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FULL PAPER

1,1,1,2,2-Pentaiododiphosphanium cations, $P_2I_5^+EI_4^-$ (E = Al, Ga or In): synthesis and characterisation by ^{31}P MAS NMR, IR and Raman spectroscopy

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The compound $P_2I_5^+AlI_4^-$ and the novel compounds $P_2I_5^+GaI_4^-$ and $P_2I_5^+InI_4^-$ have been prepared in two different ways either from PI_3 and EI_3 or from P_2I_4 and I_2/EI_3 (E = Al, Ga or In). The products have been characterised by solid-state ^{31}P MAS NMR, Raman and IR spectroscopy. The solid-state ^{31}P MAS NMR spectra are compared with NMR studies of related PI_4^+ salts and alkylphosphorus tetraiodides. Vibrational assignments for the normal modes for the solid-state species $P_2I_5^+EI_4^-$ (E = Al, Ga or In) have been made on the basis of their Raman and IR spectra. These results are in excellent agreement with density functional calculations for the $P_2I_5^+$ cation and are consistent with the ionic formulation $P_2I_5^+EI_4^-$ (E = Al, Ga or In).

Introduction

As early as in 1964 Baudler and Wetter[1] obtained a deeply coloured co-ordination compound (2 $PI_3 \cdot AlI_3$) from the reaction of PI_3 and AlI_3 in CS_2. They assumed a monomeric structure having a symmetric trigonal bipyramidal arrangement (symmetry D_{3h}) with sp^3d bond hybridisation and a co-ordination number of 5 at the aluminium atom, analogous to $(Me_3N)_2AlH_3$.[2] The 2 : 1 adduct of PI_3 and AlI_3 was structurally characterised by X-ray crystallography and identified as $P_2I_5^+AlI_4^-$ by Pohl[3] in 1983. Pohl suggested as reaction mechanism the intermediate formation of "PI_2^+" *via* I^- abstraction by the Lewis acid AlI_3 yielding AlI_4^-. In the next step the "PI_2^+" reacts with a second molecule of PI_3 forming the $P_2I_5^+$ cation *via* P–P linkage.[3] Similar to $PI_4^+AlI_4^-$,[4] the cation and anion are connected by bridging I · · · I interactions. The P–P distance in the $P_2I_5^+$ cation (2.218 Å) is very similar to that in P_2I_4 (2.21 Å).[5] Like the related alkylphosphorus tetraiodides RPI_4 (R = Me,[6] *i*-Pr,[7] *t*-Bu[7] or Me_3SiCH_2[7]) and the tetraiodophosphonium cations in $PI_4^+AlI_4^-$ [4] and $PI_4^+GaI_4^-$,[8] the $P_2I_5^+$ cation exists only in the solid state.

Recently, we published a combined theoretical and experimental study on the PI_4^+ cation.[8] It has an extremely large negative ^{31}P chemical shift which quantum chemical calculations and solid-state NMR spectroscopy showed is due to spin–orbit coupling. This investigation naturally led to further work on binary phosphorus–iodine cations. A recent MAS ^{31}P NMR study on related cationic di- and tri-tertiary phosphines in the solid state and in solution can be found in the literature.[9a,b] In this paper we report on the preparation and properties of the structurally and chemically interesting $P_2I_5^+$ cation.

Results and discussion

All the compounds reported here were prepared from the reaction of 2 equivalents PI_3 with 1 equivalent of EI_3 (E = Al **1a**, Ga **2a** or In **3a**), eqn. (1), or from the reaction of P_2I_4 with I_2

$$2\,PI_3 + EI_3 \xrightarrow{CS_2} P_2I_5^+EI_4^- \qquad (1)$$

and EI_3 E = Al **1b**, Ga **2b** or In **3b**) in a 1 : 1 : 1 molar ratio, eqn. (2), in CS_2 under nitrogen.

