



# Three new 3-D inorganic–organic coordination polymers constructed from polyoxovanadate-based heterometallic network and flexible bis(imidazole) ligand: Syntheses, structures and properties

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## ARTICLE INFO

### Article history:

Received 27 November 2009  
Received in revised form 16 December 2009  
Accepted 18 December 2009  
Available online 28 December 2009

### Keywords:

Polyoxovanadate  
Heterometallic clusters  
Crystal structure  
Electrochemical behavior

## ABSTRACT

Three new 3-D inorganic–organic polyoxovanadate-based coordination polymers  $[M_2(\text{bbi})(V_2O_6)_2(H_2O)_2]$  [ $M = \text{Co}$  (**1**),  $\text{Mn}$  (**2**)] and  $[\text{Ni}_2(\text{bbi})_3V_4O_{12}] \cdot 4H_2O$  (**3**) ( $\text{bbi} = 1,1\text{-(1,4-butanediyl)bis(imidazole)}$ ) have been synthesized under hydrothermal condition and characterized by elemental analyses, IR spectra, TG and single crystal X-ray diffraction. The 3-D networks of compounds **1** and **2** are constructed from neutral  $\{M_2V_4O_{12}\}$  [ $M = \text{Co}$  (**1**),  $\text{Mn}$  (**2**)] layers that are pillared via the coordination of organic ligands  $\text{bbi}$  to  $M$  sites. Compound **3** is a 3-D eight-connected network, in which each binuclear  $[\text{Ni}_2O_4N_6]$  node linked with other eight adjacent nodes through two  $\{V_4O_{12}\}^{4-}$  clusters and six  $\text{bbi}$  ligands. The electrochemical behaviors of **1–3** modified carbon paste electrodes (**1**-CPE, **2**-CPE and **3**-CPE) in 1 M  $H_2SO_4$  aqueous solution have been reported.

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## 1. Introduction

Hybrid solids that combine both metal–oxide and organic ligand “building blocks” are a growing class of new materials and are beginning to receive widespread attention because of their potential application in the fields of magnetism, catalysis and photochemistry [1–3]. Owing to the ability of vanadium to adopt a variety of coordinated geometries in various oxidation states, the influences of the second metal ions as well as the organic ligands on the structure could be significant. Compounds combining the flexible bridging ligands with the vanadate have received great attention [4–8]. A few prominent results have been reported recently by Su and Wang’s group in this field [9–11]. Such typical examples include  $[\text{Cu}(\text{bbi})_2V_{10}O_{26}][\text{Cu}(\text{bbi})_2] \cdot 2H_2O$  ( $\text{bbi} = 1,1\text{-(1,4-butanediyl)bis(imidazole)}$ ) [9], which is the first example of an enantiomerically pure 3-D POM-based compound with achiral ligands, the  $[V_{10}O_{26}]^{4-}$  polyoxoanion, and mixed-valence  $\text{Cu}^{II/III}$ .  $[\text{Ni}_2(\text{bbi})_2V_4O_{12}] \cdot 2H_2O$  and  $[\text{Co}(\text{bbi})(H_2O)V_2O_6]$  [10] are firstly reported chiral POM-based compounds consisting of 3-D chiral inorganic skeletons. They also reported a 3-D hetero-catenated framework  $[\text{Cu}_2(\text{biim})_3V_4O_{12}]$  ( $\text{biim} = \text{bbi}$ ) constructed from 2-D sub-layers, and a rare case of a self-catenated ‘ilc’ network  $[\text{Co}_2(\text{biim})_3V_4O_{12}] \cdot 4H_2O$  that displays an unusual  $4^{24} \cdot 5 \cdot 6^3$  topology [11].

In addition, the modification of the hydrothermal synthesis conditions, such as time, temperature, stoichiometry, pH, concentration and filling factor allows a partial control of the degree of oxoanion polymerization giving rise to different stable species in solution [12–20]. Examples of those are  $\{V_4O_{12}\}$  cyclic tetramers,  $\{VO_3\}$  metavanadate chains, or  $\{V_2O_7\}$  dimers, which may give rise to novel structural types for synergetic interaction with metal and flexible bridging ligands.

On the basis of aforementioned points, we have successfully synthesized three new inorganic–organic polyoxovanadate-based coordination polymers  $[M_2(\text{bbi})(V_2O_6)_2(H_2O)_2]$  [ $M = \text{Co}$  (**1**),  $\text{Mn}$  (**2**)], and  $[\text{Ni}_2(\text{bbi})_3V_4O_{12}] \cdot 4H_2O$  (**3**) using  $\text{bbi}$  ligands (Chart 1), vanadium source and different metal ions under different hydrothermal conditions. The isostructural compounds **1** and **2** are composed of neutral  $\{M_2V_4O_{12}\}$  [ $M = \text{Co}$  (**1**),  $\text{Mn}$  (**2**)] layers and organic ligands  $\text{bbi}$ . Compound **3** displays an eight-connected topology with the binuclear  $[\text{Ni}_2O_4N_6]$  units as nodes. Moreover, the thermal and electrochemical properties of the title compounds are investigated.

