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Intercalation processes and their application to metal-phosphonate intercalation chemistry

Komise pro obhajoby doktorských disertací v oboru Anorganická chemie

Vítězslav Zima

Ústav makromolekulární chemie AV ČR, v.v.i.

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Content

Résumé

This thesis deals with intercalation processes which occur in layered materials based on metal phosphates and phosphonates. Some phenomena accompanying the intercalation reactions are described and exemplified on intercalation reactions of water and ethanol into anhydrous vanadyl phosphate and redox intercalation of alkali metal cations into vanadyl phosphate dihydrate. Possible mechanisms of intercalation are presented which are based on: i) an idea of exfoliation of layers; ii) the formation of stages and randomly stacked layers; iii) co-existence of intercalated and non-intercalated parts of crystals of the host separated by advancing phase boundary.

The group of layered metal phosphates used as the hosts in intercalation chemistry can be enlarged when one of the oxygen atoms of the phosphate is replaced with an organic group. In this way, layered metal phosphonates can be prepared which have increased variability of the structure. In our work we focused on organophosphonates of alkaline-earth metals and tetravalent metals. We found that the formation of various forms of phenylphosphonates of alkaline-earth metals depends on the acidity of the medium in which the reaction proceeds. For the purpose of detailed investigation of these processes we have developed a method of so-called controlled additions of reagents. It was found that two types of layered compounds with general formula $MeC_6H_5PO_3\cdot yH_2O$ and $Me(C_6H_5PO_3H)_2$ can be mutually interconverted. The compounds with formula $MeC_6H_5PO_3\cdot yH_2O$ can be used as hosts for intercalation reactions with alcohols, diols, amines and nitrogen-containing heterocyclic compounds. Another host compound is strontium methylphosphonate which is able to form surprisingly stable intercalates with alcohols and diols.

As regards the organophosphonates of tetravalent metals, an important class is presented by those which contain functional groups. New way for the preparation of 4-sulfophenylphosphonic acid was proposed based on the hydrolysis of sulfamoylphenylphosphonic acid under hydrothermal conditions. 4-Sulfophenylphosphonic acid was successfully used for the preparation of zirconium sulfophenylphosphonate and zirconium phosphate sulfophenylphosphonate. Zirconium 4-sulfophenylphosphonate is a layered material which can be employed as a host for intercalation reactions with basic molecules. This material and layered alpha

modification of zirconium hydrogen phosphate were also used as hosts for intercalation of optically active push-pull systems showing an intramolecular charge-transfer. A tris[4-(pyridin-4-yl)phenyl]amine (TPPA) molecule has been selected as a model tripodal push-pull system with three peripheral basic centers that may undergo protonation. The described intercalates represent the first case when a tripodal push-pull system was incorporated in a system with restricted geometry with the aim to influence its optical properties.

Abbreviations

ACA	ε-aminocaproic acid
HT	Hendricks-Teller effect
EDX	energy-dispersive X-ray analysis
MeTPPA	tris(4-(N-methylpyridinium-4-yl)phenyl)amine
SrPP	strontium phenylphosphonate
TGA	thermogravimetric analysis
TPPA	tris[4-(pyridin-4-yl)phenyl]amine
XRD	X-ray diffraction
ZrP	zirconium hydrogen phosphate
ZrSPP	zirconium 4-sulfophenylphosphonate

Symbols

c	basal spacing
m	number of layers of guest molecules in one host interlayer space
n_C	number of carbon atoms in alkyl chain of guest
x	content of guest
y	content of water
α_I	extent of reaction of intercalate
α_H	extent of reaction of host

1. State-of the art of intercalation chemistry

The problems of intercalation chemistry are by no means exhausted in this chapter. The following text focuses on those aspects of intercalation chemistry which are in our research interest.

1.1. Intercalation – what is it?

In the IUPAC Compendium of chemical terminology[1] the term intercalation is defined as a generally reversible reaction that involves introduction of a guest species into a host structure without a major structural modification of the host. In the strictest sense, intercalation refers to insertion of a guest into a two-dimensional host. The process of intercalation is shown schematically in Figure 1.

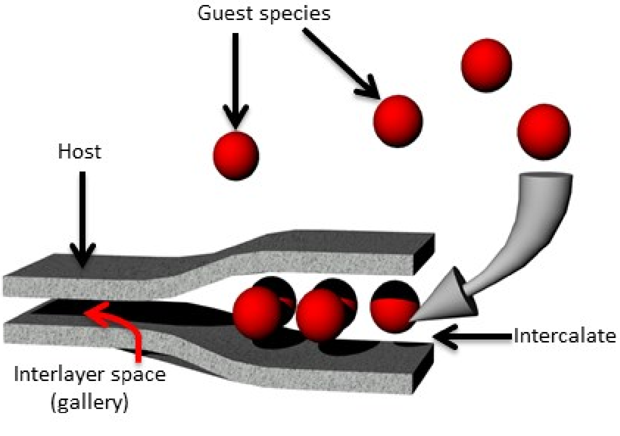


Figure 1. Schematic depiction of the intercalation process.

1.2. Basic terms used in intercalation chemistry

For the following considerations we need to define some important terms used in the intercalation chemistry. In most of the layered compounds which undergo intercalation there are covalent bonds between atoms in the same layers and non-covalent bonds (interactions) between the adjacent layers. Therefore, we can consider a single layer of such material as a giant two-dimensional macromolecule that can be stacked one above another to form a crystal of a layered compound. The space between two adjacent layers is usually called **interlayer space**, or gallery. The distance between the layers (the height of the space between them) is denoted also as the **gallery height**. The sum of the **thickness of the layer** and the gallery height is the **interlayer distance**, sometimes called **interlayer spacing** or **basal spacing**. All these terms are depicted in Figure 2. In most cases the intercalation is accompanied by enlargement of the distance between the layers.

Several ways how the intercalation proceeds will be shown on an intercalation of various species (molecules or ions) into vanadyl phosphate as a model host material.[2,D1]

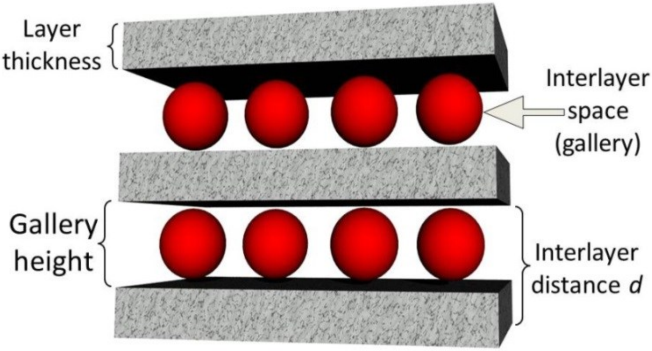


Figure 2. Basic terms used in intercalation chemistry.

1.3. Vanadyl phosphate as an example of a host material

Vanadyl(V) phosphate, $VOPO_4$, exists in several structural modifications of which the α_I-VOPO4 is the most suitable for intercalation reactions. This modification can be prepared in the form of its dihydrate with the formula $VOPO_4 \cdot 2H_2O$ by the reaction of vanadium pentoxide with phosphoric acid as described by Ladwig.[3] Thermal dehydration of layered $VOPO_4 \cdot 2H_2O$ at 400 °C leads to α_I-$VOPO_4$.[4] The layers of α_I-$VOPO_4$ are formed from phosphate tetrahedra and VO_6 octahedra as shown in Figure 3. The sixth position in each VO_6 octahedron is complemented by an oxygen atom from a neighboring layer.

The structure of the alpha modification of $VOPO_4$ is retained in $VOPO_4 \cdot 2H_2O$, with the exception of the sixth position of the VO_6 octahedron which is complemented by the oxygen of the coordinated water molecule residing in the interlayer space of the phosphate, see Figure 4. The second molecule of water is not coordinated to the host layer and is bound in the interlayer space by weak non-covalent interactions.

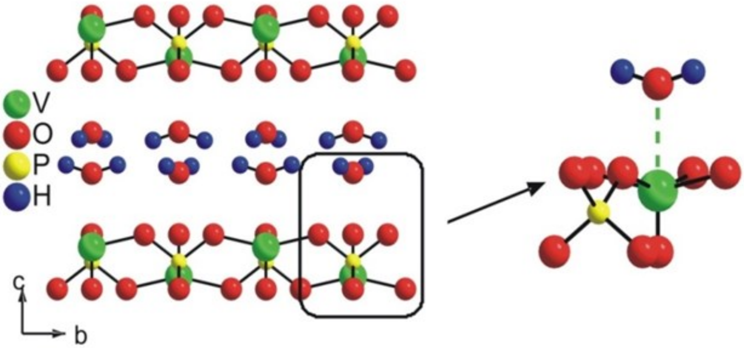


Figure 3. Structure of α_I-modification of $VOPO_4$.

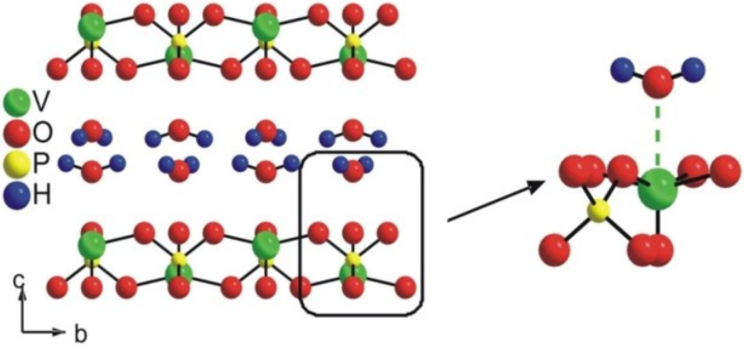


Figure 4. Structure of $VOPO_4 \cdot 2H_2O$.

