

Syntheses, structure and intercalation properties of low-dimensional phenylarsonates, $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{Tl}, \text{Na}, \text{K}$ and Rb)

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Abstract. Four new low-dimensional phenylarsonates, $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{Tl}$ (**1**), Na (**2**), K (**3**) and Rb (**4**)), have been synthesized and characterized by X-ray diffraction, spectroscopic and thermal studies. They crystallize in triclinic unit cells and have approximately planar arrangement of A^+ ions, coordinated to oxygen atoms of phenylarsonates, on both sides. Structure of thallium phenylarsonate as determined by single crystal X-ray diffraction, is one-dimensional, whereas those of alkali metal analogues are two-dimensional. Successful intercalation reactions of compounds **1** and **2** with primary *n*-alkyl amines have been demonstrated.

Keywords. Phenylarsonates; organic–inorganic hybrid composites; X-ray diffraction; low-dimensional compounds; intercalation.

1. Introduction

In the recent past, there has been a renewed interest and activity in the research on 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 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^{12–17} with extended frameworks, such as $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{O}_3\text{PPh}) \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{O}_3\text{PPh})_3 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$, $\text{La}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$, $\text{Zr}(\text{O}_3\text{PPh})_2$, $[\text{MoO}_2(\text{O}_3\text{PPh})] \cdot \text{H}_2\text{O}$, $[\text{UO}_2(\text{O}_3\text{PPh})] \cdot 0.7\text{H}_2\text{O}$. 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.

All 1:2 tri- and divalent metal phenylphosphonates, such as $\text{La}(\text{HO}_3\text{PPh})(\text{O}_3\text{PPh})$ ^{14c} and $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$,^{12b} have similar lamellar structure of $\text{Zr}(\text{O}_3\text{PPh})_2$,^{15b} with different coordinations for metals. 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^{12b,13b–f} and important from the point of view of sensors.⁹ Intercalation of primary amines has been reported for only one such 1:2 metal phenylphosphonate, $\text{Ca}(\text{HO}_3\text{PPh})_2 \cdot 2\text{H}_2\text{O}$, which involves Lewis acid–base reaction that brings a change in the coordination sphere of the metal. 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 we have recently investigated the potentiality of such compounds as Brønsted-acid hosts, for intercalation of bases such as ammonia and amines.

We reported¹⁸ the synthesis, characterization and intercalation chemistry of seven new phenylphosphonates, $A(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ ($A = \text{alkali metals}, \text{NH}_4$ and Tl). Lithium and ammonium compounds are one-dimensional, whereas others are two-dimensional. All of them undergo room-temperature intercalation reactions with primary *n*-alkyl amines and ammonia. The intercalates are polycrystalline and, therefore, have been structurally characterized by powder X-ray diffraction to a limited extent only. Single crystal X-ray structure determination of the intercalates is necessary to know the placement of the intercalated amines and thus explain the variation of interlayer distance with the chain length and the amount of amine intercalated.

Dedicated to Prof J Gopalakrishnan on his 62nd birthday

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The solid-state chemistry of metal arsonates^{3,6,19,20} with extended frameworks is rather limited. It is generally believed that the chemistry of metal phenylarsonates would be the same as that of the corresponding phenylphosphonates. Despite this common belief, we have undertaken a study of synthesis, structure and intercalation properties of $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{alkali metals, NH}_4 \text{ and Tl}$) phenylarsonates, with the hope of succeeding in the crystal growth and, therefore, X-ray single crystal X-ray diffraction study of their intercalated products. These efforts have led to the successful synthesis and intercalation of new $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{Tl(1), Na(2), K(3) and Rb(4)}$) phenylarsonates, among which the thallium compound possesses a new structure type. Our attempts of crystal growth of intercalated products were not fruitful. The results of these investigations are presented here.

2. Experimental

2.1 Synthesis

The high purity chemicals, A_2CO_3 ($A = \text{Na, K (SD Fine, India), Rb, Tl (Aldrich)}$) carbonates, phenylarsonic acid, $\text{C}_6\text{H}_5\text{AsO}_3\text{H}_2$ (Fluka) and eight primary n -alkyl amines, $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 5-9, 12, 16, 18$) (Fluka) were used, as purchased, for the synthesis. $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{Tl(1), Na(2), K(3) and Rb(4)}$) compounds were synthesized in polycrystalline form, on the scale of 1 g, by evaporating, on a steam bath, aqueous solutions of stoichiometric reactant mixtures of phenylarsonic acid and appropriate A_2CO_3 carbonate. In all the cases, the yields were almost quantitative. Crystal growth by slow evaporation, at room temperature, of the aqueous solutions of stoichiometric reactant mixtures was successful in the case of the thallium (**1**) compound only.

