

22-Isopolytungstate Fragment $[\text{H}_2\text{W}_{22}\text{O}_{74}]^{14-}$ Coordinated to Lanthanide Ions

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The novel polyanions $[\text{Ln}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{71}(\text{OH})_2]^{8-}$ ($\text{Ln} = \text{La}$ (1), Ce (2), Tb (3), Dy (4), Ho (5), Er (6), Tm (7), Yb (8), Lu (9), Y (10)) have been synthesized by reaction of WO_4^{2-} and lanthanide ions in acidic aqueous medium. The low symmetry (C_i) polyanion family $[\text{Ln}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{71}(\text{OH})_2]^{8-}$ consists of the isopolyanion $[\text{H}_2\text{W}_{22}\text{O}_{74}]^{14-}$ and two $\{\text{Ln}(\text{H}_2\text{O})_5\}^{3+}$ supporting units. The $[\text{H}_2\text{W}_{22}\text{O}_{74}]^{14-}$ cluster, which consists of two undecatungstate $\{\text{W}_{11}\}$ fragments, acts as a tridentate ligand to two Ln^{3+} ions. Polyanions **1–10** are isostructural, and the coordination number of the lanthanide ions correlates with their sizes. All compounds have been fully characterized in the solid state by Fourier transform infrared spectroscopy, single-crystal X-ray diffraction, thermogravimetric analysis, and elemental analysis. Single-crystal X-ray diffraction analyses show that **1–10** crystallize as sodium salts in the triclinic space group $P\bar{1}$.

Introduction

Polyoxometalates (POMs) represent a large class of nanosized metal-oxo anions. POMs are remarkable not only in terms of molecular and electronic structural versatility but also because of their reactivity and relevance in fields such as photochemistry, analytical chemistry, clinical chemistry, magnetism, catalysis, biology, medicine, and materials science.¹ Polyoxoanions which result from the condensation of metalate anions in acidified solutions (usually aqueous) can efficiently absorb light in the near UV–vis region and can therefore be used as photocatalysts.² The intrinsic chemical properties of POMs as electron acceptors or as very strong Brønsted acids (in their protonated form) make them useful as catalysts in organic transformations, and their abilities to form peroxo complexes or to serve as supports for catalytically active metal ions in high oxidation states are particularly useful in oxidation reactions.^{1b,3}

Although the first POM was synthesized already in 1826 by Berzelius,^{1a} the mechanism of POM formation is still not completely understood and is often described as a self-assembly. POMs can usually be isolated from aqueous solution as solid salts with appropriate counter cations which may be alkali metal cations (e.g., Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) or organic cations (e.g., guanidinium, alkylamines). Two main types of POMs are known, based on their chemical composition: isopoly and heteropoly anions. Isopolyanions are represented by the general formula $[\text{M}_m\text{O}_y]^{n-}$, where M is the addendum atom, usually molybdenum or tungsten and less frequently vanadium, niobium, or tantalum in their higher oxidation states. Heteropolyanions are represented with the general formula $[\text{X}_x\text{M}_m\text{O}_y]^{q-}$ ($x \leq m$) where X, the heteroatom, can be one of many elements of the periodic table, most commonly P^{5+} , As^{5+} , Si^{4+} , Ge^{4+} , and B^{3+} .¹

Lanthanide-containing POMs have been investigated less than their 3d-transition-metal-substituted analogues. Because of the larger size of the lanthanide ions compared to 3d metals, they are not fully incorporated into the lacunary site(s) of vacant POM precursors. Because of their higher

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coordination numbers, each lanthanide ion can be used as a linker to one or more other lacunary POM units. This approach has resulted in polymeric or unusually large molecular POM assemblies.⁴ Also, lanthanide-containing POMs can be of interest because of photoluminescence, as well as catalytic, electrochemical, and magnetic properties.⁵

Our group has also been working on lanthanide-containing heteropolytungstates. We have reported the ytterbium-containing tungstoarsenate $[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{7-}$ resulting from the interaction of the monolacunary $[\text{As}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})]^{10-}$ with Yb^{3+} ions in acidic aqueous medium. The polyanion consists of two ($\alpha\text{-As}^{\text{III}}\text{W}_9\text{O}_{33}$) fragments connected by a V-shaped $(\text{H}_2\text{O})\text{Yb}(\text{OW}(\text{H}_2\text{O}))_2$ fragment.^{4j} The monolanthanide-containing polyanion family $[\text{Ln}(\beta_2\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ ($\text{Ln} = \text{La, Ce, Sm, Eu, Gd, Tb, Yb, Lu}$) has also been synthesized and structurally characterized. These polyanions are composed of two chiral ($\beta_2\text{-SiW}_{11}\text{O}_{39}$) units sandwiching the Ln^{3+} ion.^{4s} Recently, we reported the 20 cerium containing 100-tungsto-10-germanate $[\text{Ce}_{20}\text{Ge}_{10}\text{W}_{100}\text{O}_{376}(\text{OH})_4(\text{H}_2\text{O})_{30}]^{56-}$ which is the third largest molecular polytungstate known to date.^{4t} We synthesized this polyanion by reaction of the trilacunary POM precursor $[\alpha\text{-GeW}_9\text{O}_{34}]^{10-}$ with Ce^{3+} ions in acidic aqueous medium.

