

MOLECULAR AND CRYSTAL STRUCTURES OF THREE TETRAPHENYLDICHALCOGENOIMIDO-DIPHOSPHINATES, $M[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ ($M = \text{Rb}, \text{Cs}$) AND $[\text{NMe}_4][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$

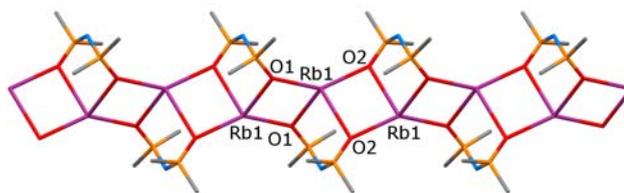
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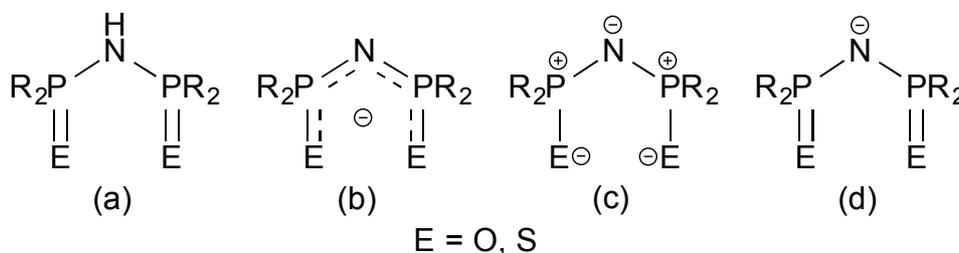
In this study, the molecular and crystal structures of three synthetically useful tetraphenyldichalcogenoimidodiphosphinates have been determined by single-crystal X-ray diffraction studies. In the solid state, the tetraphenylimidodiphosphinates $M[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ with $M = \text{Rb}$ (**1**) and Cs (**2**) are self-assembled into supramolecular 1D-chain structures. The crystal structure determination of tetramethylammonium-tetraphenyldithioimidodiphosphinate, $[\text{NMe}_4][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ (**3**) allowed the structural characterization of the uncoordinated $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ anion not involved in any cation-anion interactions in the solid state.



INTRODUCTION

The dichalcogenoimidodiphosphate anions $[\text{Ph}_2\text{P}(\text{E})\text{NP}(\text{E})\text{Ph}_2]^-$ ($\text{E} = \text{O}, \text{S}$), first introduced by Schmidpeter *et al.* in 1967,¹ after a slow beginning became an intensively investigated class of ligands.²⁻⁴ They are versatile complexing reagents with a strong

tendency to form inorganic (carbon free) chelate rings.⁵ As illustrated in Scheme 1, the parent protonated compounds $\text{Ph}_2\text{P}(\text{E})\text{NHP}(\text{E})\text{Ph}_2$ ($\text{E} = \text{O}, \text{S}$) are characterized by the presence of formal $\text{P}=\text{E}$ double bonds (a), whereas the corresponding anions can be described by three resonance forms, of which (b) is the most important.



Scheme 1 – Schematic representation of the parent dichalcogenoimidodiphosphinic acids $\text{Ph}_2\text{P}(\text{E})\text{NHP}(\text{E})\text{Ph}_2$ ($\text{E} = \text{O}, \text{S}$) and three resonance forms of their anions.

