia, which is the only product of dinitrogen conversion, is ~50% calculated per oxidized vanadium ($V^{II} \to V^{III}$). In aqueous solutions, such yields are obtained only at elevated nitrogen pressures. Dihydrogen is evolved upon the reaction in the absence of nitrogen. When the nitrogen pressure increases, the yield of ammonia increases and that of dihydrogen decreases. However, even at elevated nitrogen pressures the yield of ammonia does not exceed 75%, and 25% electrons are consumed to form dihydrogen. Thus, similarly to biological nitrogen fixation involving Mo nitrogenase, the reaction obeys the equation

$$8\,V^{2+} + N_2 + 8\,H_2O \longrightarrow$$
$$\longrightarrow 8\,V^{3+} + 2\,NH_3 + H_2 + 8\,OH^-.$$

This equation involving NH_2 evolution coupled with the reduction of N_2 reflects the polynuclear character of the intermediate complex.

Also by analogy to nitrogenase, acetylene is reduced by the V^{2+} complex with catechol to ethylene in ~100% yield, and C_2D_2 produces *cis*-dideuterioethylene. The kinetic equation for dinitrogen reduction has the following form:

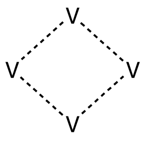
$$-d[V^{II}]/dt = k_1[V^{II}]^2[N_2] + k_2[V^{II}]^{1/2}.$$

The first term of the equation corresponds to the reduction of N_2 to NH_3, and the second term corresponds to H_2 evolution coupled with N_2 reduction.

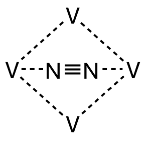
Hydrazine, which might be an intermediate, is readily reduced to ammonia in ~100% yield. When $VOSO_4$ or acid is added to the reaction mixture, a minor amount of hydrazine formed from the hydrazine derivative is evolved. The study of the kinetics of the process shows that the rate of free hydrazine reduction by at least two orders of magnitude exceeds the rate of reduction of hydrazine formed by the action of $VOSO_4$ or acid. This means that hydrazine evolved during the reaction is not in the free state.

The results of kinetic studies indicate the polynuclear character of the intermediate complex. They can be explained by the fact that dinitrogen reduction needs the formation of an octanuclear vanadium complex (upon collision of four tetranuclear complexes), while to reduce H^+, each tetranuclear complex should dissociate to two binuclear complexes. The ESR spectra, which were interpreted first as due to the presence of complexes containing three vanadium atoms,[8] confirmed this conclusion.[18a] The same conclusion follows from the kinetic data.[18b]

An important information was obtained by X-ray diffraction analysis of the structure of the complex synthesized from di-*tert*-butylcatechol.[19] This complex is a tetramer (Fig. 2), and two vanadium ions have the oxidation state II, whereas two other ions are characterized by the oxidation state III, so that the complex corresponds to the half-reduced state. The complex has a tetranuclear framework (**A**), and nitrogen can form a complex with the tetranuclear structure (**B**).



A



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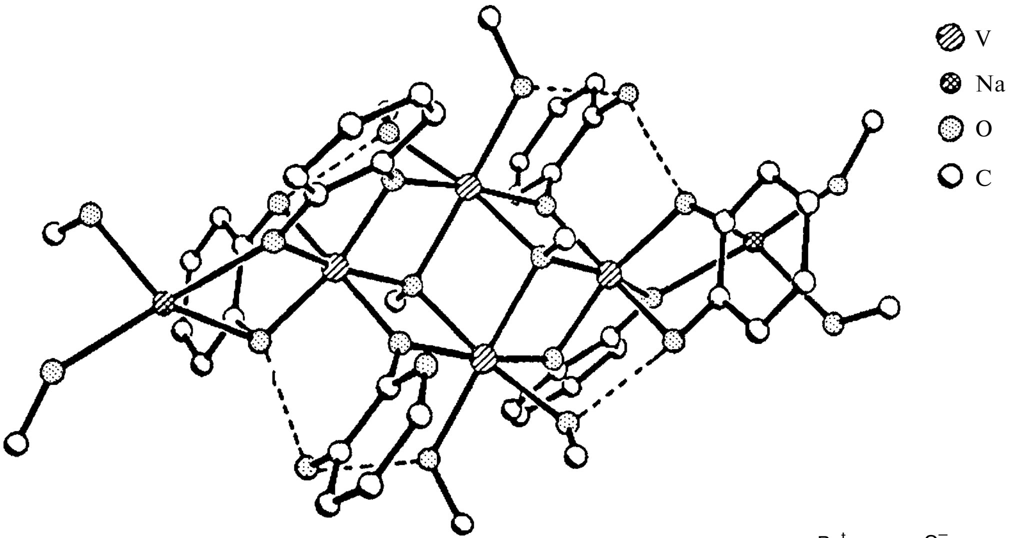
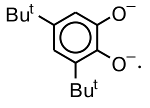


Fig. 2. Molecular structure of the $[V_4(\mu_3\text{-OMe})_2L_4(LH)_2\cdot 2MeOH]Na_2\cdot 4MeOH$ complex; L =



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The above complex is transformed into an ammonia derivative upon the interaction with another complex.

