

Syntheses, Structure and Intercalation Properties of Low-Dimensional Phenylphosphonates, $A(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ (A = Alkali Metal, NH_4 and Tl)

Koya Prabhakara Rao^[a] and Kanamalur Vidyasagar^{*[a]}

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Seven new low-dimensional phenylphosphonates, $A(\text{H}-\text{O}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ [A = Li (**1**), Na (**2**), K (**3**), Rb (**4**), Cs (**5**), NH_4 (**6**) and Tl (**7**)], have been synthesized and characterized by X-ray diffraction, spectroscopic and thermal studies. They crystallize in triclinic unit cells with two formula units and have approximately planar arrangement of A^+ ions, coordinated to oxygen atoms of phenylphosphonates, on

both sides. Compounds **1** and **6** are one-dimensional, whereas others are two-dimensional. All of them undergo room-temperature intercalation reactions with primary n -alkylamines and ammonia. Single crystal X-ray structures of compounds **1**, **2** and **6** have been determined.

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Introduction

Metal organophosphonates are a class of organic-inorganic hybrid materials, in which the organophosphonate groups are covalently bonded to the metal inorganic backbone. In the recent past, there has been a renewed interest and activity in the research arena of metal organophosphonates,^[1–6] mainly due to their varied compositions, structural diversity and potential applications^[7–11] like sorbents, ion-exchangers, sensors, and catalysts. The expansion^[1–6,12,13] of metal organophosphonate chemistry includes phosphonates and diphosphonates of s -, p -, d - and f -block metals. The structures reported for these compounds could be broadly classified into two categories, namely, zero-dimensional types^[14] such as mononuclear and complex molecular clusters and extended framework types^[15] of one-, two- and three-dimensional networks. Mostly low-dimensional, namely chain and layered, structures are observed for the compounds of second type, due to the segregation of hydrophobic regions of organic moieties from the rest of the framework.

The solid-state chemistry of phenylphosphonates constitutes a significant portion of this research area. Reported are many investigations about the synthesis, structures and properties of di-, tri-, tetra-, penta-, and hexavalent metal phenylphosphonates^[16–21] with extended frameworks, such as $\text{Ca}(\text{HO}_3\text{PPh})_2$, $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{HO}_3\text{PPh})_2$,

$\text{Zn}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$, α - and β - forms of $\text{Al}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$, $\text{Al}(\text{HO}_3\text{PPh})_3 \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{O}_3\text{PPh})_3 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$, $\text{Fe}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$, $\text{HFe}(\text{HO}_3\text{PPh})_4$, $\text{La}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$, $\text{Zr}(\text{O}_3\text{PPh})_2$, $\text{Th}(\text{O}_3\text{PPh})_2$, $[\text{VO}(\text{O}_3\text{PPh})] \cdot 2\text{H}_2\text{O}$, $[\text{MoO}_2(\text{O}_3\text{PPh})] \cdot \text{H}_2\text{O}$, $[\text{UO}_2(\text{O}_3\text{PPh})] \cdot 0.7\text{H}_2\text{O}$, $[\text{UO}_2(\text{HO}_3\text{PPh})_2(\text{H}_2\text{O})]_2 \cdot 8\text{H}_2\text{O}$, $[(\text{UO}_2)_3(\text{HO}_3\text{PPh})_2(\text{O}_3\text{PPh})_2] \cdot \text{H}_2\text{O}$. These examples illustrate the structural diversity and the compositional variations with different ratios of metal to phenylphosphonates, mono- and di-anionic forms of phenylphosphonic acid and inclusion of O^{2-} and/or H_2O in the coordination sphere of metals. One noteworthy feature of all reported phenylphosphonates is their insolubility in water that enabled their isolation as precipitates from aqueous solutions. Most of these compounds, especially those with 1:1 and 1:2 ratios of metal to phenylphosphonic acid content, are lamellar phases. They contain layers of metal atoms coordinated to oxygen atoms of phosphonate groups and, in a few cases, additionally to O^{2-} and/or H_2O as well. The hydrophobic phenyl groups of phosphonates protrude into the interlayer region, on both sides of the inorganic metal layer.

Intercalation of metal phenylphosphonates is well studied^[16b,17b–17f] and important from the point of view of sensors.^[9] For example, the lamellar 1:1 divalent metal phenylphosphonates, such as $\text{Zn}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$, are known to intercalate ammonia and amines, which occupy the interlayer region and coordinate to the metal. This intercalation involves Lewis acid–base reaction that brings a change in the coordination sphere of the metal. The dependence of interlayer distance of intercalates on the chain length of the intercalated n -alkyl primary amine, structural elucidation of intercalates and stereo selectivity towards primary amines for intercalation have been reported.^[17b–17f]

[a] Department of Chemistry,
Indian Institute of Technology Madras,
Chennai, 600036, India
E-mail: kvsagar@iitm.ac.in

All 1:2 tri- and divalent metal phenylphosphonates, such as $\text{La}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$ ^[18c] and $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$ ^[16b] have similar lamellar structure of $\text{Zr}(\text{O}_3\text{PPh})_2$ ^[19b] with different coordinations for metals. Lewis acid-base intercalation of primary amines has been reported for only one compound, $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$. These compounds contain mono $(\text{HO}_3\text{PPh})^-$ anions and are, therefore, potential solid Brønsted acids. The acid-strength would be higher for lower-valent metal phases, and the potentiality of these compounds as Brønsted-acid hosts, for intercalation of bases such as ammonia and amines, has not been investigated so far. This Brønsted acidity is distinctly different from the one reported^[22] as due to functional SO_3H group of the phenyl moiety.

