

# Polymerization of Mo<sup>V</sup>: Synthesis and Characterization of a Dinuclear Mo<sup>V</sup> and a Hexanuclear Mixed-Valence Mo<sup>V</sup>/Mo<sup>VI</sup> Complex<sup>[‡]</sup>

Marc D. Meienberger,<sup>[a]</sup> Bernd Morgenstern,<sup>[b]</sup> Stefan Stucky,<sup>[b]</sup> and  
Kaspar Hegetschweiler\*<sup>[b]</sup>

**Keywords:** Molybdenum / Oxidation / O ligands / Tripodal ligands / Mixed-valence compounds

1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci = L) reacts with MoCl<sub>5</sub> in a mixture of MeOH/water at 80 °C to yield the pale purple *syn*-[Mo<sub>2</sub>O<sub>4</sub>H(L)<sub>2</sub>]Cl<sub>3</sub>·14.5H<sub>2</sub>O (1Cl<sub>3</sub>·14.5H<sub>2</sub>O). Crystal data: space group *P*<sub>2</sub><sub>1</sub>/*n*, *a* = 8.797(2) Å, *b* = 25.439(5) Å, *c* = 23.077(5) Å, β = 90.44(3)°, *V* = 5164(2) Å<sup>3</sup>, *Z* = 4 for C<sub>24</sub>H<sub>84</sub>Cl<sub>3</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>24.5</sub>. In solutions of the dinuclear 1<sup>3+</sup>, which were exposed to air for several weeks, slow formation of deep red crystals containing a novel, hexanuclear, mixed-valence complex of composition [Mo<sub>4</sub>O<sub>8</sub>(L)<sub>2</sub>(MoO<sub>4</sub>)<sub>2</sub>]·27H<sub>2</sub>O (2·27H<sub>2</sub>O) was observed. The tetranuclear core of complex 2 was unambiguously identified by MS-FAB spectrometry, and the entire structure was char-

acterized by a crystal-structure analysis: space group *P*<sub>2</sub><sub>1</sub>/*c*, *a* = 12.224(2) Å, *b* = 15.986(3) Å, *c* = 14.220(3) Å, β = 98.95(3)°, and *V* = 2744.9(9) Å<sup>3</sup>, *Z* = 2 for C<sub>24</sub>H<sub>109</sub>Mo<sub>6</sub>N<sub>6</sub>O<sub>49.5</sub>. The structure of the hexanuclear mixed-valence complex 2 contains the well-known [Mo<sub>4</sub>O<sub>8</sub>]<sup>4+</sup> core in which two of the four Mo<sup>V</sup> centers bond to Mo<sup>VI</sup>O<sub>4</sub> units by corner sharing. The remaining two Mo<sup>V</sup> centers are each chelated by a tdci ligand. Cyclic voltammetry confirmed an irreversible reduction and oxidation of 1<sup>3+</sup> at a potential of about -1.15 V and +0.54 V vs. NHE, respectively.

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## Introduction

Polynuclear oxido complexes of the early-transition elements attracted considerable interest due to their unique structural properties and reactivity<sup>[1]</sup> and interesting applications in catalysis, materials science, and medicine.<sup>[2]</sup> Anionic representatives, the so-called polyoxometalates (POMs), have been particularly well investigated, whereas the chemistry of neutral or cationic species is somewhat less developed. In view of their electronic structure, spectroscopic properties and redox behavior, mixed-valence derivatives constitute an especially fascinating class of compounds.<sup>[3,4]</sup> As an example, the so-called molybdenum blue, a polynuclear Mo<sup>V</sup>/Mo<sup>VI</sup> complex, has attracted chemists for more than 100 years, but its structure has been elucidated just recently.<sup>[5]</sup> Papers reporting on the determination of the crystal structure of mixed-valence Mo<sup>V</sup>/Mo<sup>VI</sup> tetramers have been published in 1973 and in 1983;<sup>[6,7]</sup> however, it has been shown later that they proved to be isovalent Mo<sup>V</sup> complexes.<sup>[8]</sup> Preparation and structural characteriza-

tion of the first true mixed-valence Mo<sup>V</sup>/Mo<sup>VI</sup> derivative has been reported by Chisholm et al. in 1982.<sup>[9]</sup> Since then, a variety of discrete examples have been described.<sup>[10–20]</sup> In addition, polymers consisting of [Mo<sup>V</sup><sub>2</sub>O<sub>4</sub>]<sup>2+</sup> units and [MoO<sub>4</sub>]<sup>2-</sup> bridges are also known.<sup>[21]</sup>

Mixed-valence Mo<sup>V</sup>/Mo<sup>VI</sup> species can either be obtained by partial reduction<sup>[10,11,14,16,17,21]</sup> or partial oxidation<sup>[18]</sup> of isovalent Mo<sup>VI</sup> or Mo<sup>V</sup> precursors, respectively. However, in a variety of preparative attempts, the two types of processes, i.e. the polymerization reaction and the redox process, have been found to occur in combination. The polymerization reaction, which starts from mononuclear Mo<sup>V</sup>, yielding dinuclear species of the [Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup> core which assemble to tetranuclear complexes and further to aggregates of even higher nuclearity, is well known.<sup>[22–30]</sup> Even the formation of very large clusters, still containing the basic [Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup> unit as building block,<sup>[17]</sup> has been observed. Modéc and Brencic stated in their review on [Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup> aggregation that “traces of water have been found to severely change the reaction course, leading to mixed-valence, Mo<sup>V</sup>/Mo<sup>VI</sup> clusters. The sensitivity towards water makes the reactions irreproducible and difficult to control”.<sup>[24]</sup> We found in our laboratory that, in the presence of the tripodal triol 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci, see Scheme 1), Mo<sup>V</sup> reacts in a MeOH/H<sub>2</sub>O medium to yield a cationic [Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup> species, and this dimeric species further reacts to afford an uncharged, well defined, hexanuclear mixed-valence complex. In this paper, we will report on the molecular structures of the two complexes, which

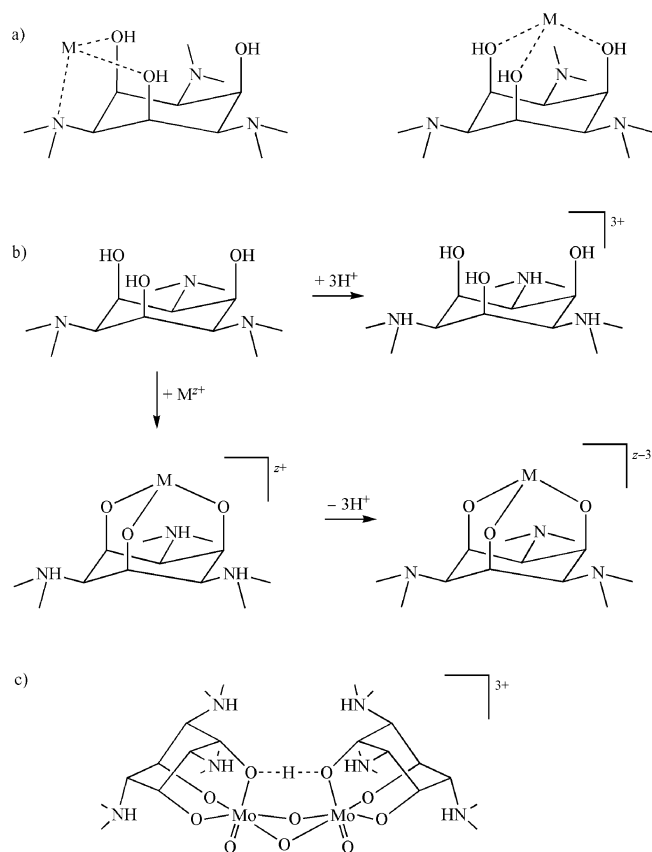
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[a] ETH Zürich,  
8092 Zürich, Switzerland

