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### Hydrothermal syntheses and crystal structures of two transition metal complexes supported by vanadate $\{V_4O_{12}\}$ : $\{[M(dpa)_2]_2V_4O_{12}\}$ ( $M = Co, Ni$ , dpa = 2,2'-dipyridylamine)

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## Hydrothermal syntheses and crystal structures of two transition metal complexes supported by vanadate $\{V_4O_{12}\}$ : $\{[M(dpa)_2]_2V_4O_{12}\}$ ( $M = Co, Ni$ , dpa = 2,2'-dipyridylamine)

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Hydrothermal reactions have been exploited in the syntheses of two new metavanadates,  $\{[Co(dpa)_2]_2V_4O_{12}\} \cdot H_2O$  (**1**) and  $\{[Ni(dpa)_2]_2V_4O_{12}\} \cdot H_2O$  (**2**), which were characterized by X-ray diffraction, IR and thermogravimetric analysis. Crystal data:  $C_{40}H_{38}N_{12}O_{13}Co_2V_4$  (**1**) monoclinic.  $P2(1)$ ,  $a = 10.126(2)$ ,  $b = 17.639(4)$ ,  $c = 12.930(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 98.356(4)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 2$ ;  $C_{40}H_{38}N_{12}O_{13}Ni_2V_4$  (**2**) monoclinic.  $P2(1)$ ,  $a = 10.1037(9)$ ,  $b = 17.6680(14)$ ,  $c = 12.8832(10)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 98.423(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 2$ . The two complexes are isomorphic and their structures consist of a  $[V_4O_{12}]^{4-}$  cluster bound to two  $[M(dpa)_2]^{2+}$  moieties through the terminal oxygen atoms in a *trans*-conformation; the  $[V_4O_{12}]^{4-}$  cluster adopts a chair-like configuration.

**Keywords:** Vanadates; Transition metal complexes; Polyoxometalates; Hydrothermal synthesis

### 1. Introduction

There has been extensive interest in the assembly of polyoxometalates with metal complex fragments for their structures and potential applications in catalysis, biochemistry, medicine, magnetism and solid-state devices [1–5]. Polyoxovanadates have been employed as polyoxometalate building blocks due to their structural diversity and flexibility [6]. Among them, a discrete tetravanadate  $[V_4O_{12}]^{4-}$  anion with a cyclic eight-membered  $\{V_4O_4\}$  core [7, 8], as a polydentate ligand, bridges metal complex subunits into polynuclear metal complexes supported by the vanadates [9–18]. Examples for such complexes include discrete clusters, such as  $\{[Zn(2,2'-bipy)_2]_2V_4O_{12}\}$  [9] and  $\{[Mn(2,2'-bipy)_2]_2V_4O_{12}\}$  [10], whose  $[V_4O_{12}]^{4-}$  clusters both possess distinct curvature and boat-like configurations, and  $\{[Zn(phen)_2]_2V_4O_{12}\}$  [9],  $\{[Co(phen)_2]_2V_4O_{12}\} \cdot H_2O$  [11],  $\{[Mn(phen)_2]_2V_4O_{12}\} \cdot 1/2H_2O$  [12],  $\{[Cd(phen)_2]_2V_4O_{12}\} \cdot 5H_2O$  [13],  $\{[Cu(H_2O)(terpy)]_2V_4O_{12}\} \cdot H_2O$ ,  $\{[Cu(ttberpy)]_2V_4O_{12}\} \cdot 2H_2O$  [14], each of which contains a distinctly chair-like configuration of  $[V_4O_{12}]^{4-}$  cluster. Such complexes also include layer structures, such as  $\{[Zn(bpy)]_2V_4O_{12}\}$  [15] and

