

Coordination between $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ and antimony(III): synthesis and characterization of sandwich complex derived from the new $\{\text{P}_2\text{W}_{13}\text{O}_{51}\}$ fragment†

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A sandwich-type anionic cluster of a new lacunary building block $[\text{P}_2\text{W}_{13}\text{O}_{51}]^{14-}$ has been prepared: $[\text{H}_6\{\text{P}_2\text{W}_{13}\text{O}_{51}\}_2\text{Sb}_4]^{10-}$ (**1**) was synthesized in a one-pot self-assembly reaction of $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ with $\text{C}_4\text{H}_4\text{K}_2\text{O}_2\text{Sb}_2 \cdot 0.5\text{H}_2\text{O}$ and characterized by single-crystal X-ray analysis, IR, thermogravimetric analysis, elemental analysis, UV, NMR and electrochemistry. **1** represents the first dimeric, antimony-containing polyoxoanion derived from a vacant Dawson-type tungstophosphate.

Introduction

The class of polyoxometalates (POMs) is unique in inorganic chemistry due to the enormous structural varieties combined with interesting properties and their widespread applications such as catalysis, magnetism and materials science.^{1–3} The Wells–Dawson-derived sandwich-type POMs are of both practical and intellectual interest.⁴ The lacunary Dawson type tungstophosphates are extensively used as the building blocks to form various sandwich polytungstate complexes. The examples for metal ion-bridged monovacant Wells–Dawson POMs are the 1:1-type dimers $[\{\text{Eu}(\text{H}_2\text{O})_3(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})\}_2]^{14-}$ and $[\{\text{Ce}(\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61})(\text{H}_2\text{O})_4\}_2]^{14-}$ (Fig. 1a, Fig. 1b)⁵; 1:2-type dimers $[\text{Lu}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$, $[\text{M}(\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{16-}$ (M = Zr and Hf) and $[\text{Ln}(\alpha_1\text{-P}_2\text{W}_{17}\text{O}_{61})_2]^{17-}$ (Ln = La³⁺, Nd³⁺, Eu³⁺, Dy³⁺ or Er³⁺) (Fig. 1c, Fig. 1d).⁶ In the case of trivalent Wells–Dawson POMs, the sandwich-type compounds are comprised of a tetranuclear $[\text{M}_4\text{O}_{14}(\text{OH})_2]$ (where M = Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) or Cd(II)) (Fig. 1e) and a hexanuclear $[\text{Yb}_6(\mu_6\text{-O})(\mu_3\text{-OH})_6(\text{H}_2\text{O})_6]$ cluster encapsulated by two trivalent $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ clusters, respectively (Fig. 1f).^{4,7,8}

In recent years, the hexavacant $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ (abbreviated as $\{\text{P}_2\text{W}_{12}\}$) has emerged as a key building block for the rational design of mixed heteropolyoxometalates with intriguing structures and properties. The polyoxoanion $\{\text{P}_2\text{W}_{12}\}$ can assemble into dimeric $[\text{H}_2\text{P}_4\text{W}_{24}\text{O}_{94}]^{22-}$ (an orthogonal C_{2v} species or a linear C_{2h} anion), U-shaped trimer $[(\text{PO}_3\text{OH})_2\text{P}_6\text{W}_{36}\text{O}_{136}]^{22-}$ and crown tetramer $[\text{H}_7\text{P}_8\text{W}_{48}\text{O}_{184}]^{33-}$.⁹ These assemblies exhibit strong reactivities on their inner surfaces with various electrophilic metal ions, such as V^v,¹⁰ Fe^{III},¹¹ Co^{II},¹² Cu^{II},¹³ Ln^{III},¹⁴ organoruthenium¹⁵ and organotin,¹⁶ etc. Nevertheless, only one sandwich compound $[\text{H}_{12}\text{P}_4\text{W}_{28}\text{Fe}_8\text{O}_{120}]^{16-}$ derived from $\{\text{P}_2\text{W}_{12}\}$ has been reported (Fig. 1g).¹⁷

Up to now, the Wells–Dawson-derived sandwich-type tungstophosphates are almost always comprised of transition metals or lanthanides encapsulated by two lacunary polyoxoan-

