Intercalated Vanadyl Vanadates: Syntheses, Crystal Structures, and Magnetic Properties

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Two compounds $(AH_2)_{0.5}V_2O_5$ (A = ethylenediamine, piperazine) have been synthesized hydrothermally (180 °C, 24 h, autogeneous pressure). They are triclinic (space group $P\bar{1}$) with the following lattice parameters: $a = 6.253(3)$ Å, $b = 6.397(4)$ Å, $c = 7.470(4)$ Å, $\alpha = 78.67(4)°$, $\beta = 80.16(4)°$, $\gamma = 77.20(4)°$ with $Z = 2$ for A = ethylenediamine; $a = 6.3913(7)$ Å, $b = 6.4151(8)$ Å, $c = 8.2041(9)$ Å, $\alpha = 94.508(7)°$, $\beta = 105.934(7)°$, $\gamma = 104.030(5)°$ with $Z = 2$ for A = piperazine. The inorganic layers are formulated $[V_2O_5]^-$ with V^{IV} and V^{V} located on two different crystallographic sites. Vanadium(IV) realizes a square pyramidal coordination. Each $V^{IV}O_5$ polyhedron shares an edge with another one to ensure $[V_2O_8]$ units in which the two terminal apices point respectively up and down relative to the middle plane constituted by the six equatorial oxygens. Vanadium(V) is tetrahedrally coordinated; each $V^{V}O_4$ tetrahedron is linked to three $[V_2O_8]$ units, the fourth oxygen being free.

Introduction

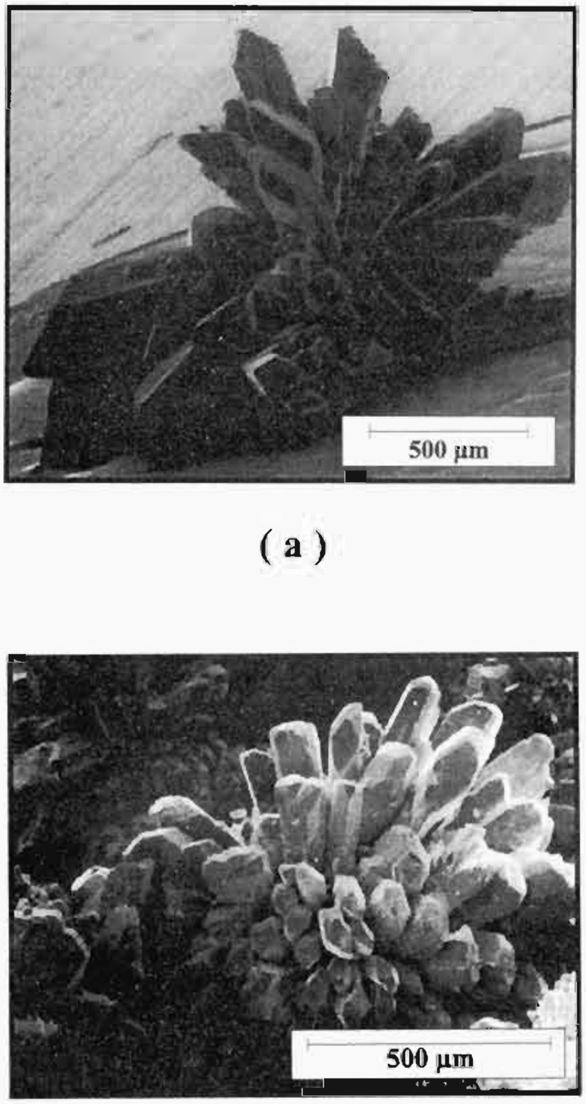
With a view to synthesizing oxyfluorinated silicovanadates possessing microporous frameworks, we have investigated the systems $V_2O_5-SiO_2-HF-H_2O$–amine and obtained large crystals of intercalated vanadium oxides free of fluorine and silicon, which only induce a better crystallization as previously reported.[1–7]

We have already described $(1,3\text{-diaminopropaneH}_2)V_4O_{10}$,[8] the first example of a vanadyl vanadate with an organic molecule intercalated between the $[V_2O_5]^-$ layers. This paper presents the syntheses and the structure determinations of two new vanadyl vanadates: $VO(VO_4)(\text{ethylenediammonium})_{0.5}$ and $VO(VO_4)(\text{piperazinium})_{0.5}$.