Until very recently, only one family of lanthanide-containing isopolyanions had been reported. Peacock and Weakley were the first to describe the sandwich-type decatungstate family of the general formula

$[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$.^{4a,6} This polyanion is now known for $\text{Ln}^{3+} = \text{La, Ce, Pr, Nd, Sm, Ho, Yb, and Y}$, and also for Ce^{4+} , all synthesized by reaction of the lanthanide ions with Na_2WO_4 in hot aqueous (pH 6.5–7.5) solution. The structure of the D_{4d} $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{n-}$ polyanions consist of two monolacunary Lindqvist based fragments $[\text{W}_5\text{O}_{18}]^{6-}$ encapsulating a central metal ion exhibiting a square-antiprismatic coordination. Yamase et al. reported the crystal structures of the Pr, Nd, Dy, Sm, Eu, Gd, and Tb derivatives with different types of alkali counter cations.⁷ The lanthanum analogue $[\text{La}(\text{W}_5\text{O}_{18})_2]^{9-}$ was reported in 2005,⁸ and also the actinide analogues $[\text{Th}(\text{W}_5\text{O}_{18})_2]^{8-}$ and $[\text{U}(\text{W}_5\text{O}_{18})_2]^{8-}$ have been studied crystallographically.^{5b,9} Very recently our group reported on the synthesis and solid state structure of the yttrium-derivative $[\text{YW}_{10}\text{O}_{36}]^{9-}$, as well as its solution properties by ^{183}W and ^{89}Y NMR.¹⁰ Very recently, Cao and co-workers reported on a pentadecatungstate ring capped by two Ce^{3+} ions.¹¹

The isopolyanion family $[\text{Ln}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-}$ ($\text{Ln} = \text{Pr, Nd, Sm, Eu, Tb, Dy}$) has shown high luminescence quantum efficiency.¹² The decatungstoterbate $[\text{Tb}(\text{W}_5\text{O}_{18})_2]^{9-}$ showed green-emissive luminescence.^{7h} Furthermore, Griffith and co-workers studied the lanthanoisopolytungstates $[\text{Ln}^{\text{III}}\text{W}_{10}\text{O}_{36}]^{9-}$ ($\text{Ln} = \text{Y, La, Ce, Pr, Sm, Eu, Gd, Dy, Er, Lu}$) as catalytic oxidants with H_2O_2 for alcohol oxidations and alkene epoxidations.^{5b} This provides an impetus to prepare other, novel isopolyanion structures coordinated to lanthanide ions.

Herein we report on the synthesis of a novel class of 22-isopolytungstates $\{\text{W}_{22}\}$ coordinated to two external lanthanide ions, $[\text{Ln}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{71}(\text{OH})_2]^{8-}$ ($\text{Ln}^{3+} = \text{La}$ (**1**), Ce (**2**), Tb (**3**), Dy (**4**), Ho (**5**), Er (**6**), Tm (**7**), Yb (**8**), Lu (**9**)) and yttrium, $[\text{Y}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{71}(\text{OH})_2]^{8-}$ (**10**).

Experimental Section

Synthesis. We used all reagent-grade chemicals as purchased without further purification.

$\text{Na}_2\text{La}_2[\text{La}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{72}(\text{OH})_2] \cdot 44\text{H}_2\text{O}$ (NaLa-1). A sample of 10.00 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (30.3 mmol) was dissolved in 20 mL H_2O , followed by dropwise addition of a solution of 1.02 g of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (2.8 mmol) in 5 mL of H_2O . Then 2.5 mL of 12 M

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HCl was added dropwise to the resulting solution (local formation and redissolution of hydrated tungsten oxide and lanthanum hydroxide was observed), and then the pH was adjusted to 2.2 using 4 M aqueous HCl. The mixture was heated to 90 °C for 1 h with vigorous stirring. A white precipitate, which had formed, was filtered off and discarded. After cooling to room temperature, the filtrate was kept in an open vial for crystallization. Colorless crystals were obtained after several days, which were filtered off and air-dried. Although additional product continued to form subsequently, it contained NaCl impurities. Yield: 0.87 g (9.2%). The compound **NaLa-1** could also be synthesized in higher yield under analogous reaction conditions by heating to 45 °C instead of 90 °C. Yield: 1.51 g (16%). IR for **NaLa-1** in cm^{-1} (only between 400–1000 cm^{-1}): 943(m), 868(sh), 820(s), 711(s), 513(w), 419(w). Anal. Calcd (%) for **NaLa-1**: Na, 0.7; W, 59.1; La, 8.1. Found (%): Na, 1.1; W, 59.7; La, 7.7.

Na₂Ce₂[Ce₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·44H₂O (NaCe-2). A sample of 10.00 g of Na₂WO₄·2H₂O (30.3 mmol) was dissolved in 20 mL of H₂O followed by dropwise addition of 2.5 mL of 12 M HCl (local formation and redissolution of hydrated tungsten oxide was observed). Then a solution of 1.03 g of CeCl₃·7H₂O (2.8 mmol) in 5 mL of H₂O was added immediately and dropwise. Finally, the pH was adjusted to 2.2 using 4 M aqueous HCl. The mixture was vigorously stirred at room temperature for 1 h. A yellow precipitate, which had formed, was filtered off and discarded. The filtrate was kept in an open vial for crystallization at room temperature. After a few hours, a yet unidentified polycrystalline material started to form and was filtered off successively until yellow crystals of **NaCe-2** started to appear. These crystals were in turn filtered off and air-dried. Yield: 0.63 g (3.8%). Although additional product continued to form subsequently, it contained NaCl impurities. IR for **NaCe-2**: 944(m), 870(sh), 820(s), 721(s), 514(w), 419(w) cm^{-1} . Anal. Calcd (%) for **NaCe-2**: Na, 0.7; W, 59.1; Ce, 8.2. Found (%): Na, 0.9; W, 58.6; Ce, 8.0.