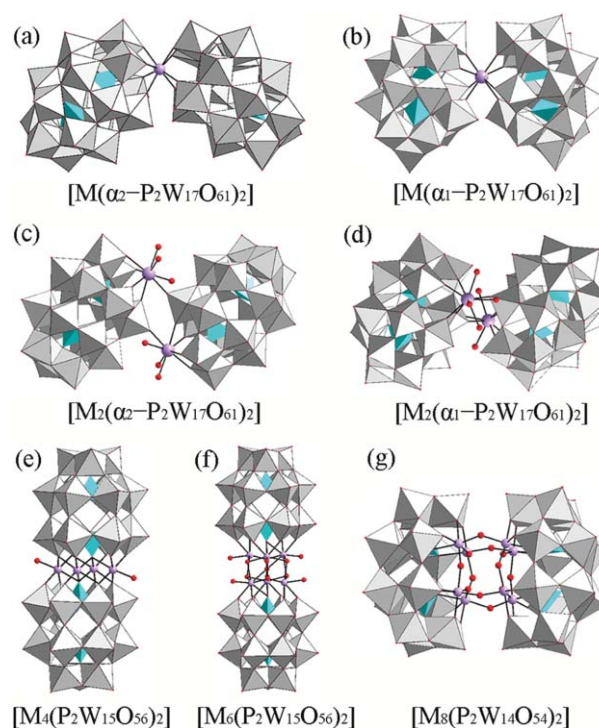


Fig. 1 Main structural types of dimeric anions built from vacant Dawson-type POMs; gray octahedral, WO₆; turquoise tetrahedral, PO₄; lavender spheres, M; red spheres, O.

ions. Contrary to this, the investigation on the sandwich-type POMs with main group metal ions remains largely undeveloped. Currently, we are exploring the reactivities of the vacant Dawson-type tungstophosphates and main-group metal elements, and $\{\text{P}_2\text{W}_{12}\}$ is a preferred such precursor because it possesses more vacant sites and stronger reactivity than other lacunary species to form novel compounds with interesting topological structures, various components and potential applications. The first Dawson sandwich compound $\text{K}_{10}[\text{H}_6\{\text{P}_2\text{W}_{13}\text{O}_{51}\}_2\text{Sb}_4] \cdot 21\text{H}_2\text{O}$ ($\text{K}_{10}\text{-1}\cdot 21\text{H}_2\text{O}$) to contain Sb(III) was successfully synthesized. Herein, we report the synthesis, crystal structure, IR, thermogravimetric, UV, NMR, and electrochemical properties. The successful isolation and structural characterization of **1** can offer a new

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† Electronic supplementary information (ESI) available: IR spectra, TG curve, UV spectra and cyclic voltammogram of **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b925682b

interesting model for the reaction between lacunary Dawson polyanions and main group metal elements.

Experimental section

Materials and methods

The $K_{12}[H_2P_2W_{12}O_{48}] \cdot 24H_2O$ was synthesized following published procedures and the purity was confirmed by infrared spectroscopy (Figure S1†) and ^{31}P NMR (Figure S2†).¹⁸ All other reagents were readily available from commercial sources and used as received without further purification. The IR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with a Mattson Alpha Centauri FT/IR Spectrophotometer. Elemental Analysis (C, H and N) was performed with a Perkin-Elmer 2400 CHN Elemental Analyzer. K, P, Sb and W were determined with a PLASMASPEC (I) ICP atomic emission spectrometer. Thermogravimetric analysis was carried out by using a Perkin-Elmer TGA7 instrument, with a heating rate of 10 $^{\circ}C\ min^{-1}$, under a nitrogen atmosphere. ^{31}P NMR spectra in D_2O solution were recorded in 5-mm outer diameter tubes on an Avance-400 Bruker NMR spectrometer. UV-Vis absorption spectra were obtained by using a 752 PC UV-Vis spectrophotometer at room temperature. Electrochemical measurements were performed with a CHI660B electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A three electrode system was employed in this study. A glassy carbon electrode ($d = 3\ mm$) was used as a working electrode, an Ag/AgCl electrode as a reference electrode and a Pt coil as a counter electrode. All potentials were measured and reported versus Ag/AgCl. All the experiments were conducted at ambient temperature (25–30 $^{\circ}C$).