2.2 Intercalation reactions

Thallium (**1**) and sodium (**2**) phenylarsonates were examined for intercalation and a more detailed study of intercalation was confined to the latter compound. Intercalation reactions of sodium (**2**) phenylarsonate were carried out, under nonaqueous conditions, by four methods. In the first method, a 2:1 molar reactant mixture of n -alkyl amine and phenylarsonate **2** was stirred in 10 ml of n -hexane solvent, at room temperature, over a period of one day. In the second

method, the same 2:1 molar reactant mixture was refluxed in 12 ml of n -hexane solvent at $\sim 80^\circ\text{C}$ for one day. In the third method, phenylarsonate **2** was added to excess of liquid n -octyl amine ($\sim 1:10$ molar ratio) and the solid immediately swelled, with the evolution of heat. The reaction mixture was left undisturbed for 2 days. The fourth one was solvothermal method intended for crystal growth of intercalates. In this method, the same 2:1 molar reactant mixture of n -octyl amine and phenylarsonate **2** was heated along with 4 ml of n -hexane solvent, at 170°C over a period of 1 day, in a 23 ml Teflon-lined acid digestion bomb and then cooled to room temperature over a period of 1 day. In all these intercalation reactions, the solid $\mathbf{2}\cdot(\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ intercalates were filtered, washed with n -hexane and finally air-dried.

Similarly intercalates of thallium (**1**) phenylarsonate, $\mathbf{1}\cdot(\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5, 8 \text{ and } 16$) were prepared by the first method. The third method was employed to prepare $\mathbf{1}\cdot(\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5 \text{ and } 8$) intercalates. Crystal growth of n -octyl amine intercalate, $\mathbf{1}\cdot(\text{CH}_3(\text{CH}_2)_7\text{NH}_2)_x$ was attempted by the fourth method.

2.3 X-ray diffraction and crystal structure

The powder X-ray diffraction (XRD) patterns of phenylarsonates, **1-4** and the intercalation products were recorded on an XD-D1 X-ray diffractometer, Shimadzu, using $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The powder XRD patterns of compounds **1-4** were simulated, using the LAZY-PULVERIX program²¹ on the basis of single crystal X-ray structures, for the purpose of ascertaining their compositions and structures.

A good quality, needle-shaped crystal of the $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ compound (**1**) was selected and mounted on a thin glass fibre with glue. The X-ray data were gathered at 25°C , using $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), on an Enraf-Nonius CAD4 automated four-circle diffractometer, by standard procedures involving $w-2\theta$ scan technique. The data were reduced by routine computational procedures. The structure solution and refinements were carried out using the program,²² SHELXL-97 and the graphic programs^{23,24} DIAMOND and ORTEP were used to draw the structures. The structure solution was obtained by the direct method and all the non-hydrogen atoms were refined anisotropically. The nonhydrogen-atom content in the asymmetric unit does not account for charge neutrality and thus indi-

icates the presence of six acidic protons of four phenylarsonic acid molecules. These acidic hydrogen atoms and also the phenyl hydrogen atoms were introduced in the calculated positions and refined with riding model restraints. The crystallographically determined composition of $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)$ ($\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5$) for thallium (**1**) compound was corroborated by the carbon and hydrogen elemental analysis (found C, 23.81; H, 2.25% requires C, 23.73; H, 2.17%). The CIF file, containing the supplementary crystallographic data, for this compound is deposited in the Cambridge Crystallographic Data Centre; deposition number, CCDC-284740. The pertinent crystallographic data, the positional parameters and the selected bond lengths for thallium (**1**) compound are given in tables 1–3.

2.4 Spectroscopic, thermal and analytical data

The samples were ground with dry KBr and pressed into transparent discs for infrared spectroscopic study. The infrared spectra, in the range 400 to 4000 cm^{-1} , were measured on a Bruker IFS 66V FT-IR spectrometer. Solid-state nuclear magnetic resonance (NMR) experiments were performed with magic angle spinning (MAS) on a Bruker DSX 300 spectrometer operating at resonance frequencies of 75.5 MHz for ^{13}C nuclei. Chemical shifts were ref-

erenced to an external standard of glycine. The recycle delay time was 2 s and the pulse length was 3.0 μs , whereas the spinning frequency was 7.0 kHz. Thermogravimetric analysis was carried out on Netzsch STA 409C instrument. The samples were heated to 1000–1200°C at a rate of 10°C per minute, under flowing nitrogen gas. The compounds were analyzed for CHN content, using elemental analyzer Perkin–Elmer Series 11 Model.

3. Results and discussion

The powder XRD patterns of three $\text{A}(\text{HO}_3\text{AsC}_6\text{H}_5)$ ($\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5$) ($\text{A} = \text{Na}$ (**2**), K (**3**) and Rb (**4**)) alkali-metal phenylarsonates are, as strikingly evident from the d -values of the first intense reflection with the two-theta value of ~ 5 (figure 1), similar to one another but different from that of $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)$ ($\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5$) (**1**). The corresponding four phenylphosphonates possess three different, but similar, layered structures and only two structure types, namely those of alkali metal compounds, were identified¹⁸ by single crystal X-ray diffraction. Thus all four of them have similar powder XRD patterns, which are comparable to those of the three alkali metal phenylarsonates, **2–4**. The observed powder XRD pattern (figure 2) of sodium (**2**) compound agrees well with the one simulated, based on the crystal structure and *also* the triclinic unit cell parameters of $\text{Na}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$. For some of

Table 1. Pertinent crystallographic data for $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ (**1**) compound.

