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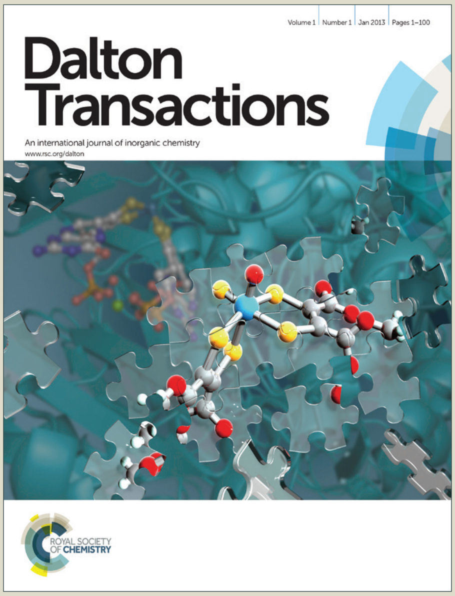

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ARTICLE TYPE

Retrosynthetic approach to design of molybdenum-magnesium oxoalkoxides

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The reaction of $MoCl_5$ methanolysis in the presence of magnesium ions was shown to produce an extensive row of heterobimetallic Mg-Mo(V, VI) oxomethoxides of different nuclearity ranging from 4 for $[Mg_2(CH_3OH)_4Mo_2O_2(OCH_3)_{10}]$ (**1**) to 26 for $[Mg(DMF)_3(CH_3OH)_3]_2[Mo_{22}Mg_4O_{48}(OCH_3)_{28}(DMF)_6]$ (**2**) with the latter possessing a ring morphology. Examination of $[Mo_6O_{12}(OCH_3)_{16}Mg_4(CH_3OH)_6]$ (**3**), $[Mo_6O_{12}(OCH_3)_{12}Mg_2(DMF)_4]$ (**4a**), and $[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_8]$ (**5a**) X-ray structures revealed the presence of the well known tetranuclear core $\{Mo_4O_8(OCH_3)_2\}^{2+}$ thus the similar reactivity patterns leading to their formation were assumed. For convenient synthesis of such heterobimetallic oxoalkoxides, the retrosynthetic approach based on speculative deconstruction of a target molecule onto simpler fragments was suggested and successfully employed. Namely, the reaction of the stoichiometric amounts of appropriately chosen Mo(V), Mo(VI) and Mg^{2+} synthons led to their assembling resulted in formation of heterometallic clusters **3, 5a** and $[Mo_6O_{12}(OCH_3)_{12}Mg_2(CH_3OH)_4]\cdot 2CH_3OH$ (**4b**) characterized by means of elemental analysis, UV-Vis, IR spectroscopy, and X-ray crystallography.

Introduction

Efficient catalytic dinitrogen reduction on a well defined metal site is a long-standing goal in the field of synthetic inorganic chemistry that still remains if not elusive but obscure despite a number of remarkable achievements providing insights on ligation, activation, and stoichiometric [1] transformations of N_2 on mononuclear and polynuclear metal centres and even on a possibility of a catalytic production of NH_3 [2-4] and its derivatives [5] on a *single* metal site [6]. Due to the fact that both industrial and biological dinitrogen reduction to ammonia are based on the cooperation of *multiple* metal sites in the course of activation and hydrogenation of N_2, protic nitrogen fixing systems suggested by Shilov and co-workers [7] which employ *polynuclear* methoxide complexes of low valence molybdenum, represent the most appropriate model for the both processes. Besides the highest activity of the protic systems [7] among known ones in terms of the number of catalytic cycles and reaction rates (the latter being close to those observed for nitrogenase enzyme [8]), another strong evidence supporting the reliability of the model comes from the comparative kinetic study of catalytic behaviour of the active site of enzyme, the iron-molybdenum cofactor (FeMoco), extracted from the MoFe protein, and that of a synthetic complex, that clearly demonstrates very similar patterns for both polynuclear compounds [9].

Unfortunately, a little is known on the structures of the active sites in the protic systems that makes the elucidation of the mechanistic details of N_2 transformations on a polynuclear complex impossible. This stimulates us to undertake a detailed investigation of the catalytic system preparation procedure [10], the general description of which could be summarized as follows: $MoCl_5$ methanolysis reaction in the absence/presence of Mg^{2+} in a weakly alkaline media followed by the reduction of the obtained mixture by the strong reducing agent (Na/Hg, Eu/Hg, Ti^{3+}, *etc*). Data on how the $MoCl_5$ methanolysis reaction is influenced by the ratio and the nature of an alkaline agent are presented in [11].

Herein we report our results on the synthesis and structures of the novel polynuclear magnesium-molybdenum oxoalkoxides formed in the reaction: $MoCl_5 + Mg^{2+} + CH_3OH + NaOCH_3$. We were able to improve the initially exploited synthetic methodology as the retrosynthetic philosophy seemed to be and then proved to be the effective and convenient strategy for the synthesis of complex heterometallic structures from simpler compounds.

Our interest to the synthesis of heterometallic alkoxides was also stimulated by their growing application as Single Source Precursors [12] in MOCVD and sol-gel technology since they combine such valuable assets as the mild decomposition