Synthesis

$K_{10}[H_6\{P_2W_{13}O_{51}\}_2Sb_4] \cdot 21H_2O$. A sample of $K_{12}[H_2P_2W_{12}O_{48}] \cdot 24H_2O$ (0.5 g, 0.13 mmol) was dissolved in a stirred solution of $C_4H_4KO_7Sb \cdot 0.5H_2O$ (0.3 g, 0.90 mmol) in 20 mL H_2O at room temperature (pH ~ 7.4). After one hour, the pH value of the mixture was adjusted to ~ 3.8 by 4M HCl, and then $C_2H_7N \cdot HCl$ (0.35 g, 4.29 mmol) was added and stirred for 2 h in air. Subsequently this mixture was heated to 75 $^{\circ}C$ for 45 min and after cooling to room temperature it was filtered. The solution was kept at room temperature with slow evaporation for four days, resulting in colorless block crystals of **1** (yield 63% based on W). Elemental Anal. Calcd (%) for $H_{48}O_{123}P_4K_{10}Sb_4W_{26}$: H, 0.62; P, 1.59; K, 5.01; Sb, 6.23; W, 61.30. Found (%): H, 0.65; P, 1.45; K, 5.27; Sb, 5.99; W, 59.81.

X-ray structure analysis

Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD diffractometer with Mo-K α monochromated radiation ($\lambda = 0.71073\ \text{\AA}$) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Empirical absorption corrections were applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS-97.¹⁹ The largest residual electron density was located less than 1.0 \AA from the W addenda atoms and was most likely

Table 1 Crystal data and structural refinement for compound $K_{10}-1 \cdot 21H_2O$

Formula	$H_{48}O_{123}P_4K_{10}Sb_4W_{26}$
Formula weight/ $gmol^{-1}$	7798.07
T/K	296 (2)
Wavelength/ \AA	0.71073
Crystal system	Monoclinic
Space group	$C2/m$
$a/\text{\AA}$	18.283 (6)
$b/\text{\AA}$	22.241 (6)
$c/\text{\AA}$	18.687 (6)
β ($^{\circ}$)	102.684 (5)
$V/\text{\AA}^3$	7413 (4)
Z	2
D_{calc} ($mg\ m^{-3}$)	3.365
μ/mm^{-1}	21.199
$F(000)$	6484
Total reflections	18685
Indep. reflections	6696
R_{int}	0.0801
Crystal size/mm	$0.215 \times 0.182 \times 0.148$
Goodness-of-fit on F^2	1.086
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0747$, $wR_2 = 0.1814$
R indices (all data)	$R_1 = 0.0882$, $wR_2 = 0.1874$

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

due to an imperfect absorption correction often encountered in the solution and refinement of polyoxotungstate structures. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except for some of the oxygens (O7, O8 and O24) which were refined using isotropic thermal parameters. Those hydrogen atoms attached to lattice water molecules were not located. In this compound, only partial lattice water molecules can be accurately assigned from the residual electron peaks. In order to improve the refinement results and estimate the number of residual solvent water molecules, the crystal data was modelled by the SQUEEZE programme²⁰ in the final refinement. Based on the SQUEEZE modelling results, as well as the elemental analysis and the TG analysis, 21 crystallization water molecules were included in the final molecular structure of **1**. Crystallographic data for the structural analysis have been deposited in the ICSD Inorganic Crystal Structure database. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666); e-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number 420983 for $K_{10}-1 \cdot 21H_2O$. The crystal data and structure refinement results of $K_{10}-1 \cdot 21H_2O$ are summarized in Table 1.

Results and discussion

Synthesis

In this experiment, a new polyoxoanion cluster $[P_2W_{13}O_{51}]^{4-}$ ($\{P_2W_{13}\}$) is obtained, although the reaction is carried out by using $\{P_2W_{12}\}$ as the starting material. It is well known that the polyoxoanion $\{P_2W_{12}\}$ is very capable of combining metal cations and is a metastable precursor which can easily decompose in aqueous solution. In this reaction, tungstate fragments arising from the (limited) decomposition of $\{P_2W_{12}\}$ compete with the extra added Sb(III) ions, which form a new polyoxoanion

cluster $\{P_2W_{13}\}$. Some experimental results have proved that $\{P_2W_{12}\}$ could be transformed into $[P_2W_{14}O_{54}]^{14-}$, $[P_2W_{17}O_{61}]^{10-}$ or $[P_2W_{18}O_{62}]^{6-}$ under acidic conditions.^{17,21} It is noteworthy that the pH of the reaction plays an obvious role in the final product obtained. In the preparation of **1**, if the pH is lower than 3, then saturated $[P_2W_{18}O_{62}]^{6-}$ can be obtained. In contrast, when the pH value is adjusted to higher than 4.5, no crystals can be isolated.

