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One-, Two-, and Three-Dimensional Coordination Polymers Built from Large Mo_{36}-Polyoxometalate Anionic Units and Lanthanide Cations

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The Mo_{36}-polyoxometalate $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$ reacts with Ln^{3+} to give crystalline solids with 1D, 2D, and 3D polymeric frameworks, depending on the size of Ln^{3+} and the reaction conditions. Reaction of $LaCl_3$ with $(NH_4)_{12}[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]$ gives $(H_3O)_2[\{La(H_2O)_5\}_2\{La(H_2O)_6\}\{La(H_2O)_5Cl\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl\cdot21H_2O$ (**1**), in whose structure the La^{3+} cations and the polyoxometalate anions are united in a 3D framework, whereas $NdCl_3$ and $SmCl_3$ give $[\{Ln(H_2O)_6\}_4\{Ln(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl_3\cdot nH_2O$ [Ln = Nd, n = 24 (**2**); Ln = Sm, n = 21 (**3**)], which have 2D frameworks. Under different conditions, large Ln^{3+} ions (La–Nd) give the one-dimensional coordination polymers $[\{Ln(H_2O)_6\}_2\{Ln(H_2O)_7\}_2\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot nH_2O$ [Ln = La, n = 29 (**4**); Ln = Ce, n = 41 (**5**), Ln = Pr; n = 40 (**6**), Ln = Nd, n = 36 (**7**)], whereas reaction with $Gd(NO_3)_3$ gives $[\{Gd(H_2O)_5\}_4\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot34H_2O$ (**8**), which has a unique 2D layered structure. Smaller Ln^{3+} ions (Tb–Lu) give isostructural 1D chain coordination polymers $(H_3O)_3[\{Ln(H_2O)_6\}_2\{Ln(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot nH_2O$ [Ln = Tb, n = 42 (**9**); Ln = Dy, n = 43 (**10**), Ln = Ho, n = 46 (**11**), Ln = Er, n = 50 (**12**); Ln = Yb, n = 56 (**13**); Ln = Lu, n = 31 (**14**)]. The first coordination polymer based on $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, namely $(H_3O)_2[\{Nd(H_2O)_5\}_2\{Mo_{36}O_{112}(H_2O)_{16}\}]\cdot40H_2O$ (**15**), was prepared from MoO_4^{2-}, NH_2OH, and Nd^{3+}. It has a 2D layered structure. All these compounds are obtained in moderate to high yields (35–93 %), and were characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray structural analysis. Direct coordination of Ln^{3+} to the oxygen atoms of terminal *cis*-MoO_2^{2+} groups is responsible for the formation of these polymeric frameworks. The coordination numbers of Ln^{3+} change from 9 (La–Sm) to 8 (Gd–Lu).

Introduction

Giant polyoxometalates (POMs) are relatively recent but increasingly fascinating objects of study owing to their potential applications in catalysis, photochemistry, sorption, magnetism, medicine, etc.[1–5] Furthermore, they are attractive building blocks for the design of new one-, two-, and three-dimensional frameworks in new functional materials because they possess both well-defined tunable structures and properties and can act as macroligands toward heterometals.[6,7] The heterometal can bring into play its own properties, such as magnetism. The oxophilic and paramagnetic lanthanide ions are especially well suited for these purposes[8,9] as they also may serve as luminescent[10–16] and Lewis acid catalytic centers.[17] Organic linkers between the lanthanide centers can also be inserted, giving rise to new hybrid organic–inorganic polymeric frameworks.[18] Lanthanide complexes of $[SiW_{11}O_{39}]^{8-}$ and $[P_2W_{17}O_{61}]^{10-}$, for example, show antiviral activity against HIV virus,[19] and there are some examples of using Anderson[20] $\{[Al(OH)_6Mo_6O_{18}]^{3-}\}$ and Keggin[21–23] $\{[XM_{12}O_{40}]^{n-}$, $[Mo_8O_{27}]^{6-}$,[24] $[Mo_9O_{30}]^{6-}$,[25] $[V_{18}O_{42}(X)]^{n-}$,[26–30] and $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}\}$ anions[31–32] as building blocks for inorganic polymers.

Herein we report a series of new compounds (**1**–**15**) with one-, two-, and three-dimensional extended structures, which were obtained by linking large Mo_{36}-polyoxometalate anionic units by lanthanide cations.

Results and Discussion

Syntheses

Orange rhombic crystals of **1**–**3** and **5**–**14** were prepared from the ammonium salt of the polyoxomolybdate $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ and the corresponding Ln^{3+} salts in a 1:4 molar ratio in moderate to high yields by the synthetic procedures described in the Experimental Section. The reactions generally occur in a straightforward manner, although only in the case of La (**1**), Ce (**5**), Pr (**6**), Nd (**7**, synthesis 2), and Gd (**8**) does the Ln/POM ratio in the product correspond to the reagent ratio. The counterion of the

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Ln salts sometimes enters the final product, as in **1**–**3**, but more often does not influence the final composition: chlorides, nitrates, and sulfates were used for the preparation of isostructural compounds **9**–**14** with equal efficiency. Some of the isolated solids could actually be metastable phases and sometimes longer crystallization times led to different products (as in the case of **1** and **4**). The POM building blocks $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ or $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ can also be generated in situ, and the compounds **4**, **7** (synthesis 1), and **15** were obtained by refluxing the mixture of $Na_2MoO_4{\cdot}2H_2O$ and $NH_2OH{\cdot}HCl$ at pH ≈ 2, followed by addition of $LaCl_3{\cdot}7H_2O$ or $NdCl_3{\cdot}6H_2O$. In the case of Nd, longer refluxing followed by slow cooling and crystallization below room temperature led to NO-free $(H_3O)_2[\{Nd(H_2O)_5\}_2\{Mo_{36}O_{112}(H_2O)_{16}\}]{\cdot}40H_2O$ (**15**). The Gd compound **8**, which was previously obtained by reaction of the ammonium salt of keplerate, $[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(CH_3COO)\}_{30}]^{42-}$, with $Gd(NO_3)_3$,[33] was obtained from $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ and Gd^{3+} in a more straightforward manner.

The compounds were characterized by elemental analysis and FT-IR spectroscopy. Compounds **1**–**14** and the parent $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]{\cdot}36H_2O$ have similar FT-IR spectra, showing only slight shifts in some band positions. All spectra show characteristic absorption bands attributable to H_2O, $\nu(Mo–O_{term})$, $\nu(Mo–\{\mu_2\text{-}O\})$, and $\nu(Mo–\{\mu_3\text{-}O\})$ groups. The $\nu(NO)$ vibrational frequency of 1617 cm^{-1} overlaps with $\delta(HOH)$ and is typical for the linear $\{MoNO\}^{3+}$ moiety.[34] There are three types of water in compounds **1**–**15**: water of crystallization, water coordinated to Ln^{3+}, and water attached to the POM anion. Theoretically, it should be possible to follow the water loss by TGA and to discriminate between the types of water leaving the structure. However, our preliminary experiments showed only one nondifferentiated step for water loss over a wide temperature range.

Structures

The structures of compounds **1**–**15** were determined by single-crystal X-ray diffraction. The main bond lengths and angles are given as Supporting Information. The structures show remarkable diversity, being 1D, 2D, or 3D, neutral or anionic frameworks where the discrete POM fragments $\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}$ (for **1**–**14**) or $\{Mo_{36}O_{112}(H_2O)_{16}\}$ (for **15**) are united by $\{Ln(H_2O)_n\}$ units depending on the identity of Ln^{3+}. The coordination environment of the lanthanide cations in **1**–**15** is summarized in Table 1.

The polyoxomolybdate anions $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ $\{Mo_{36}(NO)_4\}$, and $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ $\{Mo_{36}\}$,[34,35] which serve as building blocks, are built of two $\{Mo_{17}\}$ subunits that are joined together by two $MoO_2{}^{2+}$ groups. There are two MoL^{n+} groups (L = NO, n = 3; or L = O, n = 4) within each subunit with pentagonal-bipyramidal coordination, surrounded by five MoO_6 octahedra: three are derived from MoO^{4+} and two from *cis*-

Table 1. Coordination environment of the lanthanide cations in **1**–**15**.

