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Synthesis, Structure, and Magnetic Properties of $(NH_4)VOPO_4$: A Structure with One-Dimensional Chains of VO_6 Octahedra

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The title compound $(NH_4)VOPO_4$, (1), was synthesized hydrothermally from a mixture of $CsVO_3$, V, $CH_3PO_3H_2$, $(NH_4)_2HPO_4$, $(C_2H_5)_3CH_3NBr$, and H_2O in the mole ratios 3.96:1:4.88:11.97:4.96:1498. Phosphate (1) crystallizes in the orthorhombic space group *Pnn*2 with $a = 10.5119(2)$ Å, $b = 12.917(3)$ Å, $c = 6.462(1)$ Å, $V = 877.3(4)$ Å^3, $Z = 4$, and $R = 0.043$. The framework consists of one-dimensional chains of corner-sharing VO_6 octahedra joined together by phosphate tetrahedra which generates cation filled tunnels running parallel to the c axis. There are two unique vanadium sites, with the VO_6 octahedra connected to their neighbors through alternating *cis*-O–V–O and *trans*-O–V–O linkages. At higher temperatures, the compound is paramagnetic with isolated V^{4+} d^1 centers while complicated, short range antiferromagnetism is observed below 10 K. The framework is closely related to that of $KVOPO_4$.

INTRODUCTION

Vanadium phosphate systems are of interest for their catalytic properties (1, 2) as well as their diverse structural and magnetic characteristics. There V–P–O phases have been shown to possess a wide variety of different structural types, some examples of which are $AVOPO_4$ and $A[VOPO_4]_2$ (3), $A_2(VO)_n(P_2O_7)$ (4), $A_{0.5}VOPO_4 \cdot xH_2O$ (5), and AVP_2O_7 (6), where A = alkali or alkaline earth metal cation. Structures are also known that contain (HPO_4) or (H_2PO_4) tetrahedra (7), as well as materials that include additional transition metals besides vanadium (8). The title compound is a member of the $AVOPO_4$ class with $A = NH_4^+$. Although other oxovanadium phosphates with ammonium cations are known, such as the α- and β- forms of $NH_4(VO_2)(HPO_4)$ (9), the vanadium centers in these compounds are in +5 oxidation state rather than the +4 state observed for NH_4VOPO_4. In this paper we report the synthesis and characterization of $(NH_4)VOPO_4$, (1). The structure of (1) is composed of one-dimensional (1-D) strands of VO_6 octahedra sharing corners in a *cis–trans* arrangement in the ac plane in the spacegroup *Pnn*2. These strands are joined together via phosphate bridges, giving a connectivity that generates tunnels occupied by the ammonium cations. While compound (1) exhibits paramagnetic behavior at high temperatures, a broad maximum is observed near 4 K suggesting short range antiferromagnetic exchange. Long-range exchange results in an antiferromagnetic phase transition at 3.7 K. The framework is very similar to that of $KVOPO_4$.

EXPERIMENTAL

Synthesis. The title compound was hydrothermally synthesized from a mixture of −325 mesh vanadium metal (0.3706 mmole), −100 mesh $CsVO_3$ (1.472 mmole), $CH_3PO_3H_2$ (1.814 mmole), $(NH_4)_2HPO_4$ (4.440 mmole), $(C_2H_5)_3CH_3NBr$ (2.158 mmole), and H_2O (555.6 mmole). The mixture, in the molar ratios of $CsVO_3$:V:$CH_3PO_3H_2$:$(NH_4)_2HPO_4$:$(C_2H_5)_3CH_3NBr$:H_2O as 3.96:1:4.88:11.97:4.96:1498, was heated in a 23 ml polytetrafluoroethylene lined vessel at 200°C for four days. This afforded reddish-brown, diamond shaped crystals of the title compound. The crude product was washed several times with water, and the yield was found to be about 60% (based on total V) while an additional product was formed in approximately 40% yield. We were unable to find reaction conditions capable of suppressing the formation of the impurity phase.

Crystallography. A single crystal having the dimensions 0.15 × 0.16 × 0.10 mm was selected for indexing. Crystal data, data collection, solution, and refinement information are given in Table 1. Atomic positional parameters are presented in Table 2 and selected bond lengths and angles are found in Table 3.