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$\{[\text{Ni}(\text{dien})]_2\text{V}_4\text{O}_{12}\}$  [16], which are constructed from  $[\text{V}_4\text{O}_{12}]^{4-}$  rings linked through square pyramidal Zn sites and octahedral Ni sites into network structures, respectively. Such complexes also include 3-D frameworks, such as  $\{[\text{Co}(3,3'\text{-bpy})]_2\text{V}_4\text{O}_{12}\}$  [17], constructed from  $[\text{V}_4\text{O}_{12}]^{4-}$  anions and two-dimensional  $\{\text{Co}(\text{bpy})_2\}_n^{2n+}$  networks. Only recently, Xu and co-workers utilized the polydentate coordination of  $[\text{V}_4\text{O}_{12}]^{4-}$  anions, constructing a new self-catenated topology based on  $\{\text{CuV}_4\text{O}_{12}\}$  clusters as nodes [18]. The organic ligands are crucial to the syntheses and structures. As an extension of the synthetic approach to polyoxometalates, we have investigated the chemistry of the *M*-vanadate-2,2'-dipyridylamine (dpa) system. The dpa ligand is particularly attractive as an excellent ligand and also potential participation as the neutral dpa, the protonated  $\text{Hdpa}^+$  or  $\text{H}_2\text{dpa}^{+2}$  or even the deprotonated  $\text{dpa}^-$  [19]. A 4,4'-dipyridylamine has been introduced into metal complexes supported by chain-like vanadates  $\{\text{VO}_3\}$ , such as  $[\text{M}(\text{Hdpa})_2(\text{VO}_3)_3]$  ( $M = \text{Co}, \text{Ni}$ ) [19] and  $[\text{Cu}(\text{dpa})\text{VO}_3]$  [20]. Although 2,2'-dipyridylamine has been extensively used in syntheses of metal complexes [21, 22], few metal-dpa complexes supported by polyoxometalates have been reported [7, 23].

In this article, we describe the hydrothermal syntheses and crystal structures of two new complexes of  $[\text{V}_4\text{O}_{12}]^{4-}$ ,  $\{[\text{Co}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\} \cdot \text{H}_2\text{O}$  and  $\{[\text{Ni}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\} \cdot \text{H}_2\text{O}$ . Complexes **1** and **2** both consist of  $[\text{V}_4\text{O}_{12}]^{4-}$  clusters bound to metal ions with chair-like configurations.

## 2. Experimental

### 2.1. General considerations

All starting materials were commercially obtained and used without further purification. All syntheses were carried out in 20 mL Teflon-lined stainless steel containers under autogenous pressure. The reactants were stirred at room temperature for 20 min before heating.

### 2.2. Synthesis of $\{[\text{Co}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\} \cdot \text{H}_2\text{O}$ (**1**)

A mixture of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.1660 g, 0.65 mmol),  $\text{NaVO}_3$  (0.0950 g, 0.77 mmol), 2,2'-dipyridylamine (0.1391 g, 0.80 mmol) and  $\text{H}_2\text{O}$  (15.0 g, 0.83 mol) in the mole ratio 1:1.2:1.2:1302 was heated at 120°C for 40 h. After the mixture cooled to room temperature, red block shape crystals were manually isolated from the mixture in ca 30% yield based on  $\text{NaVO}_3$ . Anal. Calcd for  $\text{C}_{40}\text{H}_{38}\text{N}_{12}\text{O}_{13}\text{Co}_2\text{V}_4$  (%): C, 39.50; H, 3.12; N, 13.82; Co, 9.70; V, 16.75. Found: C, 38.65; H, 3.37; N, 13.82; Co, 9.69; V, 16.39.