Experimental Section

The two title compounds have been prepared hydrothermally from mixtures of $V_2O_5-SiO_2-HF$–amine (ethylenediamine or piperazine)–H_2O in molar ratios of 1:2:2:1:80, which were placed in a Teflon-lined steel autoclave and heated at 453 K for 24 h under autogeneous pressure. The pH increased from 5 to 7 during the preparation with ethylenediamine whereas it remained constant around 4 for the other preparation. The resultant products were washed with water and then dried at room temperature (yields: 90% for piperazine and 80% for ethylenediamine). The presence of unreacted silica powder was observed in both preparations in the form of fine particles easily extractable by filtering. Both phases were obtained as millimetric dark green crystals. Scanning electron micrographs of the two kinds of crystals are shown in Figure 1. The system using ethylenediamine also contained another type of orange crystal corresponding to a decavanadate species. There was no reaction if silica (quartz, α form) was missing.

The absence of fluorine and silicon in the greenish crystals was verified by EDX analysis on a JEOL-2010 TEM equipped with a



(b)

Figure 1. Scanning electron micrographs of $(pipH_2)_{0.5}V_2O_5$ (a) and $(enH_2)_{0.5}V_2O_5$ (b).

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Table 1. Crystallographic Data for $(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$ (in Italics)

$(N_2C_2H_{10})_{0.5}VO(VO_4)$	212 g		
$(N_2C_4H_{12})_{0.5}VO(VO_4)$	*226 g*		
a = 6.253(3) Å	*a = 6.3913(7) Å*	triclinic	P -1 (n°2)
b = 6.397(4) Å	*b = 6.4151(8) Å*	T = 20 °C	
c = 7.470(4) Å	*c = 8.2041(9) Å*	λ (MoKα) = 0.71073 Å	
α = 78.67(4) °	*α = 94.508(7) °*	$\rho_{calc.}$ = 2.498 (*2.422*) g.cm^{-3}	
β = 80.16(4) °	*β = 105.934(7) °*	μ = 34.548 (*31.51*) cm^{-1}	
γ = 77.20(4) °	*γ = 104.030(5) °*		
V = 283.2(3) Å^3	*V = 309.98(6) Å^3*	R1 (F_O) = 0.0181 / *0.0269*	
Z = 2	*Z = 2*	wR2 (F_O^2) = 0.0536 / *0.0658*	

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$ (in Italics)[a]

atoms	**x**	**y**	**z**	**U(eq)**
V(1)	3305(1)	1551(1)	6122(1)	11(1)
	1450(1)	*2576(1)*	*9387(1)*	*10(1)*
V(2)	1546(1)	7161(1)	5623(1)	10(1)
	3033(1)	*8050(1)*	*8975(1)*	*10(1)*
O(1)	3651(2)	1158(2)	8261(1)	24(1)
	2705(3)	*7632(3)*	*6935(2)*	*24(1)*
O(2)	-175(1)	8236(1)	3930(1)	15(1)
	3710(2)	*1179(2)*	*9746(2)*	*14(1)*
O(3)	219(2)	6994(2)	7708(1)	23(1)
	-25(2)	*2172(3)*	*882(2)*	*16(1)*
O(4)	2824(2)	4631(1)	5228(2)	19(1)
	-229(3)	*1958(3)*	*7432(2)*	*24(1)*
O(5)	3762(1)	8676(1)	5390(1)	15(1)
	2782(3)	*5288(2)*	*9751(3)*	*22(1)*
ethylenediamine				
N	2502(2)	7131(2)	608(2)	25(1)
C	5857(2)	4945(3)	9154(2)	24(1)
piperazine				
N	2821(3)	5114(4)	4014(3)	24(1)
C(1)	5087(5)	3520(5)	6247(3)	27(1)
C(2)	3123(4)	3045(4)	4619(4)	26(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Principal Distances (Å) and Angles (deg) in $(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$ (in Italics)