Compound and type of Ln atom		CN	Polyhedra type	Coordination type
$\{La_4Mo_{36}(NO)_4\_3D\}$ (**1**)	La1	9	triply capped trigonal prism	$O^A{}_2O^C{}_1O^D{}_1O^W{}_5$
	La2	9	triply capped trigonal prism	$O^A{}_2O^B{}_1O^W{}_6$
	La3	9	distorted triply capped trigonal prism	$O^A{}_2O^B{}_1O^W{}_5Cl$
$\{Nd_5Mo_{36}(NO)_4\}$ (**2**)	Nd1	9	triply capped trigonal prism	$O^A{}_2O^B{}_1O^W{}_6$
	Nd2	9	triply capped trigonal prism	$O^C{}_2O^W{}_7$
$\{Sm_5Mo_{36}(NO)_4\}$ (**3**)	Sm1	9	triply capped trigonal prism	$O^A{}_2O^B{}_1O^W{}_6$
	Sm2	9	triply capped trigonal prism	$O^C{}_2O^W{}_7$
$\{La_4Mo_{36}(NO)_4\_1D\}$ (**4**)	La1	9	triply capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_6$
	La2	9	distorted triply capped trigonal prism	$O^A{}_2O^W{}_7$
$\{Ce_4Mo_{36}(NO)_4\}$ (**5**)	Ce1	9	triply capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_6$
	Ce2	9	distorted triply capped trigonal prism	$O^A{}_2O^W{}_7$
$\{Pr_4Mo_{36}(NO)_4\}$ (**6**)	Pr1	9	triply capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_6$
	Pr2	9	distorted triply capped trigonal prism	$O^A{}_2O^W{}_7$
$\{Nd_4Mo_{36}(NO)_4\}$ (**7**)	Nd1	9	triply capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_6$
	Nd2	9	distorted triply capped trigonal prism	$O^A{}_2O^W{}_7$
$\{Gd_4Mo_{36}(NO)_4\}$ (**8**)	Gd1	8	doubly capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_5$
	Gd2	8	doubly capped trigonal prism	$O^A{}_2O^C{}_1O^W{}_5$
$\{Tb_3Mo_{36}(NO)_4\}$ (**9**)	Tb1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Tb2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Dy_3Mo_{36}(NO)_4\}$ (**10**)	Dy1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Dy2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Ho_3Mo_{36}(NO)_4\}$ (**11**)	Ho1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Ho2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Er_3Mo_{36}(NO)_4\}$ (**12**)	Er1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Er2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Yb_3Mo_{36}(NO)_4\}$ (**13**)	Yb1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Yb2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Lu_3Mo_{36}(NO)_4\}$ (**14**)	Lu1	8	dodecahedron	$O^A{}_4O^W{}_4$
	Lu2	8	distorted square antiprism	$O^A{}_2O^W{}_6$
$\{Nd_2Mo_{36}O_{112}\}$ (**15**)	Nd	9	triply capped trigonal prism	$O^A{}_4O^W{}_5$

MoO_2^{2+}. These six Mo atoms form a five-pointed star. Two such stars are held together by two pairs of edge-sharing octahedra (*cis*-MoO_2^{2+} type), and by one "inner" Mo atom with no terminal oxygen atoms, and are also octahedrally coordinated. Only the terminal MoO_2^{2+} groups coordinate lanthanide cations, and altogether 16 terminal oxygen atoms of $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ can participate in this bonding. For the sake of simplicity we will call the two octahedra attached to the $Mo(NO)^{3+}$ unit as "coordinated" (type A), those in the dimer that hold two "stars" together in each subunit as "peripheral" (type B), those holding two $\{Mo_{17}\}$ subunits together as "closing" (type C), and the MoO_2^{2+} units in the dimer that hold two "stars" together in each subunit as "inner" (type D; Figure 1). Two neighboring A-type MoO_2^{2+} groups always behave as a bidentate ligand, while the others are monodentate.

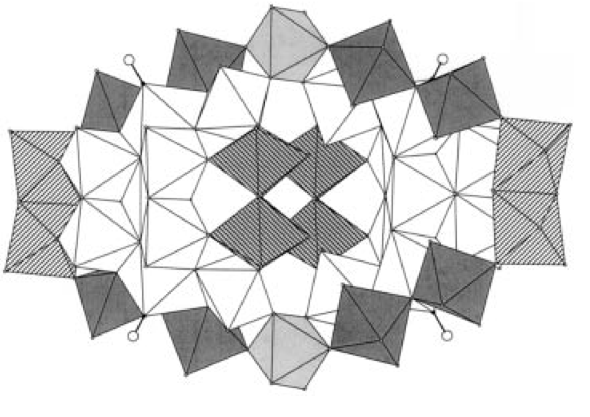

Figure 1. The structure of building block $[Mo_{36}L_4O_{108}(H_2O)_{16}]^{n-}$ (L = NO, $n = 12$; L = O, $n = 8$). Representation in polyhedra: dark-grey: type A octahedra; hatched white: type B octahedra; light-grey: type C octahedra; hatched dark-grey: type D octahedra; white: the remaining polyhedra.

The compound $(H_3O)_2[\{La(H_2O)_5\}_2\{La(H_2O)_6\}\text{-}\{La(H_2O)_5Cl\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl\cdot 21H_2O$ (**1**) is the only one in this series with a 3D-framework structure. Each POM anion is coordinated by 10 La^{3+} cations through 14 oxygen atoms. In turn, these 10 La^{3+} cations join each polyoxoanion with another eight POM anions. All possibilities for coordination of the POM anion to La^{3+} are realized in **1**: through oxygen atoms of A-type groups (eight atoms of four "bidentate ligands"), B-type groups (two atoms), C-type (two atoms), and D-type groups (two atoms). In fact, **1** is the only example of a $\{Mo_{36}(NO)_4\}$-based polymer compound where oxygen atoms of D-type groups take part in coordination to the lanthanide cation. There are two types of La^{3+} cations, with two of each type for every POM fragment. Cations of the first type ensure the binding together of POM building blocks along the crystallographic axes *a* and *b*. Each POM is coordinated by six La cations of this type, such that an A-MoO_2^{2+}–La^{3+}–D-MoO_2^{2+} sequence runs along the *a* axis, while in the other direction (along the *b* axis) the pattern of the sequence is C-MoO_2^{2+}–La^{3+}–D-MoO_2^{2+} and C-MoO_2^{2+}–La^{3+}–A-MoO_2^{2+} (Figure 2). Thus, one La^{3+} cation joins together three POM fragments to form pseudo-layers packed along the crystallographic *c* axis. Four oxygen atoms of type A, two of type C, and two of type D take part in this coordination for each POM fragment. Cations of the second type join together the aforementioned "layers" in a 3D framework along the diagonal between the crystallographic *a* and *c* axes in ay A-MoO_2^{2+}–La^{3+}–B-MoO_2^{2+} sequence. Each POM is coordinated by four La^{3+} cations of this type. Four oxygen atoms of an A-type group (as two "bidentate ligands") and two oxygens of two B-type groups, which are joined together in pairs by an inversion center, participate in this bonding. Every two neighboring POM fragments are bound together by two La cations of this type (Figure 3). Lanthanum cations of this type are disordered over two positions in such a way that in the first position La^{3+} additionally coordinates six water molecules and in the other position five water molecules and one Cl^- anion. There are two types of solvent water molecules in **1**. Two water molecules are clathrated in the inner cavity of the POM whereas the others lie in the voids of framework. There is an extended network of hydrogen bonds involving water molecules and oxygen atoms of the cluster.

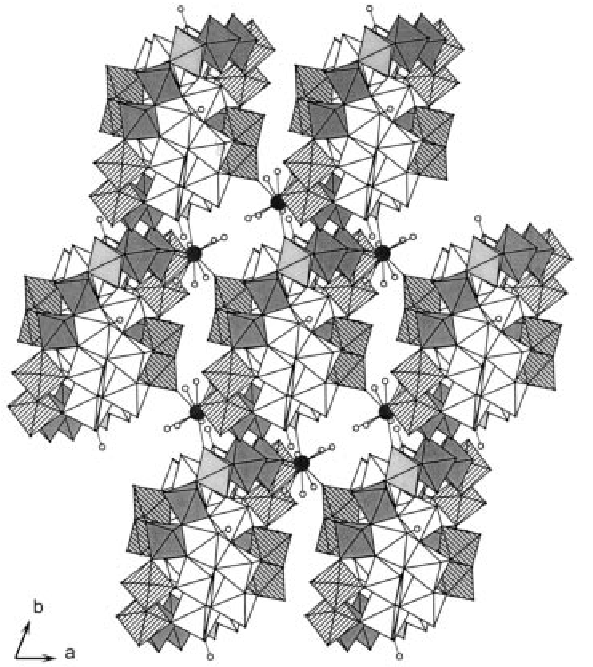

Figure 2. Connectivity pattern in the crystal structure of compound **1** in the *ab* plane. $\{La(H_2O)_5\}$ fragments in ball-and-stick representation (La: dark-grey; O: white); polyoxometalate fragments as polyhedra (for "color" legend see Figure 1).

Compounds $[Nd_5Mo_{36}(NO)_4]$ (**2**), $[Sm_5Mo_{36}(NO)_4]$ (**3**), $[Gd_4Mo_{36}(NO)_4]$ (**8**), and $[Nd_2Mo_{36}]$ (**15**) have different 2D-network structures. The networks in **2** and **3** are isostructural. Each POM anion is coordinated by ten lanthanide cations through fourteen oxygen atoms. In turn, the latter join it to another six POM anions (Figure 4). There are two types of Ln^{3+} in the structure: one is disordered

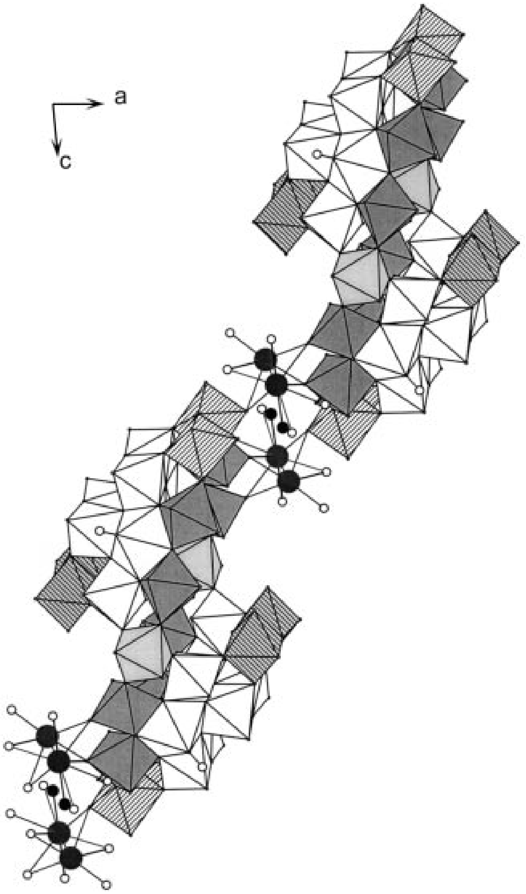

Figure 3. Connectivity pattern in the crystal structure of compound **1** along the diagonal between the crystallographic *a* and *c* axes. Lanthanum cations are disordered over two positions. $\{La(H_2O)_5Cl\}$ and $\{La(H_2O)_6\}$ fragments in ball-and-stick representation (La: dark-grey; O: white; Cl: black); polyoxometalate fragments as polyhedra (for “color” legend see Figure 1).

