

Synthesis, Crystal Structure and Magnetic Properties of a New 3D Cobalt Vanadate

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A new cobalt vanadate compound **1** [$\text{Co}^{\text{II}}(\text{H}_2\text{O})_2 \text{V}_2^{\text{V}} \text{O}_6$] has been hydrothermally synthesized and characterized by the elemental analyses and the single crystal X-ray diffraction analysis. Compound **1** crystallizes in the orthorhombic system, space group *Pmna*, with $a=0.55646$, $b=1.06900$, $c=1.18452$ nm, and $Z=4$. The magnetic susceptibility of the cobalt vanadate has been measured and indicates possible antiferromagnetic coupling between adjacent cobalt (II) (0.5432—0.5697 nm) through bond or space.

Keywords cobalt vanadate, hydrothermal synthesis, crystal structure, antiferromagnetic coupling

Introduction

A lot of work has been focused in the last few years on the synthesis and magnetic properties of transition metal complexes.¹⁻⁶ Cobalt compounds are the most befitting magnetic materials because cobalt ion (Co^{2+}) has large coercive force resulting from large anisotropy energy.^{7,8} It was found that vanadium compounds are helpful to enhance the temperature of magnetic ordering.^{7,9,10} Therefore, plenty of cobalt vanadates have been synthesized, where organonitrogen ligands were used as template¹¹⁻¹³ in general. However, only a few studies about magnetic properties of inorganic cobalt vanadates have been reported.¹⁴ We herein report the synthesis, crystal structure and magnetic properties of a new cobalt vanadate [$\text{Co}^{\text{II}}(\text{H}_2\text{O})_2 \text{V}_2^{\text{V}} \text{O}_6$].

Experimental

Preparation of cobalt vanadate

All chemicals were purchased commercially and used without further purification. The title compound was synthesized by a hydrothermal reaction. A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol, 0.238 g), NH_4VO_3 (0.01 mol, 0.117 g), and deionized water (10 mL) was sealed in a Teflon-lined autoclave and heated at 150 °C for 4 d. The crystal product was filtered and washed with distilled water, and dried at ambient temperature. The yield based on cobalt reached 86%. Anal. calcd for $\text{CoH}_4\text{O}_8\text{V}_2$: Co 20.12, H 1.38, V 34.79; found Co 20.28, H 1.33, V 34.67 (H was analyzed on a Perkin-Elmer 2400 CHN Elemental Analyzer. V and Co were determined by a Leeman inductively coupled plasma (ICP) spectrometer). The TG curve of **1** has only one step,

which is attributed to the removal of H_2O coordinated to Co^{2+} ion and occurs in the range of 200—320 °C. The observed weight loss (13.2%) is in agreement with the calculated value (12.3%) (Perkin-Elmer TGA7 thermogravimetric analyzer).

Crystallographic data collection

The structure of compound **1** was determined by single crystal X-ray diffraction analysis. A brown single crystal of **1** with dimensions 0.487 mm × 0.398 mm × 0.318 mm was mounted on a glass fiber. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo K α ($\lambda=0.071073$ nm) at 293 K in the range of $2.57^\circ < \theta < 27.45^\circ$. Empirical absorption correction (ψ scan) was applied. The structure was solved by the direct method and refined by the Full-matrix least squares on F^2 using the SHELXTL-97 software.¹⁵ All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in its calculated position. A total of 1495 (848 unique, $R_{\text{int}}=0.0160$) reflections were measured. Structure solution and refinement based on 1495 independent reflections with $I > 2\sigma(I)$ and 55 parameters gave R_1 (wR_2) = 0.0235 (0.0741) $\{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]^{1/2}\}$. A summary of crystal data and structure refinement for compound **1** is provided in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **1** are given in Table 2. The bond lengths and angles are listed in Table 3. Crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters were available in supplementary crystallographic data.

