

Hydrothermal synthesis and crystal structure of a layered vanadium oxide with an interlayer metal coordination complex: [Co(phen)₃][V₁₀O₂₆] · H₂O

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Abstract

A novel compound, [Co(phen)₃][V₁₀O₂₆] · H₂O, was hydrothermally synthesized and characterized by single-crystal X-ray diffraction. This compound crystallizes in the orthorhombic space group *Ccca* with $a = 13.447(3)$, $b = 29.936(6)$, $c = 23.252(5)$ Å, $V = 9360(3)$ Å³, $Z = 8$ and $R = 0.0285$. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K in the range of $1.36 < \theta < 24.99^\circ$. The structure of the compound consists of vanadium oxide layers, which are built up from the infinite VO₄ chains by corners and edges sharing. The [Co(phen)₃]²⁺ complexes occupy the interlayer space and contact each other via $\pi - \pi$ stacking interactions of the phen groups to form infinite one-dimensional chains.

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1. Introduction

In the past few years, there has been extensive interest in vanadium oxides for their structural diversity and potential application in the fields of catalysis, electrical conductivity, magnetism and photochemistry [1,2]. The evolution of vanadium oxide is dependent upon the synthesis of new solids possessing unique structures and properties, although synthesis of the materials remains a challenge. The recent success in the hydrothermal assembly of the vanadium oxides employing secondary metal–ligand complex subunits suggests a novel approach towards synthesis of vanadium oxides possessing unique structures and properties. A variety of novel vanadium oxides containing metal coordination complex subunits including discrete clusters, infinite chain and layer structures have been prepared by hydrothermal methods [3–8]. Among which, the secondary

metal–ligand complex $[M'L_x]^{n+}$ (M' = transition metal, L = ligand) may be directly coordinated through bridging oxo-groups, $M'-O-V$, to form a bimetallic phase [9–11], or it may be only present as an discrete charge-balancing cation [12,13]. In the latter case, the secondary metal–ligand complex $[M'L_x]^{n+}$ are limited to two forms $[M'L_2]^{n+}$ and $[M'L_3]^{n+}$ in the known complexes. Most vanadium oxides containing $[M'L_2]^{n+}$ type counteranion display two-dimensional layered structures, such as compounds [(bpy)₂Zn]₂[V₆O₁₇] [12] and (en)₂Cu[V₆O₁₄] [12]. In contrast, $[M'L_3]^{n+}$ type counteranion often occurs in the vanadium oxides with discrete clusters or one-dimensional chainlike structures, such as in compound [Zn(2,2'-bpy)₃]₂[V₄O₁₂] [13] and Ni(en)₃(VO₃)₂ [14], and no examples of layered vanadium oxide containing $[M'L_3]^{n+}$ type counteranion has been observed.

In this paper, we report the synthesis, crystal structure of a novel vanadium oxide, [Co(phen)₃][V₁₀O₂₆] · H₂O, which is the first example of layered vanadium oxides with $[M'L_3]^{n+}$ type interlamellar metal coordination complex cation.

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2. Experimental

2.1. Synthesis and characterization

The best crystals of the title compound were prepared from a reaction mixture of V_2O_5 (0.1011 g), H_3BO_3 (0.15 g), $CoCl_2$ (0.06 g), 1,10'-phen (0.055 g) in 8 mL of water. The starting mixture was adjusted to pH 7.5 by the addition of 2 M aqueous NaOH under vigorously stirring. The final solution was transferred into an 18 mL Teflon-lined autoclave and crystallized at 160°C for 6 days. After slow cooling to room temperature, red crystals were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 50% based on V. The title compound can be obtained in the pH range 7.0–8.0 and reaction at pH 7.5 give the higher yields. The red crystals were manually selected for the structural determination and other characterizations. The ICP analysis showed that the title compound contained 32.5% V and 3.6% Co (Calcd: V, 33.0; Co, 3.8%). The elemental analysis found: C, 27.7; H, 1.8; N, 5.3 (Calcd: C, 28.0; H, 1.7; N, 5.4%).