Vanadyl phosphate dihydrate can be considered as an intercalate of $VOPO_4$ with water as a guest molecule. The water molecules in the interlayer space can be replaced by other neutral molecules (stronger Lewis bases) which can play a similar role in the structure of a new intercalation compound. These reintercalation reactions of the dihydrate are often easier than an intercalation of anhydrous vanadyl phosphate with the same molecular guest. The intercalates prepared by the reactions of Lewis bases with anhydrous vanadyl phosphate or its dihydrate are characteristic for neutral organic guest compounds having a functional group with a free electron pair.

Vanadyl phosphate can be also intercalated with cations as was described by Johnson and Jacobson.[5] It was found that $VOPO_4 \cdot 2H_2O$ readily undergoes redox intercalation reaction with alkaline metal,[6] hydronium[6a,D7] and ammonium[7,D8] cations in the presence of a reducing agent.

The first review on intercalation reactions of vanadyl phosphate was published more than fifteen years ago.[8,D2] Since then, many new intercalates have been prepared and their structure or the arrangement of the guest molecules in the interlayer space has been proposed. The progress in the intercalation chemistry of vanadyl phosphate has been reviewed recently.[9,D3]

1.4. Phenomena occurring in the intercalation processes - an overview

Incorporation of molecules or ions into the interlayer space of the host can be realized in several ways. Those which proved to occur during intercalation into vanadyl phosphate are depicted in Figure 5.[2,D1] The details of each process are given in the referenced papers.

The first example is *exfoliation* (Figure 5, route 1) that is a complete separation of the host layers mostly in a liquid medium. The layers, surrounded by the guest species are then stacked again to form an intercalate. The process of exfoliation and subsequent stacking was employed for the preparation of the intercalates of $Zr(HPO_4)_2$[10,D4] and $VOPO_4$ with a homologous series of linear 1-alkanols from ethanol (n_C = 2) to 1-octadecanol (n_C = 18) and 1,ω-alkanediols from ethylene glycol (n_C = 2) to 1,10-decanediol (n_C = 10).[11,D5] This method was also used for the intercalation of alcohols and diols into $NbOPO_4$ and $NbOAsO_4$, host materials isostructural with $VOPO_4$.[12,D6]

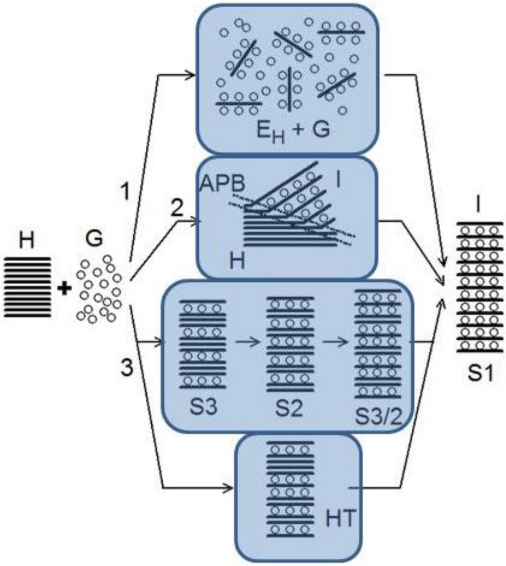


Figure 5. Several phenomena which occur during the intercalation into vanadyl phosphate - an overview.

Another type of intercalation proceeds through *advancing phase boundary* (route 2), which is typical especially for slowly intercalating species, when the driving forces of the intercalation are rather low. In this case the intercalation starts at the edge of the crystal and from this edge it slowly progresses into the center of the crystal. There is an obvious border area between the original host and the intercalate. The existence of the boundary phase usually cannot be detected by powder X-ray diffraction and can be deduced only indirectly. We encountered this phenomenon when we studied kinetics of the intercalation of ethanol into vanadyl phosphate.[13]

If the driving force is stronger, the intercalation proceeds through *stages* (route 3). It means that at a certain phase of the intercalation some interlayer spaces are filled with the guest species, while the neighboring interlayer spaces remain empty. We speak about stage three, when only every third interlayer space is intercalated, stage two, when every second interlayer space is filled, and so on. It was found that during the intercalation of sodium cations into $VOPO_4 \cdot 2H_2O$ three phases are gradually created with the compositions $Na_{0.3}V^{IV}{}_{0.3}V^{V}{}_{0.7}OPO_4 \cdot 2H_2O$, $Na_{0.5}V^{IV}{}_{0.5}V^{V}{}_{0.5}OPO_4 \cdot 2H_2O$ and $NaV^{IV}OPO_4 \cdot H_2O$. From the basal spacing of these phases it was deduced that they corresponded to stages 3, 2 and 1.[14] A similar study was carried out for the intercalation of lithium cations using LiI.[15] Also in this case the stages 3, 2 and 1 were observed. Out of the definition of staging was the phase with formula $Li_{0.66}V^{IV}{}_{0.66}V^{V}{}_{0.34}OPO_4 \cdot 2H_2O$.[14-15] The most plausible arrangement for this stage is a sequence consisting of two full galleries and one empty gallery. This phase can be then denoted as stage 3/2 in accordance with the definition coined by Fuerst et al. for the intercalates of graphite.[16]

When these galleries are filled randomly, a phenomenon called *Hendricks-Teller effect* (denoted HT in Figure 5) occurs. We observed this phenomenon, when we studied deintercalation of alcohols from the interlayer space of vanadyl phosphate.[17]

1.5. Quest for new host materials: Layered metal phosphonates

Most research efforts in current solid state chemistry are concerned with the design and prediction of new structures and materials with potential commercial applications.[18] In the field of hybrid inorganic-organic materials, a typical approach to complex materials is to combine organic molecular groups with inorganic moieties into crystalline hybrid compounds. The most important property of the hybrid materials is that they can be prepared from individual modular organic and inorganic parts, which subsequently allows a rational control over their structure and functions. Hybrid materials are often constructed and kept together through noncovalent and covalent interactions; novel combinations of organic and inorganic materials can be produced in a cooperative manner. This feature greatly enhances the toolkit available for the synthesis of new materials.

Layered metal phosphates proved to be good host materials for intercalation chemistry. This applies not only for vanadyl phosphates described above, but also for phosphates of other metals especially tetravalent metal phosphates. Probably the most studied layered phosphate from the point of its intercalation chemistry is zirconium hydrogen phosphate with formula $Zr(HPO_4)_2$.[19] It was soon realized that the OH group of this hydrogen phosphate might be replaced with an organic group as in the case of organophosphonic acids, RPO_3H_2 which might be considered as a derivative of phosphoric acid. Many layered zirconium phosphonates have been prepared[20] and this field of study was soon extended to other metals.[21]

Metal phosphonates represent a varied group of organic-inorganic hybrid solids which has not been fully explored yet. Targeted changes of their organic backbones may be carried out with the aim to obtain desired properties or to create required structures. A vast variety of metal phosphonates having open-framework or pillared structures, layered structures or one-dimensional structures have been prepared and characterized. A recent progress of the work done in this field is documented in the book on chemistry of metal phosphonates.[21] The functionality of layered metal phosphonates might be significantly enlarged by employing these materials as hosts in intercalation chemistry.[22]

2. Phenylphosphonates of alkaline-earth metals

As regards layered phosphonates of alkaline-earth metals, hydrogen phenylphosphonates with a general formula of $Me(C_6H_5PO_3H)_2$ (Me = Ca,[23] Sr,[24] Ba[25]) were prepared. To the best of our knowledge, no phenylphosphonate of other alkaline-earth metals with general formula $MeC_6H_5PO_3 \cdot yH_2O$ (except $MgC_6H_5PO_3 \cdot H_2O$[26]) was described before 2005.

2.1. Calcium phenylphosphonate as a host material[27,D10]

In the course of preparation of $Ca(C_6H_5PO_3H)_2$ according to the previously described procedure,[23] we found that another calcium phenylphosphonate with a Ca/P molar ratio of 1 was formed at higher pH. This is in accordance with the statement that the acidity of the reaction mixture plays an important role in the controlling of the resulting metal/phosphonate ratio in the products.[28] The diffraction pattern of this compound proves it has a layered structure. The formula of this compound was determined to be $CaC_6H_5PO_3 \cdot 2H_2O$.

The relationship between $CaC_6H_5PO_3 \cdot 2H_2O$ and previously described $Ca(C_6H_5PO_3H)_2$ was investigated by a reaction of a suspension of $CaC_6H_5PO_3 \cdot 2H_2O$ with phenylphosphonic acid added in small doses using a computer-controlled burette. In these reactions an aqueous solution of phenylphosphonic acid was added using the burette to an aqueous suspension of the calcium compound. The intervals between additions of the acid were chosen to be sufficiently long to ensure that practically all added acid would be consumed in the reaction with the calcium compound. The acidity of the solutions during the reactions was checked with a glass pH electrode. The value of pH at the end of the intervals, just before another addition, was then measured and its dependence on the amount of added acid is depicted in Figure 6.

At the beginning of the reaction, the values of pH remain roughly constant. After addition of about 0.33 mol of phenylphosphonic acid per 1 mol of $CaC_6H_5PO_3 \cdot 2H_2O$ (point A in Figure 6), pH starts to decrease down to about 3.2 (point B). Then there is another steep increase of pH to 3.7 and this pH is maintained constant (from point C) during further additions of the acid. Another decrease of pH follows after the addition of about 1 mol of phenylphosphonic acid per 1 mol of $CaC_6H_5PO_3 \cdot 2H_2O$ (point D). The product of the reaction was identified to be $Ca(C_6H_5PO_3H)_2$.

The shape of the curve in Figure 6 indicates formation of an intermediate during the reaction. To obtain this intermediate, we reacted $CaC_6H_5PO_3 \cdot 2H_2O$ with phenylphosphonic acid to the point B only. The product of this reaction has a relative Ca/P molar ratio of 0.745 (≈ 3/4) as found by EDX. Hence, its formula can be $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 \cdot yH_2O$. Powder X-ray diffraction data confirm that $Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 \cdot 4H_2O$ is a new compound with $c = 15.197$ Å and not a mixture of the starting compound and the product of the reaction.