and coordinates oxygens of C-type groups of two adjacent $\{Mo_{36}(NO)_4\}$ units, whereas the other coordinates oxygen atoms of A-type groups of one POM unit and oxygen atoms of B-type groups of a neighboring POM. Thus, a layered structure forms with a C-MoO_2^{2+}–Ln^{3+}–C-MoO_2^{2+} sequence along the *b* axis and an A-MoO_2^{2+}–Ln^{3+}–B-MoO_2^{2+} sequence along the diagonal between the *b* and *c* axes (Ln = Nd and Sm; Figure 5).

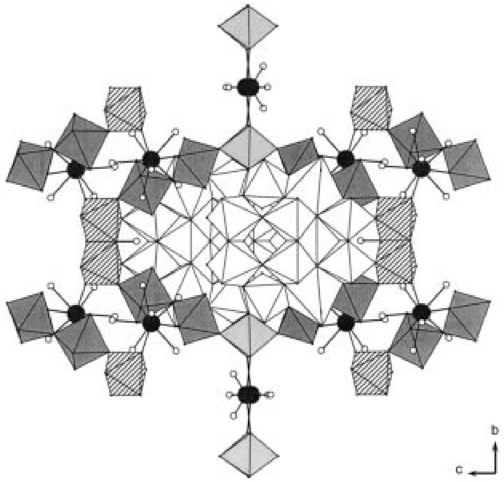

Figure 4. Connectivity pattern in the crystal structure of compounds **2** and **3**. $\{Ln(H_2O)_n\}$ fragments in ball-and-stick representation (Ln: dark-grey; O: white) and $\{Mo_{36}(NO)_4\}$ fragments as polyhedra (for “color” legend see Figure 1).

The structure of $[Gd_4Mo_{36}(NO)_4]$ (**8**) was described in detail in our previous work.[33] This compound was ob-

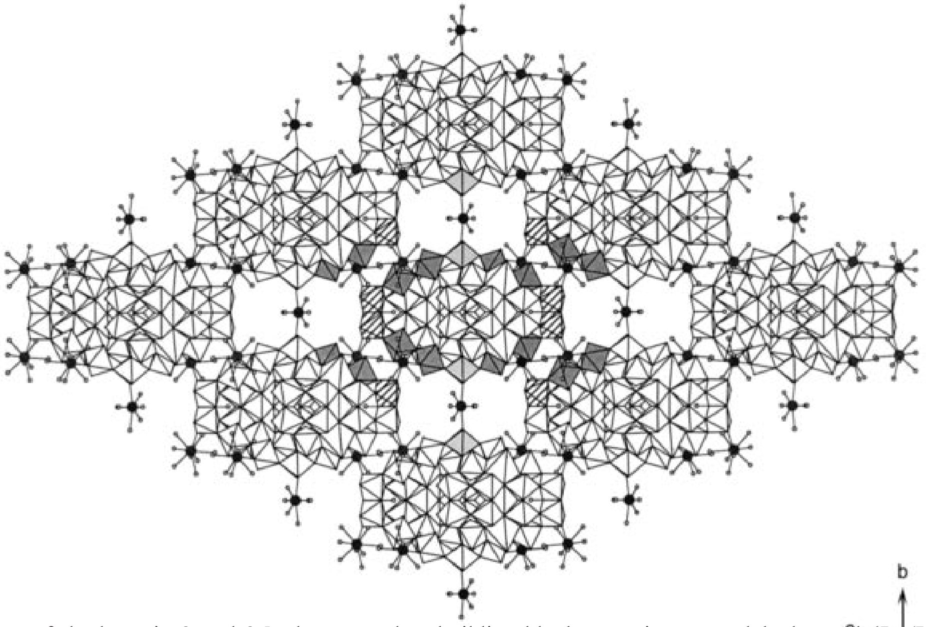

Figure 5. The structure of the layer in **2** and **3** [polyoxometalate building blocks are given as polyhedra and $\{Ln(H_2O)_nCl_m\}$ fragments in ball-and-stick representation]. Crystallization water molecules have been omitted.

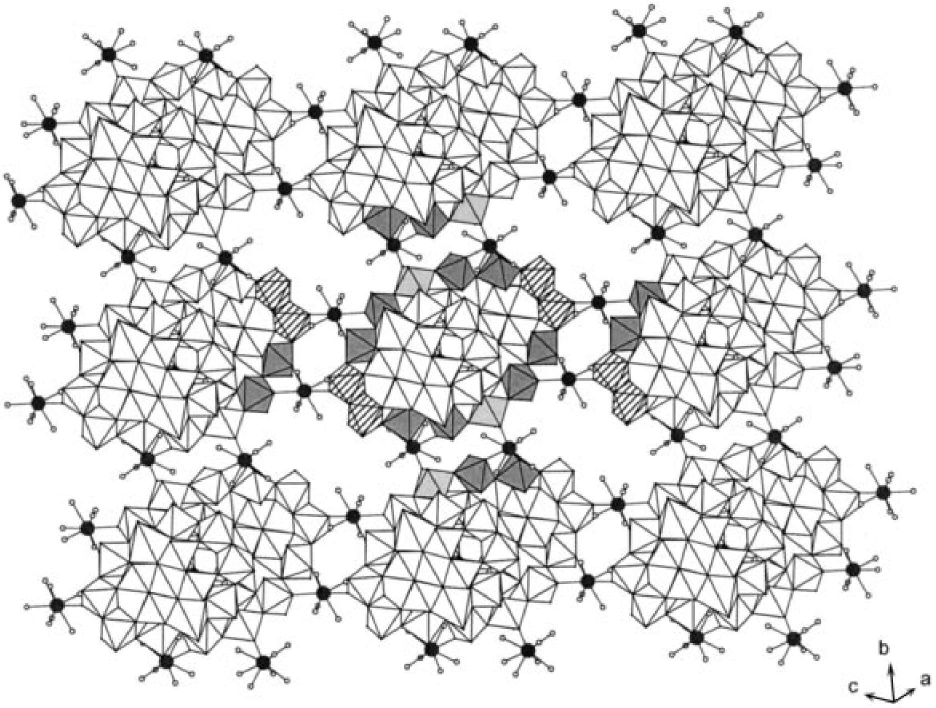

Figure 6. The structure of the layer in **8** [polyoxometalate building blocks are given as polyhedra, {Gd(H_2O)$_5$} fragments in ball-and-stick representation]. Crystallization water molecules have been omitted.

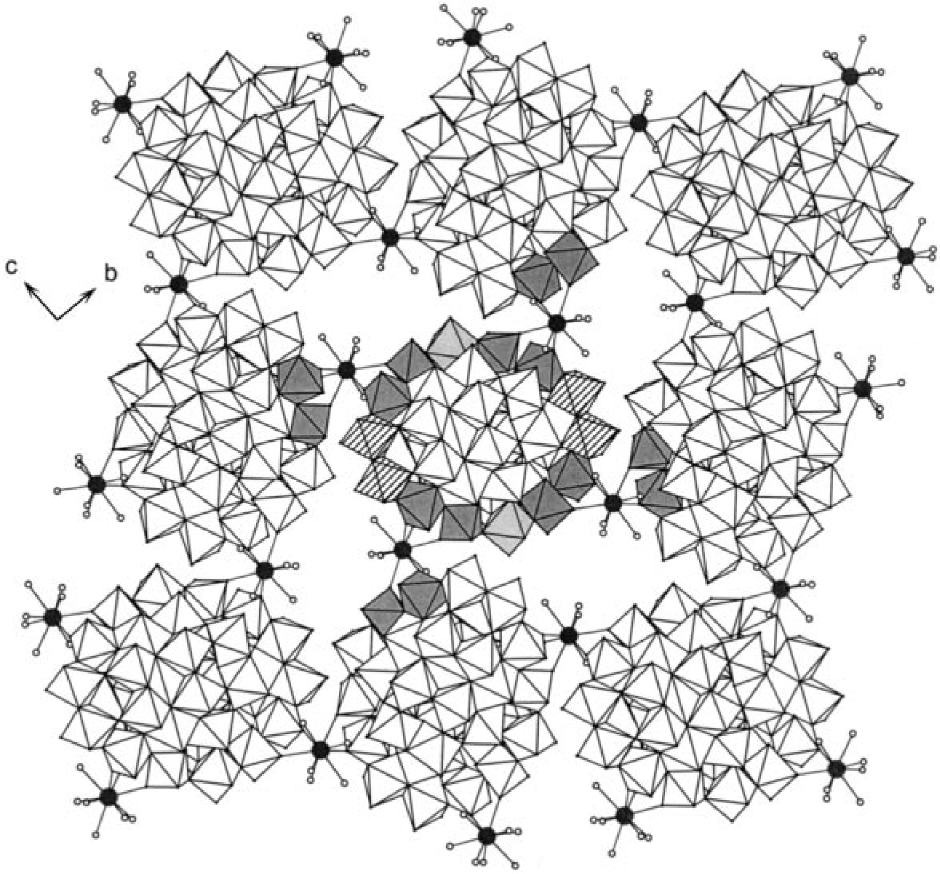

Figure 7. The structure of the layer in **15** [polyoxometalate building blocks as polyhedra, {Nd(H_2O)$_5$} fragments in ball-and-stick representation]. Crystallization water molecules have been omitted.