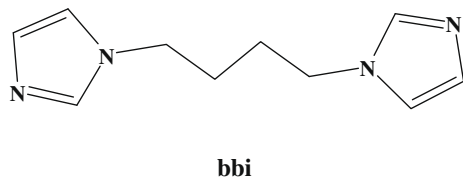
## 2. Results and discussion

### 2.1. Synthesis

In a specific hydrothermal process, many factors may affect the crystallization and structural construction of the products, such as initial reactants, pH value, temperature, etc. According to the previous reports, those isostructural compounds were usually obtained under the similar reaction conditions in which only one

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**Chart 1.** The schematic structure of the ligand bbi.

component is different. For example,  $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{bpp})_2\text{Cl}][\text{PW}_{12}\text{O}_{40}] \cdot \sim 20\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{H}_2\text{O})_2(\text{bpp})_2\text{Cl}][\text{PMo}_{12}\text{O}_{40}] \cdot \sim 20\text{H}_2\text{O}$  in Ref. [2],  $[\text{Co}_2(\text{biim})_3\text{V}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{biim})_3\text{V}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$  in Ref. [11], were produced under the same procedure, respectively, except that  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  was used instead of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  in Ref. [2],  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in Ref. [11].

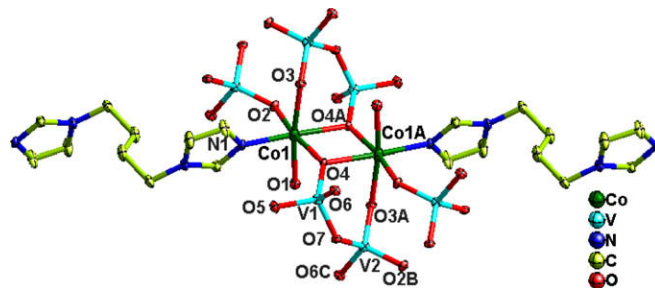
In order to investigate the effect of different reaction conditions on the hydrothermal system, we have synthesized three new coordination polymers by the tunable role of the initial reactants, pH and temperature, which are different from the reported compounds [9,11]. Initially, we obtained two complexes  $[\text{Co}_2(\text{bbi})(\text{V}_2\text{O}_6)_2(\text{H}_2\text{O})_2]$  (**1**) and  $[\text{Co}_2(\text{bbi})_3\text{V}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$  (**1a**) by reaction of  $\text{NaVO}_3$ , bbi and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  at 180 °C depending on different pH values (pH 8 for **1** and pH 10 for **1a**). But the latter has been reported in the literature [11] by reaction of  $\text{NaVO}_3$ , bbi,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$  at 120 °C for 5 days. Our experimental results showed that the  $\text{V}_4\text{O}_{12}^{4-}$  clusters were likely to form under the higher pH conditions, which is consistent with the phenomena in the literature [1,12,13,17]. Under similar condition to that of **1**, we expected that using  $\text{V}_2\text{O}_5$  in place of  $\text{NaVO}_3$  would lead to the same compound as **1**; however, we failed to isolate the expected single crystal. Only when the temperature was lowered to 120 °C, the same product **1** was obtained; but the yield was very low. According to the experimental results, we can speculate that the reactive system of  $\text{V}_2\text{O}_5$  may obtain the same compound to the system of  $\text{NaVO}_3$  by means of adjusting the pH and temperature, which is because the syntheses of these compounds are affected not only by the stoichiometries of the reactants but also by the pH of the reaction media, temperature, reaction time, and types of co-ligands in the reaction medium [12–20].

To further investigate the structural diversity that can be tuned by the nature of different transition-metal ions, we extended our studies from  $\text{Co}^{\text{II}}$  ion to the  $\text{Mn}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  ions. When  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  reacted with  $\text{V}_2\text{O}_5$  and bbi at 120 °C and pH 9, compound **2** was obtained, which is isostructural with compound **1**. Compound **3** was obtained when  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  reacted with  $\text{V}_2\text{O}_5$  and bbi at 120 °C and pH 11, which is isostructural with previously reported  $[\text{Co}_2(\text{bbi})_3\text{V}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$  that is prepared under different conditions (0.2 mmol  $\text{Na}_2\text{HPO}_4$  as pH controlled medium) [11]. These results further provide us with a useful and important guide to synthesis of inorganic–organic polyoxovanadate-based coordination polymers under hydrothermal conditions.