Magnetism. The magnetic susceptibility data were recorded on a manually selected 81.77 mg polycrystalline sample of the title compound over the temperature range 2.3–300 K using an S.H.E. Corp. SQUID susceptometer. Measurement and calibration techniques have been reported elsewhere (10). The magnetic data are reported as

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TABLE 1
Experimental Crystallographic Data

A. Crystal data	
Crystal system	orthorhombic
Space group	*Pnn*2
Unit cell dimensions	a = 10.511(2) Å
	b = 12.917(3) Å
	c = 6.462(1) Å
Volume	877.3(4) Å^3
Z	4
Formula weight	359.9
Density (calc.)	2.725 Mg/m^3
Absorption coefficient	2.548 mm^{-1}
F(000)	712
B. Data collection	
Diffractometer	Rigaku AFC 5S
Radiation	Mo$K\alpha$(λ = 0.71073 Å)
Temperature	213 (K)
Monochromator	graphite crystal
2θ range	2.0 to 45.0°
Scan type	$\theta/2\theta$
Scan speed	6.00°/min in θ
Scan range (θ)	1.10°
Standard reflections	3 out of every 100
Reflections collected	2018
Independent reflections	1209 (R_{int} = 0.023)
Observed reflections	962 [$F > 6.0\sigma(F)$]
Absorption correction	ψ scans on 5 reflections
C. Solution and refinement	
System used	Siemens SHELXTL PLUS (PC version)
Solution	direct methods
Refinement method	full-matrix least-squares
Quantity minimized	$\Sigma\, w(F_o - F_c)^2$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting	$w^{-1} = \sigma^2(F) + 0.00010F^2$
Refined parameters	85
Final R indices (obs. data)	$R(R_w)$ = 0.0433(0.0501)
R indices (all data)	$R(R_w)$ = 0.0664(0.0671)
Goodness-of-fit	2.43
Largest and mean Δ/σ	0.012, 0.002
Data-to-parameter ratio	17.9 : 1
Largest peak	0.52 e Å^{-3}
Largest hole	−0.22 e Å^{-3}

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 $\times$ 10^3) for NH_4VOPO_4

	x	y	z	U(eq)
V(1)	2406(1)	1248(1)	27(5)	7(1)
V(2)	−50(2)	2514(2)	2714(5)	7(1)
P(1)	0	5000	3318(7)	5(1)
P(2)	2590(2)	1826(1)	4962(6)	6(1)
P(3)	0	0	1715(8)	7(1)
O(1)	1169(6)	5190(5)	4747(13)	11(1)
O(2)	251(6)	4024(6)	1972(11)	8(1)
O(3)	2137(6)	6116(5)	8076(11)	9(1)
O(4)	3514(5)	7573(5)	9441(10)	8(1)
O(5)	1239(5)	7513(5)	10370(10)	7(10)
O(6)	2746(7)	6162(5)	1881(11)	9(1)
O(7)	−150(6)	963(5)	3077(11)	9(10)
O(8)	3827(6)	5128(6)	5341(12)	11(2)
O(9)	3609(6)	7209(5)	5398(11)	9(1)
O(10)	−1099(5)	2770(5)	4559(11)	8(10)
N(1)	750(8)	3859(7)	−2140(14)	24(2)
N(2)	6725(8)	5956(6)	1777(12)	16(2)

the molar magnetic susceptibility plotted as a function of temperature over the entire temperature region.

RESULTS AND DISCUSSION

The title compound was synthesised hydrothermally using $CsVO_3$, vanadium metal, $CH_3PO_3H_2$, $(NH_4)_2HPO_4$, $(C_2H_5)_3CH_3NBr$, and H_2O in the molar ratios of 3.96 : 1 : 4.88 : 11.97 : 4.96 : 1498. Although two of the starting materials, $(C_2H_5)_3CH_3NBr$ and $CH_3PO_3H_2$ do not appear in the product, omission of both of them resulted in a product that had a different X-ray powder pattern than the title compound. Omission of just the phosphonate resulted in a lower yield as did the use of other alkylammonium and phosphonium bromides such as $(CH_3)_4NBr$, $(C_2H_5)_4NBr$, $(C_4H_9)_4NBr$, and $(C_6H_5)_4PBr$. Use of V_2O_5 as the source of V^{+5} in place of $CsVO_3$ gave a multiphase, low yield of (**1**).

