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A Novel Cobalt(II) Vanadophosphate with a Quasi Zeolithic Intersecting Tunnel Structure: $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$

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A new cobalt(II) vanadophosphate $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ has been synthesized by hydrothermal method at 220 °C. Its original structure crystallizes in the $Pmc2_1$ space group with $a = 6.4394(4)$, $b = 7.4299(5)$, and $c = 9.854(1)$ Å. It can be described by the assemblage of mixed "tetrahedral-octahedral" $[VPO_7OH]_\infty$ chains with either octahedral cobalt rutile type chains or chains of edge sharing CoO_4OH pyramids. This framework delimits intersecting tunnels, where the NH_4^+ cations and the water molecules sit. This structure exhibits a quasi zeolithic character, releasing two water molecules from the tunnels when heating at 350 °C under nitrogen and slowly readsorbing 0.5 molecule of water when exposed at 25 °C to air. The zeolithic character is nevertheless limited since the structure collapses and becomes amorphous when it releases the ammonia at 460 °C.

Introduction

Transition metal oxide phosphates are of a great interest and extensively used as catalysts for oxidation reactions. For example, $(VO)_2P_2O_7$ and $Fe_7(PO_4)_6$ are highly selective in the mild oxidation of hydrocarbons.[1,2] Recent catalytic studies performed in the oxide systems indicate that their performances can be improved when multicomponent catalysts with several metals are used.[3,4] In the phosphate systems, such procedures remain rare and few binary phosphates are known. To isolate new potential catalysts, we chose to investigate the Co−V−P−O system using hydrothermal conditions. The Co phosphates and the V ones are known for their catalytic properties,[1,5] and they offer varied coordinations (from octahedral to tetrahedral) and different oxidation states able to generate new structural arrangements. In addition, recently interesting cobalt phosphates with zeolithic frameworks were reported.[5,6] Up to now, no anhydra cobalt vanadophosphate is known, and only two hydrated cobalt vanadophosphates have been reported: $Co(VO)_2(PO_4)_2{\cdot}4H_2O$[7] and $V_{0.94}Co_{0.46}[PO_4(OH)_{0.74}(OH_2)_{0.26}]$.[8] Both of them, contain divalent cobalt, with vanadium in tetravalent and trivalent oxidation state, respectively. Resulting from our studies, in reducing conditions, using hydrothermal synthesis, we present here the synthesis and structure of a new cobalt(II) vanadophosphate involving tetravalent vanadium. This monophosphate $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$, which consists of rutile "CoP" chains associated with mixed "VP" chains, can also be described as an intersecting tunnel structure, containing NH_4^+ and H_2O species.

Crystal Growth and Characterization

Light brown plate crystals of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ were synthesized by hydrothermal method. A mixture of Co_3O_4, VO_2, $H(NH_4)_2PO_4$, and H_3PO_4 (85 wt %) in ratio 0.333:2:1:1 and 2 cm^3 of water were introduced in a 25 mL Teflon container, sealed in a steel autoclave, heated at 220 °C for 20 h, and slowly cooled to 100 °C at a rate of 1°/h for 120 h. The resulting mixture was filtered, washed with water, and dried in air; it contains brown crystals of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$, pink lamellas of $NH_4CoPO_4{\cdot}H_2O$[9], and a small amount of unidentified blue powder. The presence of Co, V, and P atoms in crystals of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ was confirmed by EDS analysis. Attempts of syntheses, with stoichiometric ratios and different heating cycles, were unsuccessful to obtain a monophasic sample. They led to a mixture of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ and $NH_4CoPO_4{\cdot}H_2O$ crystals under slow cooling, and under quenching, the main powder product is $NH_4CoPO_4{\cdot}H_2O$, whereas the title phase is not formed. Despite the small size of the crystals, a small amount of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ single crystals was selected with tweezers for elemental microanalysis and TGA. The measured N/H ratios (3.26%/2.8%) are in agreement with the chemical formula and the expected ratios (3.14%/2.02%, respectively). The thermogravimetric analyses were performed on a SETARAM microbalance under argon and nitrogen atmosphere.

