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RESEARCH ARTICLE

HYDROGEN PHENYLPHOSPHONATE PHENYLPHOSPHONIC ACID WATER 1:1:1 CO-CRYSTAL AND HYDROGEN PHENYLARSONATE CYCLOHEXYLAMMONIUM SALTS: SYNTHESIS AND CRYSTAL ELUCIDATION

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Abstract

One pot reactions of phenylphosphonic acid or phenylarsonic acid with cyclohexylamine led to two new organic-inorganic hybrid salts $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$ (**1**) and $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ (**2**) which were investigated by single-crystal X-ray diffraction analysis. Salt **1** crystallizes in the monoclinic system, space group $P2_1/n$ with a = 12.3963 (4), b = 6.1123 (2), c = 28.2081 (8) Å, β = 90.426 (1)°, V = 2137.27 (12) $Å^3$ and Z = 4. Salt **2** crystallizes in the monoclinic system, space group $P2_1/c$ with a = 12.3991 (5), b = 6.5048 (2), c = 18.5466 (7) Å, β = 105.824 (2)°, V = 1439.16 (9) $Å^3$ and Z = 4. In the co-crystal **1**, the hydrogen phenylphosphonate anions are organized into dimers *via* O–H···O H-bonds, whereas the phenylphosphonic acid and the water molecules are connected, through O_{water}–H···O and O–H···O hydrogen bonding interactions, to form dimers. Inter-species O–H···O hydrogen bonds connect the alternating dimers into anionic infinite chains. The 1D infinite ribbons are linked into an anionic 2D layer-like structure, by means of water molecules through O_{water}–H···O and O–H···O_{water}. The cyclohexylammonium interacts *via* N–H···O hydrogen bonds, to consolidate the compactness of the 2D layer-like structure. In the crystal of salt **2**, the hydrogen phenylarsonate anions are organized into dimers through O–H···O H-bonds. Hydrogen bonded dimers are connected by the cyclohexylammonium cations, through N–H···O hydrogen bonds, leading to the formation of an infinite ribbon. The 1D hydrogen bonded ribbons are interlinked through N–H···O hydrogen bonding interactions giving rise to a 2D layer-like structure.

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Introduction:-

In the past, several phosphonate based metal complexes investigations exhibited catalysis (Ranocchiari and van Bokhoven, 2011; Hu and Zhao, 2017; White *et al*., 2009), gas sorption and separation (Llewellyn *et al*., 2015; Taddei *et al*., 2016; Hermer *et al*., 2017; Oschatz and Antonietti, 2018; Li and Chen, 2016), energy storage and conversion applications (Winter and Brodd, 2004). The solid state luminescent properties of a mixed phenylphosphonic acid/singly protonated phenylphosphonate copper complex (Latham *et al*., 2009) as well as magnetic properties (Bao and Zheng, 2016; Hamchaoui *et al*., 2013) and several metal phosphonates surface photovoltage, semi conductor and luminescent properties (Cai *et al*., 2018; Zhu *et al*., 2016; Shi *et al*., 2014; Zhang *et al*., 2020; Firmino *et al*., 2020; Ayhan *et al*., 2020; Jiao *et al*., 2016; Chu *et al*., 2013; Dai *et al*., 2014; Yang *et al*., 2016; Zhao *et al*., 2016) have also been reported. New materials either usable as electrodes or electrolyte components has been reported too (Peng and Chen, 2009). Related phenylarsonates with diverse substituents at the ortho, meta or para position, have widely been investigated, though hydrogen phenylarsonate compounds are most scarcely encountered in the literature (Smith and Wermuth, 2010; Reck and Schmitt, 2012; Yi *et al*., 2009; Padalwar and Vidyasagar, 2016; Padalwar *et al*., 2013; Reddy *et al*., 2006). Indeed, several singly protonated phenylarsonate crystal compounds are reported to date, according to the Cambridge Structural Database CSD (Smith and Wermuth, 2010; Reck and Schmitt, 2012; Yi *et al*., 2009; Padalwar and Vidyasagar, 2016; Padalwar *et al*., 2013; Reddy *et al*., 2006). Tetrabutylammonium hydrogen phenylarsonate–phenylarsonic acid (1/1) exhibits an acidic anionic infinite chain with alternating species grown from the junction of the dimers $PhAsO_3H^-/PhAsO_3H_2$ through O–H···O hydrogen bonds (Reck and Schmitt, 2012). $A(HO_3PPh)(H_2O_3PPh)$ (A = Li, Na, K, Rb, Cs, Tl, NH_4) phenylphosphonates as well as $Na(HO_3AsPh)(H_2O_3AsPh)$ phenylarsonate crystal structures have been reported (Padalwar *et al*., 2013); they display hydrogen bonding interaction patterns between the singly protonated forms, nevertheless the hydrogen bonding pattern investigations between species have not been deepened. In 2010, Smith and Wermuth reported the crystal structure of guanidinium phenylarsonate–guanidine–water (1/1/2) which describes extended hydrogen bonding patterns, but without usually encountered hydrogen bonding interactions between the singly protonated phenylarsonate ions. Several phosphonate based metal complexes with mixed phenylphosphonic acid/singly protonated phenylphosphonate such as $[CuX(phen)_2][(C_6H_5PO(OH)_2)(C_6H_5PO_2(OH))]$ (where X = Cl, Br, I, NCS) and $[Cu^{II}(phen)_2X][((OH)_2OPC_6H_5)((OH)O_2PC_6H_5)]$ (where X = I, Br, Cl, NCS) have earlier been reported, describing hydrogen bonded acidic ribbons (Clarke *et al*., 2005; Latham *et al*., 2007; Rao and Vidyasagar, 2005). The Dakar group has been involved in single crystal X-ray diffraction investigations of phosphonates and cyclohexylammonium co-crystallization, by describing various phenylphosphonate crystal structures exclusive dealing (Diop *et al*., 2019, 2013, 2012, 2011; Sarr *et al*., 2012), but also some cyclohexylammonium salts (Sarr *et al*., 2020, 2015a, 2015b, 2013). Continuing to widen our contribution in this field, one pot reactions of phenylphosphonic acid, $C_6H_5PO_3H_2$ and nickel(II) chloride hexahydrate, $NiCl_2.6H_2O$ or phenylarsonic acid, $C_6H_5AsO_3H_2$ with cyclohexylamine, $C_6H_{13}N$ were undertaken in solution media. These reactions led to the isolation of namely, $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$ **1** and $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ **2** whose structure elucidations were carried out by single-crystal X-ray diffraction analysis.

