

Article

Role of Bis(triphenylphosphine)iminium Cation [PNP]⁺ on the Crystal Packing of [PNP]⁺[HSeO₃][−] Solvate Salt

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Received: 14 March 2018; Accepted: 28 March 2018; Published: 29 March 2018



Abstract: Selenate(IV) and hydrogen selenate(IV) salts of bulky cations are very interesting compounds for synthetic and kinetic studies. In this work, bis(triphenylphosphine)iminium ([PNP]⁺) chloride has been used, which aims to synthesize the corresponding selenate(IV) salt by an exchange reaction in the aqueous solution and subsequent crystallization by solvent evaporation. Unexpectedly, the procedure afforded a solvate form of the [PNP]⁺[HSeO₃][−] salt (1). In this solid phase, which has a structure that is determined by Single Crystal XRD, the anion tends to maximize the interactions with itself, although it leaves the cationic moiety to have only weak interactions with the anions and the solvent molecules. In turn, the latter builds a network of effective hydrogen bonds. This behavior opposes the general tendency of selenite(IV) and hydrogen selenite(IV) compounds, since these anions are commonly found to have formed effective hydrogen bonds with surrounding chemical species. Moreover, as the exchange reaction is non-quantitative, the exceeding traces of the starting bis(triphenylphosphine)iminium chloride reagent reacted with bis(acetonitrile)dichloropalladium(II) to form the bis(triphenylphosphine)iminium hexachloropalladate (2). In the solid phase, [PNP]⁺ causes the absence of strong supramolecular interactions, which highlights the peculiar behavior of the cation in the crystal packing of its solid phases.

Keywords: hydrogen selenate(IV) compounds; crystal structure; PNP salt; hydrogen bond interactions

1. Introduction

The interest of the scientific community in the structural chemistry of selenite(IV) and tellurate(IV) has grown significantly in the last decades due to several reasons. First of all, these anions allow the formation of solid state structures characterized by the presence of cavities, which are mostly in the form of channels. These cavities are able to house the selenium or tellurium electron pairs and form open framework structures [1–6]. Moreover, it is known that the presence of pyramidal anions, such as XO₃^{2−} (X = S, Se, Te), can lead to the formation of non-centrosymmetric structures. These materials can display non-linear optical properties and other interesting properties, such as ferroelectricity and piezoelectricity [7–12]. In addition, the weak coordinative capability of Se(IV) electron lone pairs in selenate(IV) anions has been recently suggested to play a crucial role in the formation of supramolecular interactions, which was observed in the case of the [Pd₁₅(μ₃-SeO₃)₁₀(μ₃-O)₁₀Na]^{9−} anion [13]. On the other hand, the bis(triphenylphosphine)iminium cation has been used extensively as the counter ion in synthetic and kinetic studies. In fact, its salts are commonly very soluble and dissociate well in a number of aprotic solvents [14,15], thus allowing more homogeneous reactions and facilitating the study of their kinetics [16]. Moreover, the weak polarizability of this cation improves

the crystallization and the consequent isolation of many salts of anions, which would otherwise not be possible to obtain. Pursuing our interest in the chemistry of selenite(IV) metal complexes, we decided to investigate the reactivity of selenate(IV) of a bulky cation, such as bis(triphenylphosphine)iminium, in order to explore the possibility of using starting materials that are soluble in non-polar solvents. In fact, the absence of interactions between selenate(IV) anion and solvent molecules would promote the formation of coordinative interactions between the selenate(IV) anion and a metal ion. Moreover, the combination of a bulky cation, such as bis(triphenylphosphine)iminium, with the selenate(IV) anion might enhance the solubility of the selenate(IV) in a non-polar solvent. When in the presence of a cation, this combination is capable of creating interactions with anions of similar hindrance and dimensions, such as oxo- chloro- or cyanometallate, to promote the formation of crystalline phases [17]. With this idea in mind, we tried to synthesize the bis(triphenylphosphine)iminium selenate(IV) and aimed to react it with bis(acetonitrile)dichloropalladium(II).

