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Synthesis, crystal structure and properties of a neodymium(III) coordination polymer of 1D chain structure based on typical plenary Keggin cluster

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A 1D zigzag chain compound, $[\{\text{Nd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$, has been synthesized by reaction of $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, Nd_2O_3 and NMP (NMP = *N*-methyl-2-pyrrolidone) in acetonitrile–water mixture, and characterized by elemental analysis, IR and UV spectra, and X-ray single crystal structural analysis. The crystal structure indicates that the title compound forms a one-dimensional zigzag chain built from alternating polyanions and cationic units through Mo–O_l–Nd–O_t–Mo links. In the compound, Nd³⁺ are eight-coordinate with a bicapped trigonal prism geometry of oxygen atoms, from six NMP molecules and two adjacent polyanions, and two terminal oxygen atoms of the polyanions occupying the caps. The powder ESR spectrum at 110 K of the title compound after being exposed to sunshine shows the signal of Mo⁵⁺, $g = 1.96$. The CV shows that the title compound undergoes five two-electron reversible reductions and that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ are active centers for electrochemical redox in solutions; cations have a small effect on electrochemical redox.

Keywords: Polyoxometalates; Oxy-ligands; Lanthanides; Structure elucidation; Zigzag chains

1. Introduction

As a rich and diverse class of inorganic cluster systems, the polyoxometalate ions, which are characterized by fascinating structural [1], electrochemical [2], catalytic [3], magnetic [4] and medicinal properties [5], have been found to be extremely versatile inorganic building blocks in the fields of designing and assembling molecule-based materials [6–8]. Based on coordination capability of the surface oxygen atoms (bridging or terminal oxygen atoms) of the polyoxoanions, novel complexes with a discrete cluster, 1D, 2D or 3D structures can be synthesized through metal units being bound to the surface framework of the polyoxoanions or metal atoms being two-dimensionally bound to lacunary polyoxoanions. In addition, the rare earth elements have photophysical, electrochemical, magnetic, and photochemical functions and properties; their coordination number may change over wide range, so their organic compounds are

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good catalysts. Many rare earth coordination compounds based on polyoxometalates have been synthesized and reported [9–13].

Inorganic materials based on lanthanide cations and polyoxometalate building blocks exhibit unique spectroscopic and magnetic properties, with wide potential applications in many fields [14–17]. Because the lanthanide cations are highly oxophilic and polyoxometalate building blocks have surface oxygen atoms, the combination produces many interesting compounds. Using the coordination chemistry of polyoxometalates with lanthanides, we have synthesized six infinitely extended polyoxometalate-based composites: $[\{\text{Ln}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Gd}$; $\text{NMP} = N$ -methyl-2-pyrrolidone) [18, 19], $[\{\text{La}(\text{DMSO})_6(\text{H}_2\text{O})\}(\text{PMo}_{12}\text{O}_{40}) \cdot \text{H}_2\text{O}]_n$ [20] and $[\{\text{Pr}(\text{DMSO})_6(\text{H}_2\text{O})\}(\text{PMo}_{12}\text{O}_{40}) \cdot \text{CH}_3\text{CN}]_n$ [21]. X-ray single crystal structure analyses show they all contain a one-dimensional chain-like structure through $\text{Mo}-\text{O}_t-\text{Ln}-\text{O}_t-\text{Mo}$ [22] links. Here, we report the study of properties and X-ray single crystal structure analysis of a new infinitely extended polyoxometalate-based composite, $[\{\text{Nd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$.

2. Experimental

2.1. Physical measurements

C, H and N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra of samples were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrometer in the range of $4000\text{--}500\text{ cm}^{-1}$. The UV spectra were observed in aqueous with a UV-250 spectrometer in the range of $190\text{--}400\text{ nm}$ (Shimadzu). The powder ESR spectrum of the title compound was recorded on a Bruker ER-200-D-SRC spectrometer with the X-band at 110 K. Cyclic voltammograms were obtained on a LK98BII electrochemical analyzer at 25°C (Tianjin, China). A glass-carbon (diameter = 3 mm) electrode was employed as the working electrode. The electrode underwent ultrasonic washing for 5 min, and was washed with water and acetone prior to every measurement. A platinum rod (diameter = 2 mm) was used as the counter electrode. The reference electrode was SCE.