$V^{IV}O_5$ square pyramids

V(1)	**O(1)**	**O(4)**	**O(2)**	**O(5)**	**O(5)**
V(2)	***O(1)***	***O(5)***	***O(3)***	***O(2)***	***O(2)***
O(1)	**1.614(1)**	2.876(2)	2.859(1)	2.894(1)	2.921(1)
O(1)	***1.621(2)***	*2.850(3)*	*2.813(3)*	*2.926(2)*	*2.941(2)*
O(4)	108.27(8)	**1.9274(9)**	2.657(1)	3.707(1)	2.701(1)
O(5)	*107.1(1)*	***1.915(2)***	*2.656(3)*	*3.681(2)*	*2.686(2)*
O(2)	106.71(6)	86.78(5)	**1.941(1)**	2.6900(9)	3.728(1)
O(3)	*104.45(9)*	*87.38(9)*	***1.930(2)***	*2.672(2)*	*3.722(2)*
O(5)	107.33(6)	144.17(7)	86.95(4)	**1.969(1)**	2.468(1)
O(2)	*109.19(9)*	*143.53(9)*	*86.74(7)*	***1.961(1)***	*2.472(3)*
O(5)	108.47(6)	87.57(5)	144.37(5)	77.45(4)	**1.9756(9)**
O(2)	*109.36(9)*	*87.35(7)*	*145.84(8)*	*77.83(7)*	***1.975(1)***

$V^{V}O_4$ tetrahedra

V(2)	**O(3)**	**O(4)**	**O(2)**	**O(5)**
V(1)	***O(4)***	***O(5)***	***O(3)***	***O(2)***
O(3)	**1.631(1)**	2.711(2)	2.819(1)	2.845(1)
O(4)	***1.622(2)***	*2.692(2)*	*2.788(2)*	*2.886(2)*
O(4)	109.05(7)	**1.697(1)**	2.760(1)	2.809(1)
O(5)	*108.1(1)*	***1.703(1)***	*2.746(3)*	*2.839(2)*
O(2)	113.31(6)	106.70(7)	**1.742(1)**	2.950(1)
O(3)	*112.05(9)*	*105.8(1)*	***1.740(2)***	*2.973(2)*
O(5)	110.47(7)	105.55(6)	111.36(5)	**1.829(1)**
O(2)	*112.4(1)*	*106.10(8)*	*111.93(9)*	***1.847(2)***

Hydrogen bonds

O(1)—H(2): 2.178(7)	O(3)—H(5): 2.425(2)
O(2)—H(3): 1.984(6)	O(3)—H(1): 1.94(1)
O(1)—H(b): 1.954(3)	*O(3)—H(a): 2.169(3)*

KEVEX energy-dispersive X-ray spectrometer. The TGA experiments performed under an O_2 flow on a SETARAM TGDTA92 apparatus confirmed 2:1 V_2O_5: amine ratios. Moreover, in a first step (at 330 °C for $(enH_2)_{0.5}V_2O_5$ and 320 °C for $(pipH_2)_{0.5}V_2O_5$ (pip = piperazine)), one observes the loss of the amine and one oxygen (for $(enH_2)_{0.5}V_2O_5$, $\%_{exp} = 21.3$, $\%_{th} = 22.1$; for $(pipH_2)_{0.5}V_2O_5$, $\%_{exp} = 26.2$, $\%_{th} = 26.5$), the resulting product being VO_2. This transformation is immediately followed by the reoxidation of the VO_2 to V_2O_5.

The crystals were selected optically, and their quality was determined by Laue photographs. The intensities of X-ray diffraction were collected on a Siemens AED-2 four-circle diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). The conditions of data collection are summarized in Table 1. The data were corrected for Lorentz–polarization effects, and an absorption correction based on the crystal morphology was applied. Both structures were solved using the direct method of the SHELXS-86[9] option TREF. Vanadium atoms were first located and the remaining atoms deduced from Fourier difference syntheses using the SHELXL-93 program.[10]

Refinements with anisotropic thermal parameters for all atoms (except H refined with a common isotropic factor) led to the reliability factors R1 = 0.018 and wR2 = 0.054 for $(enH_2)_{0.5}V_2O_5$ and R1 = 0.027, wR2 = 0.066 for $(pipH_2)_{0.5}V_2O_5$. The atomic coordinates are listed in Table 2 and the principal bond lengths and angles in Table 3.

Magnetic susceptibility measurements were performed on a Faraday balance between 4 and 300 K.