Experimental section:-

Reagents phenylphosphonic acid, $C_6H_5PO(OH)_2$ (98 % purity), cyclohexylamine, $C_6H_{11}NH_2$ (99 % purity), nickel(II) chloride hexahydrate, $NiCl_2.6H_2O$ (99.9 % purity) and phenylarsonic acid, $C_6H_5AsO(OH)_2$ (97 % purity) were purchased from Sigma-Aldrich, Steinheim am Albuch, Germany and used without any further purification. The X-ray crystallographic data for compounds **1** and **2** were collected using a Bruker Kappa APEX-II diffractometer operating at 150 K and a Nonius Kappa CCD working at 293 K, respectively.

Synthesis and isolation of $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$ (1):-

The pooling of methanolic solutions containing two equivalents of phenylphosphonic acid, $C_6H_5PO_3H_2$ (0.816 g; 5.16 mmol), one equivalent of cyclohexylamine, $C_6H_{11}NH_2$ (0.8547 g/cm^3; 0.3 mL; 2.58 mmol) and one equivalent of nickel(II) chloride hexahydrate, $NiCl_2.6H_2O$ (0.613 g; 2.58 mmol) has afforded a cloudy solution. The resultant solution was subsequently stirred at room temperature for more than 2h then filtered. After some days of slow evaporation of the filtrate, colorless plate-like crystals suitable for single-crystal X-ray structure determination were collected within the solvent and characterized as $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$ (**1**).

Compound **1** can also be synthesized by directly reacting two equivalents of phenylphosphonic acid, $C_6H_5PO_3H_2$ with one equivalent of cyclohexylamine, $C_6H_{11}NH_2$.

Synthesis and isolation of $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ (2):-

Salt **2** has been isolated by reacting one equivalent of phenylarsonic acid, $C_6H_5AsO_3H_2$ (3.124 g; 15 mmol) with one equivalent of cyclohexylamine, $C_6H_{11}NH_2$ (1.7 mL; 15 mmol), in water. The resultant solution was subsequently stirred about 2h. Colorless prism-like crystals suitable for a single-crystal X-ray diffraction study were obtained, after some days of slow solvent evaporation at room temperature and characterized as $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ (**2**).

X-ray crystallography of $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$ (1):-

A crystal of approximate dimensions 0.246×0.103×0.050 mm was used for data collection. The X-ray crystallographic data were collected using a Bruker Kappa Apex II diffractometer operating at T = 150 (2) K. Data were measured using φ and ω scans using MoKα radiation (λ = 0.71073 Å) using a collection strategy to obtain a hemisphere of unique data determined by *Apex2* (Bruker AXS Inc., Madison, WI 53719-1173., 2012). Cell parameters were determined and refined using the *SAINT* program (SAINT (2012)). Data were corrected for absorption by multi-scan absorption using *SADABS* (SADABS2012/1). The structure of **1** was solved by dual-space analysis using *SHELXT* (Sheldrick, 2015) and refined using least-squares minimization with *SHELXL97* (Sheldrick, 2008).