Catalytic reduction of dinitrogen

The system can become catalytic in the presence of an agent reducing vanadium to the bivalent state. However, bivalent vanadium can hardly be an optimum catalyst, because in the presence of the too strong reducing agent water is decomposed to form dihydrogen. The more probable potential catalyst is Mo^{III}, which can activate N_2 in the presence of a stronger one-electron reducing agent, such as $Ti(OH)_3$, $Cr(OH)_2$, or $Ta(OH)_3$. These reducing agents can transfer electrons to the molybdenum ion, which forms a complex with dinitrogen and thus transfers electrons to nitrogen.

The first catalytic system obtained on the basis of this approach was the system containing Mo^{III} as a catalyst and Ti^{III} hydroxide as a reducing agent.[17] At elevated temperatures this system gave equimolar amounts of hydrazine and Mo^{III}. The system became catalytic in the presence of alkaline-earth metal cations Mg^{2+}, Ca^{2+}, and Sr^{2+}. In the case of $MgTi_2O_4$ as the reducing agent, the maximum yield of the products of dinitrogen reduction (to hydrazine and ammonia) achieved 170 turnovers calculated per Mo at 110 °C.

The $MgTi_2O_4$ sample is semiconducting. At 110 °C the molybdenum complex adsorbed on the reducing agent surface activates dinitrogen and attracts electrons from the support, remaining bound to the surface. As a result, the system becomes catalytic.

The $Mg[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]$ complex, whose anionic crystal structure is presented in Fig. 3, was isolated[20,21] from a methanol solution of $MoCl_5$ in the presence of $MgCl_2$. This complex becomes a good catalyst being supported on the sodium amalgam surface using a surfactant (phosphatidylcholin or polyethylene glycol) with triphenylphoshine present in a solution (Table 2). Up to 1000 turnovers were obtained with an aqueous-methanol solution at room temperature and under an atmospheric pressure, and more than 10 000 turnovers were obtained under an elevated pressure. The mechanism of dinitrogen reduction includes the electron transfer from the amalgam surface to the complex coupled with the transfer of four electrons to the coordinated nitrogen molecule. Therefore, it is inferred that there is the reductive assistance of the donor during dinitrogen reduction.

Table 2. Development of the Na/Hg and Mo catalytic systems (MeOH, 20 °C)

Catalytic system	p_{N_2} /atm	v^a /s^{-1}	Yield (N_2H_4 + 0.5 NH_3)	
			I^b	II^c
$MoCl_5$—Na/Hg	70	<0.0001	0.5	0.004
$MoCl_5$—Na/Hg—Mg^{2+}	70	0.0003	2.5	0.02
$MoCl_5$—Na/Hg—PL^d	70		25	0.25
Complex	1	1.1	100—200	~10
$Mo_8Mg_2^{2-}$—PL—R_3P	70	—	10000	30
Nitrogenase		~0.6	—	—

[a] Specific reduction rate is the ratio of concentrations of reduced dinitrogen and molybdenum.
[b] Calculated per Mo (turnover number).
[c] Calculated per reduced dinitrogen (%).
[d] Phospholipid.