Structure Determination

A 0.020 × 0.082 × 0.096 mm^3 brown plate of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ was selected for the structure

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10.1021/cm001248q CCC: \$20.00

Table 1. Crystallographic Parameters for $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$

empirical formula	$NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$
fw (g)	445.8
crystal habit	light brown plate
a (Å)	6.4394(4)
b (Å)	7.4299(5)
c (Å)	9.854(1)
V (Å3)	471.44(6)
space group (N*o*.)	$Pmc2_1$ (No. 26)
ρ_{calc} ($g \cdot cm^{-1}$)	3.14
T (°C)	20
λ(Mo Kα) (Å)	0.71073
$h_{min} \rightarrow h_{max}$	$0 \rightarrow 12$
$k_{min} \rightarrow k_{max}$	$0 \rightarrow 14$
$l_{min} \rightarrow l_{max}$	$-19 \rightarrow 19$
std reflecns	3 every 3000 s
measd reflecns:	4115
independent reflecns with $I > 3\sigma(I)$	888
μ(Mo Kα) (mm^{-1})	4.86
abs corr	Gaussian
T_{min}, T_{max}	0.717, 0.942
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2]$ with $P = (\max(F_o^2,0) + 2F_c^2)/3$
params refined	61
ρ_{max}, ρ_{min}	1.36, −0.99
$R(F_o)^a$ (%), $R_w(F_o^2)^b$ (%)	3.92, 8.55

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]\}^{1/2}$.

Table 2. Atomic Parameters for $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$

atom	x	y	z	$U_{eq}{}^a/U_{iso}$
Co	0.2504(2)	0.0275(1)	0.00000	0.0074(2)
V	0.00000	0.2856(3)	0.2583(3)	0.0043(4)
P(1)	0.50000	0.1892(5)	0.2623(4)	0.0060(5)
P(2)	0.00000	0.6825(4)	0.0894(3)	0.0069(6)
O(1)	0.1952(9)	0.7985(8)	0.1090(6)	0.012(1)
O(2)	0.50000	0.097(1)	0.1212(9)	0.008(2)
O(3)	0.50000	0.056(1)	0.3792(9)	0.011(2)
H2O(4)	0.263(1)	0.2709(8)	−0.1114(6)	0.017(1)
HO(5)	0.00000	0.049(1)	0.3668(9)	0.007(2)
O(6)	0.00000	0.170(1)	0.1131(8)	0.008(2)
O(7)	0.00000	0.537(1)	0.1992(8)	0.011(2)
O(8)	0.3080(7)	0.3112(7)	0.2722(6)	0.007(1)
O(9)	0.00000	0.590(1)	−0.0492(9)	0.009(2)
N	0.50000	0.537(2)	0.041(1)	0.021(3)

[a] $U_{eq} = (1/3)\Sigma U_{ij}$.

Table 3. Distances (Å) and Bond Valence Calculations for the Cobalt, Vanadium, Phosphorus, and Oxygen Atoms in $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$

Co−O(1): 2.043(6)
Co−O(2): 2.068(6)
Co−O(3): 2.094(6)
Co−H_2O(4): 2.118(6)
Co−HO(5): 2.156(6)
Co−O(6): 2.227(6)
$\Sigma v[Co-O]$: *1.92(7)*

V−O(6): 1.670(8)
V−O(7): 1.954(9)
V−O(8): 1.997(5)
V−O(8): 1.997(5)
V−HO(5): 2.055(9)
V−O(9): 2.110(9)
$\Sigma v[V-O]$: *3.9(2)*

P(1)−O(3): 1.52(1)
P(1)−O(8): 1.536(5)
P(1)−O(8):1.536(5)
P(1)−O(2): 1.551(9)
$\Sigma v[P(1)-O]$: *4.8(1)*

P(2)−O(9): 1.529(9)
P(2)−O(7): 1.532(9)
P(2)−O(1): 1.536(6)
P(2)−O(1): 1.536(6)
$\Sigma v[P(2)-O]$: *4.8(1)*

N−O(1): 2.84(1) 2
N−O(4): 2.92(1) 2
N−O(8): 3.09(1) 2
N−O(8): 3.13(1) 2
N−O(9): 3.363(4) 2
N−O(2): 3.37(2)