Programs used for the representation of the molecular and crystal structures: *Olex2* (Dolomanov *et al*., 2009) and *Mercury* (Macrae *et al*., 2008). The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in the caption of Figure 1.

CCDC 2172774 (**1**) contains 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,or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

X-ray crystallography of $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ (2):-

A crystal of approximate dimensions 0.22×0.12×0.02 mm was used for data collection. The X-ray crystallographic data were collected using a Nonius Kappa CCD diffractometer operating at T = 293 (2) K. Data were measured using φ and ω scans using MoKα radiation (λ = 0.71073 Å) using a collection strategy to obtain a hemisphere of unique data determined by *COLLECT* (Hooft, Nonius Kappa CCD, Nonius BV: Delft (The Netherlands), 2003). Cell parameters were determined and refined using *DIRAX* (Duisenberg, 1992). Data were corrected for absorption correction using *EVAL CCD* (Duisenberg *et al*., 2003). The structure of **2** was solved using *SHELXS* (Sheldrick, 2008) and refined using least-squares minimization with *SHELXL97* (Sheldrick, 2008).

Programs used for the representation of the molecular and crystal structures: *Olex2* (Dolomanov *et al*., 2009) and *Mercury* (Macrae *et al*., 2008). The Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and angles are listed in the caption of Figure 5.

CCDC 2172775 (**2**) contains 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, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Table 1:- Crystal data and structure refinement for compounds (**1**) and (**2**).

Parameters	Compound	
	(**1**)	(**2**)
Empirical formula	$C_{18}H_{29}NO_7P_2$	$C_{12}H_{20}AsNO_3$
Formula weight	433.36	301.21
Temperature/K	150.00	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.3963(4)	12.3991(5)
b/Å	6.1123(2)	6.5048(2)
c/Å	28.2081(8)	18.5466(7)
α/°	90	90

β/°	90.4260(10)	105.824(2)
γ/°	90	90
Volume/Å^3	2137.27(12)	1439.16(9)
Z	4	4
ρ_{calc} g/cm^3	1.347	1.390
μ/mm^{-1}	0.242	2.359
F(000)	920	624
Crystal size/mm^3	0.246 × 0.103 × 0.05	0.22 × 0.12 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.58–62.442	6.406–54.996
Index ranges	$-18 \le h \le 18$, $-8 \le k \le 8$, $-41 \le l \le 41$	$-14 \le h \le 16$, $-8 \le k \le 8$, $-24 \le l \le 24$
Reflections collected	77999	9364
Independent reflections	6887 [R_{int} = 0.0543, R_{sigma} = 0.0270]	3306 [R_{int} = 0.0333, R_{sigma} = 0.0350]
Data/restraints/parameters	6887/7/369	3306/453/252
Goodness-of-fit on F^2	1.069	1.060
Final R indexes [I>2σ (I)]	R_1 = 0.0379, wR_2 = 0.0871	R_1 = 0.0397, wR_2 = 0.1003
Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.0937	R_1 = 0.0540, wR_2 = 0.1074
Largest diff. peak/hole / e Å^{-3}	0.43/-0.36	0.71/-0.55

[a] $R_1 = \Sigma(||F_o|-|F_c||)/ \Sigma |F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/ \Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2)+(0.0435P)^2+0.7237P]$ for **1** and $w = 1/[\sigma^2(F_o^2)+(0.0506P)^2+0.9955P]$ for **2** with $P = (F_o^2)+2F_c^2)/3$; [c] goodness of fit = $[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$.

Results and Discussion:-

Compound **1** was isolated from the reaction in methanol, from a 1:1 molar ratio between phenylphosphonic acid and cyclohexylamine in the presence of nickel(II) chloride hexahydrate. Colorless single crystals grown from the filtrate (Eq. 1) and were characterized as **1**, $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$. Several X-ray investigations involving both phenylphosphonic acid and singly protonated phenylphosphonate were previously investigated (Smith and Wermuth, 2010; Wilke *et al.*, 2016a, 2016b).

