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Article

Pentadecatungstate with Dinuclear Cerium(III) Unit: Synthesis, Crystal Structure and Properties

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A novel pentadecatungstate, $[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{7-}$ (**1**), constructed by a dinuclear cerium unit and 15-member ring WO_6 units was prepared and characterized by single-crystal X-ray diffraction. Polyanion **1** exhibits blue photoluminescence with an emission maximum at 488 nm, which is characteristic of cerium(III) transitions from 5d to $^2F_{5/2}$ states. Furthermore, the study of the electrochemical property investigation of **1** shows two reversible redox peaks ascribing to two-electron processes.

Introduction

Polyoxometalates (POMs) are discrete, molecular metal−oxygen clusters with an unrivaled versatility and structural variety[1]coupled with a multitude of properties, which has led to applications in many fields such as catalysis, materials science, structural biology, medicine, and photochemistry.[2] In the large POM families, heteropolymetalates containing lanthanide ions form one of the most-interesting subgroups. This is partly due to the unique spectroscopic, electrochemical, and magnetic properties of lanthanide,[3] and another important reason is that the combination of oxophilic lanthanide ions and oxygen-rich POMs may generate POM compounds with interesting structures. Because Ripan and Todorut[4] prepared the first heteropolymetalate compounds containing lanthanide ions, many efforts have been devoted to the synthesis of this kind of compounds. However, the product often forms as precipitates, which makes the elucidation of the structure difficult. In most of the reported cases, the lanthanide ions are restricted to act as linkers to one or more other POM units, resulting in polymeric or unusually large molecular POMs.[5] Several heteropolymolybdenates based on the classic Keggin type polyanions,[6] $H_8(CeMo_{12}O_{42})\cdot(H_2O)_{18}$,[7] $(NH_4)_2H_6(CeMo_{12}O_{42})(H_2O)_{12}$,[8] and $[Gd(H_2O)_3]_3[GdMo_{12}O_{42}]\cdot 3H_2O$,[9] have been reported, in which the lanthanide ions serve as central heteroatoms. To our best knowledge, similar heteropolytungstate examples have not been reported. Hence, the synthesis of new type heteropolytungstates containing central lanthanide ion units is a great challenge for chemists. In this article, we will report

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the synthesis and characterizations of a heteropolytungstate $[H_6Ce_2(H_2O)ClW_{15}O_{54}]^{7-}$ (**1**) containing a dinuclear cerium unit.

Experimental Section

Materials and General Methods. All reagent-grade chemicals were commercially available and used without further purification. Elemental analyses were carried out on a Jobin Yvon Ultima2. Infrared (IR) spectrum was recorded with PerkinElmer Spectrum One as KBr pellets in the range 4000−400 cm^{-1}. UV−vis absorption spectra were recorded using a Lambda 35 spectrophotometer (PerkinElmer, USA). Thermogravimetric analysis (TGA) was performed using an NETZSCH apparatus (model STA449C Jupiter) from ambient temperature (~23°) to 800°, with heating rate of 5°/min, in a nitrogen atmosphere. X-ray powder diffraction was measured with a RIGAKU DMAX2500PC diffractometer using Cu Kα radiation.

Synthesis of $[Na_2(H_2O)_2K_5(H_2O)_6][H_6Ce_2(H_2O)ClW_{15}O_{54}]\cdot 6H_2O$ (Na_2K_5-1). $Na_2WO_4\cdot 2H_2O$ (2.7 g, 8.19 mmol) was dissolved in water (20 mL), and the pH was adjusted to 5.3 with 2 mol/L HCl. To the colorless solution was added dropwise 1.26 mL of 1mol/L $Ce(NO_3)_3$ aqueous solution with stirring at room temperature. A small amount of transient yellow precipitate appeared after each drop. After boiling for 60 min, the mixture was filtered and cooled to room temperature. The pH of the filtrate was adjusted to 5.0 with 2 mol/L HCl and 3.4 g of KCl was added. After boiling for 30 min, the mixture was filtered. The filtrate was kept for several weeks at ambient conditions, and yellow needle crystals of Na_2K_5-**1** were isolated in 42% yield (1.02 g, based on tungsten). Anal. Calcd for $K_5Na_2W_{15}Ce_2ClO_{69}H_{36}$: H 0.81, K 4.42, Na 1.03, Cl 0.80, Ce 6.29, W 61.90. Found: H 0.96, K 4.56, Na 0.90, Cl 0.69, Ce 6.38, W 62.11%. IR: 1621(s), 951(s), 895(m), 847(m),797(s), 512(m).