2.2. Preparation of the title compound

All organic solvents and materials used for synthesis were of reagent grade and used without further purification. $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ was prepared according to the literature method [23]. NdCl_3 was prepared through adding concentrated HCl to Nd_2O_3 (99.9%).

The formation of heteropolyacid neodymium salts was realized by neutralizing the acids. $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (3.8 g, 2 mmol) and NdCl_3 (2 mmol) were dissolved in 15 mL water, and the solution was heated on a 80°C water bath until dry. Then 2 mL of NMP was added to the dried solid (2 g) from the first stage with stirring until the mixture was a paste. After standing for 5 min, the paste was dissolved in enough acetonitrile–water (3 : 2 v/v). Finally, the solution was filtered and left to evaporate at room temperature. One or two days later, yellow crystals suitable for X-ray diffraction were obtained, yield based on $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ was about 80%.

Table 1. Crystal data for the title compound.

Formula	C ₃₀ H ₅₄ Mo ₁₂ N ₆ O ₄₆ PNd
<i>M</i>	2561.28
Crystal size (mm ³)	0.27 × 0.14 × 0.06
Crystal system	Monoclinic
Space group	C2/c
<i>Z</i>	4
<i>a</i> (Å)	25.188
<i>b</i> (Å)	12.680
<i>c</i> (Å)	22.279
β (°)	111.23
<i>V</i> (Å ³)	6633
<i>D_c</i> (g cm ⁻³)	2.565
μ (mm ⁻¹)	3.082
Reflections collected	9792
Independent reflections	5710 (<i>R</i> _{int} = 0.0339)
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0718, 0.1457
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0542, 0.1387
Largest difference peak and hole (e Å ⁻³)	1.892 and -1.488

Anal. Calcd for [Nd(NMP)₆](PMO₁₂O₄₀)_{*n*}(%): C, 14.06; H, 2.11; N, 3.28. Found: C, 14.06; H, 2.15; N, 3.40.

2.3. Crystal structure analysis

The crystal structure of the title compound was determined from single crystal X-ray diffraction data. The intensity data were collected on a Rigaku RAXIS-IV image plate area detector with Mo-K α ($\lambda = 0.71073$ Å) at 293(2) K. The crystal parameters and details of the structure solution and refinement are listed in table 1. The structure was solved by direct methods and refined using full-matrix least-squares calculations with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached and refined with individual isotropic displacement parameters. All calculations were performed using the SHELXTL-97 program [24]. Selected bond lengths and bond angles are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. IR spectra

There are four characteristic asymmetric vibrations resulting from heteropolyanions with Keggin structure, namely, $\nu_{\text{as}}(\text{Mo}=\text{O}_t)$, $\nu_{\text{as}}(\text{Mo}-\text{O}_b)$, $\nu_{\text{as}}(\text{Mo}-\text{O}_c)$, and $\nu_{\text{as}}(\text{P}-\text{O}_a)$. Comparing the IR spectra of the title compound with those of $\alpha\text{-H}_3\text{PMO}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ [23] the vibration band of the Mo=O_t bond red-shifted from 975 to 961 cm⁻¹ for the title compound; the peak duo to the Mo-O_c bonds red-shifted from 810 to 801 cm⁻¹; the P-O_a bond vibrations are red-shifted from 1067 to 1063 cm⁻¹; while the vibration band of Mo-O_b bonds blue-shifted from 870 to 879 cm⁻¹. These results indicate that the polyanions in the title compound still retain the basic Keggin structure, but are distorted due to coordination. This is in agreement with the results of the single crystal X-ray diffraction analysis. In addition, there are three characteristic asymmetric

Table 2. Selected bond lengths (Å) for the title compound.

