

## Structure and Intercalation Chemistry of Metal Phosphate Layer Compounds.

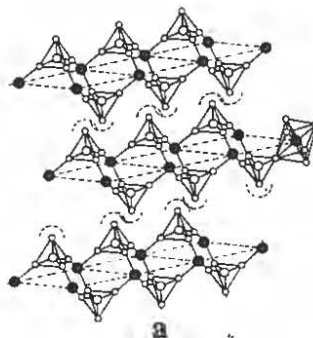
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Acid salts of tetravalent metals which have general formula  $M^{IV}(HXO_4)_2 \cdot nH_2O$  ( $M^{IV} = \text{Zr, Ti, Hf, Ce, Th}$ ;  $X = \text{P, As}$ ) are well known, but recently there has been renewed interest in these compounds [1]. This revived interest is mainly due in part to their ion exchange properties and their resistance toward high temperature and radiation.

Since 1964 several insoluble acid salts of tetravalent metals have been obtained in crystalline form and among them the most investigated acid salt is the zirconium bis(monohydrogen orthophosphate), usually obtained as a monohydrate form [2]. Its structure, **a**, has been elucidated by Clearfield and coworkers. [3]



Each layer consists of zirconium atoms lying in a plane and bridged through phosphate groups. Three oxygens of each tetrahedral phosphate are linked to three zirconium atoms so that each zirconium is octahedrally coordinated by six oxygens from six different phosphate groups. The fourth oxygen of each phosphate group bears a proton. This proton of the acid can be easily replaced by other cations; therefore much work has been done in the area of ion exchange [4]. Intensive research has also focused on the intercalation chemistry of amines [5], alcohols [6], and other polar molecules [7], as well as on the study of various catalytic properties [8] of the  $\alpha$ -zirconium phosphate. One particularly attractive feature of these layered solids is the possibility of manipulating surface textural properties by introducing organic radicals into the layered matrix. Such compounds may be considered organic derivatives of  $\alpha$ -zirconium phosphate since they have the basic  $\alpha$ -layered structure but the tetrahedral P-OH groups have been replaced by P-R or P-OR groups (R is an organic radical) [9]. Although zirconium phosphates have a layered structure, the intracrystalline pore size is small and does not allow the intercalation or ion exchange of large molecules. Therefore catalytic reactions occur only on the surface and not in the interior. Efforts to pillar the  $\alpha$ -zirconium phosphates by organic phosphates, phosphonates [10] and inorganic Keggin ion,  $[Al_{13}O_4(OH)_{24} \cdot 12H_2O]$  [11], have been performed thereby increasing the interlayer distance, pore size, and surface area.

Recently new families of layered vanadyl organophosphonates  $VO(RPO_3) \cdot H_2O$  [12],  $VO(RPO_3) \cdot 2H_2O$  [13],  $VO(RPO_3) \cdot H_2O \cdot R'OH$  (R = alkyl, phenyl; R' = benzyl) [14] have been prepared as layered compounds. Unlike  $Zr(RPO_3)_2 \cdot nH_2O$ , the structure of  $VO(RPO_3) \cdot 2H_2O$  appear to be derived from the newberyite,  $Mg(O_3POH) \cdot 3H_2O$ , structure. The structure of the dihydrated form may be compared [12] with that of the monohydrated form. The inorganic layer portion of the crystal structure of monohydrate is closely related with that of dihydrate. However, the loss of one water molecule from the dihydrate forces the intralayer formation of  $-V=O-V-$  chains which changes the way in which the organic groups pack in the

interlayer. Although the two structures can be interconverted topologically by breaking the bond between one water molecule and a vanadium atom, in practice the two phases are difficult to interconvert because of the extensive reorganization of the structure required by the packing of organic groups.  $\text{VO}(\text{RPO}_3) \cdot \text{H}_2\text{O} \cdot \text{R}'\text{OH}$  is a structural analogue of vanadyl organophosphonate dihydrate, which loses  $\text{R}'\text{OH}$  when heated in vacuo. The new compound recognizes primary alcohols in preference to secondary and tertiary alcohols, since the structure has formed around the  $\text{R}'\text{OH}$  template [14].

While the structures and properties of the acid salts of group IV metals have been intensively investigated over the past decades, the studies on the divalent phosphate and phosphonates have been carried out only for a few recent years. The divalent transition-metal phosphonate,  $\text{M}(\text{O}_3\text{PR}) \cdot \text{H}_2\text{O}$  ( $\text{M} = \text{Mn, Mg, Ni, Cu, Zn}$ ;  $\text{R} = \text{alkyl, phenyl}$ ), have been prepared by Mallouk and Clearfield independently [15]. In the divalent metal phosphonates the metal atoms are octahedrally coordinated but the 1:1  $\text{M}:\text{PO}_3\text{R}$  ratio requires a chelating arrangement of the phosphonate group as well as oxygen bridging of metal atom and the incorporation of water to complete the 6-fold coordination. In contrast, the divalent metal phosphates,  $\text{Zn}(\text{O}_3\text{POR}) \cdot \text{H}_2\text{O}$  ( $\text{R} = \text{alkyl}$ ), have layers formed by phosphate groups bridging the tetrahedral zinc atoms, which are perpendicular to the layer direction [16]. Shape-selective intercalation reactions of layered zinc and cobalt phosphonates with alkyl amines have also been investigated. Amines with the branching at the  $\alpha$ -carbon can not access the metal coordination site [17].

Various di- and tetravalent metal phosphates and phosphonates have been prepared as layered compounds and their structures have been modified. The compounds show many interesting properties such as ion exchange, sorption, intercalation, and catalytic activity. Some of the compounds show substrate-specific recognition for their coordinative intercalations, which is very desirable for the highly selective oxidation catalysts.

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