

Supporting information for

Tri-, tetra-, and hexanuclear mixed-valence molybdenum clusters: structural study and catalysis of acetylene hydrogenation

Denis A. Kuznetsov,^{*a} Tamara A. Bazhenova,^a Ivan V. Fedyanin,^b Vyacheslav M. Martynenko,^a Alexander F. Shestakov,^a Galina N. Petrova^a and Natal'ya S. Komarova^a

^a Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432, Russian Federation. E-mail: kuz_da@icp.ac.ru

^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 119991, Russian Federation.

Table S1. Crystallographic data for complexes **3-7**.

Complex	3	4	5	6	7
Formula	C ₁₀ H ₃₃ Cl ₃ Mo ₃ O ₁₀	C ₁₂ H ₃₈ Cl ₄ Mo ₄ O ₁₂	C ₁₂ H ₃₉ Cl ₃ Mo ₄ O ₁₃	C ₁₄ H ₄₄ Cl ₂ Mo ₄ O ₁₄	C ₁₂ H ₃₈ Cl ₄ Mo ₆ O ₁₈
Formula weight	707.53	899.98	881.54	891.15	1187.86
T, K	120				
Crystal system	trigonal	triclinic	monoclinic	monoclinic	monoclinic
Space group	R3m	P-1	Pn	P2 ₁ /n	P2 ₁ /n
Z / Z'	3 / 0.33	1 / 0.5	2 / 1	2 / 0.5	2 / 0.5
a, Å	16.8738(12)	8.7762(3)	7.1547(3)	9.6392(4)	12.0042(6)
b, Å	16.8738(12)	8.8015(3)	19.2160(6)	10.3534(4)	9.5495(5)
c, Å	6.7163(5)	9.9874(4)	10.1221(4)	14.8342(7)	14.9585(8)
α, °	90	68.8208(18)	90	90	90
β, °	90	89.0869(19)	104.388(2)	105.179(2)	103.0060(10)
γ, °	120	72.587(2)	90	90	90
V, Å ³	1656.1(3)	682.70(4)	1347.99(9)	1428.78(11)	1670.76(15)
d _{calc} , g cm ⁻³	2.128	2.189	2.172	2.071	2.361
radiation type	MoKα	CuKα	CuKα	CuKα	MoKα
μ, cm ⁻¹	20.82	187.66	181.27	162.97	25.69
2θ _{max} , °	60	144	142	142	60
Refls. collected / independent	7179 / 1181	11018 / 2563	14951 / 4916	25668 / 14868	28885 / 4869
Observed reflections [I > 2σ(I)]	1120	2347	4498	12199	4346
R ₁	0.0183	0.0392	0.0353	0.0759	0.0263
wR ₂	0.0361	0.0979	0.0864	0.2056	0.0681
GOF	0.991	1.023	1.075	1.066	1.061
Residual density, e Å ⁻³ (d _{max} /d _{min})	0.382/-0.370	1.380/-0.756	0.769/-0.654	1.414/-1.477	0.964/-1.401