It is in this context that 1:2 phenylphosphonates of monovalent metals, $\text{A}(\text{HO}_3\text{PPh})(\text{H}_2\text{O}_3\text{PPh})$ are envisaged to be strong solid Brønsted acids that can undergo intercalation with bases. It is surprising that no structurally characterized monovalent metal phenylphosphonate has been reported so far. $\text{Na}_2(\text{O}_3\text{PPh})$ and $\text{Na}(\text{HO}_3\text{PPh})$ are the only two compounds of this family realized by Corbridge and Tromans,^[23] who reported the powder X-ray data without any crystallographic information. In view of these observations, we undertook a study of 1:2 phenylphosphonates of alkali and thallium metals and ammonium. We report here the successful synthesis, characterization and intercalation chemistry of seven new phenylphosphonates, $\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ [$\text{A} = \text{Li}$ (1), Na (2), K (3), Rb (4), Cs (5), NH_4 (6) and Tl (7)].

Results and Discussion

X-Ray Diffraction and Crystal Structures: The powder X-ray diffraction (XRD) patterns (Figure 1) of all the seven $\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ compounds are, in general, similar to one another, corroborating the similarity of the values of their triclinic unit cell parameters. The 001 reflection, with the 2θ value of about 5° , is the most intense and the observed main reflections arise from a family of $\{00l\}$ planes. The values of unit cell volumes of 2–7 vary in accordance with the relative sizes of A ions and lithium compound 1, however, has slightly bigger unit cell volume than sodium compound 2. For the four structurally characterized compounds 1, 2, 5 and 6, the observed powder XRD patterns agree with those simulated, using the LAZY-PULVERIX program,^[24] on the basis of single-crystal X-ray structures. However, the observed relative intensities of some of the 00 l reflections are more than those calculated, due to the preferential orientation of the crystallites. The XRD powder pattern of 2 is different from those of $\text{Na}_2(\text{O}_3\text{PPh})$ and $\text{Na}(\text{HO}_3\text{PPh})$.^[23]

The values of the triclinic unit cell parameters of compounds 1–7, though similar, show that they have five types of structures. The single-crystal X-ray data sets of compounds 1, 2, 5 and 6 have enabled the identification of the four types, whereas the fifth type, namely the structure of the thallium compound (7), could not be ascertained. Com-

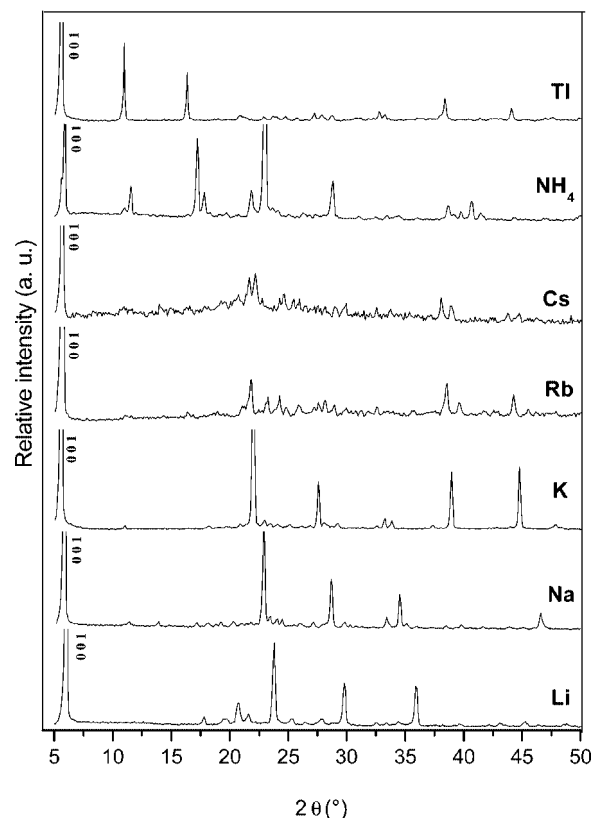


Figure 1. Powder X-ray diffraction patterns of $\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ [$\text{A} = \text{Li}$ (1), Na (2), K (3), Rb (4), Cs (5), NH_4 (6) and Tl (7)] compounds.

pounds 3 and 4 have the structure type of 5. The structural and crystallographic similarities, as deduced from XRD study, of the seven phosphonates, 1–7 are as follows: Two formula units are present in their centrosymmetric triclinic unit cells. A^+ ions are confined approximately to ab plane and coordinated to oxygen atoms of phosphonates on both sides. The phenyl groups are oriented, without *interdigitation* and π - π stacking, in approximately perpendicular fashion to the ab planes. Thus hydrophobic regions of phenyl groups separate the *inorganic* ab planes. The observed values of bond lengths and angles of these phosphonates compare well with those reported^{16–21} in the literature. The labeling Scheme followed is such that P(1) is bonded to O(1)–O(3) oxygen atoms and C(1) carbon atom of phenyl ring C(1)–C(6), whereas P(2) is similarly bonded to O(4)–O(6) and C(7) of phenyl ring C(7)–C(12).

Lithium compound (1) is, as shown in Figure 2, one-dimensional in nature. O(3) and O(6) form short P–O bonds of ca. 1.49 Å length. Lithium is tetrahedrally bonded to these two oxygen atoms of four [two P(1)O₄ and two P(2)O₄] phosphonate moieties. Each LiO₄ tetrahedron is connected to two such tetrahedra, through O(3)–O(6) edges, and also to phosphonate moieties, to form one dimensional chains of $\text{Li}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$, along a -axis. These chains are apart by 8.50 Å within the ab plane and 14.99 Å between such planes. The other four oxygen atoms form longer P–O bonds of 1.53–1.56 Å length and have acidic

hydrogen atoms.^[18d] The hydrogen bonding between these four oxygen atoms hold the chains along *b*-axis.