Structure descriptions

Polyanion **1** crystallizes in the monoclinic space group $C2/m$. Crystallographic study of **1** showed that the asymmetric unit contains seven W centers, two P centers and one Sb center with three Sb–O bonds (average Sb–O distance = 2.20 Å). Extension of the asymmetric unit reveals that two symmetrically-related $\{P_2W_{13}\}$ subunits are held together by four equivalent Sb^{III} centers (Fig. 2). It may be viewed as a sandwich type antimony complex of $\{P_2W_{13}\}$. This sandwich type assembly $[H_6\{P_2W_{13}O_{51}\}_2Sb_4]^{10-}$ has C_{2h} symmetry and contains an empty cuboid cage (about $6.31 \times 6.77 \times 3.78 \text{ \AA}^3$) in the center of the molecule. In contrast to the tetrahedrally coordinated P(v) and As(v) of the same main group, Sb(III) gives new structural information because of the stereochemical effect of the lone pair electrons located on top of the trigonal pyramid. Each Sb atom is coordinated by three oxygen atoms from different $\{P_2W_{13}\}$ subunits (O14 (W) and O16 (W) of one $\{P_2W_{13}\}$; O9 (W) of other $\{P_2W_{13}\}$) to give a SbO_3 distorted pyramidal geometry with ranges of Sb–O distances from 1.94 to 2.00 Å. These Sb centers aren't connected directly by μ -O atoms to form a metal cluster, which is different from most sandwiched metal centers (Fig. 3).²² The bond lengths of W–O (1.70–2.51 Å) and P–O (1.49–1.58 Å) are within the normal ranges and in close agreement with those described in the literature.²³ In addition, since **1** was synthesized under acidic conditions, it is common that six protons can be used to act as the charge balance cations. Moreover, this phenomenon is constantly encountered in POM chemistry.²⁴ The BVS calculations confirm that all W metal centers are in the +6 oxidation state, Sb centers are in the +3 oxidation state and P centers are in the +5 oxidation state in compound **1**.²⁵

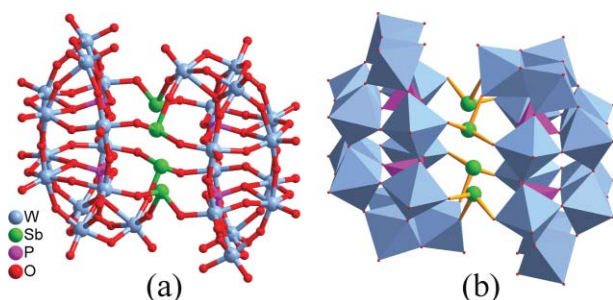


Fig. 2 (a) Ball-and-stick representation of **1** with selected labelling schemes. (b) Polyhedral representation of **1** viewed along the [010] direction.

Infrared spectrum and thermogravimetric analysis

The IR spectrum of $K_{10}\text{-}1.21H_2O$ showed a band at 664 cm^{-1} , which we assign to the absorption of $\nu(\text{Sb-O})$.²⁶ The bands at 1072 and 1020 cm^{-1} correspond to P–O antisymmetric stretching modes. The characteristic absorptions of the polyanions below 1000 cm^{-1}

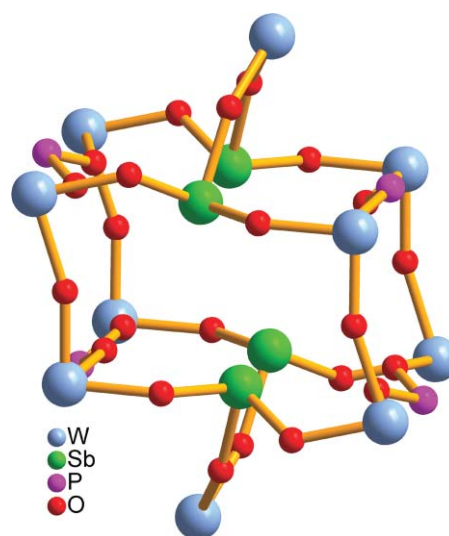


Fig. 3 The connection modes of Sb in **1**.

appearing at *ca.* 936, 897, 806, and 748 cm^{-1} are attributed to terminal W=O as well as bridging W–O–W stretching modes (Figure S3†).