Nd(1)–O(2A)	2.379(9)	Nd(1)–O(2A)#1	2.379(9)
Nd(1)–O(1A)	2.384(7)	Nd(1)–O(1A)#1	2.384(7)
Nd(1)–O(3A)	2.390(7)	Nd(1)–O(3A)#1	2.390(7)
Nd(1)–O(1)#1	2.609(6)	Nd(1)–O(1)	2.609(6)
Mo(1)–O(1)	1.656(6)	Mo(1)–O(11)#2	1.795(10)
Mo(1)–O(10)#2	1.798(9)	Mo(1)–O(8)	1.987(8)
Mo(1)–O(17)	1.991(10)	Mo(1)–O(22)	2.465(10)
Mo(2)–O(2)	1.639(7)	Mo(2)–O(14)	1.800(8)
Mo(2)–O(18)	1.809(7)	Mo(2)–O(16)	1.984(7)
Mo(2)–O(13)	2.011(7)	Mo(2)–O(19)	2.398(11)
Mo(2)–O(21)#2	2.451(12)	Mo(3)–O(3)	1.656(7)
Mo(3)–O(16)	1.802(8)	Mo(3)–O(17)	1.806(8)
Mo(3)–O(7)	1.996(6)	Mo(3)–O(12)	2.003(8)
Mo(3)–O(22)	2.388(12)	Mo(4)–O(4)	1.634(7)
Mo(4)–O(15)	1.804(7)	Mo(4)–O(12)#2	1.813(10)
Mo(4)–O(14)	1.998(9)	Mo(4)–O(10)	2.010(8)
Mo(4)–O(22)#2	2.433(11)	Mo(5)–O(5)	1.656(7)
Mo(5)–O(13)	1.793(8)	Mo(5)–O(8)	1.811(8)
Mo(5)–O(9)	1.980(10)	Mo(5)–O(15)	2.003(7)
Mo(5)–O(20)	2.478(10)	Mo(5)–O(19)	2.495(10)
Mo(6)–O(6)	1.632(7)	Mo(6)–O(7)	1.792(7)
Mo(6)–O(9)#2	1.816(8)	Mo(6)–O(11)	1.999(8)
Mo(6)–O(18)	2.009(7)	Mo(6)–O(20)#2	2.354(11)
O(9)–Mo(6)#2	1.816(8)	O(10)–Mo(1)#2	1.798(9)
O(11)–Mo(1)#2	1.795(10)	O(12)–Mo(4)#2	1.813(10)
O(20)–Mo(6)#2	2.354(11)	O(21)–Mo(2)#2	2.451(12)
O(22)–Mo(4)#2	2.433(11)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, y, -z+1/2$; #2: $-x+1/2, -y+1/2, -z$.

Table 3. Selected bond angles (°) for the title compound.

O(211)–Nd(1)–O(1A)	74.4(3)	O(2A)#1–Nd(1)–O(1A)	76.1(3)
O(211)–Nd(1)–O(1A)#1	76.1(3)	O(2A)#1–Nd(1)–O(1A)#1	74.4(3)
O(211)–Nd(1)–O(3A)	82.0(3)	O(1A)#1–Nd(1)–O(3A)	88.5(2)
O(211)#1–Nd(1)–O(3A)#1	82.0(3)	O(1A)–Nd(1)–O(3A)#1	88.5(2)
O(311)–Nd(1)–O(3A)#1	92.0(4)	O(2A)#1–Nd(1)–O(1)#1	74.7(3)
O(111)#1–Nd(1)–O(1)#1	71.2(2)	O(3A)–Nd(1)–O(1)#1	69.5(2)
O(311)#1–Nd(1)–O(1)#1	71.6(2)	O(2A)–Nd(1)–O(1)	74.7(3)
O(111)–Nd(1)–O(1)	71.2(2)	O(3A)–Nd(1)–O(1)	71.6(2)
O(311)#1–Nd(1)–O(1)	69.5(2)	O(1)#1–Nd(1)–O(1)	122.6(3)
Mo(1)–O(1)–Nd(1)	175.4(4)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, y, -z+1/2$; #2: $-x+1/2, -y+1/2, -z$.

vibrations resulting from NMP molecules, namely, $\nu_{\text{as}}(\text{C}=\text{O})$, $\nu_{\text{as}}(\text{C}-\text{N})$ and $\nu_{\text{as}}(\text{N}-\text{CH}_3)$. Comparing the IR spectra of the title compounds with those of NMP [25], the $\nu_{\text{as}}(\text{C}=\text{O})$ decreases by 26 cm^{-1} (from 1666 to 1640 cm^{-1}) for the title compound, confirming that NMP is coordinated to the rare-earth ions by their oxygen atoms. The $\nu_{\text{as}}(\text{C}-\text{N})$ and $\nu_{\text{as}}(\text{N}-\text{CH}_3)$ frequencies in the compound rise slightly by 7 and 5 cm^{-1} , respectively. This can be explained by the fact that the charge density over the oxygen and carbon atoms is decreased due to the O atoms of the $\text{C}=\text{O}$ bonds being coordinated to rare-earth ions, leading to an increase in the electron-donating effect of the methyl groups through N atoms. The IR spectral studies show that there is strong interaction between the polyanions and organic groups in solid state.