The structure of (**1**) consists of a three-dimensional (3-D) anionic framework built up from VO_6 octahedra and PO_4 tetrahedra. The VO_6 octahedra share corners in a *cis–trans* fashion and generate chains or strands that run diagonally in the **ac** plane as seen in Fig. 1. Each of the crystallographically inequivalent vanadium atoms are joined together through both short (V1–O9 1.654(6) Å, V2–O10 1.657(7) Å), and longer (V1–O6 2.042(7) Å, V2–O9 2.166(7) Å) bonds. Thus the V–O–V–O backbone of the chains has alternating long and short V–O bonds. The $[V–O–V]_\infty$ chains that run parallel to the 101 direction

TABLE 3
Selected Bond Lengths (Å)

V(1)–O(1*B*)	2.036(7)	V(1)–O(3*B*)	2.036(7)
V(1)–O(6*A*)	2.042(7)	V(1)–O(8*B*)	1.953(7)
V(1)–O(9*A*)	1.654(6)	V(1)–O(10*A*)	2.041(6)
V(2)–O(2)	2.033(8)	V(2)Z–O(7)	2.021(7)
V(2)–O(10)	1.657(7)	V(2)–O(4*A*)	1.964(6)
V(2)–O(5*A*)	1.9964(7)	V(2)–O(9*A*)	2.166(7)
P(1)–O(1)	1.557(8)	P(1)–O(2)	1.554(8)
P(2)–O(3*A*)	1.552(8)	P(2)–O(4*A*)	1.547(7)
P(2)–O(5*B*)	1.540(6)	P(2)–O(6*B*)	1.548(8)
P(3)–O(7)	1.532(7)	P(3)–O(8*A*)	1.528(7)