### 2.3. Synthesis of $\{[\text{Ni}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\} \cdot \text{H}_2\text{O}$ (**2**)

A mixture of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.0913 g, 0.37 mmol),  $\text{NaVO}_3$  (0.0876 g, 0.72 mmol), 2,2'-dipyridylamine (0.1288 g, 0.75 mmol) and  $\text{H}_2\text{O}$  (15.0 g, 0.83 mol) in the mole ratio 1:2:2:2250 was heated at 120°C for 40 h. After the mixture cooled to

room temperature, green block shape crystals were manually isolated from the mixture in *ca* 29% yield based on  $\text{NaVO}_3$ . Anal. Calcd for  $\text{C}_{40}\text{H}_{38}\text{N}_{12}\text{O}_{13}\text{Ni}_2\text{V}_4$  (%): C, 39.51; H, 3.15; N, 13.83; Ni, 9.65; V, 16.76. Found: C, 39.09; H, 3.21; N, 13.68; Ni, 9.55; V, 16.58.

#### 2.4. Physical measurements

C, H and N elemental analyses were performed on a PE240 elemental analyzer. Co, Ni and V elemental analyses were performed on a PLASMA-SPEC(I) elemental analyzer. IR spectra of samples were obtained as KBr pellets on a Bruker Axis Tensor 27 FT-IR spectrometer. TG spectra were recorded on a Pyris Diamond TG/DTA using a platinum crucible under air flow.

#### 2.5. Single crystal X-ray analyses

A suitable single crystal was carefully selected under a microscope. Crystal structure determinations for **1** and **2** were performed on a SMART APEX II-CCD X-ray single diffractometer at  $293 \pm 1$  K using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  (Mo-K $\alpha$ ) = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. An empirical absorption correction was applied. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using SHELXL-97. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were added theoretically. Some relevant crystallographic data and structure determination parameters are summarized in table 1. Selected bond lengths and angles for **1** and **2** are given in tables 2 and 3, respectively. The molecular structures are given in figures 1 and 2.

### 3. Results and discussion

#### 3.1. Structure of $\{[M(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\} \cdot \text{H}_2\text{O}$ ( $M = \text{Co}, \text{Ni}$ )

Complexes **1** and **2** crystallize in the same monoclinic crystal system with space group  $P2(1)$  and are isomorphous. As shown in figure 1, they consist of a discrete neutral hexanuclear heterometallic cluster  $\{[M(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\}$  constructed from a  $[\text{V}_4\text{O}_{12}]^{4-}$  ring bonded to two  $[M(\text{dpa})_2]^{2+}$  moieties via the terminal oxygen atoms. The  $[\text{V}_4\text{O}_{12}]^{4-}$  cluster possesses a distinctly chair-like configuration, similar to previously observed complexes [9, 11–14]. It has a cyclic eight-member  $\{\text{V}_4\text{O}_4\}$  core formed by corner sharing of four distorted  $\text{VO}_4$  tetrahedra, each defined by two bridging oxo-groups and two terminal oxo-groups. The V–O distances are in the range 1.573(9)–1.673(8) Å for  $\text{O}_t$  atoms (average V– $\text{O}_t$  = 1.639 Å) and 1.762(9)–1.827(9) Å for  $\text{O}_b$  atoms (average V– $\text{O}_b$  = 1.797 Å). The V– $\text{O}_b$ –V angles are 154.4 and 124.0° alternately within the ring. The  $\text{O}_b$ –V– $\text{O}_b$  bond angles are 106.8 and 111.4° alternately within the ring. The average  $\text{O}_t$ –V– $\text{O}_t$ ,  $\text{O}_b$ –V– $\text{O}_t$  bond angles are 110.3 and 109.8°, respectively. The four V atoms of  $[\text{V}_4\text{O}_{12}]^{4-}$  cluster are nearly located on the same plane with mean

Table 1. Summary of crystallographic data for **1** and **2**.