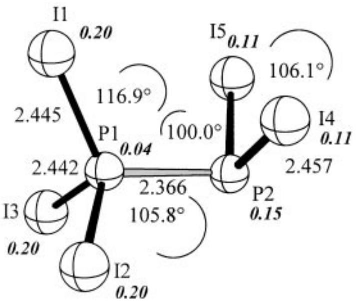

Fig. 1 Fully optimised geometry of $P_2I_5^+$ [bond lengths in Å, partial charges (italics) in e].

$$P_2I_4 + I_2 + EI_3 \xrightarrow{CS_2} P_2I_5^+EI_4^- \qquad (2)$$

The $P_2I_5^+$ cation exists only in the solid state. Dissolving $P_2I_5^+EI_4^-$ (E = Al **1**, Ga **2** or In **3**) in CS_2 gives a solution that contains essentially only PI_3 ($\delta^{31}P$ +178 in CS_2[9c]) and the corresponding triodides EI_3. Evaporation of the solvent allows recovery of the $P_2I_5^+$ compound.

Attempts to prepare $P_2I_5^+$ compounds, containing an iodine free anion, such as AsF_6^- or SbF_6^-, by treating P_2I_4 with $I_3^+AsF_6^-$ or $I_3^+SbF_6^-$ in different solvents, were unsuccessful. The reactions were carried out analogously to the preparation of $PI_4^+AsF_6^-$ [10] and $PI_4^+SbF_6^-$.[8] However, these reactions led only to decomposition into the thermodynamically more stable products PF_3, I_2, AsI_3 and SbI_3, respectively, which were identified by Raman spectroscopy. We conclude that the $P_2I_5^+$ cation can only be stabilised with anions like EI_4^- (E = Al, Ga or In).

Fig. 1 shows the B3LYP-optimised minimum structure of the free $P_2I_5^+$ cation. In addition, the geometry and frequencies of the PI_4^+ cation were calculated for comparison [B3LYP: d(P–I) = 2.431 Å, ν_1 (A_1, 0.0) 165, ν_2 (E, 0.0) 62, ν_3 (T_2, 67) 385, ν_4 (T_2, 0.0) 96 cm^{-1}]. Both cations were shown to possess stable minima at the B3LYP level (no imaginary frequencies). As expected for steric reasons, $P_2I_5^+$ displays a staggered configuration with an I1–P1–P2–I5 dihedral angle of 54.3°, and three essentially equal P–I distances for the PI_3 part and two effectively equal, but longer, P–I separations for the PI_2 unit. The

Table 1 Raman and IR wavenumbers (cm^{-1}) for $P_2I_5^+EI_4^-$ (E = Al **1a**, Ga **2a** or In **3a**)

$P_2I_5^+AlI_4^-$ **1a**		$P_2I_5^+GaI_4^-$ **2a**		$P_2I_5^+InI_4^-$ **3a**		Calculation[a]	Assignment
Raman	IR	Raman	IR	Raman	IR		
390 (1)	393m	389 (1)	392m	389 (1)	389m	394 (A′, 50.0)	ω_1
384 (2)	382m	382 (2)	380m	381 (1)	380s	382 (A″, 37.9)	ω_2
348 (0.5)	346 (sh)	347 (0.5)	343m	346 (0.5)	347m	354 (A′, 9.4)	ω_3
						350 (A″, 61.6)	ω_4
324 (1)	317 (br)	321 (2)	314 (br)	323 (2)	314 (br)	325 (A′, 24.9)	ω_5
			231s				ν_3 (EI_4^-)
			224s				ν_3 (EI_4^-)
210 (10)	209m	209 (10)	209vs	210 (10)	211vs	209 (A′, 25.1)	ω_6
147 (2)		143 (3)		138 (4)			ν_1 (EI_4^-)
129 (6)		129 (8)		127 (9)		128 (A′, 0.0)	ω_7
97 (4)		97 (5)		98 (5)		97 (A″, 0.6)	ω_8
89 (2)		88 (2)		85 (2)		94 (A″, 0.0)	ω_9
						80 (A′, 0.1)	ω_{10}
						65 (A″, 0.0)	ω_{11}
						58 (A′, 0.2)	ω_{12}
						42 (A″, 0.1)	ω_{13}
						39 (A′, 0.1)	ω_{14}
						16 (A″, 0.0)	ω_{15}

[a] See Fig. 4. [b] In parentheses: symmetry, IR intensity [km mol^{-1}].

