

# A tetrakis(amido)phosphonium cation containing 2-pyridyl (<sup>2</sup>Py) substituents, [P(NH<sup>2</sup>Py)<sub>4</sub>]<sup>+</sup> and its reactivity studies with Ag(I) salts

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**Abstract.** Poly-imido analogues of various phosphorus oxo anions have gained recent attention in inorganic chemistry. Current methods to obtain these anions require strong organometallic deprotonating agents in reaction with phosphonium salt like [(NHPh)<sub>4</sub>P]Cl or phosphoramides such as [(RNH)<sub>3</sub>P=E] (E = NSiMe<sub>3</sub>, O, S or Se) in non-polar solvents. Recently, employing salts of soft and reactive transition metal ions, we have developed methods to obtain these anions in polar and protic solvents. Herein, we have described a facile anion exchange route that stabilizes the highly labile tetrakis(2-pyridylamino)phosphonium cation as its nitrate salt, [P(NH<sup>2</sup>Py)<sub>4</sub>]NO<sub>3</sub>. This molecule exhibits a double chain structure mediated by H-bonding interactions of the pyridylamino segments (N-H...N). The phosphonium salt upon reaction with excess silver triflate results in a pentanuclear Ag(I) complex, {Ag<sub>5</sub>[P(N<sup>2</sup>Py)<sub>2</sub>(NH<sup>2</sup>Py)<sub>2</sub>]}·(F<sub>3</sub>CSO<sub>3</sub>)<sub>3</sub>, stabilized by two imido-phosphinate [P(N<sup>2</sup>Py)<sub>2</sub>(NH<sup>2</sup>Py)<sub>2</sub>]<sup>-</sup> ligands. Formation of a similar penta-nuclear cluster has been observed before when AgClO<sub>4</sub> was used as a base. Our previous results with the related phosphate precursor, [PO(NH<sup>2</sup>Py)<sub>3</sub>], in reaction with various Ag(I) salts have shown to yield complexes of the corresponding neutral, mono- and dianionic ligands. However, the stability of the Ag<sub>5</sub>-cluster within the mono-anionic casing of the [P(N<sup>2</sup>Py)<sub>2</sub>(NH<sup>2</sup>Py)<sub>2</sub>]<sup>-</sup> ligand have seemingly overwhelmed the subtle reactivity changes offered by various Ag(I) salts.

**Keywords.** P-N compounds; imido P(V) anions; silver (I) complexes; cluster compounds; N-H bond deprotonation

## 1. Introduction

Phosphorus-bound poly-imido anions have found a re-surgent research interest due to their ability to act as multi-site ligands in coordination chemistry.<sup>1</sup> Several of the P(V)-imido metal complexes have been utilized as catalysts in olefin oligomerization<sup>2</sup> and polymerization,<sup>3</sup> ring-opening polymerization of lactides,<sup>4</sup> hydroamination<sup>5</sup> and transfer hydrogenation,<sup>6</sup> etc. These imido-P(V) anions are ubiquitous in the reactions involving a phosphonium salt like [(NHPh)<sub>4</sub>P]Cl or phosphoramides such as [(RNH)<sub>3</sub>P=E] (E = NSiMe<sub>3</sub>, O, S or Se) and highly basic organometal alkyls/aryls/silylamides in aprotic non-polar medium.<sup>7,8</sup> However, their stability in protic and polar solvents has been very poor due to the highly reactive nature of the metal ions employed as well as to the presence of residual metal-alkyl/aryl/silylamide bonds in their complexes. Use of less basic reagents in these reactions did not lead to any deprotonation which sometimes have led to P-N bond

cleavage especially when the metal reagent involved is Lewis acidic in nature.<sup>9</sup> As a result, the coordination chemistry of imido-P(V) species is limited to the organometallic reagents of reactive main-group metals and to some extent alkyl/silylamide reagents of few d- and f-block elements. In view of finding a broader synthetic application for imido-P(V) ligand chemistry, we started looking at the salts of certain soft transition metal ions as a source of base for effecting the N-H bond deprotonation in polar medium. In this effort we have been using the reactive salts of Ag(I) and Pd(II) to generate imido anions isoelectronic to H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> ions. By employing Pd(OAc)<sub>2</sub>, complete deprotonation of phosphoric triamides of the type [PO(NHR)<sub>3</sub>] (R = alkyl) were realized with the exclusive formation of their corresponding trianions [PO(NR)<sub>3</sub>]<sup>3-</sup> (iso-electronic to PO<sub>4</sub><sup>3-</sup>) as their tri or hexa-nuclear Pd(II) complexes.<sup>10</sup> Using various salts of Ag(I) and by employing the phosphoric triamide of the type, [PO(NH<sup>2</sup>Py)<sub>3</sub>] (<sup>2</sup>Py = 2-pyridyl) having fairly acidic N-H groups, controlled deprotonation of the amido protons were achieved. Thus, by using AgNO<sub>3</sub>, AgClO<sub>4</sub> and AgBF<sub>4</sub> in reaction