Compound	<b>1</b>	<b>2</b>
Empirical formula	C <sub>40</sub> H <sub>38</sub> N <sub>12</sub> Co <sub>2</sub> O <sub>13</sub> V <sub>4</sub>	C <sub>40</sub> H <sub>38</sub> N <sub>12</sub> Ni <sub>2</sub> O <sub>13</sub> V <sub>4</sub>
Formula weight	1216.44	1215.96
Crystal size (mm <sup>3</sup> )	0.30 × 0.30 × 0.10	0.40 × 0.30 × 0.10
<i>T</i> (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)	<i>P</i> 2(1)
<i>a</i> (Å)	10.126(2)	10.1037(9)
<i>b</i> (Å)	17.639(4)	17.6680(14)
<i>c</i> (Å)	12.930(3)	12.8832(10)
α (°)	90	90
β (°)	98.356(4)	98.423(2)
γ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	2284.9(8)	2275.0(3)
<i>Z</i>	2	2
Density (mg m <sup>-3</sup> )	1.768	1.775
Absorption coefficient (mm <sup>-1</sup> )	1.572	1.677
<i>F</i> (000)	1224	1228
θ range (°)	1.97–21.99	2.04–26.90
Limiting indices	−8 ≤ <i>h</i> ≤ 10 −17 ≤ <i>k</i> ≤ 18 −13 ≤ <i>l</i> ≤ 11	−12 ≤ <i>h</i> ≤ 11 −22 ≤ <i>k</i> ≤ 22 −10 ≤ <i>l</i> ≤ 16
Reflections collected	8785	13,718
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.8586 and 0.6499	0.8502 and 0.5534
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	5066/1/640	8901/1/640
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.981	1.017
Final <i>R</i> indices [ <i>I</i> > 2 σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0551 <i>wR</i> <sub>2</sub> = 0.1066	<i>R</i> <sub>1</sub> = 0.0597 <i>wR</i> <sub>2</sub> = 0.1164
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0880 <i>wR</i> <sub>2</sub> = 0.1246	<i>R</i> <sub>1</sub> = 0.0990 <i>wR</i> <sub>2</sub> = 0.1345
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.402 and −0.344	0.461 and −0.786

deviation 0.0202 Å for **1** and 0.0164 Å for **2**. Consequently, the [V<sub>4</sub>O<sub>12</sub>]<sup>4−</sup> cluster is coordinated to the two [M(dpa)<sub>2</sub>]<sup>2+</sup> fragments via the terminal oxygen atoms in a *trans*-conformation.

For **1**, as shown in figure 1(a), a Co(II) atom has a {Co(dpa)<sub>2</sub>O<sub>2</sub>} distorted octahedron with dextro-*cis* geometry. The octahedron is completed with four nitrogen donors from two 2,2′-dipyridylamine ligands and two oxygen donors from two VO<sub>4</sub> tetrahedra. The quasilinear coordination angles around the cobalt ions are between 170.7(4) and 179.6(4)°, and other N–Co–N, N–Co–O bond angles are in the range 83.9(4)–94.6(4)° and 85.7(3)–94.9(4)°, respectively. The Co–N bond distances range from 2.090(10) to 2.152(10) Å, and the Co–O bond distances are within the range 2.087(8)–2.131(8) Å. For **2**, similar to **1**, the distorted octahedron has a dextro-*cis* configuration (see figure 1b). The quasilinear coordination angles around nickel are between 172.2(3) and 178.2(3)°, and other N–Ni–N, N–Ni–O bond angles are in the range 84.9(3)–95.6(3)° and 86.5(2)–94.4(2)°, respectively. The Ni–N bond distances range from 2.070(7) to 2.101(7) Å, and the Ni–O bond distances are within the range 2.086(5)–2.119(5) Å.

As shown in figure 2, the {V<sub>4</sub>O<sub>4</sub>} rings in **1** and **2** stack orderly along the *a* axis direction. Two dpa molecules connecting to M(II) array in the *a* and *c* directions.

