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An Inorganic Aggregate Based on a Sandwich-Type Polyoxometalate with Lanthanide and Potassium Cations: From 1D Chiral Ladder-Like Chains to a 3D Open Framework

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The reaction of sandwich-type polyanion $[Mn_4Si_2W_{18}O_{68}(H_2O)_2]^{12-}$, ceric sulfate, and potassium citrate in an acidic aqueous solution led to the isolation of a new compound $K_4Na_2[\{Ce(H_2O)_7\}_2Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot 21.5H_2O$ (**1**), which crystallizes in the space group $P2_12_12_1$ with $a = 12.040(2)$ Å, $b = 26.094(5)$ Å, $c = 30.043(6)$ Å, $V = 9439(3)$ Å^3, $Z = 4$, and flack parameter x = 0.63(1). X-ray diffraction analysis reveals that **1** consists of novel chiral ladder-like chains based on sandwich-type polyanions and lanthanide cations, which are further connected into a three-dimensional open framework by potassium cations.

Introduction

The use of polyoxometalates (POMs) as basic building blocks to construct novel extended materials by means of different cationic linkers is of great interest and stems not only from their intriguing variety of architectures and topologies, but also from their numerous potential applications in catalysis, sorption, nonlinear optics, magnetic materials, and bioinorganic pharmaceuticals.[1] In this field, lanthanide cations ($Ln^{3+/4+}$) are popular linkers due to their high coordination numbers and oxyphilic activities, as well as their multiple physicochemical properties.[2] To date, a series of POM-based extended aggregates linked by lanthanide ions have been extensively reported as follows: (1) Keggin[3] polyanions and their monovacant derivatives are linked by $Ln^{3+/4+}$ ions to form one-dimensional zigzag chains, such as $[Ln_n(SiW_{11}O_{39})]$,[4a] $[Ln(SiW_{11}O_{39})_2]^{13-}$,[4b] and $[Ce_2(BW_{11}O_{39})_2(H_2O)_6]^{12-}$,[4d] a two-dimensional layer $[\varepsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5-}$,[4e] and a three-dimensional framework $[Gd(H_2O)_3]_3[GdMo_{12}O_{42}]$.[4i] Further, a series of trivacant Keggin polyanions can be self-assembled with $Ln^{3+/4+}$ ions to form nanoscale inorganic aggregates, such as $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$,[4g] $[(PM_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$ (M = Eu, Y),[4h] and $[K\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$.[4f] (2) Wells–Dawson[5] polyanions and their monovacant congeners[6] are another kind of popular building blocks[7] assembled with lanthanide ions. A current report in this family is $[Ln(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})]_n^{7n-}$,[7b] which displays a series of extended structures with 1D chains and 2D layers. (3) Recently, Anderson-type polyanions have become a new class of precursors for the construction of extended inorganic aggregates,[8] such as $[La(H_2O)_7CrMo_6H_6O_{24}]^{2-}$[8a] and $[\{(C_6H_5NO_2)_2Ln(H_2O)_4\}_2\{IMo_6O_{24}\}]$.[8b] (4) Various isopolyoxoanion units connected with $Ln^{3+/4+}$ ions have also been reported,[9] exemplified by $[Ce(H_2O)(DMF)_6(W_{10}O_{32})]$,[9a] $[La(W_5O_{18})_2]^{9-}$,[9b] and $[\{Ln(H_2O)_5\}_2(H_2M_{12}O_{42})\}]^{2-}$ (M = Mo, W).[9c] (5) A series of large molybdenum and vanadium clusters have also been linked by lanthanide ions, which led to a series of infinite chains and networks.[10] As a continuation of the exploration of novel extended POM-based aggregates in this subfield with the "property-adding" feature, transition-metal-substituted POMs should be suitable precursors owing to their optical, electronic, and magnetic properties, which are largely dependent on the changeable transition metal centers.[11] In this aspect, the sandwich-type POMs with tetranuclear transitional-metal centers are an ideal class of candidates. However, no such extended inorganic aggregates based on sandwich-type POMs and lanthanide linkers have been reported. Because the pH stability ranges for sandwich-type POMs in aqueous solutions are different from those of lanthanide ions, together with the obvious reactive activity between the highly negative polyanions and strongly oxyphilic lanthanide cations,[12] most reactions between such two units result in immediate precipitates but not crystals. Thus, it is still a challenge to explore suitable synthetic conditions that would enable the acquisition of novel inorganic aggregates that are based on