2. Results and Discussion

Following the procedure reported in a previous study [18], we reacted aqueous solutions of bis(triphenylphosphine)iminium chloride and sodium selenate(IV) in a 1:5 molar ratio at 70 °C. The reaction was stirred for 10 min, before being cooled in an ice bath for 1 h. The pale gray microcrystalline powder subsequently obtained was filtered and washed with water. The powder is soluble at room temperature in acetone, methanol, ethanol, dimethylsulfide, acetonitrile, dichloromethane and chloroform. The IR spectrum of the microcrystalline product shows the typical bands of the bis(triphenylphosphine)iminium ion and two bands at 690 and 728 cm^{-1} due to the presence of Se-O groups (Figure S1). The SEM analysis conducted on the powder clearly shows the presence of chlorine, which likely belongs to the unreacted starting reagent (Figure S2). The slow solvent evaporation of a dichloromethane solution created prismatic colorless crystals suitable for single crystal X-Ray diffraction, which allowed the structure of this phase to be solved.

2.1. Crystal and Molecular Structure of Bis(triphenylphosphine)iminium Hydrogen Selenate(IV) Solvate (1)

The crystal structure of **1** consists of a bis(triphenylphosphine)iminium cation, a hydrogen selenate(IV) anion, a dichloromethane and a water molecule. The crystal structures of hydrogen selenate(IV) of alkali metals or ammonium have been largely reported in the literature [19–21], while relatively few phases containing hydrogen selenate(IV) and organic nitrogen cations have been described until now [22–29]. Some relevant features of the structure of **1** are reported in Figure 1.

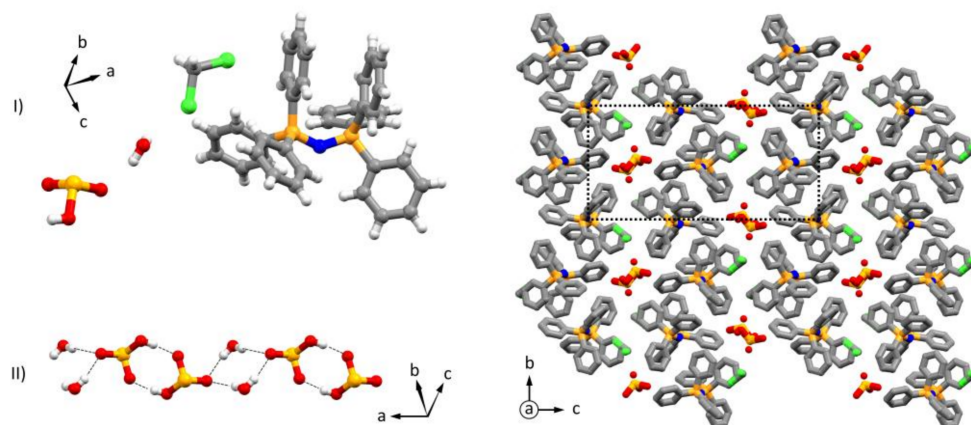


Figure 1. (I) Asymmetric unit of **1**, ball and stick representation; and (II) The chain formed by hydrogen selenite(IV) anions and water molecules is displayed in ball and stick representation. On the right, the crystal packing is shown along the crystallographic direction *a*; and the hydrogen atoms are omitted for the sake of clarity. This is shown in a capped sticks representation.

The hydrogen selenate(IV) anions are linked together by strong hydrogen bonds forming dimers ($\text{O}\cdots\text{O}$ distance 2.762(2) Å, $\text{O}\cdots\text{H}$ distance 1.964(2) Å, $\text{O}-\text{H}\cdots\text{O}$ angle 164.07(2)°). Two water molecules act as H-bond donors towards two different hydrogen selenate(IV) dimers, bridging them and forming an infinite chain of hydrogen selenate(IV) anions and water molecules. These develop along the crystallographic a axis. To the best of our knowledge, this type of arrangement has never been reported in the literature for hydrogen selenate(IV) anions. Remarkably, the selenium lone pair is not involved in any recognizable interaction, since the nearest H-bond donor, which is the adjacent aromatic $-\text{CH}$ groups of PNP, are involved in H-bond with the oxygen atoms of the anions. A dichloromethane molecule is also present in the crystal packing, which is involved in interactions with another dichloromethane and with a water molecule through the H atoms. [Distance $\text{H}\cdots\text{Cl}$ 2.858(2) Å and distance $\text{H}\cdots\text{O}$ 2.142(2) Å]. As shown in Figure 2, the overall supramolecular network forms a grid, whose apertures host the bulky cations.