Na₅Tb[Tb₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·41H₂O (NaTb-3). A sample of 10.00 g of Na₂WO₄·2H₂O (30.3 mmol) was dissolved in 20 mL of H₂O, and then 2.5 mL of 12 M HCl was added dropwise. A sample of 0.93 g of Tb(CH₃COO)₃·H₂O (2.8 mmol) in 5 mL of H₂O was added dropwise to the acidified tungstate solution, and then the pH was adjusted to 2.2 using 4 M aqueous HCl. The mixture was vigorously stirred at room temperature for 1 h, and then filtered and allowed to crystallize at room temperature. Colorless crystals were obtained after several days, which were filtered off and air-dried. Yield: 0.65 g (7.0%). Although additional product continued to form subsequently, it contained NaCl impurities. IR for **NaTb-3**: 944(m), 870(sh), 820(s), 721(s), 514(w), 419(w) cm^{-1} . Anal. Calcd (%) for **NaTb-3**: Na, 1.7; W, 60.0; Tb, 7.1. Found (%): Na, 1.8; W, 58.9; Tb, 6.6.

Na₈[Dy₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·49H₂O (Na-4), **Na₅Ho[Ho₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·45H₂O (NaHo-5)**, **Na₈[Er₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·44H₂O (Na-6)**, **Na₈[Tm₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·41H₂O (Na-7)**, **Na₈[Yb₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·46H₂O (Na-8)**, **Na₅Lu[Lu₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·44H₂O (NaLu-9)**, **Na₈[Y₂(H₂O)₁₀W₂₂O₇₂(OH)₂]·46H₂O (Na-10)**. Compounds **Na-4** through **Na-10** were synthesized using similar procedures (see Supporting Information).

In this paper, "Ln" will be used as an abbreviation for the lanthanide ions La³⁺, Ce³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺, as well as for the yttrium ion Y³⁺, since the ionic radius of the latter falls in the range of lanthanides.

Instrumentation. Infrared (IR) spectra were recorded on KBr pellets using a Nicolet Avatar 370 spectrometer. Thermogravimetric analyses (TGA) were performed using a TA Instruments SDT Q600 instrument between 20–900 °C with a 100 mL/min flow of nitrogen

and a heating rate of 5 °/min. Elemental analyses were carried out by Eurofins Umwelt West GmbH, Wesseling, Germany.

X-ray Crystallography. All crystals were mounted in Hampton cryoloops using light oil for data collection at low temperature. Indexing and data collection were performed using a Bruker X8 APEX II CCD diffractometer with kappa geometry and Mo K α radiation ($\lambda = 0.71073$ Å). Data integration and routine processing were performed using the SAINT software suite. Further data processing, including multiscans absorption corrections, was performed using SADABS.¹³ Direct method (SHELXS97) solutions successfully located the W atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms.¹⁴ Refinements were full-matrix least-squares against F^2 using all data. Some lanthanides, cations, and waters of hydration were modeled with varying degrees of occupancy, a common situation for polyoxotungstate structures. For **NaTb-3**, **NaHo-5**, and **NaLu-9**, disordered lanthanide counter cations were found in addition to the nondisordered Ln³⁺ ions bridging the {W₂₂} polyanion. In the final refinements, all non-disordered heavy atoms (W, Ln) were refined anisotropically, while the O and Na atoms and some disordered lanthanides were refined isotropically. No H atoms were included in the models. The crystallographic data are provided in Table 1.

Results and Discussion

The ten novel lanthanide containing isopolytungstates [Ln₂(H₂O)₁₀W₂₂O₇₁(OH)₂]⁸⁻ (Ln = La (**1**), Ce (**2**), Tb (**3**), Dy (**4**), Ho (**5**), Er (**6**), Tm (**7**), Yb (**8**), Lu (**9**), Y (**10**)) have been prepared by reaction of WO₄²⁻ and lanthanide ions in a ratio of 11:1 in aqueous medium at pH 2.2. We discovered that three parameters are crucial for the successful formation of pure salts of **1–10**: reaction temperature, concentration of reagents, and pH of the solution. For example, the lanthanum analogue **1** forms only if the solution is heated. If the synthesis is performed at room temperature, a different product is formed as based on IR which has not been fully characterized yet but appears to be {W₅₆} based on preliminary crystal structures (vide infra). On the other hand, the cerium analogue **2** forms only at room temperature and is isolated as a second batch using fractional crystallization. The first crop of crystals appears to be identical with the room temperature product of the La synthesis described above, as based on IR. If the synthesis solution of **2** is heated, the well-known metatungstate ion [H₂W₁₂O₄₀]⁶⁻ is formed. Polyanions **3–10** also form upon heating, but the yield is much higher at room temperature. The yield is also affected by the concentration of the starting material. A tungstate concentration as high as 1.5 M is needed to obtain a pure crystalline product. Lower concentrations result in lower yields and non-crystalline white powder as the main product. It is interesting that formation of a considerable amount of unidentified precipitate was also detected during the optimal synthetic procedure, which partially accounts for the low yields observed. This precipitate had an IR signature different from **1–10**. Finally, we discovered that the pH of the reaction solution affects the formation and yields of compounds **1–10**. A pH window of 2.0–3.5 can be considered for a successful