In summary, the reaction of $CaC_6H_5PO_3 \cdot 2H_2O$ with phenylphosphonic acid can be described by the following equations:

$$3CaC_6H_5PO_3 \cdot 2H_2O + C_6H_5PO_3H_2 \rightarrow Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 \cdot 4H_2O + 2H_2O \quad (1)$$

$$Ca_3(C_6H_5PO_3H)_2(C_6H_5PO_3)_2 \cdot 4H_2O + 2C_6H_5PO_3H_2 \rightarrow 3Ca(C_6H_5PO_3H)_2 + 4H_2O. \quad (2)$$

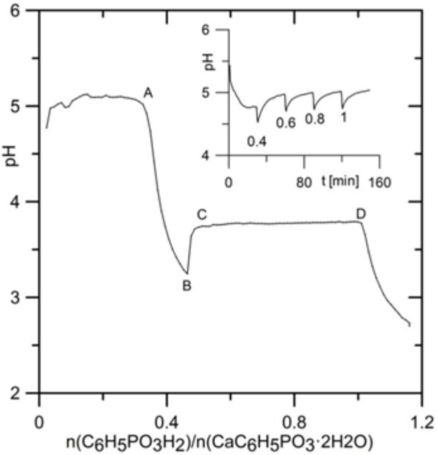


Figure 6. Reaction course of the reaction of the $CaC_6H_5PO_3 \cdot 2H_2O$ suspension with the phosphonic acid solution. The inset represents the time dependence of pH at the beginning of the reaction; the numbers in the inset indicate the amount of the added acid solution in milliliters.

2.1.1. Intercalation chemistry of calcium phenylphosphonate

Early works dealing with intercalations into layered divalent metal (Me^{II}) phenylphosphonates appeared in 1990s.[29] Generally speaking, there are two ways how these intercalation reactions are accomplished:

(i) intercalation due to an acid-base interaction. In this case basic guest molecules (usually amines) are intercalated into metal hydrogen phosphonates in which their acid PO_3H groups interact with basic functional groups (e.g., $-NH_2$) of the guest. This can be denoted as a Brønsted-type intercalation. Examples are, for instance, intercalations of amines into calcium[30] and barium[31] hydrogen phenylphosphonates with the general formula $Me(C_6H_5PO_3H)_2 \cdot yH_2O$ ($y = 0\text{-}2$).

(ii) intercalation due to coordination of a guest having a free electron pair to a metal having a free coordination site. This can be denoted as a Lewis-type intercalation. As examples can serve intercalations of amines into zinc,[32] cadmium[33] or copper[29b, 34] phenylphosphonates with the general formula $MeC_6H_5PO_3 \cdot H_2O$. The guest molecules coordinate to the metal atoms at the site vacated by water molecules.

Intercalation of nitrogen- and oxygen-containing guest compounds into $CaC_6H_5PO_3 \cdot 2H_2O$ belongs to the Lewis-type intercalation. As the guests, 1-alkylamines, 1-alkanols, 1,ω-amino alcohols, nitrogenous heterocycles (pyridine, morpholine, and piperazine) and arylamines (aniline, 1-naphthylamine) were used. The details of the intercalations are given in our paper.[35,D11]

Intercalation of alkylamines and alkanols. In contrast to alkylamines, which can be easily intercalated at room temperature, alkanols cannot be directly intercalated into $CaC_6H_5PO_3 \cdot 2H_2O$. Only propanol can be intercalated by refluxing solid $CaC_6H_5PO_3 \cdot 2H_2O$ in propanol. Other alkanols were intercalated by a replacement of butylamine in $CaC_6H_5PO_3 \cdot C_4H_9NH_2$ with the corresponding alcohol in a microwave field. Neither amines nor alkanols can be intercalated into anhydrous calcium phenylphosphonate.

The relation between the basal spacing and the number of carbon atoms in the aliphatic chains of the intercalated 1-alkylamines and 1-alkanols is shown in Figure 7.

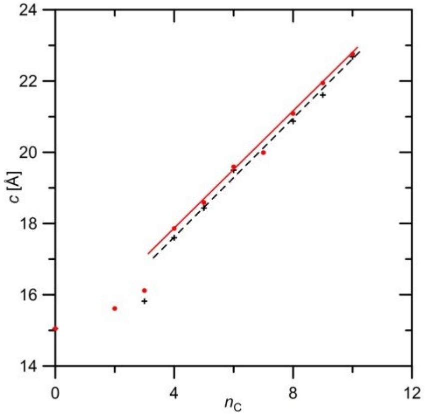


Figure 7. Dependence of the basal spacing of the intercalates of the alkylamines (circles) and alkanols (crosses) on the number of carbon atoms n_C.

In the case of the guests with more than four carbon atoms, the dependences are linear with the slope of 0.82 for both types of the intercalates. The increment in the interlayer distance for each C-C bond corresponds to the slope of the straight line correlation of the above plot, and it can be related to the inclination angle α of the axis of the carbon chain of the individual molecule with respect to the plane of the host layer according to the relation

$$\Delta c/\Delta n_C = m\ (\Delta h/\Delta n_C) \sin \alpha, \quad (3)$$

where $\Delta c/\Delta n_C$ is the slope of the dependence of the basal spacing c on the number of carbon atoms in the host chain n_C, m is the number of layers of guest molecules in one interlayer space of the host and the ratio $\Delta h/\Delta n_C$ has the value of 1.279 for both 1-alkanols and 1,ω-alkanediols (the derivation of this value was described in detail in our paper[11a]).

Using Equation (3) for these data we can infer that the amine and alkanol molecules are probably arranged in a monomolecular way and their axes are tilted at an angle of 40° to the host layers. Ethylamine, propylamine and propanol molecules are probably arranged in another way.

Intercalation of amino alcohols. In contrast to the intercalates of amines and alkanols, the intercalates of amino alcohols are stable at ambient conditions. Intercalates with shorter amino alcohols (n_C = 2-3) contain also water, while the intercalates with longer amino alcohols (n_C = 4-5) are anhydrous. The basal spacing values for all intercalates are very low compared to those for alkanols and amines. Most probably the amino alcohol molecules are arranged parallel to the host layers or they fill some cavities in the structure. The parallel arrangement of the amino alcohol molecules and the presence of the functional groups on both ends of the aliphatic chain are probably the reason of higher stability of the amino alcohol intercalates in comparison with the aliphatic amine or alcohol intercalates.

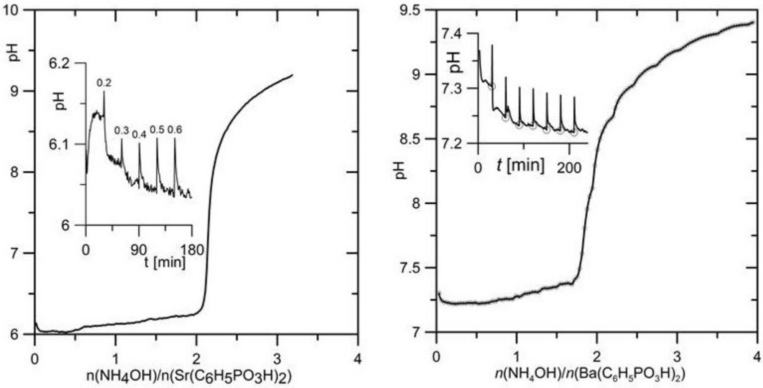
Intercalation of nitrogenous heterocycles and arylamines. The intercalates of pyridine, morpholine, piperazine, aniline and 1-naphthylamine are also stable at ambient conditions. All these intercalates contain water as can be seen in Table 1. Again, as in the case of amino alcohol intercalates, the increase of the basal spacing compared to the original host is very low.

Table 1 The basal spacings and stoichiometric quotients of the $CaC_6H_5PO_3 \cdot x(\text{guest}) \cdot yH_2O$ intercalates.

Guest	**Basal spacing [Å]**	***x***	***y***
none	15.05	0	2
pyridine	15.78	0.5	0.5
morpholine	15.61	0.35	1.0
piperazine	15.69	0.34	1.0
aniline	15.64	0.28	1.0
1-naphthylamine	15.39	0.12	1.0

2.2. Strontium and barium phenylphosphonates as host materials

Strontium and barium phenylphosphonate can be prepared in a way analogous to that for $CaC_6H_5PO_3 \cdot 2H_2O$ described above.[36,D12,D13] The formula of the prepared compound is $MeC_6H_5PO_3 \cdot 2H_2O$ (Me = Sr, Ba).



a

b

Figure 8. (a) Course of the reaction of the $Sr(C_6H_5PO_3H)_2$ suspension with ammonia in the presence of $Sr(NO_3)_2$. (Inset) Time dependence of pH at the beginning of the reaction; the numbers represent the milliliters of added NH_4OH. **(b)** Course of the reaction of the $Ba(C_6H_5PO_3H)_2$ suspension with ammonia in the presence of $BaCl_2$ solution. (Inset) Time dependence of pH at the beginning of the reaction.

New phosphonates with formula $MeC_6H_5PO_3 \cdot 2H_2O$ (Me = Sr, Ba) can be prepared from the known $Me(C_6H_5PO_3H)_2$ in a way proposed for calcium phenylphosphonate.[27,D10] This preparation is based on the reaction of $Me(C_6H_5PO_3H)_2$ with OH^- ions in a moderately basic medium and in the presence of Me^{2+} ions. The reaction was carried out by the computer-controlled addition of an ammonia solution to a suspension of $Me(C_6H_5PO_3H)_2$ in aqueous solution of $Sr(NO_3)_2$ or $BaCl_2$. The dependence of pH on the amount of added ammonia (expressed as a molar amount of added ammonia per one mol of $Me(C_6H_5PO_3H)_2$) is given in Figure 8. Since only one equivalence point was observed at $n(NH_4OH)/n(Me(C_6H_5PO_3H)_2) = 2$, the reaction proceeds according to the equation

$$Me(C_6H_5PO_3H)_2 + 2NH_4OH + Me^{2+} \rightarrow 2MeC_6H_5PO_3 \cdot 2H_2O + 2NH_4^+. \qquad (4)$$

In contrast to the analogous reaction of $Ca(C_6H_5PO_3H)_2$ with ammonia,[27] there is no formation of an intermediate.