Sv[O(1)−X]: 1.59(2)
Sv[O(2)−X]: 1.88(3)
Sv[O(3)−X]: 1.93(3)
Sv[O(4)−X]: 0.316(2)
Sv[O(5)−X]: 1.05(2)
Sv[O(6)−X]: 1.83(3)
Sv[O(7)−X]: 1.71(3)
Σv[O(8)−X]: 1.76(2)
Σv[O(9)−X]: 1.64(3)
with X = Co, V, P(1), and/or P(2)

determinations. The cell parameters were refined at 20 °C using 25 reflections. The data were collected with a CAD Enraf Nonius four circles diffractometer using the Mo Kα radiation. The data set was corrected for Lorentz and polarization effects and for absorption using Gaussian integration methods with the JANA98 software.[10] The structure resolutions, using the heavy atom method, and the refinements were performed with the SHELX97 programs.[11] The extinction conditions, $h0l$ ($l = 2n + 1$) and $00l$ ($l = 2n + 1$) are consistent with the space groups: $Pmcm$ (other setting of $Pmma$), $Pmc2_1$, and $P2cm$ (other setting of $Pma2_1$). An acceptable model was found only in the $Pmc2_1$ space group (No. 26) leading to $R(F_o) = 3.92\%$ and $R_w(F_o^2) = 8.55\%$ (Tables 1 and 2). The anisotropic thermal factors were refined for the Co, V, and P atoms only. Attempts to refine the O and N atoms led to two undefined U_{33} parameters for O(5) and O(9) because of the low ratio (observed reflections/refined parameters) (888/97) and due to the fact that the H atoms were not located. The bond valence calculated for the Co and V cations indicate that their valences are +2 and +4, respectively (Table 3). The calculations for the oxygen atoms suggest the presence of two hydrogen atoms linked to O(4) and one linked to O(5).

Structure Description and Comments

The projection of the structure of this new Co(II) vanadophosphate along a (Figure 1) shows that it can be described in two different manners, either by considering the entire framework $[Co_2(H_2O)_2HVO_2(PO_4)_2]_\infty$ (Figure 1A) or by considering that H_2O molecules are invited species in the $[Co_2HVO_2(PO_4)_2]_\infty$ host lattice (Figure 1B).

In the frame of the first description, the $Co_2(H_2O)_2HVO_2(PO_4)_2$ framework (Figure 1A) consists of PO_4 tetrahedra, VO_5OH, and $CoO_4(OH)(H_2O)$ octahedra. The structure can be described by the stacking, along b, of mixed $[Co_2VP(OH)(H_2O)_2O_7]_\infty$ layers connected through $PO_{4/2}$ tetrahedra (Figure 1A). Each cobaltovanadophosphate layer is built up from $[CoO_4]_\infty$ rutile chains (more exactly $CoO_{2.5}(OH)_{0.5}(H_2O)]_\infty$) and $[VPO_8]_\infty$ chains (more exactly $[V(OH)PO_7]_\infty$) which run along a and alternate along c (Figure 2). In the rutile chain, the common edges O(2)−O(3) and OH(5)−O(6) share alternatively their corners with two P(1) tetrahedra and two V octahedra of two adjacent chains; as a result the previous oxygen atoms are triply bonded as in the rutile structure. On the projection along a and c (Figures 1 and 3), we can see that the three dimensionnal framework delimits two types of tunnels. The first ones run along a and have a "C" shape section, with the center occupied by the water molecule H_2O(4). The second type of tunnels runs along c and exhibits a six sided section. The NH_4^+ cations sit at the intersection of the two sorts of tunnels, close to the border of the C type tunnels.

Considering the second description, the $Co_2HVO_2(PO_4)_2$ framework consists of PO_4 tetrahedra, VO_5OH octahedral, and $CoO_4(OH)$ square pyramids (Figure 1B)