[b] Anorganische Chemie, Universität des Saarlandes,  
Postfach 15 11 50, 66041 Saarbrücken, Germany  
Fax: +49-681-302-2663  
E-mail: hegetschweiler@mx.uni-saarland.de

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have been determined by single-crystal X-ray diffraction. In addition, a CV study on the  $[\text{Mo}_2\text{O}_4]^{2+}$  complex, which sheds some light on possible redox processes of this species, will be presented.



Scheme 1.

## Results and Discussion

### Synthesis and Structure of the Dinuclear Complex

The reaction of  $\text{MoCl}_5$  with a slight excess of tdc in  $\text{MeOH}/\text{H}_2\text{O}$  resulted in the formation of the dinuclear complex  $[\text{Mo}_2\text{O}_4(\text{tdci})(\text{Htdci})]^{3+}$  ( $\mathbf{1}^{3+}$ ). The complex crystallized from a  $\text{H}_2\text{O}/\text{acetone}$  mixture as a strongly hydrated trichloride salt. The resulting crystals were of sufficient quality to perform a single-crystal structure analysis (Figure 1). The cation of  $\mathbf{1}^{3+}$  contains the well-known  $\text{Mo}^{\text{V}}$  dimer with two  $\text{Mo}^{\text{V}}=\text{O}$  units that form a  $\text{Mo}-\text{Mo}$  single bond, and two  $\mu\text{-O}_{\text{oxo}}$  bridges. The tridentate tdc ligand coordinates in a tripodal fashion through the three oxygen donors, one of them in the *trans* and two of them in the *cis* position with respect to the terminal  $\text{O}_{\text{oxo}}$  ligand. Although not crystallographically imposed, the symmetry of  $\mathbf{1}^{3+}$  is  $C_{2v}$ , within significance. Both, the *syn* and *anti* orientations of the two  $\text{Mo}=\text{O}$  entities are known for such  $(\text{LMoO})(\mu_2\text{-O})_2(\text{LMoO})$  complexes.<sup>[31]</sup> However, the *syn* isomer is in general more stable and, in agreement with these findings, complex  $\mathbf{1}^{3+}$  contains a *syn*- $[(\text{MoO})_2(\mu_2\text{-O})_2]^{2+}$  structure. In agreement

with previous reports, the four-membered  $\text{Mo}_2\text{O}_2$  ring exhibits significant puckering as shown by the dihedral angle ("fold angle") between the two  $\mu_2\text{O}-\text{Mo}-\mu_2\text{O}$  planes of  $159.5^\circ$ . This value is, however, significantly larger than expected<sup>[24,28]</sup> and corresponds more closely to those found for derivatives with an additional carboxylato bridge spanning the two positions *trans* to  $\text{O}_{\text{oxo}}$  in a  $\text{Mo}-\text{O}-\text{C}(\text{R})-\text{O}-\text{Mo}$  arrangement.<sup>[32]</sup>

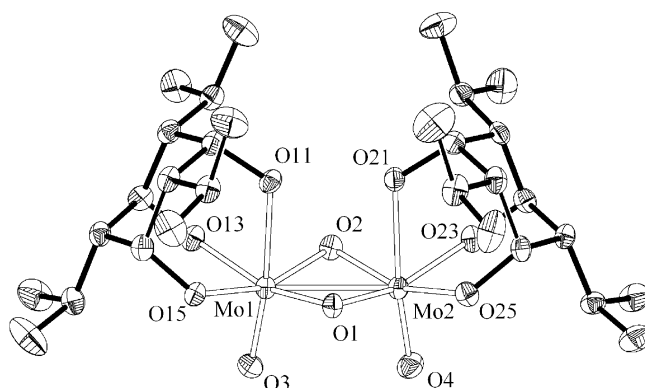


Figure 1. Molecular structure of *syn*- $[\text{Mo}_2\text{O}_4(\text{HL})(\text{L})]^{3+}$  ( $\mathbf{1}^{3+}$ ); the atomic displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity; only the labeling scheme of the inorganic core is shown. Selected bond lengths [Å] and angles [°]:  $\text{Mo1}-\text{Mo2}$  2.625(1),  $\text{Mo1}-\text{O1}$  1.945(4),  $\text{Mo1}-\text{O2}$  1.961(4),  $\text{Mo1}-\text{O11}$  2.311(4),  $\text{Mo1}-\text{O13}$  2.045(4),  $\text{Mo1}-\text{O15}$  2.079(4),  $\text{Mo1}-\text{O3}$  1.701(4),  $\text{Mo2}-\text{O1}$  1.952(4),  $\text{Mo2}-\text{O2}$  1.960(4),  $\text{Mo2}-\text{O21}$  2.329(4),  $\text{Mo2}-\text{O23}$  2.048(4),  $\text{Mo2}-\text{O25}$  2.045(4),  $\text{Mo2}-\text{O4}$  1.698(4),  $\text{O11}-\text{Mo1}-\text{O3}$  172.1(2),  $\text{Mo1}-\text{O1}-\text{Mo2}$  84.7(2),  $\text{Mo1}-\text{O2}-\text{Mo2}$  84.1(2),  $\text{O21}-\text{Mo2}-\text{O4}$  173.4(2).

The tdc ligand is known to offer two different types of metal binding sites: a triaxial *O,O,O* and an axial-equatorial-axial *O,N,O* mode (Scheme 1a).<sup>[33–39]</sup> Coordination through the three axial oxygen donors has been observed for hard, highly charged metal cations such as  $\text{Fe}^{\text{III}}$ ,<sup>[33]</sup>  $\text{Al}^{\text{III}}$ ,<sup>[33]</sup>  $\text{V}^{\text{IV}}$ ,<sup>[39]</sup> and  $\text{Ta}^{\text{V}}$ ,<sup>[35]</sup> whereas side-on-coordination through the *O,N,O* site has been found for  $[(\text{Mo}^{\text{IV}}\text{-tdci})_3\text{S}_4]^{4+}$ ,  $[(\text{Mo}\text{-tdci})_3\text{S}_4\text{CuBr}]^{3+}$ , and in a trinuclear  $\text{Pb}^{\text{II}}$  complex.<sup>[34,36]</sup> In terms of Pearson's HSAB concept, the  $\text{Pb}^{\text{II}}$  as well as  $\text{Mo}^{\text{IV}}$  centers of the thio complexes are relatively soft, whereas the  $\text{Mo}^{\text{V}}$  centers of the oxido species  $\mathbf{1}^{3+}$  should be considered to be somewhat harder. This difference is nicely reflected in the different coordination modes of tdc observed in these complexes.