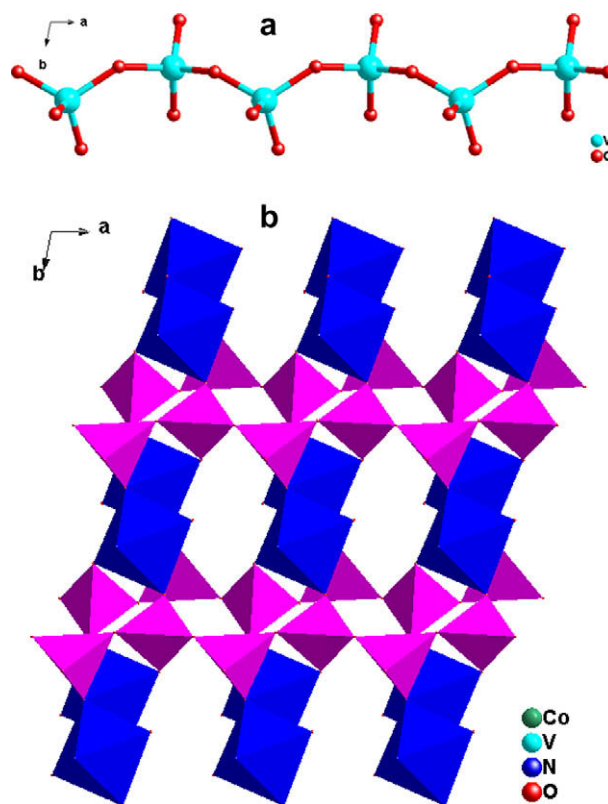
## 2.2. Description of crystal structure

$[\text{M}_2(\text{bbi})(\text{V}_2\text{O}_6)_2(\text{H}_2\text{O})_2]$  ( $M = \text{Co}$  for **1**,  $Mn$  for **2**): Single-crystal X-ray diffraction analysis reveals that the compounds **1** and **2** are isostructural with only slight differences in bond lengths and angles, whose general formula consist of one metal dimer  $[\text{M}_2^{\text{II}}(\text{bbi})(\text{H}_2\text{O})_2]^{4+}$  and two  $[\text{V}_2\text{O}_6]^{2-}$  anions cluster (Fig. 1 and Fig. S1). In this paper, we will discuss in detail the structure of **1** as an example.

In the compound **1**, the  $\text{VO}_4$  tetrahedra connect each other by corner-sharing O atoms to form oxo-vanadium cluster chain-like structure along *a* axis, as shown in Fig. 2(a). Each polyoxovanadate



**Fig. 1.** ORTEP diagram (at 30% probability level) of the coordination environment for  $\text{Co}^{\text{II}}$  ions in **1** (for clarity, the H atoms are not shown). Selected bond distances and bond angles (Å, °):  $\text{Co}(1)\text{--N}(1)$  2.056(2),  $\text{Co}(1)\text{--O}(4)$  2.061(2) ( $\times 2$ ),  $\text{Co}(1)\text{--O}(2)$  2.063(2),  $\text{Co}(1)\text{--O}(1)$  2.151(2),  $\text{Co}(1)\text{--O}(3)$  2.166(2),  $\text{V}(1)\text{--O}(5)$  1.601(2),  $\text{V}(1)\text{--O}(6)$  1.807(2),  $\text{V}(2)\text{--O}(7)$  1.766(2),  $\text{V}(2)\text{--O}(3A)$  1.679(2),  $\text{O}(4)\text{--Co}(1)\text{--O}(4A)$  80.63(7),  $\text{N}(1)\text{--Co}(1)\text{--O}(4A)$  177.40(8),  $\text{O}(5)\text{--V}(1)\text{--O}(7)$  105.91(1),  $\text{O}(7)\text{--V}(1)\text{--O}(6)$  116.02(9),  $\text{O}(3A)\text{--V}(2)\text{--O}(7)$  106.38(9).



**Fig. 2.** (a) The oxo-vanadium cluster  $\{\text{V}_2\text{O}_6\}_n^{2n-}$  chain-like structure in **1** along *a* axis; (b) 2-D layer-like mixed metal oxide framework of **1**.