tained by decomposition of Keplerate polyoxoanions, $[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_6\}_{12}\{Mo^{V}{}_2O_4(CH_3COO)\}_{30}]^{42-}$, in the presence of Gd^{3+} cations. Every POM building block in $[Gd_4Mo_{36}(NO)_4]$ is surrounded by eight Gd^{3+} cations and in that way is joined to four adjacent polyoxoanions. There are two unique gadolinium(III) atoms in the structure of **8**, each of which is octacoordinate. The Gd cations of the first type coordinate terminal oxygen atoms of two $MoO_2{}^{2+}$ groups of type A and one oxygen atom of an $MoO_2{}^{2+}$ group of type B, whereas the Gd cations of the second type coordinate two oxygens of neighboring A-type groups and one oxygen atom of an $MoO_2{}^{2+}$ C-type group. In this way the coordination polyhedron of each Gd is filled with three POM oxygen atoms, the rest being coordinated water. Thus, we have an A-$MoO_2{}^{2+}$–Gd^{3+}–C-$MoO_2{}^{2+}$ regularity along the *b* axis, while in the other direction (along the *c* axis) this pattern is A-$MoO_2{}^{2+}$–Gd^{3+}–B-$MoO_2{}^{2+}$ (Figure 6).

Each POM fragment in $[Nd_2Mo_{36}O_{112}]$ (**15**) is surrounded by four Nd^{3+} cations, all of which are equivalent. Only oxygen atoms of type A take part in coordination to form infinite layers where every polyoxoanion is bonded together with four adjacent POM blocks (Figure 7). These layers are perpendicular to the crystallographic *a* axis. Only one (molecular) complex of this polyoxoanion with a lanthanide $(NH_4)_6[Gd_2Mo_{36}O_{112}(H_2O)_{22}]\cdot 50H_2O$ has been described previously.[36]

The crystal packing of **2**, **3**, **8**, and **15** consists of adjusted neutral, in the cases of **2**, **3**, and **8**, and anionic, in the case of **15**, layers stacked in an ABAB... mode (Figure 8). There are three types of solvent water molecules in these network compounds: two water molecules are clathrated in the inner cavity of the POM, and of the rest, some are placed inside the layers and the others fill the gap between adjacent layers. There is an extended network of hydrogen bonds involving water molecules and oxygen atoms of the cluster.

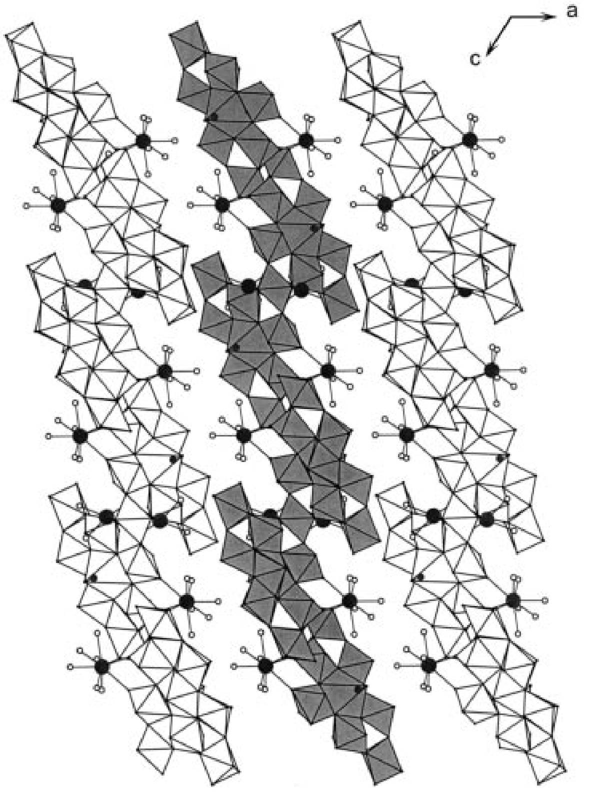

Figure 8. Three neighboring layers (view along the *b* axis) in the crystal structures of **2** and **3**. Polyoxometalate building blocks are given as polyhedra, Ln atoms in ball-and-stick representation. Polyoxometalate fragments of neighboring layers have different “colors” for clarity. Crystallization water molecules have been omitted.

The rest of the coordination polymers in this series have 1D-chain frameworks of different structure. Isostructural compounds with general formula $[\{M(H_2O)_6\}_2\{M(H_2O)_7\}_2\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot nH_2O$ were obtained for the larger lanthanides La^{3+} (**4**), Ce^{3+} (**5**), Pr^{3+} (**6**), and Nd^{3+} (**7**). There are two types of lanthanide cations in the lattice, and only one type takes part in the formation of infinite chains. It provides connection between POM fragments to give an ...A-$MoO_2{}^{2+}$–Ln^{3+}–C–$MoO_2{}^{2+}$... sequence along the *a* axis. The cations of the other type are attached to the oxygen atoms of A-type $MoO_2{}^{2+}$ groups of only one POM anion. These lanthanide cations are disordered over two positions. Every polyoxoanion is coordinated to four cations through eight A-type oxygen atoms (acting as four “bidentate ligands”) and to two C-type oxygen atoms (Figure 9). The chains run parallel to each other, forming *ac* pseudolayers which pack up in the ABAB... mode, as observed for **2**, **3**, **8**, and **15** (Figure 10).

We obtained six isostructural compounds with a different 1D chain structure by using the smaller Ln^{3+} ions Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, and Lu^{3+} as linkers, namely $(H_3O)_3[\{M(H_2O)_6\}_2\{M(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot nH_2O$ (M = Tb, Dy, Ho, Er, Yb and Lu; **9**–**14**) Here, oxygen atoms of all A-type groups of each polyoxoanion $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{8-}$ are coordinated to lanthanide cations. Two lanthanide cations coordinate only one POM fragment and another two Ln^{3+} ions coordinate oxygen atoms of A-type groups of two neighboring POMs (Figure 11). These compounds crystallize in the trigonal system in the space group $R\bar{3}c$. The infinite chains pack to form pseudo-layers perpendicular to the *c* axis. These pseudo-layers are stacked in such a way that chains of each layer are turned relative to the chains of two neighboring layers by 60° (Figure 12). There is an extended network of hydrogen bonds involving water molecules and oxygen atoms of the cluster.

There are two more $\{Mo_{36}(NO)_4\}$-based one-dimensional polymers $(H_3O)_{12}\{[Mo_2O_5(H_2O)_2][Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\}\cdot 44H_2O$ (**16**)[31] and $[La_2(MoO)_2Mo_{36}(NO)_4O_{108}(H_2O)_{28}]\cdot 56H_2O$ (**17**).[32] These were obtained by refluxing $(H_3O)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]$ with an excess of $NH_2OH\cdot HCl$ in water for no more than 30 min (in the presence La^{3+} salt in the case **17**). The $\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}$ units in **16** are connected by bridging $\{Mo_2O_4(\mu\text{-}O)(H_2O)_2\}$ groups coordinated to A-type $MoO_2{}^{2+}$ groups only (A-$MoO_2{}^{2+}$–{Mo–O–Mo}–A-$MoO_2{}^{2+}$ connectiv-

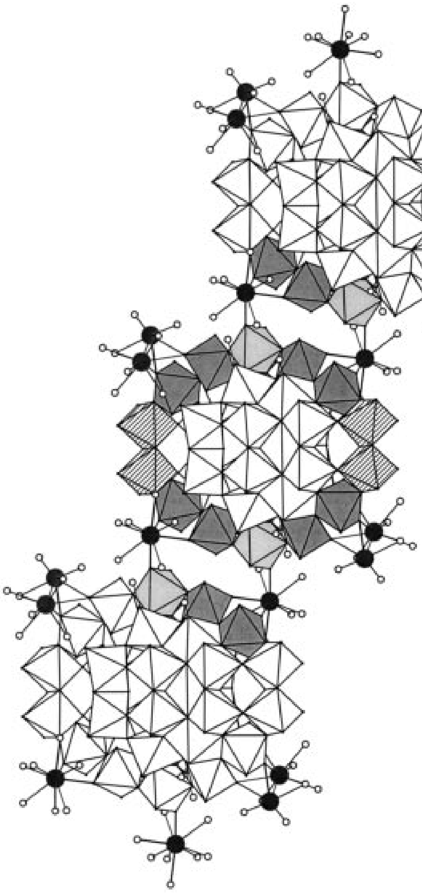

Figure 9. Connectivity pattern in the chains in compounds **4**–**7** distinguishing between the building units or constituents: $\{Ln(H_2O)_n\}$ fragments in ball-and-stick representation and $\{Mo_{36}(NO)_4\}$ fragments as polyhedra (for “color” legend see Figure 1).