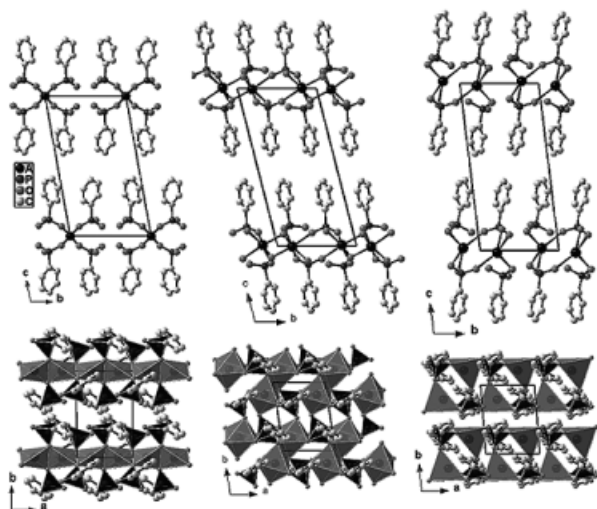


Figure 2. Unit cell of $A(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ [$A = \text{Li}$ (1) (left), Na (2) (middle) and NH_4 (6) (right)], viewed along the *a* axis (top: ball-stick representation) and the *c* axis (bottom: polyhedral representation).

Sodium compound (2) is a two-dimensional phosphonate (Figure 2). The layered framework could be conceived as being built from centrosymmetric $\text{Na}_2\text{O}_6(\text{O}_3\text{P}-\text{C}_6\text{H}_5)_4$ blocks, each of which consists of an edge-shared bioctahedral Na_2O_{10} unit, corner-connected to four phosphonates. Only five of the crystallographically distinct oxygen atoms, O(1)–O(5), are involved in octahedral coordination of sodium. Two NaO_6 octahedra share an edge, O(5)–O(5') to form a Na_2O_{10} unit, which links, at the O(5) and O(3) atoms, to four phosphonate moieties. These building blocks are linked to one another such that the phosphonates of one block are corner-connected to Na_2O_{10} units of another, resulting in the layered framework. Sodium atom is coordinated to oxygen atoms of six phosphonate groups, whereas the phosphonates of P(1) and P(2) are coordinated to three and two sodium atoms respectively. These $\text{Na}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ layers are stacked along *c*-axis, with an inter-layer distance of 15.59 Å. The three oxygen atoms, O(1), O(2) and O(4), form longer P–O bonds of 1.54–1.58 Å length and have acidic hydrogen atoms. The hydrogen bonding exists between these oxygen atoms as well as O(6).

$\text{NH}_4(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ (6) is one-dimensional compound (Figure 2). With the cut-off distance of 3.0 Å for bonding, the nitrogen atom is found to be hydrogen-bonded, in an irregular tetrahedral fashion, to four oxygen atoms, O(1), O(2), O(3) and O(5), of four phenylphosphonate moieties. This arrangement leads to ladder-like chains, parallel to *a*-axis. The layered framework is not feasible, because the nitrogen atoms are not hydrogen-bonded to oxygen atoms of neighbouring chain in the *ab* plane, even with the higher cut-off value of 3.6 Å for bonding. These chains are apart by 7.66 Å within the plane and 16.34 Å between the planes. O(3) and O(6) form longer P–O bonds

of ca. 1.56 Å length and have two acidic hydrogen atoms, H(13) and H(14), that are hydrogen-bonded to O(5) and O(2), respectively. Furthermore, O(4)–H(15) is strongly hydrogen-bonded to O(1).

The positional parameters of cesium (5) and ammonium (6) compounds are similar. However, cesium compound is two-dimensional and cesium is nine-coordinate, with the maximum value of Cs–O bond length being 3.52(2) Å. The layered framework of 5 is due to higher coordination number of cesium, which bonds additionally to oxygen atoms of those corresponding neighbouring chains in one-dimensional 6. Compounds 3 and 4 are isostructural with the layered 5, and potassium and rubidium are computed to be eight-coordinate. It could only be inferred that the structure type of thallium compound 7 has a similar arrangement of phosphonate moieties, which bond differently to thallium atoms in the *inorganic ab* plane. Thus the differences between the above five structure types stem from the different types of coordination of A^+ ions.

The reported 1:2 tetra-, tri- and divalent metal phenylphosphonates, with no additional $\text{O}^{2-}/\text{H}_2\text{O}$, have similar structural features of compounds 1–7. $\text{Zr}(\text{O}_3\text{PPh})_2$,^[19b] $\text{La}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$,^[18d] $\text{Mn}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$,^[18b] $\text{A}(\text{HO}_3\text{PPh})_2$ ($A = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$)^[16a–16e] and the compounds 1–7 are the only 1:2 metal phenylphosphonates, for which the unit cell parameters have been determined from either single-crystal X-ray data or structural elucidation. Similar unit cell lengths of $(5.36\text{--}6.16) \text{ Å} \times (7.65\text{--}10.215) \text{ Å}$ are due to analogous planar arrangement of *A* atoms. The different types of coordination of *A* atoms and stacking of planes of *A* atoms are responsible for the variations in the third axis length and unit cell angles.

