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# New Lanthanide-Containing Polytungstates Derived from the Cyclic $P_8W_{48}$ Anion: $\{Ln_4(H_2O)_{28}[K\subset P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]^{13-}\}_x$, Ln = La, Ce, Pr, Nd[†]

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The reaction of $K_{28}Li_5H_7[P_8W_{48}O_{184}]\cdot 92H_2O$ with early lanthanides under hydrothermal and conventional conditions yields novel structures of the molecular formula $Ln_4(H_2O)_{28}K_6Li_7[K\subset P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}] \cong 57H_2O$, Ln = La (**1**), Ce (**2, 2a**), Pr (**3**), Nd (**4**), in which the central cavity of the precursor anion is occupied by lanthanide cations and $H_4W_4O_{12}$ moieties. The new heteropolyanions were characterized by elemental analysis, infrared spectroscopy, $^{31}P$ NMR, and X-ray crystallography. All of the crystals are monoclinic, space group *C*2/*m*, with lattice constants (Å, E) $a = 33.061(3)$, $b = 30.986(3)$, $c = 15.1649(13)$, $\beta = 103.607(2)$, (**1**); $a = 33.0577(16)$, $b = 31.0562(15)$, $c = 15.2320(7)$, $\beta = 104.015(2)$, (**2**); $a = 33.0577(16)$, $b = 31.0562(15)$, $c = 15.2320(7)$, $\beta = 104.015(2)$, (**2a**); $a = 33.007(2)$, $b = 31.060(2)$, $c = 15.2129(10)$, $\beta = 104.0140(10)$, (**3**); $a = 32.913(19)$, $b = 31.155(18)$, $c = 15.135(9)$, $\beta = 103.495(11)$, (**4**); and $Z = 2$.

## Introduction

The incorporation of lanthanide (Ln) and actinide (An) cations within polyoxometalate[1] structures offers a possible route to the sequestration and storage of such cations present in nuclear wastes.[2] Examples of the encryption of Ln/An within the cyclic polytungstate frameworks $[P_5W_{30}O_{110}]^{15-}$ and $[As_4W_{40}O_{128}]^{28-}$ have been reported in recent years.[3] In 1985, Contant and Tézé[4] reported the anion $[P_8W_{48}O_{184}]^{40-}$, stable in aqueous solution over a broad pH range, which has a central cavity with a "diameter" of about 8 Å. The crystal structure of $K_{28}Li_5H_7[P_8W_{48}O_{184}]\cdot 92H_2O$ revealed the cavity to be occupied by about 8 potassium cations disordered over 12 sites and, presumably, disordered water molecules. We report that the reaction of $P_8W_{48}$ with early lanthanide cations under hydrothermal and conventional conditions leads to 3D networks in which the anion cavities are occupied by lanthanide and polytungstate moieties.

## Experimental Section

The Dawson anions $\alpha$-$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$, $\beta$-$K_6[P_2W_{18}O_{62}]\cdot 19H_2O$, and $\alpha$-$K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ were synthesized following

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published procedures[5] and were identified by infrared and $^{31}P$ NMR spectroscopy.

$K_{28}Li_5H_7[P_8W_{48}O_{184}]\cdot 92H_2O$ ($P_8W_{48}$) was synthesized according to a variation of the method reported by Contant and Tézé.[4] In 950 mL of water were dissolved, successively, glacial acetic acid (60 g, 1 mol), lithium hydroxide (21 g, 0.5 mol), lithium chloride (21 g, 0.5 mol), and $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ (28 g, 7 × $10^{-2}$ mol). The solution was left in an open beaker. After 9 days, the volume of the solution had evaporated to ca. 650 mL, and the crystals were collected by suction filtration on a coarse frit and washed with ethanol (50%, 40 mL), ethanol (40 mL), and ether (40 mL) and finally air-dried for 1 day. Yield: 17.5 g (66% based on tungsten). IR ($cm^{-1}$): 1138 (m), 1085 (m), 1017 (w), 979 (sh), 951 (sh), 929 (m), 916 (m), 808 (s), 687 (s), 573 (w), 527 (w), 462 (w). $^{31}P$ NMR (ppm): −7.4.