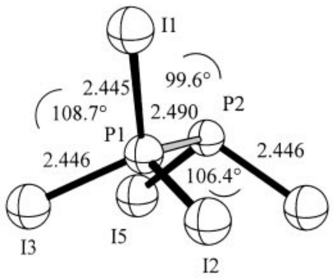

Fig. 2 Transition state for the internal rotation [bond lengths in Å].

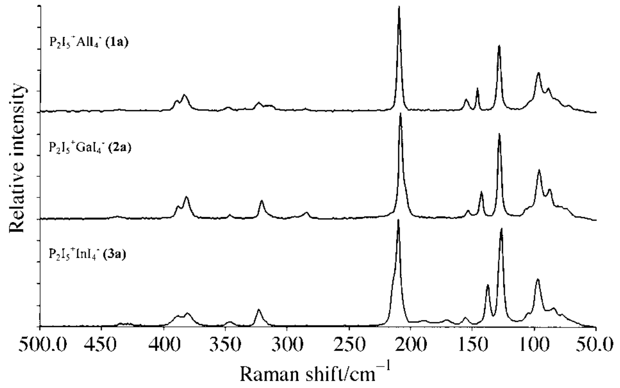

Fig. 3 Raman spectra of $P_2I_5^+EI_4^-$ (E = Al **1a**, Ga **2a** or In **3a**).

experimentally not observed eclipsed configuration (Fig. 2) represents a transition state (number of imaginary frequencies=1, −i14 cm^{-1}) describing the internal rotation about the P–P axis. The rotation barrier was calculated to be of the order E^a (B3LYP, 298 K) = 2.4 kcal mol^{-1}. The calculated NBO (natural bond orbital) partial charges (Fig. 1) reveal fairly covalent P–I bonds with the positive charge almost evenly distributed amongst all atoms.

Vibrational spectroscopy

Table 1 summarises the computed and experimentally observed vibrational frequencies of the $P_2I_5^+$ compounds synthesised (**1a**, **2a**, **3a**) in this study. Fig. 3 shows the Raman spectra of these compounds. Raman and IR spectra of all three sets of compounds (**1a**, **1b**, **2a**, **2b**, **3a**, **3b**) are very similar regardless of the method of synthesis. The measured vibrational spectra agree excellently with our theoretical calculation (B3LYP) for the isolated $P_2I_5^+$ cation. The most intense peak, observed at *ca.* 210 cm^{-1}, can be assigned to a mixture of P1–P2 stretching (ω_6, Fig. 4) and P1–I1 stretching. The P1–I1 stretching mode (ω_1) at *ca.* 390 cm^{-1} and the asymmetric P1–I2,3 stretching mode (ω_2) at *ca.* 382 cm^{-1} can be observed in all IR and Raman spectra. Similar vibrational frequencies are reported for the asymmetric P–I stretching mode, ν_3 (T_2), in $PI_4^+AlI_4^-$ [11] and $PI_4^+GaI_4^-$ [8] at *ca.* 380 cm^{-1}. The signals at *ca.* 346 cm^{-1} can be described as a mixture of the P1–P2 stretching vibration (ω_3) and the asymmetric P2–I4,5 stretching vibration (ω_4; the resolution was not sufficient enough). The predicted value for the symmetric P–I stretching vibration of the P2–I4,5 unit (ω_5), 325 cm^{-1} (Fig. 4), is most closely associated with the experimental values at *ca.* 323 (Raman) and *ca.* 314 cm^{-1} (IR), respectively. Similar P–I stretching frequencies are reported for the vibrational spectra of P_2I_4 [12] (IR: 330 cm^{-1}), PI_3 [12] (IR: 310 cm^{-1}. Raman: 325 cm^{-1}) and the adduct $PI_3{\cdot}BI_3$ [13] (IR: 304 and 329 cm^{-1}). ω_7, ω_8 and ω_9 represent P–I deformation modes (Fig. 4) with ω_7 (*ca.* 128 cm^{-1}) being one of the most intensive peak in all Raman spectra. The presence of the anions EI_4^- (E = Al **1**, Ga **2** or In **3**) is confirmed by the symmetric stretching mode, ν_1 (A_1), at 147 (**1**),