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these two building blocks. Nevertheless, some current efforts indicate that the introduction of organic N- and O-donor ligands or solvents during the preparation could somewhat stabilize the lanthanide cations, reduce the reactivity between POMs and lanthanide linkers, and improve the solubility of the final products. Therefore, the use of multidentate O-donor ligands (such as citrate, tartrate, and EDTA salts) were fully considered during our preparation of novel inorganic aggregates based on sandwich-type POMs and lanthanide cations. Although most of the sandwiching POMs possess lower symmetry in the crystal form, if they were to coordinate to different linkers they may present chirality and improve their functionality. On the basis of the above consideration, we synthesized a new compound with the assistance of citrate ligands, $K_4Na_2[\{Ce(H_2O)_7\}_2Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot 21.5H_2O$ (**1**), which represents the first extended inorganic aggregate composed of sandwich-type POMs and lanthanide linkers. The structure of **1** possesses a chiral ladder-like chain based on $[Mn_4Si_2W_{18}O_{68}(H_2O)_2]^{12-}$ polyanions and cerium cations. These chains are further connected into a 3D open framework by potassium cation linkers.

Results and Discussion

Syntheses

Compound **1** was synthesized by boiling a mixed aqueous solution of $K_4Na_6Mn[Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot{\approx}33H_2O$, $Ce(SO_4)_2\cdot 4H_2O$ and potassium citrate for 2 h. Yellow block crystals were isolated after the filtrate stood at room temperature for one week. The precursor $K_4Na_6Mn[Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot{\approx}33H_2O$ was synthesized according to the published procedure.[13] Two important problems must be fully considered during the synthesis. Firstly, the pH value of the reaction system should be carefully controlled so as to stabilize the structure of the sandwich-type polyanions and avoid early precipitation of cerium cations. However, a series of reports indicate that the surface oxygen atoms of POMs are rather active to react with the oxyphilic lanthanide ions,[12] and in most cases precipitation instead of crystallization occurs. Thus, a multidentate O-donor ligand of potassium citrate was used to stabilize the cerium ions or maybe reduce the reactivity of cerium ions owing to the high coordination ability of such organic ligand with metal ions. Although the citrate ligand was not observed in the final structure of **1**, it is definitely necessary during the preparation of **1**. It is also noteworthy that there are two obvious color changes during the reaction. At the beginning of the reaction, the yellow aqueous solution of $K_4Na_6Mn[Mn_4Si_2W_{18}O_{68}(H_2O)_2]$ immediately changed to brown when the mixed solution of $Ce(SO_4)_2\cdot 4H_2O$ and potassium citrate was added. However, the brown color changed back to yellow after boiling for 2 h. It is presumed that the redox reactions between Mn^{2+} and Ce^{4+} ions in the first step led to the formation of Mn^{3+} and Ce^{3+} ions, which exhibit the brown color. After boiling for 2 h, the disproportionation reaction of the metastable Mn^{3+} ions occurred, which resulted in the transformation of Mn^{3+} into Mn^{2+}; thus, the brown solution changed back to yellow.

Structure Description

Single-crystal X-ray diffraction analysis revealed that **1** consists of a novel chiral ladder-like chain based on sandwich-type $[Mn_4Si_2W_{18}O_{68}(H_2O)_2]^{12-}$ polyanions and cerium cation linkers. In **1**, the well-known sandwich-type polyanion (as shown in Figures 1 and S1) consists of two trivacant $[B\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ Keggin moieties sandwiching a central symmetric rhomb-like $[Mn_4O_{16}(H_2O)_2]$ segment through the W–O–Mn and Si–O–Mn connecting modes. All the W and Mn centers exhibit an octahedral coordination environment. The bond lengths of W–O are in the range 1.664(2)–2.471(2) Å, whereas the bond lengths of Mn–O are between 2.107(2) and 2.250(2) Å. It is interesting that two cerium cations are coordinated directly to the surface oxygen atoms (O45, O27, O14, O47) of the sandwich-type polyanion (see Figures 1 and S1). The bond lengths of the four Ce–O bond lengths are 2.541(2) Å, 2.492(2) Å, 2.519(2) Å, and 2.578(2) Å, respectively. The residual coordination sites of two nona-coordinated cerium cations are fulfilled by coordinated water molecules. The distances of Ce–Ow vary from 2.394(14) Å to 2.68(3) Å. Further, these Ce cations can be viewed as μ_2-bridges that link the sandwich-type polyanions into an infinite ladder-like chain along the *c* axis (Figure 2). It is also noteworthy that the central symmetric sandwich-type polyanions change into asymmetric moieties as a result of the connection with two different $[Ce(H_2O)_7]$ linkers. On the basis of the space group $P2_12_12_1$ of **1**, it is considered that a 2_1 screw axis passes through the central part of the ladder-like chain (as shown in Figure 2) and the whole chain possesses the chirality. However, the flack parameter