$Ln_4(H_2O)_{28}K_6Li_7[K\subset P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}] \cong 57H_2O$, Ln = La(**1**), Ce (**2**), Pr (**3**), Nd (**4**). The general procedure for all hydrothermal syntheses was as follows: $P_8W_{48}$ (0.5 g, 0.034 mmol) and LiCl (0.5 g, 11.795 mmol) were dissolved in water (7 mL). The pH was adjusted to 1.5 with three drops of 6 M HCl. The trivalent lanthanum salt ($Ce(NO_3)_3\cdot 6H_2O$ (0.088 g, 0.203 mmol), $La(NO_3)_3\cdot 6H_2O$ (0.088 g, 0.203 mmol), $Pr(Cl)_3\cdot 7H_2O$ (0.076 g, 0.203 mmol), or $Nd(NO_3)_3\cdot 5H_2O$ (0.085 g, 0.203 mmol)) was added, and the mixture was heated to 140 °C in an acid digestion bomb overnight. The resulting solution was separated from an insoluble residue, and crystals were obtained after 3 days in a sealed beaker. Yield: ca. 30 mg of crystals (5%) and ca. 230 mg of insoluble residue. During reproducibility checks for the syntheses, an alternative nonhydrothermal procedure for **2** was developed: $P_8W_{48}$ (1.000 g, 0.068 mmol), $H_2WO_4$ (0.136 g, 0.544 mmol), and LiCl (1.000 g, 23.590 mmol) were dissolved in water (14 mL). The pH was adjusted to 1.5 with a few drops of aqueous 6 M HCl. Then, $CeCl_3\cdot 7H_2O$ (0.152 g, 0.408 mmol) was added in small portions, and a pale-yellow precipitate appeared immediately. The reaction mixture was boiled for 6 h in a covered beaker and then filtered while hot to remove any insoluble residue (final pH was 1.3). Single crystals (**2a**) suitable for X-ray diffraction were obtained in a open beaker after 1 day (yield 0.060 g, 5%; insoluble residue, 0.460 g). The structures of the anions obtained by both synthetic methods were essentially the same by single-crystal X-ray analysis. IR: 1145 (s), 1078 (s), 1020 (w), 933 (s), 916 (s), 750 (s), 673 (sh), 532 (m), 470 (m), 431 (w). Anal. Calcd (found) for **2a**: Li 0.37(0.3); K 1.62(1.69); Ce 5.0 (4.4); P 1.47(1.44); W 61.3(61.0); $H_2O$ 10.63(10.65).

**Physical Measurements.** Elemental analysis was performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany. Water content was determined by TGA measured at TA Instruments, Darmstadt, Germany, on a TGA Q5000 analyzer under nitrogen (platinum pan, heating rate 5 K/min, room temperature to ca. 900 EC). A single dehydration step was complete by 300 EC. (Figure S1) Infrared spectra with 2 $cm^{-1}$ resolution were recorded on a Nicolet 170SX FTIR spectrophotometer with KBr pellet samples. Parr models 4746 and 4748 acid digestion bombs were used for the hydrothermal reactions. NMR spectra were recorded on a Bruker AM-300WB spectrometer operating at 7.05 T. The resonance frequency was 121.495 MHz for $^{31}P$. Chemical shifts are reported with respect to external 85% $H_3PO_4$. All of the $^{31}P$ spectra were obtained using the reaction solution without further purification and a deuterium oxide insert.