Spectroscopic and Thermogravimetric Data: Infrared spectra of compounds 2 and 6 are presented in Figure 3. The C–H stretching vibrations of the phenyl ring in the region 3090–3000 cm^{-1} , the aromatic C=C stretching vibrations at 1438 cm^{-1} , the peaks at 692 and 745 cm^{-1} representing the out-of-plane bending of the mono substituted phenyl ring, the peak at 2376 cm^{-1} , characteristic of PhPO_3H group, the peak at 1594 cm^{-1} due to phenyl group stretching, the P–O stretching vibrations in the region 1200–1000 cm^{-1} and the O–P–O bending vibrations in the region 540–410 cm^{-1} , are the common features^[18a,21a] observed in the infrared spectra of the seven compounds, 1–7. The infrared spectrum of ammonium compound (6), shows two additional peaks at 3240 and 1401 cm^{-1} corresponding to the stretching and bending vibrations of the ammonium ion.^[25] All these compounds, as illustrated in the solid-state ^{13}C and ^{31}P spectra (Figure 4) of 2, show four ^{13}C signals^[16b] between 140.0–120.0 ppm, corroborating the presence of aromatic carbon atoms and three ^{31}P signals^[18a] between –1.2 and 7.8 ppm. Thermogravimetric analysis revealed, as illustrated with the case of 2 in the Figure 5, that all compounds 1–7 are stable up to about 200 °C and then undergo weight losses of 51.5%, 48.5%, 46.0%, 42.0%, 37.0%, 71.1% and 32.50%, respectively, in the temperature range 200–700 °C in four or five steps. These values agree with those calculated for $\text{AP}_2\text{O}_{5.5}$ as the products of decom-

position for alkali and thallium metal compounds. All of them undergo further decomposition above 700 °C.

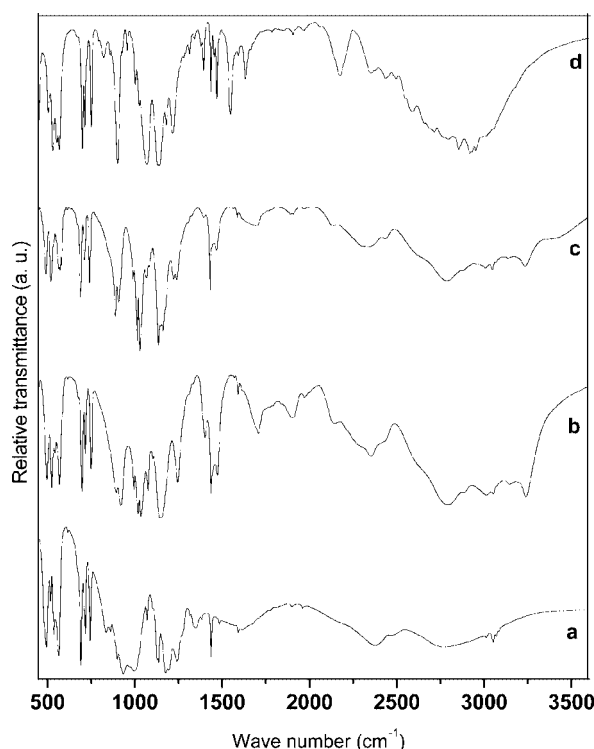


Figure 3. Infrared spectra of (a) sodium (2) and (b) ammonium (6) compounds and the intercalates of sodium compound, (c) $2 \cdot (\text{NH}_3)_{1.2}$ and (d) $2 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_{1.5}$.

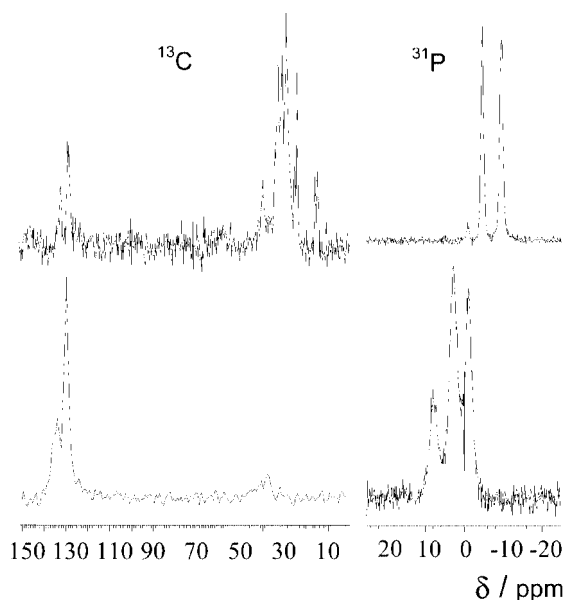


Figure 4. Solid-state ^{13}C (left) and ^{31}P (right) NMR spectra of sodium (2) compound (bottom) and its intercalate $2 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_{1.5}$ (top).

Intercalation Reactions: These seven phosphonates, 1–7 are solid Brönsted acids with a porous region between the inorganic *ab* planes. Therefore, they have been investigated from the point of view of Brönsted acid–base intercalation

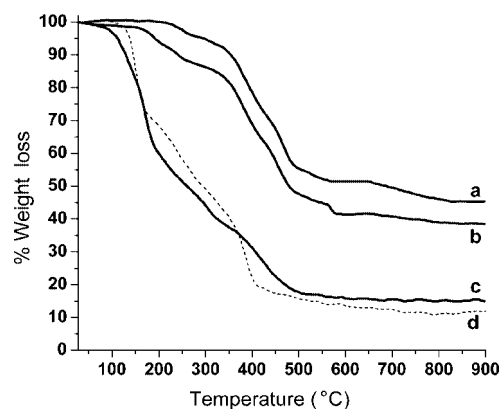


Figure 5. Thermogravimetric curves of (a) sodium (2) compound and its intercalates, (b) $2 \cdot (\text{NH}_3)_{1.2}$, (c) $2 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_{1.5}$ and (d) $2 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_{4.1}$.

reactions with ammonia and primary *n*-alkylamines, $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 4-9, 12, 16, 18$). These reactions, as determined from chemical analysis and powder XRD, spectroscopic and thermal studies, turned out to be successful.