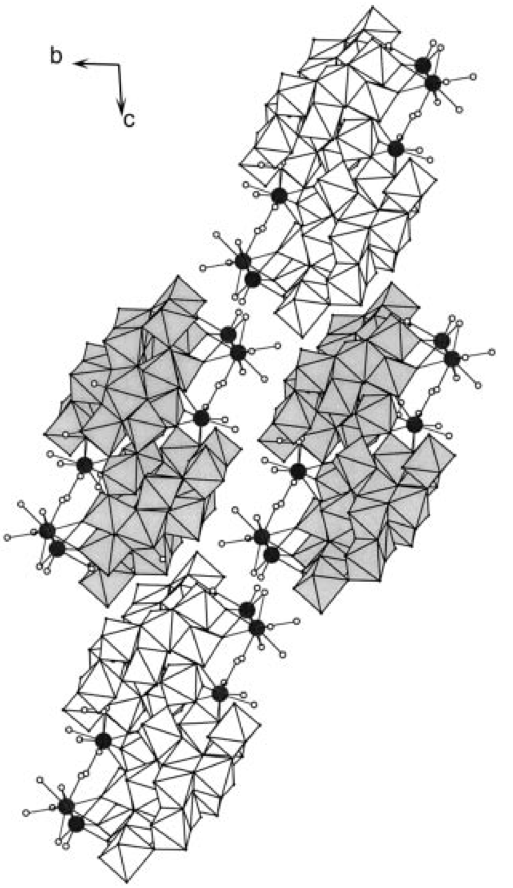

Figure 10. Packing of infinite chains in the crystal structures of **4**–**7** (view along the *a* axis). Polyoxometalate building blocks are given as polyhedra, $\{Ln(H_2O)_n\}$ fragments in ball-and-stick representation. Polyoxometalate fragments of neighboring chains have different “colors” for clarity. Crystallization water molecules have been omitted.

ity),[32] and in **17** two MoO^{3+} groups are coordinated to the A-type *cis*-MoO_2^{2+} units. Chain-building is realized through A-MoO_2^{2+}–La^{3+}–C-MoO_2^{2+} interactions.[31]

Thus, we can see that the nature of Ln^{3+} is decisive with respect to the type of framework adopted. For the same stoichiometry $\{Ln_4Mo_{36}(NO)_4\}$ and without extra ligands (except H_2O) attached to the Ln^{3+}, the larger Ln^{3+} ions (La–Nd, compounds **4**–**7**) adopt a chain structure with nine-coordinate lanthanide, in the middle of the lanthanide series another, layered arrangement appears, exemplified here by the Gd salt **8** (CN Gd^{3+} = 8), and with the smaller Ln^{3+} ions (Tb–Lu, compounds **9**–**14**) a chain-like 1D ar-

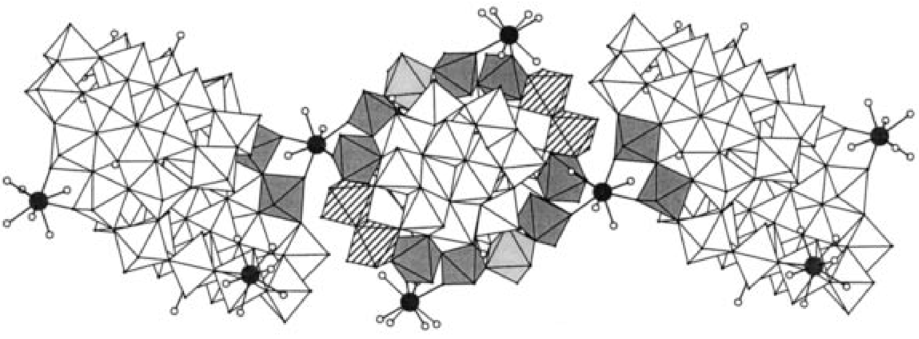

Figure 11. Connectivity pattern in chains in compounds **9**–**14** distinguishing between the building units or constituents: $\{Ln(H_2O)_n\}$ fragments in ball-and-stick representation and $\{Mo_{36}(NO)_4\}$ fragments as polyhedra (for “color” legend see Figure 1).

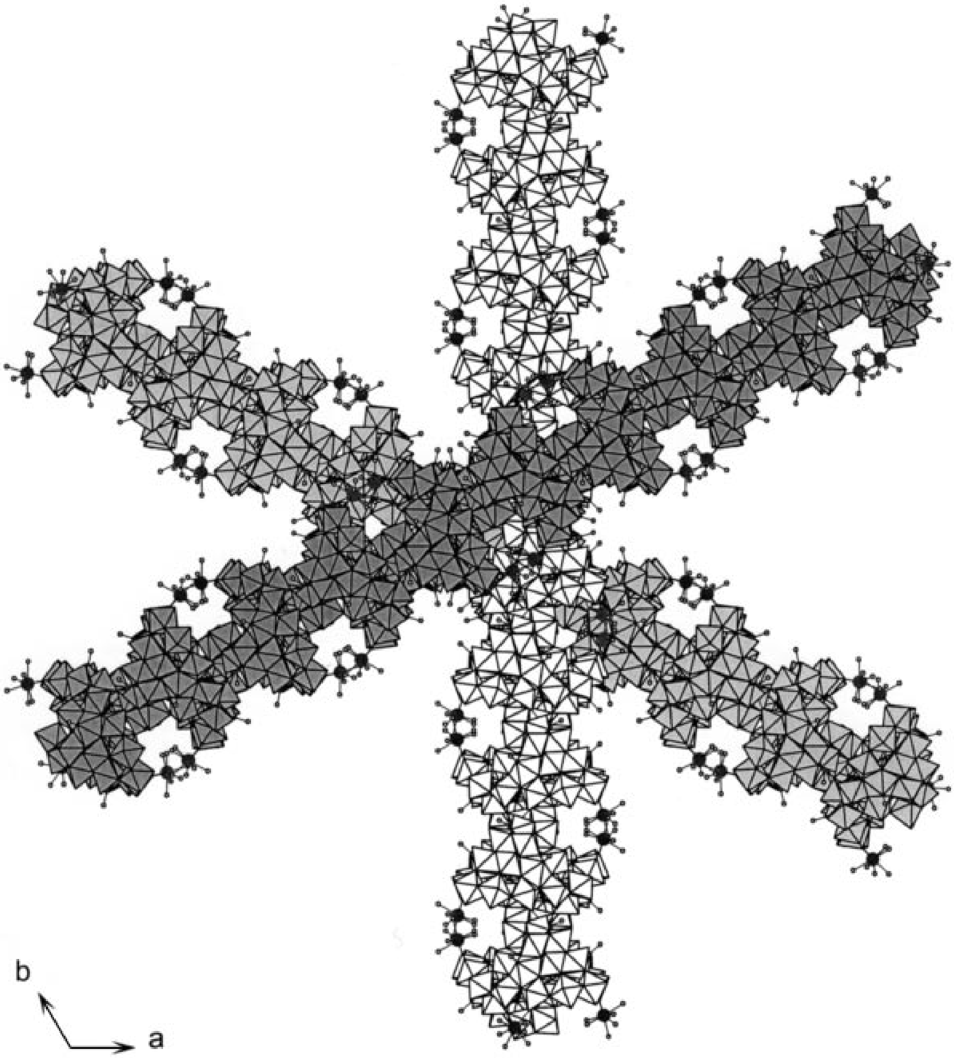

Figure 12. Packing of infinite chains in the crystal structures of **9**–**14** (view along the *c* axis). Polyoxometalate building blocks are given as polyhedra, $\{Ln(H_2O)_n\}$ fragments in ball-and-stick representation. Polyoxometalate fragments of neighboring chains have different "colors" for clarity. Crystallization water molecules have been omitted.

rangement reappears. It is, however, not identical to that found in **4**–**7** as the Ln^{3+} ions are now eight-coordinate and their coordination polyhedra correspond to a dodecahedron and a distorted square antiprism rather than the bicapped trigonal prism of **8**. A similar influence of the Ln^{3+} size can also be found for the series of 1:1 salts formed by Ln^{3+} and monovacant lacunary $[\gamma\text{-}SiW_{11}O_{39}]^{8-}$: the La and Ce salts feature a nine-coordinate lanthanide, the Eu salt is eight-coordinate, and the Yb salt is seven-coordinate. All these compounds are built from 1D chains that change from zig-zag to linear on going from La to Yb.[16]

In conclusion, we have developed a simple synthetic method that allows us to obtain polymeric compounds based on $\{Mo_{36}(NO)_4\}$ building blocks and Ln^{3+} in high yields. Only two compounds were known before our work, both of which are 1D chain polymers. We have synthesized fifteen new polymeric compounds, among which are one with a 3D framework, three with 2D networks of two different types, and eleven with 1D chains, also of two different types. We have also synthesized one 2D network, $[Nd_2Mo_{36}]$, which is the only example of a polymeric compound, based on $\{Mo_{36}O_{112}\}$ building blocks. The influence of the counterion and the reaction conditions (pH crystallization time, and temperature) on the structural type, observed in this work, allows us to expect even more complex architectures to be realized from these nanosized building blocks.

Experimental Section

Materials: $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot 33H_2O$ was prepared according to the previously published procedure.[34] All other reagents were obtained commercially and used as supplied.