chain is linked to three adjacent polyoxovanadate chains by binuclear cobalt unit  $[\text{Co}_2^{\text{II}}(\text{bbi})(\text{H}_2\text{O})_2]^{4+}$ , leading to forming a 2-D layer-like mixed metal oxide framework, as shown in Fig. 2(b) and Fig. S2. In the layer-like network there are two kinds of crystallographically independent V atoms. Both kinds of V atoms are four-coordinated showing distorted  $\text{VO}_4$  tetrahedral coordination geometry, the V(2) atom is coordinated by two O atoms [O(2), O(3)] from one adjacent  $[\text{Co}_2\text{O}_8\text{N}_2]$  building blocks and two O atoms [O(6), O(7)] from two adjacent  $[\text{V}(1)\text{O}_4]$  units, whereas the V(1) atom is coordinated by one O atom [O(4)] from a  $[\text{Co}_2\text{O}_8\text{N}_2]$  unit, two O atoms [O(6), O(7)] from two adjacent  $[\text{V}(2)\text{O}_4]$  units in the chain and one terminal O atom [O(5)]. The corresponding V–O bond lengths are in the range of 1.601(2)–1.807(2) Å and the O–V–O angles vary from 105.91(1) to 116.02(9)°, indicating

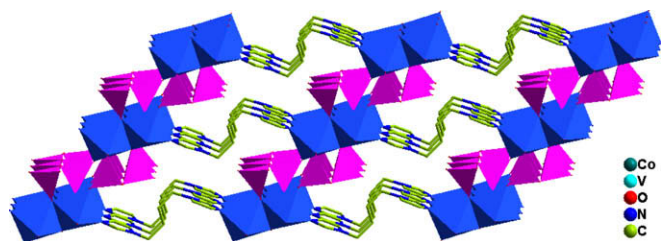


Fig. 3. Projection of the three-dimensional framework in **1** (H atoms are omitted for clarity).

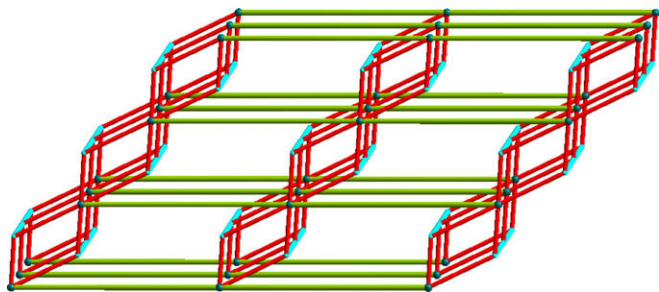


Fig. 4. The 3-D topology of bimetallic network for **1**.

that geometrical configurations of V atoms have been distorted to some extent [25].

The Co<sup>II</sup> ions display six-coordinated octahedral configuration, which are defined by one N atom [N(1)] from a bbi ligand, two O atoms [O(4), O(3)] from the adjacent [V(1)O<sub>4</sub>] and [V(2)O<sub>4</sub>] units in the same one-dimensional chains, two oxygen atoms [O(2), O(4A)] from [V(1)O<sub>4</sub>] and [V(2)O<sub>4</sub>] units in two different one-dimensional chains and one O atom [O(1)] from a water molecule. The average Co–N and Co–O bond lengths are 2.056(2) and 2.121(2) Å, respectively. The O(N)–Co–N(O) angles vary from 80.63(7) to 177.40(8)°. The bond valence sum calculations (BVS) [26] results reveal that in the compound **1**, all V centers are in the +5 oxidation state, and Co center is in the +2 oxidation state, which was consistent with the formula of [Co<sup>II</sup>(bbi)(V<sup>V</sup>O<sub>6</sub>)<sub>2</sub>].

The bbi ligand, thanks to the flexibility of the spacer, has been purposefully selected for the design and construction of intriguing structural polymers in crystal engineering [27–31]. As shown in Fig. 3, the 3-D network of compound **1** is based on the bridging ligand bbi and the heterometallic layers [Co<sup>II</sup>(V<sup>V</sup>O<sub>6</sub>)<sub>2</sub>]<sub>n</sub>, in which the bbi ligands complete the three-dimensional hybrid structure by linking cobalt dimers of 2-D bimetallic layers. The separation of Co...Co is 12.136 Å in the 2-D bimetallic layers. In order to better understand the structure of compound **1**, it is necessary to simplify the building blocks from which the 3-D framework is built. Considering the binuclear [Co<sub>2</sub>O<sub>8</sub>N<sub>2</sub>] units as nodes (dark green), keeping the {V<sub>2</sub>O<sub>6</sub>}<sup>2n-</sup> chains (light blue) and bbi ligands (light green) as spacers, a novel 3-D framework with the rare heterometallic layers is constructed (Fig. 4).<sup>1</sup>

The most interesting structural feature of **1** is that the {V<sub>2</sub>O<sub>6</sub>}<sup>2n-</sup> cluster chains and the [Co<sup>II</sup>O<sub>4</sub>N(H<sub>2</sub>O)]<sub>2</sub><sup>4+</sup> complex fragments are alternately connected to form a 2-D layer-like heterometallic network. To the best of our knowledge, some inorganic–organic heterometallic frameworks based on {V<sub>2</sub>O<sub>6</sub>}<sup>2n-</sup> cluster chains have been reported, such as 3-D open framework [Co(4,4'-bipy)V<sub>2</sub>O<sub>6</sub>]

