



## Hydrothermal synthesis and characterization of two novel inorganic-organic hybrid materials

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**Abstract:** By using different organic ligands, two 3D inorganic-organic hybrid compounds  $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$  **1** and  $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$  **2** were synthesized by hydrothermal reaction and characterized by X-ray crystallography. Crystal data: **1**. crystal system orthorhombic, space group *Pnna*,  $a=10.188(2)$  Å,  $b=11.497(2)$  Å,  $c=7.3975(15)$  Å,  $V=866.5(3)$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{calcd}}=2.705$  g/cm<sup>3</sup>; **2**. crystal system triclinic, space group  $P1\bar{1}$  (No. 2),  $a=8.3190(17)$  Å,  $b=8.4764(17)$  Å,  $c=11.183(2)$  Å,  $\alpha=95.48(3)^\circ$ ,  $\beta=92.03(3)^\circ$ ,  $\gamma=107.24(3)^\circ$ ,  $V=748.0(3)$  Å<sup>3</sup>,  $Z=2$ ,  $D_{\text{calcd}}=1.958$  g/cm<sup>3</sup>. The framework of compound **1** contains both  $\{\text{Co}(\text{C}_4\text{H}_4\text{N}_2)\}$  and infinite metavanadate chains. Crystal structure of compound **2** is constructed with inorganic  $\{\text{CoV}_2\text{O}_6\}$  layers across-linked by organic 1,2-bis(4-pyridyl) ethane ligands. The two compounds are thermally stable to approximately 410 °C and 350 °C, respectively. Their optical band gaps are determined to be 2.13 eV and 2.12 eV by UV-VIS-NIR diffuse reflectance spectra, which revealed their nature of semiconductor and optical absorption features.

**Key words:** Inorganic-organic hybrid materials, Hydrothermal synthesis, Crystal structure, Oxovanadium

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### INTRODUCTION

In recent years, there are tremendous activities in the area of inorganic-organic hybrid materials because of their diversified structures and interesting properties (Hagrman *et al.*, 1999), which endow these materials with applications to sorption, catalysis, electrical conductivity and solar energy conversion (Bruce and O'Hare, 1992; Mallouk and Lee, 1990). The inorganic-organic hybrid materials are constructed with extended inorganic covalent frameworks being linked by organic multidentate ligands through coordination bonds. Many compounds based on cobalt vanadate have been reported, such as  $[\{\text{Co}(3,3'\text{-bipy})_2\}_2\text{V}_4\text{O}_{12}]$  (3,3'-bipy=3,3'-bipyridine) (LaDuca *et al.*, 2000),  $[\text{Co}(\text{dpa})_2\text{V}_4\text{O}_{12}]$  (dpa=4,4'-dipyridylamine) (LaDuca *et al.*, 2001),  $\text{Co}(\text{bipy})(\text{H}_2\text{O})\text{V}_2\text{O}_6$  (bipy=bipyridine) (Liu *et al.*, 2002),  $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}]\text{H}_2\text{O}$  (phen=1,10-phenanthroline) (Lu *et al.*, 2004),  $\text{Co}(\text{bpy})(\text{H}_2\text{O})\text{V}_2\text{O}_6$  (bpy=bipyridine) (Li *et al.*, 2006) and  $[\{\text{Co}_2(4,4'\text{-tmdp})_4\}\text{V}_4\text{O}_{12}]$  (4,4'-tmdp=4,4'-trimethylenedipyridine) (Khan *et al.*, 2006).

In these materials, what influencing the structure are the coordination preferences of the "secondary" metal site, the ligand geometry and spatial extension. We are interested in the synthesis of metal-organic coordination polymers stabilized by metavanadate chains to useful inorganic-organic materials with high thermal stability.

Here we report the synthesis structures and characterization of two 3D inorganic-organic hybrid compounds:  $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$  **1** and  $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$  **2**. Moreover, we investigated the use of different organic bridging ligands in the cobalt vanadate system. The thermal stability and optical properties are also reported.

### EXPERIMENTS

#### General considerations

All reagents and solvents used in the synthesis were of reagent grade without further purification. Reactions were carried out in polytetrafluoroethyl-

ene-line stainless steel containers under autogenous pressure.

