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Synthesis, crystal structure and magnetic property of a new cobalt(II) vanadate

Su-Yun Zhang [a], Wen-Bin Guo [a], Ming Yang [a], Ying-Ying Tang [a,b], Nan-Nan Wang [a], Rong-Rong Huang [a], Mei-Yan Cui [a,b], Zhang-Zhen He [a,*]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

A new cobalt(II) vanadate has been synthesized by hydrothermal reaction. It exhibits 3D cobalt(II) oxide architecture with Co_{12} member ring (MR) and Co_6 MR tunnels along *c*-axis. V(2)O_4 tetrahedra are located at the center of Co_6-MR tunnels whereas V(1)O_4 tetrahedra and 'isolated' 1D Co(1)O_6 octahedral chains are located at the Co_{12}-MR tunnels. The 3D cobalt(II) oxide architecture is constructed on irregular ladder chains formed by edge- and face-sharing of Co(2)O_6 octahedra whereas the 'isolated' 1D Co(1)O_6 octahedral chain in the tunnels are formed by face-sharing of Co(1)O_6 octahedra. Magnetic property is investigated by means of magnetic susceptibility, magnetization and heat capacity measurement. Magnetic susceptibility and heat capacity measurement indicate a typical long-range spin-canting antiferromagnetic ordering below ~71 K; metamagnetic behavior was detected in the isothermal magnetization measurement at 2 K.

1. Introduction

Metal vanadates are a class of important compounds due to their wide applications as catalyst in photocatalysis [1,2], cathode materials in lithium batteries [3], multiferroic materials when combining with transition metal-ions [4,5], non-centrosymmetric materials such as second-harmonic generation, piezoelectricity, ferroelectricity, and pyroelectricity, *etc* [6,7]. Also, vanadate groups are well-known for their ability to form low-dimensional magnetic materials [8–12]. The vanadates groups serving as nonmagnetic groups play an important role in the construction of spin-lattice of magnetic ions as well as the geometrical topology of the structures. So the vanadate groups will strongly affect the magnetic properties and it is an interesting and exciting issue to investigate the magnetic properties and understand the relationships between magnetic properties and structural features of materials based on vanadate subgroups.

In addition, vanadates may give rise to a variety of frameworks that are totally different from the compounds based on inorganic main-group acid radicals with similar coordination configuration, such as $BaCu_2V_2O_8$ and $BaCu_2P_2O_8$ [13–17]. It is also noticed that vanadium(II) may exhibit three types of coordination modes, VO_4 tetrahedron, VO_5 square pyramid or trigonal bipyramid and VO_6 octahedron. The VO_x (x=4, 5, 6) may polymerize into novel polynuclear clusters or extended structures through corner- or edge-sharing. So it is believed that it is an effective way to construct magnetic materials possessing new spin lattice or geometrical topology with vanadate groups as linking subgroups.

In this context, we started a research program to systematically explore new transition metal vanadates. As far as cobalt(II) vanadates are concerned, the structurally and magnetically characterized ternary phases are really rare, including CoV_2O_6 [18,19], $Co_2V_2O_7$ [20], $Co_3V_2O_8$ [21], $Co(VO_3)_2(H_2O)_4$ [22], $Co(H_2O)_2(V_2O_6)$ [23]. Some cobalt(II) vanadates with alkaline earth(II) or lead(II) cations have also been reported [24–28]. The reported cobalt(II) vanadates have exhibit various structures and magnetic behaviors. In CoV_2O_6, edge-shared CoO_6 octahedra form linear chains while VO_5 form zigzag chains by sharing their basal edges. 1/3 magnetization plateau was observed in CoV_2O_6. In $Co_2V_2O_7$, edge-shared CoO_6 octahedra form skew chains that are separated by bitetrahedral $(V_2O_7)^{4-}$. Magnetic measurements suggested that $Co_2V_2O_7$ is a 3D antiferromagnet with two magnetic transitions at 6.0 and 13.2 K. A spin-flop-like transition was observed while magnetic field was applied along the *b*-axis. In $Co_3V_2O_8$, the interactions of CoO_6 octahedra *via* edge-sharing result in a complicated cobalt(II) oxide layer which are further connected by VO_4 tetrahedra into 3D framework; it exhibits unusual magnetic behaviors where five magnetic phase transitions occur below 15 K along the magnetic easy *a*-axis. As for $Co(VO_3)_2(H_2O)_4$, the Co^{2+} ions are connected by vanadium(V) oxide ladder chains into 3D network and it shows a

* Corresponding author at: State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China. Tel./fax: +86 591 83792649.
E-mail address: hezz@fjirsm.ac.cn (Z.-Z. He).