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Table 1. Crystal Data and Structure Refinement for NaLa-1 – Na-10

	NaLa-1	NaCe-2	NaTb-3	Na-4	NaHo-5	Na-6	Na-7	Na-8	NaLu-9	Na-10
empirical formula	H ₁₁ L _{1.4} A ₂ Na ₅ O ₃₀ W ₂₂	H _{11.4} Ce _{1.4} Na ₅ O ₃₀ W ₂₂	H _{10.4} Tb ₂ Na ₅ O ₁₂₅ W ₂₂	H _{10.9} Dy ₂ Na ₅ O ₁₃₃ W ₂₂	H _{11.2} Ho ₃ Na ₅ O ₁₂₉ W ₂₂	H _{11.2} Er ₂ Na ₅ O ₁₂₈ W ₂₂	H _{10.4} Tm ₂ Na ₅ O ₁₂₅ W ₂₂	H _{11.4} Yb ₃ Na ₅ O ₃₀ W ₂₂	H ₁₀ Lu ₃ Na ₅ O ₁₂₈ W ₂₂	H _{11.4} Y ₂ Na ₅ O ₃₀ W ₂₂
MW	6840.91	6845.75	6741.96	6802.27	6831.03	6723.73	6671.02	6769.30	6843.13	6601.35
crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group (no.)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)	P1(2)
a/Å	13.539(2)	13.4837(12)	12.4701(7)	12.570(3)	12.516(4)	12.546(4)	12.5155(11)	12.5045(6)	12.172(3)	12.5441(17)
b/Å	13.882(3)	13.9216(13)	12.7195(9)	14.176(3)	12.704(4)	14.124(5)	12.6622(14)	12.6590(7)	12.465(3)	14.107(2)
c/Å	17.407(5)	17.393(3)	19.4938(14)	17.714(5)	19.430(7)	17.720(6)	18.3682(17)	18.3630(11)	19.469(5)	17.689(3)
α/deg	104.742(17)	104.809(7)	74.144(3)	71.874(11)	74.282(18)	72.166(18)	71.828(6)	72.041(13)	78.041(13)	71.931(9)
β/deg	92.426(16)	92.404(6)	76.728(3)	75.026(11)	76.757(16)	75.056(17)	95.498(5)	95.284(4)	77.672(15)	75.018(8)
γ/deg	117.945(10)	118.043(4)	88.131(3)	83.379(10)	88.112(14)	83.375(16)	93.339(3)	93.339(3)	86.625(11)	83.382(7)
V/Å ³	2744.6(11)	2735.2(6)	2893.4(3)	2895.9(12)	2893.4(17)	2885.7(16)	2859.6(5)	2855.6(5)	2823.0(12)	2872.5(8)
Z	1	1	1	1	1	1	1	1	1	1
T/°C	-40(2)	-100(2)	-100(2)	-100(2)	-100(2)	-100(2)	-100(2)	-100(2)	-100(2)	-100(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D/Mg m ⁻³	4.07	4.09	3.83	3.87	4.06	3.88	3.85	3.85	3.88	3.82
μ/mm ⁻¹	24.60	24.78	23.70	23.18	23.95	23.42	23.71	23.82	24.18	23.08
R _I / > 2σ(I) ^a	0.057	0.049	0.055	0.052	0.074	0.106	0.049	0.043	0.048	0.034
R _w (all data) ^b	0.153	0.121	0.176	0.147	0.233	0.280	0.127	0.123	0.122	0.088

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = (\sum [w(F_o^2 - F_c^2)] / \sum w(F_o^2))^{1/2}$$

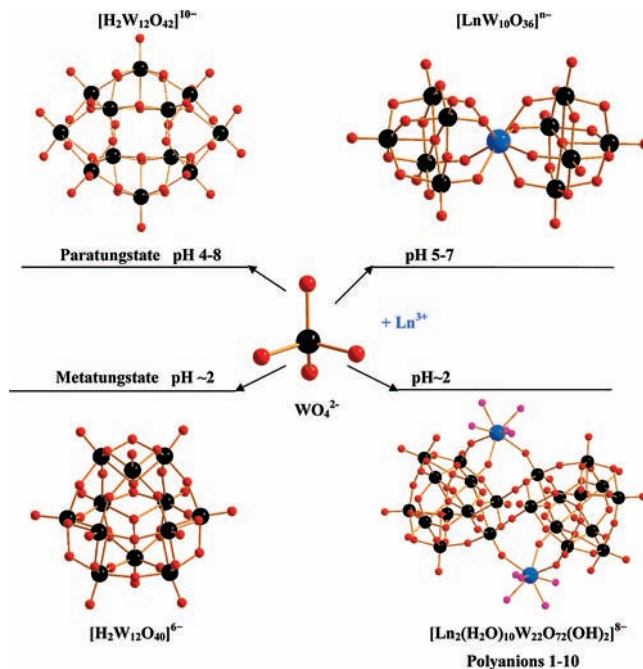


Figure 1. Formation scheme of two different isopoly dodecatungstates (left), and two lanthanide containing isopolytungstates (right) as a function of pH. The color code is as follows: W (black); O (red); Ln (blue); H₂O (pink).

synthetic procedure, with a pH of 2.2 being optimal. A pH lower than 2.0 did not result in any product, and a pH higher than 3.5 produced paratungstate ([H₂W₁₂O₄₂]¹⁰⁻) as the main product.