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. V and Co were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectrum was obtained on an Alpha Centaur FT/IR spectrometer with pressed KBr pellet in the 4000–400 cm^{-1} region. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain TGA curve in N_2 with a temperature increasing rate of 10°C min^{-1} .

2.2. Single-crystal X-ray diffraction

A red single crystal with an approximate dimension of $0.432 \times 0.296 \times 0.085$ mm³ was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on an R-AXIS RAPID IP diffractometer equipped with a normal focus, 18 kW sealed tube X-ray source (MoK α radiation, $\lambda = 0.71073$ Å) operated at 50 kV and 200 mA. Data processing was accomplished with the RAXWISH processing program. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL 97 software [15]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. The atomic positional and displacement parameters are listed in Table 2. Selected bond lengths and angles are listed in Table 3.

Table 1

Crystal data and structure refinement for $[Co(phen)_3][V_{10}O_{26}] \cdot H_2O$

Empirical formula	$C_{36}H_{26}CoN_6O_{27}V_{10}$
Formula weight	1542.96
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Ccca</i>
<i>a</i> (Å)	13.447(3)
<i>b</i> (Å)	29.936(6)
<i>c</i> (Å)	23.252(5)
Volume (Å ³)	9360(3)
<i>Z</i>	8
Calculated density (Mg m ⁻³)	2.190
Absorption coefficient (mm ⁻¹)	2.345
<i>F</i> (000)	6056
Crystal size (mm)	0.432 × 0.296 × 0.085
Reflections collected/unique	7806/4114 ($R_{int} = 0.0343$)
Data/restraints/parameters	4114/0/366
Goodness-of-fit on F^2	0.941
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0285$, $wR_2 = 0.0674$
<i>R</i> indices (all data)	$R_1 = 0.0523$, $wR_2 = 0.1030$
Largest diff. peak and hole (e Å ⁻³)	0.882 and -0.953

Note: $R_1 = \sum ||F_o| - |F_c||$; $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

3. Results and discussions

3.1. Synthesis

Hydrothermal synthesis has recently been proved a useful technique in preparation of solid-state oxides and inorganic–organic hybrid materials. In a specific hydrothermal process, many factors can affect the formation and crystal growth of products, such as the type of initial reactants, starting concentration, pH value, reaction time and temperature. In our case, the pH value of the reaction system was of crucial important for the crystallization of products. The pH values were controlled at 7.0–8.0 to obtain the crystallized product, whereas out of this pH range no product could be obtained. On the other hand, the H_3BO_3 in the preparation of products takes a role as the acid buffering agent. This species appears to be needed in the synthesis, although it is not incorporation in the final structure.

3.2. Description of structure

The structure of the title compound consists of vanadium oxide layers with $Co(phen)_3^{2+}$ complex occupying the interlamellar space. Fig. 1 shows the thermal ellipsoid plot of the compound and the coordination environment around the vanadium and cobalt atoms. Each vanadium atom has a square-pyramidal coordination environment with the apical oxygen at a distance of around 1.593(4) Å and four basal oxygens at distances in the range of 1.701(3)–2.065(3) Å. The cobalt atom has a distorted octahedral environment.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$