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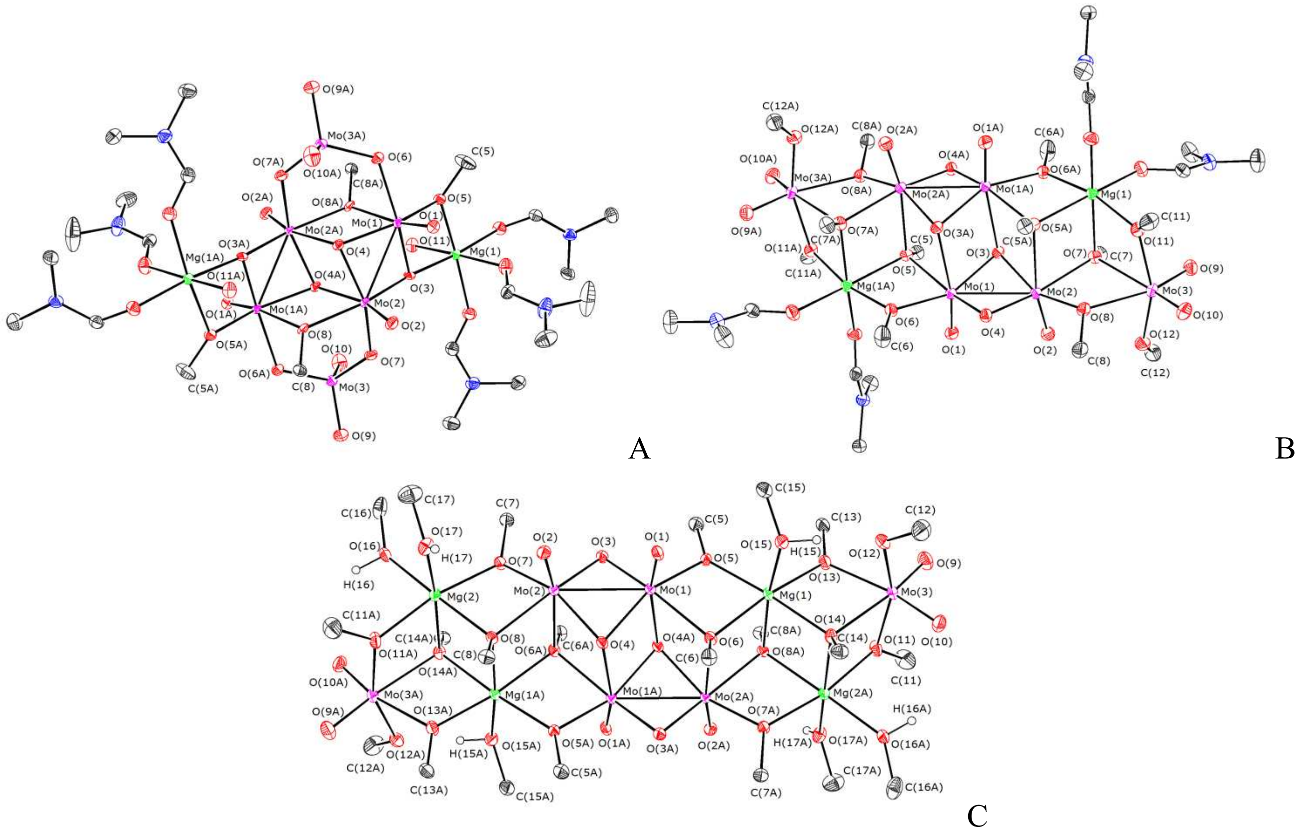

Fig. 1 ORTEP representation of the molecular structures of $[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_8]$ (**5a**) (**A**), $[Mo_6O_{12}(OCH_3)_{12}Mg_2(DMF)_4]$ (**4a**) (**B**), $[Mo_6O_{12}(OCH_3)_{16}Mg_4(CH_3OH)_6]$ (**3**) (**C**) (ρ=50%) (hydrogen atoms of methyl groups and $=CHN(CH_3)_2$ substituents at O(11) and O(11A) in **5a** are omitted from the considerations of clarity). Atomic coordinates and numbering scheme for **3** are taken from ref. [18].

conditions and feasibility to control the ratio of all the desired elements. Here, for instance, we show that the Mg/Mo ratio in the complexes we synthesized ranges from 0.27 to 1. Moreover, the scope of application of Mo-Mg oxo-compounds is not limited by N_2 activation since mixed Mo-Mg oxides are known to be effective heterogeneous catalysts for alkane dehydrogenation [13].

Results and Discussion

$MoCl_5$ methanolysis in the presence of Mg^{2+}. Descriptions of the 3, 4a and 5a structures and their analysis from the point of view of retrosynthetic philosophy

In the course of our step-by-step investigation of the structure of complexes obtained during the catalytic system preparation procedure (see above), we have studied the reaction of $MoCl_5$ + Mg^{2+} interaction with methanol in a weakly alkaline media provided by $NaOCH_3$, according to the general scheme:

$$MoCl_5 + x\ Mg^{2+} + CH_3OH + >5\ M^+A^- \rightarrow \text{“Mo-Mg oxomethoxides”}$$
$$x = 0\div2;\ M^+ = Na^+, K^+;\ A^- = OCH_3^-, OH^- \qquad (1)$$

The only structurally characterized Mo-Mg cluster isolated under the certain conditions (eq.1: $x = 0.6$, $M^+A^- = NaOH$) is $\{[Mg_2Mo_8O_{22}(MeO)_6(MeOH)_4]^{2-}[Mg(MeOH)_6]^{2+}\}\cdot6MeOH$ [10, 14], which was shown to be the high valence precursor of the catalytic active species. It was demonstrated that besides the complex above, a number of other compounds of unknown structures with different Mg/Mo ratio were formed in the course of ($MoCl_5$ + Mg^{2+}) methanolysis at $x = 0.6$, $M^+A^- = NaOCH_3$, whose reduction leads to formation of the complexes active in N_2 reduction as well [15]. Therefore, we decided to undertake a detailed study of this reaction with an intention to structurally characterize the high valence catalyst precursors and to shed some light on the reactivity patterns that take place in these systems, for being able to provide an alternative route to their syntheses. We believe that understanding the factors affecting the structure of formed compounds, could provide an opportunity to control their catalytic properties by means of fine-tuning of the catalysts' precursors structures.

The first step was to reproduce the certain reaction conditions ($x = 0.6$, $M^+A^- = NaOCH_3$ [15]) outlined in eq.1 to obtain the structural information on the compounds thus formed. By

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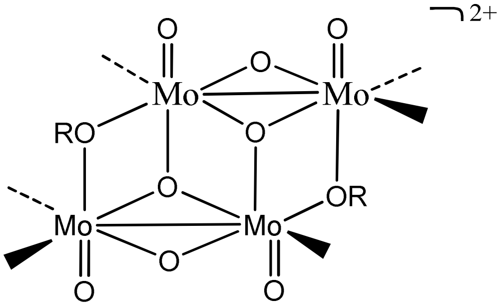

Fig. 2 Schematic representation of $\{Mo_4O_8(OR)_2\}^{2+}$ moiety.

means of recrystallization and extraction procedures we were able to isolate and then structurally characterize a row of heterobimetallic molybdenum-magnesium oxomethoxides of different geometry and nuclearity [16]. Despite apparent structural diversity, it is possible to rationalize their structures in terms of different Mo- and Mg-containing "building blocks" which they are composed of. As an example, centrosymmetric molecules **5a**, **3**, **4a** (fig. 1), **4b** (see below), can be visualized as consisting of well known [11,17] tetranuclear core $\{Mo_4O_8(OCH_3)_2\}^{2+}$ (fig. 2), representing two Mo^V-Mo^V dimers interconnected through the agency of doubly bridged methoxide groups and μ_3-oxo atoms. This core has six coordination vacancies on molybdenum atoms which are occupied with oxygen atoms of Mo^{VI}- and/or Mg-containing moieties.