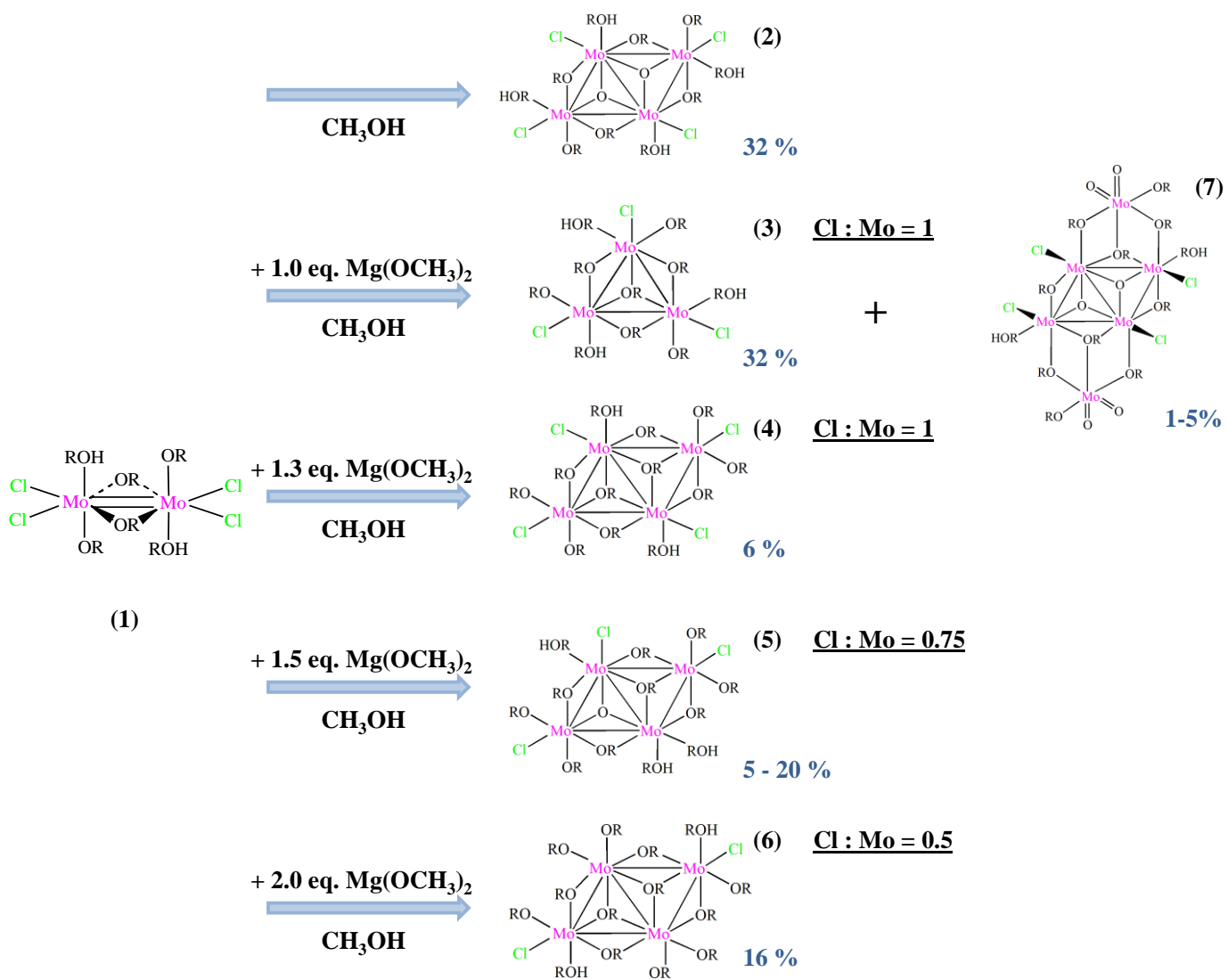
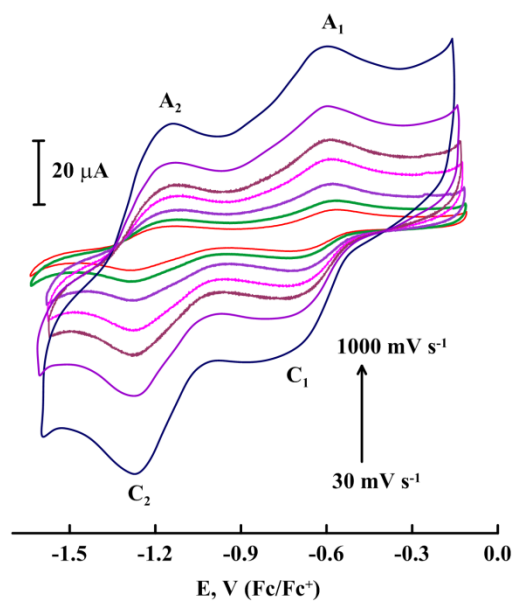
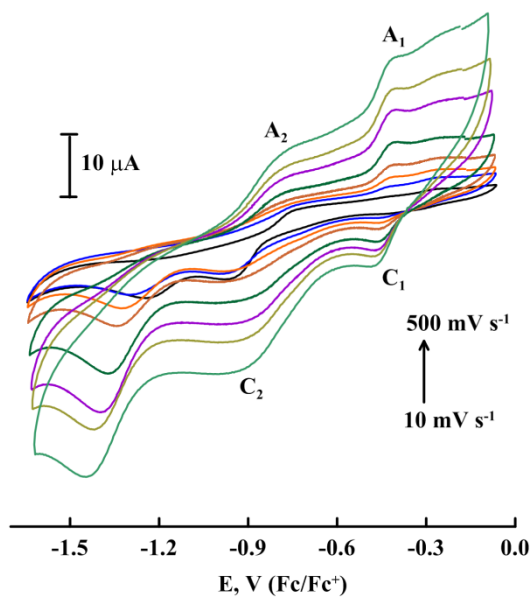


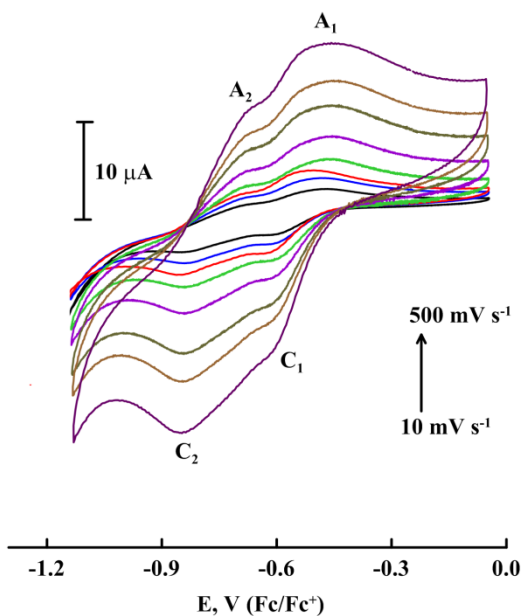
Fig. S1 Scheme illustrating the relationship between complexes 1 – 7.