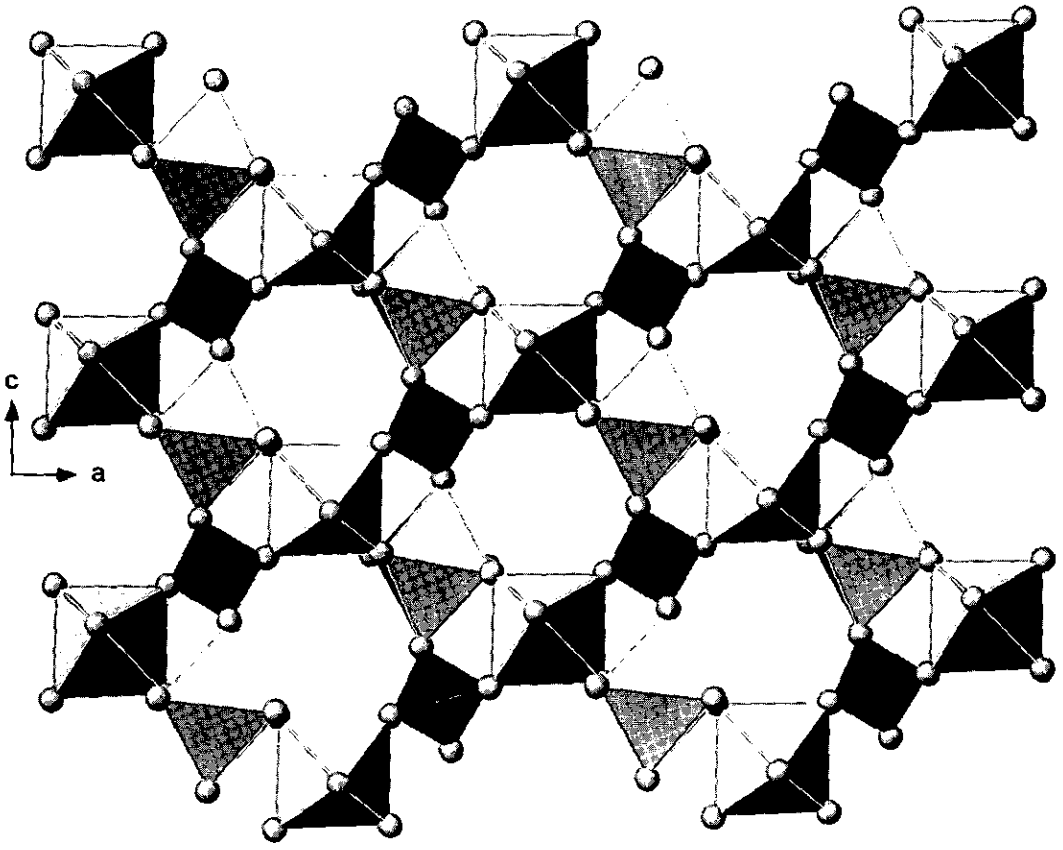

FIG. 1. View of (1) down **b**, showing the connectivity of the 1-D chains.

are in turn linked through P2. This connectivity of the octahedra and tetrahedra generates tunnels occupied by the ammonium cations, as shown in Fig. 2a.

It is of interest to note that in the $AVOPO_4$ series of vanadium(IV) phosphates (A = alkali metal or ammonium cation) only $KVOPO_4$ and NH_4VOPO_4 have this *cis–trans* mode of VO_6 octahedral connectivity. The ammonium and potassium compounds have very similar frameworks with the potassium analogue crystallizing in the space group $Pna2_1$ with a = 12.816(5) Å, b = 6.388(2) Å and c = 10.556(5) Å (3). The close similarities of the two frameworks can be seen in Figs. 2a and 2b, which shows a projection down the **c** axis for NH_4VOPO_4 and down **b** for $KVOPO_4$ respectively. Although the tunnels in both compounds are approximately the same size and provide similar environments for the cations, the location of the cations in the tunnels is different. In $KVOPO_4$, the two potassium cations are positioned in a similar manner within each tunnel, whereas in (**1**) the ammonium pairs alternate "up" and "down" with reference to an imaginary line drawn through the vanadium centers that lie in a plane parallel to the **bc** plane. This is evident in Fig. 2a as a zigzag arrangement of the NH_4^+ cations as opposed to a linear one for the K^+ cations in Fig. 2b. This observation may be rationalized by difference in the size of the cations, coupled with the fact that ammonium can H-bond to the framework. The N· · ·O distances indicate that each ammonium cation is hydrogen bonded to four framework O atoms with N1 to O1, O2, O4, and O9 distances of 2.69(1), 2.74(1), 2.85(1) Å, respectively, and N2 to O6, O7, O8, and O10 distances of 2.79(1), 2.90(1), 2.78(1) and 2.82(1) Å, respectively.

The thermal stability of the NH_4^+ cation in (**1**) was examined by thermal gravimetric analysis (TGA), which was performed under an N_2 atmosphere. At 400°C, a 9.7% weight loss was observed that corresponds to one ammonium cation per $VOPO_4$ unit being expelled from the framework, in agreement with the calculated weight loss which is 10%.

The magnetization of (**1**) was studied over the range 2.5 K < T < 300 K. At higher temperatures (T > 25 K), the magnetic susceptibility data of the title compound exhibits Curie–Weiss paramagnetism according to (Eq. [1])