In case of **4a** the coordination environment of Mo atoms of the central $\{Mo_4\}$ moiety is supplemented by coordination of 3 methoxo groups (6 total) provided by $[MoO_2(OCH_3)_4]^{2-}$ and $[Mg(DMF)_2(OCH_3)]^+$ species, both are in octahedral environment, which are interconnected in turn in edge-sharing (μ-OCH_3) mode. In **3** the ligation of molybdenum atoms of $\{Mo_4\}$ is essentially the same as in **4a**, except the $[Mg(OCH_3)_4(CH_3OH)_2]^{2-}$ moiety is present instead of $[MoO_2(OCH_3)_4]^{2-}$ fragment. To the virtually planar $Mg(\mu\text{-}OCH_3)_2Mg$ cycle, the $[Mo_2O_2(OCH_3)_2]$ moiety is attached in bidentate fashion, thus resulting in an incomplete (due to the lack of one vertex) cubane subunit (for detailed description of the structure **3** see ref. [18]).

A remarkable feature of the structures **3** and **4a** is that the substitution of molybdenum for magnesium has only a slight effect on the geometry of complex. Thus, the only significant deviation in the bond lengths within $[(OCH_3)Mg(\mu\text{-}OCH_3)_2M(OCH_3)_2]$ moiety ($M = [Mg(OCH_3)(CH_3OH)_2]^+$, $[MoO_2(OCH_3)]^+$) is an elongation of the M−O bonds *trans*- to terminal Mo=O groups in **4a**. The other bond distances have essentially the same values. Such a notable feature provides the basis for the isomorphous substitution reactions which are proved to be applicable for the synthesis of heterometallic alkoxides [19].

In **5a** the tetranuclear $\{Mo_4\}$ core is ligated by the two molybdate MoO_4^{2-} moieties in a bidentate manner. Remaining sites are occupied by the bridging methoxo groups connected with magnesium atoms that additionally coordinate μ-O groups of the Mo−Mo moieties. Octahedral coordination of magnesium atoms is supplemented by binding of four dimethylformamide molecules. In contrast to the other mixed valence compounds obtained, **5a** is the only structure containing the tetrahedrally coordinated Mo atoms ligated exclusively by the oxo-groups.

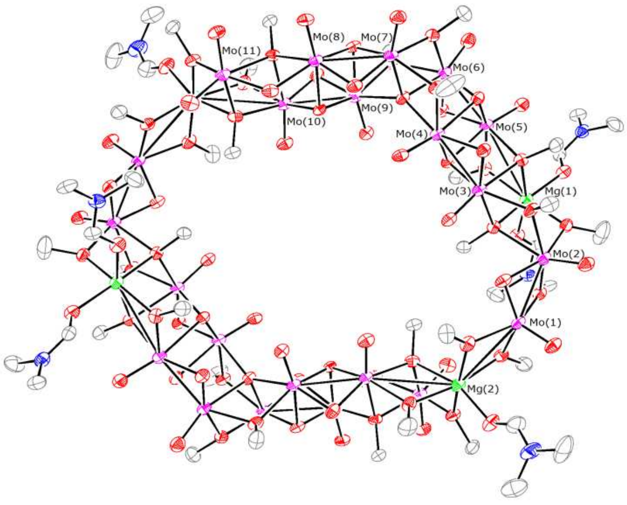

Fig.3 ORTEP view (ρ=30%) of the ring moiety of $[Mg(DMF)_3(CH_3OH)_3]_2[Mo_{22}Mg_4O_{48}(OCH_3)_{28}(DMF)_6]$ (**2**) (hydrogen atoms are omitted).

Structural description of a ring-shaped $[Mg(DMF)_3(CH_3OH)_3]_2[Mo_{22}Mg_4O_{48}(OCH_3)_{28}(DMF)_6]$ (2) polyoxometallate

The structure **2** is quite remarkable in a sense that it represents a rare polyoxometallate containing discrete main group metal polyhedra incorporated into a polymolybdenum framework. An independent part of this centrosymmetric molecule could be described as consisting of three types of Mo-containing building blocks: $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$. $\{Mo_8\}$ unit corresponds to two $\{Mo_4O_8(OCH_3)_2\}^{2+}$ moieties fused through the linkage of μ_2-methoxo and μ_3-oxo groups, with the latter replacing one of the μ_2-OCH_3 ligands in the $\{Mo_4O_8(OCH_3)_2\}^{2+}$ fragment (fig. 2). $\{Mo_2\}$ unit is the common $Mo_2O_2(\mu_2\text{-}O)_2(OCH_3)_4{}^{2-}$ edge-sharing dimeric species [17c,e, 20], while the $\{Mo_1\}$ is an octahedrally coordinated $[MoO_2L_4]^{2+}$ moiety. The pairs of $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$ units, along with four Mg^{2+} atoms, are interconnected through the agency of oxo and methoxo bridges, giving rise to a ring-shaped bimetallic anionic polyoxometallate species (fig. 3) bicapped with two $[Mg(CH_3OH)_3(DMF)_3]^{2+}$ moieties. (For the detailed discussion on the magnesium counterion coordination see Supplementary.)