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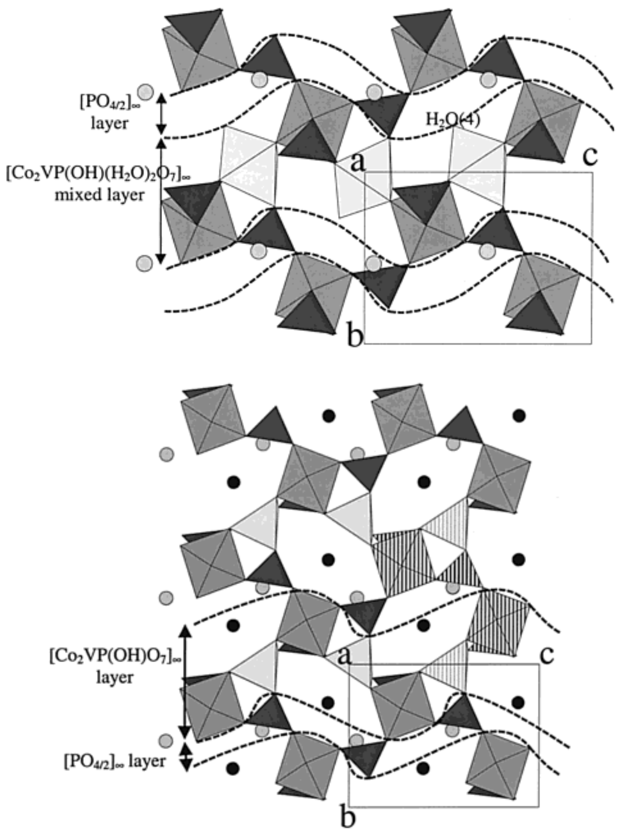

Figure 1. (A, top) Projection of the structure of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ along *a* showing the $[Co_2(H_2O)_2HVO_2(PO_4)_2]_\infty$ framework drawn with polyhedra. The $CoO_4(OH)(H_2O)$, VO_5-OH, and PO_4 polyhedra are drawn in light, medium, and dark gray; the NH_4^+ cations, with balls. (B, bottom) Projection of the structure of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ along *a* showing the $[Co_2HVO_2(PO_4)_2]_\infty$ framework drawn with polyhedra. The CoO_4-OH, VO_5OH, and PO_4 polyhedra are drawn in light, medium, and dark gray; the NH_4^+ and H_2O molecules, with light gray and black balls. The shaded polyhedra delimit the seven sided window located in the $(01\bar{2})$ plane.

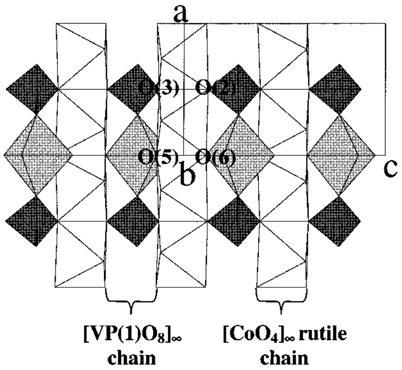

Figure 2. Projection of the $[Co_2VP(OH)(H_2O)_2O_7]_\infty$ layer along *b*.

forming large seven sided tunnels running along *a*. In this description, the buckling mixed $[Co_2VP(OH)(H_2O)_2O_7]_\infty$ layers are simply replaced by $[Co_2VP(OH)O_7]_\infty$ layers. But more importantly this description emphasizes the possible zeolithic character of this compound, the NH_4^+ cations being always located at the intersection of the two kinds of tunnels, whereas the H_2O molecules sit along the axis of the seven sided tunnels. The microporous character of this structure is also enhanced by the large size of the seven sided windows (Figure 4 and Figure 1B) oriented along $(0\bar{1}2)$ and $(O1\bar{2})$ planes, forming the [001] tunnels and which allow the communication between [100] tunnels.

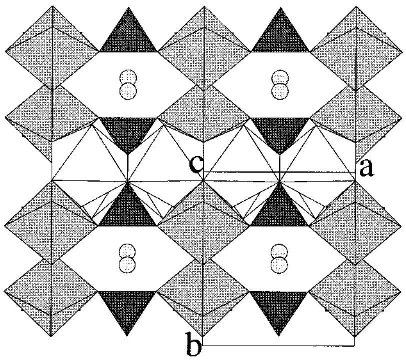

Figure 3. Projection of the structure of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ along *a*.

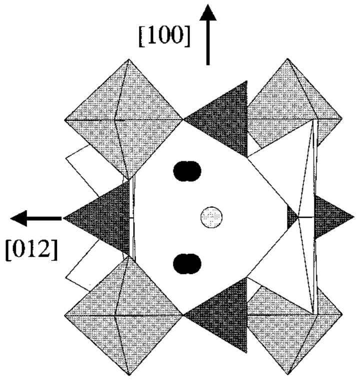

Figure 4. View of the seven sided window lying in the $(0\bar{1}2)$ plane. The CO_4OH, VO_5OH, and PO_4 polyhedra are represented in light, medium, and dark gray; the NH_4^+ and molecules, with light and dark balls.

