

# A new polyoxometalate-based helical compound with entanglement nodes: Structure, electrocatalytic and photocatalytic properties



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## ABSTRACT

A new helical compound based on polyoxovanadates,  $[\text{Ni}(\text{H}_2\text{O})_2\text{V}_2\text{O}_6]$  (**1**), has been synthesized under the hydrothermal condition. Single-crystal X-ray diffraction analysis reveals that compound **1** possesses a pair of entanglement double helixes in an inorganic framework with  $(8^1 12^4 16^1)$   $(8^2 12^2 16^2)$  topology. There are two kinds of approximately elliptical helical channels in inorganic framework. Furthermore, the electrocatalytic and photocatalytic properties of compound **1** were investigated in details.

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## 1. Introduction

In recent years, the helical structure has been attracting increased attention in materials chemistry and coordination chemistry. Up to now, many new helical compounds have been rationally designed and synthesized, which show significance in multidisciplinary areas [1–6]. Polyoxometalates (POMs) are the versatile inorganic building blocks and possess the superior potential applications in catalysis, electrochemistry and magnetism [7–12]. In virtue of their special properties, it is appealing to construct POM-based helical compounds. From the structural point of view, the incorporation of POMs into helical system leading to the formation of the helical compounds is very significant.

An excellent example of the POM-based helical compound is the first inorganic double helixes self-assembled from simple starting materials reported by Haushalter and Zubieta et al. [13]. Subsequently, thanks to the work of POM chemists, many new POM-based helical compounds have been successfully synthesized, which can be roughly divided to four types according to

number of helixes and their entangled styles: (I) right- or/and left-handed single helix [14–18], (II) entangled right- and left-handed double helixes without entanglement nodes [19–22], (III) a single of entangled right- and left-handed double helixes with entanglement nodes [23–26], and (IV) a pair of the right- and left-handed double helixes with entanglement nodes [27] (Scheme 1). The construction of POM-based helical compounds toward a specific disposition in new types is an intriguing challenge.

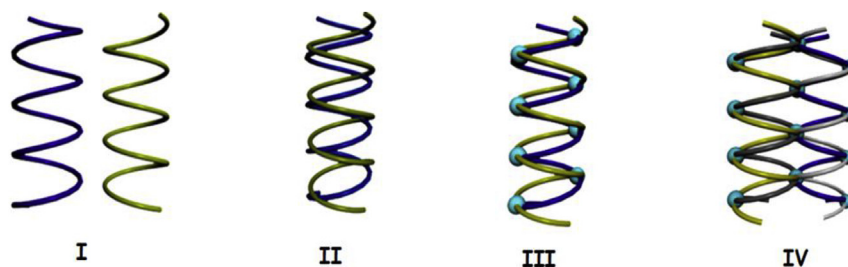
As a ramification of POMs, due to the variable oxidation states of vanadium as well as multiform coordination geometries of vanadium oxide polyhedra, polyoxovanadates (POVs) with tunable redox, catalytic and photochemical properties could be self-condensed by vanadium oxide polyhedra to form a variety of multinuclear-clusters [28–34]. Hence, the POVs could be viewed as transferable synthons for the synthesis of new helical compounds. Inspired by the aforementioned considerations, in this work, we chose  $\text{NH}_4\text{VO}_3$  as vanadium source to *in-situ* form POVs,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  as metal ions source and triethylamine as the mineralization agent. We hydrothermally synthesized an inorganic helical compound based on POVs,  $[\text{Ni}(\text{H}_2\text{O})_2\text{V}_2\text{O}_6]$  (**1**). Compound **1** shows a rare helical disposition type (IV), namely, a pair of the right- and left-handed double helixes with entanglement nodes. Furthermore, the electrocatalytic and photocatalytic properties of compound **1** were investigated.

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**Scheme 1.** Schematic representation of the four types of POM-based helical structures.

## 2. Experimental

### 2.1. Materials and general methods

All reagents and solvents for syntheses were purchased from commercial sources and used as received without further purification. The elemental analyses were of C, H and N conducted on a Perkin-Elmer 240C elemental analyzer, and that of V and Co were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. The IR spectra were recorded in the range of 4000–400  $\text{cm}^{-1}$  on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. The X-ray powder diffraction (XRPD) patterns were recorded with a Siemens D5005 diffractometer with Cu-K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The CHI760D electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a modified carbon paste electrode (CPE) as working electrode, a twisted platinum wire as counter electrode, and a commercial Ag/AgCl as reference electrode. UV–vis absorption spectra were recorded on a 756 CRT UV–vis spectrophotometer.