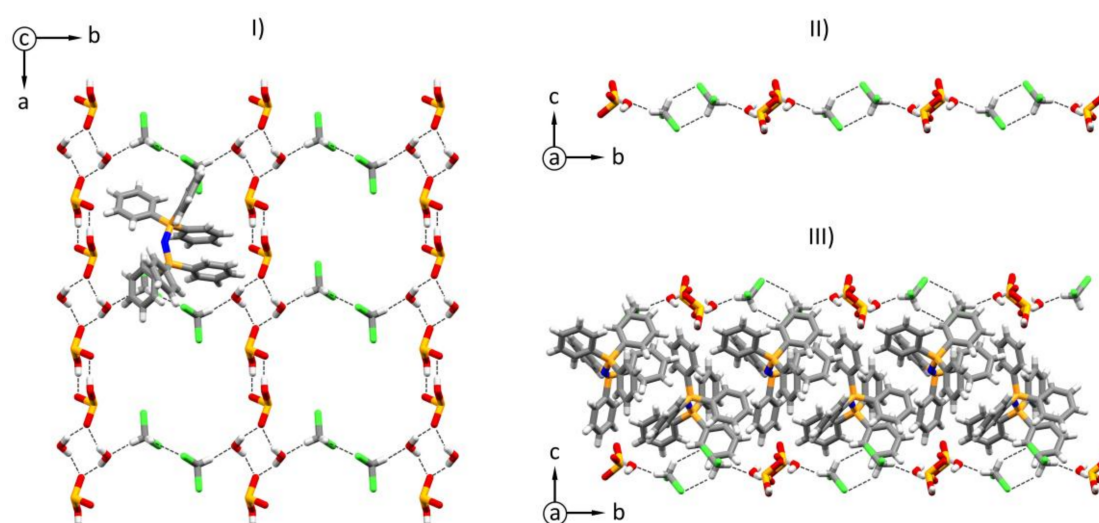


Figure 2. Supramolecular interactions in **1**. Hydrogen selenate(IV), dichloromethane and water molecules form a network of hydrogen bonds along the a and b directions (I, II). This arrangement forms square shaped apertures, where the $[\text{PNP}]^+$ cations are allocated (I; only one cation is shown for the sake of clarity), resulting in layers of cations (III). This is shown in a capped sticks representation.

Considering the structures reported in the Cambridge Crystallographic Data Centre that are comprised of hydrogen selenate(IV) anions of nitrogen containing cations, usually a strong network of hydrogen bonds developing in the entire three-dimensional array of the crystal packing is observed [22–29]. For example, the reported crystal structure of the ammonium hydrogen selenate(IV) [19], which is the simplest of this type of compounds, is consolidated by a network of hydrogen bonds, with donor \cdots acceptor distances ($\text{N}\cdots\text{O}_{(\text{Se})}$ and $\text{O}\cdots\text{O}_{(\text{Se})}$) ranging between 2.80 and 3.07 Å. In other more complexes, nitrogen-containing organic cations have been reported, such as N,N' -dimethylpiperazinium [22], anilinium [23], L-tryptophanium [29], 1-carbamoylguanidinium [24], L-argininium [25], N,N' -diphenylguanidinium [26], cytosinium [27], and several organoammonium cations described by Lukevics et al. [28]. The stabilization of the crystal packing is achieved again by forming an extended network of hydrogen bonds of the type $\text{O}-\text{H}\cdots\text{O}_{(\text{Se})}$, or $\text{N}-\text{H}\cdots\text{O}_{(\text{Se})}$. Various intermolecular hydrogen-bonding motifs, including linear and bifurcated bonds, are present and based on the $\text{O}\cdots\text{O}_{(\text{Se})}$ and $\text{N}\cdots\text{O}_{(\text{Se})}$ separations, these bonds vary in strength from fairly strong to very weak. Moreover, the directionality of the hydrogen bonds can contribute to the formation of layers or ribbons. In the crystal structure of 1-carbamoylguanidinium hydrogen selenate(IV) reported in a previous study [24], strong and short inter-selenate(IV) hydrogen bonds help to fuse molecular layers formed by the planar 1-carbamoylguanidinium ions into double sheets. In the case of the crystal structure of