In this compound, only some lattice water molecules can be directly determined by single-crystal structural analysis. The combination of elemental and thermogravimetric analysis allows us to identify the number of lattice water molecules. Such a determination method of the lattice water molecules is commonly used in giant POM species. Thermogravimetric (TG) analysis of $K_{10}\text{-}1.21H_2O$ under a nitrogen atmosphere reveals a dehydration process up to around $245 \text{ }^\circ\text{C}$ resulting in a loss of the 21 waters of crystallization and 6 protons (Figure S4†). Between $245\text{--}600 \text{ }^\circ\text{C}$, a gradual decomposition of $K_{10}\text{-}1.21H_2O$ is observed.

NMR and UV spectra

To complement our solid-state X-ray diffraction results on **1** with solution studies, we performed room-temperature ^{31}P NMR spectroscopy on $K_{10}\text{-}1.21H_2O$ redissolved at room temperature in D_2O . The ^{31}P spectrum exhibited two signals ($\delta = -11.7$ and -13.7 ppm) with approximate relative intensities 1:1 (Fig. 4), which is in complete agreement with the solid-state structure (Fig. 2). It can be seen that the $[P_2W_{12}]$ changed to $[P_2W_{13}]$ in this reaction system by the comparison of this with ^{31}P NMR

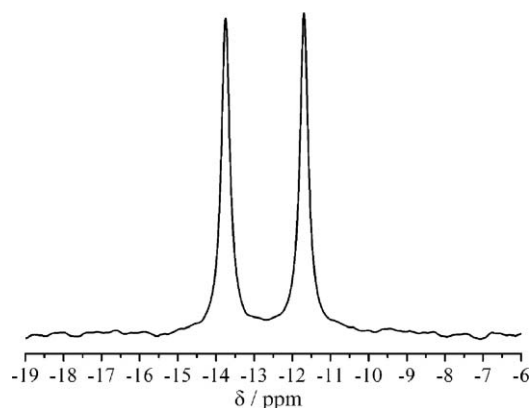


Fig. 4 ^{31}P NMR spectrum of **1** in D_2O at room temperature.

spectroscopy of $[P_2W_{12}]$ (single signal $\delta = -8.4$ ppm, Figure S2†). We have not yet obtained a decent ^{183}W NMR spectrum for **1**, probably due to the solubility problem. After polyanion **1** has been synthesized, it remains stable in the presence of air and moisture. Furthermore, the UV-vis spectra of **1** in aqueous solution (4×10^{-4} mol L $^{-1}$) were checked simultaneously and almost no changes were observed over six days (Figure S5†). In fact, the ^{31}P NMR spectrum of **1** in aqueous solution remains unchanged for weeks. These characterizations confirm that polyoxoanion **1** is structurally stable in aqueous solution.

Electrochemistry

The electrochemical behavior of **1** and the electrocatalytic properties for NO_2^- reduction were studied in 0.5 M ($CH_3COOK + CH_3COOH$) pH 4.7 buffer solution in the potential range of +400 to -1000 mV (scan rate : 40 mV s $^{-1}$, Fig. 5). There exist two reversible redox waves with midpoint potentials (E_{mid}) of -434 (II-II'), and -745 (III-III') mV, where $E_{mid} = (E_{pc} + E_{pa})/2$; E_{pc} and E_{pa} are the cathodic and anodic peak-potentials, respectively. The redox peaks II-II' and III-III' should be ascribed to the two consecutive two-electron processes of W centers.^{27,1b} In addition, the irreversible anodic peak I with the potential of -53 mV is assigned to the oxidation of the antimony centers, and its cathodic counterpart may be embedded in the reduction peak of W due to weak signal.²⁸ When the scan rate is varied from 40 to 100 mV S $^{-1}$, the peak potentials change gradually: the cathodic peak potentials shift toward the negative direction and correspondingly the anodic peak potentials shift toward the positive direction with increasing scan rates (Figure S6†).