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3D antiferromagnetic ordering at 2.5 K with a metamagnetic transition. $Co(H_2O)_2(V_2O_6)$ show a 3D framework where 'isolated' Co^{2+} ions are connected by bitetrahedral $(V_2O_7)^{4-}$ anions and it exhibits 3D antiferromagnetic ordering.

It is obviously that the incorporation of vanadate has greatly increased the diversity of the structures. Also, different molar ratios of M/V will affect the structures and magnetic properties of the compounds. Our explorations of Sr–Co–V–O quaternary phase afforded a new cobalt(II) vanadate with a non-centrosymmetric structure, namely, $Co_7V_4O_{16}(OH)_2(H_2O)$. Herein we report its synthesis, crystal structure and magnetic property.

2. Experimental section

2.1. Synthesis of $Co_7V_4O_{16}(OH)_2(H_2O)$

Dark rod-shaped single crystals of $Co_7V_4O_{16}(OH)_2(H_2O)$ were initially obtained from reaction products of a mixture of $SrCl_2 \cdot 6H_2O$ (0.060 g, 0.2 mmol), V_2O_5 (0.0182 g, 0.1 mmol), $Co(OH)_2$ (0.0372 g, 0.4 mmol) and H_2O (6 mL) in our attempt to prepare a Sr–Co–V–O phase. The mixture was sealed in an autoclave equipped with a Teflon liner (28 mL). The autoclave was put into a furnace which was then heated at 200 °C for 3 days under autogenous pressure, followed by slowly cooling to room temperature at a rate of 6 °C h^{-1}. Dark rod-shaped crystals of $Co_7V_4O_{16}(OH)_2(H_2O)$ were obtained with tiny unknown brown powders as impurity. The energy-dispersive spectrometry (EDS) elemental analysis on several single crystals gave an average molar ratio of Co/V of 1.8: 1.0 but no Sr is present (Fig. S1). After proper structural analysis, single phase of $Co_7V_4O_{16}(OH)_2(H_2O)$ was prepared by the reaction of a mixture of 0.5 mmol $CoCl_2 \cdot 6H_2O$, 0.2 mmol Na_3VO_4 in 6 mL H_2O. Then the mixture was treated as the procedure above and the furnace was heated at 190 °C for 3 days. After cooling, pure phase of dark crystals were filtered off and washed with water. The purity of the single phase was confirmed by XRD studies (Fig. S2).

2.2. Crystal structure determination

Single crystals of $Co_7V_4O_{16}(OH)_2(H_2O)$ were selected and mounted on glassy fibers for single crystal X-ray diffraction (XRD) measurements. Data collections were performed on Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo–Ka radiation (λ=0.71073 Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by Multi-scan method [29]. The structure was solved by direct method and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [30]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms associated to water molecule and aqua ligands were not refined. Bond valance calculations indicated that the total bond valences of all oxygen atoms are close to 2.0 except the oxygen atoms connecting with four Co(2) atoms. So the hydrogen atoms are associated with the oxygen atom, which is in accordance with the isostructural compound $Mg_7V_4O_{16}(OH)_2(H_2O)$ [31]. In addition, atom V (2) is disorder over two orientations V2A and V2B with a short V2A···V2B distance of 1.422(13) Å. Hence their positional occupancies were also refined with a total occupancy factor of one V2 atom. All the positions are fully occupied. The final refined structural parameters were checked by the PLATON program and no higher symmetry was suggested [32]. Crystallographic data and structural refinements are summarized in Table 1. Atomic displacement parameters are given in Table 2. Important bond distances and angels are listed in Table 3. Further details of the crystal structure studies can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247808666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD 427993.