anilinium hydrogen selenate(IV) monohydrate reported in a previous study [23], the crystal packing consists of alternating layers of anilinium cations and hydrogen selenate(IV) anions interconnected by N-H \cdots O hydrogen bonds. Water molecules are located within the anionic layers and are involved in very strong O-H \cdots O intermolecular interactions connecting the hydrogen selenate(IV) anions. On the contrary, in our case, the bulky bis(triphenylphosphine)iminium cation prevents the formation of strong intermolecular interactions between the cation and the hydrogen selenate(IV) anion. We found that the anion prefers to auto-assemble in the form of an infinite chain together with water molecules.

2.2. Reaction of the Crude Product of Bis(triphenylphosphine)iminium Chloride and Sodium Selenate(IV) with Bis(acetonitrile)dichloropalladium(II). Identification of Bis(triphenylphosphine)iminium Hexachloropalladate (2)

We know from a previous study [18] that by reacting the aqueous solutions of bis(triphenylphosphine)iminium chloride with an excess of sodium selenate(IV), the corresponding bis(triphenylphosphine)iminium selenate(IV) was formed. Therefore, we used the obtained white homogeneous microcrystalline powder in a reaction with bis(acetonitrile)dichloropalladium(II) dissolved in dichloromethane, with the aim to investigate the possibility of forming new crystalline phases containing selenate(IV) anions and bis(acetonitrile)palladium(II) cations. After stirring the reaction mixture for one hour at room temperature, the solvent was left to evaporate and red single crystals have grown. One of them was analyzed by X-Ray diffraction and the crystal structure revealed that bis(triphenylphosphine)iminium hexachloropalladate (2) was formed.

The compound is isostructural with the analogous bis(triphenylphosphine)iminium hexachlorocuprate [30]. The geometrical parameters of the bis(triphenylphosphine)iminium cation is consistent with those observed in the literature. Considering the crystal packing of the compound, the multiple pairs of approximately parallel phenyl rings are present and the bis(triphenylphosphine)iminium cations weakly interact through multiple C-H \cdots C π interactions, which has C \cdots C distances of 3.538(2)–3.757(2) Å. Moreover, six bis(triphenylphosphine)iminium cations surround a [Pd₂Cl₆]^{2−} anion through C-H \cdots Cl weak interactions [H \cdots Cl distances of 2.736(2)–3.039(2) Å], which is shown in Figure 3. Once again, the bulky cation prevents the formation of strong interactions between itself and the anionic complex.