### Synthesis

#### 1. Synthesis of $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$

A mixture of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.0476 g, 0.2 mol), pyrazine (0.032 mg, 0.4 mmol),  $\text{NH}_4\text{VO}_3$  (0.0468 g, 0.4 mmol) and  $\text{H}_2\text{O}$  (13 ml) in a mole ratio of 1:2:2:3600 was heated in a 25 ml Parr bomb for 3 d at 140 °C. After heating, the reaction vessel was allowed to cool down to room temperature. The dark red block crystals for X-ray diffraction were isolated. Anal. Calcd (%) for  $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$  is C 14.26, H 1.20, N 8.32; found C 13.78, H 1.18, N 8.40. Instrument type: Elementar Vario EL III (Germany).

#### 2. Synthesis of $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$

A mixture of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.0476 g, 0.2 mol), 1,2-bis (4-pyridyl) ethane (0.0737 g, 0.4 mmol),  $\text{NH}_4\text{VO}_3$  (0.0468 g, 0.4 mmol) and  $\text{H}_2\text{O}$  (13 ml) in a mole ratio of 1:2:2:3600 was heated in a 25 ml Parr bomb for 3 d at 150 °C. After heating, the reaction vessel was allowed to cool down to room temperature. The dark red block crystals for X-ray diffraction were isolated. Anal. Calcd (%) for  $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$  is C 29.06, H 1.94, N 6.78; found C 28.50, H 2.30, N 6.61. Instrument type: Elementar Vario EL III (Germany).

### X-ray crystallography

The single crystals of compound **1** (0.24 mm×0.15 mm×0.12 mm) and compound **2** (0.10 mm×0.10 mm×0.10 mm) were selected for X-ray diffraction measurement. Intensity data were collected using a Rigaku R-AXIS PARID image plate diffractometer equipped with graphite-monochromated Mo  $K_\alpha$  radiation ( $\lambda=0.071073$  nm) at 295 K. The raw data were corrected for LP factors and empirical absorption. The structure was solved by direct method. Hydrogen atoms were placed in the calculated positions on the relevant atoms. All non-H atoms were refined anisotropically with full-matrix least-squares on  $F^2$ . Computations were performed using the SHELX-97 program package (Sheldrik, 1997). Crystal drawings were generated with the SCHAKAL92 (Keller, 1992).

Details of the crystal data of compounds **1** and **2** and intensity collection are summarized in Table 1. Atomic positional parameters are given in Tables 2~3.

Selected bond lengths and angles are listed in Tables 4~5.

### Thermal analysis

Thermal analyses have been performed in air for

**Table 1 Crystallographic data for compounds 1 and 2**

Parameters	Crystallographic data	
	Compound 1	Compound 2
Molecular formula	$\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$	$\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$
Molecular weight	336.90	441.05
Crystal system	Orthorhombic	Triclinic
Space group	$Pnma$	$P1\bar{1}$ (No. 2)
Unit cell parameters		
$a$ (Å)	10.188(2)	8.3190(17)
$b$ (Å)	11.497(2)	8.4764(17)
$c$ (Å)	7.3975(15)	11.183(2)
$\alpha$ (°)	90	95.48(3)
$\beta$ (°)	90	92.03(3)
$\gamma$ (°)	90	107.24(3)
$V$ (Å <sup>3</sup> )	866.5(3)	748.0(3)
$Z$	4	2
$D_{\text{calcd}}$ (g/cm <sup>3</sup> )	2.705	1.958
$\mu$ (mm <sup>-1</sup> )	4.028	2.350
$F(000)$	684	438
Data collection range	$-13 \leq h \leq 13$ , $-14 \leq k \leq 14$ , $-9 \leq l \leq 9$	$0 < h < 10$ , $-11 < k < 10$ , $-14 < l < 14$
Collected $\theta$ range	$3.27^\circ \sim 27.48^\circ$	$3.25^\circ \sim 27.5^\circ$
Reflections collected/unique	3871/981	3330/3330
Independent reflections [ $I \geq 2\sigma(I)$ ]	782	2141
Goodness-of-fit on $F^2$	1.033	1.062
$R1, wR2$ [ $I > 2\sigma(I)$ ]	0.0425, 0.1188	0.0438, 0.0966
All data	0.0519, 0.1227	0.0795, 0.1217
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e/Å)	0.728, -0.617	0.879, -0.930

