The Anderson-Type Anion $(TeMo_6O_{24})^{6-}$ − A Multidentate Ligand for Trivalent Rare Earth Cations

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Dedicated to Professor Philipp Gütlich on the occasion of his 70th birthday

The syntheses and structural characterizations of four novel lanthanide polyoxomolybdates containing the Anderson-type anion $(TeMo_6O_{24})^{6-}$ are presented. Depending on the size of the trivalent rare earth cations, in the solid-state structures of $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**1**), $\{[Ce(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 7nH_2O$ (**2**), $\{[Pr(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (**3**) and $\{[Nd(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (**4**) two different arrangements of the building unit are present. The $(TeMo_6O_{24})^{6-}$ anion acts as a hexadentate ligand for La^{III} and as a tetradentate ligand for Ce^{III}, Pr^{III} and Nd^{III}, leading to two different infinite one-dimensional chains. The crystal structures of the new compounds are compared with known lanthanide polyoxomolybdates containing the $(TeMo_6O_{24})^{6-}$ anion and the influence of the Ln^{III} ionic radii is discussed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Polyoxotungstates and -molybdates[1,2] have been investigated extensively over the last years. Owing to their unusual properties such as high charges and ionic masses etc., they attract current attention in view of their potential in medicine, material science, and catalysis.[3−6] The fascination of polyoxometalate chemistry arises from the remarkable size and challenging geometry of several mixed-valence nanostructured polyoxomolybdates synthesized by the group of A. Müller.[7−10] However, complex and largely unknown self-assembly reaction mechanisms are responsible for the formation of polyoxometalates and make it difficult to develop a straightforward reaction route for their syntheses.

Lanthanide containing polyoxoanions differ fundamentally from transition metal substituted anions and exhibit unique structures because of the lanthanides' preferred coordination numbers eight and nine. In order to establish a consistent picture of lanthanide containing polyoxomolybdates, we started synthesizing and characterizing novel exponents in this class of compounds. In 2004, we were able to report the crystal structures of $[(CH_3)_4N]_x(NH_4)_{14-x}[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4] \cdot nH_2O$ (Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III}, Gd^{III}).[11] We affirmed that the well-known $[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anion reported by Yamase et al.[12] can be formed by a wide range of lanthanides.

In the case of the $(LnW_{10}O_{36})^{9-}$ anions (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, Tb^{III}, Dy^{III}), the effect of lanthanide contraction on these anions was discussed by Ozeki and Yamase.[13] Sécheresse et al. showed that the linkage of the monovacant lacunary $(SiW_{11}O_{39})^{8-}$ anions by lanthanide cations is dependent on the nature of the rare earth cation.[14] This example shows the necessity to investigate the dependency of the arrangement of different polyoxo building units on the size of the Ln^{III} atoms.

Recently, we have reported the syntheses and crystal structures of six novel lanthanide polyoxomolybdates containing the Anderson-type anion $(TeMo_6O_{24})^{6-}$. The polyoxometalates $K_{6n}(TeMo_6O_{24})_n\{[Ln(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 16nH_2O$ (Ln = Eu^{III}, Gd^{III}) and $K_{3n}\{Ln(H_2O)_5(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (Ln = Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}) exhibit lanthanide cations and $(TeMo_6O_{24})^{6-}$ anions at a ratio of 1:1. Depending on the size of the rare earth cations, two different arrangements of the building units could be found.[15] This paper describes the syntheses and structures of four novel lanthanide polyoxomolybdates with a $(TeMo_6O_{24})^{6-}:Ln^{III}$ ratio of 1:2 (Ln = La, Ce, Pr, Nd). While the cerium, praseodymium and neodymium compound show a linkage of the $(TeMo_6O_{24})^{6-}$ building units which can also be found in the europium and gadolinium compounds mentioned above, the lanthanum compound shows a novel type of combination.