Formula	$\text{C}_{12}\text{H}_{13}\text{As}_2\text{O}_6\text{Tl}$
Formula weight	607.43
Crystal system	Triclinic
a (Å)	6.644(2)
b (Å)	27.290(8)
c (Å)	9.389(3)
α (°)	90.53(3)
β (°)	110.71(2)
γ (°)	90.06(3)
V (Å ³)	1592.3(8)
Space group (No.)	$P\bar{1}$ (2)
Z	4
ρ_{calc} (g/cm ³)	2.534
I (Å)	0.71073
m (mm ⁻¹)	14.289
Total reflections	6103
Independent reflections	5573
$^a R$	0.0589
$^b R_w$	0.1754

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; \quad ^b R_w = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2]}{[\sum w|F_o|^2]^{1/2}}$$

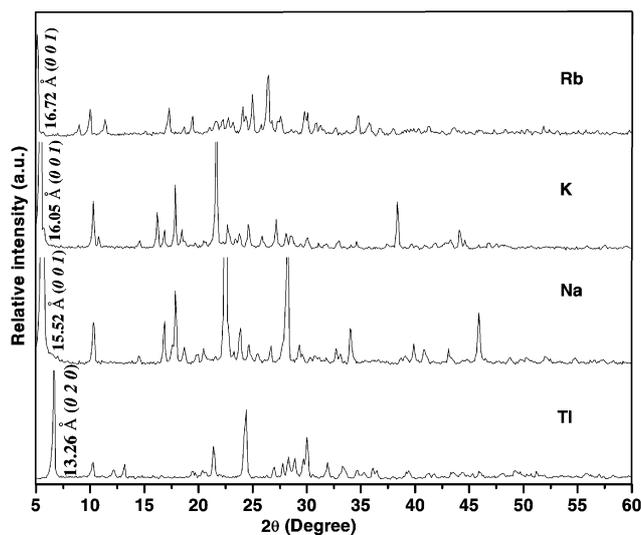


Figure 1. Powder XRD patterns of $\text{A}(\text{HO}_3\text{AsC}_6\text{H}_5)$ ($\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5$) ($\text{A} = \text{Tl}$ (**1**), Na (**2**), K (**3**) and Rb (**4**)) compounds.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of nonhydrogen atoms in $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)_2$ (**1**) compound.

Atom	<i>x</i>	<i>Y</i>	<i>z</i>	* $U_{\text{(eq)}}$
Tl(1)	0.6922(1)	0.0207(1)	0.3579(1)	0.042(1)
Tl(2)	0.3343(1)	0.4793(1)	0.6419(1)	0.042(1)
As(1)	0.1377(2)	-0.0434(1)	0.1972(2)	0.033(1)
As(2)	0.0592(2)	0.4567(1)	0.1969(2)	0.033(1)
As(3)	0.7230(2)	0.3964(1)	0.5423(2)	0.035(1)
As(4)	0.1810(2)	0.1036(1)	0.4578(2)	0.035(1)
O(1)	0.3301(17)	-0.0531(5)	0.3630(11)	0.046(3)
O(2)	0.0013(15)	0.0087(4)	0.1890(10)	0.035(2)
O(3)	0.2757(15)	-0.0371(5)	0.0713(11)	0.047(3)
O(4)	0.1912(16)	0.5080(4)	0.1897(11)	0.039(3)
O(5)	0.0357(18)	0.4469(4)	0.3669(11)	0.043(3)
O(6)	-0.2040(16)	0.4611(5)	0.0732(11)	0.047(3)
O(7)	0.5564(17)	0.4415(5)	0.4712(11)	0.048(3)
O(8)	0.8391(18)	0.3736(5)	0.4217(12)	0.050(3)
O(9)	0.9398(17)	0.4148(5)	0.6973(11)	0.051(3)
O(10)	0.0880(17)	0.0593(5)	0.5306(11)	0.043(3)
O(11)	0.4172(17)	0.1271(5)	0.5771(11)	0.049(3)
O(12)	0.2430(18)	0.0833(5)	0.3018(12)	0.053(3)
C(1)	-0.0520(20)	-0.0984(6)	0.1319(16)	0.038(4)
C(2)	0.0230(30)	0.1447(8)	0.1370(20)	0.070(6)
C(3)	-0.1080(40)	-0.1829(10)	0.0920(20)	0.082(7)
C(4)	-0.3300(30)	-0.1744(10)	0.0330(30)	0.081(7)
C(5)	-0.4160(30)	-0.1263(9)	0.0160(30)	0.076(7)
C(6)	-0.2720(30)	-0.0897(7)	0.0650(20)	0.056(5)
C(7)	0.1770(20)	0.4021(6)	0.1214(15)	0.033(3)
C(8)	0.3380(30)	0.4109(7)	0.0660(18)	0.049(5)
C(9)	0.4250(30)	0.3710(8)	0.0120(20)	0.057(5)
C(10)	0.3560(30)	0.3234(8)	0.0189(19)	0.061(5)
C(11)	0.1940(50)	0.3169(10)	0.0730(30)	0.099(9)
C(12)	0.1080(30)	0.3554(7)	0.1340(20)	0.057(5)
C(13)	0.5960(30)	0.34255(7)	0.6033(15)	0.046(5)
C(14)	0.5960(30)	0.3425(7)	0.6033(15)	0.046(5)
C(15)	0.6190(40)	0.2695(10)	0.7430(30)	0.088(9)
C(16)	0.4130(50)	0.2602(10)	0.6820(30)	0.090(8)
C(17)	0.2730(30)	0.2964(10)	0.5860(20)	0.075(7)
C(18)	0.3780(30)	0.3403(9)	0.5510(20)	0.071(6)
C(19)	0.9950(20)	0.1597(8)	0.4007(19)	0.052(5)
C(20)	0.0280(30)	0.1962(8)	0.3180(20)	0.066(6)
C(21)	0.8790(40)	0.2312(10)	0.2750(30)	0.092(8)
C(22)	0.7180(40)	0.2345(10)	0.3390(30)	0.086(8)
C(23)	0.6890(40)	0.2011(9)	0.4240(30)	0.074(7)
C(24)	0.8330(30)	0.1633(9)	0.4602(19)	0.063(6)