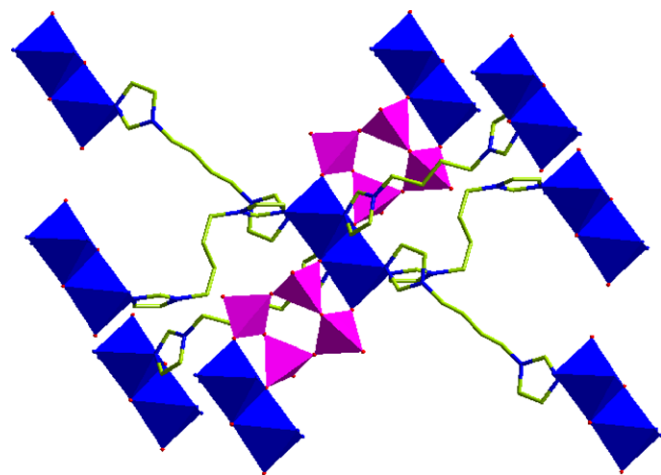


Fig. 5. View of the linkage of dinuclear core with eight adjacent cores in **3** (H atoms are omitted for clarity).

[1], 2-D layered complexes [M(dpa)V<sub>2</sub>O<sub>6</sub>] (M = Zn<sup>2+</sup> or Cu<sup>2+</sup>; dpa = 2,2'-dipyridylamine) [32], and 3-D hofmann-like networks constructed from cyanide-bridged Fe(II)–M(II) bimetallic (M = Ni, Pd, and Pt) pillared-layer [33]. Here, compound **1** is another example of 3-D inorganic–organic framework constructed from 2-D pillared-layer-type heterometallic network and organic ligands.

Ni<sub>2</sub>(bbi)<sub>3</sub>V<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O (**3**): When metal Ni<sup>II</sup> ions was chosen instead of Co<sup>II</sup> or Mn<sup>II</sup> ions, another interesting eight-connecting three-dimensional framework **3** was obtained, which is isostructural with [Co<sub>2</sub>(biim)<sub>3</sub>V<sub>4</sub>O<sub>12</sub>].4H<sub>2</sub>O that was reported by Wang and co-workers [11], and the unit cell dimensions, volumes, related bonds distances and angles vary only slightly.

X-ray study reveals that compound **3** is a 3-D coordination polymer network constructed from binuclear nickel clusters, [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> clusters and bbi linkers. As shown in Fig. S3, the building unit of **3** contains two Ni<sup>II</sup> cations, one {V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> anion, three bbi ligands, and four lattice water molecules. Each Ni<sup>II</sup> is coordinated by three nitrogen atoms [Ni(1)–N 2.059(2)–2.094(1) Å] of three bbi ligands, and three oxygen atoms [Ni(1)–O 2.073(1)–2.290(1) Å] of two {V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> anions to give a distorted octahedral geometry. As shown in Fig. 5, each binuclear nickel cluster [Ni<sub>2</sub>O<sub>4</sub>N<sub>6</sub>] is surrounded by six bbi ligands and two [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> clusters. This, therefore, defines an eight-connected node. Each binuclear [Ni<sub>2</sub>O<sub>4</sub>N<sub>6</sub>] unit is further linked to eight nearest-neighbors through two [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> clusters and six bbi ligands with distances of 9.018(2)–15.590(2) Å, thus resulting in an unusual 3-D eight-connected network. For perspicuous representation, the binuclear nickel clusters [Ni<sub>2</sub>O<sub>4</sub>N<sub>6</sub>] are considered as nodes and the bbi ligands and [V<sub>4</sub>O<sub>12</sub>]<sup>4-</sup> clusters are represented as linkers. The overall structure of the 3-D framework of **3** can be best described as an eight-connected network with the type of 4<sup>24</sup> · 5 · 6<sup>3</sup> topology [34], as shown in Fig. 6. Such topology has been found in the Reticular Chemistry Structure Resource (RCSR) database (<http://rcsr.anu.edu.au/>) [35]. To the best of our knowledge, compound **3** represents another example of the eight-connected self-catenated 3-D heterometallic framework based on inorganic polyoxovanadates and organic linkers [36–38].

### 2.3. IR spectra of compounds **1–3**

In the infrared spectra of the compounds **1–3** (Figs. S4–S6, Supplementary material), the strong bands at 1640–1087 cm<sup>-1</sup> can be assigned to the bending vibrations of the CH, NH, or the ring stretching frequency of the bbi ligands. The strong bands at 985–556 cm<sup>-1</sup> are ascribed to the vibration of V=O and V–O–Co. The

<sup>1</sup> For interpretation of color in Fig. 4, the reader is referred to the web version of this article.