Results and Discussion

The four novel compounds $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**1**), $\{[Ce(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 7nH_2O$ (**2**),

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$\{[Pr(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (**3**) and $\{[Nd(H_2O)_7]_2$-$(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (**4**) were synthesized in a two-step reaction. At first, the $(TeMo_6O_{24})^{6-}$ anion was formed by potassium molybdate and telluric acid at pH 5.5. Afterwards, the trivalent rare earth cations were added as chloride or nitrate. Single crystals of **1**−**4** formed after a few days.

All compounds crystallize in the triclinic crystal system, space group $P\bar{1}$. The asymmetric unit contains half a formula unit. The tellurium atom Te(1) is situated at an inversion center in all cases. It is located at the center of a nearly regular hexagon which is formed by the six molybdenum atoms of the $(TeMo_6O_{24})^{6-}$ anion. Consequently, all Te⋯Mo distances are almost identical in **1**−**4**. The molybdenum and tellurium atoms are nearly planar since the Te(1) atom is situated at a distance of less than 0.06 Å from the [Mo(1), Mo(2), Mo(3)] plane in all compounds. The Te^{VI} atom is surrounded octahedrally by six oxygen atoms. The Te−O bond lengths and O−Te−O bond angles summarized in Table 1 show only little distortion of the TeO_6 octahedra. The corresponding bond lengths and angles differ only slightly in all four compounds.

The corresponding molybdenum−oxygen bond lengths of the $(TeMo_6O_{24})^{6-}$ anions show great similarities in **1**−**4**. The Mo−O distances can be divided into three groups: terminal oxygen atoms, molybdenum-bridging oxygen atoms with middle oxygen−molybdenum bond lengths and oxygen atoms bound to one tellurium and two molybdenum atoms with long oxygen−molybdenum bond lengths. As expected, the terminal oxygen atoms show the shortest molybdenum−oxygen bond lengths [between 1.69(1) and 1.73(1) Å]. The long Mo−O bond lengths are located *trans* to the short Mo−O bonds and show M−O distances between 2.22(1) Å and 2.32(1) Å. The intermediate Mo−O bonds show Mo-O distances between 1.89(1) Å and 1.96(1) Å. As usual for polyoxomolybdates, the O−Mo−O bond angles differ significantly from the ideal 90° and 180° bond angles and confirm the distortion of the MoO_6 octahedra. The Mo−O bond lengths and O−Mo−O bond angles are summarized in Table 1.

In the lanthanum compound **1**, the $(TeMo_6O_{24})^{6-}$ anion acts as a hexadentate ligand for the lanthanum atoms and is bound to four La^{III} atoms. Each La atom achieves ninefold coordination by six water molecules and three terminal oxygen atoms of two $(TeMo_6O_{24})^{6-}$ anions. These nine oxygen atoms build up a tricapped-trigonal prism. Figure 1 shows a detail of the resulting infinite one-dimensional $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n$ chain. The one-dimensional chains are linked by an extensive hydrogen bond network.
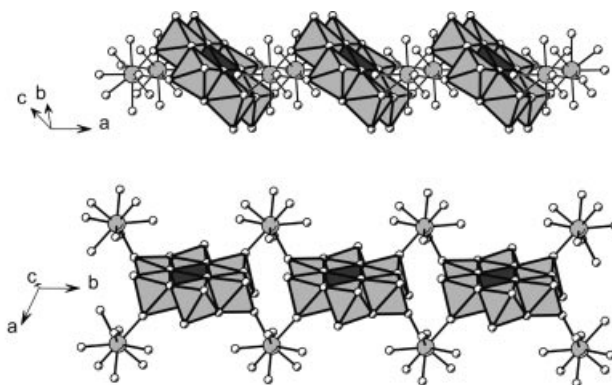

Figure 1. Details of the infinite one-dimensional chains of $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n$ in **1** (top) and of $\{[Ln(H_2O)_7]_2(TeMo_6O_{24})\}_n$ (Ln = Ce, Pr, Nd; bottom) in **2**−**4**