$D_{\text{calcd}}$  is calculated density

**Table 2 Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\times 10^3 \text{ \AA}^2$ ) for compounds 1 and 2**

Atoms	$x$	$y$	$z$	$U_{\text{eq}}$
Co	4270(1)	2500	2500	20(1)
V	7249(1)	1463(1)	981(1)	21(1)
O(1)	5676(3)	1704(3)	891(4)	26(1)
O(2)	7500	0	1712(7)	33(1)
O(3)	7920(5)	2500	2500	28(1)
O(4)	7865(4)	1685(3)	-1027(4)	31(1)
N	4560(4)	3990(4)	846(5)	26(1)
C(1)	4382(5)	5044(5)	1557(7)	32(1)
C(2)	5187(6)	3967(4)	-729(6)	30(1)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

**Table 3 Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for compound 2**

Atoms	x	y	z	$U_{\text{eq}}$	Atoms	x	y	z	$U_{\text{eq}}$
Co(1)	1.18605(9)	0.84624(9)	0.05845(6)	0.0170(19)	C(2)	1.3338(7)	0.6747(7)	-0.2840(5)	0.0313(14)
V(1)	0.73853(10)	0.75570(11)	0.02070(8)	0.0189(2)	C(3)	1.2069(7)	0.5378(7)	-0.3275(5)	0.0246(12)
V(2)	0.42093(10)	0.59254(11)	0.17680(7)	0.0170(2)	C(4)	1.0684(7)	0.4956(7)	-0.2614(5)	0.0306(14)
O(1)	0.9398(4)	0.7794(5)	0.0434(3)	0.0292(9)	C(5)	1.0652(7)	0.5888(6)	-0.1548(5)	0.0235(12)
O(2)	0.6359(4)	0.6768(5)	0.1466(3)	0.0292(9)	C(6)	1.0839(7)	1.0636(7)	0.2462(5)	0.0301(14)
O(3)	1.2906(5)	1.0625(4)	0.0009(3)	0.0293(9)	C(7)	1.0780(8)	1.1584(8)	0.3507(5)	0.0364(16)
O(4)	0.3429(5)	0.3828(5)	0.1089(3)	0.0305(9)	C(8)	1.1783(7)	1.1538(7)	0.4498(5)	0.0259(13)
O(5)	0.4091(5)	0.5966(5)	0.3192(3)	0.0335(10)	C(9)	1.2804(8)	1.0540(8)	0.4370(5)	0.0364(16)
O(6)	1.3109(5)	0.7077(5)	0.1238(3)	0.0318(10)	C(10)	1.2801(7)	0.9636(8)	0.3294(5)	0.0321(15)
N(1)	1.1897(5)	0.7225(5)	-0.1141(4)	0.0207(10)	C(11)	1.1736(8)	1.2534(7)	0.5661(5)	0.0347(15)
N(2)	1.1836(5)	0.9697(5)	0.2326(4)	0.0216(10)	C(12)	1.2163(8)	0.4363(8)	-0.4431(5)	0.0405(17)
C(1)	1.3218(7)	0.7646(7)	-0.1786(5)	0.0333(15)					