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Previously, the investigation of dichalcogenoimidodiphosphinato ligands was focused mainly on transition and post-transition metal complexes. The structures of their alkali metal salts, important starting reagents for the synthesis of complexes, were less studied. Structurally characterized alkali metal tetraphenylimidodiphosphinates mostly contain crown-ether ligands, such as the tetranuclear sodium derivatives $[\text{Na}(15\text{-crown-5})][\text{Na}_3\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}_4]$ and $[\text{Na}(\text{benzo-15-crown-5})][(\text{H}_2\text{O})\text{Na}_3\{\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2\}_4]$.⁶ In addition, the structure of the potassium 18-crown-6 complex $[\text{K}(18\text{-crown-6})][\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]\cdot\text{H}_2\text{O}$ has been reported.⁷ The other alkali metal derivatives $\text{M}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ ($\text{M} = \text{Li}, \text{Rb}, \text{Cs}$) were also previously studied as salts containing crown ethers as additional complexing agents. These are compounds in which the lithium salt is an ion-separated complex and the rubidium and cesium derivatives are monomeric chelate ring compounds. The crown ether complexation of the alkali metal cation prevents intermolecular association and affords the formation of discrete molecular complexes.⁸ The closely related tetraarylimidodiphosphates of rubidium and cesium, $\text{M}[(\text{ArO})_2\text{P}(\text{O})\text{NP}(\text{O})(\text{OAr})_2]$ ($\text{M} = \text{Rb}, \text{Cs}$; $\text{Ar} = \text{Ph}, \text{C}_6\text{H}_3\text{Me}_2\text{-3,4}$) are supramolecularly associated in the solid state.^{9,10}

Equally useful as a very versatile complexing agent is the sulfur analog tetraphenyldithioimidodiphosphinic acid, $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Ph}_2$, and its anion.² According to Scheme 1, it can coordinate to metal ions in neutral (protonated) form as $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Ph}_2$ (Scheme 1(a)) or in the anionic (deprotonated) form as $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ under formation of mainly inorganic (carbon-free) chelate rings.^{3,4} The anion has been formulated in the literature as either (b), (c) or (d) (*cf.* Scheme 1). The crystal and molecular structure of the parent compound, molecular $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Ph}_2$, is well known,¹¹⁻¹³ but there are only a few crystal structure determinations of salts which contain the uncoordinated $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ anion. This is not simple, since the tendency of the $[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ anion to form six-membered inorganic (carbon free) $\text{MS}_2\text{P}_2\text{N}$ chelate rings is so strong that even with alkali metal cations such complexes are formed.¹⁴ Thus, the potassium salt $\text{K}^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ is a supramolecular polymer consisting of self-assembled rings in the solid state.¹⁵ The sodium compound $[\text{Na}(15\text{-crown-5})]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ and the rubidium and cesium compounds $[\text{M}(18\text{-crown-6})]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$

($\text{M} = \text{Rb}, \text{Cs}$) also contain $\text{MS}_2\text{P}_2\text{N}$ chelate rings.^{8,16} In the ion separated complexes $[(\text{NH}_2)\text{Ph}_2\text{PNPPPh}_2(\text{NH}_2)]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ ¹⁷ and $[\text{Pt}(\text{H}_2\text{NC}_6\text{H}_4\text{PPh}_2)_2]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ ¹⁸ there are N-H \cdots S-P hydrogen bonds between the cation and anion, and the $[\text{Ph}_3\text{Te}]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ salt contains Te \cdots S secondary bond interactions between the anion and cation.¹⁹ Only in the lithium complex $[\text{Li}(15\text{-crown-5})]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ ⁸ and in the potassium salt, $[\text{K}(18\text{-crown-6})]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$,²⁰ the cation and anion are completely separated, without metal-sulfur interactions. In all of these compounds the anion is bent, with P-N-P bond angles around 130°. The only exception is the linear anion observed in $[\text{Ph}_3\text{PNPPPh}_3]^+[\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]^-$ ion pair, in which the anion is also "naked".²¹

In this paper we report the structure determination of two salts of the oxo ligand, namely the tetraphenylimidodiphosphinates $\text{M}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ with $\text{M} = \text{Rb}$ (**1**) and Cs (**2**), which form chelate ring complex molecules self-assembled in the solid state into supramolecular chain structures. Moreover, the crystal structure of tetramethylammonium-tetraphenyldithioimidodiphosphinate, $[\text{NMe}_4][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ (**3**) has been determined through X-ray diffraction. This compound was selected to contain a "naked" anion, not involved in any cation-anion interactions in the solid state thus enabling the determination of geometrical parameters of the anion free of any interference.