In the cerium, praseodymium and neodymium containing compounds **2**−**4**, the Anderson anion acts as a tetradentate ligand coordinating four Ce^{III}, Pr^{III} or Nd^{III} atoms by terminal oxygen atoms. The lanthanide atoms are coordinated by two terminal oxygen atoms of two $(TeMo_6O_{24})^{6-}$ anions and seven water molecules, forming a tricapped-trigonal prism. Figure 1 shows the infinite one-dimensional $\{[Ln(H_2O)_7]_2(TeMo_6O_{24})\}_n$ chain (Ln = Ce, Pr, Nd) in detail. As in **1**, the chains are connected via a hydrogen bond network. This type of chain can also be found in $K_{6n}(TeMo_6O_{24})_n\{[Eu(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 16nH_2O$ (**5**) and $K_{6n}(TeMo_6O_{24})_n\{[Gd(H_2O)_7]_2$-$(TeMo_6O_{24})\}_n \cdot 16nH_2O$ (**6**).[15] In contrast to **2**−**4**, the com-

Table 1. Bond lengths (Å) and angles (°) with standard deviations in parentheses of the polyoxometalates **1**−**4**

	1 (Ln = La)	**2** (Ln = Ce)	**3** (Ln = Pr)	**4** (Ln = Nd)
Te−O	1.903(3)−1.942(3)	1.926(4)−1.945(5)	1.921(3)−1.934(3)	1.922(3)−1.935(3)
Mo−O_t [a]	1.686(3)−1.734(3)	1.696(5)−1.733(5)	1.689(3)−1.730(3)	1.691(3)−1.732(3)
Mo−O_{Mo2} [b]	1.914(3)−1.948(3)	1.900(5)−1.962(4)	1.889(3)−1.953(3)	1.891(3)−1.960(3)
Mo−O_{TeMo2} [b]	2.223(3)−2.315(3)	2.257(5)−2.310(5)	2.253(3)−2.313(3)	2.243(3)−2.312(3)
Ln−O_{Mo} [b]	2.512(3)−2.535(3)	2.517(5)−2.548(5)	2.488(3)−2.526(3)	2.479(3)−2.512(3)
Ln−OH_2	2.511(3)−2.631(3)	2.506(5)−2.569(6)	2.471(3)−2.553(3)	2.465(3)−2.538(3)
Mo⋯Te	3.238(1)−3.278(1)	3.273(1)−3.290(2)	3.265(2)−3.282(2)	3.267(1)−3.279(2)
O−Te−O_{cis}	84.8(2)−95.2(2)	85.2(2)−94.8(2)	85.1(2)−94.9(2)	85.0(2)−95.0(2)
O−Te−O_{trans}	180.0	180.0	180.0	180.0
O−Mo−O_{cis}	70.2(1)−107.5(2)	70.2(2)−106.7(3)	70.1(1)−106.8(2)	70.1(1)−106.8(2)
O−Mo−O_{trans}	151.6(2)−164.3(2)	151.4(2)−161.3(2)	151.8(3)−161.7(2)	152.2(2)−161.8(2)
O−Ln−O	65.2(1)−141.6(1)	64.2(2)−143.4(2)	63.9(2)−142.6(2)	64.2(2)−142.7(2)

[a] Terminal. [b] The subscripts indicate the atoms bound to the oxygen atom.

pounds **5** and **6** contain two crystallographically independent $(TeMo_6O_{24})^{6-}$ anions. One of these ions acts as a tetradentate ligand for the lanthanide ions, the second one is surrounded by potassium ions and crystal water and has no bonding to the lanthanide cations.