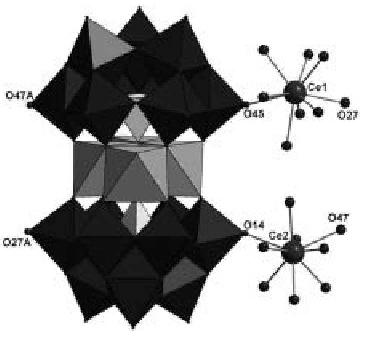

Figure 1. Polyhedral and ball-and-stick representation of the sandwich-type polyanion and the cerium cations of **1**.

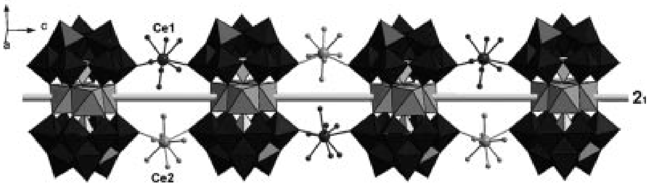

Figure 2. View of the 1D chiral ladder-like chain of **1**.

[0.63(1)] indicates that **1** is just a twin crystal containing two enantiomers simultaneously with the content of ca. 63 and 37%, respectively.[14]

In the unit cell of **1**, there are four independent potassium cations that exhibit a hepta-coordinated environment with six O atoms derived from the three different polyanions and one solvent water molecule (Figure S2). The bond lengths of $K–O_{POM}$ are in the range 2.680(2)–3.073(2) Å, whereas the distances of K–Ow is in the range 2.710(3)–2.860(5) Å. Thus, all the potassium cations can be viewed as μ_3-bridges and each of them links with three polyanion moieties (Figure S3). On the *ac* plane, adjacent ladder-like chains are connected by the four types of potassium cations to form a two-dimensional framework (Figure 3a). Interestingly, adjacent four polyanions together with four cerium linkers and four potassium linkers constitute a relatively closed space with the total volume of ca. 124.7 $Å^3$ estimated with PLATON software (Figures 3b and S4). The entrances of the closed space seem to be somewhat small with the size of ca. 7.7 × 8.0 Å (along the *a* axis) and ca. 6.2 × 12.3 Å (along the *c* axis) based on the distances among cerium, potassium, and tungsten centers. However, all the lattice water molecules and sodium cations are sealed in these "containers" during the self-assembly process of **1** (Figure S4). Furthermore, these 2D porous layers are linked by potassium cations in a stagger way to form a 3D open framework (Figures 4 and S5).

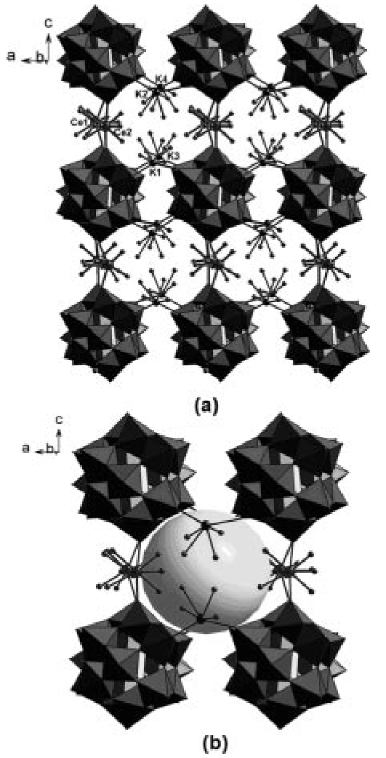

Figure 3. (a) View of the 2D double porous framework on the *ac* plane. (b) View of the simulated closed-space based on four polyanions, four $[Ce(H_2O)_7O_2]$, and four $[K(H_2O)O_6]$ linkers. The sodium cations and crystal water molecules are omitted for clarity.

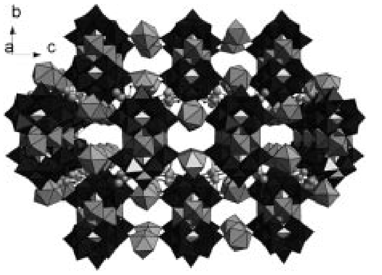

Figure 4. Polyhedral and ball-and-stick view of the 3D open framework along the *a* axis.