* $U_{\text{(eq)}}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor

the $00l$ reflections, the observed intensities are more than those calculated, indicating the preferred morphological orientations of the crystallites, which is common for compounds with such low-dimensional structures. For alkalimetal phenylarsonates, **2–4**, the d_{001} -value represents the interlayer distance and these values increase, as expected, from the sodium to the rubidium compounds (figure 1). Similarly potassium (**3**) and rubidium (**4**) phenylarsonates, as confirmed

by comparing their powder XRD patterns with the simulated ones, have the same layered structure type¹⁸ of $\text{A}(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) phenylphosphonates. The values of the triclinic cell parameters of compounds **2–4** could not be refined accurately by least square fitting of powder XRD data. However, they are deduced, from good comparison of simulated and observed powder XRD patterns, to be almost same as those of phenylphos-

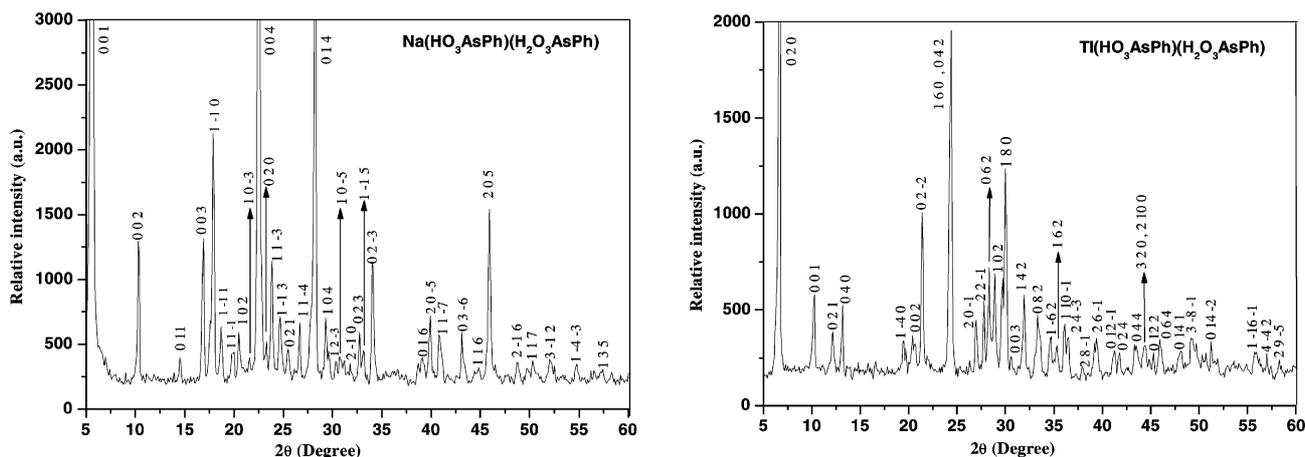


Figure 2. Powder XRD patterns of $A(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ ($A = \text{Tl}$ (**1**) and Na (**2**)) compounds.

phonate analogues. The powder XRD pattern (figure 2) and the unit cell parameters of the thallium (**1**) compound are different from those of the phenylphosphonate analogue.¹⁸ Its XRD pattern agrees well with the one simulated based on its crystal structure and the observed intensities of some of the reflections are more than those calculated.

Thus these four new phenylarsonates, **1–4**, are of three structure types, namely, known¹⁸ $A(\text{HO}_3\text{PC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{PC}_6\text{H}_5)$ ($A = \text{Na}$ and Cs) and new $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$. Some important features of two known structure types of alkali metal phenylarsonates, **2–4**, 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 phenylarsonates on both sides. The phenyl groups are oriented, without *interdigitation* and *p–p* stacking, in approximately perpendicular fashion to the ab planes. Thus hydrophobic regions of phenyl groups separate the *inorganic* ab planes. There is one layer per unit cell, with the interlayer distance of 15.52–16.72 Å.