The crystal structures of **1**−**4** differ not only in the coordination sphere of the lanthanide atoms. Figure 2 and 3 show the different arrangements of the one-dimensional chains for **1** on the one hand and **2**−**4** on the other. In **1**, the $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n$ chains run along [100], while the $\{[Ln(H_2O)_7]_2(TeMo_6O_{24})\}_n$ chains in **2**−**4** run along [010]. While the lattice parameters in **2**−**4** are very similar, they differ clearly from those found for **1**. The differences in the crystal structures can also be fixed on the Ln···Ln distances. Within the $\{[Ln(H_2O)_x]_2(TeMo_6O_{24})\}_n$ chains (x = 6, 7), the shortest La···La distance [7.82(1) Å] in **1** differs clearly from the shortest Ln···Ln distances in **2**−**4** [8.70(1) Å for **2**, 8.65(1) Å for **3**, 8.62(1) Å for **4**, respectively]. In contrast to that, the shortest Ln···Ln distances between two different chains are shorter in **2**−**4** [6.25(1) Å for **2**, 6.18(1) Å for **3**, 6.16(1) Å for **4**, respectively] than in **1** [6.77(1) Å].
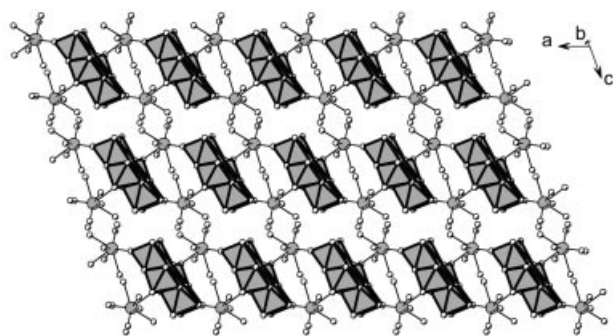

Figure 2. View of the crystal structure of $\{[La(H_2O)_6]_2$-$(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**1**). The $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n$ chains run along [100]. The hydrate water molecules are omitted partially for clarity

We have reported recently that for terbium(III), dysprosium(III), holmium(III) and erbium(III) a further linkage
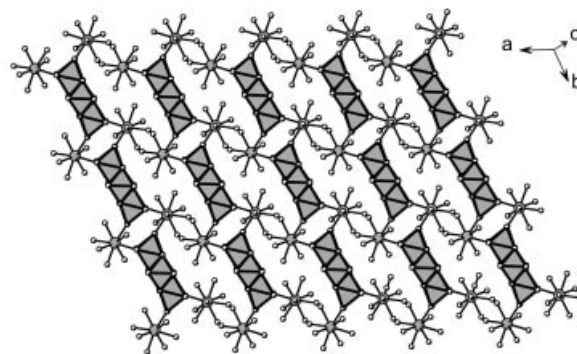

Figure 3. View of the crystal structure of $\{[Pr(H_2O)_7]_2$-$(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (**3**). The $\{[Pr(H_2O)_7]_2(TeMo_6O_{24})\}_n$ chains run along [010]. The hydrate water molecules are omitted partially for clarity

of the Anderson-type anions can be found.[15] In $K_{3n}\{Tb(H_2O)_5(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**7**), $K_{3n}\{Dy(H_2O)_5$-$(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**8**), $K_{3n}\{Ho(H_2O)_5(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**9**) and $K_{3n}\{Er(H_2O)_5(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (**10**), the $(TeMo_6O_{24})^{6-}$ anion acts as a tridentate ligand for the lanthanide atoms. As a result of the lanthanide contraction, the coordination number of these smaller rare earth cations is only eight. Within the $\{Ln(H_2O)_5(TeMo_6O_{24})\}_n^{3n-}$ chains, the Ln^{III} atoms are coordinated by five water molecules, two terminal oxygen atoms of two Anderson anions and one molybdenum-bridging oxygen atom. These eight oxygen atoms form a square-antiprismatic prism.