The optimum conditions, given in experimental section, for the first method of intercalation processes have been realized from the results of several trials, under different conditions, of intercalation reaction of sodium compound with *n*-octylamine. A variation of molar ratio of *n*-octylamine and sodium phosphonate 2, from 2:1 to 3:1 to 4:1, led to intercalates, $2 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_x$ with the corresponding *x* values of 0.9, 1.5 and 1.5, showing that the maximum intercalation at room temperature could be achieved with the reactant molar ratio of 4:1. There was no significant increase in the values of *x*, when similar reactions were carried out under reflux conditions at 70–80 °C. Similar attempts under solvothermal conditions, by heating reactant mixtures with 4 mL of *n*-hexane solvent, at 170 °C over a period of 2 days, resulted in only polycrystalline intercalates without any increase in the values of *x*. The second method involving neat liquid amines at room temperature is confined to $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 4-9, 12$) only.

The relevant data of the intercalates, $2 \cdot [\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2]_x$ and $1-7 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_x$ obtained by the first method, are presented in Table 1. The values of *x* range from 0.5 to 4.0 and do not seem to show any systematic trend with either *n* or A. The powder XRD patterns of $2 \cdot [\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2]_x$ intercalates, as shown for a few selected cases in Figure 6, contain moderate to prominent reflections at low 2θ values of 2–5° and no significant reflections with 2θ of >40°. The first reflection is found to be doubled in a few cases such as $2 \cdot [\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2]_x$. It is noteworthy that the powder XRD patterns of these intercalates, do not undergo any change, even when the samples were heated in open air at 40–50 °C for 12 h. The *d* value of the first reflection is considered to be associated with the distance between the *ab* planes. This is found to be higher than that observed for the parent phase 2, due to incorporation of the amine in the porous region, perpendicularly to the inorganic *ab* planes, with the alkyl chains aligned out of the

perpendicular. These intercalates, unlike the parent **2**, do not show higher order 00 l reflections prominently. The d value increases with n except in the case of nonylamine intercalate. The values of d do not show any systematic increase with n , probably due to the presence of *gauche* and *trans* conformations of the alkyl chains of the amines in different proportions. In general, these powder XRD patterns confirm the crystalline nature of intercalates and the topotactic intercalation of the amines. The powder XRD patterns of **1–7**·(C₈H₁₇NH₂) _{x} intercalates also contain moderate to prominent reflections at low 2θ values of 2–5° and the values of d are higher than those in the parent phases. However, the increase in the d values is not systematic with respect to both A and x . Structural elucidation of these intercalates would reveal the placement of the intercalated amines and probably explain this lack of systematic variation of d with n , x and A . There are no structurally characterized Brönsted acid–base intercalates of this type reported, for a comparison. However, structurally characterized Lewis acid–base intercalates, Zn(O₃PPh)(RNH₂) (R = C₃H₉, C₄H₁₁, C₅H₁₃), were reported^[17b] to exhibit similar nonsystematic behavior, due to coordination of the intercalated amine to the metal.

Table 1. Interplanar distance (d), number (x) of mol of amine intercalated of the **2**·[CH₃(CH₂) _{$n-1$} NH₂] _{x} (top) and **1–7**·(C₈H₁₇NH₂) _{x} (bottom) intercalates.

n	–	4	5	6	7	8	9	12	16	18
x	0.0	0.5	0.9	1.2	1.7	1.5	1.5	2.0	1.7	1.9
d [Å]	15.6	17.7	19.0	19.6	20.9	21.2	20.3	25.8	27.8	28.5
A	Li	Na	K	Rb	Cs	Tl	NH ₄			
x	2.7	1.5	2.1	1.6	1.9	2.9	4.0			
d [Å]	18.7	21.2	21.0	21.3	18.8	19.2	19.2			

The infrared spectra (Figure 3) of intercalates contain, in addition to all the features of the infrared spectrum of parent phase **2**, peaks in the region 3100–2700 cm^{–1} attributed to N–H and C–H stretching vibrations^[16b] of the amine molecules. The CH₂ bending bands observed around 1437 cm^{–1} and 1470 cm^{–1} are ascribed^[26] to *gauche* and *trans* conformations of alkyl chains of amines, respectively. The relative intensities of these two bands indicate that the alkyl chains, in the intercalates containing C₄–C₈ and C₉–C₁₈ amines, are predominantly in *gauche* and *trans* conformations, respectively. The shift of N–H stretching vibrations towards lower frequencies suggests that the amine molecules are protonated^[25] and electrostatically bonded to oxygen atoms of phosphonate moieties. The solid-state ¹³C NMR spectra (Figure 4) of the intercalates show signals between 140.0–125.0 ppm and also multiple signals in the region 45.0–15.0 ppm, indicating the presence of both aromatic carbon atoms of the phenyl group and the aliphatic carbon atoms of the amines, respectively. The ¹³C signals of alkyl carbon atoms, though not fully resolved, are in order of C₁, C₂, C₃, ..., C _{n} . The ³¹P NMR spectra consist of three signals between –0.83 and –9.37 ppm, with up-field shift