The synthetic procedures of **2–10** are very similar to Peacock and Weakley's [Ln(W₅O₁₈)₂]ⁿ⁻ and only differ in the pH of the reaction.^{4a} These authors worked at pH ~ 7, whereas we used pH ~ 2. It is well-known that pH is a crucial parameter in POM synthesis in general. For tungstates, it is also known that paratungstate, [H₂W₁₂O₄₂]¹⁰⁻, dominates in weakly acid solution, and metatungstate, [H₂W₁₂O₄₀]⁶⁻, in strongly acidic solution.^{1a} Continuous acidification leads eventually to the tungsten oxide hydrate, WO₃·2H₂O.¹⁵

Figure 1 shows the formation of different polytungstate structures in the absence and presence of lanthanide ions. Peacock and Weakley were able to isolate the sandwich-type, lanthanide-containing decatungstate [Ln(W₅O₁₈)₂]ⁿ⁻ {LnW₁₀} in a pH range where paratungstate is the major product if no lanthanide ions are present. The pH range of formation for **1–10** falls in the same range of formation for metatungstate, if no lanthanide ions are present. Therefore, the presence of lanthanide ions in solution is essential for the isolation of {LnW₁₀} at pH 5–7 and **1–10** at pH ~2.

We discovered experimentally that the presence of the lanthanide ions is needed at a very early stage in the synthesis of **2–10**. If the preacidified tungstate solution is left alone for too long before addition of the lanthanide solution, no lanthanide containing polyanion is formed but rather the metatungstate ion [H₂W₁₂O₄₀]⁶⁻. For the synthesis of **1** the situation is even more critical, as the presence of La³⁺ ions

(15) Fuchs, J.; Hartl, H.; Schiller, R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 420.

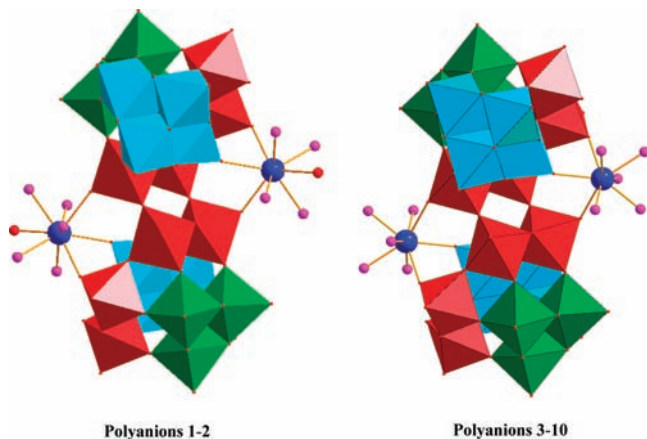


Figure 2. Polyhedral representation of $[Ln_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ (**1–2**) (left) and $[Ln_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ (**3–10**) (right). The structures of both polyanions are virtually identical, except the coordination number (8 vs 9) of the lanthanide ions (see text for details). The color code is as follows: WO_6 octahedra (light blue, green, red); Ln (blue); H_2O (pink), O (red). The WO_6 octahedra were colored differently for clarity. See also text and Figure 4.

was essential even before the first acidification step. An additional practical complication of this situation is that because of the formation of hydroxides the solution turns rather cloudy making it difficult to detect the redissolution of tungsten oxide which is formed while adding HCl_{aq} . The synthesis procedure was more straightforward for the late lanthanides Tb–Lu (**3–9**), and for the early 4d metal Y (**10**). When applying such synthesis procedure to the early lanthanides, then different products are obtained. Preliminary X-ray diffraction (XRD) analysis revealed the novel, lanthanide-containing 56-tungsten isopolyanion $\{W_{56}\}$ family $\{[Ln_2(H_2O)_{11}W_{28}O_{93}(OH)_2]^{14-}\}_2$, Ln = La–Gd. So far, we have obtained single-crystal XRD analyses for the lanthanum and cerium derivatives.¹⁶ After successive filtrations, another crystalline product is formed which turned out to be $\{Ln_2W_{22}\}$ based on IR and single crystal XRD. Polyanions **1–10** are isostructural and crystallize as hydrated sodium salts in the common triclinic space group $P\bar{1}$. This is reflected in their virtually identical IR spectra (see Supporting Information, Figure S1). Single-crystal XRD on the salts of polyanions La (**1**), Ce (**2**), Tb (**3**), Ho (**5**), and Lu (**9**) showed extra lanthanides as counter cations. These results were also confirmed by elemental analysis. The structure of polyanions **1–10** comprises the $[H_2W_{22}O_{74}]^{14-}$ isopolyanion coordinated to two $\{Ln(H_2O)_5\}^{3+}$ supporting ions. This 22-isopolytungstate consists of two undecatungstate units $\{W_{11}\}$ fused by two corner sharing W–O–W bridges (see Figure 2). Hence this structure can be described as a dimeric molecular entity composed of two $\{LnW_{11}\}$ half-units related by an inversion center, with point group symmetry C_i . Each Ln^{3+} is linked to the $\{W_{22}\}$ unit through three μ_2 -oxo bridges, two bridges to one $\{W_{11}\}$ half-unit and one bridge to the other half-unit. For the smaller lanthanides and yttrium (**3–10**), the remain-