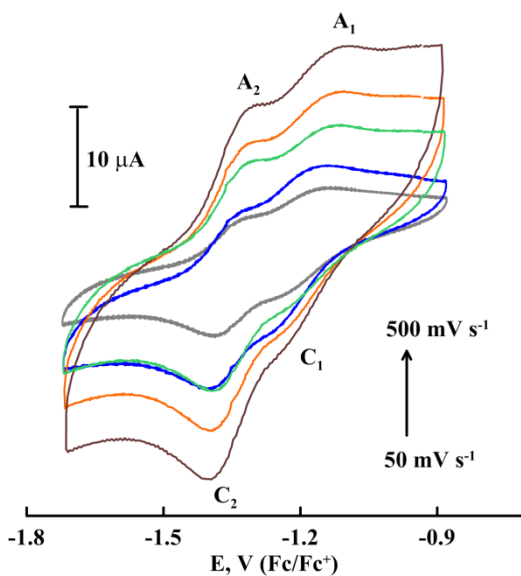
[Mo₄Cl₄O₂(OCH₃)₆(CH₃OH)₄] (2)



[Mo₃Cl₃(OCH₃)₇(CH₃OH)₃] (3)

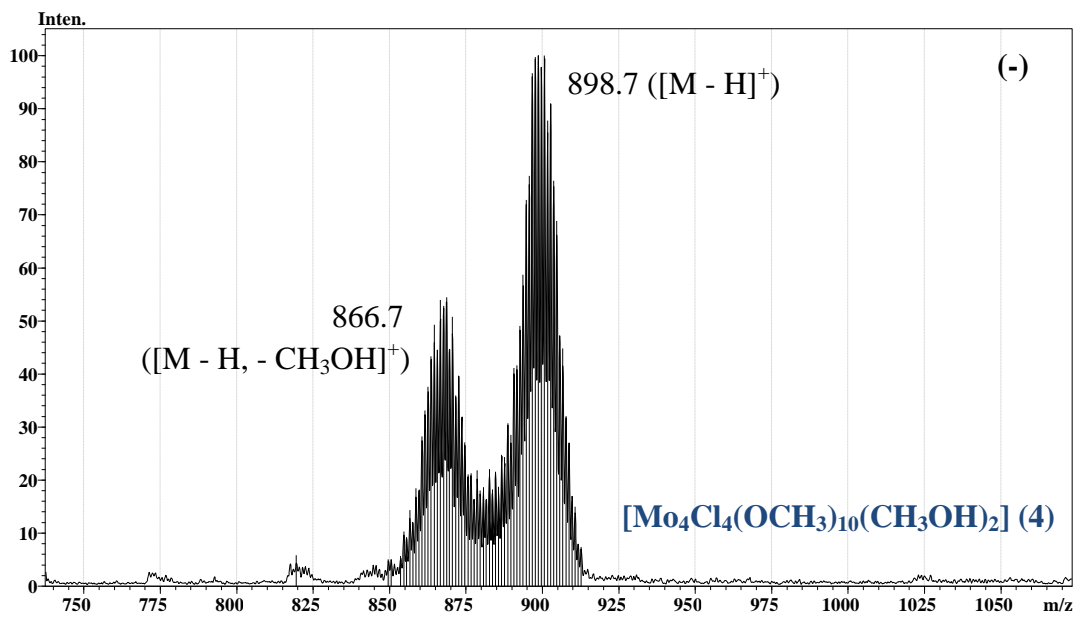
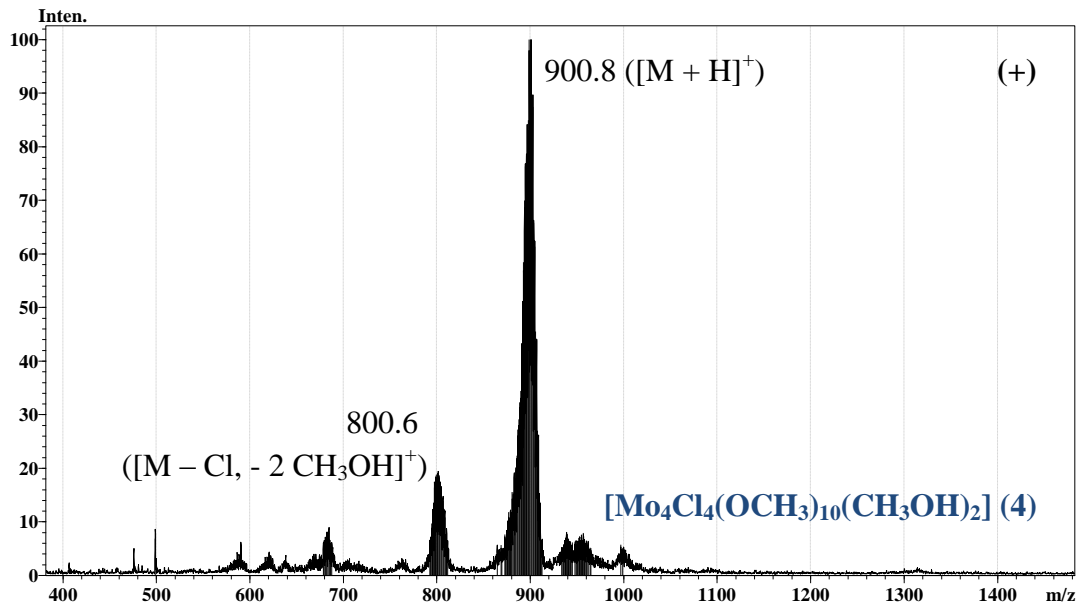
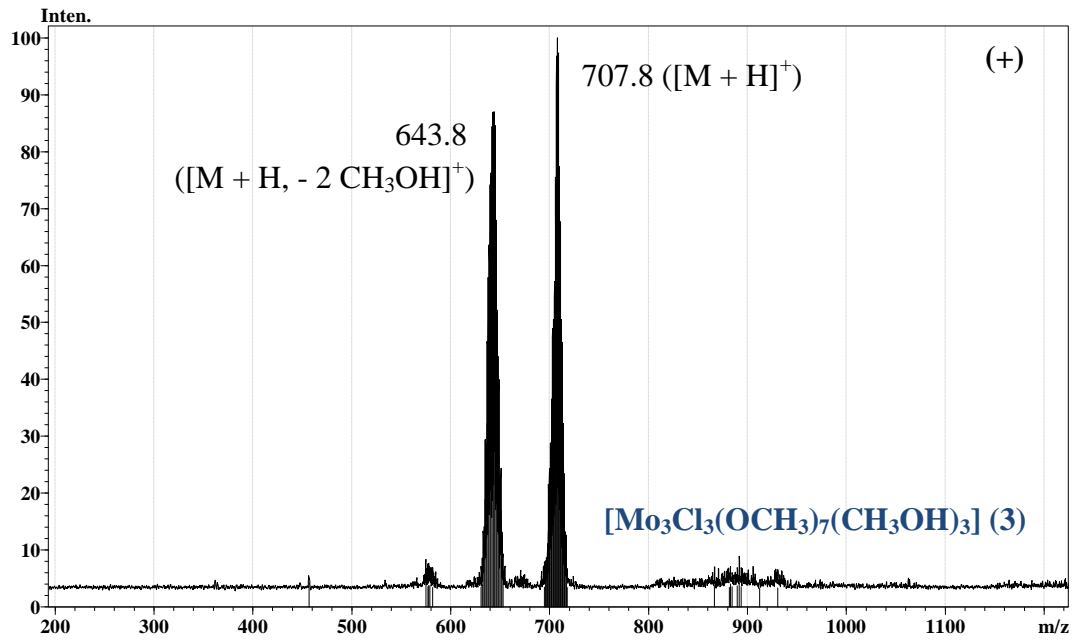