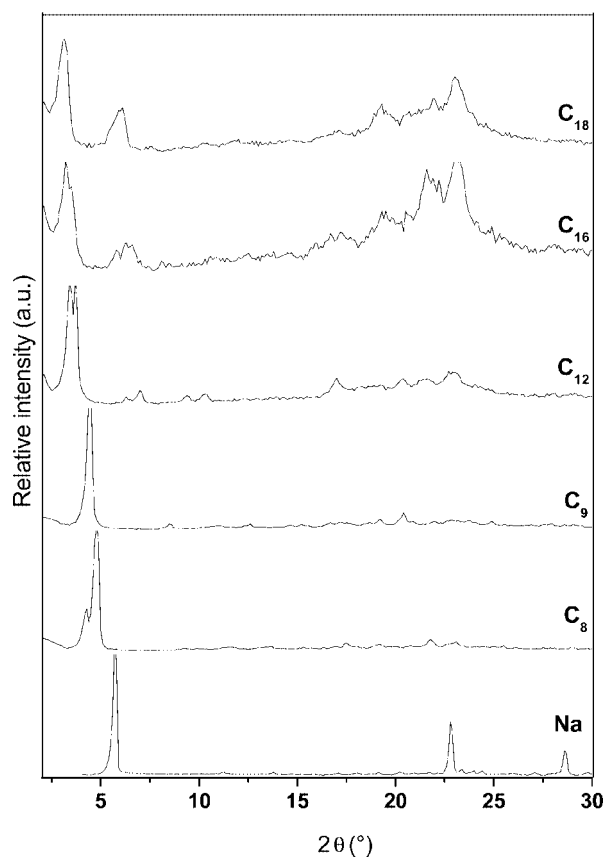


Figure 6. Powder X-ray diffraction patterns of sodium (**2**) compound and its intercalates, **2**·[CH₃(CH₂) _{$n-1$} NH₂] _{x} (n = 8, 9, 12, 16 and 18).

compared to parent phases. Thermogravimetric analysis of a few selected intercalates revealed that they undergo more percentage of decomposition than the parent phases. For example, the total decomposition of 84% for **2**·(C₈H₁₇NH₂) _{x} (Figure 5) starts at 70 °C and is completed by 600 °C. The first two stages of weight loss of 36% in the 70–200 °C range are attributable to the loss of intercalated amine, 1.5 mol of C₈H₁₇NH₂. The spectral and thermal features of other intercalates are similar to those of the sodium compound.

The second method of intercalation is compared with the first one, in terms of the compositions, the powder XRD patterns and spectral features of the corresponding intercalates. The x values of **2**·[CH₃(CH₂) _{$n-1$} NH₂] _{x} are 1.5, 2.1, 2.0, 1.4, 4.1, 2.4, 2.5 for n = 4–9 and 12, respectively. Similarly the x values of **1–7**·(C₈H₁₇NH₂) _{x} are 2.8, 4.1, 2.7, 5.0, 5.0, 3.2, 4.3, respectively. In general, the extent of intercalation, as corroborated by thermogravimetric study (Figure 5), is larger in the second method. The powder XRD patterns revealed no increase in the d values with increase in x values. There are no significant changes in their infrared and solid-state NMR spectra. The maximum amount of intercalation of primary amines reported is about two molecules per formula unit of Ca(HO₃PPh)₂·2H₂O^[16b] and 1:1 phenylphosphonates.^[17b–17f] Contrastingly, the extent of intercalation in the present 1:2 phenylphosphonates **1–7** is as high

as five molecules of amine per formula unit. This could be attributed to the Brønsted acidity of the compounds and thus intercalates with $x > 3$ and $x \leq 3$ values could be represented as $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_3^+[\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2]_{x-3}^-[\text{A}(\text{O}_3\text{PC}_6\text{H}_5)_2]$ and $[\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_3^+]_x[\text{AH}_{3-x}(\text{O}_3\text{PC}_6\text{H}_5)_2]$, respectively. Thus the amine upto the value of $x = 3$ is present as RNH_3^+ ions, whereas the amine in excess of $x = 3$ is present as RNH_2 , held together by van der Waals forces in the lattice.

The success and extent of ammonia intercalation in the intercalates, $1-7 \cdot (\text{NH}_3)_x$ have been determined from infrared spectra and the analysis of carbon and nitrogen contents. The infrared spectra contain two peaks at 3240 and 1450 cm^{-1} corresponding to the stretching and bending vibrations of the ammonium ion.^[17e] The x values of $1-7 \cdot (\text{NH}_3)_x$ are 2.0, 1.2, 1.1, 1.5, 1.7, 2.3 and 2.3, respectively, and indicate no systematic variation with A. Thus these intercalates could be represented as $[\text{NH}_4]_x[\text{AH}_{3-x}(\text{O}_3\text{PC}_6\text{H}_5)_2]$. Some of the reflections in the powder XRD patterns of ammonia intercalates are more intense than those in the parent phases. $2 \cdot (\text{NH}_3)_{1.2}$, unlike the parent phase **2**, decomposes even below 200°C and shows higher weight loss (Figure 5). The total decomposition of 59% occurs in the $160-700^\circ\text{C}$ range and the weight loss below 200°C is probably due to the loss of intercalated ammonia.

The $2 \cdot (\text{NH}_3)_{1.2}$ intercalate undergoes deintercalation, on heating. The success of deintercalation is proved by CHN analysis and absence of vibrational frequencies of NH_4^+ in the infrared spectrum of deintercalate. Moreover, its powder pattern is the same as that of parent phenylphosphonate **2**, showing that the process of intercalation and deintercalation is reversible and topotactic. This process of deintercalation is probably true for other ammonia intercalates of this study.

$\text{Zn}(\text{O}_3\text{PPh})$ and $[\text{UO}_2(\text{HO}_3\text{PPh})_2(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ have been reported^[19,21c] to be sensors and proton conductors, due to their intercalation and Brønsted acidic properties, respectively. All the seven title compounds **1-7** exhibit both these properties and could be potentially useful as sensors and proton conductors. A similar study of phenylarsonate analogues has revealed interesting structural variations, which we would report elsewhere.