The oxidation states of the lanthanide cations were checked by the bond valence method.[16] New bond-valence parameters for Ln−O bonds have been reported recently.[17] Table 2 summarizes the calculated bond valences for the lanthanide atoms of the new compounds **1**−**4** and the compounds **5**−**10** reported previously. The calculated valences vary only slightly and affirm that the lanthanide atoms are trivalent in all compounds, although the yellow color of the cerium containing compound **2** could lead to the assumption that Ce^{III} was oxidized to Ce^{IV}. The average Ln−O bond lengths show not only the influence of the lanthanide contraction but also point to the additional decrease of the

Table 2. Comparison of Ln−O bond lengths and calculated bond valences of **1**−**10**

	Ln atom	Coordination number	Range of Ln−O bond lengths	Average Ln−O bond length	Bond-valence (calcd.)
1	La(1)	9	2.511(3)−2.631(3)	2.545	3.01
2	Ce(1)	9	2.506(5)−2.569(6)	2.533	2.87
3	Pr(1)	9	2.471(3)−2.553(3)	2.511	2.95
4	Nd(1)	9	2.465(3)−2.538(3)	2.496	2.97
5	Eu(1)	9	2.398(3)−2.489(3)	2.448	2.99
6[a]	Gd(1)	9	2.393(4)−2.498(4)	2.444	2.95
	Gd(2)	9	2.391(4)−2.497(4)	2.442	2.96
7	Tb(1)	8	2.347(3)−2.422(3)	2.379	2.98
8	Dy(1)	8	2.339(5)−2.401(6)	2.367	2.97
9	Ho(1)	8	2.324(5)−2.394(5)	2.360	2.95
10	Er(1)	8	2.319(6)−2.388(6)	2.350	2.93

[a] The gadolinium compound contains two crystallographically independent Gd^{III} atoms.

Ln−O bond lengths which is caused by the change of the coordination number from 9 to 8.

Conclusions

The decrease of radii of the trivalent rare earth cations leads to three different one-dimensional chains in **1**, **2−6** and **7−10**. As a result, the solid-state structures show varieties which are not only limited to slight changes of Ln−O bond lengths, but also cause diverse coordination spheres, lattice parameters and distances between the one-dimensional chains. The influence of the size of the Ln^{III} atoms can be watched closely in the $(TeMo_6O_{24})^{6-}/Ln^{III}$ system because the $(TeMo_6O_{24})^{6-}$ anions exhibit numerous potential bonding partners for the lanthanide cations and therefore enable different arrangements of the building units with different coordination spheres of the lanthanide atoms. In the crystal structures reported, the $(TeMo_6O_{24})^{6-}$ anion can act as a tridentate, tetradentate and hexadentate ligand, respectively. Linking these discrete entities to build up solid-state materials is of great interest beyond the structural

point of view, but also for possible applications in different fields of chemistry. It still remains a challenge to investigate the dependency of the crystal structures on the lanthanide radii to establish a consistent picture of lanthanide containing polyoxomolybdates.

Experimental Section

Instrumentation and Analytical Procedures: IR spectra were measured with a Perkin−Elmer 683 spectrometer as KBr pellets. The atomic ratios of the heavy elements were determined by energy dispersive X-ray fluorescence analysis (EDX). Diffraction experiments were performed with a STOE IPDS imaging plate system (for **2**) and a BRUKER SMART APEX diffractometer with CCD detector (for **1**, **3** and **4**), both using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Structures were solved by Patterson Synthesis with the SHELXS-97[18] and refined with the SHELXL-97 program.[19] No hydrogen atoms were included during the refinement. All atoms were refined anisotropically by full-matrix least-squares calculations based on F^2. The programs SADABS[20] (for **1**, **3** and **4**) and DECAY[21] (for **2**) were applied for the absorption correction. As usual for polyoxometalates, the crystal structures of **2−4** show disorder in the crystal water part of the structure.