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with  $[\text{PO}(\text{NH}^2\text{Py})_3]$ , sequential deprotonation of the ligand amido-protons was attained to yield the respective P(V)-oxo analogous corresponding to  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  ions as their multi-nuclear Ag(I) clusters.<sup>11</sup> Using a similar approach, the homoleptic imido species  $[\text{P}(\text{N}^2\text{Py})_2(\text{NH}^2\text{Py})_2]^-$ , analogous to  $\text{H}_2\text{PO}_4^-$  ion, as its penta-nuclear Ag(I) complex was synthesized in a reaction involving the phosphonium salt  $[\text{P}(\text{NH}^2\text{Py})_4]\text{Cl}$  and  $\text{AgClO}_4$ .<sup>12</sup> Prompted by this observation, we screened the reactivity of the phosphonium salt  $[\text{P}(\text{NH}^2\text{Py})_4]\text{Cl}$  with various salts of Ag(I) in an attempt to sequentially generate its homoleptic imido-anions including the elusive tetra-imido phosphate trianion,  $[\text{P}(\text{N}^2\text{Py})_4]^{3-}$ , in protic and polar medium and the outcome of these efforts are summarised in this paper.

## 2. Experimental

All manipulations involving phosphorus halides were performed under dry nitrogen atmosphere in standard Schlenk-glassware.  $\text{PCl}_5$ , 2-aminopyridine and silver trifluoromethanesulphonate ( $\text{AgOTf}$ ) were purchased from Aldrich and used as received. Compound **1·Cl** was synthesized as per the previous procedure.<sup>12</sup> The  $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  was purchased from MERCK and used as received. NMR spectra were recorded on a 400 MHz Jeol FT spectrometer ( $^1\text{H}$  NMR: 400.13 MHz,  $^{13}\text{C}\{^1\text{H}\}$  NMR: 100.62 MHz and  $^{31}\text{P}\{^1\text{H}\}$  NMR: 161.97 MHz) at room temperature using  $\text{SiMe}_4$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as external standards. ESI and MALDI-TOF Mass spectra were obtained by Waters Q-ToF Premier & Aquity spectrometer and Applied Biosystem MALDI-TOF/TOF spectrometer, respectively. Elemental analyses were performed on a Vario-EL cube elemental analyser. FT-IR spectra were taken on a Perkin Elmer spectrophotometer with samples prepared as KBr pellets. Melting points were obtained using an Electro thermal melting point apparatus and were uncorrected.

### 2.1 Preparation of phosphonium salt **1·NO<sub>3</sub>**

To a solution of **1·Cl** (100 mg, 0.23 mmol) in methanol (4 mL) containing few drops of chloroform,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (30 mg, 0.115 mmol) was added and stirred for a few minutes. The solution was then filtered over a thick pad of celite and left for crystallization at room temperature. Colourless crystals of **1·NO<sub>3</sub>**, suitable for SCXRD, were obtained after 2 days. Yield 91% (97 mg). M.p. 195–198°C.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  3.10 (br, 4H, NH), 6.81 (dd, 4H, CH), 7.05 (d, 4H, CH), 7.68 (dd, 4H, CH), 8.01 (d, 4H,

CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  113.89, 115.71, 139.03, 147.57 and 154.38.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -0.35. FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3450, 3314 and 3113 [ $\nu$  (N–H)], 586, 610, 624, 644, 771, 874, 927, 972, 997, 1055, 1101, 1151, 1201, 1234, 1269, 1298, 1383, 1460, 1485, 1530, 1594 [ $\nu$  (P–N)]. ESI(+) spectra: 403.1546 (M+). Anal. Calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_9\text{O}_3\text{P}$ : C, 51.61; H, 4.33; N, 27.09. Found: C, 52.04; H, 4.28; N, 26.87.

### 2.2 Preparation of Ag(I) complex **2·(OTf)<sub>3</sub>**

A solution of **1·Cl** (100 mg, 0.23 mmol) in methanol (2 mL), DMF (1 mL) and with few drops of chloroform kept in a screw capped vial, was carefully layered with toluene (1 mL) followed by a solution of  $\text{AgOTf}$  (208.12 mg, 0.81 mmol) in methanol (3 mL). This results in a cloudy solution which was then kept in dark for crystallization. Colourless crystals were obtained after 3 days. Direct mixing of a solution of **1·Cl** in methanol/DMF to  $\text{AgOTf}$  in methanol yielded a white precipitate, which was washed with water and methanol and dried. This precipitate was found to give same mass, NMR and CHN analysis as that of the crystalline sample. Yield 47% (135 mg). M.p. 183–187°C.  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  4.13 (br, 4H, NH), 6.89 (br, 4H, CH), 7.19 (br, 2H, CH), 7.69 (br, 4H, CH), 7.91 (br, 2H, CH), 8.15 (br, 2H, CH), 8.69 (br, 2H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  116.53, 117.58, 121.06, 139.97, 150.35, 159.22;  $^{31}\text{P}\{^1\text{H}\}$  NMR (161 MHz,  $(\text{CD}_3)_2\text{SO}$ ):  $\delta$  -2.07; FT-IR data in KBr pellet ( $\text{cm}^{-1}$ ): 3310 [ $\nu$  (N–H)], 506, 596, 742, 819, 925, 1047, 1075, 1177, 1234, 1297, 1350, 1426, 1448, 1460, 1594 [ $\nu$  (P–N)], 1641, 623 [ $\nu$  (Ag–N)]. Anal. Calcd. For  $\text{C}_{52}\text{H}_{57}\text{F}_9\text{N}_{19}\text{O}_{12}\text{P}_2\text{S}_3\text{Ag}_5$ : C, 31.09; H, 2.86; N, 13.25; S, 4.79. Found: C, 30.74; H, 2.40; N, 12.78; S, 4.35. MALDI-TOF spectra: 1340.92 ( $[\text{Ag}_5\text{L}_2]^{3+}$ ), 1233.04 ( $[\text{Ag}_4\text{L}_2]^{2+}$ ) and 1127.14 ( $[\text{Ag}_3\text{L}_2]^+$ ).