Atom	x	y	z	U_{eq}
Co	5000	6195(1)	7500	14(1)
N(1)	4419(3)	5714(1)	7054(2)	17(1)
N(2)	3795(3)	6204(1)	7961(2)	17(1)
N(3)	5677(3)	6643(1)	7960(2)	17(1)
C(1)	3820(3)	5731(2)	6600(2)	22(1)
C(2)	3541(4)	5344(2)	6306(3)	30(1)
C(3)	3849(4)	4933(2)	6491(3)	38(2)
C(4)	4424(4)	4898(2)	6992(3)	31(1)
C(5)	4694(3)	5304(2)	7251(2)	22(1)
C(6)	4733(4)	4490(2)	7256(3)	48(2)
C(11)	3562(3)	5970(2)	8427(2)	24(1)
C(12)	2597(4)	5975(2)	8659(3)	30(1)
C(13)	1874(4)	6234(2)	8407(3)	28(1)
C(14)	2097(3)	6488(2)	7927(2)	24(1)
C(15)	3073(3)	6462(2)	7714(2)	18(1)
C(16)	1404(4)	6769(2)	7627(3)	33(2)
C(21)	5385(4)	6849(2)	8441(2)	24(1)
C(22)	6045(4)	7118(2)	8756(3)	31(1)
C(23)	7010(4)	7177(2)	8580(3)	31(1)
C(24)	7336(4)	6966(2)	8077(2)	27(1)
C(25)	6642(3)	6701(2)	7786(2)	18(1)
C(26)	8333(4)	6993(2)	7849(3)	36(2)
V(1)	4966(1)	6946(1)	4440(1)	12(1)
V(2)	6357(1)	6134(1)	4545(1)	18(1)
V(3)	2328(1)	6920(1)	4824(1)	15(1)
V(4)	3744(1)	4965(1)	4787(1)	24(1)
V(5)	3905(1)	6153(1)	4966(1)	14(1)
O(1)	5000	5000	5000	96(4)
O(2)	4886(2)	7021(1)	3764(2)	24(1)
O(3)	6706(2)	6049(1)	3896(2)	34(1)
O(4)	3670(4)	4872(2)	4118(2)	55(1)
O(5)	2500	7500	5000	22(1)
O(6)	4403(3)	6168(1)	5587(2)	32(1)
O(7)	2500	5000	5090(2)	19(1)
O(8)	6222(2)	5632(1)	4880(2)	37(1)
O(9)	1826(2)	6910(1)	4202(2)	32(1)
O(10)	1275(2)	6815(1)	5371(2)	22(1)
O(11)	3734(2)	5609(1)	4780(2)	23(1)
O(12)	2538(2)	6298(1)	5059(2)	25(1)
O(13)	3738(2)	6813(1)	4725(2)	22(1)
O(14)	5000	7500	4738(2)	17(1)
O(15)	4981(2)	6273(1)	4463(2)	15(1)
O(1W)	2500	5000	2934(6)	174(5)

It coordinates to six N atoms from three phen ligands with an average Co–N bond distance of 1.941(4) Å. Valence sum calculations [16] indicate that all V are pentavalent. This oxidation state is consistent with the overall charge balance of the compound.

A view perpendicular to one of the vanadium oxide layers is shown in Fig. 2. The network structure of the title compound is built from the VO_4 chains linked together by corners and edges, which is quite distinct from those previously reported organically templated or metal coordination complex templated two-dimensional vanadium oxides. In this compound, the VO_5 square pyramids share two corners of their base with neighboring square pyramids to form straight VO_4 chains along

Table 3

Selected bond lengths (Å) for $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$

Co–N(1)#1	1.939(4)	Co–N(1)	1.939(4)
Co–N(2)	1.942(4)	Co–N(2)#1	1.942(4)
Co–N(3)	1.942(4)	Co–N(3)#1	1.942(4)
V(1)–O(2)	1.592(4)	V(1)–O(14)	1.799(2)
V(1)–O(13)	1.822(3)	V(1)–O(10)#2	1.857(3)
V(1)–O(15)	2.014(3)	V(2)–O(3)	1.600(4)
V(2)–O(8)	1.701(4)	V(2)–O(12)#2	1.900(3)
V(2)–O(15)	1.907(3)	V(2)–O(10)#2	2.050(3)
V(3)–O(9)	1.595(4)	V(3)–O(5)	1.7994(9)
V(3)–O(10)	1.929(3)	V(3)–O(13)	1.936(3)
V(3)–O(12)	1.960(3)	V(4)–O(4)	1.585(5)
V(4)–O(1)	1.7631(8)	V(4)–O(7)	1.817(2)
V(4)–O(11)	1.929(3)	V(4)–O(8)#3	1.948(4)
V(5)–O(6)	1.594(4)	V(5)–O(11)	1.701(3)
V(5)–O(15)	1.895(3)	V(5)–O(12)	1.901(3)
V(5)–O(13)	2.065(3)		