Comments on Mo^{+6} formation

There is no unequivocal explanation of how a Mo^{+6} appears in the reaction conditions described above neither from our work nor from the literature, despite the documented evidences that Mo^{+5} methanolysis may be accompanied with the formation of Mo^{+6}

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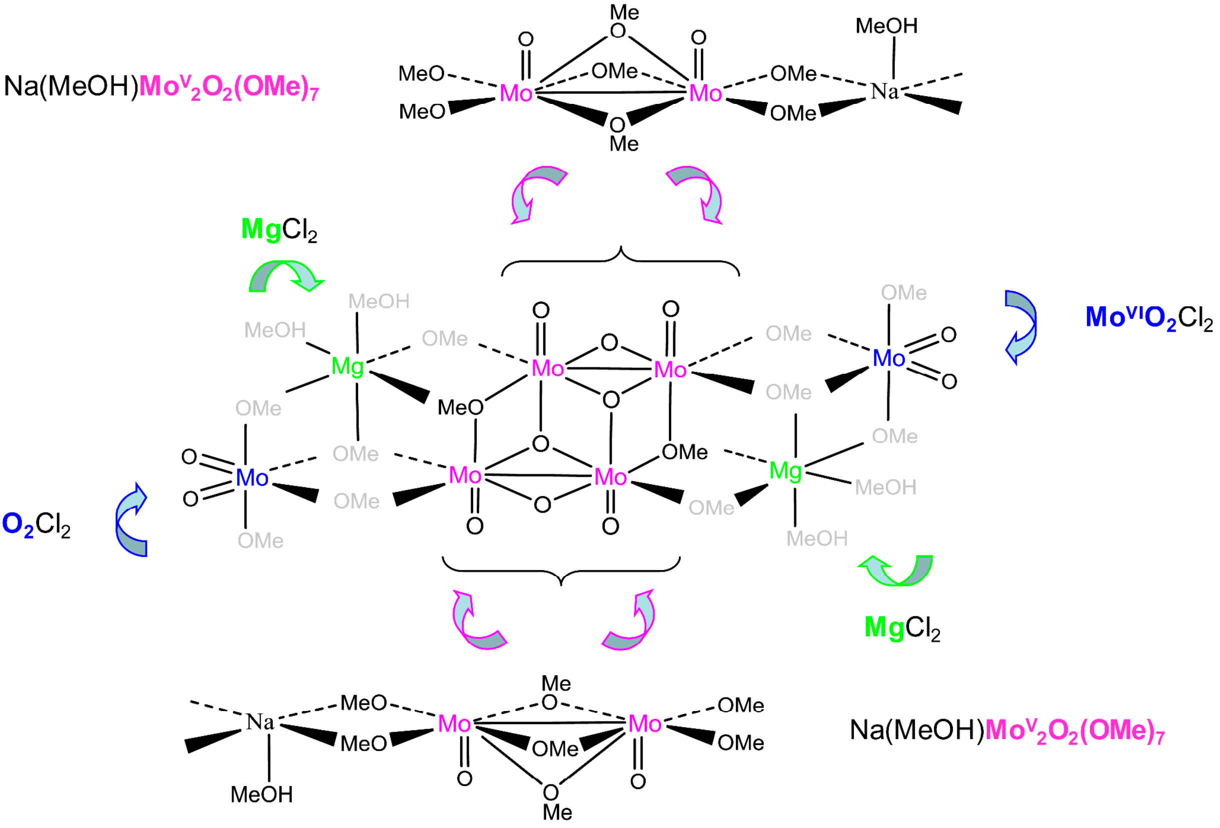

Fig. 5 Scheme of **4b** formation depicting its aggregation from "building units" (corresponding synthons are shown).

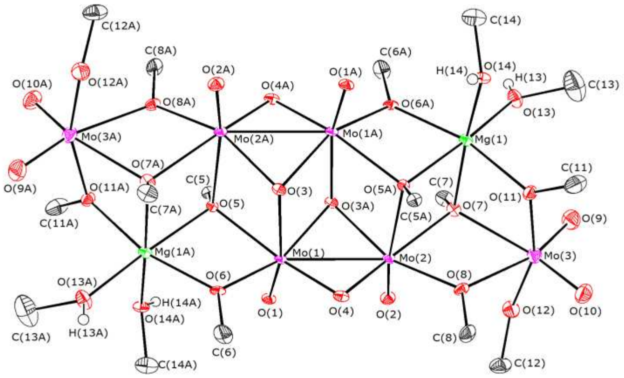

Fig. 4 ORTEP view of **4b** (ρ=50%). Hydrogen atoms of methyl groups and cocrystallized solvent molecules are omitted.

species [17b, 21]. Taking into account the fact that the oxidation reaction strongly accelerates in the presence of water [17b], one can suppose that oxidation of a metal proceeds through the formation of the hydroxo coordinated Mo-species. Such species can be deprotonated more easily in an alkaline media (in comparison with the reaction of dealkylation of alkoxo species), thus transforming into the oxo species, that makes a metal centre more nucleophilic and, hence, more susceptible to oxidation. It might be assumed that such Mo^{+5} oxo-hydroxo compounds (which could be produced in the reaction of Mo^{+5} with traces of moisture inevitably present in a solvent) could function as reducing agents in a metal mediated reduction of solvent protons producing H$_2$, while themselves oxidizing to Mo^{+6}. Though further experiments are required to prove this point, we strongly believe that intrinsic reactivity of the system is responsible for the observed transformations, rather than reactants contamination (which was assumed [17b, 21] to be the reason of this redox process)

Retrosynthetic strategy to preparation of Mo-Mg oxomethoxides [Mo$_6$O$_{12}$(OCH$_3$)$_{16}$Mg$_4$(CH$_3$OH)$_6$] (3), [Mo$_6$O$_{12}$(OCH$_3$)$_{12}$Mg$_2$(CH$_3$OH)$_4$]·2CH$_3$OH (4b), and [Mo$_6$O$_{16}$(OCH$_3$)$_4$Mg$_2$(DMF)$_8$] (5a)

Unfortunately, originally exploited synthetic pathway to Mo-Mg oxomethoxides based on (MoCl$_5$ + Mg^{2+}) methanolysis reaction (eq.1) was found to be rather inconvenient due to low and uncontrollable yields of the products and tedious work-up [16].