### 2.3 Crystallography

Reflections were collected on a Bruker Smart Apex Duo diffractometer at 100 K using  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Structures were refined by full-matrix least-squares against  $F^2$  using all data (SHELX-2013).<sup>13</sup> All non-hydrogen atoms were refined anisotropically if not stated otherwise. Hydrogen atoms were constrained in geometric positions to their parent atoms. Crystals of **1·NO<sub>3</sub>·2H<sub>2</sub>O** diffracted weakly at higher angles and hence a  $2\theta = 50^\circ$  cut-off was applied. The nitrate anion in **1·NO<sub>3</sub>·2H<sub>2</sub>O** was disordered and refined over three positions with SIMU/SAME restraints. The solvated DMF molecules and the  $\text{OTf}^-$  anions in **2·(OTf)<sub>3</sub>·**

3DMF were disordered and refined over two positions with SIMU/SAME restraints.

### 3. Results and Discussion

#### 3.1 Synthesis and spectra

The phosphonium precursor  $[P(NH^2Py)_4]Cl$  (**1·Cl**) was synthesized as reported by us earlier which involves the reaction of  $PCl_5$  and 2-aminopyridine in refluxing toluene. Attempted crystallization of **1·Cl** from its solution in methanol have lead to the formation of the neutral phosphoramidate derivative  $[PO(NH^2Py)_3]$  mediated by a P-N bond cleavage reaction. This is presumably due to the mildly acidic conditions offered by the methanolic medium where the OH protons of the solvent participates in H-bonding with the ring nitrogens which subsequently weakens one of the P-N bonds towards hydrolysis. However, under slightly basic conditions employing a dilute methanolic KOH solution the neutral phosphorane  $[P(N^2Py)(NH^2Py)_3]$  (**1-H**) derivative was obtained and could be crystallized in methanol/ $CHCl_3$  solvent mixture.<sup>12</sup> This prompted us to look for other suitable counter anion which can prevent the P-N bond hydrolysis and provide stability for **1** to exist in the slightly acidic pH of the methanol medium. We have employed the non-coordinating anions of various electropositive metal ions in the anion exchange reactions with **1·Cl** and succeeded in replacing the chloride ion with the nitrate ion using  $Mg(NO_3)_2$  (scheme 1). The  $^{31}P$ -NMR of **1·NO<sub>3</sub>** gave a single peak at  $\delta$  -0.35 which is closely matching with that of **1·Cl**. The high-resolution mass spectral analysis revealed a characteristic peak in the phosphonium region at  $m/z = 403.15$  confirming the absence of the hydrolyzed product (figure S1). Moreover, the single-crystal X-ray diffraction data was collected on the crystal of **1·NO<sub>3</sub>** which unequivocally supports its existence in the solid-state.

In order to study the stepwise deprotonation behaviour, the phosphonium salt **1·Cl** was treated with Ag(I) salts having various counter anions which offers different degrees of reactivity in metallation reactions. Thus, in an earlier report we have shown that the reaction of **1·Cl**, or its neutral analogue **1-H**, with excess  $AgClO_4$  in methanol/toluene mixtures have led to the formation of penta-nuclear Ag(I) complex stabilized by two  $[P(N^2Py)_2(NH^2Py)_2]^-$  mono-anionic ligands. The reaction was seemingly complete in less than 24 h where upon the crystals of  $\{Ag_5[P(N^2Py)_2(NH^2Py)_2]\} \cdot (ClO_4)_3$  (**2·(ClO<sub>4</sub>)<sub>3</sub>**) were recovered from the reaction vessel. In contrast, the reaction of **1·Cl** with excess  $AgNO_3$  under similar conditions have led to the in-situ