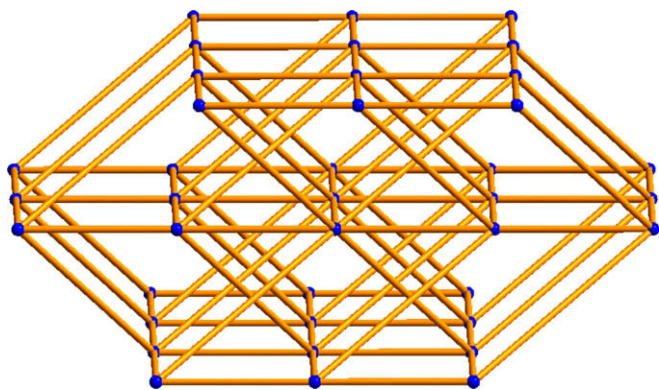


Fig. 6. The 3-D eight-connected topology based on binuclear nickel cluster  $[\text{Ni}_2\text{O}_4\text{N}_6]$  in **3**.

strong broad band at around  $3400\text{ cm}^{-1}$  is assigned to the vibrations of hydroxyl groups from water molecules.

#### 2.4. TG analysis of compounds **1–3**

To examine the thermal stability of compounds **1–3**, thermal gravimetric (TG) analyses were carried out in the temperature range of  $30\text{--}500\text{ }^\circ\text{C}$  (Figs. S7–S9, Supplementary material). The TG curves of compounds **1** and **2** were similar, exhibiting two weight loss steps, respectively. The continuous weight loss step from  $170$  to  $240\text{ }^\circ\text{C}$  is attributed to the loss of the coordinated water molecules. The weight loss is about  $5.10\%$  for compound **1** ( $4.63\%$  for **2**), in correspondence with the calculated value of  $4.87\%$  for **1** ( $4.92\%$  for **2**). The second sharp weight loss was observed in the range  $250\text{--}400\text{ }^\circ\text{C}$ , corresponding to the decomposition of organic ligands bbi (for **1**:  $25.76\%$ , calculated value of  $25.69\%$ ; for **2**:  $25.91\%$ , calculated value of  $25.97\%$ ). The remaining weight ( $69.14\%$  for **1** and  $69.46\%$  for **2**) corresponds to the percentage ( $69.44\%$  for **1** and  $69.11\%$  for **2**) of  $\text{V}_2\text{O}_5$  and  $\text{CoO}$  (or  $\text{V}_2\text{O}_5$  and  $\text{MnO}$ ) components. The TG curve of compound **3** exhibits two weight loss steps in the temperature range of  $100\text{--}460\text{ }^\circ\text{C}$ . The first weight loss step from  $100$  to  $190\text{ }^\circ\text{C}$  is attributed to the loss of the lattice water molecules. The weight loss is about  $6.58\%$ , in correspondence with the calculated value of  $6.23\%$ . The oxidation of bbi ligands and the decomposition of polyoxovanadate-framework take place at  $215\text{ }^\circ\text{C}$ , the total weight loss is about  $44.28\%$ , in the accordance with the calculated value  $44.43\%$ .

#### 2.5. Electrochemical behaviors of compounds **1–3** modified carbon paste electrodes

Among those important properties of polyoxovanadates, the abilities to undergo reversible mono-electron redox processes  $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$  endow them with very attraction in electrochemical and electrocatalytic research [11,39]. In order to study the electrochemical behavior of **1–3** in aqueous solution, the three compounds were used as solid modifiers to fabricate three-dimensional bulk-modified carbon paste electrodes (**1**-CPE, **2**-CPE and **3**-CPE) by direct mixing method due to its insolubility.

The electrochemical studies of the three compounds modified CPEs were carried out in  $1\text{ M H}_2\text{SO}_4$  aqueous solution. Fig. 7 shows the cyclic voltammograms of a bare CPE, **1**-CPE, **2**-CPE and **3**-CPE in  $1\text{ M H}_2\text{SO}_4$  aqueous solution. It can be seen from Fig. 7 that in the potential range of  $1300\text{--}100\text{ mV}$ , no peak current appeared at the bare CPE (Fig. 7, curve a). However, one quasi-reversible redox peak appears and the mean peak potentials  $E_{1/2} = (E_{pa} + E_{pc})/2$  are  $752\text{ mV}$  for the **1**-CPE,  $754\text{ mV}$  for the **2**-CPE, and  $718\text{ mV}$  for the **3**-CPE at a scan rate of  $100\text{ mV s}^{-1}$ , which can be attributed to