The oxidation states of Si, W, Mn, and Ce sites are +4, +6, +2, and +3, respectively, on the basis of the bond lengths and angles, charge balance consideration, and bond valence sum calculations.[15]

Spectroscopic and Electrochemical Analyses

The IR spectrum of **1** (Figure S6) shows the characteristic bands at 946, 905, 873, 770, 722, 536, 511, and 489 cm^{-1}, which are similar to the IR peaks of $[Mn_4Si_2W_{18}O_{68}(H_2O)_2]$[11–13] except for some slight shifts owing to the influence of coordinated cerium cations on polyanions in the range 450–1000 cm^{-1}. This similarity indicates that the polyanion of **1** still keeps the basic sandwich-type structure, which is consistent with the result of single-crystal X-ray diffraction analysis.

The UV/Vis spectrum of **1** (Figure S7) was recorded in a solution of H_2SO_4/Na_2SO_4 at pH = 3.5 and shows absorbance bands between 200 and 400 nm, which can be attributed to the characteristics of charge-transfer bands of terminal oxygen and bridging oxygen atoms to tungsten centers, respectively.

To investigate the solution properties of **1**, the cyclic voltammogram (CV) (Figure S8) was recorded for 1 mM solutions of **1** in 0.5 M H_2SO_4/Na_2SO_4 at pH = 3.50. The voltammogram shows two similar quasi reversible peaks at $E_{1/2}$ = –1.09 and –0.76 V [$E_{1/2} = (E_{pa} + E_{pc})/2$] that can be attributed to two two-electron redox cycles of W^{6+} and one quasi reversible peak at $E_{1/2}$ = +0.68 V that indicates a one-electron redox process of Ce^{3+} to Ce^{4+}. The redox peaks of Mn^{2+} are too weak to be assigned.[16] (Figures S8 and S9). The blurry redox peaks and quasi reversible CV feature of **1** probably result from slow electron transfer rather than chemical irreversibility.

TG and XRPD Analyses

Thermogravimetric (TG) analysis of compound **1** was carried out with a Perkin–Elmer TGA7 instrument under an N_2 atmosphere. The TG curve (Figure 5) exhibits a continuous weight loss step from 35 to 250 °C, attributed to the loss of all lattice and coordinated water molecules. The weight loss is about 11.51%, in correspondence with the calculated value of 11.57%. Then, no weight loss occurs in the temperature range 250–650 °C. There is another minor weight loss of 1.8% in the temperature range 650–800 °C, which might be attributable to the loss of oxygen atoms from the residual metal oxides.

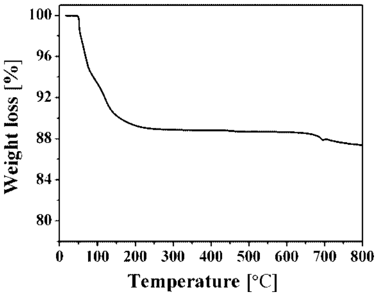

Figure 5. TG curve of **1**.

To check the stability of the open framework of **1**, the X-ray powder diffraction (XRPD) of **1** was checked at 20, 70, and 120 °C. As shown in Figure 6, the peak positions of the simulated and experimental XRPD pattern at 20 °C are in agreement with each other, which indicates the good phase purity of the compound. The differences in intensity may be due to the preferred orientation of the crystalline powder samples. The main peaks of the XRPD pattern at 20 and 70 °C are also similar to each other except for the minor differences in peak intensity, which are due to the loss of some crystal water molecules; this indicates that the open framework of **1** is still stable below 70 °C. However, most peaks of the XRPD pattern of **1** disappeared at 120 °C, which suggests that compound **1** is not in the crystalline state. This could be ascribed to a collapsed framework resulting from the loss of most of the coordinated water molecules from the cerium and potassium cation linkers.

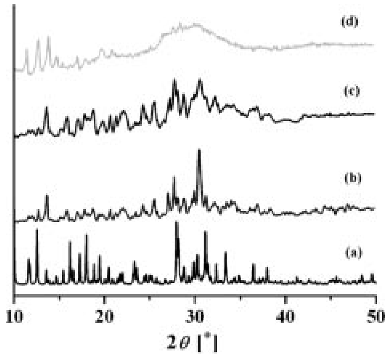

Figure 6. Stimulated and experimental XRPD patterns of **1**. (a) Stimulated XRPD; (b) XRPD at 20 °C; (c) XRPD at 70 °C; (d) XRPD at 120 °C.