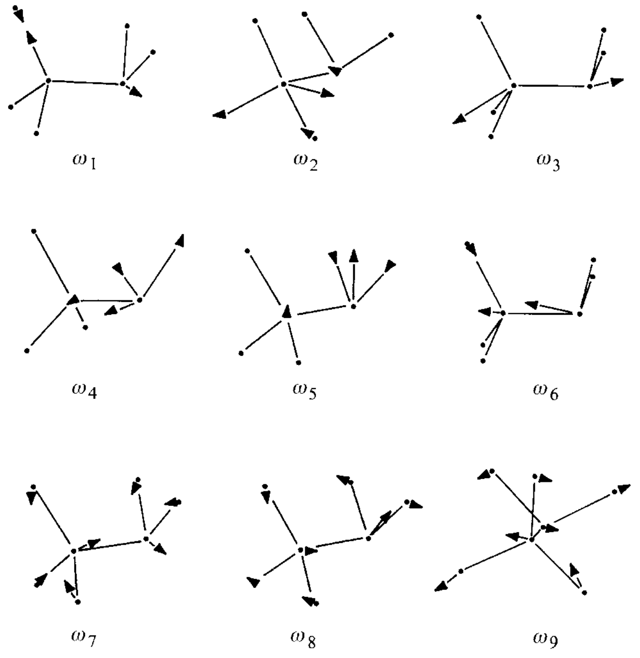

Fig. 4 Pictorial description of the calculated normal modes of $P_2I_5^+$.

Table 2 The ^{31}P NMR isotropic chemical shift (δ), chemical shift anisotropy ($\Delta\delta_{CSA}$), asymmetry parameter (η_{CSA}) and relative peak intensity (I) of the compounds $P_2I_5^+EI_4^-$ and PI_3

$P_2I_5^+EI_4^-$	δ (±0.5 ppm)	$\Delta\delta_{CSA}$[a] (±5 ppm)	η_{CSA}[b] (±0.2)	I (%) (±3%)
1, E = Al				
P1 (I_3P)	−142	−216	0	48
P2 (I_2P)	114	−124	0.4	52
2, E = Ga				
P1 (I_3P)	−142	−217	0	49
P2 (I_2P)	112	−117	0.4	51
3, E = In				
P1 (I_3P)	−139	−225	0	48
P2 (I_2P)	112	−116	0.4	52
PI_3	237	−111	0.3	—

[a] $\Delta\delta_{CSA} = \delta_{33} - \delta_{iso}$. [b] $\eta_{CSA} = |\delta_{22} - \delta_{11}|/|\delta_{33} - \delta_{iso}|$.

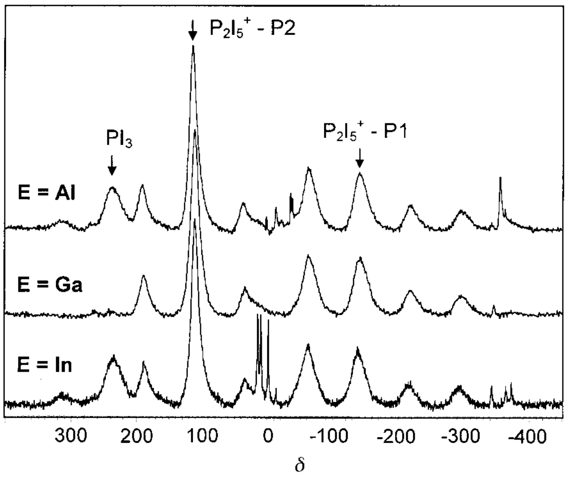

Fig. 5 ^{31}P MAS NMR spectra (ν_o = 162.96 MHz, ν_{rot} = 12.5 kHz) of $P_2I_5^+EI_4^-$ with E = Al **1**, Ga **2** or In **3**. The central lines are indicated by arrows; all the other broad peaks are spinning side bands. The sharp lines originate from impurities.