EXPERIMENTAL

The starting materials $\text{Ph}_2\text{P}(\text{E})\text{NHP}(\text{E})\text{Ph}_2$ ($\text{E} = \text{O}, \text{S}$) were prepared according to established literature procedures. Rb, Cs metals and $[\text{NMe}_4]\text{OH}$ were obtained from commercial sources and used as received. The salts $\text{M}[\text{Ph}_2\text{P}(\text{O})\text{NP}(\text{O})\text{Ph}_2]$ ($\text{M} = \text{Rb}$ (**1**), Cs (**2**)) were prepared by dissolving 2 equiv. of the alkali metals (Rb, Cs) in ethanol under nitrogen and addition of 1 equiv. of $\text{Ph}_2\text{P}(\text{O})\text{NHP}(\text{O})\text{Ph}_2$ dissolved in ethanol, followed by slow evaporation of the resulting clear solution Tetramethylammonium-tetraphenyldithioimidodiphosphinate, $[\text{NMe}_4][\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{Ph}_2]$ (**3**) was prepared by adding equivalent amounts of tetramethylammonium hydroxide to tetraphenyldithioimidodiphosphinic acid, $\text{Ph}_2\text{P}(\text{S})\text{NHP}(\text{S})\text{Ph}_2$, in ethanol solution followed by slow evaporation.

RESULTS AND DISCUSSION

Figure 1 shows the asymmetric units of the compounds **1** and **2**. Both compounds crystallize in

the monoclinic space group $P2_1/n$. Relevant crystallographic information on the two compounds is listed in Table 1. From Table 1 it can be seen that in line with the similarities in the molecular structures which are evident from Figure 1 the unit cell dimensions are also quite similar. To visualize the similarity of the two crystal structures an overlay of the two molecules has been calculated as shown in Figure 2. The striking similarity between **1** and **2** can be traced back to the rigidity of the ligand. In Table 2, selected bond length of the compounds **1** and **2** are given. First, it can be seen that the P1-O1 bond (1.498(2) Å) and the P2-O2 bond (1.500(2) Å) as well as the phosphorus-nitrogen bonds (P1-N: 1.597(2) Å, P2-N: 1.595(2) Å) within the anion in complex **1** are equal with respect to their standard deviations. In addition, the bond lengths and angles of the ligand of compound **1** match perfectly the respective values of the ligand of compound **2**. In the related crown-ether-containing structures reported by Cea-

Olivares et al.⁸ the bond lengths in the imidodiphosphinate ligand are also equal to the bond lengths reported in this study. The major differences occur in the P1-N-P2 angle. Compared to the value of 129.5(7)° for the Rb compound and 132.6(5)° for the Cs compound (*i.e.* the crown-ether complexes reported in ref. 8) the P-N-P angle is compressed in compound **1** (122.92(15)°) and **2** (123.58(13)°). This may be the consequence of the additional coordination of the bulky crown-ether ligand in the compounds reported by Cea-Olivares et al.⁸ The differences between the two compounds lie as expected in the bond distances of the oxygen atoms to the alkali metal cations. For compound **1** these are calculated to 2.932(2) Å for the Rb1-O1 bond and to 2.971(2) Å for the Rb1-O2 bond. Similarly, the bond lengths in compound **2** are calculated to 3.118(2) Å for the Cs1-O1 bond and 3.088(2) Å for the Cs1-O2 bond. This difference is obviously due to the increased ionic radius of the Cs cation.