3.2. UV spectra

The UV spectrum of the title compound measured in aqueous solution is similar to that of $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ in the same solution. There is one absorption peak at approximate 205 nm, which is the $\text{O}_t \rightarrow \text{Mo}$ charge-transfer band and strong due to the absorption of NMP molecules [25]. This suggests that the metal coordination cations and the polyanions are entirely dissociated in dilute solution. This was observed in a previous paper.

3.3. ESR spectrum

The title compound is strongly photosensitive under irradiation with sunlight, resulting in charge-transfer by oxidation of the NMP and reduction of the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. The powder ESR spectrum of the title compound after exposure to sunshine is recorded on a Bruker ER-200-D-SRC spectrometer with the X-band at 110 K. The spectrum is typical of molybdenum(V) [26] at 110 K, $g = 1.96$ (figure 1). The occurrence of the molybdenum (V) signal indicates the title compound has formed mixed valence heteropoly blue compound with unshared electrons located in metal atoms of MoO_6 octahedra, which results from the electron transfer between organic substrates and the heteropolyanions under irradiation by reduction of the heteropolyanions ($\text{Mo}^{\text{VI}} \rightarrow \text{Mo}^{\text{V}}$) and oxidation of organic units. Thus, it is assumed that charge transfer may occur through hydrogen bonds or weak intermolecular interactions between the organic groups and the polyoxometalate moieties [27–29].

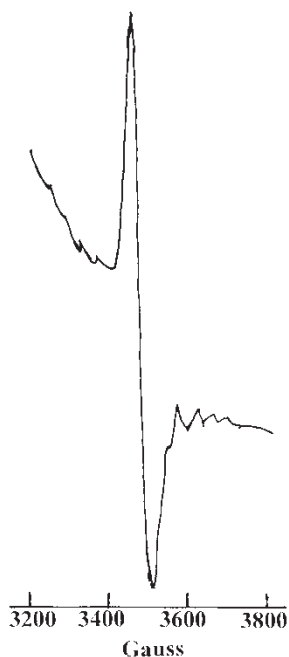


Figure 1. The ESR spectrum of the title compound (at 110 K).

Table 4. Cathodic peak potential (E_{cp}) and anodic (E_{ap}) and potential difference for $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $[\{\text{Gd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ and the title compound.

Compound	E_{cp} (V)	E_{ap} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
$\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$	0.308	0.339	31	0.324
	0.179	0.208	29	0.194
	-0.052	-0.022	30	-0.037
	-0.201	-0.17	31	-0.186
	-0.282	-0.244	38	-0.263
$[\{\text{Gd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$	0.311	0.341	30	0.326
	0.181	0.212	31	0.197
	-0.050	-0.019	31	-0.035
	-0.208	-0.176	32	-0.192
	-0.286	-0.247	39	-0.267
The title compound	0.308	0.340	32	0.324
	0.181	0.212	31	0.197
	-0.053	-0.022	31	-0.038
	-0.208	-0.179	29	-0.194
	-0.288	-0.249	39	-0.269

3.4. Cyclic voltammetric behavior

Table 4 summarizes the cathodic and anionic peak potential (V), the half-wave potential $E_{1/2}$ (V), as well as the difference potential for $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $[\{\text{Gd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ and the title compound. Figure 2 shows the CVs for $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $[\{\text{Gd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ and the title compound carried out at a sensitivity of 10 μA . For phosphopolyoxomolybdate it is difficult to obtain well-defined redox waves in cyclic voltammetry in aqueous electrolytes due to the easy hydrolysis of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. However, it is stabilized by addition of comparatively large amounts of organic solvents. Thus, cyclic voltammetry is measured in organic-aqueous solvents [50% 1,4-dioxane and 50% H_2O (secondary distilled water)] containing 0.5 mol L^{-1} H_2SO_4 as the supporting electrolyte. $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, $[\{\text{Gd}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ and the title compound undergo five two-electron reversible reductions. The reversibility criteria used was $\Delta E_p = (E_{ap}) - (E_{cp}) = 59/n$ mV (n = number of electrons). The small difference of $E_{1/2}$ (V) of three compounds shows that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions are active centers for electrochemical redox in the solutions, while cations have small effect.