**Crystallography.** Data for the structure of **2a** were collected at the International University Bremen at 173 K on a Bruker X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo anode tube and graphite monochromator.[6] Scan widths were 0.5°, and 3283 frames were collected. The remaining structures were collected at Georgetown University (**2**) and the Naval Research Laboratory (**1**, **3**, **4**) at 93 K on a Bruker SMART 1K diffractometer equipped with an Xstream LT system. Scan widths were 0.3°, and 1800 frames were collected. The SHELX software package was used to solve and refine the structures.[7] The direct methods solution located the heaviest atoms, and remaining atoms were found in subsequent Fourier difference syntheses. Crystal data for all of the compounds are summarized in Supporting Information (**1**, **2**, **2a**, **3**, **4**).

## Results and Discussion

In preliminary exploratory measurements, aqueous solutions of $P_8W_{48}$ (formed by addition of lithium chloride to the insoluble potassium salt, Experimental section) were treated with varying quantities of $Ce(NO_3)_3$ ($P_8W_{48}$/Ce ratios of 1:1 to 1:8) at temperatures ranging from 20 to 100 °C and pH values between 1 and 6. In every case, an insoluble material resulted that we were unable to recrystallize. Under hydrothermal conditions as described above, yellow crystals of the new compound were obtained from reactions carried out at pH 1.5 with $P_8W_{48}$/Ce ratios of 1:4, 1:6, and 1:8. The relative amount of an insoluble coproduct varied and increased at higher ratios. By slow evaporation in an open beaker, a second kind of colorless, sometimes pale-yellow, crystals grew. These showed a sharp single peak at −13 ppm in the $^{31}P$ NMR and were confirmed as the Dawson anion[8] $\alpha$-$[P_2W_{18}O_{62}]^{6-}$ by a partial X-ray investigation and elemental analysis. If solutions of $P_8W_{48}$ without added lanthanide were subjected to hydrothermal treatment, the Dawson anion was the only polytungstate product according to $^{31}P$ NMR.

If the reaction was carried out at higher pH (4.5), red crystals were formed. These were provisionally identified as a salt of $[Ce(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$ by $^{31}P$ NMR of the supernatant and solutions of the crystals. At lower pH values (1.0, 1.5), $^{31}P$ NMR of the solution from which the crystals eventually formed showed a major resonance for $\alpha$-$[P_2W_{18}O_{62}]^{6-}$ and five minor ones at −13.4, −17.8, −18.9, −20.7, and −23.7 ppm (Figure S2). The latter four peaks disappeared after the crystals of the product had grown, and they may indicate the signature of the new polyanion in solution (below).

The structure of the polyoxometalate anion in each of the four compounds investigated is shown in Figure 1. The central cavity of the $P_8W_{48}$ anion is occupied by two added $W_4O_{12}$ groups, and two potassium and four lanthanide cations, each of which has an occupancy of 50%.

Bond valence sum (BVS) calculations[9] indicate that each $W_4O_{12}$ moiety has four protons on terminal oxygens (BVS = 0.97 and 0.89). As a result of the imposed 2/*m* symmetry,

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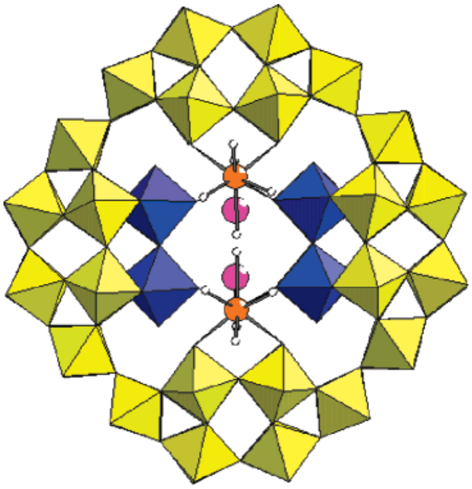

**Figure 1.** Polyhedral representation of $[K\subset P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]^{25-}$, Ln = La, Ce, Pr, Nd, viewed perpendicular to the equatorial mirror plane. The color code is as follows: tungsten (yellow and blue), lanthanide (orange), potassium (violet), and oxygen (white).