X-ray Data Collection and Structural Determination: Single crystals of the complexes were selected and mounted on a Stoe IPDS II

Table 2. Crystal data, data collection, and structure-refinement parameters for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$H_{122}Cl_2La_4Mo_{36}N_4O_{172}$	$H_{136}Cl_3Mo_{36}N_4Nd_5O_{180}$	$H_{130}Cl_3Mo_{36}N_4O_{177}Sm_5$	$H_{142}La_4Mo_{36}N_4O_{183}$	$H_{166}Ce_4Mo_{36}N_4O_{195}$
Mol. mass	7011.40	7354.52	7331.02	7136.66	7357.69
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$C2/m$	$C2/m$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.6821(7)	24.8059(8)	26.178(5)	16.415(3)	16.452(3)
b [Å]	16.4159(7)	19.7684(7)	19.389(4)	16.717(3)	16.582(3)
c [Å]	19.1401(11)	20.5187(9)	20.901(4)	19.085(4)	18.990(4)
α [°]	77.722(1)	90.00	90.00	88.29(3)	88.01(3)
β [°]	80.456(1)	121.792(1)	122.97(3)	77.32(3)	77.02(3)
γ [°]	67.389(2)	90.00	90.00	60.60(3)	60.45(3)
V [Å^3]	3860.9(3)	8552.2(6)	8900(3)	4423.4(15)	4374.0(15)
Z	1	2	2	1	1
$D_{calcd.}$ [g cm^{-3}]	3.016	2.856	2.735	2.674	2.793
T [K]	273	273	100	100	100
$2\theta_{max}$ [°]	65.46	72.02	54.16	56.56	59.56
Range h, k, l	$-20 \le h \le 15$	$-19 \le h \le 37$	$-18 \le h \le 33$	$-18 \le h \le 20$	$-13 \le h \le 21$
	$-24 \le k \le 12$	$-29 \le k \le 26$	$-24 \le k \le 24$	$-21 \le k \le 21$	$-10 \le k \le 21$
	$-28 \le l \le 28$	$-33 \le l \le 30$	$-26 \le l \le 25$	$-24 \le l \le 24$	$-20 \le l \le 24$
μ [mm^{-1}]	4.059	4.199	4.223	3.513	3.633
Reflns. measured	37088	40758	17668	25858	13432
Unique reflns.	26640	15945	8787	17053	11481
R_{int}	0.0293	0.0501	0.0567	0.0584	0.0815
Observed [$I > 2\sigma(I)$]	14647	9102	7296	14620	7178
Refined parameters	1025	601	617	1070	1093
Restraints	49	0	42	59	68
R_1[a], wR_2[b]	$R_1 = 0.0572$	$R_1 = 0.0581$	$R_1 = 0.0581$	$R_1 = 0.0823$	$R_1 = 0.0677$
[$I > 2\sigma(I)$]	$wR_2 = 0.1493$	$wR_2 = 0.1603$	$wR_2 = 0.1737$	$wR_2 = 0.2318$	$wR_2 = 0.1623$
R_1[a], wR_2[b]	$R_1 = 0.1189$	$R_1 = 0.1196$	$R_1 = 0.0675$	$R_1 = 0.0907$	$R_1 = 0.1086$
(all data)	$wR_2 = 0.1657$	$wR_2 = 0.1899$	$wR_2 = 0.1821$	$wR_2 = 0.2420$	$wR_2 = 0.1807$
Goodness-of-fit on F^2	0.950	0.949	1.035	1.036	0.939
Largest diff. peak/hole [e Å^{-3}]	5.041/–5.177	3.292/–3.599	3.471/–2.750	2.486/–3.654	1.000/–1.185

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Absorption corrections were made with SADABS.[37] The structures were solved by direct methods and refined by the full-matrix least-squares method minimization of [$\Sigma w(F_o - F_c)^2$] with anisotropic thermal parameters for all skeleton non-hydrogen atoms, and for practically all oxygen atoms of the lattice water molecules, using the SHELX 97 program package.[38] The crystallographic and refinement data are listed in Tables 2, 3, and 4. Selected bond lengths and angles of complexes **1**–**15** are given as Supporting Information.

$(H_3O)_2[\{La(H_2O)_5\}_2\{La(H_2O)_6\}\{La(H_2O)_5Cl\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl\cdot21H_2O$ [$La_4Mo_{36}(NO)_4$-3D, 1]: $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot33H_2O$ (0.300 g, 0.047 mmol) was dissolved in 25 mL of water whilst stirring and heating gently (50 °C). The solution was then allowed to cool down to room temperature and filtered. $LaCl_3\cdot7H_2O$ (0.070 g, 0.188 mmol) was added to the filtrate with stirring (5 min). Small orange crystals of the product started to appear after one hour. These were filtered off and the filtrate was kept at room temperature for three days to produce a crop of single crystals, which were collected by filtration, washed twice with a minimal amount of ice-cooled water, and dried in air. Yield: 0.236 g [72% based on $\{Mo_{36}(NO)_4\}$]. $H_{122}Cl_2La_4Mo_{36}N_4O_{172}$: calcd. H 1.74, N 0.80; found H 1.96, N 0.83. IR (KBr pellet): $\tilde{\nu}$ = 3431 cm^{-1} (s, br), 1626 (s), 1399 (m), 957 (m), 875 (s), 835 (w), 776 (m), 619 (s), 566 (s), 531 (m), 369 (m).

$[\{Nd(H_2O)_6\}_4\{Nd(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl_3\cdot24H_2O$ [$Nd_5Mo_{36}(NO)_4$], 2]: $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot33H_2O$ (0.300 g, 0.047 mmol) was dissolved in 25 mL of water whilst stirring and heating gently (50 °C). After the solution had cooled down and been filtered, $NdCl_3\cdot6H_2O$ (0.066 g, 0.184 mmol) was added to the filtrate whilst stirring (5 min). After one hour small, orange, rhombic crystals of product started to form. After one day they were collected by filtration, washed twice with a small amount of ice-cooled water, and dried in air. X-ray quality single crystals were obtained by reagent diffusion in a U-tube. Yield: 0.250 g [73% based on $\{Mo_{36}(NO)_4\}$, 93% based on $NdCl_3\cdot6H_2O$]. $H_{136}Cl_3Mo_{36}N_4Nd_5O_{180}$: calcd. H 1.87, N 0.77; found H 2.03, N 0.84. IR (KBr pellet): $\tilde{\nu}$ = 3442 cm^{-1} (s, br), 1622 (s), 1402 (m), 950 (m), 874 (s), 774 (m), 614 (s), 566 (s), 478 (m), 370 (m), 338 (m).

$[\{Sm(H_2O)_6\}_4\{Sm(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]Cl_3\cdot21H_2O$ [$Sm_5Mo_{36}(NO)_4$], 3]: Compound **3** was prepared by exactly the same protocol as **2**, but with $SmCl_3\cdot6H_2O$ (0.066 g, 0.181 mmol). Dark-orange crystals. Yield: 0.166 g [49% based on $\{Mo_{36}(NO)_4\}$, 63% based on $SmCl_3\cdot6H_2O$]. X-ray quality single crystals were grown by reagent diffusion in a U-tube. $H_{130}Cl_3Mo_{36}N_4O_{177}Sm_5$: calcd. H 1.79, N 0.77; found H 2.01, N 0.90. IR (KBr pellet): $\tilde{\nu}$ = 3393 cm^{-1} (s, br), 1617 (s), 1410 (w), 952 (m), 870 (s), 776 (m), 616 (s), 568 (m), 537 (m).

$[\{La(H_2O)_6\}_2\{La(H_2O)_7\}_2\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot29H_2O$ [$La_4Mo_{36}(NO)_4$-1D}, 4]: A suspension of $Na_2MoO_4\cdot2H_2O$ (1.500 g, 6.20 mmol), $NH_2OH\cdot HCl$ (0.900 g, 12.95 mmol), and $LaCl_3\cdot7H_2O$ (1.280 g, 3.44 mmol) in 30 mL of water was acidified with concd. HCl until the pH reached 2. The resulting mixture was refluxed for 1 h and slowly cooled to room temperature. The resulting solution was filtered and the filtrate was kept for a week at room temperature in an open dish. Orange rhombic crystals were collected by filtration, washed twice with a minimal amount of water and dried in air. Yield: 0.846 g (69% based on $Na_2MoO_4\cdot2H_2O$). $H_{142}La_4$-

Table 3. Crystal data, data collection and structure refinement parameters for **6**–**10**.