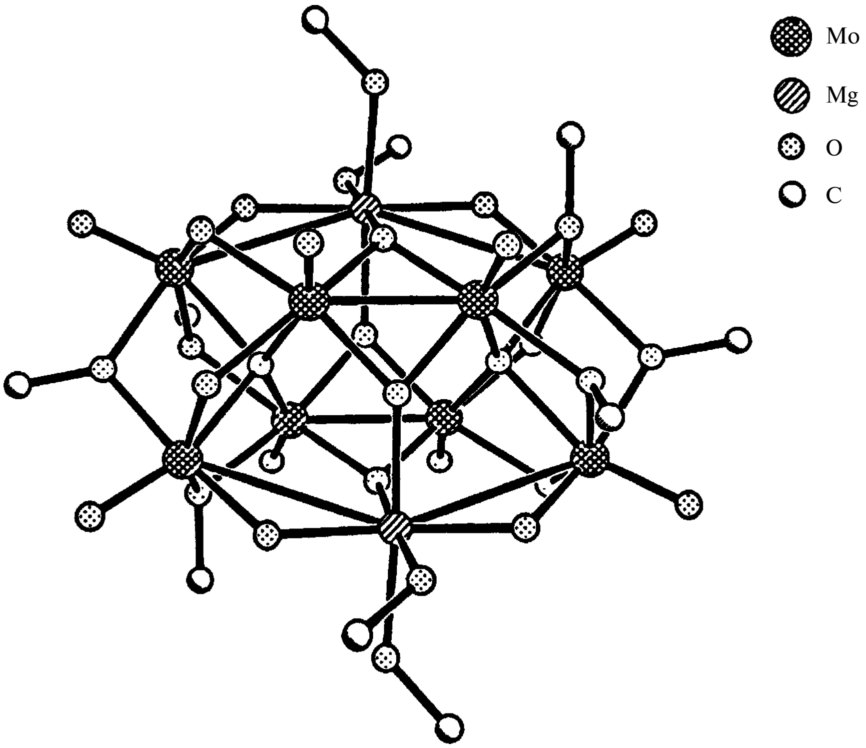

Fig. 3. Crystal structure of the $[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]^{2-}$ anion.

In the presence of the magnesium-molybdenum complex, zinc amalgam (E = –0.8 V) does not reduce dinitrogen but reduces acetylene if thiophenol is added to a solution of the complex. When the amalgam is affected by an induced potential, the reaction obeys the Tafel equation

$$E = a + b\log i.$$

This indicates that the catalyst is adsorbed on the cathode surface. Thus, the $Mg[Mg_2Mo_8O_{22}(OMe)_6(MeOH)_4]$ octanuclear (with respect to molybdenum) complex in methanol can be a catalyst for dinitrogen reduction. An increased activity can be expected from a complex with the number of nuclei higher than eight. This is indicated by the data of gel chromatography: the more polynuclear complex, which was not isolated in the crystalline state, exhibited a higher activity.

The results of studying the vanadium-catechol complex and FeMo cofactor made it possible to revise the reduction of dinitrogen with sodium amalgam catalyzed by the titanium-catechol complex with molybdenum.[22] The yields of the reaction products at different Ti : Mo ratios are presented in Fig. 4. It is seen that at the Ti : Mo ratio equal to 7 the reaction rate is maximum. This can indicate the formation of a heteropolynuclear complex (Scheme 1) containing seven Ti atoms and one Mo atom and active toward dinitrogen in the presence of sodium amalgam.

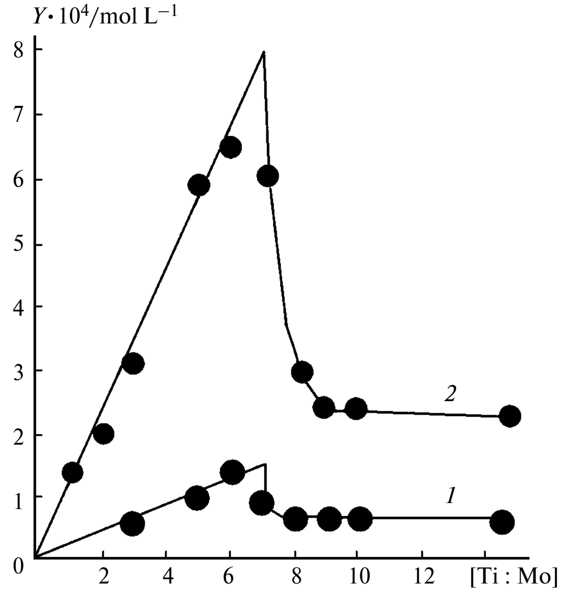

Fig. 4. Yields (Y) of hydrazine (*1*) and ammonia (*2*) at different Ti : Mo ratios. Reaction conditions: water, ~20 °C, p_{N_2} = 70 atm.