**Table 4 Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for compound 1**

Compound 1	Value	Compound 1	Value	Compound 1	Value	Compound 1	Value
Co-O(4) <sup>#1</sup>	2.029(3)	O(4)-Co <sup>#5</sup>	2.029(3)	O(4) <sup>#2</sup> -Co-N	91.99(15)	O(1)-V-O(2)	108.30(13)
Co-O(4) <sup>#2</sup>	2.029(3)	N-C(2)	1.329(6)	O(4) <sup>#2</sup> -Co-N	91.99(15)	O(4)-V-O(2)	111.58(19)
Co-O(1) <sup>#3</sup>	2.075(3)	N-C(1)	1.334(7)	O(1) <sup>#3</sup> -Co-N	83.03(15)	O(3)-V-O(2)	112.70(15)
Co-O(1)	2.075(3)	C(1)-C(2) <sup>#6</sup>	1.364(7)	O(1)-Co-N	85.96(15)	V-O(1)-Co	137.0(2)
Co-N	2.126(4)	C(2)-C(1) <sup>#6</sup>	1.364(7)	O(4) <sup>#1</sup> -Co-N <sup>#3</sup>	91.99(15)	V <sup>#4</sup> -O(2)-V	144.7(3)
Co-N <sup>#3</sup>	2.126(4)	O(4) <sup>#1</sup> -Co-O(4) <sup>#2</sup>	90.2(2)	O(4) <sup>#2</sup> -Co-N <sup>#3</sup>	99.28(15)	V-O(3)-V <sup>#3</sup>	134.7(3)
V-O(1)	1.627(4)	O(4) <sup>#1</sup> -Co-O(1) <sup>#3</sup>	177.44(13)	O(1) <sup>#3</sup> -Co-N <sup>#3</sup>	85.96(15)	V-O(4)-Co <sup>#5</sup>	146.3(2)
V-O(4)	1.633(3)	O(4) <sup>#2</sup> -Co-O(1) <sup>#3</sup>	88.58(14)	O(1)-Co-N <sup>#3</sup>	83.03(15)	C(2)-N-C(1)	115.4(4)
V-O(3)	1.776(2)	O(4) <sup>#1</sup> -Co-O(1)	88.58(14)	N-Co-N <sup>#3</sup>	164.0(2)	C(2)-N-Co	123.7(3)
V-O(2)	1.7848(18)	O(4) <sup>#2</sup> -Co-O(1)	177.44(13)	O(1)-V-O(4)	108.33(18)	C(1)-N-Co	119.1(3)
O(2)-V <sup>#4</sup>	1.7848(18)	O(1) <sup>#3</sup> -Co-O(1)	92.70(19)	O(1)-V-O(3)	106.9(2)	N-C(1)-C(2) <sup>#6</sup>	122.4(5)
O(3)-V <sup>#3</sup>	1.776(2)	O(4) <sup>#1</sup> -Co-N	99.28(15)	O(4)-V-O(3)	108.82(15)	N-C(2)-C(1) <sup>#6</sup>	122.1(5)

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup> ( $x-1/2, y, -z$ ); <sup>#2</sup> ( $x-1/2, -y+1/2, z+1/2$ ); <sup>#3</sup> ( $x, -y+1/2, -z+1/2$ ); <sup>#4</sup> ( $-x+3/2, -y, z$ ); <sup>#5</sup> ( $x+1/2, y, -z$ ); <sup>#6</sup> ( $-x+1, -y+1, -z$ )