The reverse reaction namely formation of $Me(C_6H_5PO_3H)_2$ from $MeC_6H_5PO_3 \cdot 2H_2O$ in the presence of an acid was also investigated. This reaction was accomplished using the same experimental arrangement as in the reaction of $Me(C_6H_5PO_3H)_2$ with ammonia. In this case an aqueous suspension of $MeC_6H_5PO_3 \cdot 2H_2O$ was titrated with phenylphosphonic acid. At the beginning of the additions, only a decrease of pH is observed due to the increased concentration of the H^+ ions (see insets in Figure 9). After several additions of the acid, the reaction starts as follows from the exponential increase of pH with time between the additions of the acid. The pH reaches the value of about 6 before another addition of the acid. This value of pH is then maintained roughly the same up to the molar ratio $n(C_6H_5PO_3H_2)/n(MeC_6H_5PO_3 \cdot 2H_2O) = 1$. Further additions of the acid cause a rapid decrease of pH (solid line in Figure 9). The product was identified as $Me(C_6H_5PO_3H)_2$. The same behavior was observed when chloroacetic acid instead of phenylphosphonic acid was used (dashed line in Figure 9a) in the reaction with $SrC_6H_5PO_3 \cdot H_2O$. The product of this reaction was the same as in the case of the reaction with phenylphosphonic acid and according to EDX did not contain chlorine.

It can be deduced that the reaction proceeds according to the equation

$$2MeC_6H_5PO_3 \cdot 2H_2O + 2H^+ \rightarrow Me(C_6H_5PO_3H)_2 + Me^{2+} + 2\ H_2O \qquad (5)$$

and that any acid can be used in this conversion. As in Equation (4), no formation of an intermediate was observed, in contrast to the analogous reaction of $CaC_6H_5PO_3 \cdot 2H_2O$.[27]

The difference between the above described reactions of strontium and barium phenylphosphonates is in the acidity at which the reactions proceed. As is shown in Figures 8 and 9, the value of pH at which the reactions take place is about one unit of pH lower for the Sr compound than for barium phenylphosphonate.

Strontium[37,D15] and barium[38,D16] 4-carboxyphenylphosphonates with formulae $Me(HOOCC_6H_4PO_3H)_2$ and $Me_3(OOCC_6H_4PO_3)_2 \cdot 2H_2O$ can be prepared in a way similar to that used for the phenylphosphonates. It was found that depending on the acidity of the reaction medium, $Me(HOOCC_6H_4PO_3H)_2$ can be converted to

$Me_3(OOCC_6H_4PO_3)_2 \cdot yH_2O$ and vice versa. As an intermediate in these reactions, $MeH(OOCC_6H_4PO_3)$ is formed. Copper 4-carboxyphenylphosphonate[39,D17] with formula $Cu(HOOCC_6H_4PO_3)$ in which the structure of its inorganic part resembles that of dioctahedral sheets typical for clays containing trivalent metals can be synthesized hydrothermally. Unfortunately, all these 4-carboxyphenylphosphonates do not show any intercalation behavior.

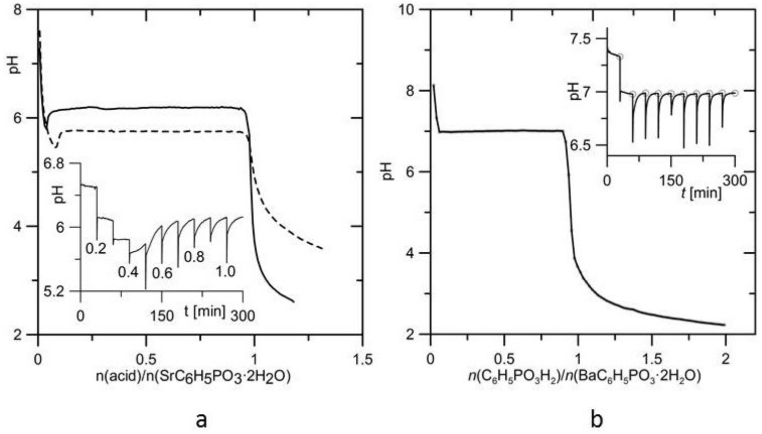


Figure 9. (a) Reaction of $SrC_6H_5PO_3 \cdot 2H_2O$ suspended in water with the phosphonic acid solution (solid line). The analogous reaction of $SrC_6H_5PO_3 \cdot 2H_2O$ with the chloroacetic acid solution (dashed line). (Inset) Time dependence of pH at the beginning of the reaction; the numbers indicate the milliliters of the added acid. **(b)** Course of the reaction of the $BaC_6H_5PO_3 \cdot 2H_2O$ suspension with the phosphonic acid solution. (Inset) Time dependence of pH at the beginning of the reaction; circles indicate the values of pH used for the pH vs. molar ratio dependence shown in the main figure.

2.2.1. Intercalation chemistry of strontium phenylphosphonate

Alcohol intercalated strontium phenylphosphonates were prepared by additions of alcohols into aqueous solutions of strontium phenylphosphonate (further denoted as **SrPP**). These intercalates are unstable and deintercalate spontaneously at ambient conditions. For the complete elucidation of their structure a combination of a single-crystal X-ray diffraction and molecular modelling was used. The structure of the host layers in methanol (**SrPP·MeOH**) and ethanol (**SrPP·EtOH**) intercalates is composed of strontium atoms which are eight-coordinated by oxygen atoms of the phosphonate groups and water molecules. The structures of **SrPP·MeOH** and **SrPP·EtOH** differ in orientation of the benzene rings. The alcohol molecules reside in the cavities formed among the benzene rings and are coordinated to the Sr atoms of the host layer by their oxygen atoms. On the basis of the structure of **SrPP·EtOH** structures of propanol and butanol intercalates and of strontium phenylphosphonate dihydrate (**SrPP·2H$_2$O**) were modeled. The proposed model of **SrPP·2H$_2$O** with three kinds of water molecules elucidates its behavior in dependence on temperature and humidity of the environment.[40,D18] Molecular modeling was also used for the elucidation of intercalation behavior of 1,n-diol intercalates of strontium phenylphosphonate.[41,D19]

2.2.2. Intercalation chemistry of barium phenylphosphonate

Barium phenylphosphonate dihydrate is a compound which undergoes intercalation reactions[42,D14] analogous to those of $CaC_6H_5PO_3 \cdot 2H_2O$.

Intercalation into barium phenylphosphonate dihydrate. In contrast to amines, which can be easily intercalated at room temperature, alkanols must be intercalated at elevated temperature. Therefore, the intercalates of alkanols (from propanol to dodecanol) were prepared by a solvothermal treatment at 160 °C. The alkanol intercalates of $BaC_6H_5PO_3$ can also be prepared by heating in a microwave field,[10-11,D4-D5] with the exception of intercalates with 1-propanol and 1-butanol, which have low boiling points and the reaction temperature cannot be achieved. All alkanol intercalates are quite stable in air, whereas the amine intercalates are less stable - they decompose during washing with toluene or hexane and new phases with lower basal spacings were sometimes formed during their drying in an evacuated ampoule. The dependence of the basal spacing on the number of carbon atoms in the guest chain is given in Figure 10. The dependence is linear with the slope of 1.29 and 1.26 for amines and alkanols intercalates, respectively. From Equation (3) it follows that the guest molecules are arranged in a monomolecular way and are perpendicular or nearly perpendicular to the host layers in the case of alkanols. The intercalates of amines have the basal spacing by about 2.5 Å higher than the intercalates of alkanols with the same number of carbon atoms.

Both aliphatic amines and alkanols can also be intercalated into anhydrous barium phenylphosphonate ($BaC_6H_5PO_3$) at room temperature.[42]

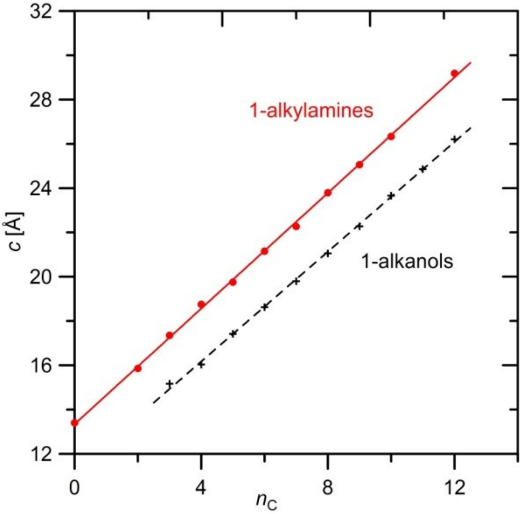


Figure 10. Dependence of the basal spacing *c* on the number of carbon atoms in the guest chain n_C for the intercalates prepared from barium phenylphosphonate dihydrate.

3. Strontium methylphosphonate as a host material[43,D20]

Strontium methylphosphonate trihydrate with formula $SrCH_3PO_3 \cdot 3H_2O$ represents a new host material related to above described $MeC_6H_5PO_3 \cdot 2H_2O$. We determined its structure and investigated its intercalation reactions.

Structure of $SrCH_3PO_3 \cdot 3H_2O$. Strontium methylphosphonate is a layered compound, the neutral layers are composed of SrO_7 pentagonal bipyramids (see Figure 11). The methylphosphonate groups are placed alternately above and below the plane of the layers. One water molecule bridges two Sr atoms, another two water molecules reside in the interlayer space, as shown in Figure 12. As it is obvious from this figure, the methyl groups are not placed evenly, so that the layers form a kind of a corrugated structure.