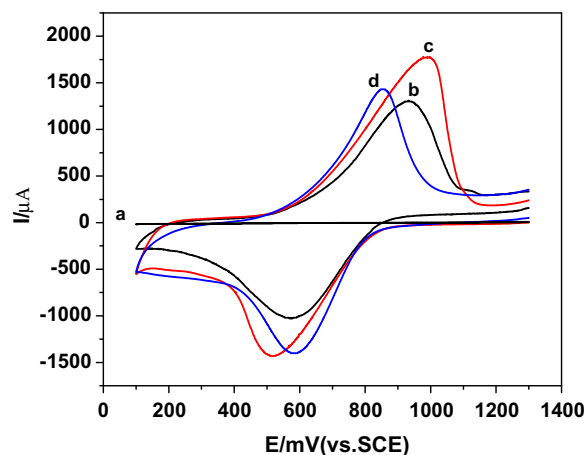


Fig. 7. Cyclic voltammograms of (a) the bare CPE, (b) **1**-CPE, (c) **2**-CPE and (d) **3**-CPE in  $1\text{ M H}_2\text{SO}_4$  solution in the potential range of  $1300\text{--}100\text{ mV}$ . Scan rate:  $100\text{ mV s}^{-1}$ .

$\text{V}^{\text{V}}/\text{V}^{\text{IV}}$  [11]. The electrochemical behaviors of the compounds modified CPEs are similar to that of Qi's report in Ref. [11], but the slight differences of the potentials may be attributed to the effect of different metal ions or the different structures of the three compounds. Although the complex fragment is  $\text{Co}/\text{bbi}$  and  $\text{Mn}/\text{bbi}$  for **1** and **2** respectively, the mean peak potentials of **1**-CPE and **2**-CPE are close, which may be assigned to the isostructural network of **1** and **2**. However, there is a big difference for the values of  $E_{1/2}$  between the complexes **3** and **1** (or **2**) due to the different crystal structure of **3**. Hence we conclude that the structures of complexes may have a significant effect on the electrochemical behavior.

#### 2.6. Conclusions

We have prepared and structurally characterized three new three-dimensional inorganic–organic coordination polymers constructed from polyoxovanadates-based heterometallic network and flexible bis(imidazole) ligand:  $[\text{Co}_2(\text{bbi})(\text{V}_2\text{O}_6)_2(\text{H}_2\text{O})_2]$  (**1**),  $[\text{Mn}_2(\text{bbi})(\text{V}_2\text{O}_6)_2(\text{H}_2\text{O})_2]$  (**2**) and  $\text{Ni}_2(\text{bbi})_3\text{V}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$  (**3**). The 3-D structure of compounds **1** and **2** are constructed from neutral  $[\text{M}_2\text{V}_4\text{O}_{12}]$  [ $\text{M} = \text{Co}$  (**1**),  $\text{Mn}$  (**2**)] layers that are pillared via the coordination of organic ligands to M sites in each layer. To the best of our knowledge, they represent the rare example of 3-D inorganic–organic framework constructed from 2-D pillared-layer-type heterometallic network and organic ligands. Compound **3** is an interesting 3-D eight-connected network based on binuclear  $[\text{Ni}_2\text{O}_4\text{N}_6]$  units as nodes, whereas the inorganic polyoxovanadates and organic bbi ligands act as linkers. The successful isolation of compounds **1–3** further confirms that the reaction conditions profoundly influence the structure of the inorganic–organic polyoxovanadate-frameworks in the hydrothermal system. In addition, the three coordination polymers modified carbon paste electrodes showed excellent electrochemical property of  $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$  couples.

### 3. Experimental

#### 3.1. Materials and instrumentation

1,1-(1,4-Butanediyl)bis(imidazole)(bbi) was prepared according to the published method [21]. All other reagents were readily available from commercial sources and were used as received without further purification.

FT-IR spectrum (KBr pellets) was taken on a Magna FT-IR 560 spectrometer and the elemental analyses (C, H, and N) were carried

out on a Perkin–Elmer 240C elemental analyzer. Thermogravimetric data for the title compounds were collected on a Pyris Diamond thermal analyzer under N<sub>2</sub> atmosphere (heating rate 10 °C/min). The electrochemical experiments were carried out using a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. The modified electrodes were fabricated according to our previous method and used as working electrodes [22]. A SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

### 3.2. Synthesis of [Co<sub>2</sub>(bbi)(V<sub>2</sub>O<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (1)

A mixture of NaVO<sub>3</sub> (1 mmol), bbi (1 mmol), CoSO<sub>4</sub>·7H<sub>2</sub>O (1 mmol), and H<sub>2</sub>O (555.6 mmol) was stirred for ca. 2 h in air until it was homogeneous. Then the pH was adjusted to 8.0 by 1 M NaOH solution. The mixture was sealed in a 23 ml Teflon-lined stainless steel container and kept at 180 °C for 3 days. After slow cooling to room temperature at 10 °C/h, the reddish brown block crystals of **1** were obtained. (yield: ca. 39% based on vanadium). Anal. Calc. for (**1**): C, 16.21; N, 7.56; H, 2.45. Found: C, 16.08; N, 7.42; H, 2.59%. IR (KBr, cm<sup>-1</sup>): 3398(s), 1640(s), 1512(s), 1449(m), 1137(m), 1098(s), 985(s), 883(s), 653(s), 558(m).