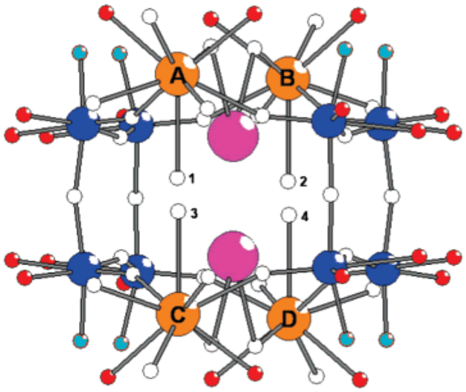

**Figure 2.** Ball-and-stick representation of the contents of the cavity of $P_8W_{48}$ in compounds **1**−**4**. Oxygen atoms of the precursor $P_8W_{48}$ anion are shown in red, protonated "terminal" oxygens in aqua. Other atoms follow the color code in Figure 1. The lanthanide and potassium cations with coordinated water molecules all have 50% occupancy.

the BVS calculation cannot distinguish between two possible cases: four terminal hydroxy groups or disorder of two terminal water ligands with terminal oxo groups. The thermal parameters of the oxygens do not appear to be larger than usual, so the atoms are not clearly disordered.

In addition, one oxygen that bridges a tungsten and the inner Ce atom has a low BVS of 1.34. Although this could indicate two or three additional (possibly disordered) protons, we believe that the disorder of the Ce atoms makes this less certain. The formula we report is our best estimate based on a combination of elemental analysis and the structural results.

A representation of the contents of the filled cavity is shown in Figure 2. The polytungstate shell therefore consists of four subunits, two $P_2W_{12}O_{48}$ and two $P_2W_{16}O_{60}$, with equivalent ones facing each other. Both subunits are derived from the well-known Dawson structure, $P_2W_{12}O_{48}$, by the loss of six adjacent $WO_6$ octahedra, two from the cap and four from the belt, and $P_2W_{16}O_{60}$, by the loss of one $WO_6$ octahedron in each cap. The W...W distances in the two different subunits are between 3.33 and 3.65 Å and agree with those found in other Dawson-like structures.

Two kinds of lanthanide atoms can be distinguished. The first kind is formed by the $Ln^{3+}$ ions inside the polyanion, which have occupancy factors of 50%, as well as the coordinated water molecules 1 and 3, which would otherwise stand too close together (Figure 2). Lanthanide atoms of a second type are connected to terminal tungstate oxygen atoms and establish eight ionic linkages between the polytungstate anions to form a 3D network (Figure 3). Similar linkages between poloxometalate anions have been observed in the dimeric and polymeric derivatives of lanthanide complexes of $[As_4W_{40}O_{140}]^{28-}$.[10]

Both internal and external cerium cations exhibit an approximate monocapped square-antiprismatic coordination geometry.

The crystallographic occupancy factors of 50% for the two internal potassium cations are consistent with the short interatomic distances between K(1) and K(2) (3.18 Å). Similar disordered positions of the encrypted cations within the Preyssler anion $[MP_5W_{30}O_{110}]^{n-}$ have been noted.[3c,e,11]

Geometric considerations indicate that an individual $P_8W_{56}$ anion shell can accommodate the two lanthanide cations only in positions A and B or A and D (Figure 2) or their symmetry-equivalent arrangements. There seems to be no major reason to favor one arrangement over the other unless the potassium cation assists in stabilizing the AB arrangement. One might speculate (but cannot prove) that the remaining internal sites could be occupied by one or more lithium cations or disordered water molecules.

As a result of the lanthanide contraction, the change in size of the $Ln^{3+}$ ions from $La^{3+}$ (1.17 Å) to Lu $^{3+}$ (1.00 Å) means that homologous compounds of lanthanides with appreciably different radii may differ in structure. As shown in this work, the behavior of $La^{3+}$, $Pr^{3+}$, and $Nd^{3+}$ was identical to that of $Ce^{3+}$ (Table S1). However, experiments with the smaller lanthanide cations $Eu^{3+}$ and $Lu^{3+}$ under the same conditions yielded no solid material.