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Co(1)–O(1)	2.131(8)	V(1)–O(10)	1.661(8)
Co(1)–O(2)	2.087(8)	V(1)–O(6)	1.762(9)
Co(1)–N(1)	2.137(10)	V(1)–O(5)	1.796(8)
Co(1)–N(2)	2.152(10)	V(2)–O(9)	1.603(8)
Co(1)–N(4)	2.134(10)	V(2)–O(1)	1.673(8)
Co(1)–N(5)	2.090(10)	V(2)–O(5)	1.804(8)
V(1)–O(2)	1.654(8)	V(2)–O(8)	1.813(8)
O(2)–Co(1)–N(5)	92.2(4)	O(6)–V(1)–O(5)	106.8(4)
O(2)–Co(1)–O(1)	89.3(3)	O(9)–V(2)–O(1)	109.9(4)
N(5)–Co(1)–O(1)	91.9(3)	O(9)–V(2)–O(5)	108.1(4)
O(2)–Co(1)–N(4)	174.4(3)	O(1)–V(2)–O(5)	106.5(4)
N(5)–Co(1)–N(4)	85.5(4)	O(9)–V(2)–O(8)	109.6(4)
O(1)–Co(1)–N(4)	85.7(3)	O(1)–V(2)–O(8)	111.7(4)
O(2)–Co(1)–N(1)	91.5(4)	O(5)–V(2)–O(8)	110.8(4)
N(5)–Co(1)–N(1)	172.3(4)	V(1)–O(5)–V(2)	124.3(5)
O(1)–Co(1)–N(1)	94.9(4)	V(1)–O(6)–V(4)	154.1(6)
N(4)–Co(1)–N(1)	91.4(4)	V(3)–O(7)–V(4)	123.5(5)
O(2)–Co(1)–N(2)	91.0(4)	V(3)–O(8)–V(2)	153.3(5)
N(5)–Co(1)–N(2)	88.5(4)	V(2)–O(1)–Co(1)	136.5(5)
O(1)–Co(1)–N(2)	179.6(4)	V(1)–O(2)–Co(1)	140.3(5)
N(4)–Co(1)–N(2)	94.0(4)	C(10)–N(7)–Co(2)	118.7(10)
N(1)–Co(1)–N(2)	84.7(4)	C(6)–N(7)–Co(2)	122.7(8)
O(2)–V(1)–O(10)	109.7(4)	C(5)–N(8)–C(1)	117.8(11)
O(2)–V(1)–O(6)	112.8(5)	C(5)–N(8)–Co(2)	118.9(9)
O(10)–V(1)–O(6)	110.3(5)	C(1)–N(8)–Co(2)	120.8(8)
O(2)–V(1)–O(5)	107.2(4)	C(10)–N(7)–C(6)	118.6(12)
O(10)–V(1)–O(5)	109.9(4)	C(1)–N(9)–C(6)	129.4(11)

Table 3. Selected bond lengths (Å) and angles (°) of **2**.