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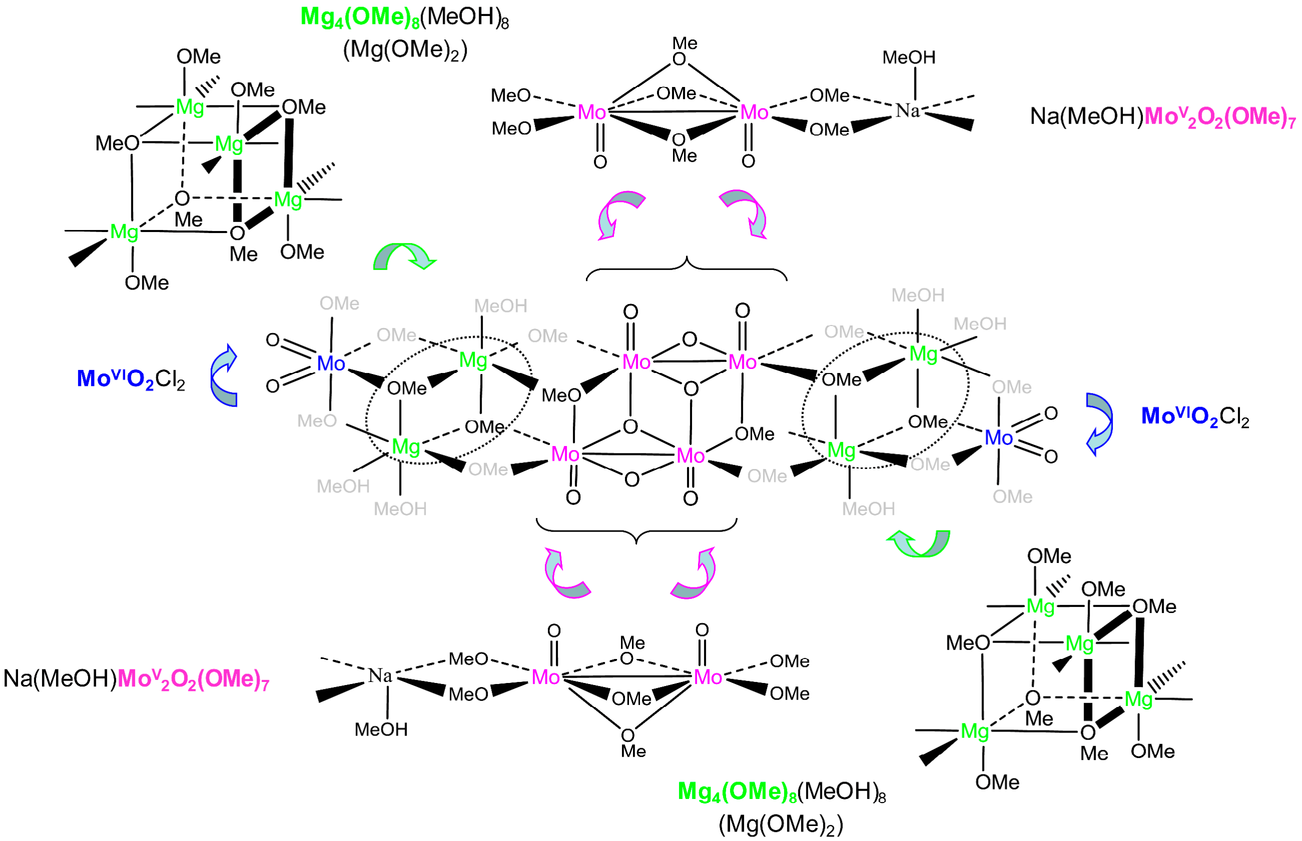

Fig. 6 Scheme of **3** formation *via* aggregation of “building units” (corresponding synthons are shown).

To study the reactivity of this type of compounds further, it was necessary to elaborate an alternative strategy to their syntheses.

As it was underlined, a speculative deconstruction of a complex compound into the smaller “building blocks” could be effectively utilized for a description of its structural peculiarities. The most prominent advantage of this strategy came with the finding that such building blocks could be considered as retrons in what is usually referred to as retrosynthesis [22].

Inspired with the known tendency of alkoxo compounds to aggregate into complicated structures from the smaller ones, including heterometallic (often in a rather unpredictable manner despite attempts to rationalize the reactivity of alkoxides [19, 23]), and taking into account the known reactivity [18] of Mo−Mo containing dimeric complex [Na(CH_3OH)$Mo_2O_2(OCH_3)_7$] [11], we were intrigued to examine whether the retrosynthetic strategy can be employed in the preparation of Mo-Mg complexes obtained in the reaction of the metal chlorides methanolysis.

Summarizing the structural features of **3**, **4a** (and **4b** [24], see fig. 4 and Table 1) and **5a**, one might repeat that these compounds could be considered as consisting of different Mo^{+5}, Mo^{+6} and Mg^{2+} containing moieties. Schemes of formation of **3** and **4b** depicting deconstruction of the complex molecule onto corresponding retrons and demonstrating the synthetic equivalents of the latter are shown on Fig.5 and Fig.6, respectively [25].

Thus, the reaction of the stoichiometric amounts of Mo^V-Mo^V and Mo^{VI} (in a form of [Na(CH_3OH)$Mo_2O_2(OCH_3)_7$] and MoO_2Cl_2, respectively) with either 1 or 2 equivalents of $Mg(OCH_3)_2$ [26] per Mo^V-Mo^V unit and water (apparently hydrolyzing methoxo-bridged $[Mo_2O_2(OCH_3)_7]^-$ dimers) leads to the formation of clusters **4b** or **3**, according to eq. 2 and 3.

$$2\ Mo^{VI}O_2Cl_2 + 2\ Mg(OCH_3)_2 + 2\ [Na(CH_3OH)Mo^V{}_2O_2(OCH_3)_7] + 4\ H_2O \rightarrow [Mo^V{}_4O_8(OCH_3)_{12}Mo^{VI}{}_2O_4Mg_2(CH_3OH)_4]\ (\mathbf{4b}) + 2\ NaCl + 2\ HCl + 4\ CH_3OH \qquad (2)$$

$$2\ Mo^{VI}O_2Cl_2 + 4\ Mg(OCH_3)_2 + 2\ [Na(CH_3OH)Mo^V{}_2O_2(OCH_3)_7] + 4\ H_2O \rightarrow [Mo^V{}_4O_8(OCH_3)_{16}Mo^{VI}{}_2O_4Mg_4(CH_3OH)_6]\ (\mathbf{3}) + 2\ NaCl + 2\ HCl + 2\ CH_3OH \qquad (3)$$

It is clear from the eq. 2 and 3 that outcome of the process markedly depends on the alkalinity of the media in the initial stage of the reaction (*i.e.* $Mg(OCH_3)_2/MoO_2Cl_2$ ratio taken). This

