Formation of Large Clusters in the Reaction of Lanthanide Cations with Heptamolybdate

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A series of new lanthanide polyoxomolybdates was synthesised by reaction of lanthanide cations with the heptamolybdate anion $(Mo_7O_{24})^{6-}$. The heteropolyanions $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III}, Gd^{III}) were isolated as either their ammonium or tetramethylammonium salts and characterised by X-ray structure analysis, energy dispersive X-ray fluorescence analysis, and IR and Raman spectroscopy. The central $[Ln_4(MoO_4)(H_2O)_{16}]^{10+}$ core of the anion is coordinated by four heptamolybdate groups. Each Ln^{III} atom in the core exhibits ninefold coordination by oxygen atoms belonging to H_2O, $(MoO_4)^{2-}$ and $(Mo_7O_{24})^{6-}$ units; the central molybdenum atom is coordinated tetrahedrally by four oxygen atoms.

Introduction

Because of their multifunctional applications in the fields of catalysis, chemical analysis and medicine, the chemistry of polyoxometalates is a research area of growing interest.[1−3] The selective synthesis of heteropolymetalates is made difficult by the large number of equilibrium reactions during the formation of the resulting anions. The characterisation of novel compounds and functional investigations are required for identification of structural characteristics and for understanding the different mechanisms that are responsible for biological and catalytic activity.

In recent years, a number of very large polyoxomolybdate clusters have been synthesised and structurally characterised. The Müller group has reported several giant mixed-valence nano-structured polyoxomolybdates with well above one hundred molybdenum atoms.[4−7] In polyoxotungstate chemistry quite different structures have been described; the $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$ anion is the largest anion yet known.[8]

Lanthanide-containing polyoxometalates constitute a type of compound of great impact.[9] Structural studies of lanthanide polyoxotungstates have been investigated and a number of compounds, for example $Na_6H_2[Ce(W_5O_{18})_2]\cdot 30H_2O$,[10] $K_{16}[Ce(P_2W_{17}O_{61})_2]\cdot 50H_2O$[11] and $K_{15}H_3[Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]\cdot 25.5H_2O$,[12] have been reported. In connection with the discovery of the anti-HIV activity of the polyoxometalate PM-104 by Yamase et al. and of the substances $K_{13}[Ln(SiW_{11}O_{39})_2]\cdot nH_2O$ and $K_{17}[Ln(P_2W_{17}O_{61})_2]\cdot nH_2O$, synthesised by Francesconi et al., investigations relating to structure-activity correlations were reported.[13,14]

There are still only a few crystal structure analyses of lanthanide-containing polyoxomolybdates. In 1991 Yamase et al. reported the synthesis and characterisation of the compound $(NH_4)_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 18H_2O$, the luminescence properties of which are of great interest.[15] A similar structure of nonluminescent dimeric $[Pr_4(MoO_4)(Mo_7O_{24})_4]_2{}^{28-}$ was reported in 1987.[16] The synthesis and crystal structure of the neodymium-containing compound $Na_4(NH_4)_{10}[Nd_4(MoO_4)(Mo_7O_{24})_4]\cdot 34H_2O$ was published in 1997.[17]

In this paper we report the syntheses and structural characterisation of five new lanthanide containing polyoxomolybdates of the general structure $[(CH_3)_4N]_x[NH_4]_{14-x}[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot nH_2O$. Polyoxoanions of this type, which are isotypic with Yamase's europium compound, were prepared for Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III} and Gd^{III} and their complete crystal structures are reported here.

Results and Discussion

$[(CH_3)_4N]_x[NH_4]_{14-x}[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot nH_2O$ crystals (Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III}, Gd^{III}) were obtained from aqueous solution at a pH of about 5. The syntheses succeeded in a direct and straightforward way from an aqueous solution of heptamolybdate by addition of salts of the trivalent lanthanides in water. The inserted amounts of

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lanthanide ions in relation to heptamolybdate are not stoichiometric and vary from 1:5 for Ln = Sm^{III}, Ce^{III} and Pr^{III} to 2:5 for Ln = Gd^{III} and La^{III}. $[(CH_3)_4N]_{1.33}[NH_4]_{12.67}[La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 12H_2O$ (**1**), $[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 22H_2O$ (**4**) and $[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 16H_2O$ (**5**) crystallise in the cubic crystal system, space group $I\bar{4}3d$. The asymmetric unit consists of one quarter of the whole molecule, and the unit cell contains 12 anions. $[NH_4]_{14}[Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 36H_2O$ (**2**) crystallises in the triclinic crystal system, space group $P\bar{1}$, containing one formula unit per asymmetric unit and two formula units per unit cell. $[NH_4]_{14}[Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 29H_2O$ (**3**) crystallises in the monoclinic crystal system, space group $C2/c$. The asymmetric unit contains half a molecule and the unit cell includes four anions.