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

Empirical formula	H ₄ CoO ₈ V ₂
Formula weight	292.84
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	$a=0.55646(11)$ nm $\alpha=90^\circ$
	$b=1.0690(2)$ nm $\beta=90^\circ$
	$c=1.1845(2)$ nm $\gamma=90^\circ$
Volume	0.7046(2) nm ³
Z	4
D_c	2.761 g/cm ³
Absorption coefficient	4.923 mm ⁻¹
$F(000)$	564
Crystal size	0.487 mm × 0.398 mm × 0.318 mm
θ range for data collection	2.57° to 27.45°
Limiting indices	$-7 \leq h \leq 7$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$
Reflections collected	1495
Independent reflections	848 [$R(\text{int})=0.0160$]
Completeness to $\theta=27.48^\circ$	100.0%
Absorption correction	Empirical
Max. and min. transmission	0.209 and 0.110
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	848/0/55
Goodness-of-fit on F^2	0.995
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0235$, $wR_2=0.0741$
R indices (all data)	$R_1=0.0270$, $wR_2=0.0762$
Largest diff. peak and hole	663 and -716 e ⁻ nm ⁻³

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (nm² × 10²) for compound **1**

Atom	x	y	z	U_{eq}^a
V(1)	0.1953(1)	0.4689(1)	0.1740(1)	0.008(1)
Co(1)	-0.0160(1)	0.2500	-0.0401(1)	0.009(1)
O(3)	0.1214(3)	0.3863(2)	0.0636(2)	0.020(1)
O(2)	0.1675(3)	0.6194(2)	0.1454(2)	0.018(1)
O(1)	0.0001(3)	0.4289(2)	0.2897(2)	0.017(1)
O(W2)	-0.3408(5)	0.2500	0.0529(2)	0.018(1)
O(W1)	0.3025(5)	0.2500	-0.1306(3)	0.026(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Bond lengths (nm) and angles (°) for compound **1**

V(1)—O(3)	0.16308(18)
V(1)—O(2)	0.16511(19)
Co(1)—O(3)	0.20531(18)
Co(1)—O(3)#2	0.20531(18)
Co(1)—O(2)#3	0.20530(18)
O(2)—Co(1)#4	0.20530(18)
V(1)—O(1)	0.18003(17)
V(1)—O(1)#1	0.18020(16)
Co(1)—O(2)#4	0.20530(18)
Co(1)—O(W1)	0.2071(3)
Co(1)—O(W2)	0.2117(3)
O(1)—V(1)#5	0.18020(16)
O(3)-V(1)-O(2)	109.89(10)
O(3)-V(1)-O(1)	109.25(9)
O(2)-V(1)-O(1)	109.34(9)
O(3)-Co(1)-O(3)#2	90.39(11)
O(3)-Co(1)-O(2)#3	177.19(7)
O(3)#2-Co(1)-O(2)#3	91.94(8)
O(3)-Co(1)-O(2)#4	91.94(8)
O(3)#2-Co(1)-O(2)#4	177.19(7)
O(2)#3-Co(1)-O(2)#4	85.69(10)
O(3)-Co(1)-O(W1)	89.48(8)
O(3)#2-Co(1)-O(W1)	89.48(8)
V(1)-O(3)-Co(1)	163.33(12)
O(3)-V(1)-O(1)#1	107.48(9)
O(2)-V(1)-O(1)#1	111.63(9)
O(1)-V(1)-O(1)#1	109.22(5)
O(2)#3-Co(1)-O(W1)	92.12(8)
O(2)#4-Co(1)-O(W1)	92.12(8)
O(3)-Co(1)-O(W2)	90.38(7)
O(3)#2-Co(1)-O(W2)	90.38(7)
O(2)#3-Co(1)-O(W2)	88.03(7)
O(2)#4-Co(1)-O(W2)	88.03(7)
O(W1)-Co(1)-O(W2)	179.80(11)
V(1)-O(2)-Co(1)#4	145.62(11)
V(1)-O(1)-V(1)#5	133.90(10)

Symmetry transformations used to generate equivalent atoms: #1 $x+1/2, y, -z+1/2$; #2 $x, -y+1/2, z$; #3 $-x, y-1/2, -z$; #4 $-x, -y+1, -z$; #5 $x-1/2, y, -z+1/2$.