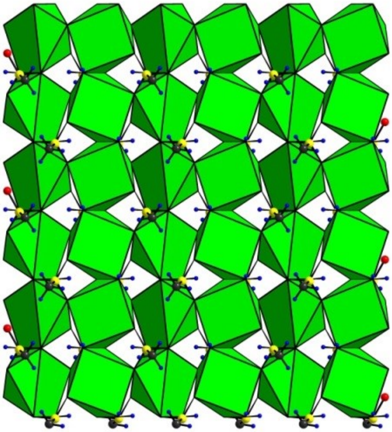


Figure 11. Strontium phosphonate layer viewed in the direction perpendicular to the plane of the $SrCH_3PO_3$ layers. SrO_7 polyhedra are shown in green, P atoms in yellow.

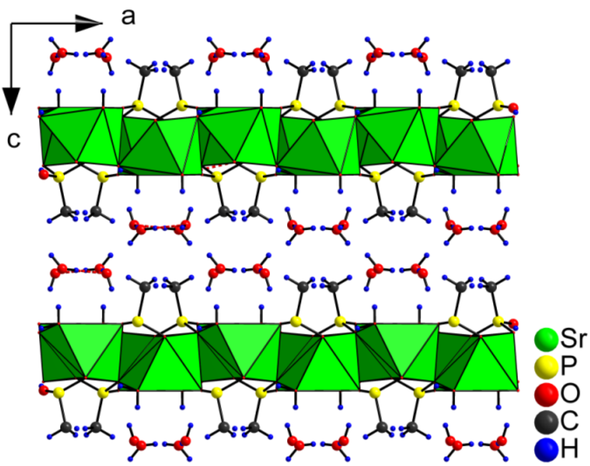


Figure 12. Stacking of the methylphosphonate layers.

3.1. Intercalation chemistry of strontium methylphosphonate

The ability of strontium methylphosphonate to intercalate organic neutral compounds was studied predominantly on straight-chained amines and alcohols that is on primary monoamines, monoalcohols, 1,ω-alkanediols and 1,2-alkanediols.[43,D20]

Aliphatic amines can be intercalated at room temperature, but the prepared intercalates are very unstable. They lose the guest during washing with toluene or hexane or during drying in an evacuated ampoule and therefore the guest content cannot be determined. As shown in Figure 13, the basal spacing of the amine intercalates (with $n_C = 3\text{-}8$) increases linearly with the length of the carbon chain. The slope, $\Delta c/\Delta n_C$, is 2.26. Using Equation (3) we infer that the amine molecules are deposited in the interlayer space of the host in two layers with the aliphatic chain inclined at angle of 62° with respect to the plane of the host layers.

Three types of alcohols were intercalated into strontium methylphosphonate: (i) 1-alkanols, (ii) 1,ω-alkanediols, and (iii) 1,2-alkanediols. In contrast to the amines, the alcohol intercalates are generally stable at ambient conditions and can be easily isolated by evaporating the excess of the guest or by washing the intercalate with toluene or hexane. The intercalates do not contain water and, on the basis of thermogravimetry and elemental analyses, their general formula can be written as $SrCH_3PO_3 \cdot x$(alcohol).

The content of the alcohol decreases with increasing length of its carbon chain. Probably, the longer chains prevent the full intercalation of the alcohols into the interlayer space and the products remain partially hydrated. In the case of 1,2-diols, only 1,2-ethanediol is fully intercalated into strontium methylphosphonate, with the formula of the intercalate $SrCH_3PO_3 \cdot HOCH_2CH_2OH$. Although 1,2-ethanediol can be considered as a diol with terminal OH groups (1,ω-diol), its amount in the intercalate ($x = 1.0$) indicates that this diol is bound to the phosphonate layer by only one of its OH groups.

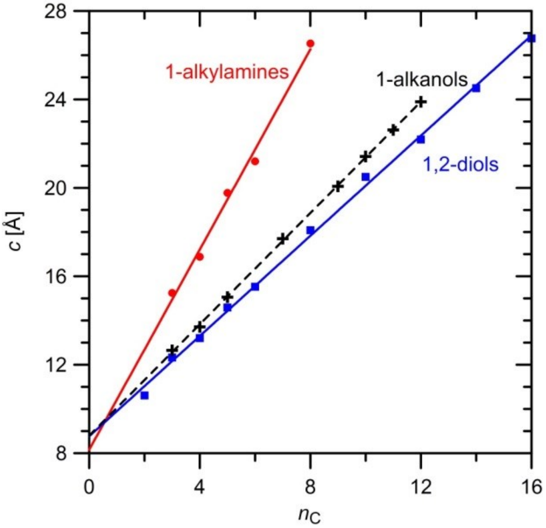


Figure 13. Dependence of the basal spacing c on the number of carbon atoms in the guest chain n_C for the intercalates of strontium methylphosphonates with amines (circles), 1-alkanols (triangles and crosses) and 1,2-alkanediols (squares).

In contrast to 1,2-alkanediols, intercalations of 1,ω-alkanediols do not proceed easily and the intercalates formed are usually accompanied by strontium methylphosphonate monohydrate or anhydrous strontium methylphosphonate. Only the 1,5-pentanediol intercalate, containing a half of the 1,5-pentanediol molecule per formula unit, was prepared in a pure form.

As in the case of the amine intercalates, the basal spacing c of the 1-alkanol intercalates depends linearly on the number of carbon atoms in the alkyl chain n_C (except for the 1-hexanol and 1-octanol intercalates) with the slope of 1.26 (Figure 13). The angle α at which the straight carbon chains are tilted with respect to the plane of the host layers calculated according to Equation (3) is 80° and the 1-alkanol molecules are deposited in the interlayer space of the host as a monolayer. Linear dependence was found also for 1,2-alkanediols with the slope of 1.13 and the angle of tilting $\alpha = 62°$. Also in this case a monolayer of the guest molecules is presumed. Most probably the secondary hydroxyl group is attracted to the host layers and this effect is the cause of the smaller tilting angle.

The reason why the alcohol intercalates are more stable than the amine ones can be explained in the following way: In the structure of $SrCH_3PO_3 \cdot 3H_2O$, the bridging water molecule is coordinated to two Sr atoms through its two free electron pairs. The position of this water molecule is the most favorable for this coordination as indicated by the Sr-Ow-Sr angle of 103.6° (where Ow is the oxygen atom of the coordinated water molecule). We can presume that the position of this coordinated water molecule is retained also in $SrCH_3PO_3 \cdot H_2O$. The oxygen atom of the alcohol molecules in the intercalates can be expected to be in the same position, with the same coordination arrangement as in $SrCH_3PO_3 \cdot 3H_2O$ or in $SrCH_3PO_3 \cdot H_2O$. This assumption is supported by the fact that the value of c for $n_C = 0$ calculated from the linear dependence c vs. n_C for the 1-alkanol and 1,2-alkanediol intercalates is 8.79 Å and 8.77 Å, respectively. These values are very close to the basal spacing found for $SrCH_3PO_3 \cdot H_2O$ (8.50 Å). The stability of the intercalates is influenced by free electron pairs present on a donor atom – oxygen or nitrogen in alcohols or amines. Two electron pairs of the oxygen donor atom in $SrCH_3PO_3 \cdot H_2O$ are bound more strongly to the two metal centers whereas one electron pair of nitrogen in an amine molecule can be bound more weakly. The coordinated water molecule can be replaced by the oxygen atom of the alcohol molecule and thus form a relatively strong bond between the host layer and the guest. Such bonding is suppressed in the case of intercalated amines and the coordination of the amine molecules is expected to be weaker.

Oxygen-containing oligomers and polymers, namely di(ethylene glycol) (DEG), tri(ethylene glycol) (TEG) and poly(ethylene glycol) (with average molecular weight of 1000, further denoted as PEG 1000), form stable intercalates with formulae $SrCH_3PO_3 \cdot 0.5$ DEG, $SrCH_3PO_3 \cdot 0.5$ TEG and $SrCH_3PO_3 \cdot 1.0(C_2H_4O)$ (where C_2H_4O is a monomeric unit of PEG 1000). These intercalates were prepared by hydrothermal treatment of the glycols with $SrCH_3PO_3 \cdot$1-pentanol at 100 °C. The glycol/$SrCH_3PO_3$ ratios indicate different ways of the arrangement of glycols in the interlayer space. The DEG and TEG guests are anchored as 1,ω-diols (glycol/$SrCH_3PO_3 = 0.5$, the value analogous to that found for 1,ω-diols) whereas PEG 1000 coordinates to the strontium atoms through its etheric oxygen atoms and the PEG chains lie parallel to the host layers.

In general, strontium methylphosphonate represents a new layered material with a simple composition and a facile preparation. The structure of its trihydrate was determined by single-crystal X-ray diffraction of crystals prepared by slow sorption of ethanol vapors into a saturated aqueous solution of strontium methylphosphonate. Layered $SrCH_3PO_3 \cdot 3H_2O$ can serve as a host material for an intercalation of organic compounds containing atoms with free electron pairs. The driving force for this intercalation is coordination of the nitrogen or oxygen atoms of the guest to the strontium atoms of the host. Since the structure of the host compound, strontium methylphosphonate, is known, the way of deposition of the guest molecules into the interlayer space and the way how the guest molecules are anchored to the host layers can be deduced. The possibility to intercalate polymeric guests, as proven by the intercalation of PEG 1000 into strontium methylphosphonate, means that this host material is prospective for the preparation of polymeric nanocomposites.

4. Zirconium 4-sulfophenylphosphonate as a host material

The organophosphonates of tetravalent metals, especially those of zirconium, are mostly robust compounds. From the numerous studies of various layered zirconium phosphonates it was inferred that the structure of these compounds was derived from the structure of alpha modification of zirconium hydrogen phosphate monohydrate, $Zr(HPO_4)_2 \cdot H_2O$, in which the OH groups were replaced by an organic radical.