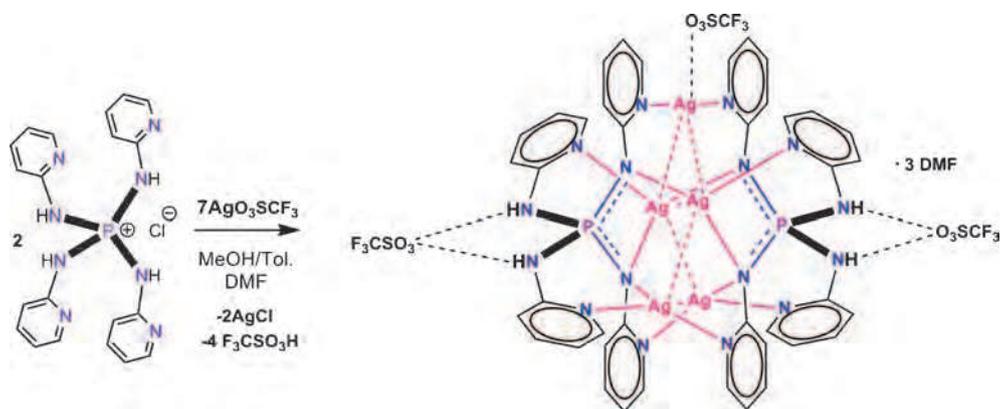
**Scheme 1.** Anion exchange reaction leading to the phosphonium cation **1·NO<sub>3</sub>**.

formation of the phosphoramidate ligand  $[PO(NH^2Py)_3]$  which binds to three Ag(I) ions in a complex of composition  $\{Ag_3[PO(NH^2Py)_3]\} \cdot (NO_3)_3$ , **3·(NO<sub>3</sub>)<sub>3</sub>** as observed before.<sup>11</sup> This reaction was relatively sluggish owing to the time that is required for the in-situ formation of the phosphoramidate ligand from **1·Cl**. From these observations it can be inferred that higher the reactivity of Ag(I) salt, higher the probability to effect the deprotonation of **1·Cl** as well as to stabilize the tetra-amido/imido P(V) backbone. Thus we chose to react the phosphonium salt **1·Cl** in presence of the more reactive silver triflate salt ( $AgOTf$ ) with the possible view of forming the fully deprotonated tetra-imido phosphate trianion  $[P(N^2Py)_4]^{3-}$  in its complex. Although the reaction proceeded spontaneously forming the crystalline material in less than 72 h, the structural determination of this compound revealed the formation of a similar penta-nuclear Ag(I) complex **2·(OTf)<sub>3</sub>** stabilized by the bis-imido phosphoramidate  $[P(N^2Py)_2(NH^2Py)_2]^-$  ( $L^-$ ) mono-anion (scheme 2).

The  $^{31}P$ -NMR data on the crystalline samples of **2·(OTf)<sub>3</sub>** showed a peak at  $\delta$  -2.07 very similar to that observed for **2·(ClO<sub>4</sub>)<sub>3</sub>**. The MALDI-TOF mass spectroscopy of **2·(OTf)<sub>3</sub>**, obtained in methanol with few drops of DMSO, is similar to that of **2·(ClO<sub>4</sub>)<sub>3</sub>** and shows prominent peaks at  $m/z$  centred at 1340.92, 1233.04 and 1127.14 consistent with cationic species of formula  $[Ag_5L_2]^{3+}$ ,  $[Ag_4L_2]^{2+}$  and  $[Ag_3L_2]^+$  respectively (figure 1).

#### 3.2 Crystal Structures

Crystals of **1·NO<sub>3</sub>·2H<sub>2</sub>O** suitable for single crystal X-ray diffraction (SC-XRD) were obtained from the slow evaporation of its solution in methanol (table 1). The molecular structure was solved in the triclinic space group P-1 comprising of the phosphonium cation, one nitrate ion in three disordered positions and two solvated molecules of water in its asymmetric unit