**Table 5 Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for compound 2**

Compound 2	Value	Compound 2	Value	Compound 2	Value	Compound 2	Value
Co(1)-O(1)	1.953(3)	C(2)-C(3)	1.352(7)	O(1)-V(1)-O(3) <sup>#1</sup>	109.8(2)	C(5)-N(1)-Co(1)	120.2(3)
Co(1)-O(6)	1.956(4)	C(3)-C(4)	1.367(8)	O(1)-V(1)-O(4) <sup>#2</sup>	109.74(18)	C(6)-N(2)-C(10)	117.0(4)
Co(1)-O(3)	1.962(4)	C(3)-C(12)	1.501(7)	O(3) <sup>#1</sup> -V(1)-O(4) <sup>#2</sup>	107.97(18)	C(6)-N(2)-Co(1)	117.8(3)
Co(1)-N(1)	2.112(4)	C(4)-C(5)	1.372(7)	O(1)-V(1)-O(2)	108.50(19)	C(10)-N(2)-Co(1)	125.1(3)
Co(1)-N(2)	2.124(4)	C(6)-C(7)	1.364(7)	O(3) <sup>#1</sup> -V(1)-O(2)	110.79(18)	N(1)-C(1)-C(2)	122.4(5)
V(1)-O(1)	1.634(4)	C(7)-C(8)	1.374(8)	O(4) <sup>#2</sup> -V(1)-O(2)	110.02(19)	C(3)-C(2)-C(1)	120.6(5)
V(1)-O(3) <sup>#1</sup>	1.668(4)	C(8)-C(9)	1.367(7)	O(5)-V(2)-O(6) <sup>#3</sup>	109.40(19)	C(2)-C(3)-C(4)	116.9(5)
V(1)-O(4) <sup>#2</sup>	1.753(4)	C(8)-C(11)	1.490(7)	O(5)-V(2)-O(2)	108.42(19)	C(2)-C(3)-C(12)	121.9(5)
V(1)-O(2)	1.757(4)	C(9)-C(10)	1.363(7)	O(6) <sup>#3</sup> -V(2)-O(2)	109.15(19)	C(4)-C(3)-C(12)	121.2(5)
V(2)-O(5)	1.596(4)	C(11)-C(12) <sup>#5</sup>	1.499(8)	O(5)-V(2)-O(4)	109.4(2)	C(3)-C(4)-C(5)	119.8(5)
V(2)-O(6) <sup>#3</sup>	1.656(4)	C(12)-C(11) <sup>#6</sup>	1.499(8)	O(6) <sup>#3</sup> -V(2)-O(4)	110.90(18)	N(1)-C(5)-C(4)	122.4(5)
V(2)-O(2)	1.776(4)	O(1)-Co(1)-O(6)	122.35(17)	O(2)-V(2)-O(4)	109.56(18)	N(2)-C(6)-C(7)	124.0(5)
V(2)-O(4)	1.784(4)	O(1)-Co(1)-O(3)	113.03(17)	V(1)-O(1)-Co(1)	169.6(3)	C(6)-C(7)-C(8)	119.0(5)
O(3)-V(1) <sup>#1</sup>	1.668(4)	O(6)-Co(1)-O(3)	124.61(17)	N(2)-C(10)-C(9)	122.3(5)	C(9)-C(8)-C(7)	117.3(5)
O(4)-V(1) <sup>#2</sup>	1.753(4)	O(1)-Co(1)-N(1)	90.51(15)	C(8)-C(11)-C(12) <sup>#5</sup>	113.5(5)	C(9)-C(8)-C(11)	121.9(5)
O(6)-V(2) <sup>#4</sup>	1.656(4)	O(6)-Co(1)-N(1)	88.43(16)	V(1)-O(2)-V(2)	133.9(2)	C(7)-C(8)-C(11)	120.7(5)
N(1)-C(1)	1.315(7)	O(3)-Co(1)-N(1)	90.92(16)	V(1) <sup>#1</sup> -O(3)-Co(1)	143.9(2)	C(10)-C(9)-C(8)	120.3(5)
N(1)-C(5)	1.318(6)	O(1)-Co(1)-N(2)	89.77(16)	V(1) <sup>#2</sup> -O(4)-V(2)	148.3(3)	C(11) <sup>#6</sup> -C(12)-C(3)	114.1(5)
N(2)-C(6)	1.312(6)	O(6)-Co(1)-N(2)	91.12(16)	V(2) <sup>#4</sup> -O(6)-Co(1)	178.4(3)		
N(2)-C(10)	1.339(7)	O(3)-Co(1)-N(2)	89.31(16)	C(1)-N(1)-C(5)	117.8(4)		
C(1)-C(2)	1.365(7)	N(1)-Co(1)-N(2)	179.55(16)	C(1)-N(1)-Co(1)	121.7(3)		

Symmetry transformations used to generate equivalent atoms: <sup>#1</sup> ( $2-x, 2-y, -z$ ); <sup>#2</sup> ( $1-x, 1-y, -z$ ); <sup>#3</sup> ( $-1+x, y, z$ ); <sup>#4</sup> ( $1+x, y, z$ ); <sup>#5</sup> ( $x, 1+y, 1+z$ ); <sup>#6</sup> ( $x, -1+y, -1+z$ )

compounds **1** and **2** on a Rigaku TG analyzer. The powder samples of 3.00 mg and 4.64 mg were loaded into an alumina pan and heated in air with a ramp rate of 10 °C/min from room temperature to 600 °C.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was selected as the reference.