Phosphorus-31 NMR of the resulting solutions showed the presence of the Dawson anion and free phosphate only. These results suggest that only the larger lanthanide cations trap an intermediate during the hydrothermal conversion of the $P_8W_{48}$ anion into the thermodynamically stable Dawson anion.

## Conclusions

A family of four new lanthanide-substituted polyoxotungstates have been synthesized and characterized by single-crystal X-ray diffraction, IR, and elemental analysis. Although the original report of the $P_8W_{48}$ anion implied that occupancy of this lacunary polytungstate by "guest" cations was unlikely, the present work and recent results by Kortz[12]

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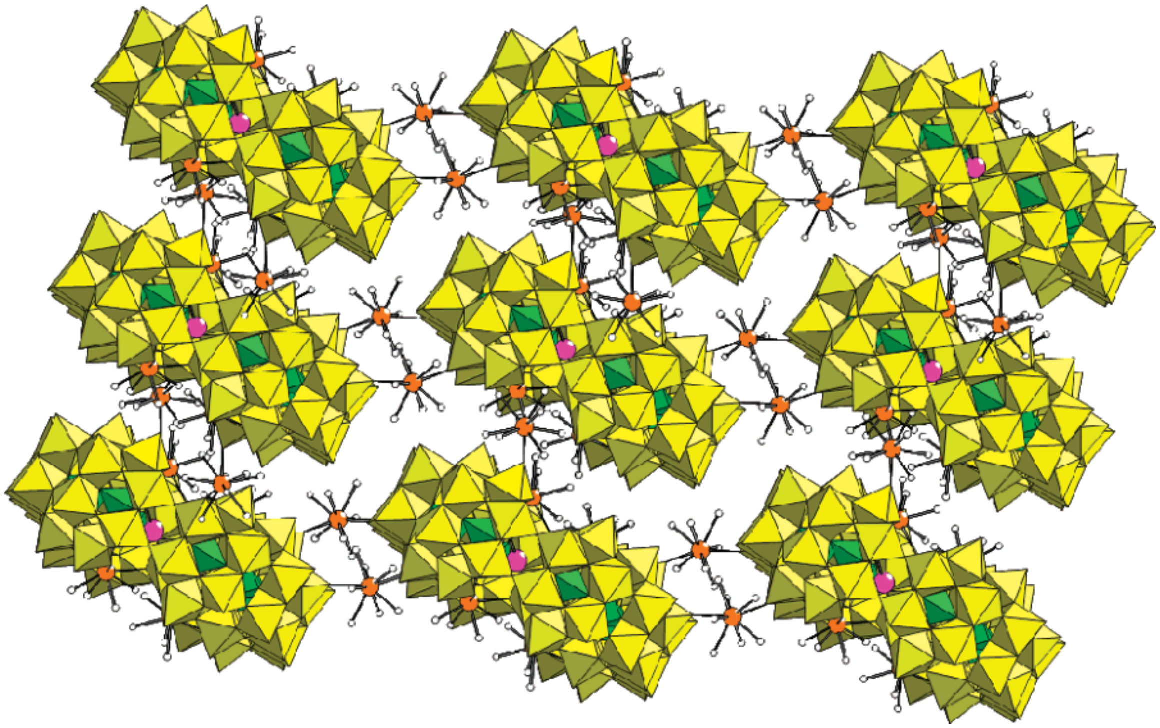

**Figure 3.** Representation of the 3D network of **1**−**4**. Color code as in Figure 1 with $PO_4$ tetrahedra (green).

indicate otherwise and demonstrate that further chemistry of this 20-year-old anion will be developed.

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**Supporting Information Available:** Crystal data for **1**−**4** and five X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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