Ni(1)–N(4)	2.070(7)	V(1)–O(1)	1.651(5)
Ni(1)–N(1)	2.076(7)	V(1)–O(8)	1.769(6)
Ni(1)–N(2)	2.081(8)	V(1)–O(5)	1.781(6)
Ni(1)–N(5)	2.083(7)	V(2)–O(10)	1.597(6)
Ni(1)–O(2)	2.100(6)	V(2)–O(2)	1.663(6)
Ni(1)–O(1)	2.101(6)	V(2)–O(6)	1.818(6)
V(1)–O(9)	1.644(5)	V(2)–O(5)	1.821(6)
N(4)–Ni(1)–N(1)	172.2(3)	O(10)–V(2)–O(2)	110.7(3)
N(4)–Ni(1)–N(2)	90.6(3)	O(10)–V(2)–O(6)	109.3(3)
N(1)–Ni(1)–N(2)	86.7(3)	O(2)–V(2)–O(6)	112.7(3)
N(4)–Ni(1)–N(5)	84.9(3)	O(10)–V(2)–O(5)	107.0(4)
N(1)–Ni(1)–N(5)	88.1(3)	O(2)–V(2)–O(5)	106.7(3)
N(2)–Ni(1)–N(5)	94.8(3)	O(6)–V(2)–O(5)	110.4(3)
N(4)–Ni(1)–O(2)	94.7(3)	V(1)–O(5)–V(2)	123.7(3)
N(1)–Ni(1)–O(2)	92.4(2)	V(3)–O(6)–V(2)	154.8(4)
N(2)–Ni(1)–O(2)	87.0(3)	V(3)–O(7)–V(4)	124.4(3)
N(5)–Ni(1)–O(2)	178.2(3)	V(1)–O(8)–V(4)	155.2(4)
N(4)–Ni(1)–O(1)	90.9(3)	V(1)–O(1)–Ni(1)	141.0(3)
N(1)–Ni(1)–O(1)	92.4(3)	V(2)–O(2)–Ni(1)	136.3(3)
N(2)–Ni(1)–O(1)	175.7(3)	V(3)–O(3)–Ni(2)	140.7(3)
N(5)–Ni(1)–O(1)	89.4(2)	V(4)–O(4)–Ni(2)	138.9(3)
O(2)–Ni(1)–O(1)	88.8(2)	C(1)–N(1)–Ni(1)	121.3(6)
O(9)–V(1)–O(1)	110.9(3)	C(5)–N(1)–Ni(1)	118.8(6)
O(9)–V(1)–O(8)	111.4(3)	C(6)–N(2)–Ni(1)	122.8(6)
O(1)–V(1)–O(8)	111.4(3)	C(10)–N(2)–Ni(1)	119.4(6)
O(9)–V(1)–O(5)	108.7(3)	C(6)–N(2)–C(10)	117.8(8)
O(1)–V(1)–O(5)	106.8(3)	C(6)–N(3)–C(1)	127.5(7)
O(8)–V(1)–O(5)	107.4(3)		