Table 3. Crystallographic data for $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n \cdot 6nH_2O$ **(1)**, $\{[Ce(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 7nH_2O$ **(2)**, $\{[Pr(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ **(3)** and $\{[Nd(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ **(4)**

	1	**2**	**3**	**4**
Formula	$La_2TeMo_6O_{42}H_{36}$	$Ce_2TeMo_6O_{45}H_{42}$	$Pr_2TeMo_6O_{46}H_{44}$	$Nd_2TeMo_6O_{46}H_{44}$
M (g·mol^{-1})	1689.34	1745.81	1765.41	1772.07
Crystal size (mm^3)	$0.10 \times 0.06 \times 0.02$	$0.14 \times 0.12 \times 0.07$	$0.23 \times 0.14 \times 0.05$	$0.18 \times 0.16 \times 0.09$
Crystal color	colorless	yellow	light green	purple
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	9.396(2)	9.626(2)	9.569(2)	9.569(2)
b (Å)	10.188(2)	10.285(2)	10.230(2)	10.236(2)
c (Å)	10.694(2)	11.632(2)	11.572(2)	11.563(2)
α (°)	101.64(3)	97.72(3)	98.01(3)	98.30(3)
β (°)	108.09(3)	101.27(3)	101.29(3)	101.21(3)
γ (°)	106.50(3)	114.33(3)	114.13(3)	114.17(3)
V (Å^3)	884.6(3)	998.9(3)	982.9(3)	981.3(3)
Z	1	1	1	1
$\rho_{calcd.}$ (g·cm^{-3})	3.171	2.902	2.983	2.999
μ (mm^{-1})	5.350	4.888	5.133	5.305
T (K)	173(2)	213(2)	173(2)	173(2)
2θ Range	$4.22 \leq 2\theta \leq 62.68$	$8.84 \leq 2\theta \leq 52.30$	$3.70 \leq 2\theta \leq 63.08$	$3.70 \leq 2\theta \leq 62.98$
Index range	$-13 \leq h \leq 13$	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$	$-12 \leq k \leq 12$	$-14 \leq k \leq 14$	$-14 \leq k \leq 14$
	$-15 \leq l \leq 15$	$-14 \leq l \leq 14$	$-16 \leq l \leq 16$	$-16 \leq l \leq 16$
Reflections collected	10455	7260	11723	11718
Independent reflections	5309 [R(int) = 0.0321]	3640 [R(int) = 0.0818]	5917 [R(int) = 0.0342]	5882 [R(int) = 0.0291]
Parameters	232	260	268	268
R_1[a] [$I > 2\sigma(I)$]	0.0313	0.0387	0.0328	0.0307
wR_2[b] [$I > 2\sigma(I)$]	0.0827	0.1079	0.0827	0.0746
R_1[a] (all data)	0.0334	0.0430	0.0373	0.0354
wR_2[b] (all data)	0.0839	0.1111	0.0846	0.0763
GooF[c] on F_0^2	1.131	1.068	1.042	1.045
Weighting scheme[b]	$a = 0.0393$; $b = 0.3916$	$a = 0.0523$; $b = 4.6743$	$a = 0.0362$; $b = 1.0403$	$a = 0.0300$; $b = 1.9405$
$(\Delta/\rho)_{max.}$ (e$^-$/Å^3)	1.440	1.745	1.660	1.242
$(\Delta/\rho)_{min.}$ (e$^-$/Å^3)	−2.592	−2.190	−2.255	−1.358

[a] $R_1 = \Sigma\,||F_{obsd.}| - |F_{calcd.}||/\Sigma\,|F_{obsd.}|$. [b] $wR_2 = \{\Sigma\,[w(F_{obsd.}^2 - F_{calcd.}^2)^2]/\Sigma\,[w(F_{obsd.}^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_{obsd.}^2) + (aP)^2 + bP]$; with $P = [\max.(F_{obsd.}^2, 0) + 2F_{calcd.}^2]/3$. [c] goof $= [\Sigma w(F_{obsd.}^2 - F_{calcd.}^2)^2/(n - p)]^{1/2}$, n = number of reflections, p = parameters used.

FULL PAPER

Syntheses of Heteropolymolybdates: All starting materials and chemicals were used without further purification.