The five new heteromolybdate anions $[La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (anion in compound **1**), $[Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (anion in compound **2**), $[Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (anion in compound **3**), $[Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (anion in compound **4**) and $[Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ (anion in compound **5**) are isostructural to the europium-containing anion that is known from the literature.[15] Figure 1 shows the arrangement of the $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anion seen from two different directions.

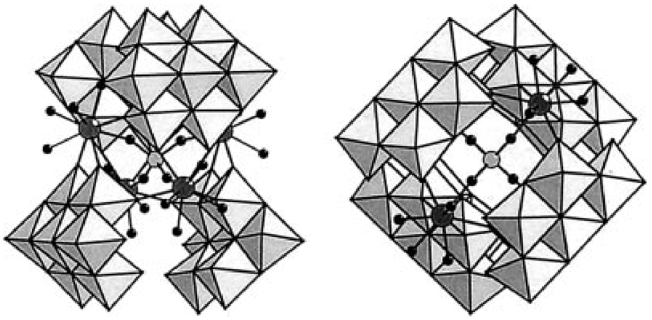

Figure 1. Polyhedron representation of the $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anion viewed in two different projections

All the examples of this type contain a centered molybdenum atom (Mo1) that is coordinated tetrahedrally by four oxygen atoms. The O−Mo1−O bond angles differ only slightly from the perfect tetrahedral angle. The bond lengths between Mo1 and the four oxygen atoms [1.75(1)−1.77(1) Å] show that these bonds have partial double-bond character. Each oxygen atom of the central $(MoO_4)^{2-}$ unit is bonded to a lanthanide atom; the corresponding Mo1−O bond lengths show that an exchange of lanthanide atoms has no influence on the dπ-pπ bonding between molybdenum and oxygen atoms.

Each of the four lanthanide atoms in the $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anion shows ninefold coordination by the oxygen atoms, approximating a tricapped trigonal prism, by attachment of one oxygen atom from the central $(MoO_4)^{2-}$ unit, four oxygen atoms from three $(Mo_7O_{24})^{6-}$ units and four oxygen atoms from four aqua ligands. The bond lengths and bond angles of the central $[Ln_4(MoO_4)(H_2O)_{16}]^{10+}$ unit (Ln = La^{III}, Ce^{III}, Pr^{III}, Sm^{III}, Eu^{III}, Gd^{III}) are given in Table 1 and 2. As shown in Table 2, all the lanthanide ions are coordinated by oxygen atoms in a very similar way. The observed decrease of Ln−O and Ln−OH$_2$ bond lengths in the series La > Ce > Pr > Sm > Eu > Gd is to be expected as an effect of the lanthanide contraction. The lanthanide atoms are well separated, with intramolecular Ln···Ln distances of between 6.28(1) and 7.67(1) Å for **1** and 6.15(1) and 7.50(1) Å for **5**. The decrease of these Ln···Ln distances is also an effect of the lanthanide contraction.

Figure 2 shows a schematic description of the $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anion. Each $(Mo_7O_{24})^{6-}$ unit can be regarded as a tetradentate ligand bonded to three lanthanide atoms. Two of the seven MoO$_6$ octahedra of the $(Mo_7O_{24})^{6-}$ unit provide two terminal oxygen atoms for the Ln−O bonds.

It has been shown by Evans et al. that a characteristic feature of the heptamolybdate anion in $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ is that all the MoO$_6$ octahedra contain two terminal or quasi-terminal bonds to oxygen atoms in *cis* positions.[18] This structural signature can also be found in the $(Mo_7O_{24})^{6-}$ units of all $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anions. The short Mo−O$_t$ bond lengths of the terminal and quasi-terminal oxygen atoms correspond well in the heptamolybdate anion and the $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ anions (Table 3). The coordination of the lanthanide cations by such terminal oxygen atoms does not lead to a significant expansion of these Mo−O bond lengths.