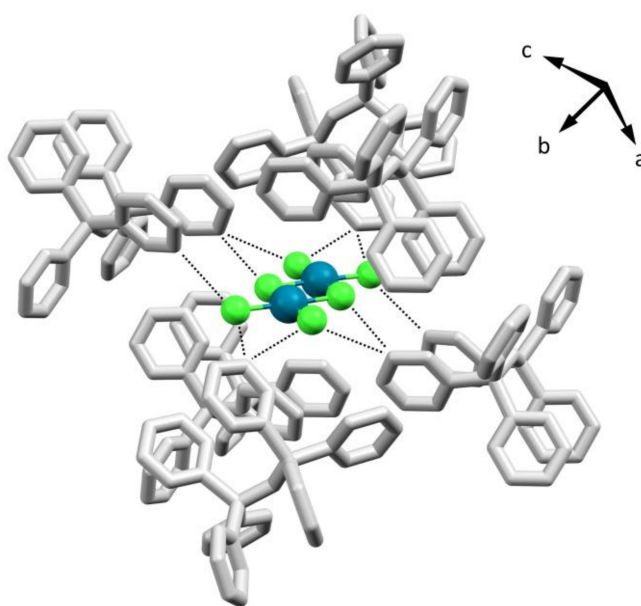


Figure 3. Crystal packing of 2 showing the six cationic molecules (capped sticks representation depicted in gray for clarity) that surrounds the hexachloropalladate anion.

In the crystal packing of the compound viewed along the crystallographic *a* axis (Figure 4), it is evident that the cations and hexachloropalladate anions tend to pile one over the other, forming infinite pillars of cations and anions.

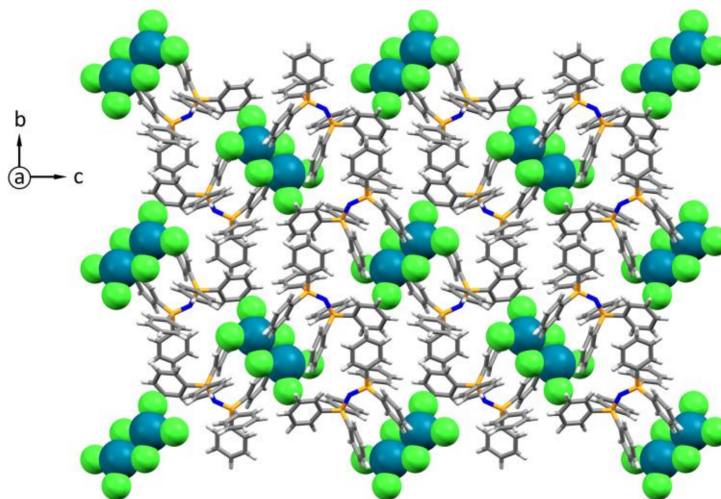


Figure 4. Crystal packing of **2** along the crystallographic axis *a*, highlighting the isolation of the chloro-anions (in ball and stick representation) by means of bis(triphenylphosphine)iminium cations (in capped sticks representation).

2.3. Crystal and Molecular Structure of a Novel Phase of Bis(triphenylphosphine)iminium Chloride Bihydrate (**3**)

In order to better investigate the nature of the microcrystalline powder obtained by reacting bis(triphenylphosphine)iminium chloride with an excess of sodium selenate(IV), a dichloromethane solution of the crude product was left to evaporate, creating two crystal phases with slightly different morphologies. The first type was the bis(triphenylphosphine)iminium hydrogen selenate(IV) solvate described above, while the second one was unambiguously identified as an unreported hydrated phase of bis(triphenylphosphine)iminium chloride (**3**). Several bis(triphenylphosphine)iminium chloride structures containing solvate molecules have been determined [31] and in our case, the principal geometrical parameters of the cations are in the expected range for similar bond distances and angles reported in the literature. On the other hand, we want to comment on the crystal packing of the bihydrated bis(triphenylphosphine)iminium chloride, highlighting once again the fact that the bulky bis(triphenylphosphine)iminium cations prevent the formation of strong intermolecular interactions between the cationic and the anionic parts of the compound. In fact, as shown in Figure 5, two water molecules and a chlorine atom are connected by hydrogen bonds and four bis(triphenylphosphine)iminium cations surround this aggregate, which interact by means of hydrogen bonds.