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

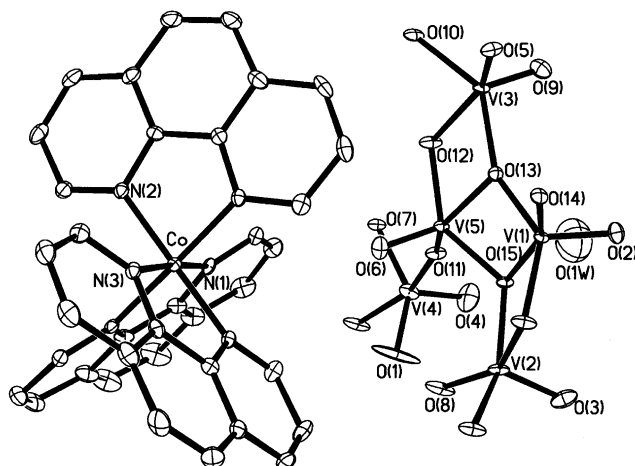


Fig. 1. Thermal ellipsoid (30% level) plot of $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$ showing the coordination environment around the V and Co atoms.

the [100] direction in such a way that the axial vertices point to the both sides of the slabs with a sequence “two up–two down”. The VO_4 chains in the compound are present in two distinct forms: one is VO_4 single chain, which has not yet been observed in other reported vanadium oxides; the other is zigzag double-chain ribbon which is composed of two VO_4 chains connected through edges sharing. Two of the latter are further linked together by corners to form a double-ribbon strip. Finally, the double-ribbon strips and VO_4 single chains are alternately connected together by corners sharing to form the infinite two-dimensional layer.

Fig. 3 shows the packing of the inorganic sheets along the a -axis direction. In the title compound, the inorganic layers are arranged in parallel and stack in an $ABAB\cdots$ sequence. The interlayer separation is approximately 11.63 Å, as measured from V-atom-plane to V-atom-plane, which is occupied by the $\text{Co}(\text{phen})_3^{2+}$ complexes

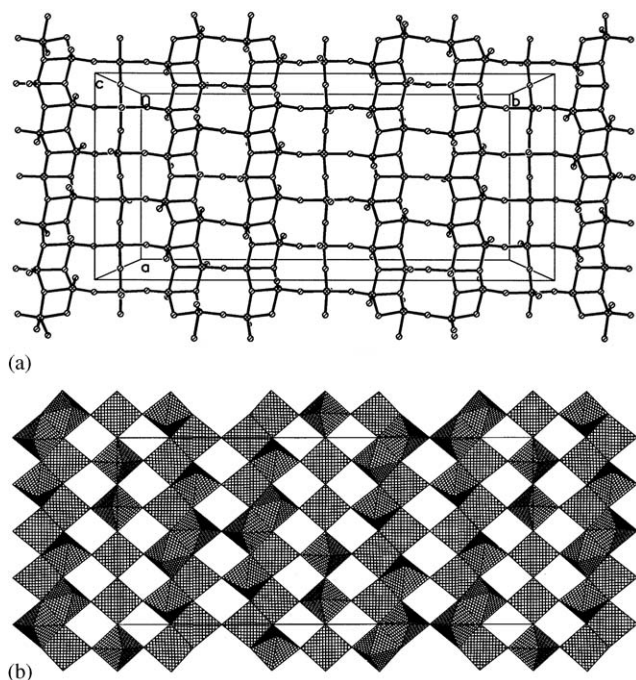


Fig. 2. (a) 2D layer of $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$, viewed along the c -axis direction; (b) polyhedral representation of the 2D layer in $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$.

and water molecules. The water molecules are not involved in any hydrogen-bonding interactions with the oxide layers. It is worth noting that the $\text{Co}(\text{phen})_3^{2+}$ complexes contact each other via π - π stacking interactions of the phen groups to form one-dimensional infinite zigzag chains viewed along the c -axis as shown in Fig. 4.

3.3. Characterization

The IR spectrum of the title compound exhibits a series of bands in the 1100 – 1600 cm^{-1} region associated with the $1,10'$ -phen groups; the compound also possesses strong bands at 989 , 835 , 788 , 717 , 551 cm^{-1} attributed to the $\nu(\text{V}=\text{O})$ or $\nu(\text{V}-\text{O}-\text{V})$ vibration.