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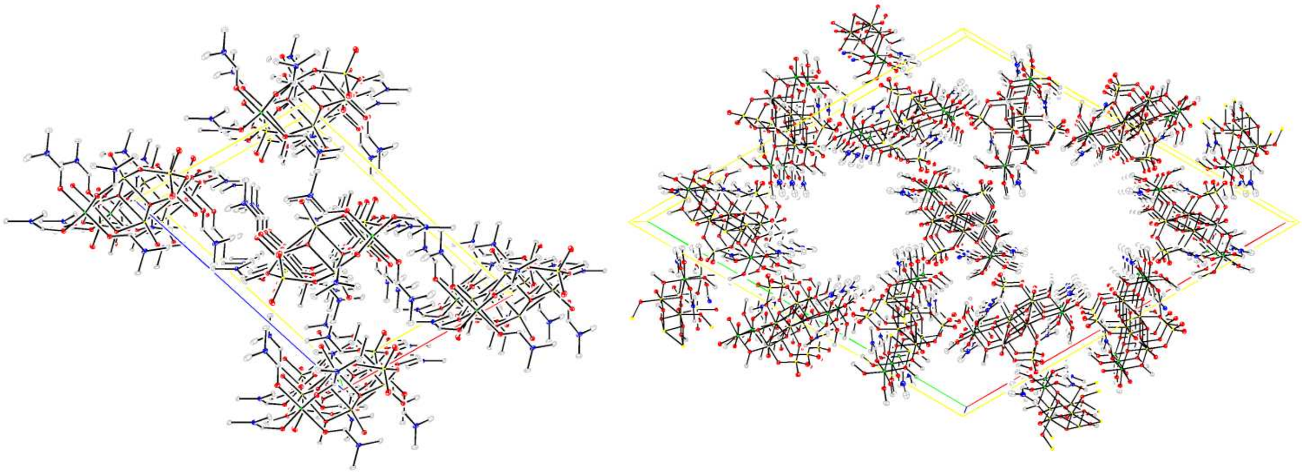

Fig. 7 Crystal packings of **5a** ($P2_1/n$) (left) (view along *b* axis) and **5b** (R-3) (view along *c* axis). Mo, yellow; Mg, green; O, red; N, blue; C, grey.

Table 1 Bond lengths (Å) in isostructural Mo-O framework of complexes 4, **4a**·2CH_3OH, **4b**.

	4a	**4a**·2CH_3OH	**4b**
Mo(1)-Mo(2)	2.5763(4)	2.5715(4)	2.5733(10)
Mo(1)-O(1)	1.684(2)	1.6839(19)	1.696(5)
Mo(1)-O(3A)	1.987(2)	1.9787(18)	1.979(5)
Mo(1)-O(3)	2.311(2)	2.3007(18)	2.296(5)
Mo(1)-O(4)	1.949(2)	1.9428(18)	1.940(6)
Mo(1)-O(5)	2.141(2)	2.1234(18)	2.131(5)
Mo(1)-O(6)	2.024(2)	2.0247(18)	2.016(6)
Mo(2)-O(2)	1.685(2)	1.6763(19)	1.688(6)
Mo(2)-O(3)	1.979(2)	1.9781(19)	1.982(6)
Mo(2)-O(4)	1.948(2)	1.9361(19)	1.942(6)
Mo(2)-O(5A)	2.351(2)	2.3558(18)	2.340(5)
Mo(2)-O(7)	2.149(2)	2.1463(18)	2.151(6)
Mo(2)-O(8)	2.050(2)	2.0383(18)	2.026(6)
Mo(3)-O(7)	2.293(2)	2.2604(18)	2.278(6)
Mo(3)-O(8)	2.223(2)	2.2391(19)	2.228(6)
Mo(3)-O(9)	1.718(2)	1.718(2)	1.711(7)
Mo(3)-O(10)	1.710(2)	1.703(2)	1.699(7)
Mo(3)-O(11)	2.045(2)	2.0373(19)	2.020(6)
Mo(3)-O(12)	1.897(2)	1.890(2)	1.932(7)

is due to the fact that it is alkalinity of the media that influences an equilibrium shift in the reaction $\{Mg_1\}^{2+} \leftrightarrow \{Mg(\mu\text{-}OCH_3)_2Mg\}^{2+}$. In close to neutral media $\{Mg_1\}^{2+}$ predominates that results in formation of **4b**, while under strongly alkaline conditions dimeric species $\{Mg(\mu\text{-}OCH_3)_2Mg\}^{2+}$ (which are the "half" of magnesium methoxide $[Mg_4(OMe)_8(MeOH)_8]$ molecule) are more stable and **3** is the main isolable product.

The same reaction scheme as for **4b** synthesis seemed to be applicable to the preparation of **5a**, but except instead of MoO_2Cl_2, molybdate was used as a source of Mo^{+6}. This suggestion was justified since we were able to synthesize **5a** in such a manner. Additionally, using the same synthetic approach, we were able to obtain compound $[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_4(CH_3OH)_4]$ (**5b**) which differs from **5a** in ligation of magnesium ions and in crystal packing (Fig.7). Unfortunately, yield of **5a** synthesized according to this scheme appeared to be poorly reproducible. Yet we were lucky to find that dissolution of either **4a** or **4b** in DMF leads to theirs high yield transformation into **5a**. One may speculate that the mechanism of the latter reaction includes dissociation of **4a** or **4b** into species structurally close to those proposed as retrons in **4b** formation scheme, (fig.5) since the conversion of **4a** (or **4b**) into **5a** represents essentially the rearrangement of the molecule accompanied with dealkylation of some methoxo groups. Almost complete transformation could be rationalized in terms of Le Chatellier's principle since **5a** is completely insoluble in DMF.

Mo(V, VI)-Mg oxomethoxides as precursors of N_2 fixing catalysts

Investigation of structural and electronic properties of the compounds obtained upon reduction of the high valence precursors as well as exploration of alternative synthetic schemes leading to polynuclear low valence molybdenum (and molybdenum-magnesium) oxomethoxides are in progress. The next step of the study presented here is the reduction of the synthesized compounds and testing of the products as the catalysts of dinitrogen reduction in methanol. Preliminary studies have demonstrated very inspiring results as the products of the reduction of certain compounds described above were active in

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Table 2 Crystallographic data for **2** [a], **4a**, **4a**·2CH_3OH, **4b** [a], **5a** [a], **5b**.