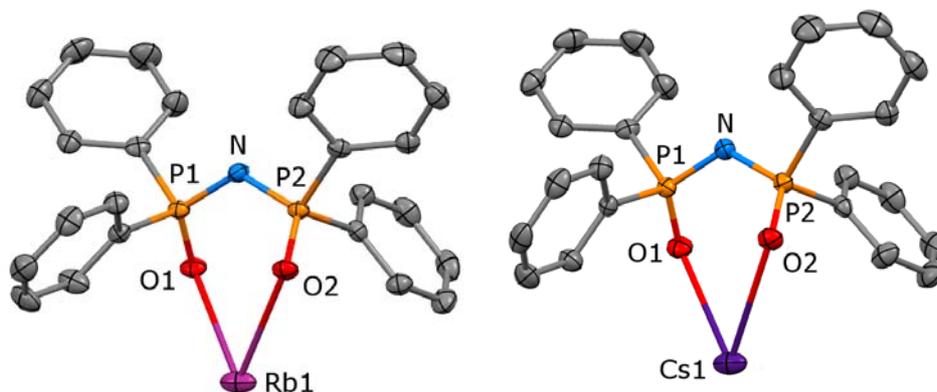


Fig. 1 – Representation of the asymmetric units of compounds **1** (left) and **2** (right). Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms are omitted for clarity.

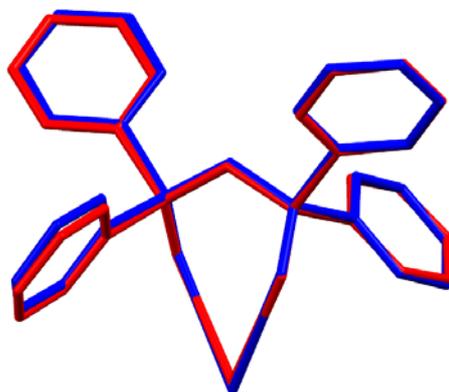


Fig. 2 – Structure overlay of the compounds **1** (red) and **2** (blue).

Table 1

Crystallographic information for compounds **1** and **2**

Compound	1	2
Empirical formula	C ₂₄ H ₂₀ NO ₂ P ₂ Rb	C ₂₄ H ₂₀ CsNO ₂ P ₂
CCDC identifier	1831161	1831160
Formula weight	501.82	549.26
Temperature [K]	173(2)	173(2)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
Unit cell dimensions [Å / °]	a = 13.0008(2) b = 7.9238(2) c = 22.1910(4) β = 105.4470(10)	a = 13.0998(14) b = 8.0652(10) c = 22.080(2) β = 106.393(8)
Absorption coefficient [mm ⁻¹]	2.413	1.818
Crystal size [mm]	0.500 x 0.250 x 0.060	0.550 x 0.500 x 0.150
Theta range for data collection [°]	1.650 to 25.350	3.001 to 24.997
Reflections collected	11661	4937
Independent reflections	4046 [R(int) = 0.0411]	3942 [R(int) = 0.0233]
Completeness to theta = 24.997°	99.90%	99.70%
Absorption correction	empirical	empirical
Max. and min. transmission	1.000 and 0.816	1.000 and 0.596
Data / restraints / parameters	4046 / 0 / 271	3942 / 0 / 271
Goodness-of-fit on F ²	1.059	1.019
R indices (all data)	R ₁ = 0.0597, wR ₂ = 0.0816	R ₁ = 0.0307, wR ₂ = 0.0594
Largest diff. peak and hole [eÅ ⁻³]	0.413 and -0.359	0.436 and -1.034

Table 2

Selected bond lengths [Å] and angles [°] for the compounds **1** and **2**

Compound 1				Compound 2			
P1	O1		1.503(2)	P1	O1		1.498(2)
P2	O2		1.503(2)	P2	O2		1.500(2)
P1	N		1.598(3)	P1	N		1.597(2)
P2	N		1.598(2)	P2	N		1.595(2)
Rb1	O1		2.932(2)	Cs1	O1		3.118(2)
Rb1	O2		2.971(2)	Cs1	O2		3.088(2)
P2	N	P1	122.92(15)	P2	N	P1	123.58(13)
O1	P1	N	119.04(13)	O1	P1	N	119.46(10)
O2	P2	N	119.33(13)	O2	P2	N	119.45(10)
P2	O2	Rb1	113.48(11)	P2	O2	Cs1	116.11(9)
P1	O1	Rb1	114.22(10)	P1	O1	Cs1	116.66(9)

Considering the packing of the crystal structures, a 1D-coordination polymer can be found. These strands can be imagined as M₂O₂ four

membered rings which are connected at one corner by an M atom and additionally bridged by an imidodiphosphate ligand (*cf.* Figure 3).