Compound	**6**	**7**	**8**	**9**	**10**
Formula	$H_{164}Mo_{36}N_4O_{194}Pr_4$	$H_{156}Mo_{36}N_4Nd_4O_{190}$	$H_{140}Gd_4Mo_{36}N_4O_{182}$	$H_{157}Mo_{36}N_4O_{189}Tb_3$	$H_{159}Dy_3Mo_{36}N_4O_{190}$
Mol. mass	7342.83	7284.09	7192.00	7168.90	7194.65
Crystal system	triclinic	triclinic	triclinic	trigonal	trigonal
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$R\bar{3}c$	$R\bar{3}c$
a [Å]	16.419(3)	16.292(3)	13.5035(14)	35.955(5)	36.209(5)
b [Å]	16.568(3)	16.604(3)	16.2894(17)	35.955(5)	36.209(5)
c [Å]	19.025(4)	19.003(4)	18.905(2)	83.285(17)	83.795(17)
α [°]	88.47(3)	89.45(3)	77.376(2)	90.00	90.00
β [°]	77.21(3)	77.47(3)	80.336(2)	90.00	90.00
γ [°]	60.30(3)	60.95(3)	76.042(2)	120.00	120.00
V [Å^3]	4362.7(15)	4359.1(15)	3908.8(7)	93241(26)	95145(27)
Z	1	1	1	18	18
$D_{calcd.}$ [g cm^{-3}]	2.795	2.775	3.055	2.298	2.261
T [K]	200(2)	200(2)	120(2)	200(2)	120(2)
$2\theta_{max}$ [°]	63.52	63.86	52.00	50.70	54.36
Range h, k, l	$-11 \le h \le 21$	$-22 \le h \le 12$	$-16 \le h \le 16$	$-39 \le h \le 35$	$-42 \le h \le 46$
	$-14 \le k \le 21$	$-20 \le k \le 12$	$-20 \le k \le 19$	$-43 \le k \le 24$	$-46 \le k \le 46$
	$-27 \le l \le 23$	$-23 \le l \le 24$	$-23 \le l \le 23$	$-100 \le l \le 76$	$-107 \le l \le 107$
μ [mm^{-1}]	3.715	3.789	4.587	3.215	3.208
Reflns. measured	29538	24097	34353	41957	170198
Unique reflns.	18902	17738	15291	17483	23281
R_{int}	0.0571	0.0343	0.0859	0.0538	0.1274
Observed [$I > 2\sigma(I)$]	13029	15253	6856	12725	16795
Refined parameters	1123	1097	987	1090	1097
Restraints	73	35	0	66	0
R_1[a], wR_2[b]	$R_1 = 0.0659$	$R_1 = 0.0637$	$R_1 = 0.0781$	$R_1 = 0.0871$	$R_1 = 0.0792$
[$I > 2\sigma(I)$]	$wR_2 = 0.1773$	$wR_2 = 0.1825$	$wR_2 = 0.1599$	$wR_2 = 0.2372$	$wR_2 = 0.1913$
R_1[a], wR_2[b]	$R_1 = 0.0922$	$R_1 = 0.0728$	$R_1 = 0.1703$	$R_1 = 0.1126$	$R_1 = 0.1001$
(all data)	$wR_2 = 0.2198$	$wR_2 = 0.2002$	$wR_2 = 0.1848$	$wR_2 = 0.3647$	$wR_2 = 0.2048$
Goodness-of-fit on F^2	1.036	1.053	1.012	1.056	1.343
Largest diff. peak/hole [e Å^{-3}]	4.340/–3.314	4.864/–6.864	4.543/–4.027	4.493/–2.887	2.658/–1.802

$Mo_{36}N_4O_{183}$: calcd. H 1.99, N 0.79; found H 2.13, N 0.96. IR (KBr pellet): $\tilde{\nu}$ = 3516 cm^{-1} (m), 3441 (m), 3328 (s, br), 3179 (s, br), 1606 (m), 1402 (w), 953 (m), 879 (s), 777 (m), 624 (m), 566 (m), 538 (m), 367 (m), 334 (w).

[{Ce(H$_2$O)$_6$}$_2${Ce(H$_2$O)$_7$}$_2${Mo$_{36}$(NO)$_4$O$_{108}$(H$_2$O)$_{16}$}]·41H$_2$O [Ce$_4$Mo$_{36}$(NO)$_4$, 5]: $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot 33H_2O$ (0.300 g, 0.047 mmol) were dissolved in 25 mL of water with stirring and slight heating (about 50 °C), then the reaction solution was cooled to room temperature and filtered. $CeCl_3\cdot 7H_2O$ (0.066 g, 0.177 mmol) was then added to the filtrate whilst stirring (5 min). The reaction mixture was kept in a closed flask at 5 °C for 2 d, and the resulting orange rhombic crystals were collected by filtration, washed twice with a little iced water, and dried in air. Crystallization at room temperature gave some white precipitate formed together with orange crystals of the product. Yield: 0.237 g [69% based on {Mo$_{36}$(NO)$_4$}]. $H_{166}Ce_4Mo_{36}N_4O_{195}$: calcd. H 2.26, N 0.76; found H 2.12, N 0.71. IR (KBr pellet): $\tilde{\nu}$ = 3398 cm^{-1} (s, br), 3194 (s, br), 1617 (s), 1410 (w), 952 (m), 874 (s), 776 (m), 616 (s), 568 (m), 542 (m).

[{Pr(H$_2$O)$_6$}$_2${Pr(H$_2$O)$_7$}$_2${Mo$_{36}$(NO)$_4$O$_{108}$(H$_2$O)$_{16}$}]·40H$_2$O [Pr$_4$Mo$_{36}$(NO)$_4$, 6]: The compound was prepared by exactly the same protocol as **5**, but with $PrCl_3\cdot 6H_2O$ (0.066 g, 0.187 mmol), to give dark-orange crystals. Yield: 0.231 g [67% based on {Mo$_{36}$(NO)$_4$}]. $H_{164}Mo_{36}N_4O_{194}Pr_4$: calcd. H 2.23, N 0.76; found H 2.01, N 0.90. IR (KBr pellet): $\tilde{\nu}$ = 3437 cm^{-1} (s, br), 1620 (s), 1405 (m), 957 (m), 875 (s), 776 (m), 619 (s), 566 (m), 531 (m), 369 (m).

[{Nd(H$_2$O)$_6$}$_2${Nd(H$_2$O)$_7$}$_2${Mo$_{36}$(NO)$_4$O$_{108}$(H$_2$O)$_{16}$}]·36H$_2$O [Nd$_4$Mo$_{36}$(NO)$_4$, 7]. Synthesis 1: A suspension of $Na_2MoO_4\cdot 2H_2O$ (0.500 g, 2.07 mmol) and $NH_2OH\cdot HCl$ (0.300 g, 4.32 mmol) in 30 mL of water was acidified with concd. HCl until pH 2. The resulting mixture was refluxed for 5 min and slowly cooled to room temperature. The deep-orange solution was filtered and then $NdCl_3\cdot 6H_2O$ (0.150 g, 0.418 mmol) was added to the filtrate with vigorous stirring for 5 min. The solution was kept for 2 d at 5 °C. Orange rhombic crystals were collected by filtration, washed twice with a minimum amount of ice-cooled water, and dried in air. Yield: 0.309 g (74% based on $Na_2MoO_4\cdot 2H_2O$).
Synthesis 2: $AgNO_3$ (0.093 g, 0.552 mmol) was added to a solution of $NdCl_3\cdot 6H_2O$ (0.066 g, 0.184 mmol) in 5 mL of water. The resulting mixture was filtered and the filtrate was added to a solution of $(NH_4)_{12}[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]\cdot 33H_2O$ (0.300 g, 0.047 mmol) in 25 mL of water whilst stirring. Small orange crystals of the product started to appear after one hour. After two days orange crystals were collected by filtration, washed twice with a minimal amount of ice-cooled water, and dried in air. Yield: 0.230 g [67% based on {Mo$_{36}$(NO)$_4$}]. X-ray quality single crystals were grown by reagent diffusion in a U-tube. $H_{156}Mo_{36}N_4Nd_4O_{190}$: calcd. H 2.14, N 0.77; found H 2.13, N 1.05. IR (KBr pellet): $\tilde{\nu}$ = 3421 cm^{-1} (s, br), 3174 (s, br), 1617 (m), 1406 (m), 952 (m), 878 (s), 776 (m), 624 (m), 565 (m).

[{Gd(H$_2$O)$_5$}$_4${Mo$_{36}$(NO)$_4$O$_{108}$(H$_2$O)$_{16}$}]·34H$_2$O [Gd$_4$Mo$_{36}$(NO)$_4$, 8]: This compound was prepared by exactly the same protocol as **5**, but with $Gd(NO_3)_3\cdot 5H_2O$ (0.080 g, 0.185 mmol), to give an orange crystalline product. Yield: 0.205 g [{61% based on $Mo_{36}(NO)_4$}]. $H_{140}Gd_4Mo_{36}N_4O_{182}$: calcd. H 1.96, N 0.78; found H 2.09, N 0.85. IR (KBr pellet): $\tilde{\nu}$ = 3414 cm^{-1} (s, br), 1620 (s), 1399 (m), 957 (m), 875 (s), 776 (m), 619 (s), 566 (m), 531 (m), 369 (w), 322 (w).

(H$_3$O)$_3$[{Tb(H$_2$O)$_6$}$_2${Tb(H$_2$O)$_4$}{Mo$_{36}$(NO)$_4$O$_{108}$(H$_2$O)$_{16}$}]·42H$_2$O [Tb$_3$Mo$_{36}$(NO)$_4$, 9]: This compound was prepared by exactly the

Table 4. Crystal data, data collection and structure refinement parameters for **11**–**15**.