Conclusions

A new compound, $K_4Na_2[\{Ce(H_2O)_7\}_2Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot 21.5H_2O$ (**1**), was successfully synthesized with the assistance of a citrate ligand, and this complex represents the first extended inorganic aggregate composed of sandwich-type POMs and lanthanide cations. Compound **1** consists of novel chiral ladder-like chains based on $[Mn_4Si_2W_{18}O_{68}(H_2O)_2]^{12-}$ polyanions and two different $[Ce(H_2O)_7]^{3+}$ linkers, which are further connected by potassium cations into a 3D open framework with a space volume of ca. 124.7 Å^3 per unit cell. TG and XRD analyses indicate that the porous framework of **1** is stable (around 70 °C) just before losing most of its coordinated water molecules. The successful synthesis of **1** suggests a new model for the construction of POM-based extended frameworks. The properties and functionalities of such compounds might be adjusted by the choice of different transition-metal ions in the sandwich sites and lanthanide cation linkers. More work in this field is underway.

Experimental Section

Materials: All chemicals purchased were of reagent grade and used without further purification.

Physical Methods: Elemental analyses W, Mn, and Ce were determined with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range of 400–4000 cm^{-1} with an Alpha Centaurt FT/IR Spectrophotometer with pressed KBr pellets. UV/Vis absorption spectra were obtained with the use of a 752 PC UV/Vis spectrophotometer. TG analyses were performed with a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. The electrochemical measurement was carried out with a CHI 660 electrochemical workstation at room temperature (25–30 °C). X-ray powder diffractometry (XRPD) studies of **1** were performed with a NETZSCH STA 449C instrument, with a Panalytical X-Pert pro diffractometer and Cu-K_α radiation.

Compound 1: The precursor $K_4Na_6Mn[Mn_4Si_2W_{18}O_{68}(H_2O)_2]\cdot{\approx}33H_2O$ was synthesized according to the published procedure.[13] The molecular formula was presumed by elemental analysis and thermogravimetric analysis. An aqueous solution (15 mL, pH = 4.5) of $Ce(SO_4)_2\cdot 4H_2O$ (0.16 g, 0.4 mmol) and potassium citrate (0.12 g, 0.4 mmol) was added to an aqueous solution (15 mL) of $K_4Na_6Mn[\{SiMn_2W_9O_{34}(H_2O)\}_2]\cdot 33H_2O$ (1.12 g, 0.2 mmol) with stirring. The color changed from yellow to brown. The solution was then heated to boiling for 2 h, and the color changed again from brown to yellow. After cooling to room temperature, the final yellow suspension was filtered, and the pH value of the filtrate was ca. 3.5. The filtrate was slowly evaporated at room temperature. The yellow columnar crystals of **1** were isolated after 10 d (yield 60% based on W). $H_{79}Ce_2K_4Mn_4Na_2O_{105.5}Si_2W_{18}$ (5835.49): calcd. Ce 4.80, Mn 3.77, W 56.71; found Ce 4.71, Mn 3.87, W 56.85.

X-ray Crystallography: Crystallographic data for **1** was collected at 298 K with a Rigaku R-axis Rapid IP diffractometer with the use of graphite monochromatic Mo-K_α radiation (λ = 0.71073 Å) and IP technique. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 by using the SHELXTL-97 crystallographic software package.[17] Anisotropic thermal parameters were used to refine all atoms on polyanions, cerium, potassium, and sodium cations. All the water molecules were refined isotropically. Non-hydrogen atoms were included. Some crystal water molecules were disordered. Their occupancies were determined by fixing the atomic displacement parameter factors (0.08) at the beginning, and then occupancy numbers were fixed to refine their atomic displacement parameter factors. Atoms with occupancies lower than 0.25 were ignored. Further details of the X-ray structural analysis are given in Table 1. Further details of the crystal-structure investigation may be obtained from the

Table 1. Crystal Data and Structure Refinement for **1**.

Chemical formula	$H_{79}Ce_2K_4Mn_4Na_2O_{105.5}Si_2W_{18}$
Formula weight	5835.49
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	12.040(2)
b [Å]	26.094(5)
c [Å]	30.043(6)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	9439(3)
Z	4
D [mg m^{-3}]	4.107
T [K]	293(2)
Reflections collected	85946
Reflections unique	21490
Goodness of fit on F^2	0.947
R_1[a]	0.0618
wR_2[b]	0.1074

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

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Supporting Information (see footnote on the first page of this article): Ball-and-stick view of the structure of **1**, view of the coordination environments of potassium cations, view of the packing arrangement of **1**. IR and UV/Vis spectra of **1**, selected bond lengths and angles of **1**.

Acknowledgments

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