3.5. Structure description

The molecular structure of the title compound is shown in figure 3. The title compound consists of one-dimensional infinite zigzag chains built from alternate polyanions and $[\text{Nd}(\text{NMP})_6]^{3+}$ units in the crystal (figure 4). The coordination environment of Nd^{3+} is shown in figure 5. The coordination numbers of Nd^{3+} ions are eight, six O atoms are from the NMP ligands, and the remaining two O atoms are from two adjacent heteropolyanions. The coordination polyhedra around the Nd^{3+} ions can be described as a bicapped trigonal prism, a common coordination geometry for complexes with coordination number of eight [30]. In the title compound, each Nd^{3+} ion has six NMP molecular forming two trigonal planes, and two terminal oxygen atoms of the polyanions occupy the caps due to steric hindrance of the polyanions. The O(1)#1–Nd(1)–O(1) bond angle is 122.6(3) $^\circ$, resulting in zigzag chains.

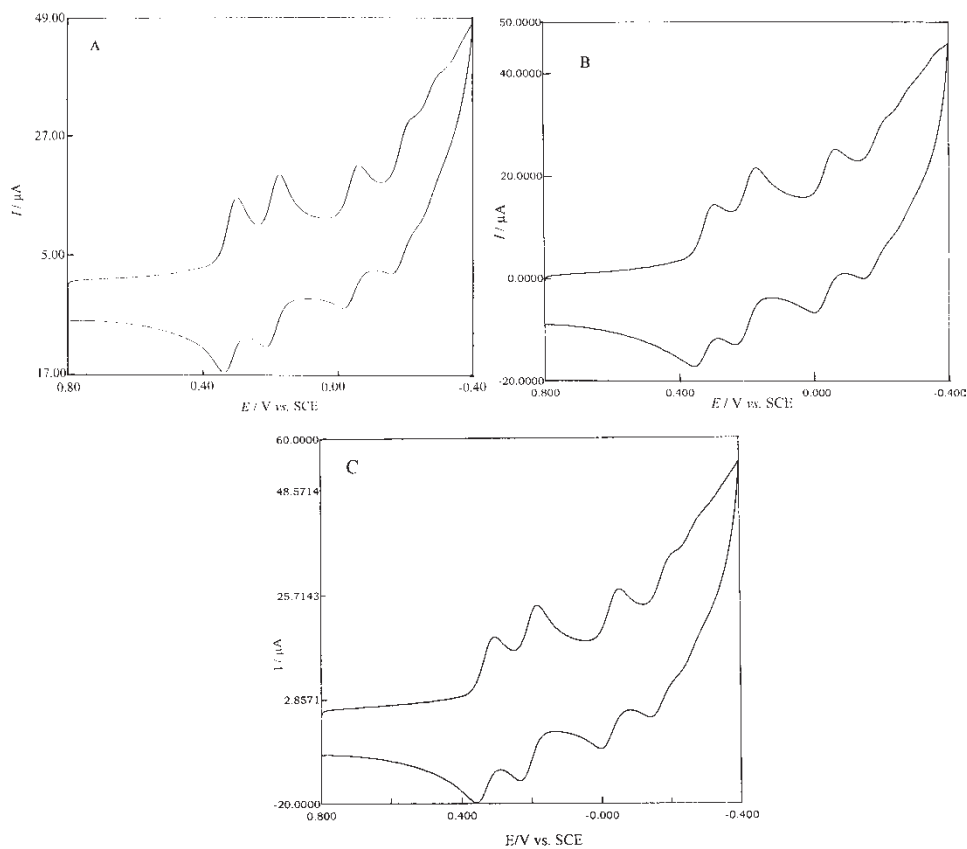


Figure 2. (A) CV of $\alpha\text{-H}_3\text{PMO}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ (1 mmol L^{-1}) in a mixture of 50% 1,4-dioxane and 50% H_2O containing 0.5 mol L^{-1} H_2SO_4 as supporting electrolyte, sensitivity $10 \mu\text{A}$, $V = 50 \text{ mV s}^{-1}$; (B) CV of the title compound (1 mmol L^{-1}) in a mixture of 50% 1,4-dioxane and 50% H_2O containing 0.5 mol L^{-1} H_2SO_4 as the supporting electrolyte, sensitivity $10 \mu\text{A}$, $V = 50 \text{ mV s}^{-1}$; (C) CV of $[\{\text{Gd}(\text{NMP})_6\}(\text{PMO}_{12}\text{O}_{40})]_n$ (1 mmol L^{-1}) in a mixture of 50% 1,4-dioxane and 50% H_2O containing 0.5 mol L^{-1} H_2SO_4 as supporting electrolyte, sensitivity $10 \mu\text{A}$, $V = 50 \text{ mV s}^{-1}$.