The compound **2** was isolated from the reaction in water, from a 1:1 molar ratio between amounts of phenylarsonic acid and cyclohexylamine. This yielded the compound $[(C_6H_{14}N)(C_6H_5AsO_3H)]$ (**2**) collected as colorless crystals (Eq. 2). To our knowledge, very few examples of non-substituted hydrogen arsonate containing compounds have been isolated and characterized by X-ray study (Yi *et al.*, 2009; Padalwar and Vidyasagar, 2016; Padalwar *et al.*, 2013; Adelani *et al.*, 2013). The yields of the reactions reported herein are 53 and 95%, respectively.

$$2C_6H_5PO_3H_2 + C_6H_{11}NH_2 + H_2O \xrightarrow[\text{room temperature (r.t)}]{NiCl_2.6H_2O/CH_3OH} \underset{\text{compound } \mathbf{1}}{\mathbf{[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]}} \quad (1)$$

$$C_6H_5AsO_3H_2 + C_6H_{11}NH_2 \xrightarrow[\text{r.t}]{H_2O} \underset{\text{compound } \mathbf{2}}{\mathbf{[(C_6H_{14}N)(C_6H_5AsO_3H)]}} \quad (2)$$

Compound **1**, $[C_6H_{14}N][C_6H_5PO_3H.C_6H_5PO_3H_2.H_2O]$, crystallizes as colorless plate-like crystals in the monoclinic space group $P2_1/n$. The asymmetric unit is comprised of a cyclohexylammonium, a hydrogen phenylphosphonate anion, a molecule of phenylphosphonic acid, and a water molecule both connected through N–H···O and O–H···O hydrogen bonds. The molecular structure of the compound **1** is represented in Figure 1.

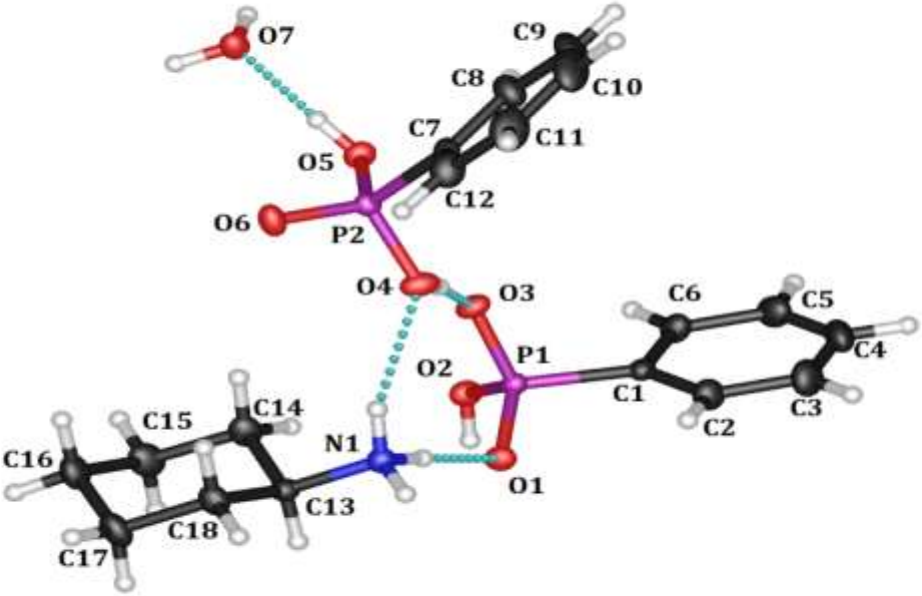

Fig. 1:- Molecular view of **1** showing 50% probability ellipsoids for atoms and the crystallographic numbering scheme [atom color code: C, black; H, white; O, red; N, blue; P, pink]. Selected bond lengths and angles (Å, deg): P1–O1 1.5097 (9), P1–O2 1.5646 (10), P1–O3 1.5152 (9), P1–C1 1.7959 (13), P2–O4 1.5509 (10), P2–O5 1.5511 (10), P2–O6 1.4915 (10), P2–C7 1.7912 (13), C13–N1 1.4987 (16); O1–P1–O2 112.42 (5), O1–P1–O3 115.21 (5), O3–P1–O2 105.20 (5), O1–P1–C1 108.64 (6), O2–P1–C1 106.95 (6), O3–P1–C1 105.20 (5), O5–P2–O4 105.84 (5), O6–P2–O5 114.05 (5), O6–P2–O4 111.38 (6), O4–P2–C7 106.95 (6), O5–P2–C7 108.06 (6), O6–P2–C7 110.21 (6), N1–C13–C18 110.25 (10), N1–C13–C14 109.72 (10).