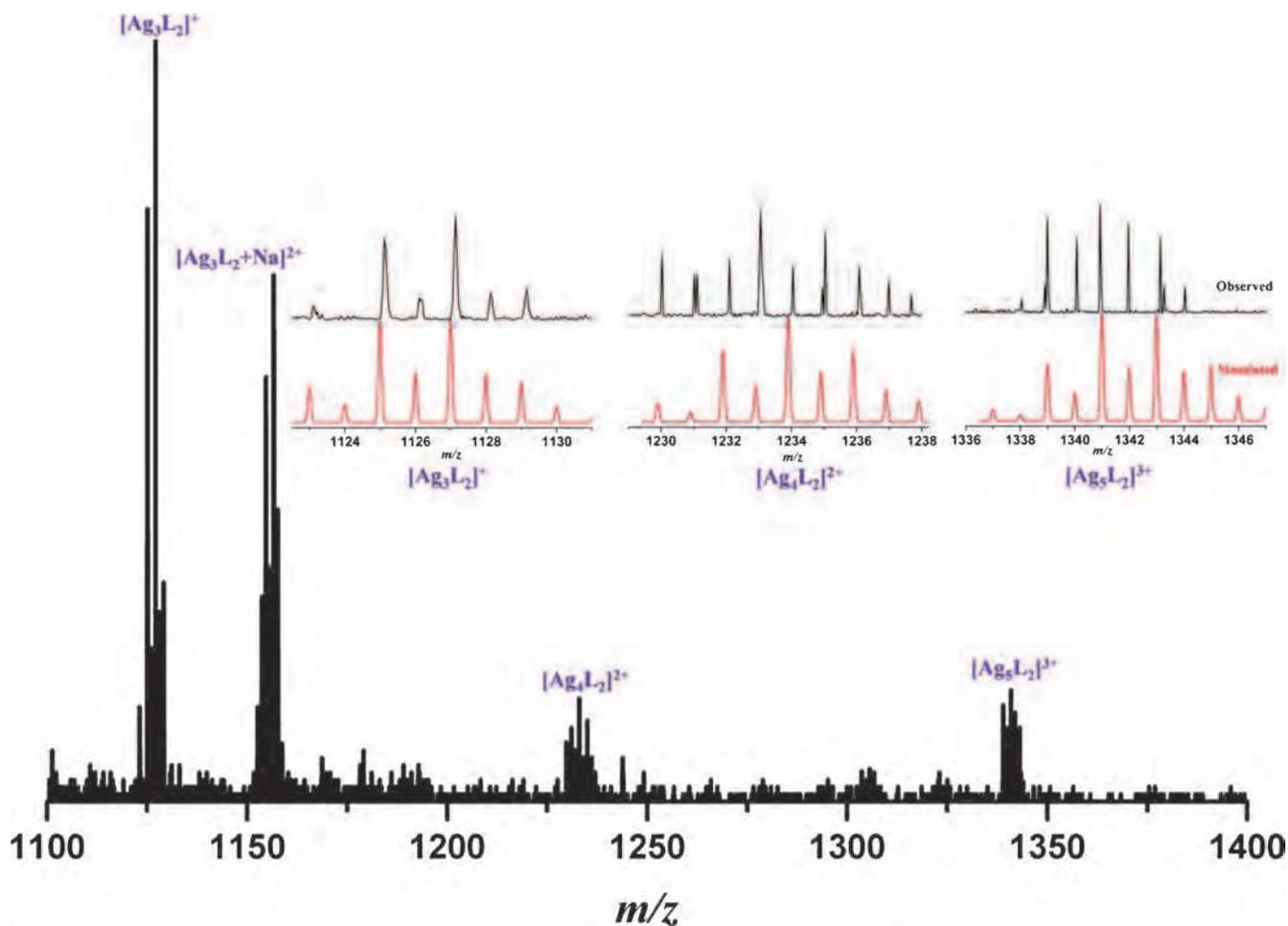


**Scheme 2.** Synthesis of the penta-nuclear Ag(I) complex **2**·(OTf)<sub>3</sub>.

(figure 2a). The observed P-N bond distances were found to be in the range between 1.598 and 1.646 Å as observed for related aryl- or alkylamino phosphonium compounds (table S1).<sup>14</sup> Two of the four N-H bonds were involved in inter-molecular hydrogen bonding interactions with pyridyl N-sites originating from same segments (from two other molecules) in a complementary fashion. These N-H...N interactions

thus propagate in a head to tail fashion and result in the formation of a 1D-double chain structure (figure 2b).

The remaining N-H sites are projected away from the double-chain (above and below) and involved in hydrogen bonding interactions with the solvated water molecules and one of the disordered nitrate motifs. These hydrogen bonded water molecules further interact with the nitrate ions and connect the adjacent chains



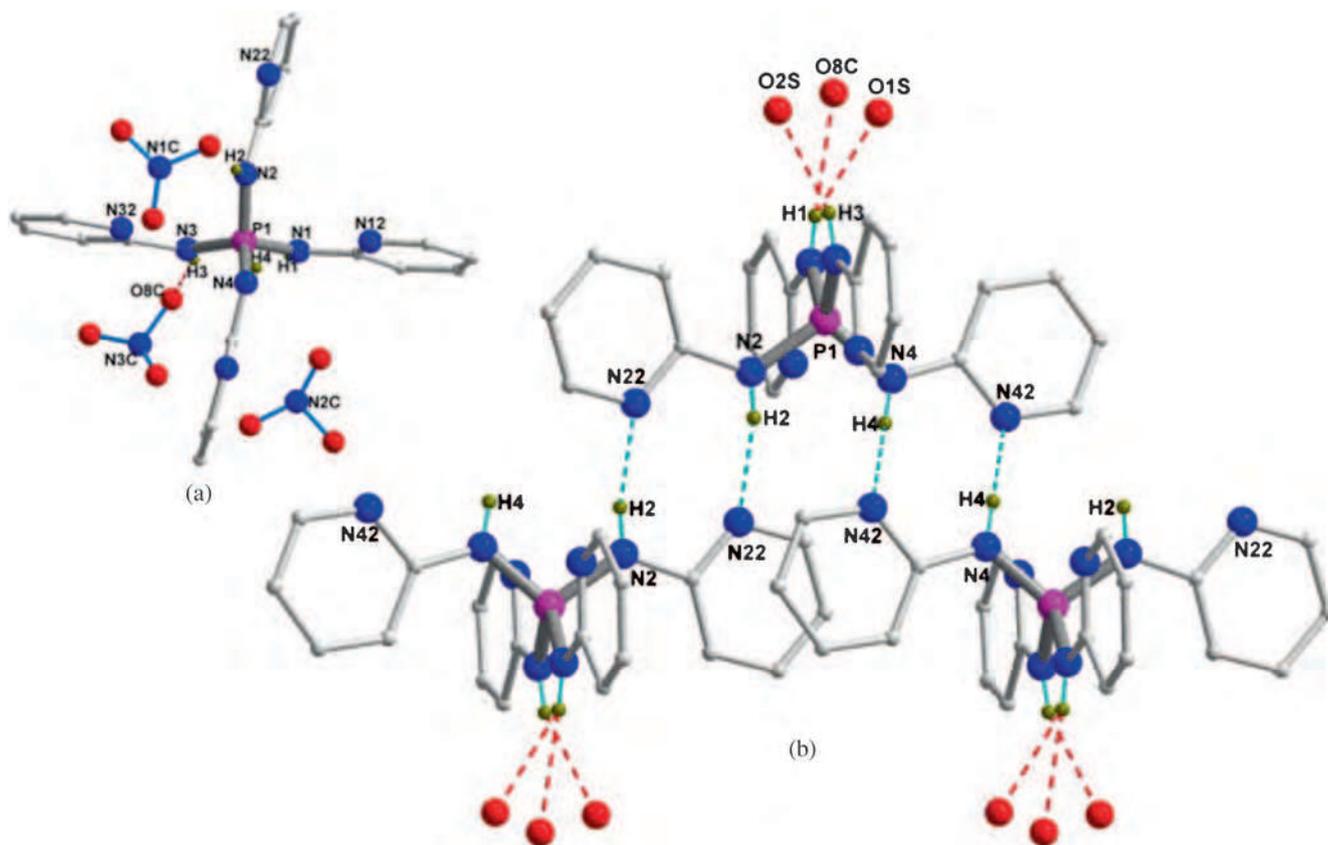
**Figure 1.** MALDI-TOF mass spectra of the penta-nuclear Ag(I) complex **2**·(OTf)<sub>3</sub>.