As well as the two short Mo−O bonds, each MoO$_6$ octahedron contains two intermediate Mo−O bonds and two long Mo−O bonds. The two long Mo−O bonds are located *trans* to the short Mo−O bonds and show Mo−O distances of between 2.09(1) Å and 2.51(1) Å (**1−5**) and 2.16(1) Å and 2.42(1) Å $[(NH_4)_6(Mo_7O_{24})\cdot 4H_2O]$. The intermediate Mo−O bonds show Mo−O distances of between 1.87(1) Å and 2.01(1) Å (compounds **1−5**) and 1.90(1) Å and 1.97(1) Å $[(NH_4)_6(Mo_7O_{24})\cdot 4H_2O]$.[18]

A comparison of the lanthanide-containing polyoxomolybdates **1−5** with the heptamolybdate anion in $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ given in Table 3 shows rather similar distances within the limits of error. The variation of the lanthanide atoms belonging to the central $[Ln_4(MoO_4)(H_2O)_{16}]^{10+}$ unit has no significant influence on the coordinating heptamolybdate units.

According to the required charge balance, 14 cations per formula unit are needed. Compounds **2** and **3** contain only ammonium counterions. In this case, the cations cannot be distinguished crystallographically from the water molecules. To achieve better crystallisation, tetramethylammonium ions were added during the preparation of **1**, **4** and **5**. Compounds **4** and **5** contain 3.33 of these counterions each, with the lanthanum-containing compound **1** only having 1.33 tetramethylammonium ions. The fractional numbers result from the special positions of carbon and nitrogen atoms in the unit cell. Elemental analyses validate the content of

Table 1. Comparison of selected Mo1−O, Ln···Ln, Ln−O and Ln−Ow[b] bond lengths with standard deviations of the anions $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ with Ln = $\mathrm{La^{III}}$, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, $\mathrm{Sm^{III}}$, $\mathrm{Eu^{III}}$,[15] $\mathrm{Gd^{III}}$

Mo1−O (Å)		Ln···Ln (Å)		Ln−O (Å)		Ln−Ow (Å)	
$\mathrm{Mo1{-}O_{LaMo}}$ [a]	1.76(1)	La···La	6.28(1)−7.67(1)	La−O	2.46(1)−2.57(1)	La−Ow[b]	2.53(1)−2.68(1)
$\mathrm{Mo1{-}O_{CeMo}}$[a]	1.75(1)−1.76(1)	Ce···Ce	6.25(1)−7.61(1)	Ce−O	2.44(1)−2.46(1)	Ce−Ow[b]	2.52(1)−2.65(1)
$\mathrm{Mo1{-}O_{PrMo}}$[a]	1.76(1)−1.77(1)	Pr···Pr	6.23(1)−7.60(1)	Pr−O	2.42(1)−2.52(1)	Pr−Ow[b]	2.51(1)−2.62(1)
$\mathrm{Mo1{-}O_{SmMo}}$[a]	1.77(1)	Sm···Sm	6.19(1)−7.55(1)	Sm−O	2.38(1)−2.50(1)	Sm−Ow[b]	2.44(1)−2.61(1)
$\mathrm{Mo1{-}O_{EuMo}}$[a]	1.76(2)−1.77(1)	Eu···Eu	6.17(1)−7.51(1)	Eu−O	2.38(1)−2.48(2)	Eu−Ow[b]	2.43(2)−2.59(2)
$\mathrm{Mo1{-}O_{GdMo}}$[a]	1.76(1)−1.77(1)	Gd···Gd	6.15(1)−7.50(1)	Gd−O	2.36(1)−2.47(1)	Gd−Ow[b]	2.40(1)−2.63(1)

[a] The subscripts indicate the atoms bonded to the oxygen atom. [b] Ow = oxygen atom of a water molecule.