Magnetic measurement

Magnetic susceptibility data of compound **1** were measured by using an Oxford MagLab2000 magnetometer in the temperature range of 2—300 K with an applied field of 1T.

Results and discussion

Description of crystal structure

The single crystal X-ray diffraction analysis reveals that compound **1** exhibits a three-dimensional (3D) framework, formed by $\{VO_4\}$ tetrahedra and $\{Co(H_2O)_2O_4\}$ octahedra via the corner-sharing mode. The asymmetric unit of compound **1** (Figure 1) shows the coordination environment around the vanadium and cobalt atoms. There are one crystallographically independent V atom and one crystallographically independent Co atom in this structure. The V(1) center shows a distorted tetrahedral coordination geometry with four bridging oxygen atoms, two of which are linked with two Co(1) atoms and another two linked with two V(1) atoms. The V—O bond lengths are in the range of 0.16308(18)—0.18020 (16) nm and the O—V—O angles $107.48(9)^\circ$ — $111.63(9)^\circ$. The Co center adopts an octahedral geometry being coordinated by two oxygen atoms of two water molecules, and four bridging oxygen atoms which are linked with four V(1) atoms. The Co—O bond lengths vary from 0.20530(18) nm to 0.2117(3) nm. The O—Co—O angles are in the range of $85.69(10)^\circ$ — $179.80(11)^\circ$.

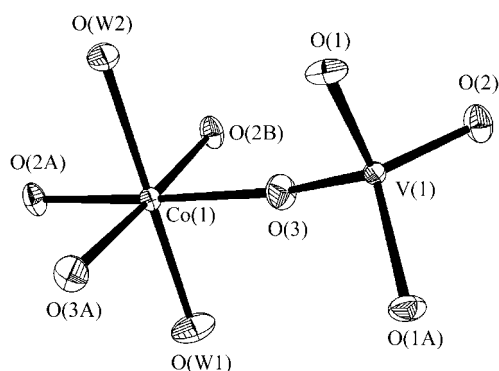


Figure 1 ORTEP drawing of compound **1** with thermal ellipsoids at 50% probability.

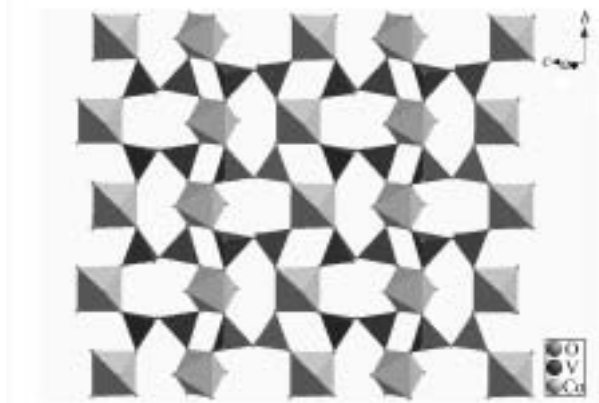


Figure 2 The $CoO_4(H_2O)_2V_2O_7$ layer of compound **1** viewed approximately parallel to *a*-axis.

As shown in Figure 2, two $\{VO_4\}$ tetrahedra share a corner to give rise to a V_2O_7 moiety, which is linked with four adjacent $\{Co(H_2O)_2O_4\}$ octahedra through corner-sharing to form a two-dimensional (2D) network (Figure 2). The 2D layer consists of 4- and 6-membered rings. All two-dimensional (2D) networks are parallel to each other and adjacent 2D networks are connected together by V(1)—O(1)—V(1) bond to produce 3D framework (Figure 3). The 3D framework contains hexagonal channels (*ca.* 0.5437 nm \times 0.4680 nm) parallel to *a*-axis (Figure 4). The two distances between two cobalt ions which are linked by Co—O—V—O—Co and Co—O—V—O—V—O—Co are 0.5432 nm and 0.5697 nm, respectively.