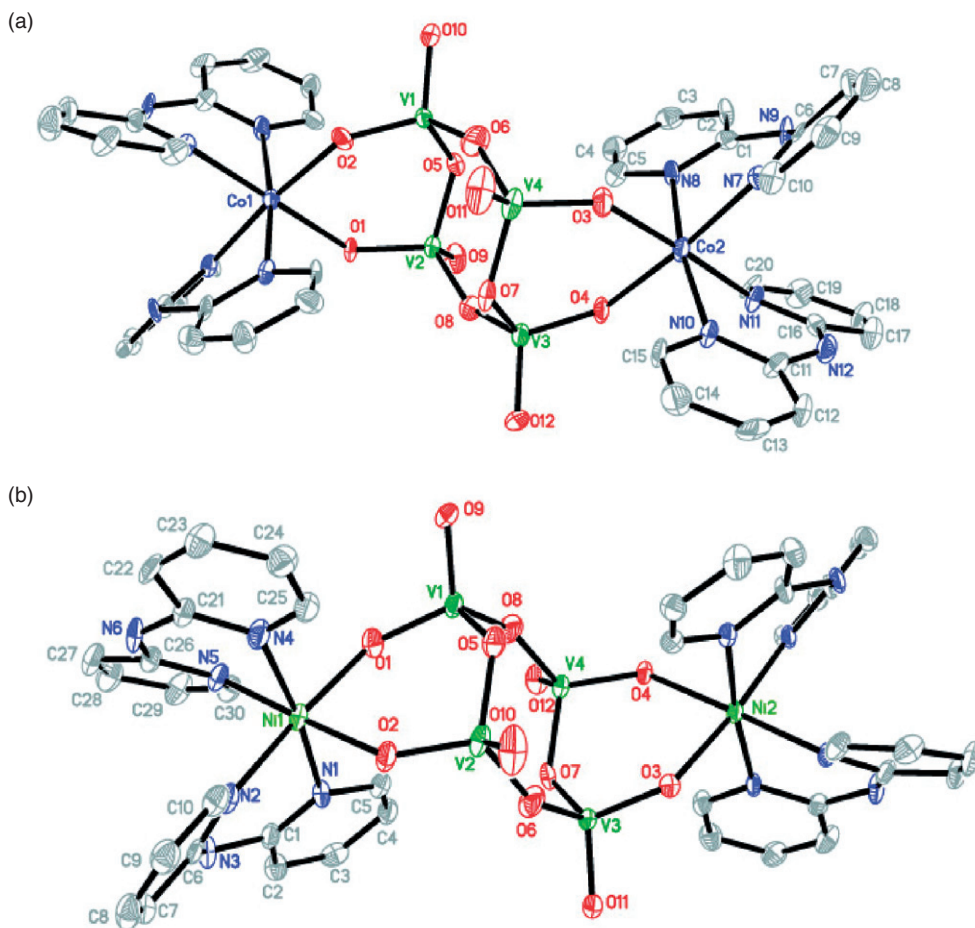


Figure 1. (a) The structure of  $\{[\text{Co}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\}$  (**1**); (b) The structure of  $\{[\text{Ni}(\text{dpa})_2]_2\text{V}_4\text{O}_{12}\}$  (**2**).

### 3.2. TG analysis

As shown in figure 3, the TG analyses of **1** and **2** in the temperature range 50–800°C are divided into two stages. The first weight loss of 1.55 and 1.49% in the temperature range 50–245 and 50–350°C, respectively, corresponds to the release of crystallization water molecules (Calcd 1.48%), and a second weight loss of 56.31 and 56.35% between 245–550 and 350–520°C corresponds to release of organic ligands (Calcd 56.29 and 56.31%, respectively). The whole weight losses (57.85 and 57.84%) were in agreement with calculated values (57.77 and 57.79%).

### 3.3. FT-IR spectra

As shown in figure 4, the infrared spectra exhibit characteristic bands in the range 1200–1650  $\text{cm}^{-1}$  associated with the C=C and C=N ring stretches of the ligands.