A peculiar property of tdc is the ability of the non-coordinating dimethylamino groups to act as internal bases,<sup>[37]</sup> deprotonating the coordinating hydroxy groups and thus generating a zwitterionic form of the ligand within a complex (Scheme 1b). Moreover, the resulting ammonium groups may act as a reservoir of weakly acidic protons. Their deprotonation would lead to an anionic form of the ligand. On the other hand, protonation of a coordinated alkoxo group of the zwitterionic form is also possible. This would then generate a cationic form of tdc. The possibility of tdc to coordinate in all these various forms is certainly

a particularly fascinating aspect, since it allows alteration of the overall charge over a wide range (Scheme 1b).<sup>[35,38,39]</sup> However, because of this flexibility, it is often difficult to ascertain unambiguously the overall charge of the resulting complexes. This problem can be particularly troublesome, because it is sometimes difficult to locate the positions of the hydrogen atoms by X-ray diffraction experiments. In the structure presented here, the overall charge of  $1^{3+}$  clearly follows from a charge-balance consideration (the Mo/Cl ratio, which has been determined by elemental analysis, is exactly 2:3, see Experimental Section). On the basis of an analysis of the bond lengths (Table 1) with values of 2.625(1) Å for the Mo–Mo single bond, 1.698(4), 1.701(4) Å for the Mo=O<sub>oxo</sub> double bonds, and 1.945(4)–1.961(4) Å for μO–Mo bridges, the +5 state is the only chemically sensible oxidation number for the two Mo centers in this complex.<sup>[22–28]</sup> Consequently, one of the tdc ligands must bear a positive charge. Inspection of the Mo–O bond lengths for the two tdc ligands revealed values of 2.045(4)–2.079(4) Å (mean: 2.054 Å) for the four tdc oxygen donors in the *cis* position of O<sub>oxo</sub>. For the oxygen donors in the *trans* position, M–O distances are, however, 2.329(4) and 2.311(4) Å. These values are too large for a Mo<sup>V</sup>–O<sub>alkoxo</sub> bond, even if a considerable *trans* influence of the terminal O<sub>oxo</sub> ligand is taken into account.<sup>[8,28]</sup> The elongation of these Mo–O bonds becomes, however, understandable, if protonation of the alkoxo groups is proposed. We were not able to locate any proton in the proximity of the *trans*-O<sub>tdci</sub> atoms. However, the observations that (i) the O(11)–Mo(1)–Mo(2)–O(21) torsional angle of 1.9° indicates an almost ideal eclipsed orientation of the two Mo–O<sub>trans</sub> bonds, (ii) the *trans*-O<sub>tdci</sub>–Mo–Mo angle of 88° is smaller than 90°, thus indicating some attraction between the two *trans*-O<sub>tdci</sub> atoms and (iii) the *trans*-O<sub>tdci</sub>...*trans*-O<sub>tdci</sub> distance of 2.460 Å is *very* short, are all in support of a probably symmetric O<sub>tdci</sub>...H...O<sub>tdci</sub> hydrogen-bonding system. The entire protonation scheme of  $1^{3+}$  is summarized in Scheme 1c; it comprises a zwitterionic form of the two tdc systems with a total of six protons, located at the dimethylammonium groups, four deprotonated alkoxo groups in the *cis* position of the two MoO<sub>oxo</sub> groups, and one mononegative RO...H...OR group.

Table 1. Summary of Mo–O bond lengths [Å] in  $1^{3+}$  and **2**.

	<b>2</b>	$1^{3+}$
O <sub>oxo</sub> –Mo <sup>V</sup>	1.697, <sup>[a]</sup> 1.701 <sup>[b]</sup>	1.698, <sup>[c]</sup> 1.701 <sup>[c]</sup>
μ <sub>2</sub> O <sub>oxo</sub> –Mo <sup>V</sup>	1.918, <sup>[b]</sup> 1.973 <sup>[d]</sup>	
μ <sub>3</sub> O <sub>oxo</sub> –Mo <sup>V</sup>	2.009, <sup>[e]</sup> 2.031, <sup>[d]</sup> 2.192 <sup>[f]</sup>	
O <sub>alkoxo</sub> –Mo <sup>V</sup>	2.025, <sup>[a]</sup> 2.097 <sup>[g]</sup>	2.045–2.079 <sup>[g,h]</sup>
μ <sub>2</sub> O <sub>alkoxo</sub> –Mo <sup>V</sup>	2.188, <sup>[g]</sup> 2.244 <sup>[f]</sup>	
H <sub>0.5</sub> O <sub>tdci</sub> –Mo <sup>V</sup>		2.311, <sup>[f]</sup> 2.329 <sup>[f]</sup>
Mo <sup>V</sup> –μ <sub>2</sub> OMo <sup>VI</sup>	2.063	
Mo <sup>V</sup> μ <sub>2</sub> O–Mo <sup>VI</sup>	1.877	
Mo <sup>VI</sup> –O <sub>oxo</sub>	1.707–1.745	

[a] *trans* to μ<sub>3</sub>O<sub>oxo</sub> [b] *trans* to μ<sub>2</sub>O<sub>alkoxo</sub> [c] *trans* to H<sub>0.5</sub>O<sub>tdci</sub> [d] *trans* to O<sub>alkoxo</sub> [e] *trans* to OMo<sup>VI</sup>O<sub>3</sub> [f] *trans* to O<sub>oxo</sub> [g] *trans* to μ<sub>2</sub>O<sub>oxo</sub> [h] Mean value: 2.054.

## Spectroscopy and Electrochemistry of the Dinuclear Complex

**1**Cl<sub>3</sub> exhibited a UV/Vis spectrum in aqueous solution, typical for a *syn*-(LMoO)(μ<sub>2</sub>-O)<sub>2</sub>(LMoO) complex, showing a charge-transfer band at λ<sub>max</sub> = 325 nm (ε = 6 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>). In comparison with corresponding tridentate N-donors [L = 1,4,7-triazacyclononane: λ<sub>max</sub> = 284 nm, ε = 7 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>; L = 1,5,9-triazacyclododecane: λ<sub>max</sub> = 299 nm (ε = 5 × 10<sup>3</sup> L mol<sup>-1</sup> cm<sup>-1</sup>)],<sup>[31]</sup> the band of complex  $1^{3+}$  with its tridentate oxygen donor tdc is displaced to a slightly longer wavelength. Corresponding species with an *anti*-[Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup> core exhibited an additional characteristic band in the range 520–550 nm (300 < ε < 600 L mol<sup>-1</sup> cm<sup>-1</sup>). In accordance with the *syn*-configuration, assigned from the crystal structure analysis, such a band has not been observed in the spectrum of  $1^{3+}$ . Also the IR spectroscopic characteristics of **1**Cl<sub>3</sub> with strong absorptions at 963 cm<sup>-1</sup> (Mo=O<sub>i</sub>) and 730 cm<sup>-1</sup> (Mo–O<sub>b</sub>) are indicative of the *syn*-(LMoO)(μ<sub>2</sub>-O)<sub>2</sub>(LMoO) structure.<sup>[27,28]</sup>