Discussion

$(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$ exhibit some topological similarities to $VO(HPO_4){\cdot}0.5H_2O$.[11,12] They present bidimensional frameworks with inorganic and organic layers alternating along [001] (Figure 2). The two structures differ only by the composition of their organic parts and by the linkages between

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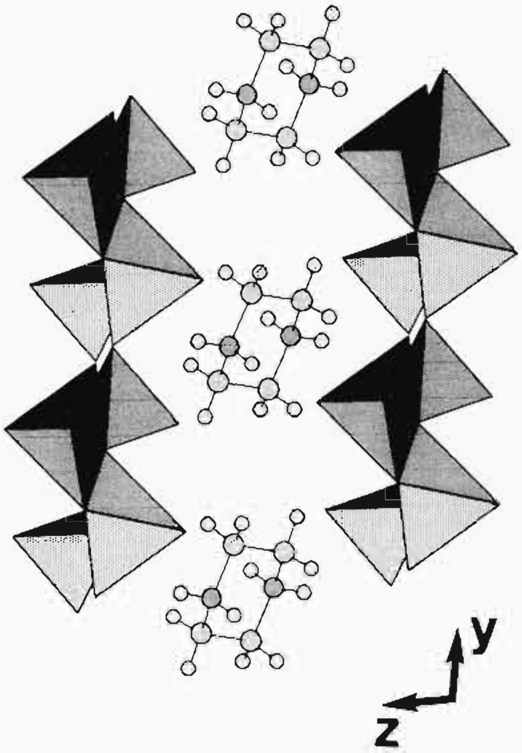

Figure 2. Projection of $(pipH_2)_{0.5}V_2O_5$ along [100].

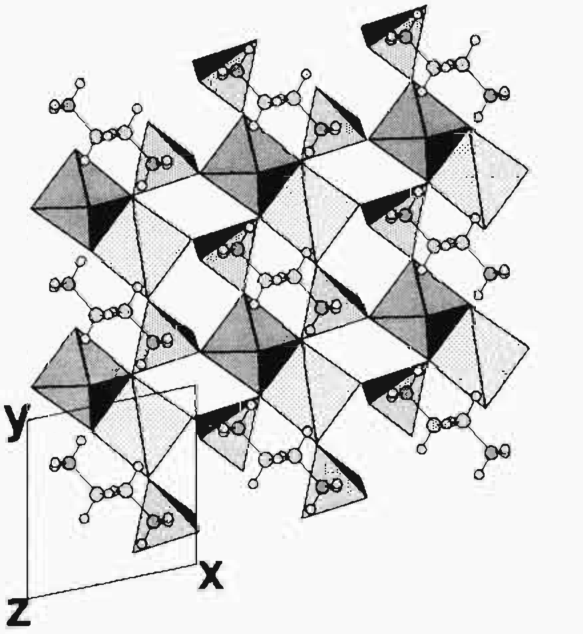

Figure 3. Projection of $(enH_2)_{0.5}V_2O_5$ along [001]. *The diagonals which appear on the light squares are an artifact of the drawing, but the basal plane is strictly square.*

the amines and the inorganic layers. The relations between the metric parameters correspond to $a_{en} \leftrightarrow b_{pip}$, $b_{en} \leftrightarrow a_{pip}$, and $c_{en} \leftrightarrow c_{pip}$ with significant differences for the angular parameters due to the shape of each amine. The increase in the *c* parameter from the ethylenediamine to the piperazine compound (7.470(4) vs 8.2041(9) Å) is explained by the larger size of the piperazine.

In the inorganic layers formulated $[V_2O_5]^-$ (Figure 3), V^{IV} and V^V are located on two different crystallographic sites. In the $V^{IV}O_5$ tetragonal pyramids, the V−O bonds corresponding to the basal plane lie in the range 1.915−1.976 Å, while the shorter distances (1.614(1) and 1.621(2) Å) correspond to the free apices of the $V^{IV}O_5$ square pyramids. Each of them shares an edge with another one to ensure $[V_2O_8]$ units in which the two terminal apices point respectively up and down relative to the middle plane constituted by the six equatorial oxygens.