[Mo₄Cl₄(OCH₃)₁₀(CH₃OH)₂] (4)



[Mo₄Cl₂(OCH₃)₁₂(CH₃OH)₂] (6)

Fig. S2 Cyclic voltammograms of the complexes [Mo₄Cl₄O₂(OCH₃)₆(CH₃OH)₄] (2), [Mo₃Cl₃(OCH₃)₇(CH₃OH)₃] (3), [Mo₄Cl₄(OCH₃)₁₀(CH₃OH)₂] (4), [Mo₄Cl₂(OCH₃)₁₂(CH₃OH)₂] (6) in CH₃OH (C(Mo) = 1–6 mM; 0.1 M Bu₄NPF₆) at different scan rates. Data for complex 2 are adapted from ref. [S1] (ref. [9] in the main text).



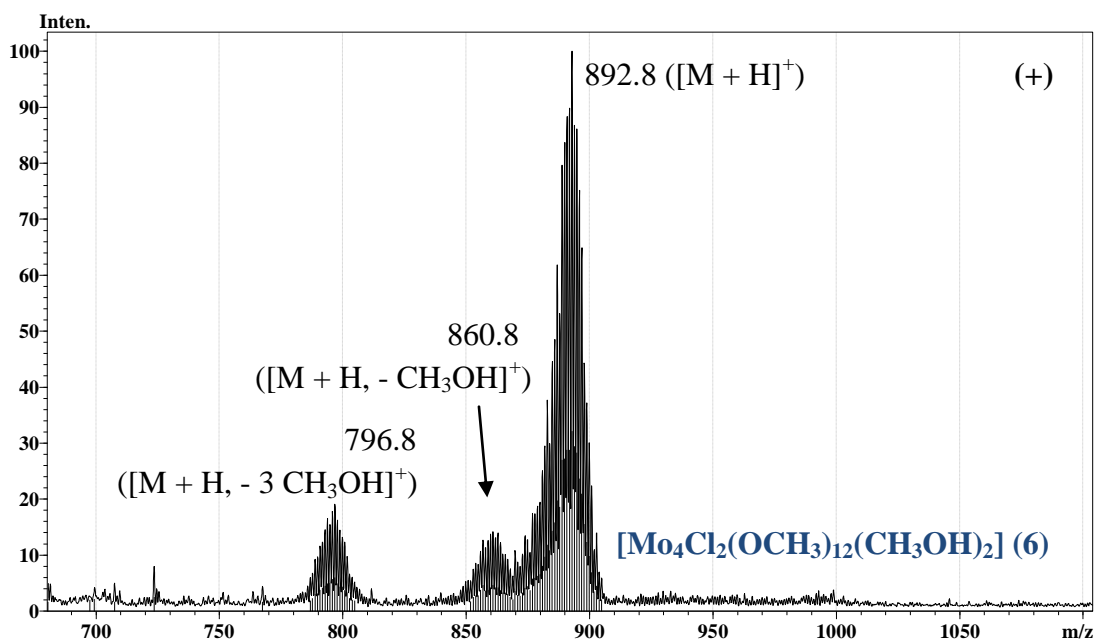
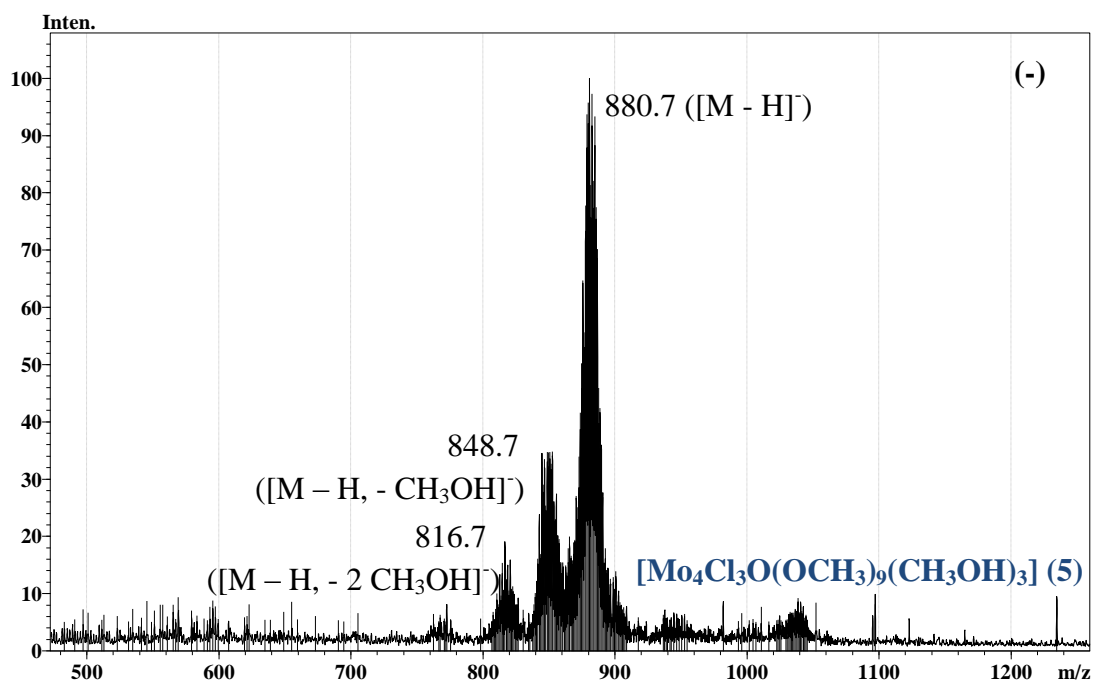


Fig. S3 ESI-MS spectra of the complexes $[Mo_3Cl_3(OCH_3)_7(CH_3OH)_3]$ (3) (toluene + CH_3OH , 2:1 v/v), $[Mo_4Cl_4(OCH_3)_{10}(CH_3OH)_2]$ (4) ($CHCl_3$ + CH_3OH , 1:1 v/v), $[Mo_4Cl_3O(OCH_3)_9(CH_3OH)_3]$ (5) (CH_3OH), $[Mo_4Cl_2(OCH_3)_{12}(CH_3OH)_2]$ (6) (CH_3OH).