143 (**2**) and 138 cm^{-1} (**3**). They are consistent with literature values [ν_1 (AlI_4^-) 146;[14] ν_1 (GaI_4^-) 145;[15] ν_1 (InI_4^-) 138 cm^{-1} [15]]. The IR spectra of **2** show two strong peaks at 231 and 224 cm^{-1} that can be assigned to the asymmetric stretching mode, ν_3 (T_2), of GaI_4^- [ν_3 (GaI_4^-) 222 cm^{-1} [15]].

Solid-state NMR spectroscopy

Fig. 5 shows the ^{31}P MAS NMR spectra of the three compounds $P_2I_5^+EI_4^-$ with E = Al **1**, Ga **2**, or E = In **3**. Table 2 summarises the isotropic chemical shifts (δ), chemical shift anisotropies ($\Delta\delta_{CSA}$), asymmetry parameters (η_{CSA}), and relative signal intensities obtained from spectra simulations. As an example, the details of the simulation for $P_2I_5^+AlI_4^-$ **1** are presented in Fig. 6. Besides the resonance of a PI_3 impurity (component 3, see below, δ^{31}P +160 to +185 in solution,[9c] +237 in the solid state[16]), two partially overlapping side band patterns can be identified (components 1 and 2) which correspond to the two P atoms in the $P_2I_5^+$ cation. The different intensity distributions of the spinning side bands indicate different chemical shift anisotropies of the two resonances, but the total intensities are in the expected ratio of 1 : 1 (Table 2). The spectrum of the PI_3 impurity could be unequivocally identified by the ^{31}P MAS NMR spectrum measured at a pure solid PI_3 sample (see Table 2). The weak narrow lines in the ranges of δ 0 to 40 and −340 to −360 are due to very small amounts of other impurities. It should be noted that no indications of scalar ^1J(PP) couplings of the two inequivalent P atoms of the $P_2I_5^+$ cation could be observed. Obviously, these splittings cannot be resolved due to the large linewidths (half-width about 3500–4000 Hz for P1 and 2000–2500 Hz for P2).

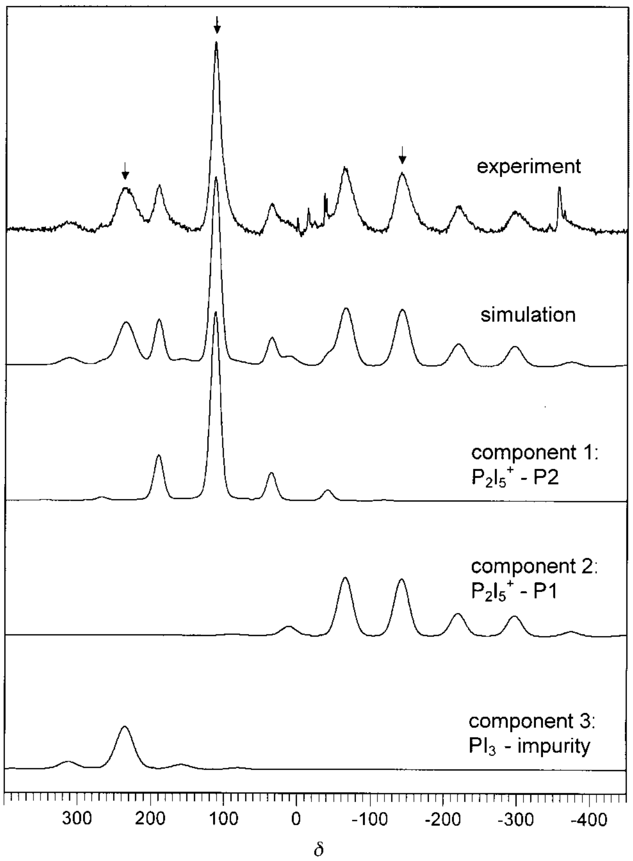

Fig. 6 Experimental and simulated ^{31}P MAS NMR spectra of $P_2I_5^+AlI_4^-$. The central lines of the spinning side band patterns are indicated by arrows in the experimental spectrum. The simulated spectrum is the sum of the three component spectra.