The P–O length values are in accordance with the published values (Diop *et al*., 2013, 2012, 2011; Sarr *et al*., 2012, 2020; Beckmann *et al*., 2003) and evidence single (O1, O3) and double (O2, O4) bonds. The geometric parameters within the cyclohexylammonium well corroborate the yet reported values (Sarr *et al*., 2020, 2015a, 2015b; Lemmerer, 2011; Grimball *et al*., 2017; Tang *et al*., 2015). In the crystal structure of compound **1**, the hydrogen phenylphosphonate anions are organized into dimers through strong O–H···O hydrogen bonds forming $R_2^2(8)$ rings (see Figure 2). The phenylphosphonic acid and the water molecules likewise form dimers through three strong O_{water}–H···O and one O–H···O_{water} hydrogen bonds affording $R_4^3(10)$ rings (see Figure 2). Inter species O–H···O hydrogen bonding interactions connect these dimers into anionic infinite chains in which they alternate. Each hydrogen bonded anionic chain is linked to its neighbours *via* O_{water}–H···O and O–H···O_{water} hydrogen bonds involving the phenylphosphonic acid and water molecules, leading to the formation of an anionic layer (see Figure 2 and Table 2).

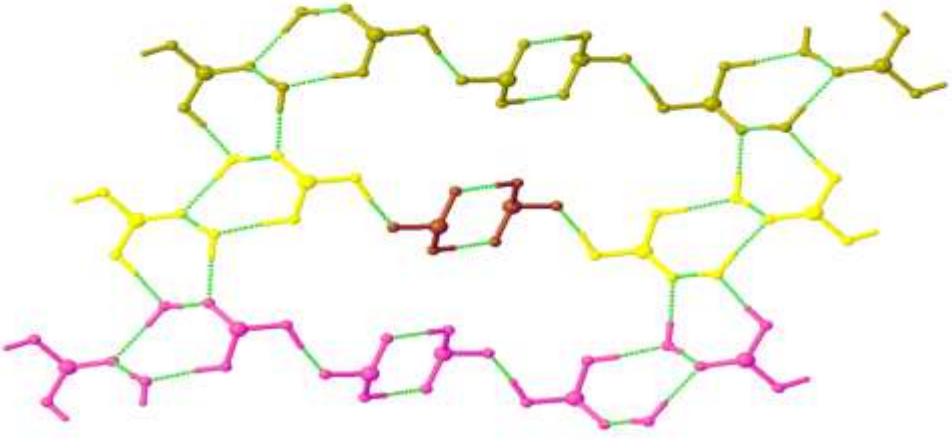

Fig. 2:- Molecular view of **1** showing 50% probability ellipsoids for atoms, showing the two different dimers and chains connected into an anionic layer network. Phenyl groups are omitted for clarity.

The cyclohexylammonium cations slipped in between the chains that they link *via* N–H···O hydrogen bonds, to consolidate the compactness and the stability of the 2D network. These hydrogen bonding interactions enable H-bonded cyclic patterns: 8-membered $R_2^2(8)$ and 10-membered $R_4^3(10)$ rings alternating within the chains and, 8-membered $R_3^3(8)$, 10-membered $R_4^3(10)$, 16-membered $R_6^4(16)$, and 14-membered $R_5^4(14)$ rings from the junction of chains and cyclohexylammonium ions, leading to a layer-like structure along [101] plane (Figure 3). However, this compound exhibits a curve pleated sheet whose molecular packing diagram is depicted in Figure 4.

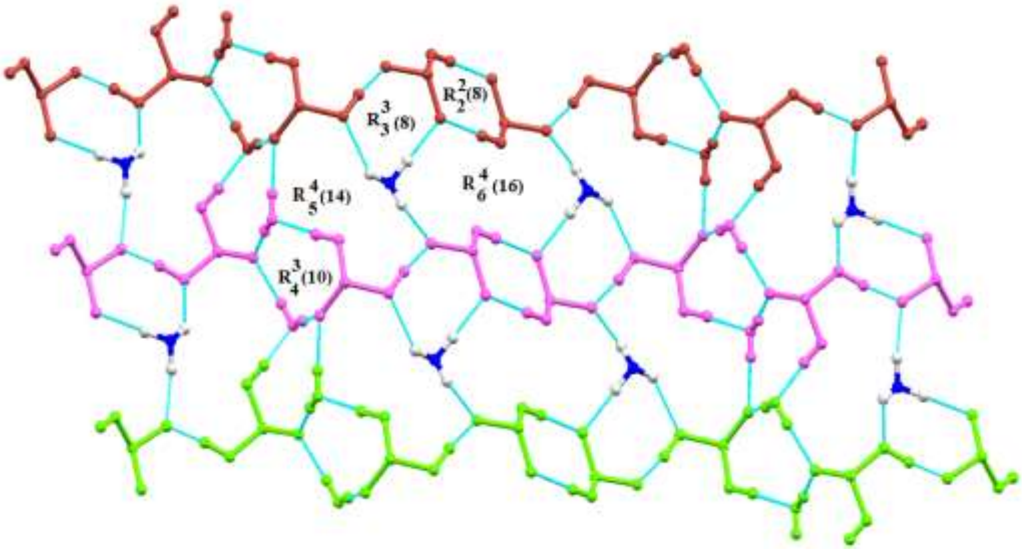

Fig. 3:- Molecular view of **1** showing 50% probability ellipsoids for atoms, showing the interactions of cations slipped in between the chains growing the layer network. Phenyl and cyclohexyl groups are omitted for clarity.