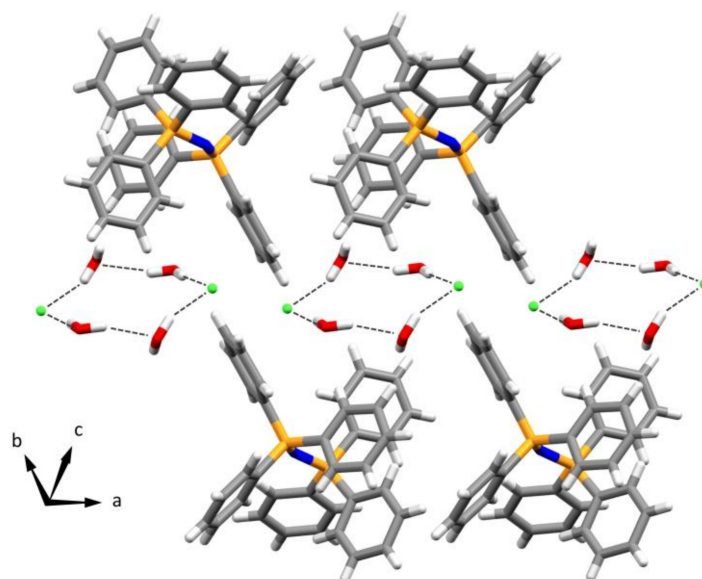


Figure 5. Crystal packing of **3**, showing the formation of hydrogen bonds between water molecules and chlorine atoms. This is shown in a capped sticks representation.

3. Conclusions

The synthesis of the bis(triphenylphosphine)iminium selenate(IV) is not easily predicted in a previous study [18], leading to the formation of the corresponding hydrogen selenate(IV) salt (**1**), which is shown by X-ray diffraction analysis. Moreover, the reaction does not fully complete, leaving traces of bis(triphenylphosphine)iminium chloride in the reaction mixture, although the exchange reaction has been carried out in the presence of an excess of sodium selenate(IV). The presence of chloride anions in the reaction mixture together with the scarce coordination ability of the acetonitrile ligands and the high stability of hexachloropalladate anion caused the formation of compound **2**, whose identity has been unequivocally confirmed by X-ray diffraction analysis. Further efforts aiming to purify the reaction mixture are needed to obtain a 100% yield of **1**. We observed that dissimilar to other ionic selenate(IV) and hydrogen selenate(IV) compounds reported in the CCDC (Cambridge Crystallographic Data Center), the anion does not interact with the bulky cation in the crystal packing of **1**, preferring to build 2D networks of hydrogen selenate(IV) and solvent molecules. A comparison between the crystal packing of the compound and the structural motifs reported in literature involving hydrogen selenate(IV) of organic nitrogen containing cations confirms that the presence of the bulky bis(triphenylphosphine)iminium cation prevents the formation of hydrogen bond interactions with the anionic part of the compounds. This behavior has also been shown in the case of the crystal structure of **2**, in which the cations and hexachloropalladate anions tend to pile one over the other, forming infinite pillars of cations and anions without any appreciable strong interactions between them.

4. Materials and Methods

4.1. General Remarks

All the preparations were carried out at room temperature in the presence of air. Bis(triphenylphosphine)iminium chloride, sodium selenate(IV), bis(acetonitrile)dichloropalladium(II) and solvents of acetone, methanol, ethanol, dimethylsulfide, acetonitrile, dichloromethane and chloroform were purchased and used as received (Merck KGaA, Darmstadt, Germany). FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond). SEM analysis was taken by a Scanning Electron Microscope (SEM) Jeol

6400 with Energy Dispersive System (EDS) Oxford INCA (15–20 kV, 1.2 nA, electronic beam diameter of 1 mm, acquisition time of 60 s).

4.1.1. Preparation of 1

A water solution (10 mL) of Na_2SeO_3 (0.7635 g, 4.35 mmol) was added to a water solution (15 mL) containing PNPCL (0.5002 g, 0.87 mol) at 70 °C. The colorless solution was stirred at the same temperature for 10 min. After this, the solution was cooled at 0 °C using an ice bath for one hour. The white precipitate formed was filtered on a Buchner and washed with water. The microcrystalline solid is soluble in acetone, methanol, ethanol, dimethylsulfide, acetonitrile, dichloromethane and chloroform. This crystallizes by slow evaporation when dissolved again in dichloromethane, forming a small amount of colorless crystals suitable for X-ray analysis together with very few morphologically different ones, which were subsequently identified as hydrated PNPCL salts (see Section 2). The FTIR of the identified bis(triphenylphosphine)iminium hydrogen selenate(IV) (Diamond crystal HATR, cm^{-1}) was at ν of 498 cm^{-1} , 531 cm^{-1} , 690 cm^{-1} , 728 cm^{-1} , 1002 cm^{-1} , 1117 cm^{-1} , 1227 cm^{-1} , 1265 cm^{-1} , 1441 cm^{-1} and 3057 cm^{-1} .