ing coordination sphere is filled by five aqua ligands, giving a total coordination number of eight for each metal ion resulting in idealized square-antiprismatic geometry (see Figure 2). For the lanthanum and cerium derivatives, **1** and **2**, an extra coordination site was found due to the larger size of the early lanthanides, hence leading to a coordination number of nine and idealized monocapped antiprismatic geometry (see Figure 2). This extra coordination site has important consequences with respect to the solid state structures of **1** and **2**. We observed an extra μ_2 -oxo bridge between the lanthanum/cerium ions of one polyanion to a tungsten center of an adjacent polyanion, resulting in two intermolecular bridges and an overall 1D chain arrangement of the polyanions in the solid state (see Figure 3). Average Ln–O bond lengths were calculated for **1–10** and are shown in Table 2. As expected, a difference of about 0.2 Å was observed between the Ln–O bonds of the early (La and Ce) and late (Tb–Lu) lanthanides. For yttrium, the average Y–O bond lengths fall in the range of the late lanthanides.

The undecatungstate subunit $\{W_{11}\}$, two of which comprise the $\{W_{22}\}$ fragment in **1–10**, can be considered an assembly of four distinct “building blocks”, see Figure 4:

- One tetratungstate $\{W_4\}$ fragment (light blue in Figure 4) formed from four edge-shared WO_6 octahedra connected via a μ_4 -oxo bridge. This tetratungstate fragment can be viewed as a dilacunary form of the Lindqvist structure.¹
- One tritungstate $\{W_3\}$ fragment (green in Figure 4) formed from three edge-shared WO_6 octahedra connected via a μ_3 -hydroxo bridge (vide infra). This fragment can be viewed as a single “triad” of the well-known Keggin or Wells-Dawson ions.¹
- Two ditungstate $\{W_2\}$ fragments (red in Figure 4), each formed from two edge-shared WO_6 octahedra, which are corner-sharing on one side.

This undecatungstate fragment $\{W_{11}\}$ was first reported by Fuchs in 1988.¹⁷ Here we report on the lanthanide capped 22-isopolytungstate $\{W_{22}\}$, which represents two $\{W_{11}\}$ fragments fused via two W–O–W’ bridges (see Figure 4). Recently Cronin et al. reported on $\{W_{36}\}$ which is a cyclic trimer of $\{W_{11}\}$ linked via three extra WO_6 bridges and stabilized by a central potassium ion.¹⁸ Figure 5 summarizes the three isopolytungstate structures $\{W_{11}\}$, $\{W_{36}\}$, and $\{W_{22}\}$ and the respective formation conditions. The $\{W_{22}\}$ isopolytungstate as such offers two tridentate ligand sites, which are coordinated to two Ln^{3+} centers in **1–10**. To the best of our knowledge, polyanions **1–10** represent the largest lanthanide-containing isopolytungstates known to date.

We also tried to synthesize the lanthanide-free isopolyanion $[H_2W_{22}O_{74}]^{14-}$ by following the same synthetic procedure as **1–10** but in the absence of lanthanides. We were able to isolate a solid compound with an IR spectrum very similar to that of **1–10** (Supporting Information, Figure S2) and different from paratungstate and metatungstate (Supporting Information, Figure S3).

(16) The cerium derivative $\{[Ce_2(H_2O)_{11}W_{28}O_{93}(OH)_2]^{14-}\}_2$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 21.629(2)$ Å, $b = 26.869(3)$ Å, $c = 31.611(3)$ Å, $\alpha = 80.463(3)^\circ$, $\beta = 72.936(4)^\circ$, $\gamma = 75.999(4)^\circ$, $V = 16951.2$ Å³, and $Z = 2$. The full characterization will be published soon.

(17) Lehmann, T.; Fuchs, J. Z. *Naturforsch. B* **1988**, *43*, 89.

(18) Long, D-L.; Abbas, H.; Kögler, P.; Cronin, L. *J. Am. Chem. Soc.* **2004**, *126*, 13880.

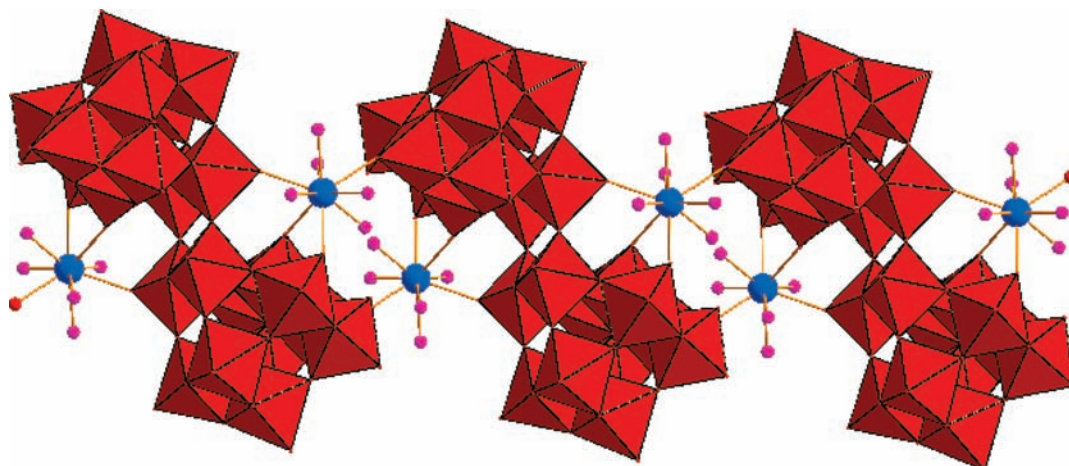


Figure 3. Polyhedral representation of polyanions **1** and **2** forming 1D chains in the solid state. The color code is as follows: WO_6 octahedra (red); La or Ce (blue); H_2O (pink), O (red).