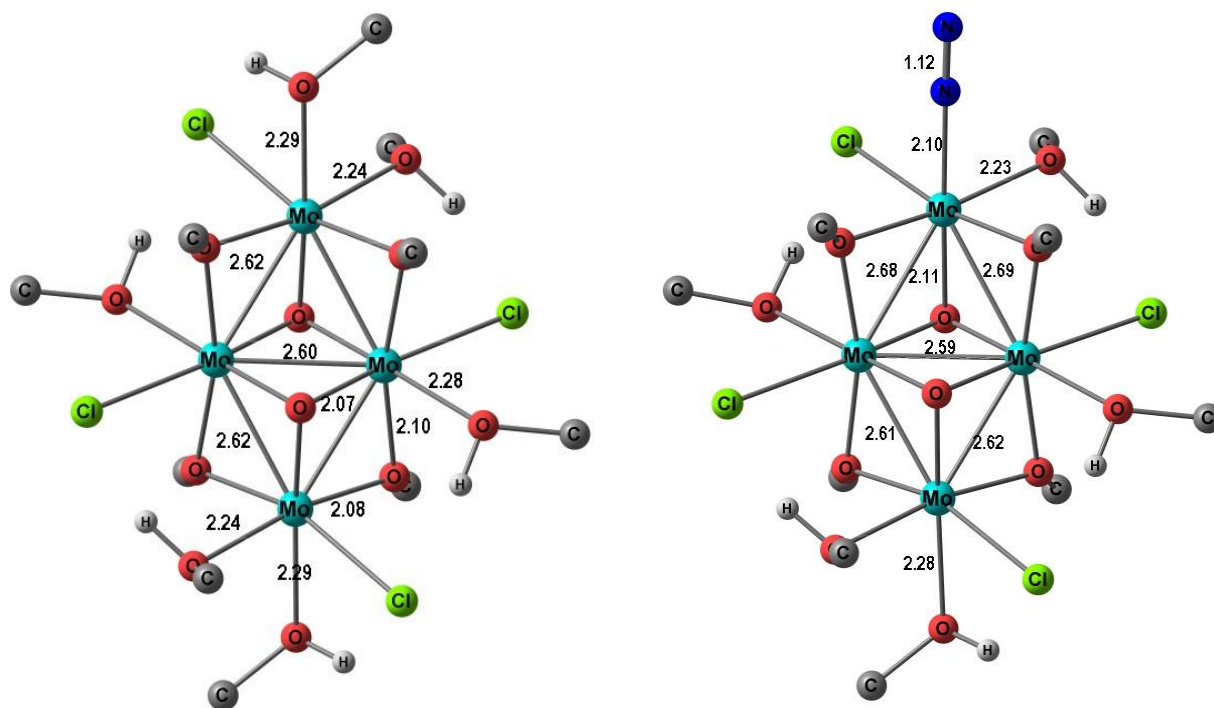


Fig. S4 Molecular structure of $[\text{Mo}^{+3}_4\text{Cl}_4\text{O}_2(\text{OCH}_3)_4(\text{CH}_3\text{OH})_6]$ (**2red**) (left) and $[\text{Mo}^{+3}_4\text{Cl}_4\text{O}_2(\text{OCH}_3)_4(\text{CH}_3\text{OH})_5(\text{N}_2)]$, according to DFT calculations. Hydrogen atoms of methyl groups are not shown. Bond lengths are given in angstroms.

Reaction of **2red** with N_2 is thermodynamically favorable (-12.7 kcal/mol - for the case of substitution of CH_3OH ligand coordinated on an acute angle of $\{\text{Mo}_4\}$ rhombus, -4.7 kcal/mol – for that coordinated on a blunt angle). However, activation of N_2 , upon coordination, is rather weak (only negligible lengthening of $\text{N}\equiv\text{N}$ bond is observed) that correlates with an inability of **2** to catalyze N_2 reduction.

Since the information on protonation state of the methanol/methoxide ligands in complexes under investigation (therefore, Mo oxidation state assignment) could not be extracted purely from the crystallographic data, additional experimental/theoretical data were analyzed. Argumentation supporting the stated assignment is provided below.

Complex 3. Three methanol ligands are protonated, thus molybdenum oxidation states are Mo(+3), Mo(+3), Mo(+4).

This is the only structure, in which direct identification of protonated moiety is not possible due to disorder by symmetry. However, long Mo-O distance is one of the indicators that the group is protonated.

1) High symmetry of the complex **3** in the solid state (C_{3v}) implies that the following formulations of the structure **3** are possible: $[Mo_3Cl_3(OCH_3)_7(CH_3OH)_3]$ (**A**) (3 methoxides are protonated) and $[Mo_3Cl_3(OCH_3)_{10}]$ (**B**) (all methoxides are deprotonated). For the latter structure, electron count gives an odd number of cluster electrons, 5 $[Mo(+4), Mo(+4), Mo(+5)]$, i.e. the complex is paramagnetic. This would result in lowering of the symmetry, since the Mo atoms are no more equivalent, but according to the structural data, Mo atoms in **3** are undistinguishable. Thus, only the formulation $[Mo_3Cl_3(OCH_3)_7(CH_3OH)_3]$ is in agreement with experimental results.

2) Calculations performed on DFT level also predict lowering of the symmetry as well as substantial elongation of the Mo-Mo bond lengths within $\{Mo_3\}$ unit for the structure **B** (2.77 – 2.95 Å).

3) Bands in the region 2800 – 3000 cm^{-1} corresponding to O-H stretching vibrations are observed in the IR spectrum.