X-ray Crystallography. Diffraction data for Na_2K_5-**1** was collected with a crystal with dimensions 0.20 × 0.10 × 0.04 mm^3 using a Rigaku Mercury CCD area detector (Mo Kα, λ = 0.71073 Å), at 173 K. Empirical absorption corrections were applied to the data using the *CrystalClear* program.[10] The structure was solved by direct methods[11] and refined on F^2 by full-matrix least-squares using the *SHELXTL-97* program package.[12] All heavy atoms except oxygen atoms of water molecules were refined anisotropically; hydrogen atoms of water molecules could not be located from the difference Fourier map and were not included in the refinements. The crystallographic data for Na_2K_5-**1** are listed in Table 1 and selected bonds and angles in Table 2. Crystallographic data for the structure reported in this article has been deposited in the Inorganic Crystal Structure Database with ICSD number 416677 for Na_2K_5-**1**.

Photoluminescence Spectroscopy. A photoluminescence (PL) spectrum was obtained on a Cary Eclipse spectrofluorometer, and the excitation and emission spectra were recorded at ambient temperature. The Ex. Slit and Em. Slit are 2.5 and 5 nm, respectively.

Electrochemical Measurement. The electrochemical experiment was carried out on a Model Epsilon Analyzer (BAS Inc., USA) in a three-electrode cell: glassy carbon electrode (GCE, diameter 3 mm) as the working electrode, platinum wire as the counter electrode, and Ag/AgCl/KCl (3 M) as reference electrode. The solution of **1** (5×10^{-4} mol/L) was used immediately after their preparation and deaerated with prepurified nitrogen for at least 15 min. Formal potential E_p of the redox couples was estimated and reported as the average value of the anodic E_{pa} and cathodic E_{pc} peak potential.

Table 1. Crystal Data and Structure Refinement Parameters for Na_2K_5-**1**

compound	Na_2K_5-**1**
chemical Formula	$H_{36}O_{69}Na_2ClK_5Ce_2W_{15}$
fw	4455.00
cryst syst	monoclinic
space group	*P*2(1)/*c*
a (Å)	13.304 (2)
b (Å)	19.803(3)
c (Å)	25.261(4)
β (°)	95.746(9)
V (Å^3)	6622.0(2)
D_{calcd} (g/cm^3)	4.400
absolute coefficient (mm^{-1})	27.758
Z	4
T (K)	173(2)
wavelength (Å)	0.71073
F(000)	7584
R1 indices [$I > 2.0\sigma(I)$][a]	0.0767
wR2 indices[$I > 2.0\sigma(I)$]	0.2027
R1 indices (all data)	0.0907
wR2 indices (all data)	0.2170

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\ \Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Results and Discussion

Synthesis. Na_2K_5-**1** was isolated from the aqueous reaction of tungsten(VI) originals of Na_2WO_4, and the XRPD result shows the observed patterns are in good agreement with the simulated ones, indicating that Na_2K_5-**1** is pure (Supporting Information, Figure S1). It deserves to be mentioned that the Cl^- was used in the synthetic reaction acting as a ligand, which is crucial to obtain **1**, similar to the synthesis of $[V_{16}O_{38}Cl]^{6-}$ anion.[13]Under similar reaction conditions, except that HCl and KCl were replaced by HNO_3 and KNO_3, no product of **1** was obtained. As known, the pH value of the synthetic reaction generally has a decisive influence on the formation of the product in polyoxometalate chemistry; in our reaction the optimized pH value for generation of Na_2K_5-**1** is 5.0.

Crystal Structure of Polyanion 1. X-ray structural analysis reveals that polyanion $[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{7-}$ (**1**) has an approximate C_3 symmetry. The anion consists of 15 WO_6 octahedral and 2 9-coordinate cerium(III) atoms at the center (Figure 1). The frequency (1621 cm^{-1}) attributed to the O−H (bending) and the O−H region indicates water of crystallization.[14] The strong band at 951 cm^{-1} in the infrared spectrum of Na_2K_5-**1** are ascribed to bonds $\upsilon(W-O_t)$. Multiple bands attributed to the bridging (W−O−W (Ce))-group absorptions are found in the 900−410 cm^{-1}