Table 2. Average Ln–O Bond Lengths (Å) $[\text{Ln}_2(\text{H}_2\text{O})_{10}\text{W}_{22}\text{O}_{72}(\text{OH})_2]^{8-}$ (La (**1**), Ce (**2**), Tb (**3**), Dy (**4**), Ho (**5**), Er (**6**), Tm (**7**), Yb (**8**), Lu (**9**), Y (**10**))

Ln	average Ln–O(W)	average Ln–OH ₂
La (1)	2.551(15)	2.562(18)
Ce (2)	2.523(11)	2.533(12)
Tb (3)	2.324(13)	2.337(15)
Dy (4)	2.382(10)	2.388(12)
Ho (5)	2.339(11)	2.388(12)
Er (6)	2.36(3)	2.33(4)
Tm (7)	2.310(11)	2.350(11)
Yb (8)	2.302(8)	2.344(8)
Lu (9)	2.301(11)	2.328(12)
Y (10)	2.339(7)	2.361(7)

Bond valence sum (BVS) calculations for **1–10** confirmed that all tungsten atoms are in the +6 oxidation state and that all lanthanide ions and yttrium are in the +3 oxidation state.¹⁹ The main purpose of our BVS studies on **1–10** was indeed to check all polyanion oxygens for possible protonation. As stated above, one monoprotonated oxygen was identified in the asymmetric half-unit, namely the μ_3 -oxo bridge of the $\{\text{W}_3\}$ fragment connecting the three tungsten atoms W5, W6, and W7 (see Supporting Information, Figure S4). This results in two OH groups for the dimeric form and a total charge of -8 for all polyanions **1–10**. As usual, terminal $\text{W}=\text{O}$ oxygen BVS values are low (~ 1.5) but this is typical for the distorted $\text{W}=\text{O}$ geometry and does not indicate additional protonation.

Polyanions **1–10** represent the first examples of lanthanide-containing isopolyanions with “exposed” lanthanide centers, bearing aqua ligands, which are expected to be labile. These water molecules represent good candidates for ligand substitution by other mono- or polydentate ligands, including chiral ones. The resulting chiral polyanions could be interesting for catalytic applications. Also, lipophilic alkyl ammonium salts of **1–10** could be useful for homogeneous catalysis applications in organic media. We plan to perform such studies in the near future.

Thermogravimetric analyses (TGA) were performed on the salts of **1–10** to determine the respective degree of

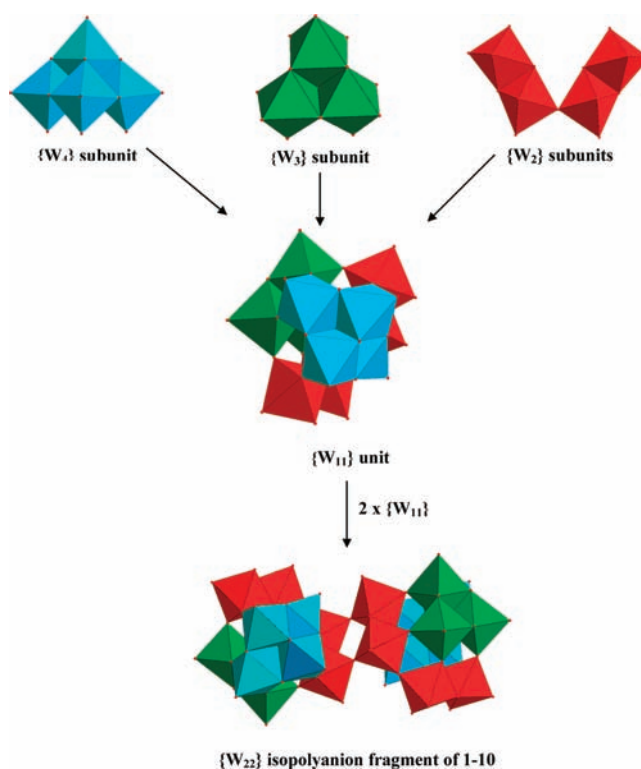


Figure 4. Polyhedral representation of the $\{\text{W}_{22}\}$ unit of **1–10** which is composed of two $\{\text{W}_{11}\}$ half-units. The latter are composed of di-, tri- and tetrameric tungsten-oxo building blocks shown in different color: $\{\text{W}_4\}$ (light blue), $\{\text{W}_3\}$ (green), $\{\text{W}_2\}$ (red).

hydration and the thermal stability. The TGA graphs of all ten compounds showed a region of weight loss due to dehydration (see Supporting Information, Figures S5–S14). This region corresponds to a two-step weight loss in the range of ~ 25 – 200 °C and ~ 200 – 400 °C for the salts of derivatives **3–10**. The first step is attributed to the release of all lattice water molecules, and the second step to the release of the coordinated water molecules, corresponding approximately to the calculated 10 waters per molecular formula. For the La and Ce derivatives **1** and **2**, this region exhibits a one-step only weight loss in the range ~ 25 – 400 °C making the steps for the loss of crystal and coordinated water molecules indistinguishable. This reflects nicely the

(19) Altermatt, D.; Brown, I. D. *Acta Crystallogr.* **1985**, *B41*, 244.