Comparing the title compound with $[\{\text{Gd}(\text{NMP})_6\}(\text{PMO}_{12}\text{O}_{40})]_n$ [19], the striking difference lies in the type of zigzag chain. In $[\{\text{Gd}(\text{NMP})_6\}(\text{PMO}_{12}\text{O}_{40})]_n$ for each $[\text{PMO}_{12}\text{O}_{40}]^{3-}$, two terminal oxygen atoms, O(11) and O(7), are in the place of almost 90° in the Keggin-type cage, however, in the title compound, O(1) and O(1)#1 are in almost para position, Mo(1)–O(1)–Nd(1) bond angle is 175.4° .

For Nd^{3+} ions in the title compound, two trigonal planes are composed by O1A, O2AA, O3AA, and O2A, O1AA, O3A, respectively; coplanar O1A, O2A, O1AA, O2AA, form one square face (the average plane deviation is 0.0638 \AA); and coplanar O3A, O1AA, O2AA, O3AA, form another square face (the average plane deviation is 0.0207 \AA), with O1B as a cap, and coplanar O1A, O2A, O3A, O3AA, form one square face (the average plane deviation is 0.0207 \AA), with O1 as a cap. In addition, the Nd–O bond distances range from 2.379 to 2.609 \AA and the average bond distance for all Nd–O bonds is 2.441 \AA . The mean Nd–O(NMP) bond distance, 2.384 \AA , is shorter than the average Nd–O_t bond distance, 2.609 \AA , indicating that the

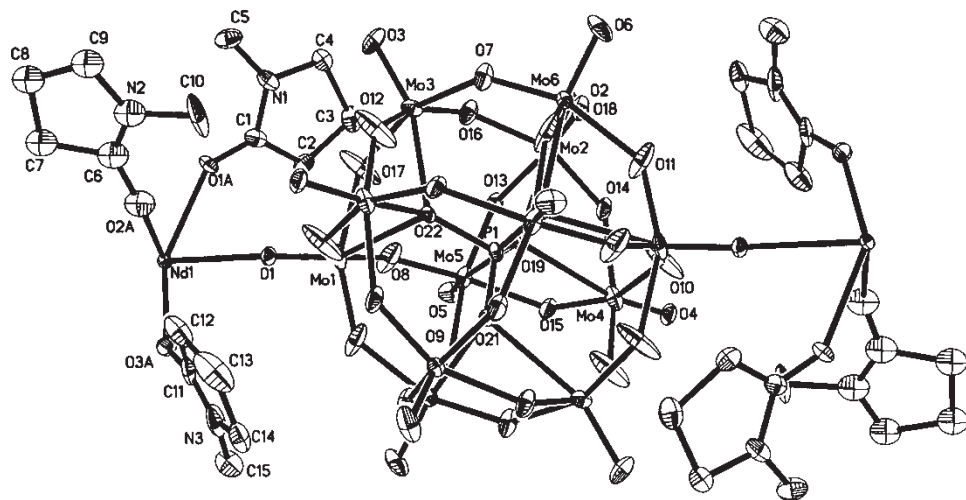


Figure 3. Molecular structure unit with atom labeling of the title compound and ellipsoids are at 30% probability. The hydrogen atoms are omitted for clarity.