The organic backbone of the phosphonate can be modified by various functional groups enhancing the ability of this layered host material to interact with proper guest species. The mostly used type of the organic backbone contains a benzene ring attached to the phosphonate group, as the benzene ring can be easily functionalized using current methods of organic chemistry. One of the functional groups most interesting is the sulfonic group, SO_3H, for its high acidity; the solids containing this group are in many cases good protonic conductors. Regarding the metal phosphonates with the sulfonic group, mostly 3-sulfophenylphosphonates are reported in the literature, as 3-sulfophenylphosphonic acid can be prepared directly by sulfonation of phenylphosphonic acid.[44] Recently, 4-sulfophenylphosphonic acid has been synthesized from 4-bromo(diethyl)sulfonate by the reaction with triethylphosphite in the presence of $NiCl_2$ (the Tavs reaction).[45] We prepared this compound in a slightly different way, by acid catalyzed hydrolysis of 4-sulfamoylphenylphosphonic acid ($NH_2SO_2C_6H_4PO_3H_2$).[46] The reaction scheme is shown in Figure 14 and the details of the synthesis are given in the paper.[47,D9] This 4-sulfophenylphosphonic acid was then used for the preparation of layered zirconium 4-sulfophenylphosphonate dihydrate (further denoted as **ZrSPP·2H₂O**).

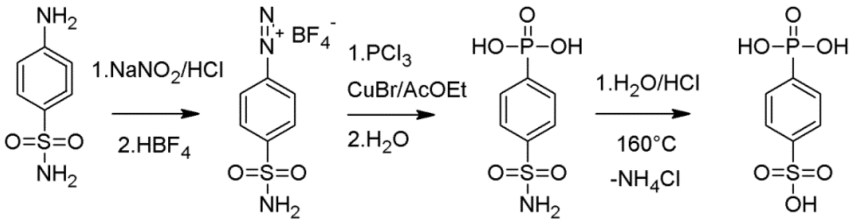


Figure 14. Scheme of synthesis of $HO_3SC_6H_4PO_3H_2$.

Zirconium 4-sulfophenylphosphonate dihydrate with the formula $Zr(HO_3SC_6H_4PO_3)_2·2H_2O$ is a layered compound with the interlayer distance of 19.94 Å, according to its powder X-ray diffraction pattern. It can be dehydrated by heating to 300 °C.

The nature of the layered zirconium phosphates and phosphonates allows preparation of mixed layered compounds as is layered mixed zirconium phosphate 4-sulfophenylphosphonate with formula $Zr(HPO_4)_{0.7}(HO_3SC_6H_4PO_3)_{1.3}·2H_2O$. The advantage of the mixed compounds rests in the possibility to "tune" the amount of the functionalized part that is to change the concentration of the functional groups present on the layer of the host material. Based on similar features of powder patterns of α-**ZrP** and **ZrSPP** we suppose that the structure of **ZrSPP** contains zirconium phosphonate layers of the α-**ZrP** type, from which the 4-sulfophenyl groups are jutting out above and below. The proposed structure of **ZrSPP** is shown in Figure 15. The sulfonic groups, placed in the middle of the interlayer space, are responsible for the high acidity of this material and consequently for its high reactivity with basic compounds.

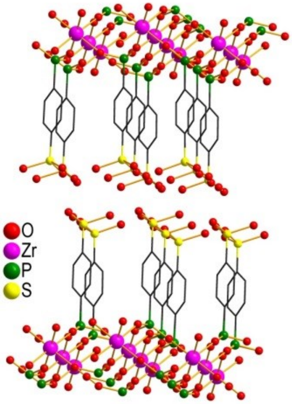


Figure 15. Assumed structure of zirconium 4-sulfophenylphosphonate.

The FT IR and solid state NMR measurements confirmed the presence of strongly acidic hydrogen on the sulfonic group.[47,D9] Based on the NMR findings, the structure of hydrogen bonding network in the interlayer space was proposed. Due to their insolubility in water, good thermal stability and a considerably high protonic conductivity, **ZrSPP** and the derived layered compounds are promising candidates for applications as components of proton exchange membranes in fuel cells.

4.1. Intercalation chemistry of zirconium 4-sulfophenylphosphonate[48,D21]

Due to the acidity of the sulfonic group, **ZrSPP** can easily be intercalated with organic bases, for instance amines.

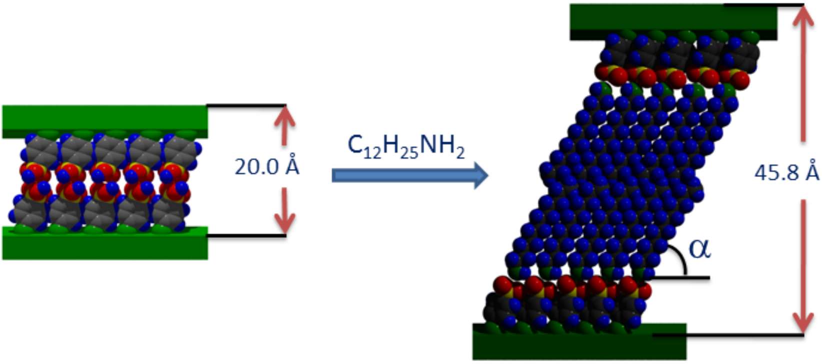


Figure 16. Intercalation of 1-dodecylamine into **ZrSPP** - schematic depiction.

By intercalation of amines the interlayer space is enlarged, as shown schematically in Figure 16 for 1-dodecylamine as a host. The corresponding increase of the interlayer distance can be very high, for instance in the 1-dodecylamine intercalate it is more than 45 Å. The dependence of the basal spacing c (equal to the interlayer distance) on the number of carbon atoms n_C of the aliphatic chain is linear in the homologous series of amines, from methylamine to dodecylamine. From the value of the slope, $\Delta c/\Delta n_C = 2.108$ it follows, according to Equation (3), that the amine molecules are deposited in the interlayer space in two layers ($m = 2$) with the inclination of the carbon chains to the host layers α of 55° with respect to the plane of the host layers.

Alberti et al. in the work on zirconium phosphate-alkylamine intercalates predicted[49] from the cross-sectional diameter of the alkyl chains (4.4 Å) and the distance between the hydrogen phosphate functional groups that the angle α should be around 56° for a compact arrangement of the alkylamine molecules, which is in a good agreement with our observations.

As inferred from the thermogravimetric analysis, the amine intercalates contain 1.8 amine molecules per formula unit and no water. The intercalates are quite stable, for instance the basal spacing of the hexylamine intercalate only slightly decreases on drying in air at room temperature from 33.4 to 32.8 Å. Also other N-containing guests can be intercalated into **ZrSPP**. These intercalates are listed in Table 2.

Structural considerations on these **ZrSPP** intercalates and probable arrangement of the guest molecules in the interlayer space are described in detail in our paper.[48,D21]

Table 2 Intercalates of N-containing guests (other than alkylamines) with general formula **ZrSPP·*x*(guest)·*y*(H_2O)**

Guest	**Basal spacing [Å]**	***x***	***y***
none	19.96	0	2.3
1,4-phenylenediamine	23.62	1.0	6.0
p-toluidine	32.18	1.8	1.0
1,8-diaminonaphthalene	25.07	0.8	2.0
1-aminopyrene	35.23	1.5	1.0
imidazole	22.63	1.0	1.0
pyridine	23.65	0.2	1.2
poly(ethylene imine)	21.70	1.3	1.8
glycine	24.83	1.0	1.0
3-aminopropionic acid	27.02	1.4	0
6-aminocaproic acid	33.01	2.0	3.0

5. Intercalation of optically active organic molecules into layered host materials

In the last part of this text intercalations of organic compounds interesting from the point of their optical properties will be described.[50,D22] Organic π-conjugates, in which donor and acceptor functional groups are present, are interesting compounds as an intramolecular charge-transfer (ICT) might occur in them, forming a dipole. Such compounds can serve as active optical materials for miscellaneous applications in nonlinear optics and optoelectronics. An example is a tripodal push-pull system, based on triphenylamine, intercalated into layered materials having acidic functional groups. Triphenylamine based compounds represent a $(A\text{-}\pi)_3\text{-}D$ type of Y-shaped push-pull molecules featuring a central amino donor and three acceptor-substituted π-branches. As the guest compound of this type we have chosen tris[4-(pyridin-4-yl)phenyl]amine (**TPPA**), whose structure is shown in Figure 17. By its quarternization (either N-alkylation or protonation) the electron withdrawing ability of pyridine can be improved and consequently the ICT effect enhanced.

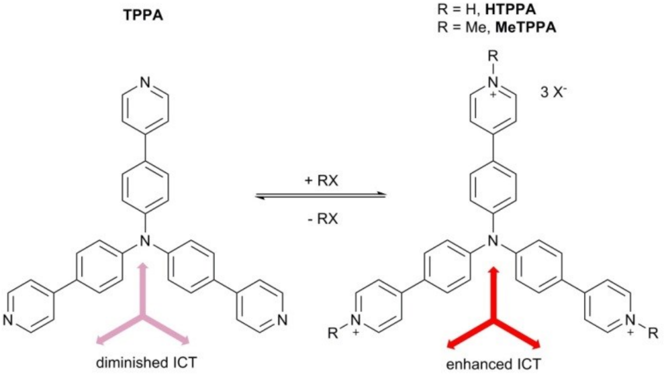


Figure 17. TPPA and its quaternized forms. Influence on the intramolecular charge-transfer.