### UV-VIS-NIR diffuse reflectance spectrum

Reflectance spectrum of the crystal was taken on a UV-3100 recording spectrophotometer from 250 nm to 2500 nm. BaSO<sub>4</sub> was selected as the reference (reflectivity was ordered 100%), and specimen was prepared by the reported method (Rabenau, 1985; Lu et al., 1999).

## RESULTS AND DISCUSSION

### Crystal structures

The structure of  $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$  **1** is built up from corner-sharing metavanadate chains running along the *b*-axis and  $\{\text{Co}(\text{C}_4\text{H}_4\text{N}_2)\}_n$  chains (Fig.1). There are two types of  $\{\text{Co}(\text{C}_4\text{H}_4\text{N}_2)\}_n$  chains in the lattice, oriented in the (011) and (01-1) directions, respectively. The flexible  $\{\text{VO}_3\}_n$  chains link the  $\{\text{Co}(\text{C}_4\text{H}_4\text{N}_2)\}_n$  chains to form a 3D framework structures. As shown in Fig.2, each  $\text{Co}^{2+}$  is coordinated in an octahedron, and the two nitrogen atoms from two equivalent pyrazine ligands occupy the axial positions of each cobalt octahedron [Co-N 2.126(4) Å]. The nitrogen atoms which come from the same ligand are connected to the different Co. The four equatorial sites are occupied by four oxygen atoms from three  $\{\text{VO}_3\}_n$  chains [Co-O 2.075(3) Å, 2.029(3) Å]. In the inorganic layer (Fig.3), vanadium is tetrahedrally coordinated by four oxygen atoms with the V-O bond length 1.627(4) Å, 1.633(3) Å, 1.776(2) Å, 1.7874(18) Å and the O-V-O angles 106.9(2)°, 108.82(15)°, 108.30(13)°, 111.58(19)°, 112.70(15)°. The two tetrahedron are connected to form a  $[\text{V}_2\text{O}_7]^-$  by sharing corner O(3) atom. The  $[\text{V}_2\text{O}_7]^-$  is connected to other two  $[\text{V}_2\text{O}_7]^-$  by sharing O(2) atoms. Thus it forms an infinite cluster along *b*-axis.

The structure of  $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$  **2** is built up with inorganic bimetallic oxide  $[\text{CoV}_2\text{O}_6]$  layers and organic 1,2-bis(4-pyridyl) ethane ligands bridging the layers. As shown in Fig.4, each  $\text{Co}^{2+}$  is coordinated in a trigonal bipyramid, where the equatorial plane comprises three oxygen atoms, O(1), O(4) and

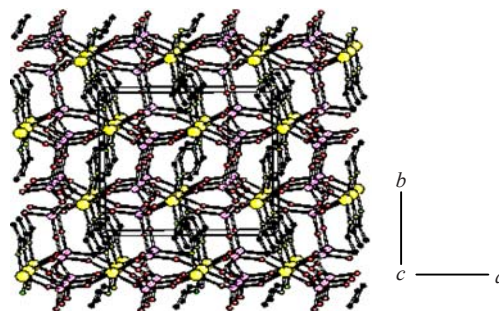


Fig.1 View of the structure of compound **1** along the *c*-axis. Hydrogen atoms are omitted

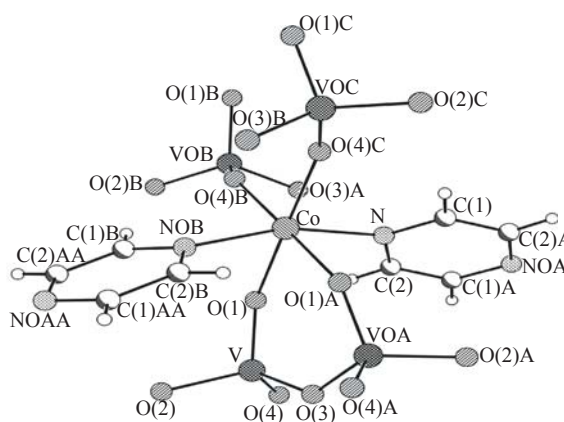


Fig.2 An ORTEP diagram with 50% probability displacement ellipsoids showing the atoms in the asymmetric unit of compound **1**