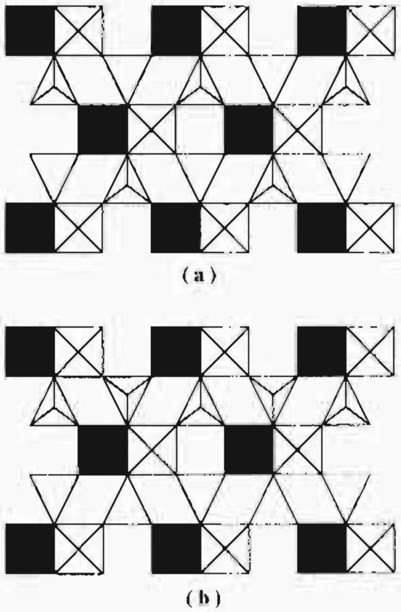

Figure 4. Schematic representations of the $[VO(VO_4)]^-$ layers in $(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$ (a) and in CsV_2O_5 (b).

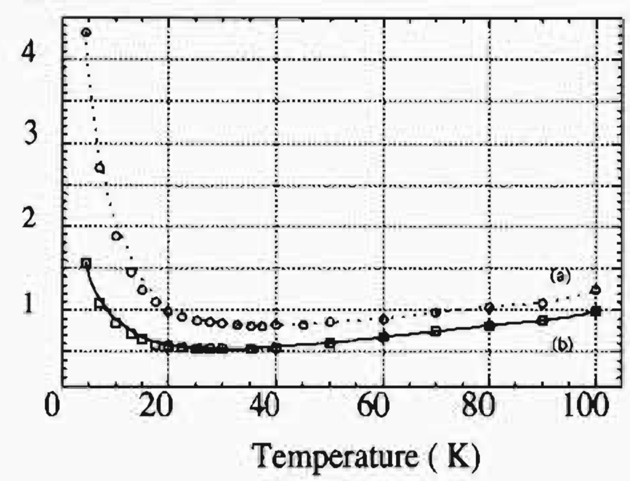

Figure 5. Thermal variation of the inverse of the magnetic susceptibility (per gram) for $(pipH_2)_{0.5}V_2O_5$ (a) and $(enH_2)_{0.5}V_2O_5$ (b).

Vanadium(V) is tetrahedrally coordinated with four V−O distances in the range 1.622−1.847 Å. The longest V−O distance occurs with an oxygen atom of the common edge of a bipyramidal unit, the two intermediate distances occur with two different $[V_2O_8]$ groups, and the shortest corresponds to the free apex of the V^VO_4 tetrahedron. This terminal oxygen points toward the organic layers and alternatively up and down from one tetrahedron to the other. The same type of V_2O_5 layers is already encountered in the compound synthesized with 1,3-diaminopropane as the organic intercalate.[8] The two frameworks differ only by the mode of stacking of the inorganic layers. In $(enH_2)_{0.5}V_2O_5$ and $(pipH_2)_{0.5}V_2O_5$, one observes the exact superposition of the same V_2O_5 layers whereas, in V_4O_{10} (1,3-DAP) one layer alternates with its equivalent by a symmetry transformation; consequently the *c* parameter is twice as large. The substitution of the protonated amine by a Cs^+ cation leads to CsV_2O_5, a compound described by Mumme et al.[13] Its structure is closely related to ours and is built from the same

$[V_2O_8]$ bipyramidal units and V^VO_4 tetrahedra. The connections are identical, but the bipyramidal units are linked by rows of V^VO_4 tetrahedra alternatively all up or all down. The topologies of these two kinds of V_2O_5 layers are schematically illustrated in the Figure 4.

The stability of the structure is ensured by strong hydrogen bonds between the hydrogens of the amino groups and the terminal oxygens of the inorganic layers. In $(enH_2)_{0.5}V_2O_5$ the strongest hydrogen bonds occur with the terminal oxygen of the V^VO_4 tetrahedra whereas in $(pipH_2)_{0.5}V_2O_5$ they occur with the free apices of the $V^{IV}O_5$ square pyramids. This may be due to the different steric hindrances of the amines.

Magnetic Measurements. The thermal variation of the inverse susceptibility is illustrated in Figure 5, which clearly shows that the two compounds order antiferromagnetically below 25(3) K. The characteristics of the curves are very closely related to those described by Trombe et al.[14] for $VOSeO_3$. In the latter compound, the lone pair of the Se^{IV} substitutes for the free apices of the V^VO_4 tetrahedra in our vanadyl vanadates. The magnetic behavior proposed by the authors for $VOSeO_3$ strictly applies to our cases.

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Supporting Information Available: Listings of structure determination details, atomic coordinates, thermal parameters, and bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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