FAB mass spectrometry in the positive-ion mode proved to be a rather efficient tool to characterize the complexes formed (Figure 2). Due to the multi-isotope nature of naturally occurring molybdenum, the Mo-containing species displayed a characteristic isotope distribution pattern, which helps significantly in the identification of mononuclear, dinuclear and tetranuclear species (Figure 2b). Moreover, the fragmentation pattern displayed in the spectrum reflects processes in the matrix rather than in the gas phase, and consequently, an analysis of the fragmentation products provides valuable information about possible high-energy solution reactions. In the FAB<sup>+</sup> mass spectrum of **1**Cl<sub>3</sub>, a series of mononuclear and dinuclear species could be identified in the range 350 < *m/z* < 500 and 700 < *m/z* < 800, respectively. The signal with the most intense line at 777 corresponds to the pseudomolecular ion [Mo<sub>2</sub>O<sub>4</sub>(tdci)<sub>2</sub>-H]<sup>+</sup>, in which one of the tdc ligands is present as an anion. This species eliminates two molecules of H<sub>2</sub>O, as indicated by the peaks with *m/z* at 759 and 741. A third elimination yields an additional peak at *m/z* = 724. The resulting difference of Δ*m/z* = 17 indicated, however, elimination of OH<sup>-</sup> rather than H<sub>2</sub>O. In terms of the relevant reaction in the matrix, we interpret this elimination as a two-step process, comprising an elimination of OH<sup>-</sup> and a reduction of Mo<sup>V</sup> to Mo<sup>IV</sup>. It is well known that, under FAB conditions, the glycerol matrix can act as a strong reducing agent.<sup>[40]</sup> The observed fragmentation pattern is well understandable if one considers that the parent [Mo<sub>2</sub>O<sub>4</sub>(tdci)<sub>2</sub>-H]<sup>+</sup> species still contains a total of five weakly acidic protons (Scheme 1). Two of them, together with either a bridging or terminal O<sub>oxo</sub> ligand, constitute one H<sub>2</sub>O entity. However, after the second H<sub>2</sub>O elimination, the above-mentioned reservoir contains only one single proton, and the final elimination of OH<sup>-</sup>, followed by a reduction of one of the Mo<sup>V</sup> centers, results in the formation of the completely deprotonated, mixed-valence [(H<sub>3</sub>-tdci)-Mo<sup>V</sup>-O-Mo<sup>IV</sup>(H<sub>3</sub>-tdci)]<sup>+</sup>. We tentatively assign a μ<sub>2</sub>-O structure for this final product of this process.

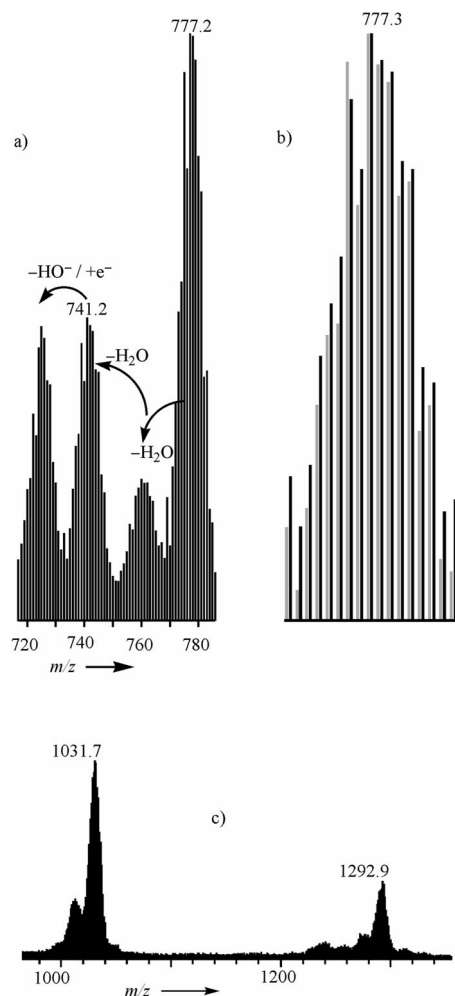


Figure 2. FAB<sup>+</sup>-mass spectra of  $1\text{Cl}_3 \cdot 12.5\text{H}_2\text{O}$  and  $2 \cdot \sim 27\text{H}_2\text{O}$ . (a) Section of the spectrum of  $1\text{Cl}_3 \cdot 12.5\text{H}_2\text{O}$ . (b) Observed (black) and calculated (gray) isotope distribution for the pseudo-molecular-ion  $[\text{Mo}_2\text{O}_4(\text{tdci})_2\text{H}]^+$ . (c) Section of the spectrum of  $2 \cdot \sim 27\text{H}_2\text{O}$ .

The formation of a mixed-valence  $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{IV}}$  complex as observed in the FAB-MS spectrum induced us to study the redox properties of  $1^{3+}$  by means of cyclic voltammetric measurements in aqueous solution. CV measurements were performed at pH 9 (Figure 3). Reduction of  $1^{3+}$  occurred at a strongly negative potential, and a hanging-drop Hg working electrode was therefore used to avoid evolution of  $\text{H}_2$ . CV measurements revealed irreversible redox behavior with a single reduction wave at about  $-1.15\text{ V}$  (vs. NHE) and at least three oxidation waves at  $-0.95$ ,  $-0.85$ , and  $-0.55\text{ V}$  (Figure 3a). The peak current of the reduction wave depended linearly on the square root of the scan rate, thus indicating a diffusion-controlled reaction. In analogy to similar observations for  $[\text{Mo}_2\text{O}_4]^{2+}$  complexes, we tentatively assign this process to a four-electron reduction of the  $\text{Mo}^{\text{V}}$  dimer.<sup>[41,42]</sup> Obviously, further chemical transformations must be taken into account at the reduced stage to explain three distinct oxidation waves.<sup>[41]</sup> It appears, however, that a major portion of the original  $1^{3+}$  is reformed in these oxidation steps, as indicated by the observation that the same reduction wave is observed in a second and a third

scan. The range of positive potentials was investigated with a gold working electrode, and a single oxidation wave at  $0.54\text{ V}$  vs. NHE (Figure 3b) assignable to a two-electron  $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$  transition<sup>[43]</sup> was observed. The absence of the reduction peak is indicative of an EC mechanism with a fast subsequent structural rearrangement at the  $\text{Mo}^{\text{VI}}$  stage. The peak current of this wave proved to be directly proportional to the scan rate, thus indicating an adsorption-controlled, rather than a diffusion controlled process. It is well known that complexes of the dinuclear, doubly bridged  $[\text{OMo}(\mu\text{O})_2\text{--MoO}]^{2+}$  core can be oxidized in aqueous solution by chemical oxidizing agents such as  $\text{Ce}^{4+}$ . The final product of this irreversible reaction is  $\text{Mo}^{\text{VI}}$  with a mixed-valence  $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{VI}}$  species as intermediate.<sup>[44]</sup> A different behavior has been described by Wiegardt et al. for the dinuclear, monobridged  $[\text{LO}_2\text{Mo}^{\text{VI}}\text{--}\mu\text{O--Mo}^{\text{VI}}\text{O}_2\text{L}]^{2+}$  complex ( $\text{L} = N,N',N''\text{-trimethyl-1,4,7-triazacyclononane}$ ), where a diffusion controlled, reversible two-step reduction was observed with the mixed-valence  $\text{Mo}^{\text{VI}}\text{--}\text{Mo}^{\text{V}}$  as an intermediate.<sup>[45]</sup>