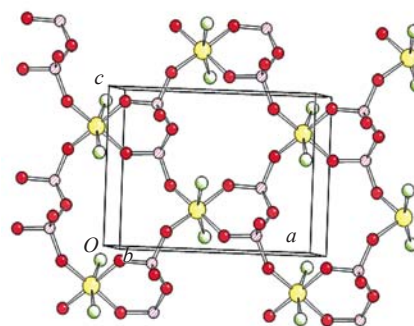


Fig.3 Structure of an inorganic layer in (010) plane of compound **1**

O(5) respectively from three different tetraoxovanadates to form the  $[\text{CoV}_2\text{O}_6]$  layers parallel to the (001) plane and the apical positions are occupied by two pyridyl nitrogen atoms N(1) and N(2), respectively from two different 1,2-bis(4-pyridyl) ethane ligands to bridge the  $[\text{CoV}_2\text{O}_6]$  layers along the *c*-axis direction through coordination bonds. In the 3D covalent framework, O(6) atoms of V(2) coordination tetrahedra are still terminal atoms, and which are

located in bigger channels in the  $a$ -axis direction. In the inorganic layer (Fig.5), two crystallographically distinct vanadium atoms, V(1) and V(2), are both tetrahedrally coordinated by oxygen atoms. [V(1)O(1)O(2)O(3)O(4)] and [V(2)O(2)O(3)O(5)O(6)] tetrahedrons are alternately connected to form a tetraoxovanadate cluster  $[V_4O_{12}]^{4-}$  by sharing corner O(2) and O(3) atoms. The  $[V_4O_{12}]^{4-}$  contains a centrosymmetric eight-membered ring [-V(1)-O(2)-V(2)-O(3)-V(1)-O(2)-V(2)-O(3)-]. The crystal structure determination revealed a 3D inorganic-organic covalent framework for  $Co(C_{12}H_{12}N_2)(VO_3)_2$  **2**, as shown in Fig.6.

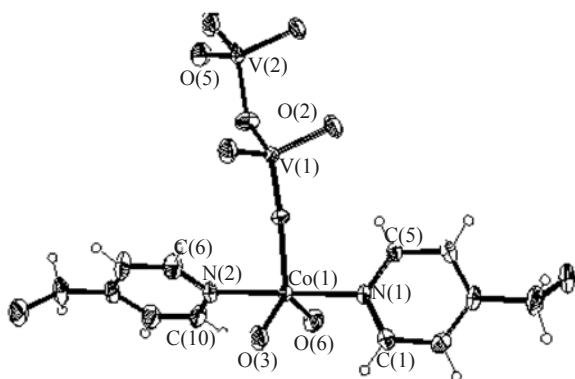


Fig.4 An ORTEP diagram with 50% probability displacement ellipsoids showing the atoms in the asymmetric unit of compound **2**

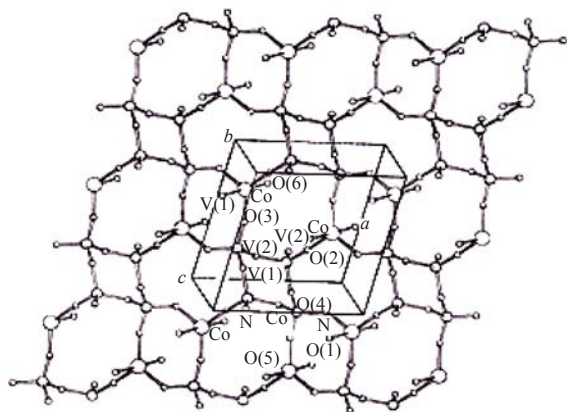


Fig.5 Structure of the inorganic layer  $[CoV_2O_6]$  of compound **2**

In compound **1**, the infinite metavanadate chain can be crystallized. When 1,2-bis(4-pyridyl) ethane ligand replaces pyrazine, the  $V_4O_{12}$  tetramers are formed. It is clear that the bridging ligand influences different vanadium oxide polymeric units.