**Table 1.** Crystal Data.

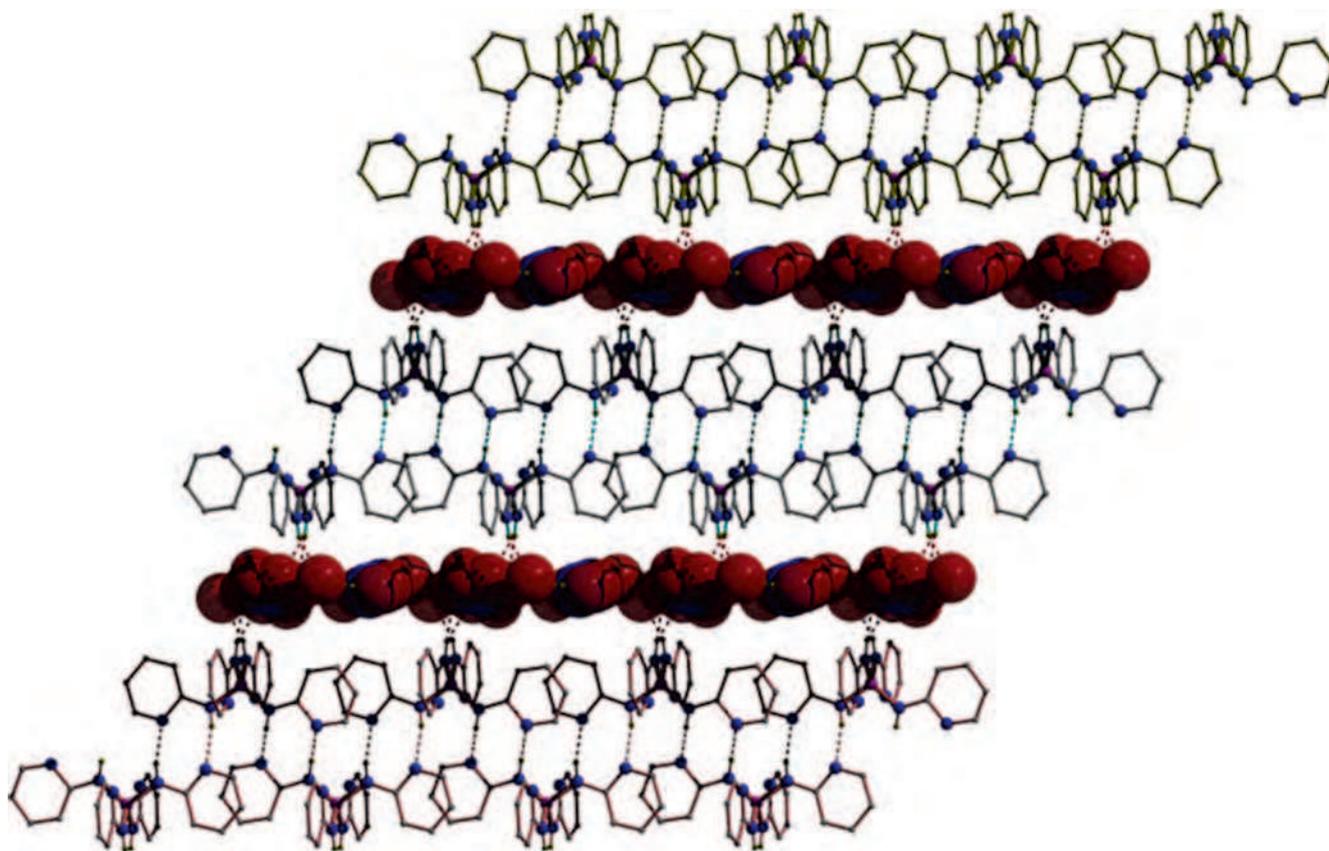
Compound	1·NO <sub>3</sub> ·2H <sub>2</sub> O	2·(OTf) <sub>3</sub> ·3DMF
Chemical formula	C <sub>20</sub> H <sub>24</sub> N <sub>9</sub> O <sub>5</sub> P	C <sub>52</sub> H <sub>57</sub> Ag <sub>5</sub> F <sub>9</sub> N <sub>19</sub> O <sub>12</sub> P <sub>2</sub> S <sub>3</sub>
Formula weight	501.45	2008.64
Temperature	100(2)K	100(2)K
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å); α (°)	9.037(3); 72.948(7)	11.624(4); 80.501(6)
b (Å); β (°)	9.746(4); 80.443(7)	16.726(5); 74.225(7)
c (Å); γ (°)	14.391(5); 86.902(7)	19.060(6); 78.162(6)
V (Å <sup>3</sup> ); Z	1194.9(8); 2	3466.6(19); 2
ρ (calc.) mg <sup>-3</sup>	1.394	1.940
μ(Mo K <sub>α</sub> ) mm <sup>-1</sup>	0.166	1.622
2θ <sub>max</sub> (°)	50	50.06
R(int)	0.0770	0.0522
Completeness to θ	92.4 %	99.5 %
Data / parameters	3894 / 339	12199 / 890
GOF	1.055	1.018
R1 [F>4σ(F)]	0.0864	0.0516
wR2 (all data)	0.2601	0.1442
max. peak/hole (e.Å <sup>-3</sup> )	0.970/ -0.668	2.548/ -1.182