$$x = C/(T - \theta) = [Ng^2\mu_B^2 S(S + 1)]/3k(T - \theta) \quad [1]$$

with C = 0.834 emu–K/mole and θ = −4.7 K. The

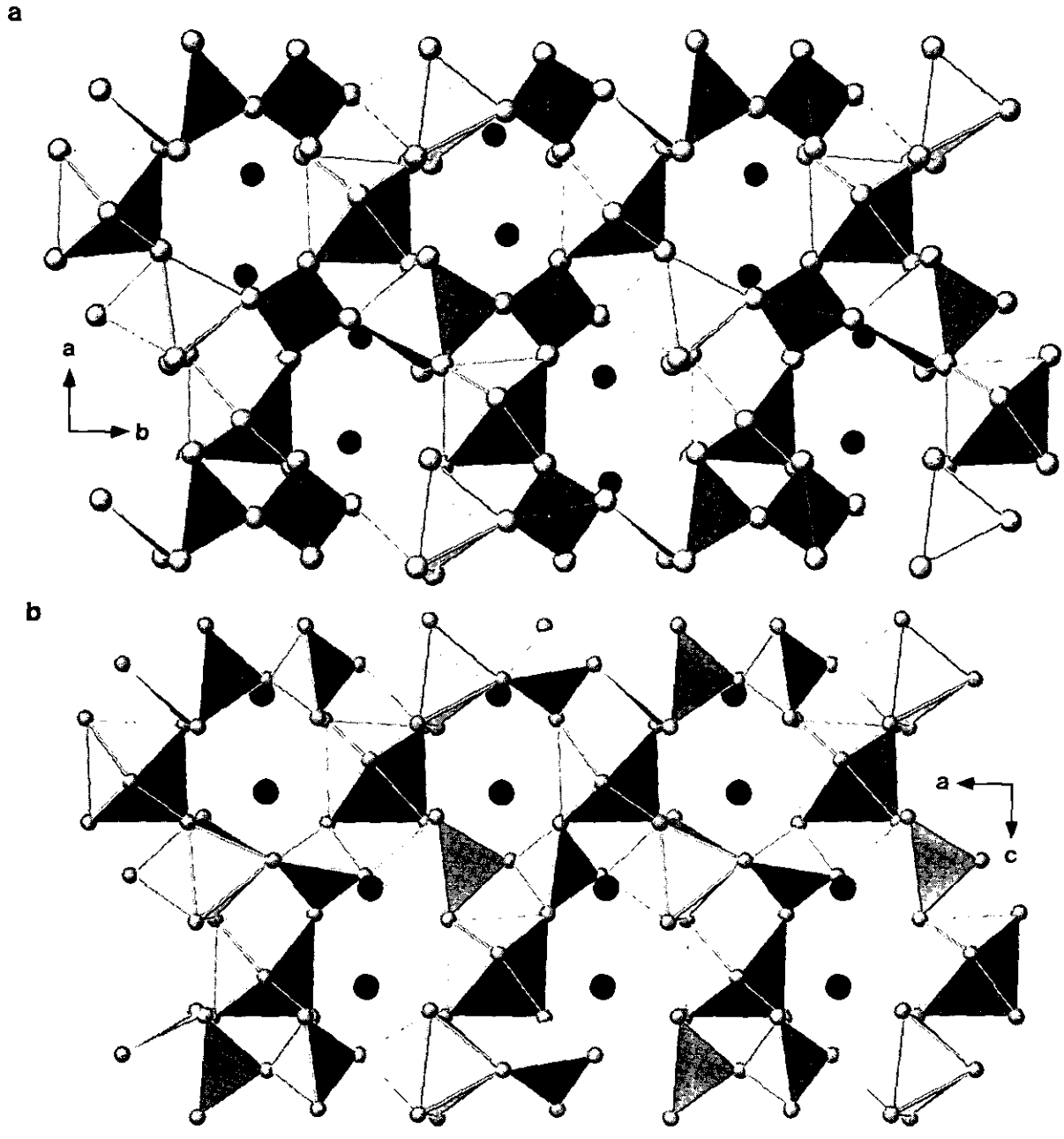

FIG. 2. (a) View of (1) down **c**, showing the ammonium cations in the cavities (b) view of $KVOPO_4$ down **b**, showing the location of the potassium cations and the similarity of the frameworks.

electron structure of $(NH_4)VOPO_4$ corresponds to one unpaired electron per V(IV) formula unit, resulting in a Curie–Weiss g-value of $g = 2.10$ for the V(IV) ions. This g value of 2.10 seems quite high in comparison to many materials containing isolated V^{4+} centers but appeared reproducible. The source of the deviation is not clear but could be due to the fact that the unpaired spin is not confined to a single V atom of the chain. The dark brown color of (**1**), in contrast to the usual blue or green color of vanadyl compounds, suggest that there may be some delocalization of the electrons on the 1-D chains.

As the temperature is lowered to around 5 K, the magnetic susceptibility of the sample passes through a broad maximum and then decreases at lower temperatures. This behavior is expected when short range antiferromagnetic exchange occurs in a crystal lattice. These short range interactions are most likely within the 1-D chains, whereas the long-range interactions result from the exchange between the chains via the phosphate bridges.

