A Chain-like Polyoxotungstate Constructed from
[CeW_{10}O_{36}]^{9-}, [Na_{5}(H_{2}O)_{17}Cl]^{4+}, and [Na_{2}(H_{2}O)_{8}]^{2+} Units:
(NH_{4})_{3}[Na_{5}(H_{2}O)_{17}Cl][[Na(H_{2}O)_{4}]_{2}[CeW_{10}O_{36}]]·6 H_{2}O

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An unusual cerium-containing decaoxotungstate complex, (NH_{4})_{3}[Na_{5}(H_{2}O)_{17}Cl][[Na(H_{2}O)_{4}]_{2}[CeW_{10}O_{36}]]·6 H_{2}O (1) has been synthesized and characterized by IR, TG, and single crystal X-ray diffraction studies (yellow crystals, orthorhombic, space group Imm2, a = 11.473(2), b = 15.225(3), c = 17.646(7) Å, V = 3082.3(15) Å^3, Z = 2, R = 0.046). In this compound, sandwich-type [CeW_{10}O_{36}]^{9-} clusters are linked by binuclear [Na_{2}(H_{2}O)_{8}]^{2+} units by sharing oxygen atoms into linear chains, which are further extended into a 2D supramolecular network via pentanuclear [Na_{5}(H_{2}O)_{17}Cl]^{4+} units by strong hydrogen bonding interactions.

Key words: Polyoxotungstate, Cerium, Cluster, Crystal Structure

Introduction

Polyoxometalates (POMs), as early transition metal oxide clusters, show unusual properties and a variety of compositions and structures that make them attractive for applications in catalysis, separation, imaging, materials science, and medicine [1 – 3]. The extension of discrete POM subunits by using various kinds of linkages into one-, two- and three-dimensional networks continues to be a focus of considerable ongoing research not only from a structural point of view, but also because the as-synthesized materials may possess novel properties owing to synergistic effects. Up to now, classic Keggin [4 – 8], Wells-Dawson- [9], Silverton- [10], Lindqvist- [11], and Anderson-type polyxoanion clusters [12] have been successfully used as building blocks for the construction of extended inorganic aggregates. For example, Zubieta et al. employed transition metal ion complexes as inorganic bridging ligands linking hexa-molybdate clusters into a two-dimensional network [11]. Sècheresse’s group prepared several 1D and 2D frameworks with ε-Keggin polyoxometalates through the linking of organic groups [5], while Lu’s group isolated a novel three-dimensional framework formed by [GdMo_{12}O_{42}]^{9-} anions and rare earth cations [10], and recently our group has reported a series of extended architectures assembled from Anderson-type polyxoanions [13].

Among the reported POM clusters, lanthanide-containing POM anions are the focus of research due to their antiviral and anti-HIV properties as well as their excellent photoluminescence behavior. The [LnW_{10}O_{36}]^{9-} polyxoanions, where Ln = La^{3+} [14], Ce^{3+} [15a], Pr^{3+} [16], Nd^{3+} [16], Sm^{3+} [16–18], Eu^{3+} [19–21], Gd^{3+} [16, 22], Tb^{3+} [16, 23], and Dy^{3+} [16] have been isolated as discrete clusters, however, examples for utilizing them for the design and synthesis of POMs with extended structures have never been reported. As a continuation of work on various POM derivatives, we are trying to construct novel extended structures based on the [CeW_{10}O_{36}]^{9-} anion. Herein, we report the synthesis, characterization and crystal structure of a new polyoxotungstate complex (NH_{4})_{3}[Na_{5}(H_{2}O)_{17}Cl][[Na(H_{2}O)_{4}]_{2}[CeW_{10}O_{36}]]·6 H_{2}O (1) which exhibits a linear chain based on [CeW_{10}O_{36}]^{9-} polyxoanions and binuclear [Na_{5}(H_{2}O)_{17}Cl]^{4+} units. These chains are further con-
Fig. 1. ORTEP drawing of the fundamental building blocks of 1, highlighting the three types of metal-oxygen units.

connected by pentanuclear [Na₅(H₂O)₁₇Cl]⁴⁺ units into a 2D supramolecular framework via extensive hydrogen-bonds. To our knowledge, compound 1 represents the first extended structure composed of the [CeW₁₀O₃₆]⁹⁻ polyoxoanion since it was first isolated by Weakley in 1971 [15b].