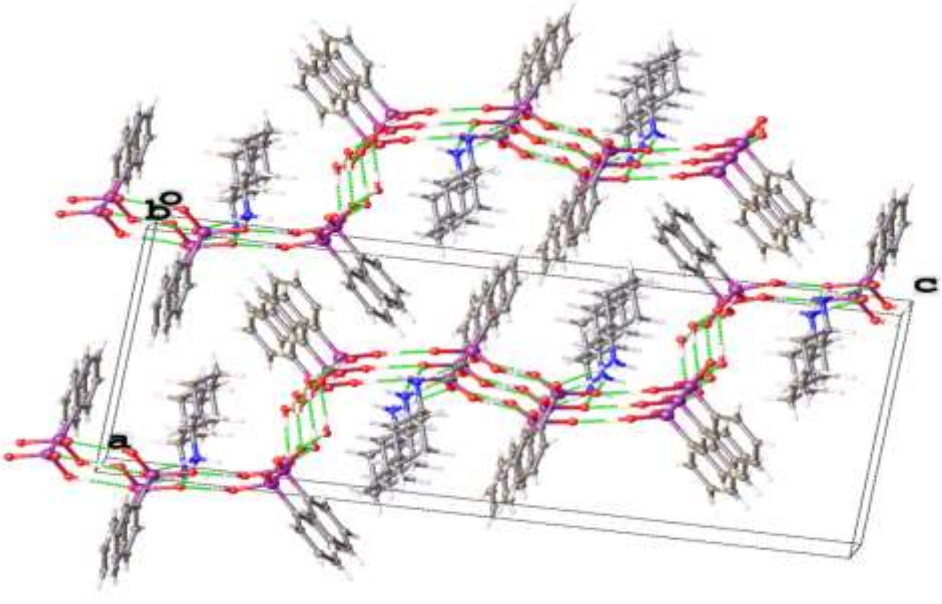

Fig. 4:- Molecular partial packing diagram of **1** showing 50% probability ellipsoids for atoms, showing the pleated layer network.

Table 2:- Hydrogen bond and interaction geometries (Å, deg) in the crystal of **1** (symmetry codes: (i) -x+1, -y+1, -z+1; (ii) x, y-1, z; (iii) x, y+1, z; (iv) -x+1/2, y+1/2, -z+3/2.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
O4–H4···O3	0.88 (2)	1.60 (2)	2.4691 (14)	171 (3)
O2–H2···O1^{i}	0.85 (2)	1.75 (2)	2.6001 (13)	177 (2)
N1–H1A···O4	0.90 (1)	2.20 (2)	2.9570 (15)	141 (1)

N1–H1B⋯O3^{ii}	0.91 (1)	1.89 (1)	2.7982 (14)	172 (2)
N1–H1C⋯O1	0.91 (1)	1.86 (1)	2.7662 (14)	175 (2)
O7–H7A⋯O6^{iii}	0.87 (2)	1.81 (2)	2.6824 (14)	176 (2)
O7–H7B⋯O6^{iv}	0.88 (2)	1.84 (2)	2.7126 (13)	174 (2)
O5–H5⋯O7	0.83 (2)	1.68 (2)	2.4995 (14)	173 (3)

The compound **2**, [($C_6H_{14}N$)($C_6H_5AsO_3H$)], crystallizes as colorless prism-like crystals in the monoclinic space group $P2_1/c$. The asymmetric unit contains one cyclohexylammonium and one hydrogen phenylarsonate ions. The molecular structure of the compound **2** is shown in Figure 5.