Compound	**11**	**12**	**13**	**14**	**15**
Formula	$H_{165}Ho_3Mo_{36}N_4O_{193}$	$H_{173}Er_3Mo_{36}N_4O_{197}$	$H_{185}Mo_{36}N_4O_{203}Yb_3$	$H_{135}Lu_3Mo_{36}N_4O_{178}$	$H_{138}Mo_{36}Nd_2O_{180}$
Mol. mass	7258.99	7338.04	7463.48	7018.87	6761.42
Crystal system	trigonal	trigonal	trigonal	trigonal	monoclinic
Space group	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$	$R\bar{3}c$	$P2_1/c$
a [Å]	36.006(5)	36.153(5)	35.945(5)	35.991(5)	32.022(6)
b [Å]	36.006(5)	36.153(5)	35.945(5)	35.991(5)	24.209(5)
c [Å]	83.540(17)	83.700(17)	83.550(17)	83.475(17)	21.914(4)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	90.00	90.00	90.00	90.00	90.18(3)
γ [°]	120.00	120.00	120.00	120.00	90.00
V [Å^3]	93792(27)	94742(27)	93485(26)	93640(27)	16988(6)
Z	18	18	18	18	4
$D_{calcd.}$ [g cm^{-3}]	2.313	2.315	2.386	2.240	2.644
T [K]	100(2)	100(2)	150(2)	200(2)	293(2)
$2\theta_{max}$ [°]	54.60	49.94	56.56	63.74	41.64
Range h, k, l	$-46 \le h \le 46$	$-27 \le h \le 42$	$-46 \le h \le 35$	$-40 \le h \le 52$	$-32 \le h \le 31$
	$-42 \le k \le 46$	$-37 \le k \le 42$	$-46 \le k \le 45$	$-43 \le k \le 45$	$-24 \le k \le 24$
	$-106 \le l \le 107$	$-91 \le l \le 96$	$-96 \le l \le 52$	$-106 \le l \le 103$	$-10 \le l \le 21$
μ [mm^{-1}]	3.319	3.357	3.545	3.597	3.281
Reflns. measured	178561	37156	73313	91224	47825
Unique reflns.	23019	17547	21807	28866	17427
R_{int}	0.0920	0.0579	0.0867	0.0866	0.0865
Observed [$I > 2\sigma(I)$]	17350	14150	15390	15582	15221
Refined parameters	1116	1100	1196	1156	2098
Restraints	48	54	96	102	546
R_1[a], wR_2[b]	$R_1 = 0.0630$	$R_1 = 0.0674$	$R_1 = 0.1088$	$R_1 = 0.1009$	$R_1 = 0.1044$
[$I > 2\sigma(I)$]	$wR_2 = 0.1832$	$wR_2 = 0.2033$	$wR_2 = 0.2765$	$wR_2 = 0.2662$	$wR_2 = 0.2509$
R_1[a], wR_2[b]	$R_1 = 0.0804$	$R_1 = 0.0815$	$R_1 = 0.1409$	$R_1 = 0.1837$	$R_1 = 0.1142$
(all data)	$wR_2 = 0.1957$	$wR_2 = 0.2179$	$wR_2 = 0.3107$	$wR_2 = 0.3247$	$wR_2 = 0.2659$
Goodness-of-fit on F^2	1.033	1.042	1.049	1.063	1.138
Largest diff. peak/hole [e Å^{-3}]	2.513/–1.525	3.236/–1.803	4.019/–3.374	5.498/–3.404	3.346/–2.204

same protocol as **5**, but with $TbCl_3\cdot 6H_2O$ (0.069 g, 0.185 mmol), to give an orange crystalline product. Yield: 0.175 g [52% based on $\{Mo_{36}(NO)_4\}$]. $H_{157}Mo_{36}N_4O_{189}Tb_3$: calcd. H 2.19, N 0.78; found H 1.87, N 0.94. IR (KBr pellet): $\tilde{\nu}$ = 3437 cm^{-1} (s, br), 1626 (s), 1397 (m), 1106 (w), 956 (m), 871 (s), 777 (m), 614 (s), 562 (m), 532 (m), 367(w).

$(H_3O)_3[\{Dy(H_2O)_6\}_2\{Dy(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot 43H_2O$ [$Dy_3Mo_{36}(NO)_4$, 10]: This compound was prepared by exactly the same protocol as **5**, but with $Dy(NO_3)_3\cdot 5H_2O$ (0.081 g, 0.185 mmol), to give an orange crystalline product. Yield: 0.143 g [42% based on $\{Mo_{36}(NO)_4\}$]. $H_{159}Dy_3Mo_{36}N_4O_{190}$: calcd. H 2.21, N 0.78; found H 1.99, N 0.87. IR (KBr pellet): $\tilde{\nu}$ = 3414 cm^{-1} (s, br), 1615 (s), 1405 (m), 1247(w); 957 (m), 870 (s), 770 (m), 613 (s), 560 (m), 531 (m), 363(w).

$(H_3O)_3[\{Ho(H_2O)_6\}_2\{Ho(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot 46H_2O$ [$Ho_3Mo_{36}(NO)_4$, 11]: This compound was prepared by exactly the same protocol as **5**, but with $Ho(NO_3)_3\cdot 5H_2O$ (0.081 g, 0.184 mmol), to give an orange crystalline product. Yield: 0.202 g [59% based on $\{Mo_{36}(NO)_4\}$]. $H_{169}Ho_3Mo_{36}N_4O_{193}$: calcd. H 2.32, N 0.77; found H 2.13, N 0.82. IR (KBr pellet): $\tilde{\nu}$ = 3431 cm^{-1} (s, br), 1626 (s), 1400 (m), 957 (m), 872 (s), 780 (m), 617 (s), 564 (m), 532 (m), 357(w).

$(H_3O)_3[\{Er(H_2O)_6\}_2\{Er(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot 50H_2O$ [$Er_3Mo_{36}(NO)_4$, 12]: This compound was prepared by exactly the same protocol as **5**, but with (0.082 g, 0.185 mmol) of $Er(NO_3)_3\cdot 5H_2O$, to give an orange crystalline product. Yield: 0.200 g [58% based on $\{Mo_{36}(NO)_4\}$]. $H_{173}Er_3Mo_{36}N_4O_{197}$: calcd. H 2.36, N 0.76; found H 2.13, N 1.05. IR (KBr pellet): $\tilde{\nu}$ = 3424 cm^{-1} (s, br), 1614 (m), 1406 (w), 958 (m), 868 (s), 774 (m), 611 (s), 562 (m), 534 (m), 366 (m).

$(H_3O)_3[\{Yb(H_2O)_6\}_2\{Yb(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot 56H_2O$ [$Yb_3Mo_{36}(NO)_4$, 13]: This compound was prepared by exactly the same protocol as **5**, but with (0.072 g, 0.186 mmol) of $YbCl_3\cdot 6H_2O$, to give an orange crystalline product. Yield: 0.208 g [59% based on $\{Mo_{36}(NO)_4\}$]. $H_{185}Mo_{36}N_4O_{203}Yb_3$: calcd. H 2.48, N 0.75; found H 1.95, N 0.96. IR (KBr pellet): $\tilde{\nu}$ = 3420 cm^{-1} (s, br), 1620 (m), 1405 (w), 957 (m), 869 (s), 770 (m), 613 (s), 561 (m), 531 (m), 369 (w).

$(H_3O)_3[\{Lu(H_2O)_6\}_2\{Lu(H_2O)_4\}\{Mo_{36}(NO)_4O_{108}(H_2O)_{16}\}]\cdot 31H_2O$ [$Lu_3Mo_{36}(NO)_4$, 14]: This compound was prepared by exactly the same protocol as **5**, but with $Lu(NO_3)_3\cdot 5H_2O$ (0.066 g, 0.183 mmol), to give an orange crystalline product. Yield: 0.132 g [40% based on $\{Mo_{36}(NO)_4\}$]. $H_{135}Lu_3Mo_{36}N_4O_{178}$: calcd. H 1.92, N 0.80; found H 1.77, N 0.90. IR (KBr pellet): $\tilde{\nu}$ = 3390 cm^{-1} (s, br), 3190 (s, br), 1606 (s), 1406 (w), 1246 (w), 956 (m), 866 (s), 769 (m), 608 (s), 565 (m), 537 (m).

$(H_3O)_2[\{Nd(H_2O)_5\}_2\{Mo_{36}O_{112}(H_2O)_{16}\}]\cdot 40H_2O$ [Nd_2Mo_{36}, 15]: A suspension of $Na_2MoO_4\cdot 2H_2O$ (0.500 g, 2.07 mmol) and $NH_2OH\cdot HCl$ (0.300 g, 4.32 mmol) in 30 mL of water was acidified with concd. HCl until pH 2. The resulting mixture was refluxed for 30 min and then slowly cooled down to room temperature. The deep-orange solution was filtered and $NdCl_3\cdot 6H_2O$ (0.150 g, 0.418 mmol) was added to the filtrate with vigorous stirring for five minutes. The reaction solution was kept at room temperature in an open beaker. The amorphous solids that separated were removed by filtration from time to time. After 10 days colorless rhombic crystals of **15** were collected by filtration, washed twice with a minimum amount of ice-cooled water, and dried in air. Yield: 0.136 g (35% based on Mo). $H_{138}Mo_{36}Nd_2O_{180}$: calcd. H 2.04; found H 1.98. IR (KBr pellet): $\tilde{\nu}$ = 3415 cm^{-1} (s, br), 1623 (m), 1384 (w), 938 (m), 897 (m), 864 (m), 839 (m), 778 (w), 711 (m), 653 (m), 552 (m), 500 (w), 402 (w), 374 (w), 346 (w).

Further crystallographic details may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-415381 (for **1**), -415403 (for **2**), -415441 (for **3**), -415401 (for **4**), -415400 (for **5**), -415404 (for **6**), -415402 (for **7**), -391260 (for **8**), -415398 (for **9**), -415383 (for **10**), -415385 (for **11**), -415384 (for **12**), -415399 (for **13**), -415397 (for **14**), and -415382 (for **15**).

Supporting Information (see footnote on the first page of this article) includes the bond lengths and angles for compounds **1**–**15**.

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