Results and Discussion

Structure description

Single crystal X-ray diffraction analysis has revealed that compound 1 contains three types of metal-oxygen clusters: a sandwich-type [CeW₁₀O₃₆]⁹⁻ polyoxoanion, the binuclear [Na₂(H₂O)₈]²⁺ unit, and a pentanuclear [Na₅(H₂O)₁₇Cl]⁴⁺ unit. The sandwich-type polyoxoanion, as shown in Fig. 1, consists of two [W₅O₁₈]⁶⁻ moieties and a central Ce³⁺ cation fixed in the cavity of each anion via W–O–Ce connecting modes. Each [W₅O₁₈]⁶⁻ subunit is made up of five edge-sharing {WO₆} octahedra (Fig. 2). The W–O bonds can be divided into three groups, i.e. W–O(t) bonds, W–O(μ₂) bonds, and W–O(μ₅) bonds, whose bond lengths fall in the ranges 1.716(11)–1.742(12), 1.750(17)–2.034(14), and 2.29(3)–2.324(2) Å, respectively. These values are comparable to those of other isomorphous [LnW₁₀O₃₆]⁹⁻ anions. The coordination polyhedron around the central Ce³⁺ cation can be described as a square antiprism. The Ce–O bond lengths are in the range of 2.489(17)–2.499(15) Å and the O–Ce–O bond angles range from 73.4(3) to 142.4(3)°. It is interesting that these sandwich-type polyoxoanions are not isolated but linked together through binuclear [Na₂(H₂O)₈]²⁺ units into a 1D chain along the a axis (Fig. 2) by sharing two terminal oxygen atoms (O1 and O1A) at opposite sides of each polyoxoanion. For each binuclear [Na₂(H₂O)₈]²⁺ unit, the Na⁺ cations adopt distorted octahedral coordination environments and the non-bonding Na···Na distance is 3.536(15) Å. The Na–OPOM bond length is 2.474(12) Å. The residual coordination sites of each sodium ion are occupied by water molecules. The distances Na–Ow vary from 2.33(3) to 2.39(3) Å. The bond valence sum (BVS) calculations [26] for O(17), O(23), O(24) give the values 0.782, 0.784 and 0.802, respectively, indicating that they are diprotonated oxygen atoms in view of the bond valence contribution of ~0.8 for an O–H bond. It is noteworthy that the composition of the [Na₂(H₂O)₈O₂] unit in 1 is different from that of [Na₂(H₂O)₁₀]²⁺ contained in a previously reported compound Na₂(NH₄)₂[La(W₅O₁₈)₂]·16 H₂O [14] in that all the oxygen atoms bonded to the Na⁺ cations of [Na₂(H₂O)₁₀]²⁺ come from water molecules. This distinction results in the [LaW₁₀O₃₆]⁹⁻ anions being isolated rather than being linked into chains as in 1.

Interestingly, apart from the binuclear [Na₂(H₂O)₈]²⁺ unit, a new type of pentanuclear [Na₅-
(NH₄)₃[Na₅(H₂O)₁₇Cl] {[Na(H₂O)₄]²⁺[CeW₁₀O₃₆]}·6H₂O

Fig. 4. The 2D layered framework of 1 formed by the extensive hydrogen bonds among [CeW₁₀O₃₆]⁹⁻, [Na₂(H₂O)₁₀]²⁺, and [Na₅(H₂O)₁₇Cl]⁴⁺. NH₄⁺ ions were omitted for clarity.

Fig. 5. IR spectrum of compound 1.