The spectra of the corresponding $P_2I_5^+GaI_4^-$ **2** and $P_2I_5^+InI_4^-$ **3** compounds are very similar to that of $P_2I_5^+AlI_4^-$ **1** (see Fig. 5) and were simulated in the same way. No impurities were found in the ^{31}P NMR spectrum of **2**. The two central peaks of the $P_2I_5^+$ cation in each of the three compounds were located by variation of the spinning frequency and are consistently observed at δ *ca.* −140 (P1) and +112 (P2), respectively (Table 2). The resonance at δ +112 (P2) with a non-axial anisotropy tensor (η_{CSA} = 0.4) can be assigned to a three-co-ordinated phosphorus atom, *i.e.* to the I_2P fragment of the $P_2I_5^+$ cation. The shift is very close to that of P_2I_4 (δ +106 in solution[17] and +127 in the solid state[18]). The ^{31}P chemical shift δ *ca.* −140 (P1) is attributed to the four-co-ordinated phosphorus atom in the I_3P fragment of the $P_2I_5^+$ cation. In accord with the C_{3v} symmetry of this fragment,[3] this resonance shows an axially symmetric anisotropy tensor (η_{CSA} = 0). The strong low-frequency (high-field) ^{31}P shift of δ *ca.* −267 from the P_2I_4 resonance can be interpreted as a result of spin–orbit interactions due to the presence of three iodine substituents at the four-co-ordinated phosphorus atom in the I_3P fragment. Using density functional calculations, Kaupp *et al.*[8] have recently shown that the extremely large low-frequency shift observed for the related compounds $PI_4^+AlI_4^-$ (δ −304), $PI_4^+GaI_4^-$ (δ −295), $PI_4^+AsF_6^-$ (δ −519), and $PI_4^+SbF_6^-$ (δ −517)[8] is entirely due to spin–orbit contributions from the four heavy iodine substituents, transmitted to the phosphorus nucleus by a very effective Fermi-contact mechanism. Equally, for *t*-$BuPI_4$ (δ −49.2) the ^{31}P NMR resonance in the solid state is shifted by −215 ppm to high field from the adduct *t*-$BuPI_2$ (δ +165).[7]

Owing to the close similarity of the isotropic chemical shifts and anisotropies of the $P_2I_5^+$ cation of all three $P_2I_5^+EI_4^-$ compounds, it can be concluded that the structures of $P_2I_5^+GaI_4^-$ **2** and $P_2I_5^+InI_4^-$ **3** are very similar to the known structure of $P_2I_5^+AlI_4^-$ with weak I···I interactions between cation and anion.[3] However, no crystals suitable for X-ray diffraction analyses could be grown up to now.

Conclusion

The results indicate that compounds such as $P_2I_5^+AlI_4^-$, $P_2I_5^+GaI_4^-$, $P_2I_5^+InI_4^-$, including the 1,1,1,2,2-pentaiododiphosphanium cation, can be prepared in two different ways. The solid-state ^{31}P MAS NMR results show two different peaks, which can be assigned to a PI_2 and a PI_3^+ fragment, respectively. Our calculations agree excellently with the experimental wavenumbers of Raman and IR spectra. Solid-state ^{31}P MAS NMR and vibrational results suggest that these compounds exist as ionic species in which the $P_2I_5^+$ cations possess only weak I···I interactions to the anions. It can be considered that the novel compounds $P_2I_5^+GaI_4^-$ and $P_2I_5^+InI_4^-$ have similar structures to that found in $P_2I_5^+AlI_4^-$.[3]