Concluding Remarks

A series of seven, new low-dimensional phenylphosphonates, $\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ (A = alkali metal, NH_4 and Tl) have been synthesized and characterized by X-ray diffraction and spectroscopic studies. Lithium and ammonium compounds are one-dimensional in nature, whereas others are layered compounds. These compounds are solid Brønsted acids and undergo room-temperature intercalation reactions with primary *n*-alkylamines and ammonia. The deintercalation of ammonia occurs on heating.

Experimental Section

Synthesis: The high-purity chemicals, A_2CO_3 [A = Li, Na, K, NH_4 (SD Fine, India), Rb, Cs and Tl (Aldrich)] carbonates, phenylphos-

phonic acid, $\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$ (Fluka) and primary *n*-alkylamines, $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 4-9, 12, 16, 18$) (Fluka) were used, as purchased, for the synthesis.

$\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ [A = Li (**1**), Na (**2**), K (**3**), Rb (**4**), Cs (**5**), NH_4 (**6**) and Tl (**7**)] compounds were synthesized, on the scale of 1–2 grams, by evaporating aqueous solutions of stoichiometric reactant mixtures of phenylphosphonic acid and appropriate A_2CO_3 carbonate. Slow evaporation, at room temperature, led to the formation of compounds as colourless flaky crystals. However, evaporation on a steam bath yielded products in polycrystalline form. In all the cases, the yields were almost quantitative. These seven compounds were ascertained to be pure from the analysis of their CHN content, using elemental analyzer, Perkin–Elmer series 11 Model. $\text{C}_{12}\text{H}_{13}\text{LiO}_6\text{P}_2$ (**1**) (322.10): calcd. C 44.75, H 4.07; found C 44.29, H 4.11. $\text{C}_{12}\text{H}_{13}\text{NaO}_6\text{P}_2$ (**2**) (338.15): calcd. C 42.62, H 3.88; found C 42.75, H 4.04. $\text{KP}_2\text{O}_6\text{C}_{12}\text{H}_{13}$ (**3**) (354.26): calcd. C 40.70, H 3.70; found C 40.59, H 3.77. $\text{C}_{12}\text{H}_{13}\text{O}_6\text{P}_2\text{Rb}$ (**4**) (400.63): calcd. C 36.00, H 3.27; found C 36.23, H 3.21. $\text{C}_{12}\text{H}_{13}\text{CsO}_6\text{P}_2$ (**5**) (448.06): calcd. C 32.17, H 2.90; found C 32.47, H 2.97. $\text{C}_{12}\text{H}_{17}\text{NO}_6\text{P}_2$ (**6**) (333.21): calcd. C 43.20, H 5.14, N 4.20; found C 43.70, H 4.89, N 4.50. $\text{C}_{12}\text{H}_{13}\text{O}_6\text{P}_2\text{Tl}$ (**7**) (519.56): calcd. C 27.74, H 2.52; found C 27.45, H 2.46.

Intercalation Reactions: Intercalation reactions of *n*-alkylamines with the water-soluble phosphonates, **1-7** were carried out under nonaqueous conditions by two methods at room temperature. In the first method, a 4:1 molar reactant mixture of *n*-alkylamine and phosphonate (**1-7**), along with 15 mL of *n*-hexane, was stirred for 1.5 days. The solid products were in the form of waxy material. In the second method, the phosphonate (**1-7**) was added to excess of liquid *n*-alkylamine ($\approx 1:10$ molar ratio) and the solid immediately swelled, with the evolution of heat. The reaction mixture was left undisturbed for 7 days. The waxy solid products, in both methods of intercalation reactions, turned out to be dry powders after filtration, washing with *n*-hexane and then air drying. Intercalation of ammonia was achieved by passing ammonia gas for 2 h, over solid phosphonates (**1-7**). In summary, all these trials pertain to intercalation of nine amines, $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 4-9, 12, 16, 18$), into sodium compound (**2**), intercalation of *n*-octylamine into other six phosphonates and intercalation of ammonia into all seven phosphonates. The amount of intercalated amine/ammonia was determined from the analysis of the carbon and nitrogen contents of the solid intercalates, $2 \cdot [\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2]_x$, $1-7 \cdot (\text{C}_8\text{H}_{17}\text{NH}_2)_x$, and $1-7 \cdot (\text{NH}_3)_x$.

Ammonia Deintercalation: Ammonia deintercalation of sodium compound intercalate, $2 \cdot (\text{NH}_3)_{1.2}$ was carried out by heating the sample in air-oven at 170°C over a period of 12 h.

X-Ray Diffraction and Crystal Structure: The powder X-ray diffraction (XRD) patterns of the compounds **1-7** and their intercalation products were recorded on XD-D1 X-ray diffractometer, Shimadzu, using Cu-K_α ($\lambda = 1.5406\text{ \AA}$) radiation. Thin plate-like single crystals, suitable for X-ray diffraction, were selected and mounted with glue, on thin glass fibers in the case of compounds **2** and **4** and in glass capillaries along with the mother liquor, for other five compounds. The X-ray data were gathered successfully from the crystals of only four compounds, **1**, **2**, **5** and **6**, at 25°C , on an ENRAF-NONIUS CAD4 automated four-circle diffractometer, by the standard procedures involving ω - 2θ scan techniques. There was no decay of crystals during X-ray data collection. Empirical absorption corrections, based on psi-scans, were applied to the data sets of **1** and **2** only. In the case of **5** and **6**, these corrections were not applied because of abnormal shape and bigger size of the crystals employed. These data sets were reduced by routine computa-

Table 2. Pertinent crystallographic data for A(HO₃PC₆H₅)(H₂O₃PC₆H₅) [A = Li (**1**), Na (**2**), NH₄ (**6**)] compounds.