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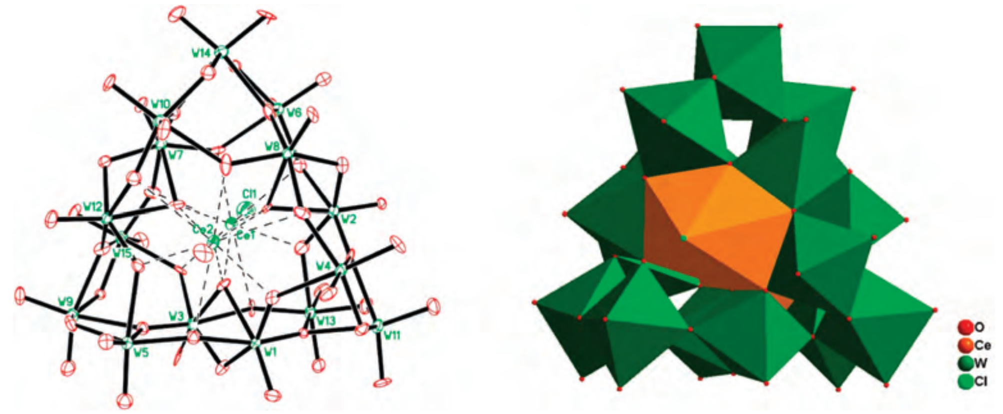

Figure 1. ORTEP view (left) (thermal ellipsoids are drawn at the 30% probability level) and polyhedral (right) representations of **1.**

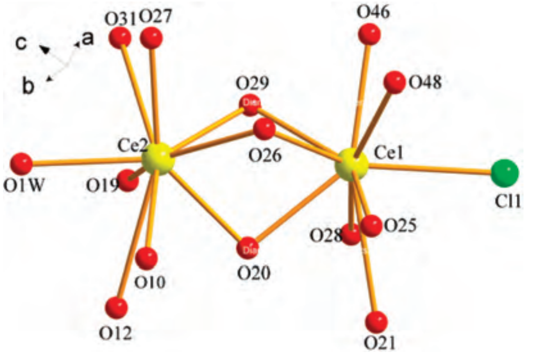

Figure 2. Ball-stick representations of $\{Ce_2O_{13}(H_2O)Cl\}$.

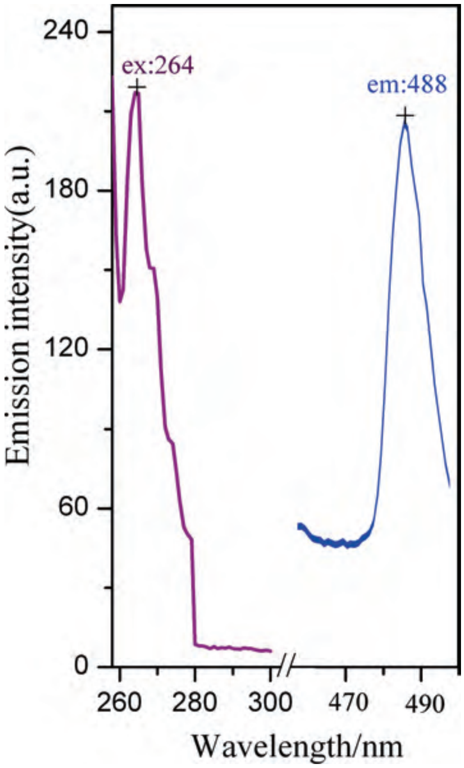

Figure 3. Solid-state excitation and emission spectra of Na_2K_5-**1**.

range. The basic building units of **1** are $\{W_5O_{18}\}$ and $\{Ce_2O_{13}(H_2O)Cl\}$, which are linked via adjacent W−O−Ce bonds. As shown in Figure 2, $\{W_5O_{18}\}$ unit is constructed by three edge-sharing WO_6 with two corner-sharing WO_6 octahedrons. Three $\{W_5O_{18}\}$ units are joined to a 15-member ring by corner-sharing WO_6 octahedron with two cerium ions stabilizing the asymmetrical ring of 15 WO_6 units. The W−O bond lengths can be divided into different categories according to their coordination modes: The first group belongs to terminal oxo groups with $W-O_{oxo}$ distances in the range of 1.69(2)−1.74(4) Å, which is comparable to those reported in the literature.[15] The second one presents $W-O_t$ (O_t for terminal oxygen atoms) distances in the range 1.76(2)−1.778(2) Å. The distances exceed the normal range of $W-O_{oxo}$ distances is probably due to the existence of partial atomic charge, which comes from the 6 delocalized hydrogen atoms within the host cluster,[16] on these oxygen sites. These bonds may be better described as W−OH bonds, according to the structure of **1**. The third one belongs to μ_2-bridge oxygen atoms with $W-O_{\mu 2}$ distances in the range of 1.89(2)−1.96(2) Å; the fourth one ascribes to μ_3-bridge oxygen atoms with $W-O_{\mu 3}$ distances in the range of 1.81(2)−2.32(2) Å; the last one assigns to μ_4-bridge oxygen atom with $W-O_{\mu 4}$ distances from 2.15(2) to 2.23(2) Å. Each cerium(III) is 9-coordinate in highly distorted tricapped trigonal prism, one is coordinated by an aqua ligand with a Ce−O distance of 2.42(2) Å and 8 oxygen atoms from $\{W_5O_{18}\}$ units, the other is coordinated by a chlorine atom with a Ce−Cl distance of 2.71(1) Å and 8 oxygen atoms from $\{W_5O_{18}\}$ units, leading to an approximate C_3 symmetry of **1**. The two cerium(III) atoms are linked via three Ce−O−Ce bonds to form the dinuclear central unit of **1** (Figure 3). The bond valence sum calculation reveals that, in Na_2K_5-**1**, the oxidation state of all tungsten centers is +6 and −2 for all oxygen centers. Because the oxidation state is +3 for cerium and +1 for potassium and sodium, 6 protons are present in the anion for charge balance.