4.1.2. Preparation of 2

A dichloromethane solution (5 mL) containing 0.078 g of bis(acetonitrile)dichloropalladium(II) was added dropwise to 10 mL of a dichloromethane solution, which contained 0.204 g of the white microcrystalline powder that was prepared according to Section 4.1.1. The solution is stirred at room temperature for 1 h and the color changed to deep red. Under slow evaporation of the solvent, several red crystals are formed and analyzed by X-ray diffraction methods.

4.2. X-ray Data Collection, Structure Solution, and Refinement

The intensity data of the three compounds were collected at room temperature on a Bruker APEX II single crystal diffractometer [32,33] equipped with an area detector using a graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Crystallographic and experimental details of the reported structures are summarized in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares procedures (based on Fo^2) using SHELXL-2014/7 [34]. This is first conducted with isotropic thermal parameters, before using anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined depending on the corresponding parent atoms, except for the hydrogen atoms of the water molecules in 1 and in 3. CCDC 1829597, 1829598 and 1829599 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Summary of crystallographic data for **1**, **2** and **3**.

	[PNP][HSeO ₃]·H ₂ O·CH ₂ Cl ₂ 1	[PNP] ₂ [Pd ₂ Cl ₆] 2	[PNP]Cl·2H ₂ O 3
Formula	C ₃₇ H ₃₅ Cl ₂ N ₄ O ₄ P ₂ Se	C ₇₂ H ₆₀ N ₂ P ₄ Pd ₂ Cl ₆	C ₃₆ H ₃₄ ClNO ₂ P ₂
FW	769.46	1502.6	610.03
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> , Å	10.8664(11)	9.1894(4)	10.6243(9)
<i>b</i> , Å	12.6743(13)	22.3661(10)	12.6404(11)
<i>c</i> , Å	26.029(3)	16.2595(7)	23.595(2)
β, deg	95.727(2)	103.657(1)	101.558(2)
<i>V</i> , Å ³	3567.0(6)	3247.4(2)	3104.4(5)
<i>Z</i>	4	2	4
<i>D</i> _{calcd} , g cm ^{−3}	1.433	1.537	1.305
<i>F</i> (000)	1576.0	1520.0	1280.0
μ, cm ^{−1}	1.333	0.944	0.260
rfns collected	34915	50951	49398
rfns unique	5605	9552	9461
rfns observed [<i>I</i> > 2σ(<i>I</i>)]	4326 [<i>R</i> _{int} = 0.0335]	7832 [<i>R</i> _{int} = 0.0334]	6719 [<i>R</i> _{int} = 0.0435]
Parameters	428	388	385
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0963; <i>wR</i> 2 = 0.3612	<i>R</i> 1 = 0.0319; <i>wR</i> 2 = 0.0817	<i>R</i> 1 = 0.0652; <i>wR</i> 2 = 0.1825
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1141; <i>wR</i> 2 = 0.3953	<i>R</i> 1 = 0.0425; <i>wR</i> 2 = 0.0867	<i>R</i> 1 = 0.0918; <i>wR</i> 2 = 0.2039

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)].$$

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/8/4/151/s1>, Figure S1: IR pattern of bis(triphenylphosphine)iminium hydrogen selenite, Figure S2: SEM analysis on the microcrystalline powder obtained by reaction between bis(triphenylphosphine)iminium chloride and sodium selenite in 1:5 molar ratio.

Author Contributions: Both authors contributed equally to the research and writing of the present paper.

Conflicts of Interest: The authors declare no conflict of interest.

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