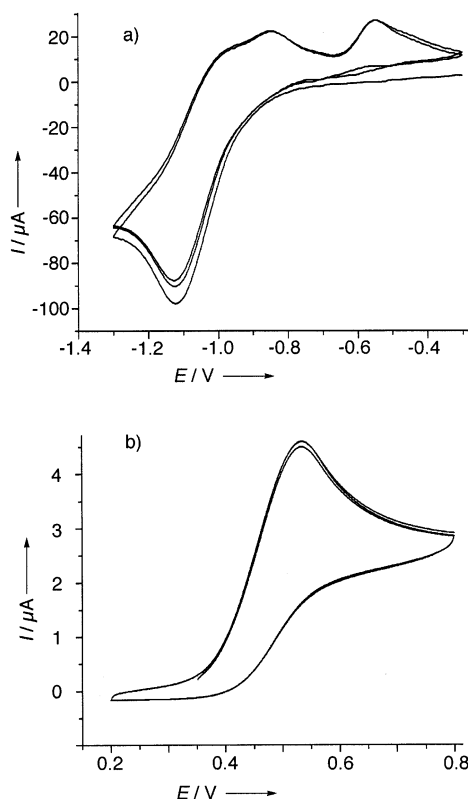


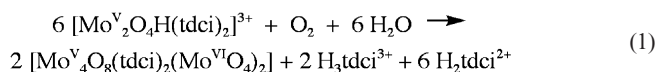
Figure 3. Cyclic voltammograms for  $1^{3+}$  in aqueous solution ( $23\text{ }^{\circ}\text{C}$ , pH 9, potentials are referenced against NHE). (a) Hg hanging-drop working electrode, scan rate =  $200\text{ mV s}^{-1}$ . (b) Au working electrode, scan rate =  $20\text{ mV s}^{-1}$ .

### Synthesis and Characterization of the Hexanuclear Complex

A solution of  $1^{3+}$  in  $\text{MeOH}/\text{H}_2\text{O}$ , upon prolonged standing open to the air over a period of several weeks, formed



a small amount of deep red crystals of composition  $[\text{Mo}_4\text{O}_8(\text{tdci})_2(\text{MoO}_4)_2] \cdot \approx 27\text{H}_2\text{O}$  (**2**· $\approx 27\text{H}_2\text{O}$ ) according to Equation (1).



The crystals, which proved to be air-stable, were insoluble in water and acetone. They could be used for single-crystal analysis. The molecular structure of the uncharged complex  $[(\text{MoO}_4)_4(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\text{tdci})_2(\text{MoO}_4)_2]$  (**2**) is depicted in Figure 4. It represents a mixed-valence Mo<sup>V</sup>–Mo<sup>VI</sup> species consisting of the well-known  $[\text{Mo}_4\text{O}_8]^{4+}$  core,<sup>[22–28]</sup> which is ligated by two facially coordinating tdcI entities and by two  $[\text{Mo}^{\text{VI}}\text{O}_4]^{2-}$  units coordinating in a monodentate fashion. The oxidation state of +6 for Mo3 was confirmed by bond-valence calculations (5.95).<sup>[46]</sup> The  $[\text{Mo}_4\text{O}_8]^{4+}$  core can be regarded as a dimer of two  $\text{Mo}_2\text{O}_4$  units, which are fused in an *anti* (i.e. head-to-tail) arrangement. The two Mo centers in these units are connected by a Mo–Mo single bond, and the two Mo centers together with the bridging oxygen donors form a four-membered Mo–O–Mo–O ring. It is worthy to note that the Mo–Mo distance (2.625 Å in **1**<sup>3+</sup>, 2.671 Å in **2**) is slightly longer in the tetramer; in addition, the tetramer exhibits some increased puckering of the four-membered ring: the deviation of the mean plane is 0.167 Å for **2** but only 0.089 Å for **1**<sup>3+</sup>.

In analogy to **1**<sup>3+</sup>, an exclusive coordination of tdcI through the three oxygen donors is observed in **2**. Although an unequivocal location of the hydrogen atomic positions was again not possible by means of the crystal structure analysis, a zwitterionic form with protonated nitrogen and deprotonated oxygen donors was assigned (Scheme 1b) on the basis of charge balance considerations. As mentioned above, such a zwitterionic form has been observed in several mononuclear metal complexes.<sup>[33]</sup> The binding mode of tdcI in **2** differs, however, from **1**<sup>3+</sup> in so far, as for each tdcI entity, only two alkoxo groups coordinate in a terminal fashion, whereas the third alkoxo group serves as a  $\mu_2$ -alkoxido bridge. Consequently, only two of the Mo centers are connected to all three oxygen donors of the tdcI ligands, whereas the remaining two Mo centers, which are only coordinated to the  $\mu_2$ -alkoxo bridge, complete their coordination sphere by binding a  $\text{MoO}_4^{2-}$  unit.

The eight oxygen atoms of the entire  $[\text{Mo}_4\text{O}_8]^{4+}$  core together with the six alkoxo oxygen atoms of the two tdcI ligands, and the two bridging oxygen atoms of the  $\text{MoO}_4^{2-}$  moieties form an aggregate of four fused, edge-sharing octahedra. The symmetry for an idealized geometry with regular octahedra would be  $C_{2h}$ . Owing to the formation of two Mo–Mo single bonds and the coordination of the two tdcI and  $\text{MoO}_4^{2-}$  ligands, the geometry of this core is, however, severely distorted, and the symmetry is reduced to  $C_i$ . The various Mo–O bond lengths are summarized in Table 1 and correspond to expectations.<sup>[8,22–28]</sup> The observed order:  $\text{O}_{\text{oxo}}\text{--Mo}^{\text{V}} < \mu_2\text{O}_{\text{oxo}}\text{--Mo}^{\text{V}} < \mu_3\text{O}_{\text{oxo}}\text{--Mo}^{\text{V}} \approx \text{O}_{\text{alkoxo}}\text{--Mo}^{\text{V}} < \mu_2\text{O}_{\text{alkoxo}}\text{--Mo}^{\text{V}}$  can be correlated to the decreasing  $\pi$ -