UV−vis Spectrum and Photoluminescence. . The UV−vis spectrum (Figure S2, Supporting Information) displays one intense absorption band centered at 264 nm and one broad

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band centered at 330 nm. The higher energy band at 264 nm can be attributed to O → W charge transfer of **1**, and band at 330 nm may be attributed to O → Ce charge transfer. Interestingly, the UV−vis spectra under different pH values of 1 and 6 are almost same, indicating that **1** is stable in a large pH value range from 1 to 6. The photoluminescence behaviors of POMs containing lanthanide cations have been extensively investigated by various groups.[17] Generally, the POMs containing lanthanide cations exhibits the photoluminescence of lanthanide cations such as $[EuP_5W_{30}O_{110}]^{12-}$, $[EuW_{10}O_{36}]^{9-}$, and so on. The photoluminescence spectrum at room temperature of Na_2K_5-**1** is shown in Figure 2. Na_2K_5-**1** exhibits blue photoluminescence when excited with energy close to the higher energy band. More specifically, compound Na_2K_5-**1** displays photoluminescence at 488 nm when excited at 264 nm, which is characteristic of cerium(III) transitions from 5d to $^2F_{5/2}$ states. The photoexcitation of the O → W LMCT band (264 nm) of **1** gave the emission of cerium(III), indicating the occurrence of an intramolecular energy transfer from the O → W LMCT states to cerium(III) in the polyanion **1** lattice,[18]and Na_2K_5-**1** may be a candidate for blue-light photoactive material.

Cyclic Voltammetry of 1 in Aqueous Solution. Figure S4 (Supporting Informationshows cyclic voltammogram of 5×10^{-4} mol/L **1** in 0.2 mol/L $CH_3OONa + CH_3COOH$ (pH 5.0) solution. In the potential range from −1500 to 200 mV, polyanion **1** displays two waves C1 (−659 mV) and C2 (−1190 mV) during the cathodic sweep, whereas the counterpart to the two anionic peaks are A1 (−570 mV) and A2 (−1159 mV), respectively. The mean peak potentials $E_{1/2} = (E_{cp} + E_{ap})/2$ are −614.5 and −1174.5 mV, respectively. Two redox peaks C1−A1 and C2−A2 correspond to two consecutive two-electron reduction of W^{VI}/W^{V} like $[Ce^{III}P_2W_{17}O_{61}]^{7-}$.[19]The two-electron processes of **1** can be described as follows:[20]

$$[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{7-} + 2e^- \rightarrow [H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{9-} \quad (1)$$

$$[H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{9-} + 2e^- \rightarrow [H_6Ce_2(H_2O)Cl(W_5O_{18})_3]^{11-} \quad (2)$$

The peak-to-peak separations between the corresponding anodic and cathodic peaks (ΔE_p) for two redox couples are 89 and 31 mV.

Conclusion

In summary, we have synthesized a blue luminescent pentadecatungstate, Na_2K_5-**1**, constructed by a central dinuclear cerium unit and a 15-member ring WO_6 octahedral. **1** is a novel Ln−POM example that two lanthanide (III) cations locate at the POM's center. The result is significant not only for producing a novel type of polyanions cluster but also for further exploration of heteropolymetalate compounds containing lanthanide ions.

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Supporting Information Available: X-ray crystallographic files (CIF), UV−vis spectrum, PXRD spectrum, TGA curve, cyclic voltammograms of Na_2K_5-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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