to form a 2D-layered structure (figure 3). The metric parameters associated with these H-bonds point to very strong interactions (table S3). As a result of these

H-bonding interactions, two varied types of N-P-N bonds were found in the structure deviating from the tetrahedral angle (109.4°). The shortest angle of



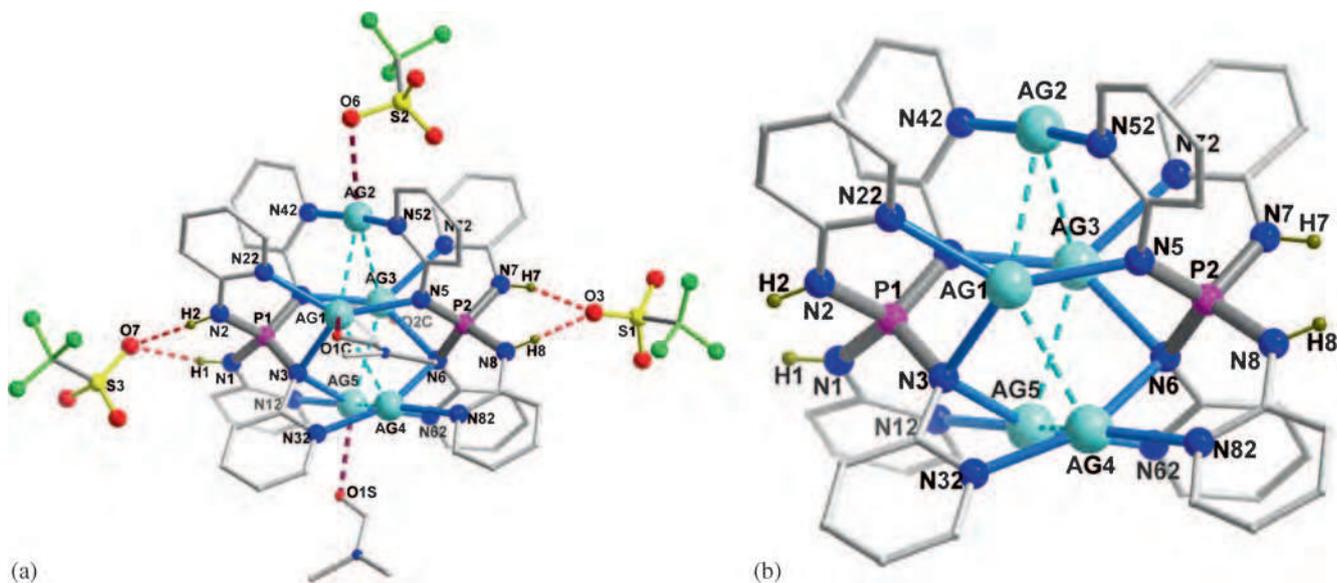
**Figure 2.** (a) Molecular structure of 1·NO<sub>3</sub>·2H<sub>2</sub>O; (b) view of the segment of a 1D-double chain structure in 1·NO<sub>3</sub>·2H<sub>2</sub>O mediated by head to tail type H-bonding interactions.



**Figure 3.** View of the 2D-layered structure formed by the interaction of the water and nitrate anion with the amino protons of the double chain segments.