4) Despite the fact that the ion multiplets in ESI MS spectrum are broad that does not allow for precise localization of its centre (this m/z value is nearly equal, for a given case, to an average mass), m/z value of 705.5 corresponding to the tentative $[Mo_3Cl_3(OCH_3)_{10}H]^+$ ion is rather rough approximation.

Complex 6. Two methanol ligands are protonated, thus molybdenum oxidation states are Mo(+3), Mo(+3), Mo(+4), Mo(+4), average oxidation state is Mo(+3.5).

1) One of the main evidence for protonation of the O6 atom is the presence of very strong hydrogen bond between O6 and O1 atom. The hydrogen atom is found as a 1 electron peak and can be refined with a reasonable thermal parameter, but was refined in a rigid body approximation due to high adsorption and twinning. Considering the Mo-O distances, see the discussion for complex **4** below.

2) According to redox titration with NH_4VO_3 , the value of an average oxidation state of molybdenum is +3.6.

3) Mo-Mo distances within $\{Mo_4\}$ unit (2.68 - 2.72 Å) are close to those for complex $[Mo_4Cl_4O_2(OCH_3)_6(CH_3OH)_4]$ (2.55 - 2.62 Å) [S1], comprising molybdenum atoms in an average oxidation state +3.5 (slightly larger values are due to different μ_3 -capping ligands for these compounds).

4) Bands in the region 2800 – 3000 cm^{-1} corresponding to O-H stretching vibrations are observed in the IR spectrum.

5) Calculations performed on DFT level predict substantial elongation of the Mo-Mo bond lengths within $\{\text{Mo}_4\}$ unit for the $\{\text{Mo}(+4)\}_4$ complex (all methoxides are deprotonated) compared to experimentally observed ones (2.92 Å for Mo(1)-Mo(2A), 2.94 Å for Mo(2)-Mo(2A) bond; experimentally observed values are 2.72 and 2.68 Å, respectively). The calculated bond lengths for $\{\text{Mo}(+4)\}_4$ complex are expectedly close to those observed for analogous planar tetranuclear tungsten(+4) cluster $[\text{W}_4(\text{OC}_2\text{H}_5)_{16}]$ [S2]: 2.94 ($\{\text{W}_4\}$) vs. 2.92 ($\{\text{Mo}_4\}$) Å for the “long” metal-metal distances, 2.65 ($\{\text{W}_4\}$) vs. 2.71 ($\{\text{Mo}_4\}$) for the “short” contacts.

6) Ionization pattern observed in the positive mode of the ESI MS spectrum points to the presence of the two coordinated methanol ligands as the the quasimolecular ion multiplet $[\text{M} + \text{H}]^+$ is accompanied with the multiplet centered lower by 96 units on a m/z scale $[\text{M} + \text{H}, - 3 \text{CH}_3\text{OH}]^+$ (protonation of one of the methoxides upon ionization gives three methanol ligands per molecule **6**).

Complex 4. Two methanol ligands are protonated, thus molybdenum oxidation states are Mo(+3), Mo(+3), Mo(+4), Mo(+4), average oxidation state is Mo(+3.5).

1) The density peaks of about 0.5 electrons are found close to O1 and O6 atoms, and one of these peaks can be refined as a hydrogen atom with acceptable thermal parameter. This hydrogen atom is involved in very strong hydrogen bond with O1...O6 distance of ca. 2.4 Å, and this is the reason why Mo-O distances are almost equal. It is very typical for quasi-symmetric X-O-H...O-X hydrogen bonds: the stronger the bonds, the closer the O-X distances are (this is also true for other structures in this study: in complex **6** (see above) with comparably strong H-bond, the Mo-O distances are very close, and in other structures where H-bonds are weaker, the Mo-X distances differ more).

2) Mo-Mo bond lengths distribution in **4** is close to that for the complexes $[\text{Mo}_4\text{Cl}_4\text{O}_2(\text{OCH}_3)_6(\text{CH}_3\text{OH})_4]$ (**2**) [S1] and **6** (see discussion above), Mo-Mo distances within $\{\text{Mo}_4\}$ unit are 2.68 - 2.70 Å for **4** (for comparison: 2.55 - 2.62 Å for **2**, 2.68 - 2.72 Å for **6**).

3) Bands in the region 2800 – 3000 cm^{-1} corresponding to O-H stretching vibrations are observed in the IR spectrum.

4) Calculations performed on DFT level predict substantial elongation of the Mo-Mo bond lengths within $\{\text{Mo}_4\}$ unit for the $\{\text{Mo}(+4)\}_4$ complex **4** (all methoxides are deprotonated) compared to experimentally observed ones (2.99 vs. 2.70 Å for Mo(1)-Mo(2A), 2.85 vs. 2.68 Å for Mo(2)-Mo(2A) bond).

5) Ionization patterns observed in the negative mode of the ESI MS spectrum of **4** points to the presence of the coordinated methanol ligands as the the quasimolecular ion multiplet $[\text{M} - \text{H}]^-$ is accompanied with the multiplet centered lower by 32 ($[\text{M} - \text{H}, - \text{CH}_3\text{OH}]^-$) units on a m/z scale. Such an ionization pattern implies the loss of O-H hydrogen following detachment of the remaining methanol ligand.