By intercalation of **TPPA** into acid-function bearing layered materials we tried both to quarternize this compound and simultaneously to order its molecules in the confined space of the layered host. In addition, the intercalates prepared should have better thermal stability compared to the original organic guest.[50,D22]

As the host materials we used the α-modification of zirconium hydrogen phosphate ($Zr(HPO_4)_2$, **ZrP**) and zirconium 4-sulfophenylphosphonate, whose ability to intercalate nitrogen-containing heterocycles is described above. Two compounds with the formulae $Zr(HPO_4)_2 \cdot 0.21(C_{33}H_{24}N_4) \cdot 2.5H_2O$ and $Zr(HO_3SC_6H_4PO_3)_{1.3}(C_6H_5PO_3)_{0.7} \cdot 0.35(C_{33}H_{24}N_4) \cdot 2.5H_2O$ (further denoted as **ZrP·TPPA** and **ZrSPP·TPPA**) were prepared.

From geometrical considerations it follows that the **TPPA** molecules are arranged in the interlayer space of **ZrP** in a way depicted in Figure 18. The same arrangement is assumed for **ZrSPP·TPPA**.

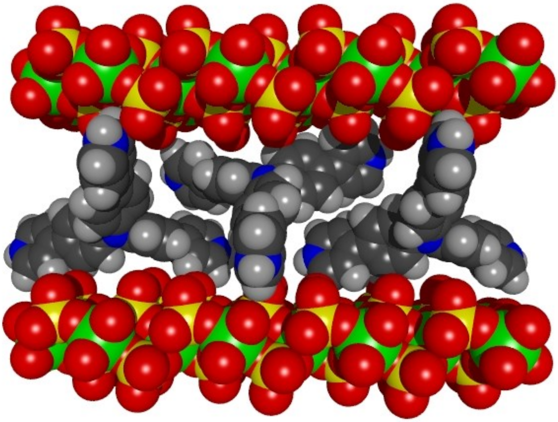


Figure 18. Schematic arrangement of the **TPPA** molecules in the interlayer space of **ZrP**. Atoms: Green - Zr, yellow - P, red - O, dark grey - C, light grey - H, blue - N.

The driving force for the intercalation process in **ZrP** is a proton transfer from the host HPO_4 group to the intercalated amine. During the intercalation the pyridine nitrogen atoms are protonated, while the OH groups of the phosphate are deprotonated. The protonated nitrogen atoms should be as close to the acidic oxygen atoms of the phosphate groups as possible. This condition can be fulfilled when the **TPPA** molecules are placed on the host layer in a manner shown in Figure 18.

It follows from the structure of **ZrP** that on the surface of the host layer is a "free area" of 24 Å^2 associated to each phosphate group. Hence, for each $Zr(HPO_4)_2$ formula unit we have 2 × 24 = 48 Å^2 free area that can be covered with the guest. Let us consider that the triangular **TPPA** molecule is anchored to one layer of **ZrP** by its base (side) and to the another neighboring layer by its apex (corner). Cross section of the base (the area which is covered by this part of the **TPPA** molecule) is about 116 Å^2. Cross section at the apex of **TPPA** is about 21 Å^2. The area covered by the **TPPA** molecule in **ZrP·TPPA** is therefore 0.21 × (116 + 21) = 29 Å^2, which is an area much smaller than that provided by the **ZrP** host. In the case of **ZrSPP·TPPA**, the area covered by the **TPPA** molecule is 0.35 × (116 + 21) = 48 Å^2, which indicates that the whole surface of the **ZrSPP** layer is covered by the guest molecules. Consequently, the amount of **TPPA** intercalated into **ZrSPP** (0.35 per formula unit) represents the maximum amount which can be intercalated into this type of the host.

The van der Waals volume of the **TPPA** molecule calculated by a Hyperchem software[51] is 462 Å^3. The molecular geometry was optimized by PM3 and PM7 semi-empirical methods implemented in programs ArgusLab[52] and MOPAC2012.[53] The volume accessible for the intercalated entities might be calculated as the "free area" (24 Å^2) multiplied by the gallery height. Thus for **ZrP·TPPA** the accessible volume is 24 × 12.2 = 293 Å^3 and for **ZrSPP·TPPA** it is 24 × 16.4 = 394 Å^3. **ZrP·TPPA** contains 0.21 molecules of **TPPA** per formula unit, and the space occupied by **TPPA** is therefore 0.21 × 462 = 97 Å^3 and in **ZrSPP·TPPA** it is 0.35 × 462 = 162 Å^3. In both cases there is enough space for water molecules to be placed among the **TPPA** molecules.

Characterization of the intercalated TPPA. To determine, whether the **TPPA** guest present in the intercalate is protonated or neutral, the IR spectra of **TPPA** and its methylpyridinium derivative (tris(4-(N-methylpyridinium-4-yl)phenyl)amine, **MeTPPA**) were measured and compared with the IR spectra of **ZrP·TPPA** and **ZrSPP·TPPA**. Due to the similarity of the bands between 1585 and 1484 cm^{-1} found in **MeTPPA**, **ZrP·TPPA** and **ZrSPP·TPPA** we conclude that in both intercalates the **TPPA** guest is present in the protonated form.

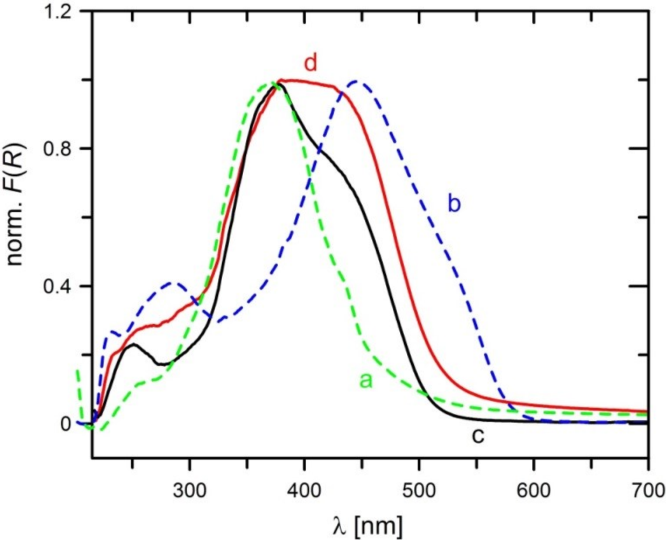


Figure 19. UV-Vis spectra of **(a) TPPA**, **(b) MeTPPA**, **(c) ZrP·TPPA**, **(d) ZrSPP·TPPA**. The diffuse reflectance *F*(*R*) was calculated using the Kubelka–Munk function.

On the other hand, from the comparison of the UV-Vis spectra of **TPPA**, **MeTPPA** and those of the intercalates it follows that both intercalates contain **TPPA** both in protonated and deprotonated forms in an equilibrium, see Figure 19. This finding is in discrepancy with the IR spectra measurements, as the bands of deprotonated **TPPA** were not found in the IR spectra of **ZrP·TPPA** and **ZrSPP·TPPA**. To solve this problem, we measured IR spectra of **TPPA** protonated to one half. The IR spectrum of the resulting product was different from that of **TPPA** and corresponded to the spectrum of **MeTPPA**. It means that the IR spectrum of even partially protonated **TPPA** completely loses the character of the spectrum of deprotonated **TPPA** and corresponds to the fully protonated form. Thus both the UV-Vis and IR spectra confirmed that the **TPPA** guest in **ZrP·TPPA** and **ZrSPP·TPPA** was partially protonated.

Deconvolution of the longest-wavelength absorption maxima λ_{max} of **ZrP·TPPA** and **ZrSPP·TPPA** revealed two peaks appearing at ~370 and 450 nm that fit the positions of ICT peaks of **TPPA** and **MeTPPA**. The observed bathochromic shift with $\Delta\lambda_{\max} \sim 80$ nm is similar to that observed in the solution (see above) and indicates enhanced ICT in both intercalates. In the case of **ZrP·TPPA** the shape of the spectrum implies that the deprotonated form is present in the intercalate in a higher relative amount than in **ZrSPP·TPPA** and hence the interlayer environment of the **ZrSPP** host is more acidic than that of **ZrP**. The question arises whether this partially protonated **TPPA** in the intercalates might be further protonated by exposing the intercalates to an acidic environment. When the **ZrP·TPPA** and **ZrSPP·TPPA** intercalates are subjected to HCl vapors overnight, their UV-Vis spectra change distinctly and are identical with that of **MeTPPA** (see Figure 20 for **ZrP·TPPA**). The powder XRD pattern of **ZrP·TPPA** after the exposition is identical with that before exposition. It means that no deintercalation occurred in this case. On the other hand, the powder XRD pattern of **ZrSPP·TPPA** after the exposition is identical with that of **ZrSPP**; it means the **TPPA** guest molecules are deintercalated in an acidic environment.[50,D22]

The prepared materials represent the first example of a tripodal push-pull organic molecule which was confined in layered materials with the aim to influence its optical properties. In view of the current interest in novel inorganic-organic hybrid materials, this structure-property relationships study would serve as a useful guide for designing new intercalates with tunable optical properties.

We proved that the incorporation of optically active organic molecules can enhance the nonlinear optical properties when we intercalated three push‑pull aminopyridine derivatives with the formulae shown in Figure 21 into **ZrSPP** and **ZrP.** The measured SHG efficiencies of the intercalates are larger than those observed for the pure organic push‑pull chromophores. Hence, the methodology of intercalation turned out to be very useful strategy for property tuning of NLO-active organic molecules.[54,D23]

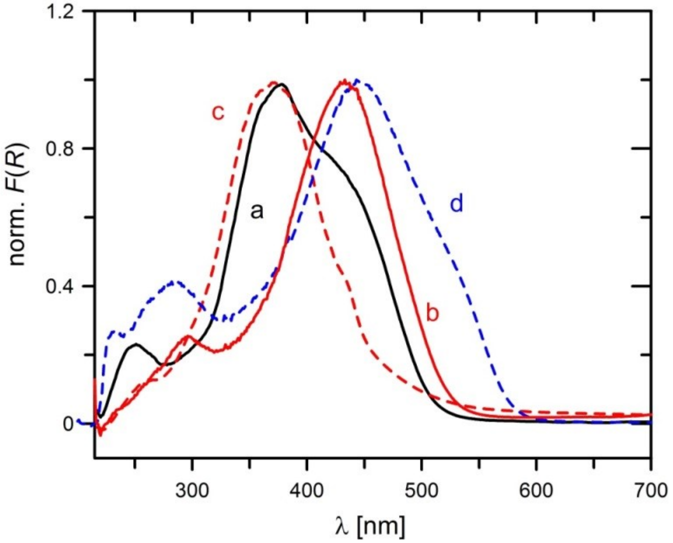


Figure 20. UV-Vis spectra of **(a) ZrP·TPPA**, **(b) ZrP·TPPA** treated with HCl, **(c) TPPA**, **(d) MeTPPA**.