Our realization, from powder XRD study, that the $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ (**1**) has a new type of structure and our success in growing its single crystals have prompted us to undertake its structural elucidation, by single crystal X-ray diffraction. The present study revealed that the thallium (**1**) phenylarsonate is a one-dimensional compound (figure 3), with the values of bond distances (table 3) and angles comparable to those reported in the literature.^{3,6,19,20} Four formula units are present in its centrosymmetric triclinic unit cell. Tl^+ ions are confined approximately to the ac plane and also its parallel plane at

$y = 0.5$. Thallium is coordinated to six oxygen atoms of six phenylarsonate groups on both sides and only two oxygen atoms of each phenylarsonate group are bonded to metal. TlO_6 polyhedron (figure 4) is non-uniform with effectively no interacting atoms on one side of the coordination sphere, indicating the stereo active nature of $6s^2$ lone pair of electrons of thallium. The bonding between the metal and the arsonate moiety extends in the direction parallel to the a -axis only (figure 3) and thus the compound has one-dimensional chains, parallel to the a -axis, of $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$. These one-dimensional chains are staggered along the b -axis (figure 3) and separated from one another by 13.26 Å and 8.78 Å along the b - and c -axes, respectively. The phenyl groups are oriented, without *interdigitation* and *p–p* stacking, in slanted fashion to the chains and thus accounts for the lower d_{020} value (figure 1). Had there been also a similar bonding in the direction parallel to the c -axis, this compound would have been two-dimensional and structurally similar to its phenylphosphonate analogue, the phenylphosphonates and phenylarsonates of sodium, potassium and rubidium metals. The difference between the structures of the phenylphosphonate and phenylarsonate of thallium seems to stem from the absence or presence of the stereo activity of $6s^2$ lone pair of electrons of thallium. The six oxygen atoms, O(3), O(6), O(8), O(9), O(11) and O(12), form longer As–O bonds of 1.694–1.742 Å length and have acidic hydrogen atoms. Hydrogen bonding exists between this set and another set of oxygen atoms, O(1), O(2), O(4) and O(5). The two oxygen atoms, O(7) and O(10), form very short As–O bonds of 1.638 and

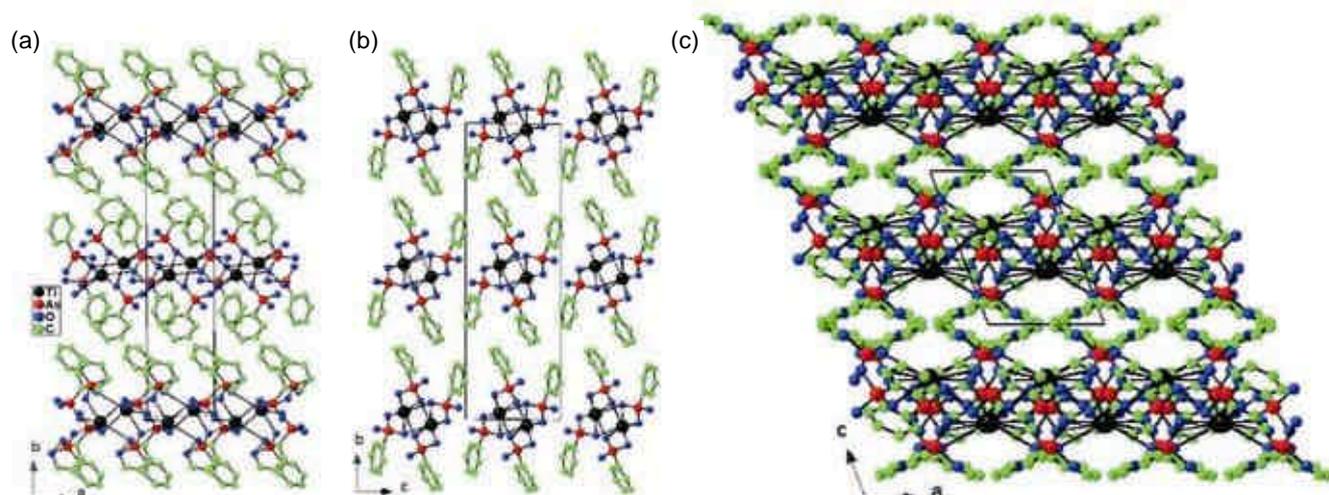


Figure 3. Ball-stick representation of unit cell of $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ viewed along (a) c -axis, (b) a -axis and (c) b -axis.

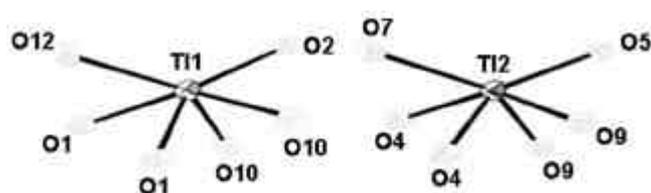


Figure 4. ORTEP diagrams of TlO_6 polyhedra in $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$.

Table 3. Selected Bond lengths (\AA) for $\text{Tl}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ (**1**) compound.

As(1)–O(1)	1.65(1)	Tl(1)–O(10)	2.64(1)
As(1)–O(2)	1.67(1)	Tl(1)–O(10)	2.76(1)
As(1)–O(3)	1.742(9)	Tl(1)–O(1)	2.81(1)
As(2)–O(4)	1.67(1)	Tl(1)–O(2)	3.02(1)
As(2)–O(5)	1.682(9)	Tl(1)–O(1)	3.15(1)
As(2)–O(6)	1.73(1)	Tl(1)–O(12)	3.33(1)
As(3)–O(7)	1.64(1)	Tl(2)–O(9)	2.62(1)
As(3)–O(8)	1.69(1)	Tl(2)–O(9)	2.74(1)
As(3)–O(9)	1.72(1)	Tl(2)–O(4)	2.78(1)
As(4)–O(10)	1.62(1)	Tl(2)–O(5)	3.01(1)
As(4)–O(11)	1.69(1)	Tl(2)–O(4)	3.16(1)
As(4)–O(12)	1.74(1)	Tl(2)–O(7)	3.35(1)
As(1)–C(1)	1.91(2)		
As(2)–C(7)	1.93(2)		
As(3)–C(13)	1.89(2)		
As(4)–C(19)	1.93(2)		

1.620 \AA length respectively and are not involved in hydrogen bonding.