Preparation of $\{[La(H_2O)_6]_2(TeMo_6O_{24})\}_n \cdot 6nH_2O$ (1): K_2MoO_4 (1 g, 4.2 mmol) was dissolved in 30 mL of water, to which telluric acid (0.160 g, 0.7 mmol), dissolved in 10 mL of water, was added. The pH was adjusted to 5.5 by adding 4 M hydrochloric acid. The colorless solution was heated to 80 °C and stirred for 30 min. $La(NO_3)_3 \cdot 6H_2O$ (0.303 g, 0.7 mmol) was dissolved in 4 mL of water and added slowly to the hot solution while stirring. After 15 minutes, the solution was filtered. Colorless single crystals suitable for X-ray diffraction were obtained from the solution after two days. $La_2TeMo_6O_{42}H_{36}$ (1689.34). Yield: 340 mg (57%, based on La). IR (KBr disc, cm^{-1}): $\tilde{\nu} = 3434$ vs (br), 3245 s (br), 1638 s, 1454 w, 1385 w, 1120 w, 941 s, 914 s, 893 s, 869 m, 679 s, 614 s, 446 s. EDX: found (calcd.) for $La_2TeMo_6O_{42}H_{36}$: La:Te:Mo = 1.95:0.97:6.00 (2.00:1.00:6.00).

Preparation of $\{[Ce(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 7nH_2O$ (2): This compound was prepared similarly to **1**, with $CeCl_3 \cdot 7H_2O$ (0.261 g, 0.7 mmol) instead of $La(NO_3)_3 \cdot 6H_2O$. Yellow single crystals were obtained from the solution after two days. $Ce_2TeMo_6O_{45}H_{42}$ (1745.81). Yield: 349 mg (57%, based on Ce). IR (KBr disc, cm^{-1}): $\tilde{\nu} = 3444$ vs (br), 3164 s, 1636 s, 1384 w, 942 s, 918 s, 890 s, 665 s, 614 m, 494 s, 449 s. EDX: found (calcd.) for $Ce_2TeMo_6O_{45}H_{42}$: Ce:Te:Mo = 1.88:0.93:6.00 (2.00:1.00:6.00).

Preparation of $\{[Pr(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (3): This compound was prepared similarly to **1**, with $Pr(NO_3)_3 \cdot 6H_2O$ (0.305 g, 0.7 mmol) instead of $La(NO_3)_3 \cdot 6H_2O$. Green single crystals suitable for X-ray diffraction were obtained from the solution after two days. $Pr_2TeMo_6O_{46}H_{44}$ (1765.41). Yield: 362 mg (58%, based on Pr). IR (KBr disc, cm^{-1}): $\tilde{\nu} = 3437$ vs (br), 3167 s, 1634 s, 1385 s, 940 s, 914 s, 872 s, 668 s, 614 s, 492 m, 449 m. EDX: found (calcd.) for $Pr_2TeMo_6O_{46}H_{44}$: Pr:Te:Mo = 2.10:0.93:6.00 (2.00:1.00:6.00).

Preparation of $\{[Nd(H_2O)_7]_2(TeMo_6O_{24})\}_n \cdot 8nH_2O$ (4): This compound was prepared similarly to **1**, with $NdCl_3 \cdot 6H_2O$ (0.251 g, 0.7 mmol) instead of $La(NO_3)_3 \cdot 6H_2O$. After one day light pink single crystals suitable for X-ray diffraction were obtained from the solution. $Nd_2TeMo_6O_{46}H_{44}$ (1772.02). Yield: 297 mg (48%, based on Nd). IR (KBr disc, cm^{-1}): $\tilde{\nu} = 3386$ vs (br), 1634 s, 1384 w, 942 s, 914 s, 870 m, 673 s, 614 s, 490 m, 448 s. EDX: found (calcd.) for $Nd_2TeMo_6O_{46}H_{44}$: Nd:Te:Mo = 1.88:1.03:6.00 (2.00:1.00:6.00).

Further details on the crystal structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldhafen, Germany [Fax: (internat.) +49-7247-808666; E-mail: crysdata@fiz-karlsruhe.de], on quoting the depository number CSD-414132 (for **1**), -414133 (for **2**), -414134 (for **3**) and -414135 (for **4**).

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