Scheme 1

$$Mo^{III} + [Ti_7] \xrightleftharpoons{\text{Cat}} Ti_7MoCat_n$$

$$Ti_7MoCat_n + [Ti] \xrightleftharpoons{K} [Ti_7MoCat_n]Ti$$

Cat is catalyst

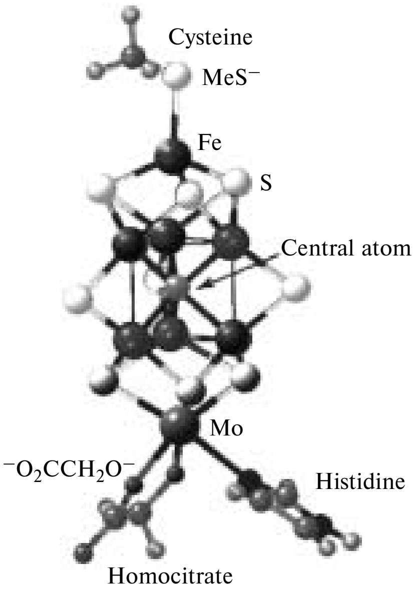

Fig. 5. Structure of the FeMo cofactor according to the X-ray diffraction data.[23]

FeMo Cofactor as a catalyst of reduction of amalgam substrates on the amalgam surface

FeMo Cofactor of nitrogenase (Fig. 5) is the Fe_7MoS_9N (homocitrate) polynuclear complex and, according to all data, is the center on which dinitrogen and other nitrogenase substrates are activated. Although it was isolated in 1977,[24] its catalytic activity outside protein was established only in 1997.[25] This is probably reasoned by the fact that in native nitrogenase the substrate is reduced simultaneously with the electron transfer from the P cluster located at a distance of 14 Å from the FeMo cofactor, while the cofactor reduction outside the protein occurs in a homogeneous system with $NaBH_4$.

We have found[26] that the FeMo cofactor in a DMF solution is an active catalyst of reduction of acetylene and other nitrogenase substrates by zinc, europium, and sodium amalgams. The reaction occurs on the amalgam surface using thiophenol as the cocatalyst.[26] Some properties of the cofactors, such as the hydrogenation of acetylene to ethylene and ethane, deactivation by carbon monoxide, hydrogen formation, and others, are similar to those observed in the interaction of the cofactor in the protein composition. As for dinitrogen, it inhibits acetylene reduction and, according to published data,[27] the inhibition effect is quantitatively identical to that observed when the FeMo cofactor is in the nitrogenase composition. It is significant for dinitrogen reduction that protons would directionally be transferred to the N atom. This can be provided only by the native state of nitrogenase.

In addition to the FeMo cofactor, the iron-vanadium (FeVco) and only iron-containing (FeFeco) cofactors are known, whose reduction of dinitrogen is likely less selective[28,29] (Scheme 2).

Scheme 2

$$N_2 + 8\,H^+ + 8\,e \xrightarrow{\text{FeMoco}} 2\,NH_3 + H_2$$

$$N_2 + 12\,H^+ + 12\,e \xrightarrow{\text{FeVco}} 2\,NH_3 + 3\,H_2$$

$$N_2 + 21\,H^+ + 21\,e \xrightarrow{\text{FeFeco}} 2\,NH_3 + 7.5\,H_2$$

FeS—H_2S System as a model of the prebiotic catalyst of dinitrogen reduction

The FeS—H_2S system can be considered as a model of only iron-containing nitrogenase cofactor. The reduction of dinitrogen to ammonia has been observed in the recent work[30]

$$N_2 + 3\,FeS + 3\,H_2S \longrightarrow 2\,NH_3 + 3\,FeS_2,$$

$$FeS + H_2S \longrightarrow FeS_2 + H_2.$$

Since the reduction of dinitrogen can be accompanied by the formation of ammonia from admixtures, the authors intensely purified nitrogen. Although the yield of ammonia was only 0.1% calculated per FeS for 7 days, the presence of NH_3 in the products was checked by labeled nitrogen. The replacement of one of the Fe atoms by the V or Mo atom makes it possible to obtain the model of vanadium or molybdenum nitrogenase, respectively, and, according to known data,[29] should result in an increase in the yield of ammonia.

Conclusion

Considerable progress has been achieved for 40 years in studying the low-temperature nitrogen fixation in solutions, which was started in the works of Vol´pin and Shur. Russian scientists contributed greatly to the development of this area.

The complexes (at least octanuclear) were synthesized, which can reduce dinitrogen to hydrazine and ammonia at room and lower temperatures. The unique octanuclear complex is also involved in the anaerobic process. Since iron is a relatively weak reducing agent, sulfur enhances the reductive properties. In addition, ATP is used in the living nature. The central atom (perhaps N) favors the enhancement of the reductive properties: the transformation of the complex with dinitrogen into the hydrazine derivative is facilitated due to an increase in the energy of the remaining bond of the Fe atom with the N atom.

It cannot be ruled out that further improvement of the catalyst occurs *via* the aerobic reduction of dinitrogen.[31]

In this case, we can assume that oxygen enhances the withdrawing properties of dinitrogen due to the formation of N_2O.[32,33]

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Received July 15, 2003