

A new polymeric chain constructed from isopolyanions and lanthanide cations: Synthesis, crystal structure, and properties of $(\text{NH}_4)_5[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Gd}, \text{Dy}, \text{Ho}$)

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Abstract

A series of 1:1 composite compounds prepared with the isopolyanions and lanthanide cations, $(\text{NH}_4)_5[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Ce}^{\text{III}}$ (**1**); Pr^{III} (**2**); Nd^{III} (**3**); Gd^{III} , $n = 1$ (**4**); Dy^{III} (**5**); Ho^{III} , $n = 1$ (**6**)) were synthesized at room temperature and characterized by single-crystal X-ray structural analysis, elemental analyses, IR spectra, thermogravimetry analyses and cyclic voltammetry. X-ray structural analysis reveals that these structures are isostructural: polyanions are bridged by Ln ions *via* the coordination of the bridging oxygen atoms and terminal oxygen atoms, forming a W–O_t–Ln–O_b–W linkage; and through the W–O_t–Ln–O_b–W linkage a one-dimension infinite linear chain with alternating cations and anions is formed. Compounds **1–6** represent the first example where two types of inorganic oxoanions (NO_3^- and $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$) simultaneously coordinating to Ln^{III} , in which the NO_3^- ions act as the bidentate ligands coordinating to the Ln^{III} , forming a four-membered ring. The room temperature luminescent studies indicate that **3** exhibits strong luminescence in the near-IR region.

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1. Introduction

Selecting suitable polyoxoanions to prepare novel compounds containing different coordination cations is of great interest for applications in different areas, not only because of their intriguing variety of architectures and topologies, but also owing to their numerous potential applications in non-linear optics, catalysis, medicine, optical, magnetic and conductive materials [1].

Polyoxometalates (POMs) [1a,2], the highly tunable nature of the polyoxoanions, may be versatile inorganic building blocks for the construction of molecular-based materials. Continuing interest in the field of POMs largely focuses on the rational syntheses of complexes with extended polymeric structure. To date, many examples of extended architectures in which well-

characterized POMs, such as Keggin-[3], Wells–Dawson-[4], Anderson-[5] and Lindquist-type [6] heteropolyanions serving as the building blocks have been successfully reported.

Among the various types of polyanions, the anion $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ possesses some particular structural features, and provides a variety of possibilities of intermolecular linkages. However, examples utilizing this anion for the design and synthesis of POMs with extended structures are rarely reported. On the other hand, as we know, by means of the multiple coordination requirements and oxophilicity of the POMs, lanthanide cations have been introduced into POMs acting as an effective bridge to link discrete entities forming new classes of materials with potentially useful electronic, magnetic and photosensitive properties [7]. Furthermore, lanthanide (4f) ions are known for their luminescence properties which make them interesting candidates for luminescent applications such as biochemical sensors, fluoroimmunoassays and electro-luminescent devices [8]. Among the lanthanide ions, Nd^{III}

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complexes emitting in the 800–1700 nm are the most popular near-IR luminescent compounds for application in laser systems [9].

Hence, our current synthetic strategy is to choose the isopolyanion $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ [10] as the building block to construct Ln complexes, and we have successfully prepared six novel compounds with the 1D linear structure. In this paper, we present the synthesis, the structural characterization and some properties of $(\text{NH}_4)_5[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$ (Ln = Ce^{III} (**1**); Pr^{III} (**2**); Nd^{III} (**3**); Gd^{III}, $n = 1$ (**4**); Dy^{III} (**5**); Ho^{III}, $n = 1$ (**6**)).

2. Experimental section

2.1. General methods and materials

The materials used for synthesis were of reagent grade and used without further purification. $\text{Ln}(\text{NO}_3)_3$ (Ln = Pr, Nd, Gd, Dy and Ho) were prepared by addition of concentrated HNO_3 to Ln_2O_3 (99.9%). $(\text{NH}_4)_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$ was synthesized according to the literature [11] and characterized by IR spectroscopy and TG analyses. W, Ce, Pr, Nd, Gd, Dy and Ho were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaur FT-IR spectrophotometer using KBr Pellets. The Ammonium-N and $\text{NO}_3\text{-N}$ were determined by ion chromatography (DIONEX 100 with DIONEX CDM-1). The TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C min}^{-1}$. The near-IR emission spectrum of compound **3** was recorded on an Edinburgh Analytical Instruments FLS920 equipped with a laser diode from the PicoQuant Company as the light source. Cyclic voltammetric measurements were performed by using an LK98 microcomputer-based electrochemical analyzer (LANLIKE, Tianjin, China). Electrochemical measurements were performed for 1.0 mM compound **1** in NaCl solution at room temperature. The reference electrode was an Ag/AgCl electrode and the working electrode was a glassy carbon electrode with a platinum wire as the counter electrode.