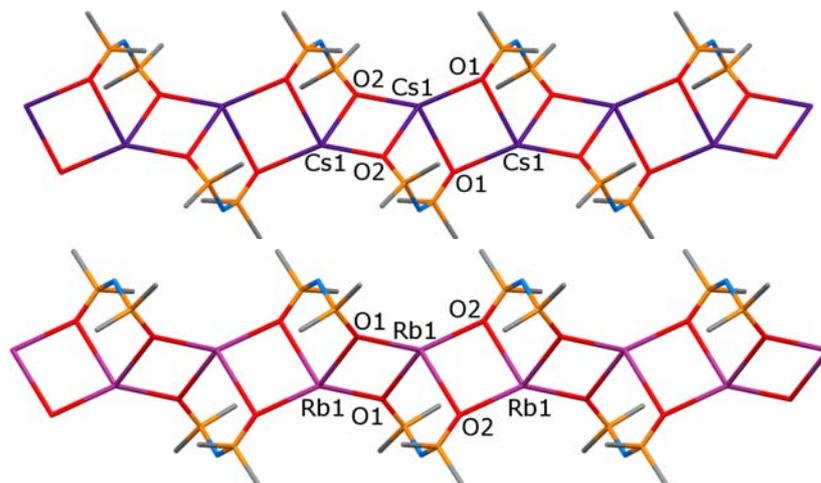


Fig. 3 – Section of the 1D-coordination polymer formed by compound **1** (top) and compound **2** (bottom).

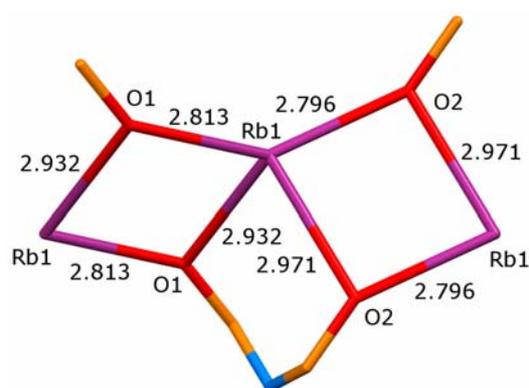


Fig. 4 – Detail of the 1D-coordination polymer for compound **1** consisting of two Rb_2O_2 four membered rings. Bond length are given in units of Å.

Table 3

Bond lengths and angles within the Cs_2O_2 four membered rings in compound **2**

Atom 1	Atom 2	Atom 2	d [Å] / δ [°]
Cs1	O1		3.118
Cs1	O1		2.94
Cs1	O2		3.088
Cs1	O2		2.952
O1	Cs1	O1	87.02
Cs1	O1	Cs1	92.98
O2	Cs1	O2	88.62
Cs1	O2	Cs1	91.38

In Figure 4, a detail of the coordination polymer of compound **1** is displayed. The Figure shows that the polymeric chain consists of two different Rb_2O_2 four-membered rings. For both of the rings a shorter and a longer Rb-O distance can be found. The rings are parallelograms. The corresponding angles are O2-Rb1-O2 $85.47(6)^\circ$, Rb1-O2-Rb1 $94.53(6)^\circ$, O1-Rb1-O1 $86.17(6)^\circ$, Rb1-O1-Rb1 $93.83(6)^\circ$. The same applies for compound **2**. The

corresponding bond lengths and angles can be taken from Table 3. For atom labeling refer to Figure 3. The formation of edge- or corner-linked four-membered rings is a commonly observed phenomenon in s-block metal chemistry.²²⁻²⁴

The structure of **3** has also been determined by single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit contains a separated ion pair of a

tetramethylammonium-cation and a tetraphenyldithioimidodiphosphinate-anion (*cf.* Figure 5).

Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N1-P1 1.601(2), N1-P2 1.592(2), P1-S1 1.973(1), P2-S2 1.977(1), P1-N1-P2 133.11(11), N1-P1-S1 120.07(6), N1-P2-S2 120.87(6).