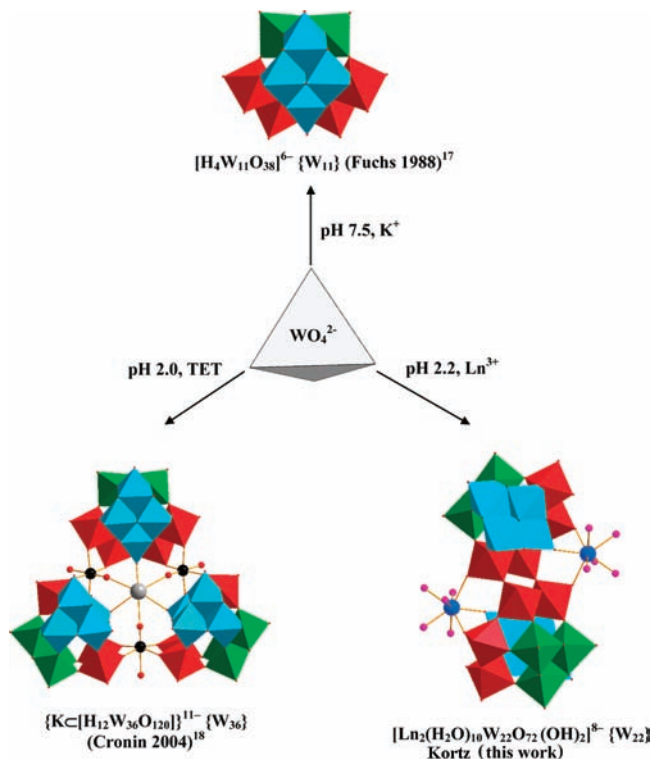


Figure 5. Polyhedral/ball-and-stick representation of isopolytungstates containing the $\{W_{11}\}$ unit. The color code is the same as in Figure 4: tungsten (black); potassium (gray); oxygen (red).

different solid state packing of **1** and **2**, compared to **3–10** (vide supra). The degree of hydration was calculated for all compounds and gave a range of 41–49 water molecules per formula unit. These results were also supported by elemental analysis. Furthermore, the absence of any additional weight loss indicated that all 10 compounds, after loss of the water molecules, were thermally stable up to 800–900 °C (see the Supporting Information).

We tried very hard to obtain solution ^{183}W NMR spectra of the diamagnetic derivatives **9** and **10** (Lu and Y analogues) but without success. The same also applies for ^{89}Y NMR. Both compounds were not very soluble. Although heating to ~80 °C eventually led to partial dissolution, ^{183}W NMR of these solutions resulted in a single peak for metatungstate ($[H_2W_{12}O_{40}]^{6-}$) indicating decomposition of **9** and **10** at this temperature. The ^{89}Y spectrum of polyanion **10**, when dissolved upon heating, showed a signal typical for free Y^{3+} ions. We also tried cation exchange using a Li^+ loaded resin, which led eventually to complete dissolution of the polyanion salts. However, the ^{183}W NMR spectra for both **9** and **10** were not conclusive and showed a large number (>11) of peaks probably arising from a mixture of species in solution.

(20) Miras, H. N.; Yan, J.; Long, D.-L.; Cronin, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 8420.

We speculate that Li^+ ion exchange may have stripped the Lu^{3+} and Y^{3+} from the polyanion framework, thus initiating a decomposition pathway resulting in various products. We also performed ^{183}W NMR studies on Fuchs' original $\{W_{11}\}$, but we observed too many signals which we attributed to a mixture of $[H_2W_{12}O_{42}]^{10-}$ and $\{W_{11}\}$.

Conclusions

We have successfully synthesized and structurally characterized by IR spectroscopy, TGA, and single crystal X-ray diffraction 10 novel isopolyoxotungstate anions containing lanthanides: $[Ln_2(H_2O)_{10}W_{22}O_{72}(OH)_2]^{8-}$ ($Ln^{3+} = La$ (**1**), Ce (**2**), Tb (**3**), Dy (**4**), Ho (**5**), Er (**6**), Tm (**7**), Yb (**8**), Lu (**9**), Y (**10**)). These polyanions were synthesized in aqueous acidic medium starting from sodium tungstate and Ln^{3+} salts. Polyanions **1–10** were isolated as sodium or mixed sodium/lanthanide salts, and they all crystallized in the triclinic space group $P\bar{1}$. Single crystal X-ray structural analysis showed that all polyanions are isostructural and are composed of a 22-tungsten isopolyanion unit $\{W_{22}\}$ coordinated to two lanthanide ions bearing terminal aqua ligands. The 22-tungstate unit $\{W_{22}\}$ is assembled from two $\{W_{11}\}$ subunits fused via two corner-sharing W–O–W bridges. The undecatungstate subunit has been reported before in a monomeric and trimeric form. Possible applications of polyanions **1–10** in the field of homogeneous catalysis may prove possible if pure lipophilic organic salts can be prepared. Chiral derivatives of **1–10** can be envisioned by replacing the terminal water ligands on the lanthanide centers by chiral organic ligands. This will be the scope of further studies.

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Note Added after ASAP Publication. After ASAP publication, ref 20 and related text in the Acknowledgment section was added. This article was published ASAP on December 30, 2008. The corrected article was published ASAP on January 12, 2009.

Supporting Information Available: Further details are given in Figures S1–S14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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