Complex	**2**	**4a**	**4a**·2CH_3OH	**4b**	**5a**	**5b**
Formula	$C_{68.6}H_{189.21}Mg_6Mo_{22}N_{12}O_{94}$ [b]	$C_{24}H_{64}Mg_2Mo_6N_4O_{28}$	$C_{26}H_{72}Mg_2Mo_6N_4O_{30}$	$C_{18}H_{60}Mg_2Mo_6O_{30}$	$C_{28}H_{68}Mg_2Mo_6N_8O_{28}$	$C_{20}H_{56}Mg_2Mo_6N_4O_{28}$ [b]
Formula weight	4942.78 [b]	1481.05	1545.14	1380.92	1589.16	1424.95 [b]
T, K	100(2)					
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Hexagonal
Space group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$	$P2_1/n$	R-3
Z/Z'	2/0.5	1/0.5	2/0.5	2/0.5	2/0.5	9/1
a, Å	16.983(2)	9.6698(6)	7.9676(8)	8.8482(10)	12.086(2)	39.690(4)
b, Å	24.133(3)	11.2114(7)	17.3716(18)	28.556(3)	13.745(3)	39.690(4)
c, Å	21.952(3)	13.5351(8)	19.067(2)	9.6563(11)	17.615(4)	9.2538(9)
α, °	90	100.7970(10)	90	90	90	90
β, °	90.464(2)	104.1670(10)	94.353(2)	105.008(2)	106.75(3)	90
γ, °	90	114.3590(10)	90	90	90	120
V, $Å^3$	8996.7(18)	1225.11(13)	2631.4(5)	2356.6(5)	2802.2(10)	12624(2)
d_{calc}, g cm^{-3}	1.825	2.007	1.950	1.946	1.883	1.687 [b]
μ, cm^{-1}	15.83	16.03	14.99	16.59	14.1	13.96*
$2\theta_{max}$, °	54	60	60	54	60	60
Reflections collected /independent	75322/19607	20020/7107	28396/7675	39675/5148	19548/8112	42295/8154
Observed reflections [$I>2\sigma(I)$]	12030	6066	6229	4143	7287	6224
Number of refined parameters	933	299	318	263	336	297
R_1	0.0644	0.0306	0.0315	0.0579	0.0339	0.0375
wR_2	0.1933	0.0840	0.0647	0.1362	0.0922	0.1006
GOF	1.061	1.027	1.036	1.073	1.047	1.028
Residual density, e$Å^{-3}$ (d_{max}/d_{min})	1.946/-0.888	1.420/-0.887	0.741/-0.694	1.742/-1.204	1.024/-0.815	2.038/-0.782

[a] Additional comments on **2**, **4b**, **5a** crystallographic characterization are given in Supporting information; [b] We were unable to identify the solvent disordered in voids in **2** and in "channels" along the -3 axis in **5b**. Randomly distributed residual peaks were removed using the SQUEEZE procedure. In both cases the crystals were obtained by recrystallization from a CH_3OH / DME / DMF (*ca.* 5:2:2) mixture. Since the real content of the voids is unknown we did not include the solvent into the total formula.

catalysis of N_2 reduction [27] (data not shown). These results clearly indicate that suggested step-by-step strategy based on the reproduction of the protic catalytic system preparation procedure, may be considered as an effective way to characterize the active sites functioning in these systems.

Conclusions

The reaction of ($MoCl_5$ + Mg^{2+}) methanolysis in the presence of base leads to a row of the heterobimetallic Mg-Mo(V, VI) oxomethoxides of different nuclearity characterized by means of elemental analysis, UV-Vis, IR spectroscopy, X-ray crystallography: $[Mg_2(CH_3OH)_4Mo_2O_2(OCH_3)_{10}]$ (**1**), $[Mg(DMF)_3(CH_3OH)_3]_2[Mo_{22}Mg_4O_{48}(OCH_3)_{28}(DMF)_6]$ (**2**), $[Mo_6O_{12}(OCH_3)_{16}Mg_4(CH_3OH)_6]$ (**3**), $[Mo_6O_{12}(OCH_3)_{12}Mg_2(DMF)_4]$ (**4a**), $[Mo_6O_{12}(OCH_3)_{12}Mg_2(DMF)_4]\cdot 2CH_3OH$ (**4a**·$2CH_3OH$) and $[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_8]$ (**5a**). X-ray structures of **2**, **4a**, **4a**·$2CH_3OH$, **5a**, as well as $[Mo_6O_{12}(OCH_3)_{12}Mg_2(CH_3OH)_4]$ (**4b**), and $[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_4(CH_3OH)_4]$ (**5b**) were determined for the first time. It was shown that **3** and **4b** could be conveniently prepared from appropriate "building units" selected on a basis of examinations of their structures from the point of view of retrosynthetic philosophy.

We believe the study presented here contributes to the continuing efforts in the nitrogenase modelling, since the combination of polynuclearity and bimetallic nature of the catalyst (that is exemplified here on the structure of precursors) remains the unique feature of the catalytic protic nitrogen fixing systems, that makes them the most reliable nitrogenase structural and functional models.

Experimental

General techniques

All procedures described below were carried out using standard Schlenk techniques under argon atmosphere. Commercially available $MoCl_5$ (Aldrich), MoO_2Cl_2 (Aldrich) were used without further purification. Methanol solution of $[Na(CH_3OH)Mo_2O_2(OCH_3)_7]$ (**NaMo**) was prepared by vacuum transferring of CH_3OH to a solid sample of **NaMo** which was obtained as described [11]. Solution of $Mg(OCH_3)_2$ was prepared by the reaction of magnesium turnings with methanol. Solution of $NaOCH_3$ was prepared by dissolving of sodium in CH_3OH. Methanol was dried upon boiling with magnesium methoxide followed by distillation and was stored under argon atmosphere. Dimethylformamide (DMF) was distilled twice at reduced pressure. Diethyl ether was dried by distillation over $LiAlH_4$. Dimethoxyethane (DME) (≥ 99.5%, Aldrich) was used as received. DMF, diethyl ether and DME were stored over molecular sieves 4Å under argon atmosphere.

The infrared spectra were measured on solid samples using a Perkin Elmer Spectrum 100 Fourier Transform infrared spectrometer. UV-Vis spectra were recorded using HP 8451A DIODE ARRAY Spectrophotometer. Elemental analyses have been carried out by the Analytical Department service at the Institute of Problems of Chemical Physics RAS. In case of CH_3OH containing compounds (**3**, **4b**) convenient C, H, N analysis gave permanently low results of C content. In these cases Mo and Mg content was measured. Molybdenum content was determined spectrophotometrically in form of thiocyanate complex. Magnesium content was determined by EDTA titration.