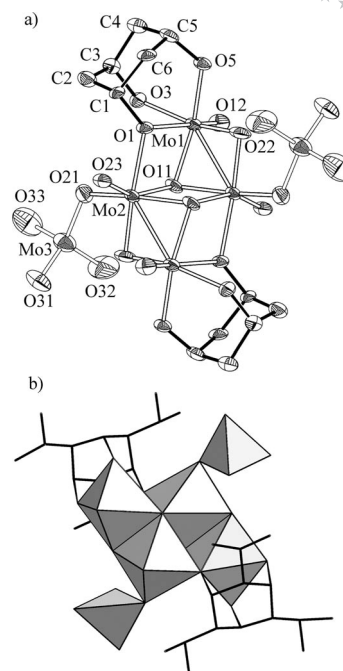


Figure 4. Molecular structure of the neutral complex  $[\text{Mo}_4\text{O}_8(\text{L})_2(\text{MoO}_4)_2]$  (**2**). (a) Numbering scheme and atomic displacement ellipsoids drawn at the 50% probability level; dimethylamino groups and hydrogen atoms are omitted for clarity. (b) Polyhedral representation for the hexanuclear core with Mo<sup>V</sup>O<sub>6</sub> octahedra and Mo<sup>VI</sup>O<sub>4</sub> tetrahedra; the organic residue is drawn as a black stick model. Selected bond lengths [Å] and angles [°]: Mo1–Mo2 2.671(1), Mo1–O12 1.701(5), Mo1–O11 2.031(5), Mo1–O1 2.244(5), Mo1–O3 2.097(6), Mo1–O5 2.025(5), Mo2–O1 2.188(5), Mo2–O22' 1.918(5), Mo1–O22 1.973(6), Mo2–O23 1.697(5), Mo2–O11 2.192(5), Mo2–O11' 2.009(6), Mo2–O21 2.063(6), Mo3–O21 1.877(6), Mo3–O31 1.745(7), Mo3–O33 1.707(9), Mo3–O32 1.740(8), O1–Mo1–O12 165.4(3), O3–Mo1–O22 160.7(2), O5–Mo1–O11 152.9(2), O23–Mo2–O11 103.4(2), Mo1–O1–Mo2 106.0(2), Mo1–O11–Mo2 113.8(2), Mo2–O11–Mo2' 103.3(2), Mo3–O21–Mo2 122.9(3), Mo1–O22–Mo2' 86.7(2).

bonding ability of the different types of oxygen donors, and the observed differences within the same donor class can simply be discussed in terms of a *trans* influence (push-pull mechanism): strong  $\pi$ -bonding generally results in a more significant weakening of the Mo–O bond in the *trans* position.<sup>[47]</sup>

Formation of the  $[\text{Mo}_4\text{O}_8]^{4+}$  core was further confirmed by FAB mass spectrometry (Figure 2c). In the range  $980 < m/z < 1320$ , several signals displaying an isotope distribution characteristic of tetranuclear species were detected in the spectrum in the positive-ion mode. The most intense signal centered at  $m/z = 1031$  was assigned to  $[\text{Mo}_4\text{O}_8(\text{tdci})_2\text{--}3\text{H}]^+$ . It can be regarded as the remaining fragment of **2** after dissociation of the two  $\text{MoO}_4^{2-}$  entities. As a matter of fact, the spectrum did not show any significant amount of penta- or hexanuclear species, thus indicating that the  $\text{MoO}_4^{2-}$  entities are only loosely bonded to the  $[\text{Mo}_4\text{O}_8]^{4+}$  core. Similar to **1**<sup>3+</sup>, the elimination of H<sub>2</sub>O is observed, as indicated by a peak at  $m/z = 1013$  assignable to  $[\text{Mo}_4\text{O}_7(\text{tdci})_2\text{--}5\text{H}]^+$ . In addition, a series of signals at  $1200 < m/z < 1300$  indicated the binding of an additional

tdci ligand. The signal centered at  $m/z = 1292$  was assigned to  $[\text{Mo}_4\text{O}_8(\text{tdci})_3\text{H}]^+$ . Elimination of  $\text{H}_2\text{O}$  resulted in the formation of  $[\text{Mo}_4\text{O}_7(\text{tdci})_3\text{H}]^+$  ( $m/z = 1274$ ),  $[\text{Mo}_4\text{O}_6(\text{tdci})_3\text{H}]^+$  ( $m/z = 1256$ ), and  $[\text{Mo}_4\text{O}_5(\text{tdci})_3\text{H}]^+$  ( $m/z = 1238$ ); the latter species corresponds to the product in which all three tdci ligands are completely deprotonated. In addition, some signals of weaker intensity observed in the range  $700 < m/z < 800$  indicated the formation of dinuclear species such as  $[\text{Mo}_2\text{O}_4(\text{tdci})_2\text{H}]^+$  ( $m/z = 777$ ). Obviously, the aggregation reaction, yielding the tetramer as a dimer of dimers, is reversible under FAB conditions.

## Conclusions

The reaction of  $\text{MoCl}_5$  with tdci resulted in the direct formation of  $[\text{Mo}_2\text{O}_4(\text{tdci})(\text{Htdci})]^{3+}$  ( $\mathbf{1}^{3+}$ ) which was subsequently converted into the mixed-valence species  $[\text{Mo}^{\text{V}}_4\text{O}_8(\text{tdci})_2(\text{Mo}^{\text{VI}}\text{O}_4)_2]$  ( $\mathbf{2}$ ) by means of an oxidatively induced polymerization process. Formation of the  $[\text{Mo}^{\text{V}}_4\text{O}_8]^{4+}$  core by dimerization of  $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$  complexes is well established, and a variety of  $[\text{Mo}^{\text{V}}_4\text{O}_8]^{4+}$  complexes with alkoxido ligands have been reported in the literature.<sup>[26,28]</sup> The present investigation provides, however, some new aspects for this reaction type:

(i) Our study confirmed the formation of a mixed-valence  $\text{Mo}^{\text{V}}\text{--}\text{Mo}^{\text{VI}}$  species in a partially aqueous system, as postulated by Modéc and Brenicé (see Introduction).<sup>[24]</sup>

(ii) Coordination of the  $\text{MoO}_4^{2-}$  unit in polynuclear Mo complexes is well established. However, in most of these complexes, the  $\text{MoO}_4^{2-}$  units undergo a bridging coordination mode. A terminal, monodentate coordination to a polynuclear (oxido)molybdenum core appears to be rather scarce,<sup>[48,49]</sup> and we are only aware of one example<sup>[11]</sup> where this type of coordination mode has been described in a mixed-valence  $\text{Mo}^{\text{V}}\text{Mo}^{\text{VI}}$  species.

(iii) It is of interest to compare the hydrolytic polymerization process of  $\text{Mo}^{\text{V}}$  with  $\text{Ta}^{\text{V}}$  under similar conditions. In analogy to the results reported here for  $\text{Mo}^{\text{V}}$ , two discrete  $\text{Ta}^{\text{V}}$  complexes, the mononuclear  $[\text{H}_2\text{Ta}(\text{tdci})_2]^{3+}$  and the heptanuclear  $[\text{H}_{11}\text{Ta}_7\text{O}_{12}(\text{tdci})_6]$  have been obtained by the reaction of  $\text{TaCl}_5$  with tdci in  $\text{MeOH}/\text{H}_2\text{O}$ .<sup>[35]</sup> However, the structural differences clearly reflect the specific properties of the  $d^1$  and  $d^0$  electron configuration. As is well known,  $\text{Mo}^{\text{V}}$  has a pronounced tendency to form a  $\text{Mo--Mo}$  single bond. Consequently, formation of a mononuclear complex as observed for  $\text{Ta}^{\text{V}}$  was not observed. Moreover, the formation of  $\text{Mo--Mo}$  bonds resulted in a much denser packing of the  $\text{MoO}_6$  octahedra (Figure S1, Supporting Information): The  $\text{Mo}_4\text{O}_{16}$  substructure of  $\mathbf{2}$  is exclusively made up of edge-sharing  $\text{MoO}_6$  octahedra, whereas in the corresponding  $\text{Ta}_7\text{O}_{30}$  substructure, the  $\text{TaO}_6$  octahedra are connected by common vertices.