Table 1
Crystal data and structure refinements for $Co_7V_4O_{16}(OH)_2(H_2O)$.

Formula	$Co_7V_4O_{16}(OH)_2(H_2O)$
Fw	924.30
Space group	$P6_3mc$
a (Å)	12.917(2)
b (Å)	12.917(2)
c (Å)	5.0944(7)
α (°)	90
β (°)	90
γ (°)	120
V (Å)	736.12(19)
Z	2
D_{calcd} (g cm^{-3})	4.170
μ(Mo–Ka) (mm^{-1})	10.186
GOF on F^2	1.164
*R*1, w*R*2[I > 2σ (I)][a]	0.0466, 0.1136
*R*1, w*R*2 (all data)	0.0492, 0.1155

$R1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR2 = \{\sum w[(Fo)^2 - (Fc)^2]^2\}/\sum w[(Fo)^2]^2\}^{1/2}$.

Table 2
The Wyckoff positions, atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $Co_7V_4O_{16}(OH)_2(H_2O)$.

Atom	Wyck.	*X*	*y*	*z*	*U*(eq)
Co(1)	2*a*	0	0	6545(9)	35(1)
Co(2)	12*d*	4267(1)	3510(1)	−1790(2)	15(1)
V(1)	6*c*	3012(2)	1506(1)	3506(4)	14(1)
V(2A)	2*b*	6667	3333	−1830(20)	15(1)
V(2B)	2*b*	6667	3333	968(12)	15(1)
O(1)	6*c*	1501(8)	750(4)	4090(20)	24(2)
O(2)	12*d*	3419(5)	2779(5)	1654(11)	16(1)
O(3)	6*c*	4736(4)	5264(4)	71(17)	18(2)
O(4)	6*c*	3887(7)	1944(4)	−3674(15)	17(2)
O(5)	6*c*	5958(4)	4042(4)	−330(20)	24(2)
O(6)	2*b*	6667	3333	−5400(70)	74(9)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Important bond length (Å) for $Co_7V_4O_{16}(OH)_2(H_2O)$.

Co(1)–O(1)#1	2.093(10)	Co(1)–O(1)	2.093(10)
Co(1)–O(1)#2	2.093(10)	Co(1)–O(1)#3	2.122(10)
Co(1)–O(1)#4	2.122(10)	Co(1)–O(1)#5	2.122(10)
Co(2)–O(2)#6	2.027(5)	Co(2)–O(2)	2.033(5)
Co(2)–O(4)	2.064(4)	Co(2)–O(5)	2.074(7)
Co(2)–O(3)#7	2.165(7)	Co(2)–O(3)	2.243(7)
V(1)–O(1)	1.717(9)	V(1)–O(2)	1.734(6)
V(1)–O(2)#8	1.734(6)	V(1)–O(4)#9	1.739(8)
V(2A)–O(5)#10	1.759(11)	V(2A)–O(5)#11	1.759(11)
V(2A)–O(5)	1.759(11)	V(2A)–O(6)	1.82(4)
V(2B)–O(5)#11	1.716(9)	V(2B)–O(5)#10	1.716(9)
V(2B)–O(5)	1.716(9)	V(2B)–O(6)#9	1.85(4)

Symmetry transformations used to generate equivalen:
#1 $-x+y, -x, z$; #2 $-y, x-y, z$; #3 $x-y, x, z+1/2$; #4 $y, -x+y, z+1/2$; #5 $-x, -y, z+1/2$; #6 $y, x, z-1/2$; #7 $-x+1, -y+1, z-1/2$; #8 $x, x-y, z$; #9 $x, y, z+1$; #10 $-x+y+1, -x+1, z$; #11 $-y+1, x-y, z$.

2.3. Magnetic measurements

Magnetic and heat capacity measurements were performed using a commercial Quantum Design Physical Property Measurement System (PPMS or MPMS). Powdered samples (15.7 mg) of $Co_7V_4O_{16}(OH)_2(H_2O)$ were placed in a gel capsule sample holder which was suspended in a plastic drinking straw. Magnetic susceptibility was measured at 0.1 T from 300 to 2 K. Magnetization was measured at 2 K and in applied field from −8 to 8 T (field scan of 0.1 T/step). Heat capacity was