Compound	1	2	6
Formula	C ₁₂ H ₁₃ LiO ₆ P ₂	C ₁₂ H ₁₃ NaO ₆ P ₂	C ₁₂ H ₁₇ NO ₆ P ₂
Formula weight	322.10	338.15	333.21
Crystal system	triclinic	triclinic	triclinic
<i>a</i> [Å]	5.4561(8)	5.754(1)	6.036(9)
<i>b</i> [Å]	8.638(1)	7.904(2)	7.732(9)
<i>c</i> [Å]	15.235(3)	16.173(3)	16.61(1)
<i>α</i> [°]	100.26(2)	103.41(1)	96.43(8)
<i>β</i> [°]	91.18(2)	95.848(9)	97.63(8)
<i>γ</i> [°]	89.90(1)	97.03(1)	93.4(1)
<i>V</i> [Å ³]	706.4(2)	703.6(3)	761.3(2)
Space group (no.)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)
<i>Z</i>	2	2	2
$\rho_{\text{calcd.}}$ [g/cm ³]	1.514	1.596	1.454
λ [Å]	1.54180	0.71073	0.71073
μ [mm ⁻¹]	3.023	0.363	0.311
Total reflections	2885	2754	2947
Independent reflections	2590	2481	2662
<i>R</i> ^[a]	0.0446	0.0564	0.0618
<i>R</i> _w ^[b]	0.1255	0.1378	0.1243

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(|F_o|^2)]^{1/2}$.

tional procedures. The structure solution and refinements were carried out by the program^[27] SHELXL-97 and the graphic program^[28] DIAMOND was used to draw the structures. The structure solutions were obtained by direct method and all the non-hydrogen atoms were refined anisotropically. The non-hydrogen atom content in the asymmetric unit does not account for charge neutrality and thus indicates the presence of three acidic protons of two phenylphosphonic acid moieties. These acidic hydrogen atoms were located in the difference Fourier maps and refined with riding model restraints. The phenyl hydrogen atoms were introduced in the calculated positions and refined isotropically. The ammonium hydrogen atoms of compound **6** were similarly located in the difference Fourier map and refined with riding model restraints. The structure refinement proceeded smoothly for **1** and **2**. In the case of **6**, the final difference Fourier map showed no residual peak with electron density of $> 1 \text{ e}/\text{\AA}^3$ and the final *R* value was ca. 12%. Absorption correction, based on the isotropically refined model, was applied to the X-ray data using the program DIFABS^[29] and *R* value had come down to ca. 6.2%. Similar absorption correction was applied to the X-ray data of cesium compound **5**. The ten peaks with electron density of $> 1 \text{ e}/\text{\AA}^3$ found in the final difference Fourier map, were ghosts. The final *R* value was ca. 8.6% and the crystal structure of **5** is, nevertheless, qualitatively correct. The pertinent crystallographic data of **1**, **2** and **6** are presented in Table 2. CCDC-276185 (for **1**), CCDC-276186 (for **2**) and CCDC-276187 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

For lithium compound **1**, an alternate triclinic unit cell, with $a = 5.4561(8)$, $b = 10.209(2)$, $c = 15.235(3) \text{ \AA}$, $\alpha = 98.03(2)$, $\beta = 91.17(2)$, $\gamma = 122.2(2)^\circ$ and $V = 706.4(2) \text{ \AA}^3$, is possible. However, our choice was based on the least deviation of unit cell angles from the value of 90° . The crystals of the remaining four compounds were good enough for only the determination of their triclinic unit cell parameters, listed below.

3: $a = 5.861(3)$, $b = 7.865(3)$, $c = 16.45(1) \text{ \AA}$, $\alpha = 96.77(4)$, $\beta = 97.57(9)$, $\gamma = 94.82(5)^\circ$, $V = 742.7(8) \text{ \AA}^3$.

4: $a = 5.9183(5)$, $b = 7.9212(9)$, $c = 16.860(2) \text{ \AA}$, $\alpha = 96.948(5)$, $\beta = 93.352(2)$, $\gamma = 94.519(9)^\circ$, $V = 771.0(2) \text{ \AA}^3$.

5: $a = 6.16(1)$, $b = 7.650(7)$, $c = 16.96(2) \text{ \AA}$, $\alpha = 97.38(7)$, $\beta = 97.7(1)$, $\gamma = 93.9(1)^\circ$, $V = 775.5(6) \text{ \AA}^3$.

7: $a = 5.946(9)$, $b = 7.999(3)$, $c = 17.11(6) \text{ \AA}$, $\alpha = 90.1(5)$, $\beta = 107.6(2)$, $\gamma = 99.9(2)^\circ$, $V = 763(4) \text{ \AA}^3$.

Spectroscopic Data: The infrared spectra in the range 400 to 4000 cm⁻¹, were measured with a Bruker IFS 66V FT-IR spectrometer. The samples were ground with dry KBr and pressed into transparent discs for infrared spectroscopic study. Solid-state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) with Bruker DSX 300 and Avance 400 series spectrometers with the spinning frequency of 7.0 kHz and recycle delay times of 2 and 5 s for ³¹P and ¹³C, respectively. The first instrument operated at resonance frequencies of 121.5 and 75.5 MHz with the pulse lengths of 4.75 and 3.0 μs for ³¹P and ¹³C, respectively. Similarly resonance frequencies of 162 and 100.5 MHz with the pulse lengths of 5.0 and 5.0 μs for ³¹P and ¹³C, respectively, were employed in the second one. Chemical shifts were referenced to an external standard of 85% H₃PO₄ for ³¹P and glycine for ¹³C.

Thermal Analysis: Thermogravimetric analytical data were collected with a Netzsch STA 409C instrument. The samples were heated to 1000 °C at a rate of 10 °C per minute under a stream of nitrogen gas.

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