The thermal analysis of the compound exhibits three steps of weight losses. The first weight loss is 1.3% in the temperature range 50 – 180°C , corresponding to the release of crystal water. The remaining two weight losses amount to 36.2% from 480°C to 700°C , and are ascribed to the release of $1,10'$ -phen group. The whole weight loss (37.5%) agrees well with the calculated value (36.2%). The calcined product was identified by XRD as an amorphous phase.

4. Conclusions

In this paper, a novel layered vanadium oxide with the formula $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$ was synthesized

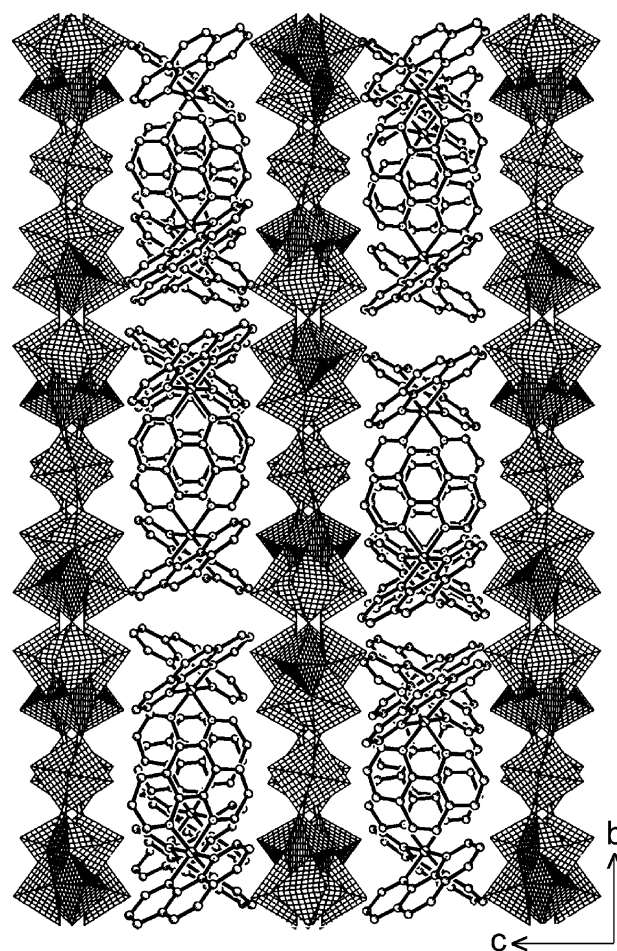


Fig. 3. View of the packing of $[\text{Co}(\text{phen})_3][\text{V}_{10}\text{O}_{26}] \cdot \text{H}_2\text{O}$ along the a -axis direction.

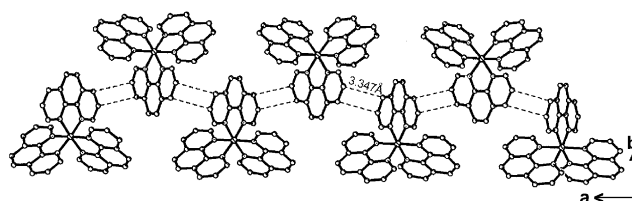


Fig. 4. View of the zigzag chain formed by $\text{Co}(\text{phen})_3^{2+}$ cation via π - π stacking interactions along c -axis.

under mild hydrothermal conditions. The structure of the compound consists of vanadium oxide layers with $\text{Co}(\text{phen})_3^{2+}$ complexes occupying the interlamellar space. Although several layered vanadium oxides containing interlamellar metal coordination complex are known, the title compound is the first example of the layered vanadium oxide containing $[\text{M}'\text{L}_3]^{n+}$ type counteranion in the interlayer space. The compound has a novel $[\text{V}_{10}\text{O}_{26}]^{2-}$ layer, which is quite distinct from those previously reported organically templated or metal coordination complex templated two-dimensional

vanadium oxides. This suggests that interlayer cation may profoundly influence the resulted structural complexity. This work also shows that the hydrothermal technique is a powerful method for the synthesis of novel structural vanadium oxides.

Acknowledgments

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Supplementary materials

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-212321. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; <mailto:deposit@ccdc.cam.ac.uk>).

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