The magnetic exchange that is expected in the d^1 vanadium(IV) centers with spin $S_{total} = \frac{1}{2}$ is the isotropic Heisenberg spin Hamiltonian,

$$\mathcal{H} = -2JS_1S_2. \quad [2]$$

Within the context of the crystal structure of this material, the exchange from this spin Hamiltonian may be propagated via a one-dimensional exchange interaction.

The behavior of a one-dimensional Heisenberg linear chain has been described by Bonner and Fisher (11). The Bonner–Fisher Heisenberg linear chain model was applied to the data to determine if the short-range order arises from a one-dimensional magnetic interaction. The high temperature data in the Curie–Weiss region could be fit adequately with this model; however, the Bonner–Fisher model did not fit, in a satisfactory manner, the temperature region in the vicinity of the maximum. Moreover, at a temperature of about 3.7 K, there is an abrupt deviation of the magnetic susceptibility data from the broad maximum. Since there is obvious cross exchange through the phosphate bridges, a molecular field correction to the linear chain model was used to approximate the effect of interchain interactions.

The equation that describes the effect of a molecular exchange field is shown by (Eq. [3]),

$$\chi = \frac{\chi'}{1 - (zJ/Ng^2\mu_B^2)\chi'} + \text{TIP}, \quad [3]$$

where χ' is the magnetic susceptibility of the linear chains in the absence of the exchange field, and χ is the molecular exchange field influenced magnetic susceptibility that is actually measured. The exchange field coupling parameter is zJ', where z is the number of exchange coupled neighbors. The addition of the molecular field exchange correction improved the fit to the data only slightly.

The results of the fit of the Bonner–Fisher model to the magnetic data, neglecting the data at temperatures below 4.0 K, is illustrated as the smooth curve in the inset of (Fig. 3). The parameters used in the fit were $g = 2.10$, $J/k = -3.26$, and $zJ'/k = -2.1$. The need for a large interchain coupling parameter (zJ') is apparent from the onset of the three-dimensional phase transition. The magnitude of this parameter requires that it be viewed with caution; however, the model shows excellent agreement with the measured magnetic susceptibility data until the onset of long range order at $T = 3.7$ K. The fact that none of these models quantitatively describes the observed data indicates that the actual situation is more complicated than our simple models suggests probably due to many competing interactions at lower temperatures.

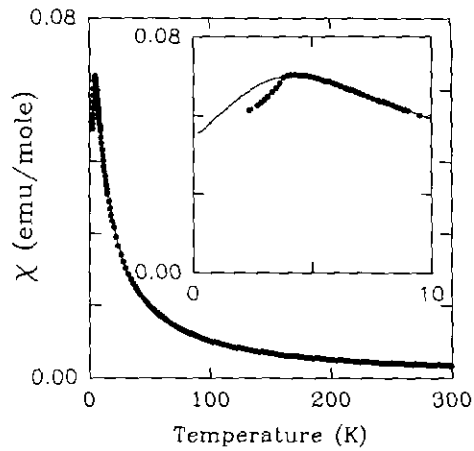

FIG. 3. The magnetic susceptibility of (1) plotted as a function of temperature over the 2.3–300 K temperature region. The inset shows an expansion of the 2.3–10 K temperature region. The curves through the data are the fits to the theoretical models as described in the text.

CONCLUSIONS

The title compound is the ammonium derivative for the class of compounds of the type $AVO(PO_4)$ (A = Li, Na, K). The structure is very similar to that of KVOPO4, but with slight distortions of the framework due to the hydrogen bonding of the ammonium cations to framework O atoms. Thermogravimetric results show one ammonium cation per vanadium which is in agreement with the crystallographic results. The magnetic data show complicated short range antiferromagnetic behavior occuring at $T <$ 10 K.