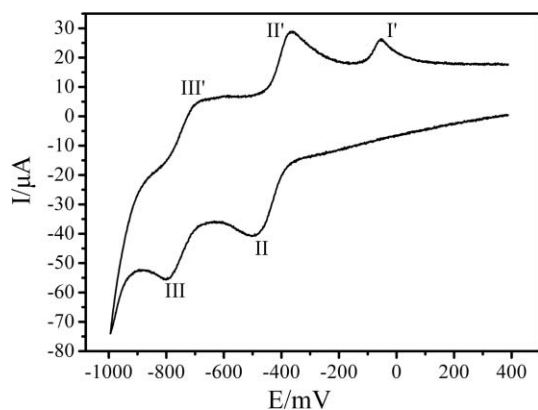


Fig. 5 Cyclic voltammogram of 1.0 mM solutions of **1** in 0.5 M $CH_3COOK + CH_3COOH$ (pH = 4.7) medium at a scan rate of 40 mV s $^{-1}$, the working electrode was glassy carbon, and the reference electrode was Ag/AgCl.

Catalytic reduction of NO_x species, especially of nitrite, by POMs has become a classical test for their electrocatalytic abilities. And the electrocatalytic reduction of nitrate remains a challenge in the NO_x series because a complete process requires several electrons. Therefore, electrocatalytic reduction of NO_2^- by **1** constitutes a further step in the search for its electrocatalytic activity. We found that **1** displays electrocatalytic activity to reduce nitrite (Fig. 6). On addition of NO_2^- , all the reduction peak currents increase, and the corresponding oxidation peak currents decrease dramatically, which indicates that both the two reduced

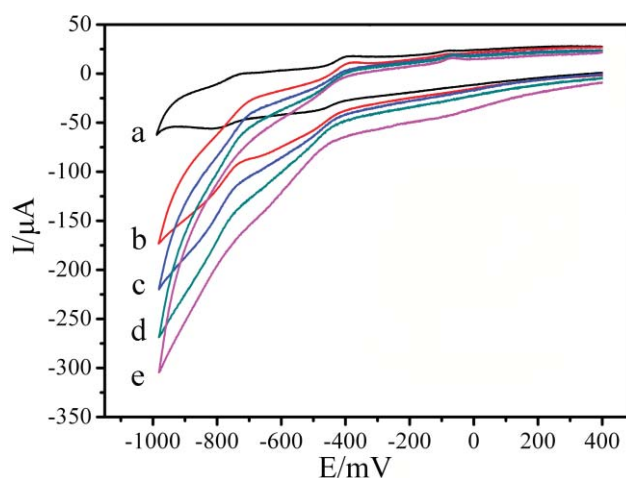


Fig. 6 Cyclic voltammograms of **1** (1.0 mM) in the pH 4.7 (0.5 M $CH_3COOK + CH_3COOH$) buffer solution containing (a) 0 mM, (b) 5 mM, (c) 10 mM, (d) 15 mM, and (e) 20 mM $NaNO_2$. Scan rate: 100 mV s $^{-1}$, the working electrode was glassy carbon, and the reference electrode was Ag/AgCl.

species show electrocatalytic activities toward the reduction of nitrite. In comparison, no reduction of nitrite took place on the GC electrode in the absence of **1**.

Conclusions

In conclusion, a novel cluster $[H_6\{P_2W_{13}O_{51}\}_2Sb_4]^{10-}$ has been successfully synthesized, representing the first derivative of the new $\{P_2W_{13}\}$ fragment and the first reaction between the lacunary $\{P_2W_{12}\}$ and main group metal ions. Note that in previous reports the structure of $\{P_2W_{12}\}$ is usually retained, but $\{P_2W_{12}\}$ change to new $\{P_2W_{13}\}$ in this experiment because of the self-assembly of POMs mechanism. Examination of cyclic voltammograms shows a good electrocatalytic activity toward the reduction of nitrite. The polyanion **1** is stable in solution, as shown by UV spectra and ^{31}P NMR spectroscopy. Due to the excellent stability of **1**, it is promising for use as a new polyoxometalate precursor to research its extensional structures.

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