Four phenylarsonates, **1–4** could be considered as solid Bronsted acids, with a porous region and,

therefore, two selected compounds, **1** and **2**, have been studied from the point of view of acid-base intercalation reactions with primary n -alkyl amines, $\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2$ ($n = 5-9, 12, 16, 18$). These reactions, as determined from chemical analysis and powder XRD, spectroscopic and thermal studies, turned out to be successful.

The occurrence of intercalation of primary amines into sodium (**2**) phenylarsonate is evident from the elemental CHN analysis, in the sense that the contents of carbon, hydrogen and nitrogen in the intercalated products, $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$, are more than those found for the parent phase, **2**. The amount (x) of intercalated amine is calculated from the carbon content and the values of hydrogen and nitrogen contents, expected for such compositions of intercalated products, agree reasonably with the observed values. The x values of 0.57, 0.83, 0.70, 0.72, 1.00, 1.00, 1.00 and 1.45 are found for $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ intercalates with $n = 5-9, 12, 16$ and 18, respectively obtained by the first method of stirring at room temperature. These x values show no systematic trend with n .

The powder XRD patterns (figure 5) of these $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ intercalates contain moderate to prominent reflections at 2θ values of ~ 5 degrees and no significant higher order $00l$ reflections with 2θ of > 40 degrees. The first reflection is doubled in a few cases. The d -value of the first reflection at $2\theta \sim 5$ is considered to be d_{001} , which is associated with the distance between the ab planes. This d_{001} value is, as expected, higher for $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$

($n = 7, 8$ and 9) intercalates than 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. The d_{001} values of intercalates with $n \geq 10$ are still higher, with $2q$ values of <5 and thus the observed reflections at $2q = 5$ represent higher order d_{00l} reflections. On the other hand, the lower d_{001} -values of intercalates with $n = 5$ and 6 represent the shrinking of inter-lamellar region, probably due to rearrangement and interdigitation of phenyl groups of the intercalates.^{13b} In general, these powder XRD patterns confirm the crystalline nature of intercalates and the topotactic intercalation of the amines.

Infrared spectra of the parent phenylarsonates, **1–4** are similar and some of these observed frequencies could be reasonably accounted for, on the basis of literature^{14a,17a} available on phenylphosphonates. The C–H stretching vibrations of the phenyl ring in the region $3090\text{--}3000\text{ cm}^{-1}$, 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 PhAsO₃H group, the peak at 1594 cm^{-1} due to phenyl group stretching, the As–O stretching vibrations in the region $1200\text{--}1000\text{ cm}^{-1}$ and the O–As–O bending vibrations in the region $540\text{--}410\text{ cm}^{-1}$, are the common features observed in the infrared spectra of compounds, **1–4**. The infrared spectra of $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ intercalates contain, in addition to all the features of the in-

frared spectrum of parent phase **2**, peaks in the region $3100\text{--}2700\text{ cm}^{-1}$ attributed to N–H and C–H stretching vibrations^{12b} of the amine molecules. The shift of N–H stretching vibrations towards lower frequencies suggests that the amine molecules are protonated²⁵ and electrostatically bonded to oxygen atoms of phosphonate moieties. The solid-state ¹³C NMR spectra of $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ intercalates show signals between $140.0\text{--}125.0\text{ ppm}$ and also multiple signals in the region $42.0\text{--}14.0\text{ ppm}$, indicating the presence of both aromatic carbon atoms of the phenyl group and the aliphatic carbon atoms of the amines respectively.

The effect of method of intercalation on the composition and powder XRD pattern (figure 6) of the intercalate is illustrated with the example of n -octyl amine intercalate, $2 \cdot (\text{CH}_3(\text{CH}_2)_7\text{NH}_2)_x$. The second method involves reflux conditions and resulted in structurally similar product, but with more ($x \sim 0.95$) intercalated amine. The third method employs excess liquid amine at room temperature without stirring and yielded structurally different product, but with even further ($x \sim 1.23$) intercalated amine. The CHN contents of the crystalline product obtained, under solvothermal conditions, by the fourth method are less than those of the parent phase, indicating that these reactions are unsuccessful.