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REFERENCES

1. G. Centi, F. Trifiro, J. R. Ebner, and V. M. Franchetti, *Chem. Rev.* **88,** 55 (1988).
2. B. L. Hodnett, *Catal. Rev. Sci. Eng.* **27,** 373 (1985).
3. For $AVOPO_4$ (A = alkali metal): $NaVOPO_4$, K. H. Lii, C. H. Li, T. M. Chen, and S. L. Wang, *Z. Kristallogr.* **197,** 67 (1991). $KVOPO_4$, M. L. F. Phillips, W. T. A. Harrison, T. E. Gier, G. D. Stucky, G. V. Kulkarni, and J. K. Burdett, *Inorg. Chem.* **29,** 2158 (1990). α-$LiVOPO_4$. A. V. Lavrov, V. P. Nikolaev, G. G. Sadikov, and M. A. Porai-Koshits, *Sov. Phys.-Dokl. Engl. Transl.* **27,** 680 (1982). β-$LiVOPO_4$, K. H. Lii, C. H. Li, C. Y. Cheng, and S. L. Wang, *J. Solid State Chem.* **95,** 352 (1991). For $A[VOPO_4]_2$ (A = alkali earth metal): $Ca[VOPO_4]_2$, K. H. Lii, B. R. Chueh, H. Y. Kang, and S. L. Wang, *J. Solid State Chem.* **99,** 72 (1992). $Ba[VOPO_4]_2$, A. Grandin, J. Chardon, M. M. Borel, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **99,** 297 (1992).
4. For $Cs_2V_3P_4O_{17}$: K. H. Lii, Y. P. Wang, and S. L. Wang, *J. Solid*

State Chem. **80,** 127 (1989). For β-$K_2V_3P_4O_{17}$: K. H. Lii, H. J. Tsai, and S. L. Wang, *J. Solid State Chem.* **87,** 396 (1990). For $A_2VOP_2O_7$ (A = Cs, Rb): K. H. Lii, and S. L. Wang, *J. Solid State Chem.* **82,** 239 (1989).

5. For $A_{0.5}VOPO_4 \cdot xH_2O$ (A = Na, x = 2.0; A = K, x = 1.5): S. L. Wang, H. Y. Kang, C. Y. Cheng, and K. H. Lii, *Inorg. Chem.* **30,** 3496 (1991). For $K_2(VO)_2P_3O_9(OH)_3 \cdot 1.125H_2O$: K. H. Lii, and H. J. Tsai, *Inorg. Chem.* **30,** 446 (1991).
6. For AVP_2O_7 (A = Li–Cs): K. H. Lii, Y. P. Wang, Y. B. Chen, and S. L. Wang, *J. Solid State Chem.* **86,** 143 (1990) and references therein. For $RbV_3P_3O_{17+x}$: K. H. Lii and C. S. Lee, *Inorg. Chem.* **29,** 3298 (1990).
7. For $K_2(VO)_3(HPO_4)_4$: K. H. Lii and H. J. Tsai, *J. Solid State Chem.* **91,** 331 (1991). For $Ca_2V(PO_4)(HPO_4)_2 \cdot H_2O$ and $Ca_2V(PO_4)(P_2O_7)$: K. H. Lii, N. S. Wen, C. C. Su, B. R. Chen, *Inorg. Chem.* **31,** 439 (1992). For α- and β-$Rb(HPO_4)_2$: R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, in press. For $Cs[V_2(PO_4)(HPO_4)_2(H_2O)_2]$ and $K[V_2O(HPO_4)_3(H_2O)_2]$: R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, *Inorg. Chem.*, in press. For $K_2[V_3O_2(PO_4)_2(HPO_4)(H_2PO_4)(H_2O)_2]$: R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, in press.
8. For $Zn_2VO(PO_4)_2$: K. H. Lii and H. J. Tsai, *J. Solid State Chem.* **90,** 291 (1991). For $Ni_{0.5}VOPO_4 \cdot 1.5H_2O$: K. H. Lii and L. F. Mao, *J. Solid State Chem.* **96,** 436 (1992). For $\{Ni(H_2O)_4\}[VO(PO_4)_2]$: R. C. Haushalter, V. Soghomonian, Q. Chen, and J. Zubieta, in press.
9. For α-$NH_4(VO_2)(HPO_4)$: P. Amoros and A. Le Bail, *J. Solid State Chem.* **97,** 283 (1992). For β-$NH_4(VO_2)(HPO_4)$: S. Pulvin, E. Bordes, M. Ronis, and P. Courtine, *J. Chem. Res. Synop.* 362 (1981).
10. C. J. O'Connor, *Prog. Inorg. Chem.* **29,** 203 (1982).
11. J. C. Bonner and M. E. Fisher, *Phys. Rev. A* **135,** 640 (1964).