(iv) Two new coordination modes of the tdci ligand are reported: In  $\mathbf{1}^{3+}$  two tdci units are bridged by a (possibly symmetrical)  $\text{M--(R)O}\cdots\text{H}\cdots\text{O(R)--M}$  bridge. A related type of bridging is known in the chemistry of aqua complexes, where a first intermediate in the so-called olation reaction

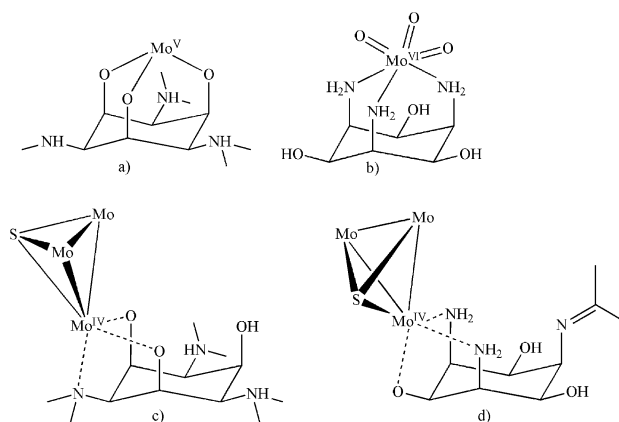
is believed to be a dimer of the type  $\text{M--O(H)--H}\cdots\text{O(H)--M}$ .<sup>[50]</sup>

In  $\mathbf{2}$ , both tdci ligands bridge two  $\text{Mo}^{\text{V}}$  centers. Each tdci ligand exhibits a facial tridentate and a monodentate coordination mode in which two of the alkoxo groups coordinate in a terminal fashion and the third oxygen donor serves as a  $\mu_2$ -alkoxo group.

(v) Owing to the different coordination modes offered by the tdci system (Scheme 1), this ligand can be used as an indicator to investigate the preference of a given metal center for binding either nitrogen or oxygen donor atoms, as expressed by Equation (2):<sup>[51]</sup>



Our investigation points to preferential binding of the harder oxygen donor to  $\text{Mo}^{\text{V}}$ , whereas binding to the softer nitrogen donor of tdci has been observed in a series of  $\text{Mo}^{\text{IV}}$  thio complexes (Scheme 2). It should, however, be noted that this question cannot be discussed simply in terms of HSAB arguments. Although  $\text{Mo}^{\text{VI}}$  is expected to be even harder than  $\text{Mo}^{\text{V}}$ , the molybdenum center in  $[(\text{taci})\text{--}\text{MoO}_3]$  is exclusively bonded to the nitrogen donors of the taci ligand (Scheme 2b).<sup>[52]</sup>



Scheme 2. Coordination modes for molybdenum complexes with 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci). (a) *syn*- $[\text{Mo}_2\text{O}_4\text{H}(\text{tdci})_2]^{3+}$  (this work), (b)  $[\text{MoO}_3(\text{taci})]$  (ref.<sup>[52]</sup>), (c)  $[\text{Mo}_3\text{S}_4(\text{tdci})_3]^{4+}$  (ref.<sup>[46]</sup>) and (d)  $[\text{Mo}_3\text{S}_4(\text{taci})_3 + 3\text{acetone} - 3\text{H}_2\text{O} - 4\text{H}^+]$  (ref.<sup>[46]</sup>).

## Experimental Section

**Physical Measurement and Analyses:** The IR spectrum of  $1\text{Cl}_3 \cdot 14.5\text{H}_2\text{O}$  was measured with a Bruker Vector 22 FT IR spectrometer equipped with a Golden Gate ATR unit. FAB<sup>+</sup> mass spectra were recorded with a VG ZAB VSEQ instrument. The samples were measured as aqueous solutions by using a glycerol matrix. Cyclic voltammetry was performed at ambient temperature ( $23 \pm 2^\circ\text{C}$ ) in a BAS C2 cell equipped with a BAS 100B/W2 potentiostat, by using a Au or Hg (hanging-drop) working electrode, a platinum counterelectrode, and a Ag/AgCl reference electrode. The measurements were performed in an aqueous medium (12 mM total Mo concentration, 0.5 M KCl as supporting electrolyte), and the pH was adjusted to 9 by using additional tdci (12 mM) as buffer.

C, H, N analyses were performed by D. Manser (Laboratorium für Organische Chemie, ETH Zürich); the Cl analysis (argentometric titration) and Mo analysis (ICP-OES) were performed by K. Hametner (Laboratorium für Anorganische Chemie, ETH Zürich).

**Materials:** MoCl<sub>5</sub> was purchased from Aldrich and was used without further purification. Tdci was prepared as described previously.<sup>[53]</sup>

**[Mo<sub>2</sub>O<sub>4</sub>H(tdci)<sub>2</sub>]Cl<sub>3</sub>·12.5H<sub>2</sub>O:** Anhydrous MoCl<sub>5</sub> (2.13 g, 7.796 mmol) was added carefully to frozen MeOH (60 g). The mixture was warmed up slowly to room temperature, resulting in a green, clear solution. An aliquot of this solution (1.21 g, 0.153 mmol Mo) was added to a solution of tdci (0.1 g, 0.383 mmol) dissolved in MeOH (2.5 mL). After 15 min., a portion of H<sub>2</sub>O (2.5 mL) was added, and a color change from green to brown was noted. The solution was stirred and heated to 80 °C until complete evaporation of MeOH. The resulting solution was cooled to room temperature and was layered with an equal volume of acetone. Ruby-colored prismatic crystals (56 mg, 66%), which formed within a period of about 14 h at 4 °C, were isolated by filtration and dried in a desiccator over P<sub>2</sub>O<sub>5</sub> to yield 1Cl<sub>3</sub>·10.5H<sub>2</sub>O. C<sub>24</sub>Cl<sub>3</sub>H<sub>76</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>20.5</sub> (1075.1): calcd. C 26.81, H 7.13, N 7.82; found C 26.50, H 6.86, N 7.76. The dried product was allowed to stand open to humid air until a constant weight was reached, to yield 1Cl<sub>3</sub>·12.5H<sub>2</sub>O. C<sub>24</sub>Cl<sub>3</sub>H<sub>80</sub>Mo<sub>2</sub>N<sub>6</sub>O<sub>22.5</sub> (1111.2): calcd. C 25.94, H 7.26, N 7.56, Cl 9.57, Mo 17.27; found C 25.93, H 7.18, N 7.44, Cl 9.60, Mo 17.31. IR:  $\tilde{\nu}$  = 3345, 1633, 1462, 1414, 1363, 1229, 1184, 1155, 1127, 1003, 963, 924, 888, 841, 712, 534 cm<sup>-1</sup>. MS-FAB<sup>+</sup>:  $m/z$  = 777.2 [Mo<sub>2</sub>O<sub>4</sub>(tdci)<sub>2</sub> – H]<sup>+</sup>. Single crystals of composition 1Cl<sub>3</sub>·14.5H<sub>2</sub>O were grown by layering an aqueous solution of the complex with acetone.