Table 2. Comparison of O−Mo1−O and O−Ln−O bond angles with standard deviations of the anions $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ with Ln = $\mathrm{La^{III}}$, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, $\mathrm{Sm^{III}}$, $\mathrm{Eu^{III}}$,[15] $\mathrm{Gd^{III}}$

Anion	O−Mo1−O (°)	O−Ln−O (°)	O−Ln−Ow[a] (°)	Ow−Ln−Ow[a] (°)
$[\mathrm{La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	109.1(2)−110.3(4)	68.1(2)−136.7(2)	65.0(2)−143.0(2)	66.9(2)−131.4(3)
$[\mathrm{Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	109.3(4)−110.2(4)	68.7(3)−136.3(3)	65.5(3)−141.1(3)	67.8(3)−138.3(4)
$[\mathrm{Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	108.6(6)−110.0(4)	68.9(3)−136.7(3)	66.4(3)−140.8(3)	67.7(4)−134.5(4)
$[\mathrm{Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	108.7(2)−110.0(3)	68.4(2)−137.2(2)	65.3(2)−142.5(2)	67.3(2)−132.6(2)
$[\mathrm{Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	108.0(7)−110.2(8)	69.4(6)−136.8(6)	67.1(6)−140.4(6)	66.9(6)−135.3(6)
$[\mathrm{Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	109.0(2)−110.4(4)	70.2(2)−137.2(2)	65.6(2)−143.1(2)	67.4(3)−131.9(3)

[a] Ow = oxygen atom of a water molecule.

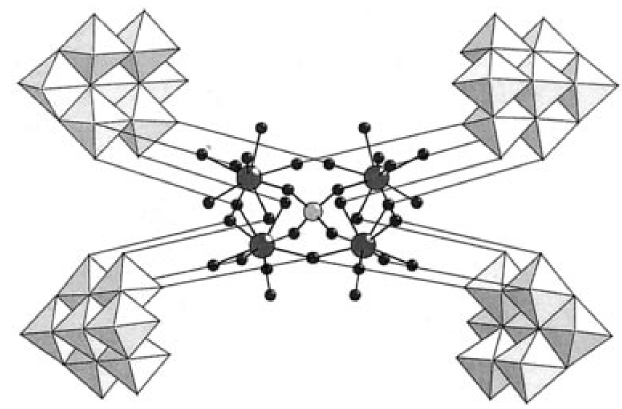

Figure 2. Schematic presentation of the $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ anion

ammonium and tetramethylammonium ions. There is no evidence for protonation of the crystal water molecules or the $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ anions.

The spectroscopic data of all $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ anions show great similarities in the most important bands of the IR and Raman spectra. The characteristic region of the Mo−O vibrations in the Raman spectra are observed in the region between 1000 and 800 $\mathrm{cm^{-1}}$ for all analysed compounds. In the IR spectra the characteristic $\mathrm{Mo{-}O_t}$ bands are observed around 893 $\mathrm{cm^{-1}}$.

Conclusion

The selective and aimed syntheses of five novel lanthanide-containing polyoxomolybdates $[\mathrm{(CH_3)_4N}]_x[\mathrm{NH_4}]_{14-x}[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]\cdot n\mathrm{H_2O}$ **(1−5)** are reported.

Table 3. Mo−O-bond lengths with standard deviations of the heptamolybdate unit of the $[\mathrm{Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$ anion with Ln = $\mathrm{La^{III}}$, $\mathrm{Ce^{III}}$, $\mathrm{Pr^{III}}$, $\mathrm{Sm^{III}}$, $\mathrm{Eu^{III}}$,[15] $\mathrm{Gd^{III}}$ and the heptamolybdate anion in $\mathrm{(NH_4)_6(Mo_7O_{24})\cdot 4H_2O}$[18]

	Region of Mo−O bond lengths (Å)		
Anion	Short bond	Intermediate bond	Long bond
$[\mathrm{La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.70(1)−1.75(1)	1.88(1)− 2.00(1)	2.11(1)−2.48(1)
$[\mathrm{Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.68(1)−1.74(1)	1.87(1)−1.99(1)	2.09(1)−2.51(1)
$[\mathrm{Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.67(1)−1.74(1)	1.88(1)−2.00(1)	2.12(1)−2.50(1)
$[\mathrm{Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.71(1)−1.74(1)	1.89(1)−1.99(1)	2.12(1)−2.48(1)
$[\mathrm{Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.68(2)−1.75(2)	1.88(3)−1.99(3)	2.13(3)−2.54(2)
$[\mathrm{Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4}]^{14-}$	1.70(1)−1.74(1)	1.89(1)−2.01(1)	2.12(1)−2.50(1)
$[\mathrm{Mo_7O_{24}}]^{6-}$	1.71(1)−1.75(1)	1.90(1)−1.97(1)	2.16(1)−2.42(1)

All compounds were completely characterised by X-ray structure analysis. The $[Ln_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]^{14-}$ clusters are built up by a central $[Ln_4(MoO_4)(H_2O)_{16}]^{10+}$ unit surrounded by four heptamolybdate groups, each of which can be regarded as a tetradentate ligand. The building blocks are connected by four lanthanide atoms which are coordinated by nine oxygen atoms. Investigations of the oxidation catalysis and anti-tumour and anti-HIV activity of the present compounds are in progress.