Complex 5. Three methanol ligands are protonated, thus molybdenum oxidation states are Mo(+3), Mo(+3), Mo(+4), Mo(+4), average oxidation state is Mo(+3.5).

1) Again, the presence of relatively strong hydrogen bonds is a solid evidence for protonation of oxygen atoms. In this case, the peaks were found from difference Fourier synthesis near O6 and O12 atoms, and their position is in line with the presence of H-bonding. In this complex, the hydrogen bond is weaker than in complexes **4** and **6**, and the distances Mo-O for protonated and deprotonated moieties differ more.

2) Mo-Mo bond lengths distribution in **5** is close to that for the complexes $[\text{Mo}_4\text{Cl}_4\text{O}_2(\text{OCH}_3)_6(\text{CH}_3\text{OH})_4]$ (**2**) [S1], **4** and **6** (see discussion above), Mo-Mo distances within $\{\text{Mo}_4\}$ unit are 2.59 - 2.68 Å for **5** (for comparison: 2.55 - 2.62 Å for **2**, 2.68 - 2.70 Å for **4**, 2.68 - 2.72 Å for **6**).

3) Bands in the region 2800 – 3000 cm^{-1} corresponding to O-H stretching vibrations are observed in the IR spectrum.

4) Ionization patterns observed in the negative mode of the ESI MS spectrum of **5** points to the presence of the coordinated methanol ligands as the the quasimolecular ion multiplet $[\text{M} - \text{H}]^-$ is accompanied with the multiplets centered lower by 32 ($[\text{M} - \text{H}, - \text{CH}_3\text{OH}]^-$) and 64 ($[\text{M} - \text{H}, - 2 \text{CH}_3\text{OH}]^-$) units on a m/z scale. Such an ionization pattern implies the loss of O-H hydrogen following detachment of the remaining methanol ligands.

Complex 7. Two methanol ligands are protonated. Tentative assignment of molybdenum oxidation states are Mo(+3), Mo(+3), Mo(+4), Mo(+4), Mo(+6), Mo(+6).

Apart from the crystallographic evidence, the given oxidation states assignment is also supported by the analysis of the ligand environment of the molybdenum atoms. Mo(3) is clearly Mo(+6): presence of two cis oxo-groups is characteristic for this oxidation state, moreover, if we remove the corresponding $[\text{MoO}_2(\text{OCH}_3)]^+$ moiety from the structure, dianionic tetranuclear fragment is obtained whose structural parameters are virtually identical to those observed for the complex **2** (2.55 – 2.62 Å for **2**, 2.57 – 2.64 Å for **7**). Assignment of the oxidation states within the $\{\text{Mo}_4\}$ unit (the average oxidation state is +3.5) is analogous to that for the complex **2**.

Table S2. Comparison of the metal-metal bond lengths distribution within complexes **4-6** with available data for planar tetranuclear tungsten and molybdenum clusters comprising metals in different average oxidation states.

Complex	Metal-metal bond lengths within {M ₄ } cluster (edge bonds/diagonal bond), Å	Reference
4	2.69 – 2.70 / 2.68	This work
5	2.63 – 2.68 / 2.59	This work
6	2.68 – 2.72 / 2.68	This work
[Mo ^{+3.5} ₄ Cl ₄ O ₂ (OCH ₃) ₆ (CH ₃ OH) ₄]	2.60 – 2.62 / 2.55	[S1]
[W ⁺⁴ ₄ (OC ₂ H ₅) ₁₆]	2.65 (“short” bond), 2.94 (“long” bond) / 2.76	[S2]
[W ⁺³ ₄ (O- <i>i</i> -C ₃ H ₇) ₁₂]	2.50 (“short” bond), 2.73 (“long” bond) / 2.81	[S3]

References

- [S1] D. A. Kuznetsov, I. V. Fedyanin, N. S. Komarova, G. V. Shilov, V. M. Martynenko, S. G. Vasil’ev, A. G. Krivenko, K. A. Lyssenko and T. A. Bazhenova, *Eur. J. Inorg. Chem.*, 2015, 715-724.
- [S2] (a) M. H. Chisholm, J. C. Huffman and J. Leonelli, *J. Chem. Soc., Chem. Commun.*, 1981, 270; (b) M. H. Chisholm, J. C. Huffman C. C. Kirkpatrick, J. Leonelli and K. Folting, *J. Am. Chem. Soc.*, 1981, **103**, 6093-6099.
- [S3] (a) M. H. Chisholm, D. L. Clark, K. Folting and J. C. Huffman, *Angew. Chem., Int. Ed.*, 1986, **25**, 1014-1015; (b) M. H. Chisholm, D. L. Clark, K. Folting, J. C. Huffman and M. Hampden-Smith, *J. Am. Chem. Soc.*, 1987, **109**, 7750-7761.