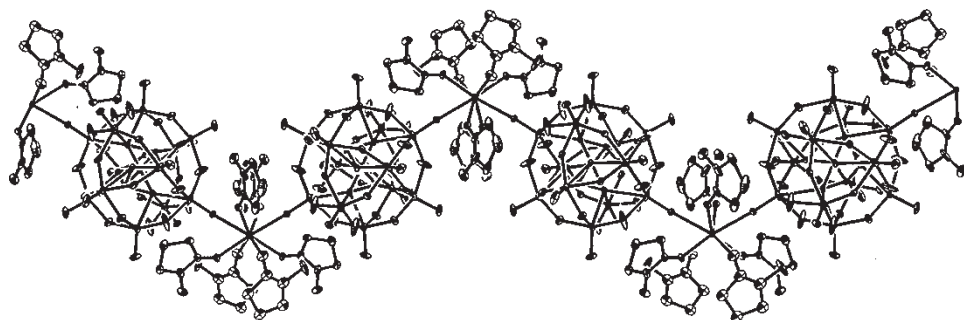


Figure 4. View of the one-dimensional chain in the title compound. The hydrogen atoms are omitted for clarity.

Nd–O(NMP) bonds are more stable than the Nd–O_t bonds, probably because the charge density over the oxygen of C=O is bigger than that of O_t, resulting from the electron-donating effect of the methyl groups through the N atoms in NMP molecules and the electron-withdrawing effect of the polyanions. The variation of Ln–O average bond separations along the Nd and Gd series [Nd–O (2.441 Å) > Gd–O (2.376 Å)] is consistent with the effects of the lanthanide contraction (ionic radius: Nd³⁺ > Gd³⁺).

The P–O bond distances range from 1.441 to 1.608 Å for the title compound, and the O–P–O bond angles range from 102.6 to 116.7°. These results show that the PO₄ tetrahedrons are distorted. The Mo–O_t bond distances range from 1.632 to 1.656 Å, mean 1.642 Å; the Mo–O_a [18] bond distances range from 2.354 to 2.495 Å, mean 2.440 Å; the Mo–O_{b,c} [22] bond distances range from 1.792 to 2.010 Å. These results show that the MoO₆ octahedra of the polyanions in the title compounds are severely distorted because of the influence of the outer coordination cations.

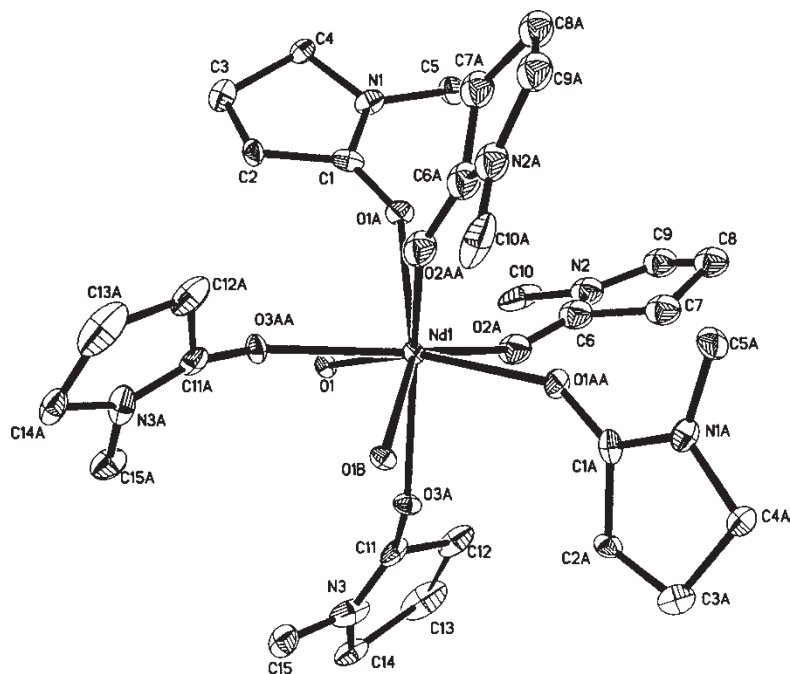


Figure 5. Coordination environment of Nd^{3+} in the title compound. The hydrogen atoms are omitted for clarity.

Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center with the deposited numbers CCDC Number 207527. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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