Now we refer to the results of intercalation reactions of one-dimensional $\text{Ti}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ (**1**). x values of 1.53 , 1.65 and 1.68 are found for $n = 5, 8$ and 16 respectively in $1 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$

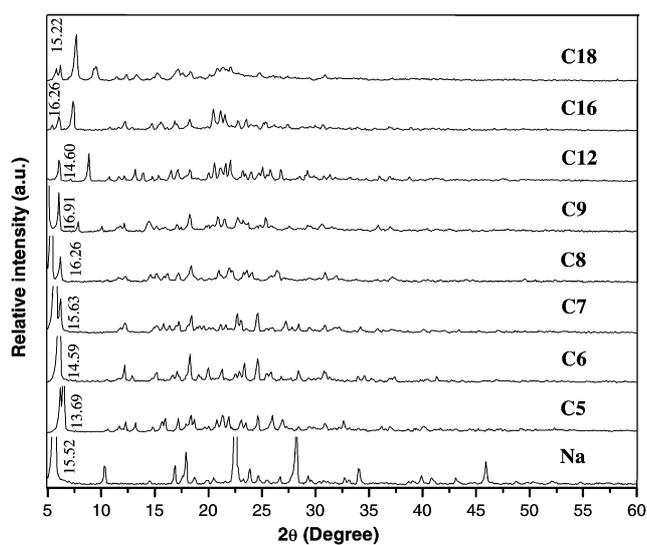


Figure 5. Powder XRD patterns of parent sodium (**2**) phenylarsonate and its amine intercalates, $2 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5\text{--}9, 12, 16$ and 18).

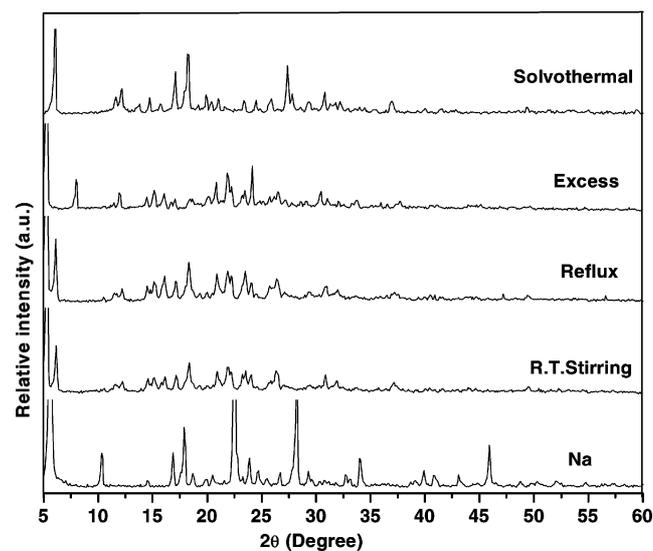


Figure 6. Powder XRD patterns of parent sodium (**2**) phenylarsonate and its n -octyl amine intercalate, $2 \cdot (\text{CH}_3(\text{CH}_2)_7\text{NH}_2)_x$ prepared by four methods.

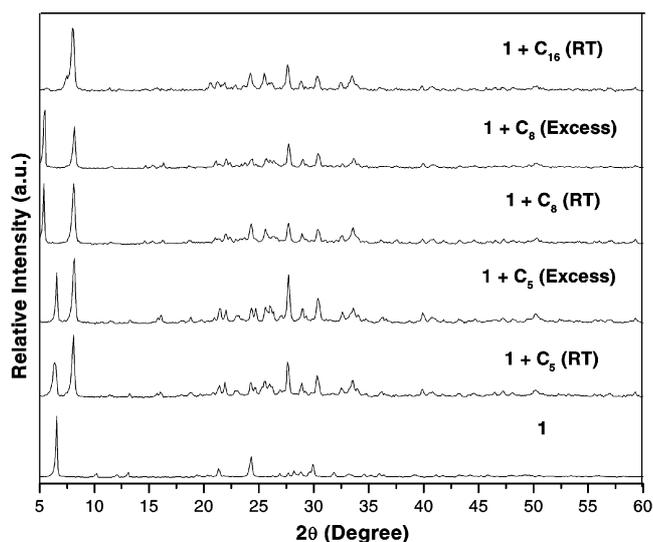


Figure 7. Powder XRD patterns of parent thallium (**1**) phenylarsonate and its amine intercalates, $1 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5, 8$ and 16) prepared by two methods.

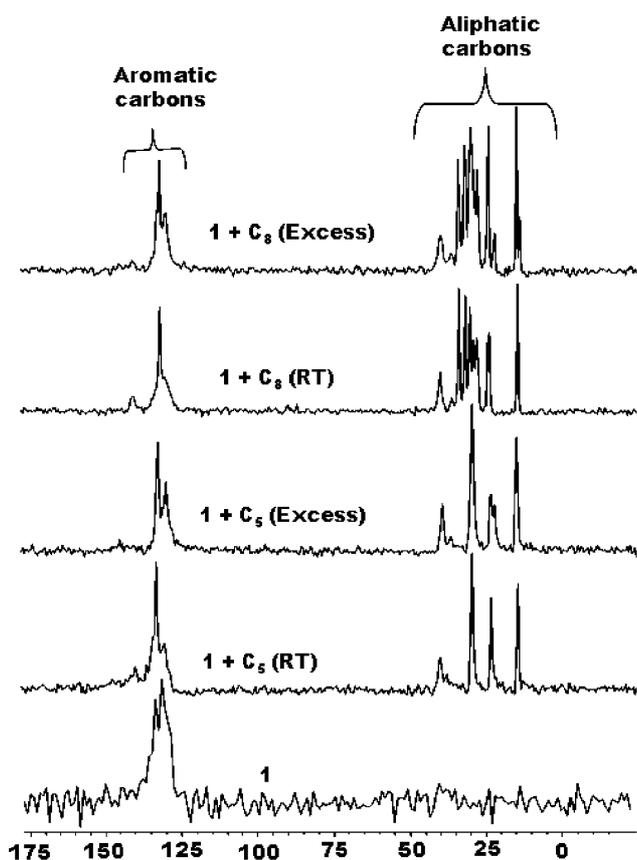


Figure 8. CP MAS ^{13}C NMR spectra of parent thallium (**1**) phenylarsonate and its amine intercalates, $1 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5$ and 8) prepared by different methods.