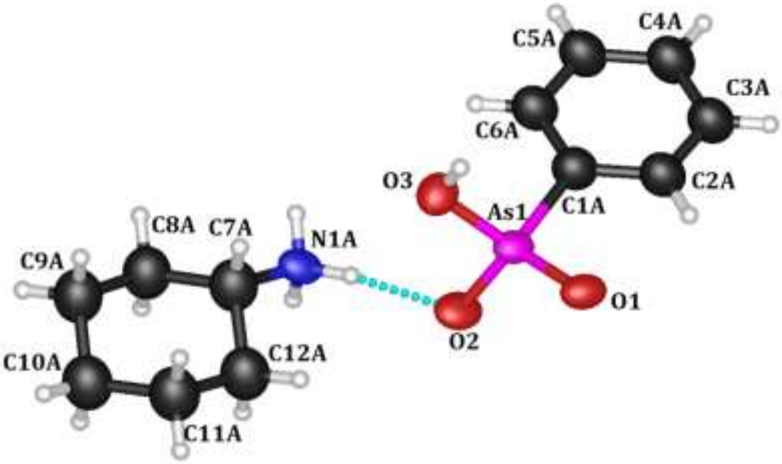

Fig. 5:- Molecular view of **2** showing 50% probability ellipsoids for atoms and the crystallographic numbering scheme adopted [atom color code: C, black; H, white; O, red; N, blue; As, pink]. Only one fragment of the disordered species is shown. Selected bond lengths and angles (Å, deg): O1–As1 1.662 (2), O2–As1 1.649 (2), O3–As1 1.719 (2), As1–C1A 1.927 (5), As1–C1B 1.890 (5), N1A–C7A 1.477 (7), N1B–C7B 1.477 (7); O1–As1–O2 115.53 (11), O1–As1–O3 111.13 (11), O1–As1–C1A 107.3 (2), O1–As1–C1B 108.5 (2), O2–As1–O3 103.84 (11), O2–As1–O1 104.03 (11), O2–As1–C1A 110.6 (2), O2–As1–C1B 110.2 (2), O3–As1–C1A 108.3 (2), O3–As1–C1B 107.3 (2), N1A–C7A–C8A 109.3 (6), N1A–C7A–C12A 109.3 (6), N1B–C7B–C8B 117.1 (19), N1B–C7B–C12B 115.8 (19).

The As–O distances indicate single and double bonds and are in the expected range (Smith and Wermuth, 2010; Reck and Schmitt, 2012; Yi *et al*., 2009; Padalwar and Vidyasagar, 2016; Padalwar *et al*., 2013; Reddy *et al*., 2006). The geometric parameters within the cyclohexylammonium are closely similar to those in compound **1**, and are in accordance with the earlier published values (Sarr *et al*., 2020, 2015a, 2015b; Lemmerer, 2011; Grimball *et al*., 2017; Tang *et al*., 2015). In the crystal of compound **2**, the hydrogen phenylarsonate anions are organized into dimers through strong O–H⋯O hydrogen bonds exhibiting a $R_2^2(8)$ ring. Each hydrogen bonded dianionic dimer is linked to its neighbor *via* two cyclohexylammonium cations, through N–H1A⋯O and N–H1B⋯O hydrogen bonds, leading to the formation of an infinite chain which describes two alternating and fused rings $R_2^2(8)$ and $R_6^4(16)$ (see Figure 6 and Table 3). In the chains, the cyclohexylammonium cations and the dianionic dimers alternate. The chains are then linked *via* the remaining nitrogen H atoms of the cations through N–H1C⋯O2 hydrogen bonds, leading to a layer-like structure along [100] plane (Figure 6). The interconnections between chains exhibit only 10-membered hydrogen bonded rings $R_4^3(10)$ (see Figure 6). The molecular packing diagram of the compound **2** is depicted in Figure 7.

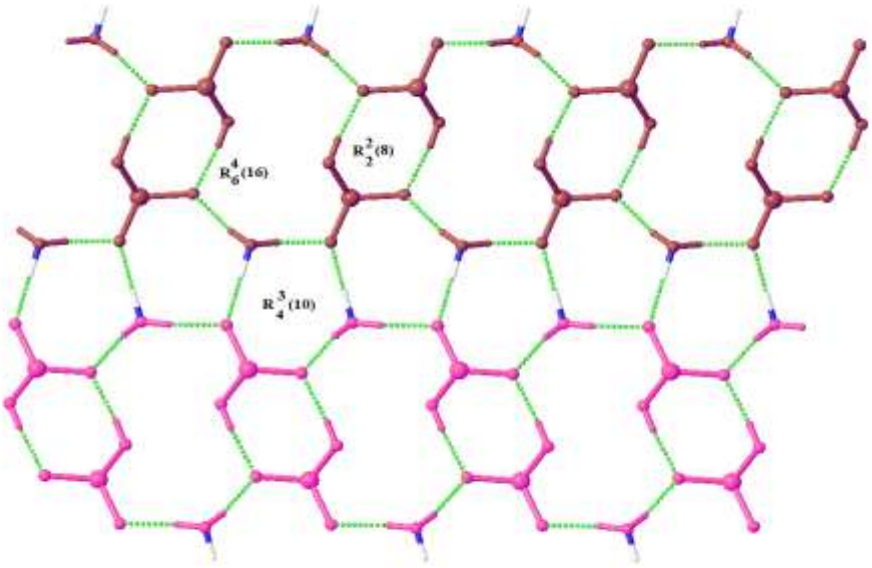

Fig. 6:- Molecular view of **2** showing 50% probability ellipsoids for atoms, showing the propagation of the infinite chain network. Phenyl and cyclohexyl groups are omitted for clarity.