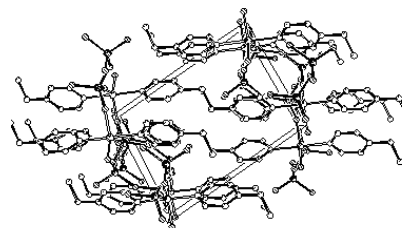


Fig.6 A packing view of compound **2** along the  $a$ -axis, including the crystallographic

### Thermal stability

The two TG curves (Fig.7) both show a one-step, sharp decomposition process, with the maximum rate at 410 °C and 350 °C, respectively. The weight losses for **1** (from 410 to 490 °C) and **2** (from 350 to 440 °C) are about 25% and 44%, due to the broken Co-N coordination bonds in the crystal and the removed organic ligands (calcd.: 23.7% for **1** and 41.8% for **2**). It is shown that the two compounds are thermally stable up to 410 °C and 350 °C, respectively.

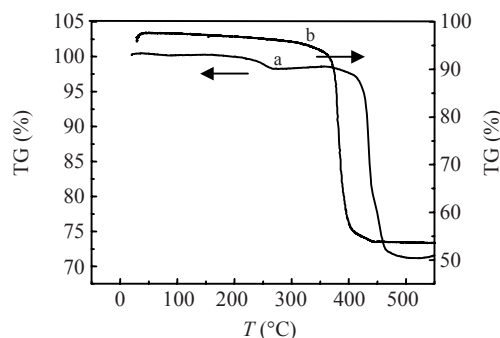


Fig.7 TG curves for compounds **1** (curve a) and **2** (curve b)

### Optical properties

The measurement of diffuse reflectivity can be used to obtain the value of band gap which agrees quite well with the value obtained by absorption measurement from single crystal of the same compound (McCarthy *et al.*, 1993). Absorption data were calculated from the reflectance data using the Kubelka-Munk (K-M) function,  $F=(1-R_\infty)^2/(2R_\infty)$ , where  $R_\infty$  is the reflectance of an infinitely thick layer at a given wavelength (Kotum, 1969). The band gap ( $E_g$ ) was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a  $F$  vs  $E$  plot (Pankove, 1971). The  $F$  vs  $E$  plots of the two compounds exhibit steep absorption edge from which the  $E_g$  can be assessed at 2.13 eV and at 2.12 eV (Fig.8).

The reflectance spectrum measurement revealed the nature of semiconductor and strong selective absorption to the solar radiation for these two compounds.

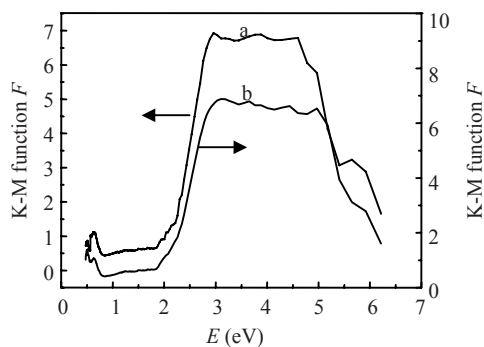


Fig.8  $F$ - $E$  curves for compounds 1 (curve a) and 2 (curve b)

## CONCLUSION

In summary, two novel cobalt vanadate compounds  $\text{Co}(\text{C}_4\text{H}_4\text{N}_2)(\text{VO}_3)_2$  **1** and  $\text{Co}(\text{C}_{12}\text{H}_{12}\text{N}_2)(\text{VO}_3)_2$  **2** have been synthesized by employing pyrazine and 1,2-bis(4-pyridyl) ethane bridging ligands by hydrothermal methods. Compound **1** contains metavanadate chains, and compound **2** includes cyclic  $\text{V}_4\text{O}_{12}$  tetramers. The two compounds are thermally stable up to 410 °C and 350 °C, respectively. It can be concluded that the thermal stabilities of coordination polymers are increased by the combination of vanadate oxide. Studies on optical properties for the powder sample suggest that both compounds are semiconductors with a band gap of 2.13 eV and 2.12 eV, and have strong selective absorption to the solar radiation.

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