Experimental

General

All experiments were carried out in a dry-box under dry nitrogen. The compounds PI_3, P_2I_4, AlI_3, GaI_3, InI_3 (Aldrich) and I_2 (Merck) were used as received; CS_2 was refluxed with P_4O_{10} and distilled before use. The ^{31}P NMR spectra were measured at 161.96 MHz with a Bruker MSL-400 NMR spectrometer under magic angle spinning (MAS) conditions. A standard double-bearing MAS probe for 4 mm rotors was used with spinning frequencies up to 12.5 kHz. Single pulse acquisition with 1 µs pulse width (corresponding to a 25° flip angle) and 5 s pulse repetition was applied. The samples were filled in 4 mm zirconia rotors under a nitrogen atmosphere in a glove-box. The spectra were referenced to 85% aqueous phosphoric acid. Spectral simulations were carried out with the PC program WINFIT of the Bruker WINNMR software package. Raman spectra were obtained on powdered solid samples contained in glass capillary tubes with a Perkin-Elmer 2000 NIR spectrometer in the range 500–50 cm^{-1}, IR spectra on Nujol mulls between CsI plates in the range 500–200 cm^{-1} on a Nicolet 520 FT IR spectrometer. For the determination of decomposition points, samples were heated in sealed glass capillaries in a Büchi B450 instrument.

Preparations

The compounds $P_2I_5^+EI_4^-$ (E = Al, Ga or In) were prepared by addition of PI_3 in CS_2 to CS_2 solutions of EI_3 (E = Al, Ga or In) (**1a**, **2a**, **3a**) or by addition of P_2I_4 and I_2 in CS_2 to CS_2 solutions of EI_3 (E = Al, Ga or In) (**1b**, **2b**, **3b**) by stirring at room temperature. After 24 h the solvent was removed under dynamic vacuum, leaving the solid compound.

$P_2I_5^+AlI_4^-$ 1a. Starting materials: 0.84 g of PI_3 (2.00 mmol), 0.41 g of AlI_3 (1.00 mmol). Yield: 1.13 g (92%) of dark red crystals, mp 90 °C (decomp.).

$P_2I_5^+AlI_4^-$ 1b. Starting materials: 0.57 g of P_2I_4 (1.00 mmol), 0.25 g of I_2 (1.00 mmol), 0.41 g of AlI_3 (1.00 mmol). Yield: 1.08 g (88%) of dark red crystals, mp 90 °C (decomp.).

$P_2I_5^+GaI_4^-$ 2a. Starting materials: 0.84 g of PI_3 (2.00 mmol), 0.45 g of GaI_3 (1.00 mmol). Yield: 1.10 g (86%) of red solid, mp 111 °C (decomp.).

$P_2I_5^+GaI_4^-$ 2b. Starting materials: 0.57 g of P_2I_4 (1.00 mmol), 0.25 g of I_2 (1.00 mmol), 0.45 g of GaI_3 (1.00 mmol). Yield: 1.10 g (86%) of red solid, mp 111 °C (decomp.).

$P_2I_5^+InI_4^-$ 3a. Starting materials: 0.84 g of PI_3 (2.00 mmol), 0.50 g of InI_3 (1.00 mmol). Yield: 1.28 g (99%) of dark red solid, mp 84 °C (decomp.).

$P_2I_5^+InI_4^-$ 3b. Starting materials: 0.57 g of P_2I_4 (1.00 mmol), 0.25 g of I_2 (1.00 mmol), 0.50 g of InI_3 (1.00 mmol). Yield: 1.28 g (99%) of dark red solid, mp 84 °C (decomp.).

Computational methods

The structure and vibrational data for PI_4^+ and $P_2I_5^+$ were calculated by using density functional theory with the program package GAUSSIAN 94.[19] For phosphorus a standard 6-31G(d,p) basis set was used and for I a quasi-relativistic pseudopotential (ECP46MWB)[20] and a (5s5p1d)/[3s3p1d]-DZ+P basis set.[21] The computations were carried out at the DFT level using the hybrid method B3LYP which includes a mixture of Hartree–Fock exchange with DFT exchange correlation. Becke's 3 parameter functional where the non-local correlation is provided by the LYP expression (Lee, Yang, Parr correlation functional) was used which is implemented in GAUSSIAN 94. For a concise definition of the B3-LYP functional see ref. 22.

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