intercalates obtained by the first method. The x values changed to 1.63 and 1.96 for $n = 5$ and 8 respectively, when the third method involving excess liquid amine is employed. The powder XRD patterns of parent compound **1** and three intercalated products, obtained by the first method of stirring at room temperature, are presented in figure 7, from which the crystalline nature and structural similarity of the intercalated products are evident. The d -value of the first reflection at $2\theta \sim 5$ is considered to be d_{020} , associated with the distance between the adjacent planes of Tl^+ ions. This d_{020} value is, as expected, higher for the intercalates than for the parent phase **1**. The d_{020} values of the intercalates seem to increase, in general, with increasing number of carbon atoms of intercalated n -alkyl amines. This is indicative of the enlargement of porous region between the chains, along the b -axis, due to accommodation of intercalated amine. The third method of intercalation employing excess liquid amine has given rise to products with more intercalated amine and similar powder XRD patterns (figure 7). The fourth method of solvothermal reactions led to the decomposition of the parent phase, yielding As_2O_3 .

Infrared and solid-state ^{13}C NMR spectra (figure 8) of amine intercalates of thallium (**1**) phenylarsonate are similar to those of sodium (**2**) phenylarsonate intercalates. Thermogravimetric curves of thallium (**1**) phenylarsonate and some of its intercalated products are presented in figure 9. All five compounds undergo total weight loss of 100% over the temperature range 30–1100°C. For the parent phase,

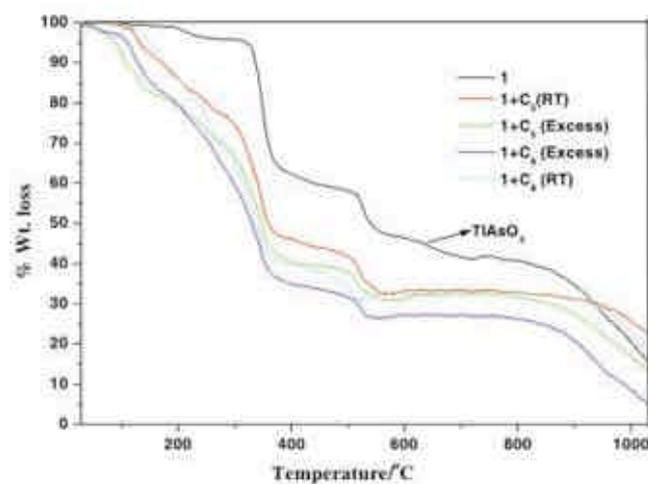


Figure 9. Thermogravimetric curves of thallium (**1**) phenylarsonate and its amine intercalates, $1 \cdot (\text{CH}_3(\text{CH}_2)_{n-1}\text{NH}_2)_x$ ($n = 5$ and 8) prepared by two methods.

the total weight loss occurs in five stages, the major weight loss of 36.6% being in the 210–400°C range. The weight loss ~4% in the 30–210°C range corresponds to loss of one water molecule, whereas the stage at 590°C corresponds to the formation of TlAsO_3 . The intercalated products, when compared to parent phase, undergo more weight loss in the 30–300°C range, indicating the loss of intercalated amine. After 300°C, their thermal behaviour seems to be similar to that of the parent phase. These plots show, as expected, more weight loss for *n*-octyl amine product than for *n*-pentyl amine product. Similarly the intercalated product by the third method shows more weight loss than the product by the first method. The values of weight loss of 60.6% and 66% for octyl amine products, $1 \cdot (\text{CH}_3(\text{CH}_2)_7\text{NH}_2)_{1.65}$ and $1 \cdot (\text{CH}_3(\text{CH}_2)_7\text{NH}_2)_{1.96}$, correspond to the formation of TlAsO_3 . Thus TlAsO_3 definitely seems to be a product in the intermediate stages of decomposition of these products.

4. Concluding remarks

Four new monovalent metal phenylarsonates, $\text{A}(\text{HO}_3\text{AsC}_6\text{H}_5)(\text{H}_2\text{O}_3\text{AsC}_6\text{H}_5)$ (A = Tl(**1**), Na(**2**), K(**3**) and Rb(**4**)), have been synthesized and characterized by X-ray diffraction and spectroscopic studies. Alkalimetal phenylarsonates are isostructural with phenylphosphonate analogues and have layered structures, whereas thallium (**1**) phenylarsonate has, as determined by single crystal X-ray diffraction study, new one-dimensional structure. Compounds **1** and **2** undergo intercalation of primary *n*-alkyl amines to yield polycrystalline intercalates.

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