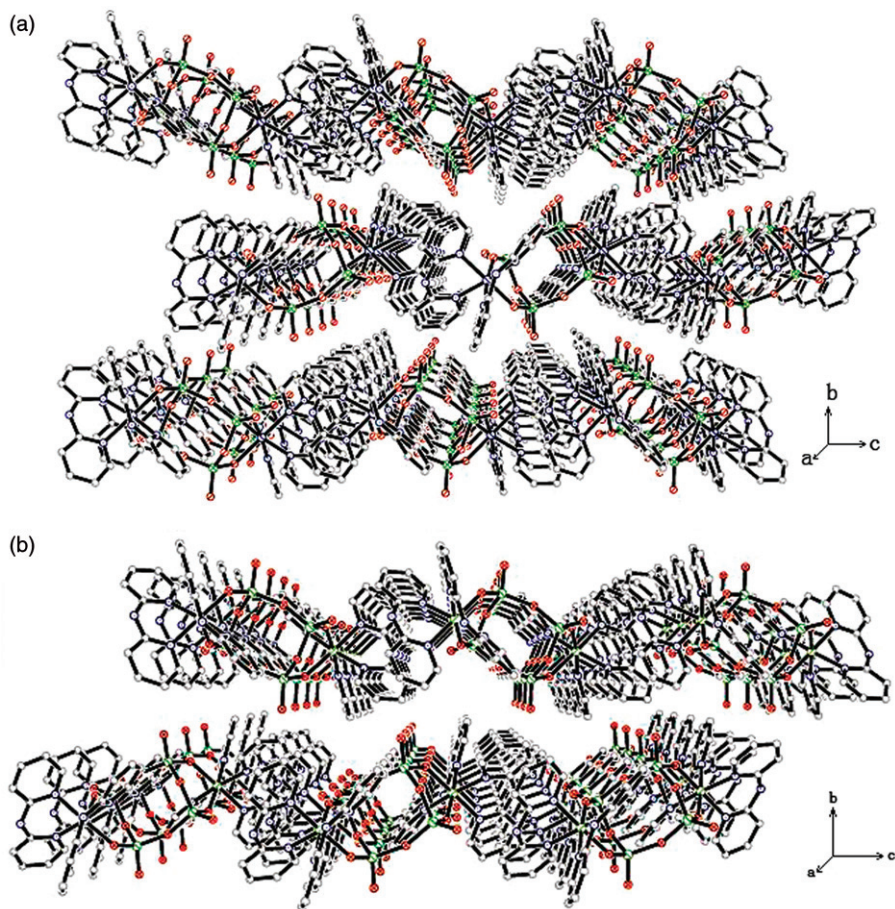


Figure 2. (a) View of the packing of **1** along the a axis; (b) View of the packing of **2** along the a axis.

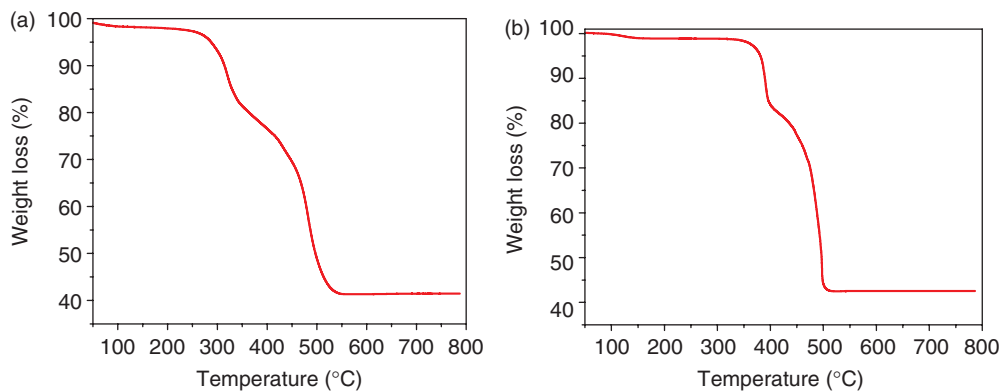


Figure 3. (a) The TG curve of **1**; (b) The TG curve of **2**.



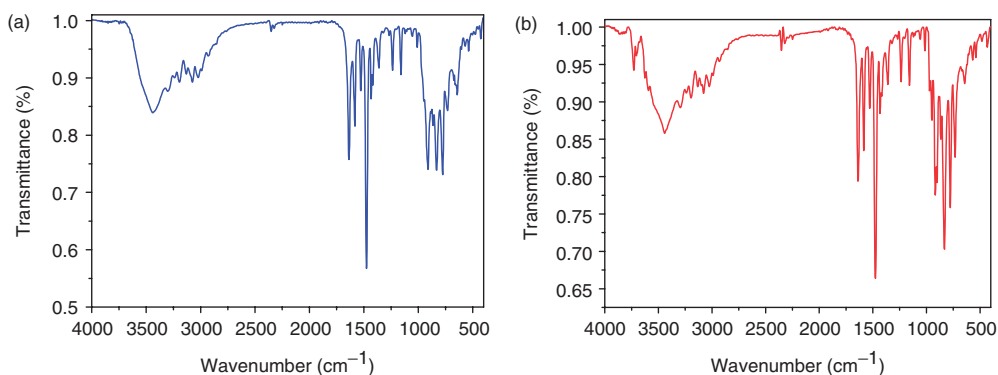


Figure 4. (a) The IR spectrum of **1**; (b) The IR spectrum of **2**.

The bands at  $913\text{ cm}^{-1}$  in **1** and  $917\text{ cm}^{-1}$  in **2** are attributed to  $\nu(\text{V}=\text{O})$ ;  $834\text{ cm}^{-1}$  and  $776\text{ cm}^{-1}$  bands in **1** and  $833\text{ cm}^{-1}$  and  $780\text{ cm}^{-1}$  bands in **2** are assigned to  $\nu(\text{V}-\text{O}-\text{V})$ .

### Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center as supplementary publications, CCDC reference numbers 634362 and 634363. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223/336 033; Email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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