Preparations

$[Mo_6O_{12}(OCH_3)_{16}Mg_4(CH_3OH)_6]$ (3). 1.24 ml of a freshly prepared solution of MoO_2Cl_2 in CH_3OH (0.19 M, 0.236 mmol) were placed in a flask equipped with magnetic stirring bar and 0.75 ml of $Mg(OCH_3)_2$ solution in methanol (0.78 M, 0.585 mmol) were added. Immediate precipitation of white solid was observed. Solution was then diluted with 4 ml of methanol. After 30 min of stirring to this slurry 10 ml of **NaMo** in CH_3OH were added ([Mo] = 0.047 M, 0.470 mmol) and resulting mixture was allowed to stir for 2 h. 0.47 ml of H_2O solution in CH_3OH (1M, 0.470 mmol) were then added. At this point the solution turned cloudy and change of colour from red to orange was observed. Following 30 min of stirring, yellow precipitate initially formed was mostly dissolved and mixture was filtered. From this solution orange crystallinic solid precipitated continuously in a course of *ca.* 3 weeks. Precipitate was washed with methanol (5 + 5 ml) and dried in vacuo. Isolated yield: 45÷50% (per Mo^V). (After 2 days of standing the yield was 32 %). IR (cm^{-1}): 2940 w, 2824 w, 1635 w, 1442 w, 1393 w, 1052 s, 1023 vs, 1012 vs, 955 vs, 929 s, 910 s, 880 vs, 749 m, 700 s. UV-Vis [DMF; λ_{max}/nm (ε/M^{-1} cm^{-1})]: 304 (12540), 272 (10350). Calc. for $C_{22}H_{72}O_{34}Mo_6Mg_4$, (%): Mo, 37.1; Mg, 6.3. Found, (%): Mo, 36.7; Mg, 6.0. (For alternative preparative procedure starting from **NaMo** and Mg-Mo^{VI} oxoalkoxide see ref. [18]).

$[Mo_6O_{12}(OCH_3)_{12}Mg_2(CH_3OH)_4]\cdot 2CH_3OH$ (4b). 1.24 ml of a freshly prepared solution of MoO_2Cl_2 in CH_3OH (0.19 M, 0.236 mmol), 0.39 ml of $Mg(OCH_3)_2$ solution in methanol (0.78 M, 0.304 mmol) and 4 ml of CH_3OH were consequently loaded into a flask equipped with magnetic stirring bar. After 30 min of stirring, to a pale-yellow solution obtained 10 ml of **NaMo** in CH_3OH were added ([Mo] = 0.047 M, 0.470 mmol). The resulting mixture was stirred for 2 h. 0.47 ml of H_2O solution in CH_3OH (1M, 0.470 mmol) were then added. Following stirring overnight, 0.06 ml of $Mg(OCH_3)_2$ in methanol (0.78 M, 0.047 mmol) were added and after 30 min of stirring flask was left standing undisturbed for 4 days. Solution was decanted from orange precipitate formed. The latter was washed with methanol (5 + 5 ml) and dried in vacuo. Isolated yield: 51÷56% per Mo^V. IR (cm^{-1}): 2939 w, 2828 w, 1638 m, 1452 w, 1032 s, 1012 s, 993 s, 956 s, 937 vs, 917 s, 898 s, 746 s, 695 s. Calc. for $C_{17}H_{56}O_{29}Mo_6Mg_2$ (corresponds to the loss of 50% of cocrystallized CH_3OH molecules), (%): Mo, 42.7; Mg, 3.6. Found, (%): Mo, 42.7; Mg, 3.9.

$[Mo_6O_{16}(OCH_3)_4Mg_2(DMF)_8]$ (5a). A sample of **4b** (20 mg) was dissolved in 5 ml of DMF + DME + CH_3OH mixture (10:2:1 vol. %) forming orange solution from which orange crystals of **5a** precipitated in a course of 2 weeks in >70% yield. Crystals were washed with DMF (3 + 3 ml) and then DME (3 ml) and dried in vacuo. IR (cm^{-1}): 2932 vw, 2817 vw, 1689 m, 1651 vs, 1503 w, 1435 w, 1384 m, 1254 w, 1110 m, 1054 s, 955 vs, 941 m, 921 m, 892 s, 800 vs, 777 vs, 736 s, 686 m. UV-Vis [CH_3OH; λ_{max}/nm (ε/M^{-1} cm^{-1})]: 306 (13340), 206 (96330). Calc. for $C_{28}H_{68}O_{28}N_8Mo_6Mg_2$, (%): C, 21.15; H, 4.31; N, 7.05. Found, (%): C, 20.90; H, 4.47; N, 6.96.

X-ray crystallographic studies

Data collection for all samples except **4a**·$2CH_3OH$ was performed on a Bruker Apex II diffractometer, for **4a**·$2CH_3OH$ on a Bruker APEX DUO diffractometer (both equipped with CCD detectors, MoKα radiation, graphite monochromator, ω-scans). The frames were integrated using the Bruker SAINT software package [28] using a narrow-frame integration algorithm. A semiempirical absorption correction was applied with the SADABS [29] (TWINABS [30] in the case of **5a**) program using the intensity data of the equivalent reflections.

The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2_{hkl} in the anisotropic–isotropic approximation. The positions of hydrogen atoms, except those of the coordinated methanol moieties, were calculated geometrically and refined in the riding model with $U_{iso} = 1.2U_{eq}$ ($1.5U_{eq}$ for methyl groups) of the connected non-hydrogen atom. All calculations were performed with SHELX software package [31]. Detailed crystallographic information is given in Table 2.

Acknowledgments

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26 To neutralize HCl formed in the reactions of **4b** and **3** formation (eq. 2 and 3, respectively), additional 0.5 equivalents of $Mg(OCH_3)_2$ per Mo^V-Mo^V unit had being taken in the syntheses (see Experimental).

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Facile synthetic strategy based on retrosynthetic philosophy was developed and employed for the preparation of the polynuclear Mo-Mg oxomethoxides - high valence precursors of N_2 fixing catalysts.