Experimental Section

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

$[(CH_3)_4N]_{1.33}[NH_4]_{12.67}[La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 12H_2O$ (1): $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ (0.93 g, 0.75 mmol) was dissolved in 20 mL of water, and 1 mL of CH_3OH was added. An aqueous solution (5 mL) containing $La(NO_3)_3\cdot 6H_2O$ (0.13 g, 0.3 mmol) was added dropwise to the above solution with stirring at room temperature. $(NMe_4)Br$ solution (0.5 mL; 1 M in water) was added to the resulting solution (pH ≈ 5). The reaction vessel was kept closed at room temperature for 48 h. Colorless single crystals were obtained from the solution. Yield: 0.37 g (86% based on La). $C_{5.33}H_{122.67}La_4Mo_{29}N_{14}O_{128}$ (5769.6): calcd. C 1.11, H 2.14, N 3.40; found C 1.06, H 2.22, N 3.43. IR data (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (s) [ν(O−H)]; 1614 (s) [δ(N−H)]; 1389 (s) [δ(O−H)]; 941 (m); 893 (s) [ν(Mo-O$_t$)]; 621 (s) [ν(Mo-O)]; 488 (w). Raman data: $\tilde{\nu}$ = 946 cm^{-1} (s) (Mo-O$_t$); 891 (m); 863 (w); 363 (w); 222 (m). EDAX: calcd. Mo:La = 7.25:1; found Mo:La = 7.36:1.

$[NH_4]_{14}[Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 36H_2O$ (2): $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ (0.93 g, 0.75 mmol) was dissolved in 9 mL of water, and 1 mL of CH_3OH was added. An aqueous solution (5 mL) containing $CeCl_3\cdot 7H_2O$ (0.056 g, 0.15 mmol) was added dropwise to the above solution with stirring at room temperature. The resulting solution (pH ≈ 5) was kept in a closed reaction flask at 278 K for 18 h. Red single-crystals were obtained from the solution. Yield: 0.18 g (78% based on Ce). $H_{160}Ce_4Mo_{29}N_{14}O_{152}$ (6132.5): calcd. H 2.63, N 3.20; found H 2.61, N 3.17. IR data (KBr): $\tilde{\nu}$ = 3142 cm^{-1} (s, br) [ν(O−H)]; 1620 (m) [δ(OH$_2$)]; 1401 (s) [δ(NH$_4$)]; 893 (s, br) [ν(Mo-O$_t$)]; 634 (m, br) [ν(Mo-O)]; 486 (w). Raman data: $\tilde{\nu}$ = 944 cm^{-1} (s) (Mo-O$_t$); 916 (m); 860 (w); 364 (w); 219 (m). EDAX: calcd. Mo:Ce = 7.25:1; found Mo:La = 6.56:1.

$[NH_4]_{14}[Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 29H_2O$ (3): This compound was prepared similarly to **2**, with $Pr(NO_3)_3\cdot 5H_2O$ (0.062 g, 0.15 mmol) instead of $CeCl_3\cdot 7H_2O$. Green single-crystals were ob-

Table 4. Crystallographic data for $[(CH_3)_4N]_{1.33}[NH_4]_{12.67}[La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 12H_2O$ (**1**), $[NH_4]_{14}[Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 36H_2O$ (**2**), $[NH_4]_{14}[Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 29H_2O$ (**3**), $[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 22H_2O$ (**4**) and $[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 16H_2O$ (**5**)

