

# Chemistry of Intercalated Vanadyl(IV, V) Phosphates: Synthesis, Structure and Magnetic Properties

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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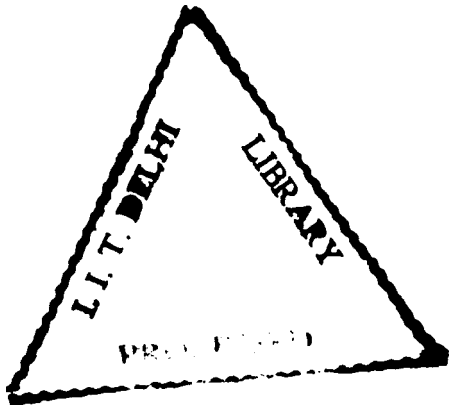


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## CERTIFICATE

This is to certify that the thesis entitled "**Chemistry of vanadyl (IV, V) phosphates: Synthesis, structure and magnetic properties**" being submitted by **Mr. P. Ayyappan** to the Indian Institute of Technology, New Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. Mr. P. Ayyappan has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached requisite standard.

The results contained in the dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

September, 1999

  
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***Dedicated to  
my mother, brothers and sisters***

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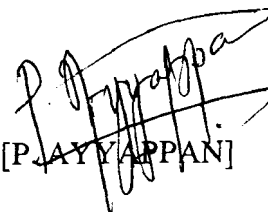
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[P. AYYAPPAN]

## ABSTRACT

Since the discovery of vanadium phosphate as an active and selective catalyst for the mild oxidation of n-butane to maleic anhydride, there has been extensive research work towards synthesizing new vanadium phosphates. Particular emphasis has been placed on metal incorporation into vanadyl phosphates. The present study is directed towards developing hydrothermal reactions for the synthesis of novel metal intercalated layered vanadyl phosphates. We report here the synthesis, characterization and magnetic properties of eight new vanadyl phosphates. This thesis is divided into four chapters with the contents therein detailed below.

Chapter I describes a brief review on structure, synthesis and properties of metal/organic molecule intercalated vanadyl phosphates along with the parent  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  reported in the literature. Like many inorganic solids, vanadyl phosphates are capable of undergoing intercalation reaction with small ions such as  $\text{H}^+$ ,  $\text{Li}^+$  and  $\text{Na}^+$ . The host solid in these reactions undergoes reduction, with the inserted cation occupying formerly empty sites of the host. In the presence of metal iodides as reducing agents, cations  $\text{M}^+$  can be reductively intercalated to form  $\text{M}_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$  ( $\text{A}=\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ). In recent years, hydrothermal reactions have been found to be an effective route to prepare new intercalated materials,  $\text{M}_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$  ( $\text{M}=\text{Na}$ ,  $\text{K}$ ,  $\text{Ca}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ,  $\text{Pb}$ ,) as well as to grow suitable single crystals for detailed structural characterization. A brief summary of the structure, synthesis and properties of layered vanadyl phosphates is reported in this chapter. In addition, we have

also described vanadium phosphates templated with organic molecule that exhibits 1D, 2D, 3D network structures and their interesting magnetic properties.

Chapter II describes the preparation and characterisation of metal intercalated vanadyl phosphates,  $M_xVOPO_4 \cdot yH_2O$  ( $M=Na, K, Mg, Fe, Co, Ni, Cu, Zn, Cd, Ag, Sn, Mo, W$ ) and organic molecule (ethylenediamine, 1,4-diaminobenzene, ferrocene, cobaltacene) intercalated vanadyl phosphates. Effect of hydrothermal technique to grow mono-phasic vanadium phosphates is discussed. Use of metal powder as the reducing agents as well as counter cation has yielded several new transition and alkaline earth metal intercalated vanadyl phosphates. We have demonstrated the use of alkylborohydrides for the synthesis of alkali metal ion intercalated vanadyl phosphates. Amount of water appears to be crucial in the formation of  $M_xVOPO_4 \cdot yH_2O$  and  $VO(H_2PO_4)_2$  through hydrothermal reaction. A new method for the preparation of  $VO(H_2PO_4)_2$  in good yield with reproducible structural characteristics is presented.

Chapter III describes the full structures of metal intercalated vanadyl phosphates(VPO),  $M_xVOPO_4 \cdot 2H_2O$  ( $M= Ag, Cu, Zn$ ), ethylenediamine intercalated vanadyl phosphate and  $VO(H_2PO_4)_2$ . The structures are related to that of  $VOPO_4 \cdot 2H_2O$  but with a different stacking sequence. In  $VOPO_4 \cdot 2H_2O$ , the VPO layers stack *directly* on top of each other so that each V=O group is oriented towards the water molecule which is weakly co-ordinated *trans* to the V=O group of an adjacent layer. In the Cu and Zn compounds, adjacent layers are offset from one another so that all atoms of the same kind (e.g., all V or all P) form strings parallel with the triclinic *c* axis. However, the VPO

layers in the M=Ag compound are offset so that alternating V and P atoms lie in strings parallel with the triclinic  $c$  axis. This results in the doubling of the  $c$  axis in AgVPO relative to CuVPO and ZnVPO. The structure of  $(en)_{0.5}[VO_2PO_4\{P(OH)_2\}_{0.44}]$  contains layers made of  $VO_5$  square pyramids and  $PO_4$  tetrahedra sharing vertices on  $ab$ -plane. An interesting feature of this structure is that  $VO_5$  on adjacent layers are connected through disordered tetrahedral  $PO_2(OH)_2$  units to form a three-dimensional network. The crystal structure of  $VO(H_2PO_4)_2$  is built up from single chains of  $VO_6$  running parallel to the  $c$ -axis and linked together via corner sharing tetrahedral  $PO_2(OH)_2$  units. Single chain of  $VO_6$  octahedra, along the  $c$ -axis lead to a sequence of disordered short and long vanadium oxygen bonds.

Chapter IV describes magnetic properties of metal intercalated layered vanadyl phosphates  $M_xVOPO_4 \cdot yH_2O$  ( $M=Na, Mg, Ag, Cu, Zn$ ),  $enVPO$  and  $VO(H_2PO_4)_2$ . The susceptibility data of all  $M_xVOPO_4 \cdot yH_2O$  were modelled over the complete temperature range (300-2K) according to a modified Curie-Weiss equation,  $1/\chi = (T-\theta)/[\chi_0(T-\theta)+C]$ , where  $\chi$  is magnetic susceptibility,  $\theta$  is Weiss constant,  $C$  is Curie constant,  $T$  is the absolute temperature and  $\chi_0$  is temperature independent paramagnetism(TIP). All the materials exhibited unusual magnetic behaviour ranging from ferro to anti-ferromagnetic interaction at low temperatures(<50 K). NaVPO, AgVPO and enVPO show ferromagnetic behaviour while MgVPO, CuVPO, ZnVPO, and  $VO(H_2PO_4)_2$  show antiferromagnetic behaviour. The data reveal that the magnetic behaviour depends not only on the type of metal ion incorporated but also on the arrangement of vanadate and phosphate groups within the layers. Our studies clearly demonstrate that preparation of

well-characterized materials in terms of structure and phase purity is essential to interpret the magnetic properties unambiguously.

Due acknowledgement has been made to other investigators wherever the work described is based on their findings. The author apologizes for any omission or mistakes, which might have occurred due to oversight.

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