### 2.2. Syntheses of compound 1

A mixture of  $\text{NH}_4\text{VO}_3$  (187 mg, 1.6 mmol),  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (149 mg, 0.8 mmol), triethylamine (0.1 mL) was dissolved in 15 mL  $\text{H}_2\text{O}$  at room temperature. The pH value was adjusted to 5 by 1.0 M HCl solution, and then the solution was transferred and sealed in a 30 mL Teflonlined stainless steel container, and kept at 160  $^\circ\text{C}$  for 4 days. After slow cooling to room temperature at a rate of 10  $^\circ\text{C h}^{-1}$ , green block crystals of compound 1 were obtained (Fig. S1) (42% yield based on Ni). Elemental analyses Calcd for  $\text{NiH}_4\text{O}_8\text{V}_2$  (292.84): Ni, 20.13; H, 1.38; V, 34.80%. Found: Ni, 20.44; H, 1.41; V, 34.58%.

### 2.3. X-ray crystallography

Single-crystal X-ray diffraction data for compound 1 was recorded on a Bruker Apex CCD diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Absorption corrections were applied using multi-scan technique. The structure was solved by Direct Method of SHELXS-97 [35] and refined by full-matrix least-squares techniques using the SHELXL-97 program [36]. The hydrogen atoms of water molecule for the compound 1 could not be positioned reliably. The detailed crystallographic data and structure refinement parameters are summarized in Table 1.

## 3. Results and discussion

### 3.1. Structure description of compound 1

Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the orthorhombic space group  $Pnma$  (No. 62). The asymmetric unit of 1 includes one  $\text{Ni}^{2+}$  cation, one  $[\text{V}_2\text{O}_6]^{2-}$  anion and

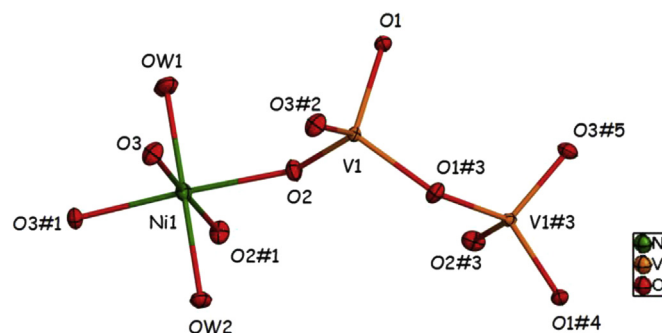
**Table 1**  
Crystal data and structure refinement for 1.

Formula	$\text{NiH}_4\text{O}_8\text{V}_2$
Formula weight	292.57
Crystal system	Orthorhombic
Space group	$Pnma$
$a/\text{\AA}$	5.5670 (5)
$b/\text{\AA}$	10.6837 (9)
$c/\text{\AA}$	11.840 (1)
$V/\text{\AA}^3$	704.20 (11)
$\alpha$ , deg	90
$\beta$ , deg	90
$\gamma$ , deg	90
Z	4
$D_{\text{calcd}}/\text{g cm}^{-3}$	2.722
T/K	273 (2)
$\mu/\text{mm}^{-1}$	5.243
Refl. Measured	4086
Refl. Unique	728
$R_{\text{int}}$	0.0165
GoF on $F^2$	0.913
$R_1/wR_2 [I \geq 2\sigma(I)]$	0.0244/0.0617

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}.$$

two coordinated water molecules (Fig. 1). The Ni(1) atom is six-coordination in an elongated octahedral geometry, constructed by six oxygen atoms from two water coordinated molecules and four  $\{\text{VO}_4\}$  tetrahedra. The average of Ni–O bond length is ca. 2.067  $\text{\AA}$  and the O–Ni–O angles are in the range of 87.97 ( $9^\circ$ )–179.54 ( $9^\circ$ ). There is one crystallographically independent V atom in  $[\text{V}_2\text{O}_6]^{2-}$  anion cluster. The V (1) atom, residing in a distorted tetrahedral environment, is coordinated by four bridging oxygen atoms from one  $\{\text{Ni}(\text{H}_2\text{O})_2\text{O}_4\}$  octahedron and three identical  $\{\text{VO}_4\}$  tetrahedral (Fig. 1). The V–O bond lengths are in the range of 1.634 (11)–1.807 (11)  $\text{\AA}$  and the average distance of V–O bond length is ca. 1.725  $\text{\AA}$ .

Compound 1 is a rarely example of the POM-based helical



**Fig. 1.** ORTEP diagram (at 30% probability level) of the basic building blocks in 1 and the coordination environment for the  $[\text{V}_2\text{O}_6]^{2-}$  cluster and  $\text{Ni}^{2+}$  ion in 1 (The H atoms of coordinated water molecules are omitted for clarity, symmetry codes: #1:  $x, 1.5-y, z$ ; #2:  $2-x, 1-y, 1-z$ ; #3:  $0.5+x, y, 1.5-z$ ; #4:  $1+x, y, z$ ; #5:  $2.5-x, 1-y, 0.5+z$ ).

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