The broad band at ca. 3366 cm⁻¹ is attributed to the vibration of the water ligand (Fig. 5).

IR spectroscopy

In the IR spectrum of compound 1, the peaks at 943, 839, 783 and 702 cm⁻¹ can be attributed to v(W-O₁), v(W-O₅) and v(W-O₆) of the polyoxoanion skeleton.

Thermal analysis

The result of the TG analysis basically agrees with that of the structure determination (Fig. 6). The first step (4.30 %) in the temperature range 70 – 98 °C corresponds to the release of all lattice water and ammonia molecules (4.22 %). The second step (4.39 %) in the temperature range of 98 – 230 °C corresponds to the loss of the coordinated water molecules of the [Na₂(H₂O)₈]²⁺ unit (4.28 %). The weight loss of 9.86 % in the range 300 – 880 °C corresponds to the demolishing of the [Na₅(H₂O)₁₇Cl]⁴⁺ units (10.18 %). Above 880 °C, no further weight loss was found.

Conclusion

In summary, we have synthesized and crystallized a new compound (NH₄)₃[Na₅(H₂O)₁₇Cl] {[Na(H₂O)₄]²⁺[CeW₁₀O₃₆]}·6H₂O.
Table 1. Crystal data and structure refinements for compound 1.

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\[\text{[CeW}_{10}\text{O}_{36}]\cdot6\text{H}_2\text{O}\] from an aqueous solution system. Compound 1 represents the first extended structure based on the [Ce(W_{10}O_{36})]^{12⁻} polyoxoanion. This work demonstrates that many other interesting compounds with extended architectures can be obtained by using various POM clusters as building blocks. More work along this line is underway in our laboratory.

Experimental Section

Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Na_{4}[W_{10}O_{32}] was prepared according to the literature method [24]. An FTIR spectrum was recorded in the range 400 – 4000 cm⁻¹ on an Alpha Centaurt FTIR spectrophotometer using a KBr pellet. Elemental analysis of N was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Ce, W, Na, and Cl were determined by a Leeman inductively coupled plasma (ICP) spectrometer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C min⁻¹.

Synthesis

Freshly prepared Na_{4}[W_{10}O_{32}] (1.22 g, 0.5 mmol) was dissolved in 40 mL of an aqueous NaCl (0.117 g, 2.0 mmol) solution with stirring. Then, a solution of Ce(NO₃)₃·6H₂O (0.217 g, 0.5 mmol) in distilled water (15 mL) was drop-wise added. The pH value of the mixture was carefully adjusted to 4.8 using 1 M HCl. The final solution was heated to 80 °C for 1 h and then a solution of 4 M NH₄Cl (20 mL) was added to the reaction mixture at the same temperature. After being cooled to r.t., the final yellow suspension was filtered. The filtrate was kept for slow evaporation at r.t. The yellow columnar crystals of 1 were isolated after one week (yield 45 % based on W). Elemental analysis for H₂₂Ce₁₃N₃Na₅W₁₀CeO₇: calcd. Cl 1.05, N 1.25, Na 4.78, W 54.66, Ce 4.17; found Cl 1.29, N 1.42, Na 4.56, W 54.80, Ce 3.89.

X-Ray crystallography

A yellow single crystal with dimensions 0.31 \(\times\) 0.26 \(\times\) 0.23 mm³ was glued on a glass fiber. Data were collected on a Rigaku R-axis RAPID IP diffractometer at 293 K using graphite-monochromated MoKα radiation (λ = 0.71073 Å).
and IP techniques in the range $3.21^\circ < \theta < 24.99^\circ$. An empirical absorption correction was applied. The structure was solved by Direct Methods and refined by full-matrix least-squares methods on $F^2$ using the SHELXS/L-97 crystallographic software package [25]. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The hydrogen atoms of NH$_4^+$ were located from difference Fourier maps and the other hydrogen atoms were included at idealized positions. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CSD-417858 contains the supplementary crystallographic data for this paper. This data may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de).

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