	1	2	3	4	5
Formula	$La_4Mo_{29}O_{128}N_{14}C_{5.33}H_{122.67}$	$Ce_4Mo_{29}O_{152}N_{14}H_{160}$	$Pr_4Mo_{29}O_{145}N_{14}H_{146}$	$Sm_4Mo_{29}O_{138}N_{14}C_{13.33}H_{158.67}$	$Gd_4Mo_{29}O_{132}N_{14}C_{13.33}H_{146.67}$
Mol. mass (g/mol)	5769.56	6132.15	6009.06	6107.79	6027.25
Crystal color/habit	colorless rhombic crystals	red rhombic crystals	light-green rhombic crystals	light-yellow rhombic crystals	colorless rhombic crystals
Crystal size (mm)	0.22 × 0.18 × 0.16	0.15 × 0.10 × 0.10	0.15 × 0.10 × 0.10	0.26 × 0.15 × 0.14	0.48 × 0.44 × 0.40
Crystal system	cubic	triclinic	monoclinic	cubic	cubic
Space group	$I\bar{4}3d$	$P\bar{1}$	$C2/c$	$I\bar{4}3d$	$I\bar{4}3d$
a (Å)	35.800(4)	17.121(3)	19.781(4)	35.533(4)	35.487(4)
b (Å)	35.800(4)	19.914(4)	43.872(9)	35.533(4)	35.487(4)
c (Å)	35.800(4)	24.328(5)	20.454(4)	35.533(4)	35.487(4)
α (°)	90	84.96(3)	90	90	90
β (°)	90	87.65(3)	117.28(3)	90	90
γ (°)	90	65.25(3)	90	90	90
V (Å^3)	45884(9)	7503.5(25)	15776.2(55)	44864(9)	44689(9)
Z	12	2	4	12	12
$d_{\text{calcd.}}$ (g/cm^3)	2.463	2.666	2.538	2.651	2.631
μ (mm^{-1})	3.485	3.639	3.542	4.003	4.217
T (K)	173	213	293	173	213
Measured refl.	237745	41899	36455	234219	163082
Independent refl.	9506	21826	9805	9261	7229
Unique refl. [$I > \sigma(I)$]	9160	16012	8099	9256	7008
R_{int}	0.0574	0.0508	0.1187	0.046	0.2026
Refined parameters	392	1673	854	425	427
2θ range (°)	4.24 < 2θ < 56.69	8 < 2θ < 48	8 < 2θ < 46	5.21 < 2θ < 56.6	8.1 < 2θ < 52.1
R [$I > 2\sigma(I)$]	R_1 = 0.0437[a] wR_2 = 0.1106[b]	R_1 = 0.0550[a] wR_2 = 0.1218[b]	R_1 = 0.0576[a] wR_2 = 0.1480[b]	R_1 = 0.0339[a] wR_2 = 0.0864[b]	R_1 = 0.0566[a] wR_2 = 0.1004[b]
R (all data)	R_1 = 0.0469[a] wR_2 = 0.1145[b]	R_1 = 0.0853[a] wR_2 = 0.1443[b]	R_1 = 0.0744[a] wR_2 = 0.1874[b]	R_1 = 0.0339[a] wR_2 = 0.0864[b]	R_1 = 0.0579[a] wR_2 = 0.1014[b]
Goof[c]	1.092	1.106	1.047	1.236	1.038
$(\Delta\rho)_{\max}$ (e$^-$/Å^3)	2.57	1.24	1.39	1.42	1.02
$(\Delta\rho)_{\min}$ (e$^-$/Å^3)	−1.81	−2.98	−2.46	−1.76	−1.24

[a] $R_1 = \Sigma||F_{\text{obsd.}}| - |F_{\text{calcd.}}||/\Sigma|F_{\text{obsd.}}|$. [b] $wR_2 = \{\Sigma[w(F_{\text{obsd.}}^2 - F_{\text{calcd.}}^2)^2]/\Sigma[w(F_{\text{obsd.}}^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + xP + (yP)^2]$; with $P = (F_o^2 + 2F_c^2)/3$ and x = 1053.774, y = 0.0532 (**1**), x = 0.0000, y = 0.0437 (**2**); x = 578.45, y = 0.085 (**3**); x = 792.964, y = 0.0314 (**4**); x = 926.793, y = 0.0597 (**5**). [c] goof = $[\Sigma w(F_{\text{obsd.}}^2 - F_{\text{calcd.}}^2)^2/(n-p)]^{1/2}$, where n = number of reflections, p = parameter used.

tained from the solution after 18 h. Yield: 0.18 g (80% based on Pr). $H_{146}Mo_{29}N_{14}O_{145}Pr_4$ (6009.1): calcd. H 2.45, N 3.26; found H 2.49, N 3.17. IR data (KBr): $\tilde{\nu}$ = 3152 cm^{-1} (s, br) [ν(O−H)]; 1621 (m) [δ(OH_2)]; 1401 (s) [δ(NH_4)]; 939 (w); 893 (s, br) [ν(Mo-O_t)]; 634 (m, br) [ν(Mo-O)]; 485 (w). Raman data: $\tilde{\nu}$ = 945 cm^{-1} (s) (Mo-O_t); 922 (m); 860 (w); 365 (w); 219 (m). EDAX: calcd. Mo:Pr = 7.25:1; found Mo:Pr = 7.09:1.