2.2. Synthesis

2.2.1. Synthesis of $(\text{NH}_4)_5[\text{Ce}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}]$ (**1**)

$(\text{NH}_4)_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$ (0.0752 g, 0.025 mmol) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.050 mmol) were dissolved in 18 mL of water. The pH value was adjusted to 2.61 with 1 mol L^{-1} HNO_3 before heating. The solution was heated at 60 $^\circ\text{C}$ with stirring for 15 min. After standing for ca. 20 min the solution was filtered and left standing to get concentrated under ambient conditions. After 20 d, yellow crystals suitable for X-ray diffraction were obtained (47% yield, based on Ce). Anal. Calcd for $\text{H}_{28}\text{N}_7\text{CeO}_{49}\text{W}_{12}$ (3256.56): N, 3.01; Ce, 4.30; W, 67.75; found: N, 2.87; Ce, 4.23; W, 67.23; IR (solid KBr pellet/ cm^{-1}): 1620 (m), 1400 (m), 1320 (m), 1041 (w), 936 (m), 881 (m), 766 (s), 609 (w), 419 (m).

2.2.2. Synthesis of $(\text{NH}_4)_5[\text{Pr}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}]$ (**2**)

An identical procedure with **1** was followed to prepare **2** except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (41% yield, based on Pr). Anal. Calcd for $\text{H}_{28}\text{N}_7\text{O}_{49}\text{PrW}_{12}$ (3257.35): N, 3.01; Pr, 4.33; W, 67.73; found: N, 2.83; Pr, 4.16; W, 66.09; IR (solid KBr pellet/ cm^{-1}): 1620 (m), 1420 (m), 1303 (m), 942 (m), 889 (m), 750 (s), 609 (w), 419 (m).

2.2.3. Synthesis of $(\text{NH}_4)_5[\text{Nd}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}]$ (**3**)

An identical procedure with **1** was followed to prepare **3** except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (39% yield, based on Nd). Anal. Calcd for $\text{H}_{28}\text{N}_7\text{NdO}_{49}\text{W}_{12}$ (3260.68): N, 3.01; Nd, 4.42; W, 67.66; found: N, 2.94; Nd, 4.36; W, 66.77; IR (solid KBr pellet/ cm^{-1}): 1640 (m), 1400 (m), 1317 (m), 1041 (w), 935 (m), 876 (m), 771 (s), 607 (w), 419 (m).

2.2.4. Synthesis of $(\text{NH}_4)_5[\text{Gd}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$ (**4**)

An identical procedure with **1** was followed to prepare **4** except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (31% yield, based on Gd). Anal. Calcd for $\text{H}_{30}\text{N}_7\text{GdO}_{50}\text{W}_{12}$ (3291.71): N, 2.98; Gd, 4.78; W, 67.02; found: N, 2.88; Gd, 4.49; W, 67.38; IR (solid KBr pellet/ cm^{-1}): 1630 (m), 1430 (m), 1300 (m), 1049 (w), 942 (m), 874 (m), 768 (s), 606 (w), 419 (m).

2.2.5. Synthesis of $(\text{NH}_4)_5[\text{Dy}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}]$ (**5**)

An identical procedure with **1** was followed to prepare **5** except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (30% yield, based on Dy). Anal. Calcd for $\text{H}_{28}\text{N}_7\text{DyO}_{49}\text{W}_{12}$ (3278.94): N, 2.99; Dy, 4.96; W, 67.28; found: N, 2.81; Dy, 4.89; W, 67.59; IR (solid KBr pellet/ cm^{-1}): 1626 (m), 1407 (m), 1323 (m), 1048 (w), 936 (m), 878 (m), 761 (s), 589 (w), 420 (m).

2.2.6. Synthesis of $(\text{NH}_4)_5[\text{Ho}(\text{NO}_3)_2(\text{H}_2\text{O})_3][\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot \text{H}_2\text{O}$ (**6**)

An identical procedure with **1** was followed to prepare **6** except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (33% yield, based on Ho). Anal. Calcd for $\text{H}_{30}\text{N}_7\text{HoO}_{50}\text{W}_{12}$ (3299.39): N, 2.97; Ho, 4.99; W, 66.87; found: N, 2.79; Ho, 4.74; W, 66.08; IR (solid KBr pellet/ cm^{-1}): 1634 (m), 1429 (m), 1308 (m), 1039 (w), 940 (m), 881 (m), 770 (s), 609 (w), 416 (m).

2.3. X-ray crystallography

Suitable single crystals of **1–6** were selected for single-crystal X-ray diffraction analysis. Intensity data were collected with a Bruker Smart Apex CCD diffractometer with Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at 293 K using the ω -scan technique. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the *SHELXTL* 97 [12] package. Intensity data were collected for empirical absorption. All of the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms attached to

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