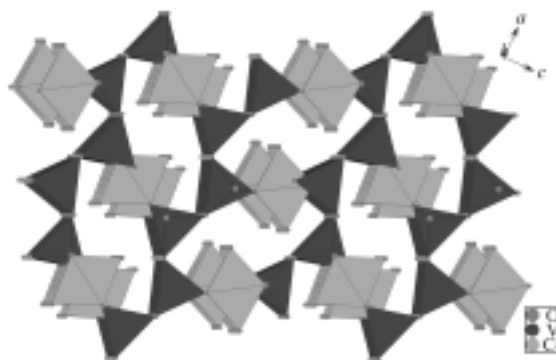


Figure 3 Perspective view parallel to *b*-axis of compound **1**.

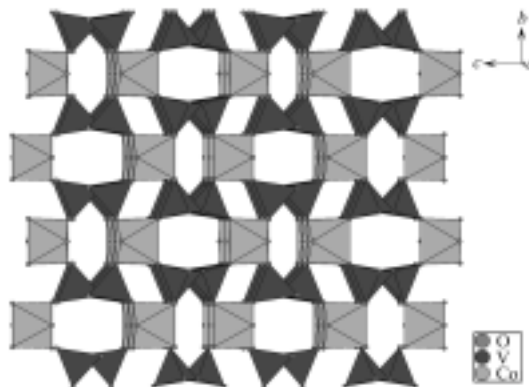


Figure 4 Perspective view parallel to *a*-axis of compound **1**.

Magnetic properties

The temperature dependence of the magnetic susceptibility for compound **1** is shown in Figure 5, in the form of χ_m^{-1} vs. *T* and $\chi_m T$ vs. *T* plots. The $\chi_m T$ value of compound **1** exhibits a continuous decrease upon cooling from 4.10 (297.5 K) to 2.03 $cm^3 \cdot mol^{-1} \cdot K$ (2.2 K). The decline of $\chi_m T$ with the lowered temperature indicates that there is possible antiferromagnetic coupling between the cobalt ions at low temperature.^{1,16} Both Co—O—V—O—Co (0.5432 nm) and Co—O—V—O—V—O—Co (0.5697 nm) may contribute to the antiferromagnetic coupling through bond or space. Comparing with the cyanide or oxalate^{17,18}, there are no proper pathways to

propagate magnetic interactions for compound **1**, so no long-range magnetic ordering was observed in Figure 5 down to 2 K.

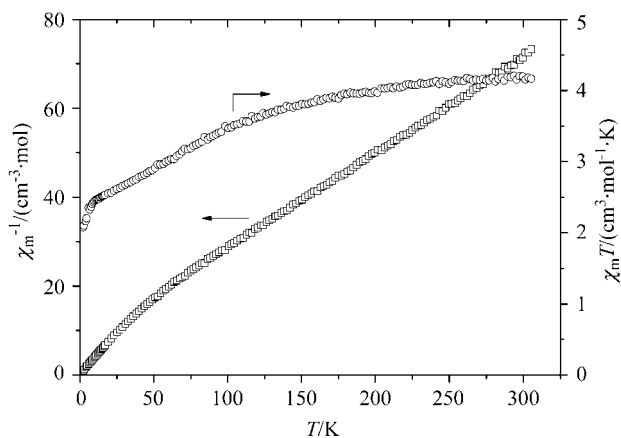


Figure 5 Temperature dependence of χ_m^{-1} and $\chi_m T$ for compound **1**.

In summary, a new 3D cobalt vanadate has been successfully synthesized, the magnetic measurement indicates possible antiferromagnetic coupling between the cobalt ions.

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