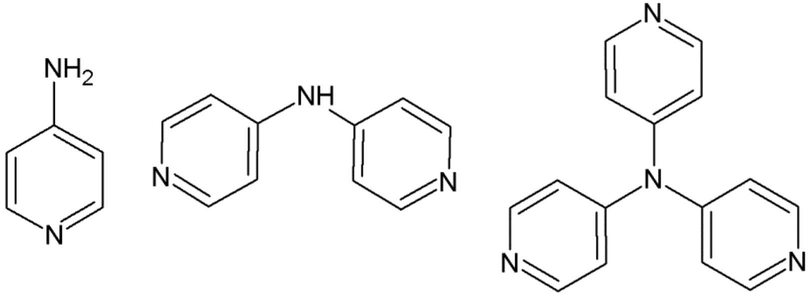


Figure 21. Aminopyridine derivatives intercalated into **ZrSPP** and **ZrP**.

6. Conclusions and future trends

The aim of the presented text is to acquaint the reader with some research fields studied in our laboratory. In the first part, the rich intercalation chemistry of vanadyl phosphate was introduced and some intercalation methods and processes were presented. In the second part, several new layered metal phosphonates were described and their ability to intercalate selected guest materials was reported. It was shown that even the intercalation chemistry of quite simple layered compounds, which can be easily prepared at mild conditions, is an unexplored field of chemistry and can produce new interesting materials.

Intercalation properties of $VOPO_4$. As follows from the intercalation studies done for the $VOPO_4$ intercalates, the term rigidity or flexibility of the layers as a factor determining the behavior of the host during intercalation cannot be considered *per se* but in every case the nature of the intercalated species must be taken into consideration. As we saw for the α_I-modification of vanadyl phosphate, its behavior depends on how the interactions between the $VOPO_4$ layers and the intercalated species are strong. Alkali metals intercalates prepared by redox reactions form quite stable compounds indicating a strong interaction between the host layers and the guest species. Neutral organic molecules, like alcohols, on the other hand form weak bonds between the host structure and the guest molecules. In addition, the intercalation of alcohols into $VOPO_4$ is a slow process, allowing the formation of transitive structures in which a part of the interlayer space in the $VOPO_4$ crystals are filled with the guest while there are still areas where the structure of the original starting material is retained.

Vanadyl phosphate is one of a few materials which are able to form two types of intercalation compounds: either intercalates with neutral molecules with weak host-guest interactions, in which the driving force is a coordination of electron-donor atom of the guest to an appropriate site on the host layer, or redox intercalates with rather strong electrostatic interactions between positively charged guest cation and negatively charged host layer of $VOPO_4$ in which a part or all vanadium(V) atoms were reduced to V(IV). Thus we had at our disposal a material which exhibited a various mechanisms of the intercalation processes. From this point of view the intercalation chemistry of $VOPO_4$ is almost educational example for how rich, diverse and interesting the intercalation chemistry might be.

Intercalation into phosphonates of alkaline-earth metals. To the best of our knowledge, our papers devoted to the intercalations into alkaline-earth metal phenylphosphonates and into strontium methylphosphonate are the first descriptions of coordinative intercalations of neutral organic guests into such compounds. The advantage of these host materials is their facile preparation and relatively cheap starting materials. A disadvantage might be in some cases a low stability of the prepared intercalates and especially the fact that these host materials can decompose in acidic environment. On the other hand, it can be an advantage in cases when a need of a targeted delivery of intercalated species is needed. Intercalated guest materials can be protected by being incorporated between the layers of the host, and then can be released from the intercalate by the increase of the acidity of the medium in which they are placed. Preliminary experiments with methylphosphonates of other alkaline-earth metal alkylphosphonates indicate that they behave in a way analogous to that of $SrCH_3PO_3$.

Intercalation into zirconium-based layered host materials. We have prepared a new layered host material based on 4-sulfophenylphosphonic acid with formula $Zr(HO_3SC_6H_4PO_3)_2 \cdot 2H_2O$. The 4-sulfophenylphosphonate ligand can be combined with other ligands as exemplified in $Zr(HPO_4)_{0.7}(HO_3SC_6H_4PO_3)_{1.3} \cdot 2H_2O$. Such combinations form a base for a new class of layered materials which could serve as hosts in intercalation chemistry, catalysts for heterogeneous acid-catalyzed reactions, ion-exchangers or proton conductors. Zirconium 4-sulfophenylphosphonate has proved to be a good host material for the intercalation of organic guest molecules, both aliphatic and aromatic, containing amino groups.

By intercalation of a homologous series of aliphatic amines a set of intercalates is obtained in which the alkyl chains are oriented in the same fashion. This uniform arrangement results in a linear dependence of the interlayer distance of the intercalate on the number of carbon atoms of the intercalated guest. While mono substituted amines are arranged in the interlayer space of the host in a bilayer fashion, disubstituted amines, like p-phenylenediamine, form monolayer pillared structures. Functionalized amines, like amino acids, can be also intercalated. For a homologous series of intercalated amino acids, the same effect as for the series of amines was observed and also in this case the bilayer arrangement of the guest molecules is formed. We succeeded also in intercalation of polymers, namely poly(ethylene imine).

Zirconium 4-sulfophenylphosphonate was also applied as a host for intercalation of optically active molecules. In the case presented in this work, tris[4-(pyridin-4-yl)phenyl]amine was successfully intercalated into zirconium 4-sulfophenylphosphonate and also into α-modification of zirconium phosphate. It was found that the guest amine is protonated during the intercalation on the peripheral pyridine-4-yl moieties. The UV-Vis spectra suggested an equilibrium between the protonated and non-protonated forms of the amine. Based on the amount of the intercalated species and the enlargement of the interlayer space caused by the intercalation the probable arrangement of the molecules of the guest in the intercalate was suggested.

Future trends in this research field. From the structural point of view, metal phosphonates offer a large variation of possibilities - one of them is the variation of the organic skeleton to introduce various shapes of the interlayer space in the host or functionalization of the organic part of the phosphonate to introduce functional groups able to interact with the guest species. Another might be the variation of the metals used for the preparation of the host compounds - this is interesting from the point of their potential application in catalysis, or in optoelectronics (presence of luminescent trivalent lanthanides).

The field of intercalation chemistry is by no means exhausted. There are many new challenges lying ahead of scientists working on layered materials. In connection with nanotechnology it is a question of preparation of nanosheets from these materials (an example is exfoliation of $VOPO_4$), nanocomposites (one way leading to nanocomposites might be intercalation of polymers into layered host materials, as was mentioned in the chapter on intercalation chemistry of strontium methylphosphonate), application in optoelectronics (which was a subject of our recent research grant, see the previous chapter).

7. Publications that form the basis of the dissertation

D1. Beneš, L.; Melánová, K.; Zima, V.; Kalousová, J.; Votinský, J., Possible mechanisms of intercalation. *J. Incl. Phenom. Macrocycl. Chem.* **1998,** *31* (3), 275-286.

D2. Kalousová, J.; Votinský, J.; Beneš, L.; Melánová, K.; Zima, V., Vanadyl phosphate and its intercalation reactions. A review. *Collect. Czech. Chem. Commun.* **1998,** *63* (1), 1-19.

D3. Beneš, L.; Melánová, K.; Svoboda, J.; Zima, V., Intercalation chemistry of layered vanadyl phosphate: a review. *J. Incl. Phenom. Macrocycl. Chem.* **2012,** *73* (1-4), 33-53.

D4. Costantino, U.; Vivani, R.; Zima, V.; Beneš, L., Microwave-assisted intercalation of 1-alkanols and 1,omega-alkanediols into alpha-zirconium phosphate. Evidence of conformational phase transitions in the bimolecular film of alkyl chains. *Langmuir* **2002,** *18* (4), 1211-1217.

D5. Beneš, L.; Melánová, K.; Zima, V.; Kalousová, J.; Votinský, J., Preparation and probable structure of layered complexes of vanadyl phosphate with 1-alkanols and 1,omega-alkanediols. *Inorg. Chem.* **1997,** *36* (13), 2850-2854.

D6. Beneš, L.; Melánová, K.; Zima, V., Intercalation of 1-alkanols and 1,omega-alkanediols into NbOPO4 and NbOAsO4. *J. Solid State Chem.* **1998,** *141* (1), 64-69.

D7. Zima, V.; Kilián, M.; Casciola, M.; Massinelli, L., Intercalation compounds of vanadyl phosphate dihydrate with rubidium ion and their electrical properties. *Chem. Mater.* **1999,** *11* (11), 3258-3262.

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D11. Beneš, L.; Melánová, K.; Svoboda, J.; Zima, V., Intercalation behavior of calcium phenylphosphonate dihydrate CaC6H5PO3·2H2O. *J. Incl. Phenom. Macrocycl. Chem.* **2010,** *66*, 279–284.

D12. Zima, V.; Svoboda, J.; Beneš, L.; Melánová, K.; Trchová, M., New strontium phenylphosphonate: synthesis and characterization. *Solid State Sci.* **2006,** *8* (11), 1380-1385.

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