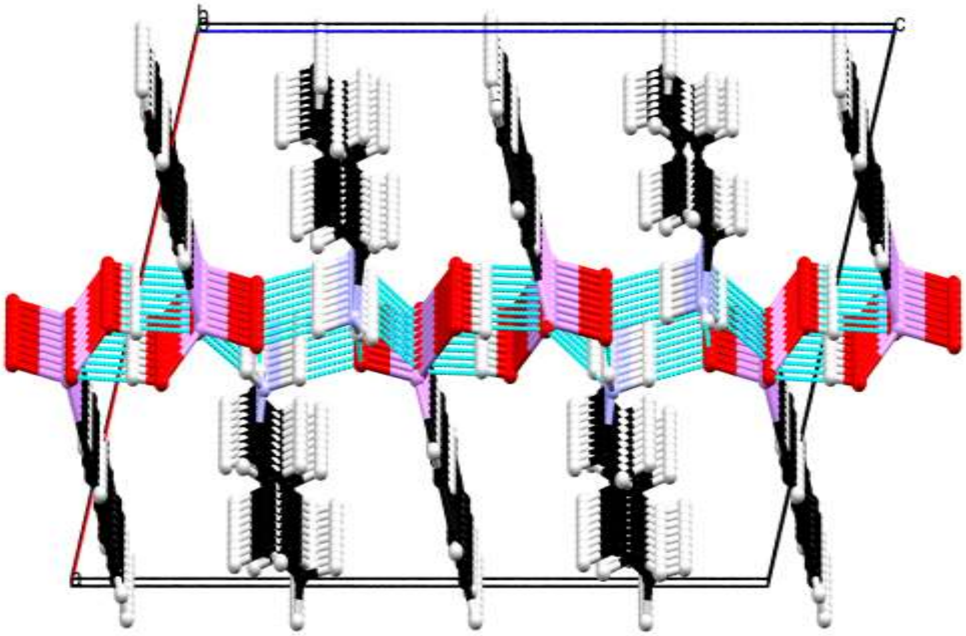

Fig. 7:- Molecular packing of **2**, approximately along [010] direction, showing 50% probability ellipsoids for atoms, showing the propagation of the layer network.

Table 3:- Hydrogen bonds in crystals of **2** (symmetry codes: (i) -x+2, -y, -z; (ii) x, y+1, z; (iii) -x+2, y+1/2, -z+1/2.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(D–H···A)
O3–H3···O1^{i}	0.82	1.80	2.618 (3)	175
N1A–H1AA···O1^{ii}	0.89	1.83	2.719 (12)	177
N1A–H1AB···O2^{iii}	0.89	1.85	2.740 (13)	176
N1A–H1AC···O2	0.89	1.85	2.728 (12)	169
N1B–H1BA···O1^{ii}	0.89	1.95	2.83 (4)	170
N1B–H1BB···O2^{iii}	0.89	1.97	2.81 (5)	157
N1B–H1BC···O2	0.89	1.95	2.83 (4)	172

Conclusion:-

The desired nickel phosphonate complex has not been isolated by carrying the reaction between cyclohexylamine, phenylphosphonic acid and nickel(II) dichloride hexahydrate. Two cyclohexylammonium salts of phenylphosphonic acid and phenylarsonic acid have been synthesized by one pot reaction and investigated by X-ray diffraction analysis. Both compounds **1** and **2** exhibit extended hydrogen bonds, even those in **1** are more extensive, evidencing five ring types *ie* $\mathrm{R}_2^2(8)$, $\mathrm{R}_3^3(8)$, $\mathrm{R}_4^3(10)$, $\mathrm{R}_5^4(14)$ and $\mathrm{R}_6^4(16)$ whereas **2** describes only three ring types *viz* $\mathrm{R}_2^2(8)$, $\mathrm{R}_4^3(10)$ and $\mathrm{R}_6^4(16)$. In **1**, phenylphosphonate anions as well as phenylphosphonic acid and the water molecules lonely form H-bonded dimers connected into infinite ribbons which are linked into an anionic 2D layer-like structure. The cyclohexylammonium cations fit in the anionic 2D layer, strengthening its stability and compactness. Pooling to form dimers, the phenylarsonate ions interconnections with cyclohexylammonium in **2** describes infinite ribbons whose hydrogen bonding linkages give rise to a 2D layer-like structure. In the attempt to synthesize and characterize new complexes of various metallic reagents, further works involving salts **1** and **2** are in progress.

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