Relevant crystallographic information for compound **3** is summarized in Table 4. The anion and cation can be regarded as independent of each other because no interaction that can be classified as classical short contact (sum of van-der-Waals radii divided by two) are present. This makes the free anionic ligand molecule a perfect candidate to study it without the influence of a coordinated cation.

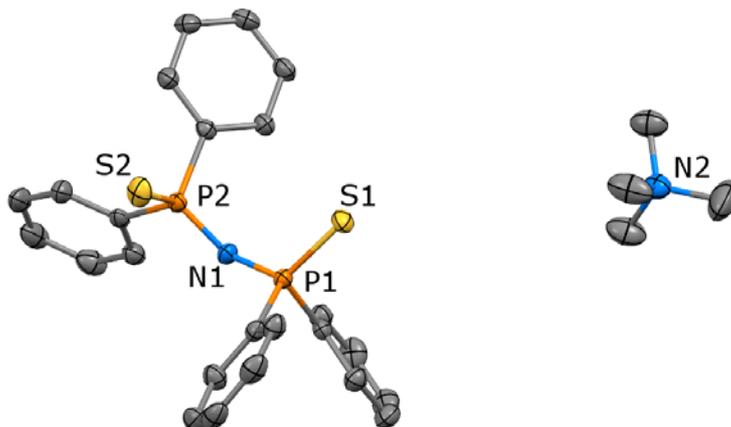


Fig. 5 – The asymmetric unit of compound **3**. Thermal ellipsoids are displayed at the 50% probability level.

Table 4

Crystallographic information for compound **3**

Empirical formula	C₂₈H₃₂N₂P₂S₂
CCDC identifier	1831159
Formula weight	522.61
Temperature	173(2) K
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Unit cell dimensions	a = 9.19880(10) Å
	b = 20.9811(3) Å
	c = 14.1817(2) Å
	β = 92.0320(10)°
Absorption coefficient	0.331 mm ⁻¹
Crystal size	0.400 x 0.400 x 0.040 mm
Theta range for data collection	1.734 to 28.303°
Reflections collected	18305
Independent reflections	6723 [R(int) = 0.0390]
Completeness to theta = 25.242°	100.00%
Absorption correction	Empirical
Max. and min. transmission	1.000 and 0.814
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6723 / 477 / 311
Goodness-of-fit on F²	1.018
R indices (all data)	R ₁ = 0.0700, wR ₂ = 0.1047
Largest diff. peak and hole	0.440 and -0.353 eÅ ⁻³

Within the parent compound tetraphenyldithioimidodiphosphinic acid, the bonding situation is best described by the distribution of single and double bonds as shown in Scheme 1a. The bond length of the P-N bonds has been determined to 1.652(7) Å and 1.700(2) Å. The corresponding P=S bond lengths are 1.915(3) Å and 1.927(3) Å.¹³ In compound **3** however, the bond length of the P-N bonds is significantly shortened (P1-N1 1.601(2) Å and P2-N2 1.592(2) Å) while the P-S bonds are elongated (P1-S1 1.973(1) Å and P2-S2 1.973(1) Å). This clearly supports the delocalized bonding situation shown in Scheme 1b. The bond lengths found within this structure are also in close agreement with the previously published structure of K(18-crown-6)-tetraphenyldithioimidodiphosphinate.²⁰

CONCLUSIONS

To summarize the work reported here, three synthetically useful tetraphenyldichalcogenoimidodiphosphinate salts have been structurally characterized by single-crystal X-ray diffraction. The tetraphenyldiphosphinates $M[Ph_2P(O)NP(O)Ph_2]$ with $M = Rb$ (**1**) and Cs (**2**) form supramolecular 1D-chain structures in the solid state. In contrast, the crystal structure determination of tetramethylammonium-tetraphenyldithioimidodiphosphinate, $[NMe_4][Ph_2P(S)NP(S)Ph_2]$ (**3**) revealed the presence of uncoordinated $[Ph_2P(S)NP(S)Ph_2]^-$ anions which are not involved in any cation-anion interactions in the solid state.

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