100.24(2)° is found in the N2-P1-N4 segment involved in the complementary N-H...N interaction and is part of an eight-membered  $R_2^2/8$  ring (graph set notation).<sup>15</sup> Similarly the shorter angle of 104.39(2)° is found for the N1-P1-N3 segment located on the other side of the

double chain. Whereas, the remaining four distances were longer and range between 110.54(2) and 116.73(2)° and were associated with the mixed N-H...N and N-H...O interactions located inside and above the double-chain, respectively.



**Figure 4.** (a) Molecular structure of 2·(OTf)<sub>3</sub>·3DMF; (b) core view of the [Ag<sub>5</sub>L<sub>2</sub>]<sup>3+</sup> cationic cluster.

The complex  $2 \cdot (\text{OTf})_3$  crystallizes as  $2 \cdot (\text{OTf})_3 \cdot 3\text{DMF}$  from its reaction mixture in methanol, toluene and DMF. SC-XRD analysis shows that it crystallizes in the triclinic space group P-1. The asymmetric unit consists of the complete  $[\text{Ag}_5\text{L}_2]^{3+}$  core, three disordered triflate ( $\text{OTf}^-$ ) anions and three DMF molecules. The core structure of  $2 \cdot (\text{OTf})_3$  resembles very closely to that of  $2 \cdot (\text{ClO}_4)_3$  featuring two doubly deprotonated hexadentate ligands ( $\text{L}^-$ ) bonded to a tricationic cluster of five Ag(I) ions (figure 4). The P- $\text{N}_{\text{imido}}$  distances (P1-N3, P1-N4, P2-N5 and P2-N6; average, 1.604(5) Å) are slightly shorter than the P- $\text{N}_{\text{amido}}$  distances (P1-N1, P1-N2, P2-N7 and P2-N8; average, 1.668(5) Å) suggesting the delocalized nature of the anionic charge between the two imido moieties housed on each P-atom (table S2). Four of the five Ag(I) ions in **2** are found in a tricoordinate environment of which two of them (Ag1 & Ag3) contains two  $\text{N}_{\text{imido}}$  and one  $\text{N}_{\text{pyridyl}}$  contacts. The remaining three Ag(I) ions have two  $\text{N}_{\text{pyridyl}}$  bonds each as Ag5 does not make any  $\text{N}_{\text{imido}}$  contacts. While, two of the three disordered triflates were engaged in H-bonding interactions with the Lewis acidic bidentate amido protons (HN-P-NH) in a chelating fashion, the third triflate is bonded to one of the Ag(I) ion at a slightly longer distance (Ag5-O1S: 2.595(16) Å). Unlike  $2 \cdot (\text{ClO}_4)_3$  where the solvated methanol and toluene were located in the porous channels arising from the grid-like packing of the cluster and anions, the three DMFs in  $2 \cdot (\text{OTf})_3 \cdot 3\text{DMF}$  are coordinated to three Ag(I) ions (Ag1, Ag3 and Ag5) resulting in the formation of a densely packed structure in which two distinct cavities were observed for DMF and triflates (figure S2). The average Ag-Ag distances were measured to be 2.984(10) Å which is slightly longer than those found in metallic silver (2.880 Å).<sup>16</sup>

In several instances, it has been observed that Ag(I) complexes featuring Ag-N bonds are labile and can adopt to interesting kinds of structural architectures depending upon, Ag(I) precursor, reaction conditions and steric and electronic effects of the ligand. However, formation of the Ag5-complex in the present instance seems to be driven by the thermodynamically stable product formation in which the pentanuclear Ag(I)-complex is perfectly sandwiched between two cisoidal imido-phosphinate ligand moieties. Our previous results with the related phosphate precursor,  $[\text{PO}(\text{NH}^2\text{Py})_3]$ , in reaction with various Ag(I) salts have shown to yield complexes of the corresponding neutral, mono- and dianionic ligands.<sup>11</sup> However, the stability of the Ag5-cluster within the mono-anionic casing of the  $[\text{P}(\text{N}^2\text{Py})_2(\text{NH}^2\text{Py})_2]^-$  ligand have seemingly overwhelmed the subtle reactivity changes offered by various Ag(I) salts.

## 4. Conclusion

Employing an anion exchange route, synthesis of a stable tetrakis(2-pyridylamino)phosphonium cation as its nitrate salt,  $[\text{P}(\text{NH}^2\text{Py})_4]\text{NO}_3$  has been described. The rich head to tail kind of H-bonding interactions offered by the pyridyl amino segments may have played a vital role in neutralizing the internal acid-base effects of the cation and stabilize the molecule in solution as well as in the solid-state. Further, the formation of a tricationic pentanuclear Ag(I) complex  $2 \cdot (\text{OTf})_3$  has been observed in the reaction of **1**·Cl with AgOTf similar to that observed in the reaction of AgClO<sub>4</sub>. These observations have demonstrated the thermodynamic stability of the complex in presence of various counter anions and solvents.

## Supplementary Information

The supplementary information available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci) contains tables (S1–S3) of bond-lengths and angles, H-bonding table and additional figures (S1 and S2). Crystal data for the compounds are deposited at the Cambridge crystallographic data centre with the CCDC numbers 966611-966612 and can be obtained via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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