### 3.3. Synthesis of [Mn<sub>2</sub>(bbi)(V<sub>2</sub>O<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (2)

A mixture of V<sub>2</sub>O<sub>5</sub> (1 mmol), bbi (1 mmol), MnSO<sub>4</sub>·H<sub>2</sub>O (1 mmol), and H<sub>2</sub>O (555.6 mmol) was stirred for ca. 2 h in air until it was homogeneous. Then the pH was adjusted to 9.0 by 1 M NaOH solution. The mixture was sealed in a 23 ml Teflon-lined stainless steel container and kept at 120 °C for 3 days. After slow cooling to room temperature at 10 °C/h, the red crystals of **2** were obtained. (yield: ca. 28% based on vanadium). Anal. Calc. for (**2**): C, 16.55; N, 6.89; H, 2.50. Found: C, 16.38; N, 6.71; H, 2.63%. IR (KBr, cm<sup>-1</sup>): 3438(s), 1638(s), 1520(s), 1458(m), 1216(m), 1087(s), 982(s), 878(s), 806(s), 656(s), 556(m).

### 3.4. Synthesis of [Ni<sub>2</sub>(bbi)<sub>3</sub>V<sub>4</sub>O<sub>12</sub>]·4H<sub>2</sub>O (3)

Green block crystals **3** were obtained by adopting the same procedure as that for **2** only with NiSO<sub>4</sub>·6H<sub>2</sub>O instead of MnSO<sub>4</sub>·H<sub>2</sub>O and the starting pH of the reactive system adjusted to 11.0 by 1 M NaOH solution (yield: ca. 20% based on vanadium). Anal. Calc. for (**3**): C, 31.14; N, 14.53; H, 4.36. Found: C, 31.28; N, 14.42; H, 4.48%. IR (KBr, cm<sup>-1</sup>): 3435(s), 1640(s), 1510(s), 1455(m), 1232(m), 1107(s), 966(s), 841(m), 803(s), 738(s), 667(s), 577(m).

### 3.5. X-ray crystallography study

Crystallographic data for compounds **1–3** were collected at 293 K on a Bruker Smart 1000 CCD diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) by  $\omega$  and  $\theta$  scan mode. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [23,24]. Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on  $F^2$ . The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined with fixed thermal parameters.

A summary of the crystallographic data and structure refinements for compounds **1–3** are given in Table 1. Selected bond lengths and angles are given in Tables S1–S3.

**Table 1**

Crystal data and structure refinement parameters for compounds **1–3**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>5</sub> H <sub>9</sub> CoN <sub>2</sub> O <sub>7</sub> V <sub>2</sub>	C <sub>5</sub> H <sub>9</sub> MnN <sub>2</sub> O <sub>7</sub> V <sub>2</sub>	C <sub>15</sub> H <sub>25</sub> N <sub>6</sub> NiO <sub>8</sub> V <sub>2</sub>
Formula weight	369.95	365.96	577.98
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	5.898(5)	5.898(5)	9.0181(1)
<i>b</i> (Å)	7.825(7)	7.941(5)	10.576(2)
<i>c</i> (Å)	11.908(1)	12.000(5)	11.892(2)
$\alpha$ (°)	99.140(6)	101.093(5)	87.674(2)
$\beta$ (°)	102.321(5)	101.662(5)	81.384(1)
$\gamma$ (°)	98.686(6)	98.265(5)	85.241(1)
<i>V</i> (Å <sup>3</sup> )	520.3(5)	530.3(6)	1117.1(3)
<i>Z</i>	2	2	2
<i>D</i> (g cm <sup>-3</sup> )	2.3615	2.292	1.718
$\mu$ (mm <sup>-1</sup> )	3.361	2.923	1.707
<i>F</i> (0 0 0)	364	360	590.0
$\theta_{\max}$ (°)	26.0	28.3	27.6
Goodness-of-fit (GOF)	1.06	1.098	1.029
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0250	0.0327	0.0255
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0642	0.0894	0.0712

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ .

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20871022) and the Talent-supporting Program Foundation of Liaoning Province (No. 2009R03).

## Appendix A. Supplementary material

CCDC 686482, 691499 and 692508 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.12.020](https://doi.org/10.1016/j.jorganchem.2009.12.020).

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