**[Mo<sub>4</sub>O<sub>8</sub>(tdci)<sub>2</sub>(MoO<sub>4</sub>)<sub>2</sub>]·≈27H<sub>2</sub>O:** A crystalline sample of [Mo<sub>2</sub>O<sub>4</sub>H(tdci)<sub>2</sub>]Cl<sub>3</sub>·12.5H<sub>2</sub>O (50 mg, 45 μmol) was dissolved in a mixture of MeOH (1 mL) and H<sub>2</sub>O (1 mL). The solution was allowed to stand open to the air in such a way that very slow evaporation of the solvent was possible. After a period of four weeks, the solution was concentrated to a total volume of about 0.5 mL, and the deposition of a small amount (≈ 5%) of dark red crystals was noted. MS-FAB<sup>+</sup>:  $m/z$  = 1031.5 ([Mo<sub>4</sub>O<sub>8</sub>(tdci)<sub>2</sub> – 3H]<sup>+</sup>).

**X-ray Diffraction Analysis:**<sup>[54]</sup> Suitable crystals of 1Cl<sub>3</sub>·14.5H<sub>2</sub>O and 2·≈27H<sub>2</sub>O were directly taken from the mother liquor and mounted on the diffractometer. Diffraction data were collected at 200 K with a Siemens Stoe IPDS diffractometer, using monochromated Mo-*K*<sub>α</sub> radiation. Crystal data for the two compounds are presented in Table 2. A total of 32137 and 16631 reflections were collected in the range 1.94° <  $\theta$  < 24.10° and 2.11° <  $\theta$  < 23.93° for 1Cl<sub>3</sub> and 2, respectively. Both data sets were empirically corrected for absorption effects. The two structures were solved by direct methods (SHELXS-97).<sup>[55a]</sup> In the structure of 1Cl<sub>3</sub>, 18 peaks were located in the electron-density map accounting for the total of 14.5 water molecules. Eleven of them (O1w–O11w) corresponded to a fully occupied water position, O12w–O16w had an occupancy of only 50%. O17w was found to be disordered over two sites with occupancies of 60 and 40%. In the structure of 2, one methyl group (C42) of a peripheral dimethylammonium moiety was found to be disordered, exhibiting two split positions, each having 50% site occupancy. Moreover, in the asymmetric unit, only three water molecules (O1w, O2w, O4w) were located at well-defined positions. The remaining water molecules were found to be badly disordered. In a first attempt, a total of eleven additional peaks (O3wA, O3wB, O5w, O6wA, O6wB, O7wA, O7wB, O8wA, O8wB, O9wA, O9wB) were assigned to partially occupied sites. However, there remained several minor peaks, having an electron density in the range 1–

1.5 e<sup>–</sup>Å<sup>–3</sup>, in the difference Fourier map, thus indicating that the problem of the disordered water molecules was not completely solved.

Table 2. Crystallographic data for 1Cl<sub>3</sub>·14.5H<sub>2</sub>O and 2·≈27H<sub>2</sub>O.

	1Cl <sub>3</sub> ·14.5H <sub>2</sub> O	2·≈27H <sub>2</sub> O
Empirical formula	C <sub>24</sub> H <sub>84</sub> Cl <sub>3</sub> Mo <sub>2</sub> N <sub>6</sub> O <sub>24.5</sub>	C <sub>24</sub> H <sub>109</sub> Mo <sub>6</sub> N <sub>6</sub> O <sub>49.5</sub>
FW [g mol <sup>–1</sup> ]	1147.2	1849.8
Crystal size [mm]	0.5 × 0.3 × 0.3	0.2 × 0.2 × 0.2
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> <sub>2</sub> / <i>m</i> (No. 14)	<i>P</i> <sub>2</sub> / <i>c</i> (No. 14)
<i>a</i> [Å]	8.797(2)	12.224(2)
<i>b</i> [Å]	25.439(5)	15.986(3)
<i>c</i> [Å]	23.077(5)	14.220(3)
$\beta$ [°]	90.44(3)	98.95(3)
<i>V</i> [Å <sup>3</sup> ]	5164(2)	2744.9(9)
<i>Z</i>	4	2
<i>T</i> , [K]	200(2)	200(2)
$\lambda$ [Å]	0.71073 (Mo- <i>K</i> <sub>α</sub> )	0.71073 (Mo- <i>K</i> <sub>α</sub> )
$\rho_{\text{calcd}}$ [g cm <sup>–3</sup> ]	1.476	2.238
$\mu$ [cm <sup>–1</sup> ]	7.19	14.62
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.050	0.056
<i>wR</i> <sub>2</sub> (all data)	0.167	0.137

Both structures (5364 unique reflections, 568 parameters for 1Cl<sub>3</sub> and 2692 unique reflections, 261 parameters for 2) were refined by using full-matrix least-squares calculations on *F*<sup>2</sup> (SHELXL-97).<sup>[55b]</sup> All non-hydrogen atomic positions except the two split positions of the disordered methyl group C42 in 2 were refined anisotropically. Several of the H(-C) and H(-N) hydrogen atomic positions could be located in the difference Fourier map. However, some of them exhibited rather poor *U*<sub>iso</sub> values. We therefore decided to use calculated positions by the riding model, *U*<sub>iso</sub> = 1.5 × *U*<sub>eq</sub> and 1.2 × *U*<sub>eq</sub> of the pivot atom for the methyl groups and the other H(-C) and H(-N) positions, respectively. The atomic positions of the hydrogen atoms of the water molecules were not considered.

At this stage, the refinement of 2 resulted in agreement factors of *R*1 = 5.80% for *I* > 2 $\sigma$ (*I*) and *wR*<sub>2</sub> = 14.47% for all data. Because of the above mentioned unsatisfactory situation for the water molecules, the SQUEEZE program of the PLATON package<sup>[56]</sup> was now applied to subtract the electron density of all water molecules. The program removed 137.2 e<sup>–</sup>, corresponding to a total of 13.75 solvent H<sub>2</sub>O molecules in the asymmetric unit. In the final refinement, the agreement factors diminished, however, only slightly to *R*1 = 5.65% for *I* > 2 $\sigma$ (*I*) and *wR*<sub>2</sub> = 13.67 for all data.

**Supporting Information** (see footnote on the first page of this article): Figure S1 showing the complex core (polyhedra) of [H<sub>–11</sub>Ta<sub>7</sub>O<sub>12</sub>(tdci)<sub>6</sub>] and [Mo<sup>V</sup><sub>4</sub>O<sub>8</sub>(tdci)<sub>2</sub>(Mo<sup>VI</sup>O<sub>4</sub>)<sub>2</sub>].

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The FAB mass spectra have been measured by R. Häfliger and Dr. W. Amrein (ETH Zürich). An early crystal structure analysis of 1Cl<sub>3</sub>·14.5H<sub>2</sub>O and 2·≈27H<sub>2</sub>O was performed by Prof. Dr. V. Gramlich, Dr. S. Leoni and Dr. M. Wörle (all ETH Zürich); the data sets presented in this investigation have been collected by Dr. Volker Huch (University of des Saarlandes). Financial support by the Schweizerischer Nationalfonds (for M. D. M.) is gratefully acknowledged.



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- from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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