$[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 22H_2O$ (4): $(NH_4)_6(Mo_7O_{24})\cdot 4H_2O$ (0.93 g, 0.75 mmol) was dissolved in 20 mL of water, and 1 mL of CH_3OH was added. An aqueous solution (5 mL) containing $Sm(NO_3)_3\cdot 6H_2O$ (0.07 g, 0.15 mmol) was added dropwise to the above solution while stirring at room temperature. $(NMe_4)Br$ solution (0.5 mL; 1 M in water) was added to the resulting solution (pH ≈ 5). The reaction flask was kept closed at 278 K for 24 h. Light-yellow single-crystals were obtained from the solution. Yield: 0.19 (83% based on Sm). $C_{13.33}H_{158.67}Mo_{29}N_{14}O_{138}Sm_4$ (6107.8): calcd. C 2.62, H 2.62, N 3.21; found C 2.55, H 2.44, N 3.17. IR data (KBr): $\tilde{\nu}$ = 3135 cm^{-1} (s) [ν(O−H)]; 1622 (s) [δ(N−H)]; 1385 (s) [δ(O−H)]; 941 (m); 894 (s) [ν(Mo-O_t)]; 629 (s) [ν(Mo-O)]; 485 (w). Raman data: $\tilde{\nu}$ = 951 cm^{-1} (s) (Mo-O_t); 897 (w); 862 (w); 368 (w); 219 (w). EDAX: calcd. Mo:Sm = 7.25:1; found Mo:Sm = 7.53:1.

$[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 16H_2O$ (5): This compound was prepared similarly to **1**, with $Gd(NO_3)_3\cdot 5H_2O$ (0.013 g, 0.30 mmol) instead of $La(NO_3)_3\cdot 6H_2O$. Colorless single-crystals were obtained from the solution after 24 h. Yield: 0.31 g (69% based on Gd). $C_{13.33}H_{146.67}Gd_4Mo_{29}N_{14}O_{132}$ (6027.3): calcd. C 2.65, H 2.45, N 3.25; found C 2.45, H 2.37, N 3.23. IR data (KBr): $\tilde{\nu}$ = 3422 cm^{-1} (s) [ν(O−H)]; 1626 (s) [δ(N−H)]; 1408 (s) [δ(O−H)]; 941 (m); 893 (s) [ν(Mo-O_t)]; 634 (s) [ν(Mo-O)]; 485 (w). Raman data: $\tilde{\nu}$ = 951 cm^{-1} (s) (Mo-O_t); 921 (m); 895 (w); 865 (w); 370 (w); 220 (w). EDAX: calcd. Mo:Gd = 7.25:1; found Mo:Gd = 7.79:1.

Instrumentation and Analytical Procedures: IR spectra were measured on a Perkin−Elmer 683 spectrometer as KBr pellets. Elemental analyses were carried out on an Elementar Vario EL III analyzer. The atomic ratios of the heavy elements were determined by energy-dispersive X-ray fluorescence analysis (EDAX).

Diffraction experiments were performed on a STOE IPDS imaging plate system (for **1**, **2** and **3**) and a Bruker Smart Apex diffractometer with CCD detector (for **4** and **5**), both using Mo-K_α radiation (λ = 0.71073 Å). Structures were solved by direct methods with SHELXS-97 and refined with SHELXL-97.[19] No hydrogen atoms were included. The nitrogen atoms of the ammonium cations were modeled as oxygen atoms because nitrogen atoms could not be distinguished from oxygen atoms.

All atoms except the oxygen atoms belonging to water molecules were refined anisotropically by full-matrix least-squares calculations based on F^2. As usual for polyoxometalates, the crystal structures show disorder in the counterions and crystal water part of the structure. The details of data collection and refinement are summarised in Table 4.

Further details on the crystal structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldhafen, Germany [Fax: +49-(0)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de], on quoting the depository number CSD-413732 (for **1**), -413730 (for **2**), -413733 (for **3**), -413734 (for **4**) or -413731 (for **5**).

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