The geometry of the polyhedra of this structure is classical as shown from the interatomic distances and angles (Table 3). The $CoO_4OH(H_2O)$ octahedron is distorted with Co−O distances ranging from 2.043(6) to 2.227(6) Å, as well as the CoO_4OH pyramid. The VO_5-OH octahedron is characterized by a short V−O bond, characteristic of vanadyl (1.670(8) Å) as opposed to the longest one (2.110(9) Å), whereas the four other ones are intermediate (1.954(9)−2.055(9) Å). Note that the vanadyl group is directly connected to cobalt, leading for the V═O−Co bond to a large Co−O distance (2.227(6) Å). This shows the great ability of cobalt to accommodate large distortions of its polyhedra. The monophosphate groups $P(1)O_4$ and $P(2)O_4$ are regular with P−O distances ranging from 1.52(1) to 1.551(9) Å. The NH_4^+ cation is surrounded by eleven oxygen atoms with N−O distances ranging from 2.84(1) to 3.37(2) Å. This structural study confirms the ability of cobalt to form chains of CoO_6 octahedra, when associated with PO_4 tetrahedra. Rutile chains have indeed been evidenced in $NaCoPO_4$,[12] whereas chains of cis and trans edge sharing octahedra, and chains of face sharing octahedra were observed in $CaCo_3(P_2O_7)_2$[13] and $V_{0.94}Co_{0.46}[PO_4(OH)_{0.74}(H_2O)_{0.26}]$,[8] respectively.

The above description of this structure suggests the possibility of topotactic dehydration of this compound.

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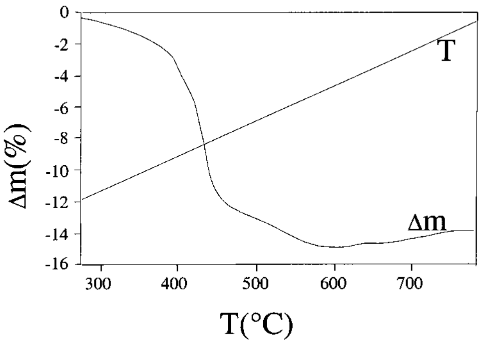

Figure 5. TGA of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ under Ar.

The investigation of the thermal stability under inert atmospheres was performed. Under argon, $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ loses 15% of its weight in two steps (Figure 5). The first weight loss, equal to 12%, occurs between 285 and 460 °C and corresponds to the release of the two water molecules located in the tunnels and then to the release of the ammonia molecule ($\Delta m_{th} = -12\%$); the second one, equal to 3.5% occurs between 460 and 600 °C and corresponds to the release of the water molecule formed by the hydroxyl group O(5)H and the H^+ cations left by the loss of ammonia ($\Delta m_{th} = -4\%$). A second TGA measurement was performed under N_2 in order to confirm and study the dehydration of this compound. At 350 °C, the mass loss is equal to 8.8% and corresponds to the release of the two water molecules contained in the tunnels; the elemental analysis of this dehydrated compound confirms that at this temperature NH_4^+ cations are still present, showing a nitrogen content of 3.3% in agreement with the chemical formula $NH_4Co_2HVO_2(PO_4)_2$. When the dehydrated compound is exposed to air at 25 °C, it exhibits limited rehydration properties, reabsorbing slowly only up to 0.5 water molecule. In fact the zeolithic character of $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ is limited by the low stability of this structure, which loses ammonia at 460 °C under N_2, leading to an amorphous compound.

In conclusion, a new cobalt(II) vanadophosphate has been evidenced despite the existence of very few compounds in this system. This original structure, built up of rutile chains, is, after the hydrate $Co(VO)_2(PO_4)_2 \cdot 4H_2O$,[7] the second example of cobalt vanadophosphate with an intersecting tunnel structure. The cobalt vanadium phosphate framework is stable under inert atmosphere up to 350 °C, where the water molecules can be removed from the tunnels without structural changes of the framework as shown by XRPD. Although $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ collapses at 460 °C, it shows that vanadium phosphates containing cobalt are interesting candidates for isolating new stable zeolithic structures with vanadium. Further research of this system is in progress.

Supporting Information Available: Tables giving anisotropic thermal parameters and the list of structure factors for $NH_4Co_2(H_2O)_2HVO_2(PO_4)_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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