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Ionic Isomerism. 2. Calculations of Thermodynamic Properties of Phosphorus(V) Chloride Isomers: $\Delta H_f^{\ominus}(PCl_4^+(g))$ and $\Delta H_f^{\ominus}(PCl_6^-(g))$

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Received January 20, 1981

Lattice energy calculations have been made for the following three ionic models of phosphorus(V) chloride: $PCl_4^+PCl_6^-$ ("normal", phase II), $2PCl_4^+{\cdot}PCl_6^-{\cdot}Cl^-$ ("metastable", phase III) and a postulated species, $PCl_4^+{\cdot}Cl^-$. These values lead to estimates of $\Delta H_f^{\ominus}(PCl_4^+(g)) = 462.4$ and $\Delta H_f^{\ominus}(PCl_6^-(g)) = -880.4$ kJ mol^{-1} from which chloride ion affinities of PCl_5 and PCl_4^+ can be derived. Further estimates predict (i) only borderline thermodynamic stability for alkali-metal hexachlorophosphates, $MPCl_6$ (M = K, Cs), and (ii) no apparent thermodynamic barrier to the formation of a $PCl_4^+Cl^-$ type structure. Thermochemical radii of 1.50 Å and 3.46 Å are estimated for PCl_4^+ and PCl_6^-, respectively.

Recently, interest has been revived[1-4] in solid-state modifications of phosphorus(V) chloride. Whalley et al. have reported the production of a metastable phase (phase III) by application of pressure to normal, tetragonal PCl_5 (phase II, $PCl_4^+PCl_6^-$); investigations of phase diagrams,[1] Raman spectra,[2] and solid-state ^{31}P NMR spectra[3] are reported. Raman spectra of phase III are identical with those of products obtained previously by sublimation[5-8] and chemical methods.[4,9] From measurements of the intensities of the ^{31}P resonances,[3] the phase III modification was formulated as $2PCl_4^+{\cdot}PCl_6^-{\cdot}Cl^-$, confirming quantitatively an earlier suggestion[9] of the presence of single halide ions in the lattice. The ionization $PCl_6^- \rightarrow PCl_4^+ + 2Cl^-$ was represented as the first known example of pressure-induced ionization in solids, a phenomenon well-known in liquids, e.g., in molten salts.[10] Work in these laboratories has shown that such solid-state ionic isomerism is not rare,[11,12] and that important consequences for inorganic chemistry are entailed, e.g., in the preparation and stability of complex halides. In this paper we report calculations of the lattice energies of phase II and phase III and discuss, inter alia, wider implications, including hexachlorophosphate salt stabilities.

Table I. Crystal Parameters for the Proposed Model for Phase III, $2PCl_4^+{\cdot}PCl_6^-{\cdot}Cl^-$ ($a = b = 9.22$ Å, $c = 22.32$ Å)[b]

		x	y	z
P (PCl_4^+ basal cell planes)	6e[a]	0.25	0.25	0.0
P (PCl_4^+ arising from dissociated PCl_6^-)	2a	0.25	0.75	0.5400
P (PCl_6^- ions)	2a	0.25	0.75	0.2067
	2a	0.25	0.75	0.8734
Cl (PCl_4^+ basal cell planes)	8f	0.3100	0.0840	0.0500
	8f	0.3100	0.0840	0.7167
	8f	0.3100	0.0840	0.3533
Cl (PCl_4^+ arising from dissociated PCl_6^-)	8f	0.6650	0.0460	0.4600
Cl (PCl_6^- ions, equatorial Cl)	8f	0.6650	0.0460	0.1267
	8f	0.6650	0.0460	0.7934
Cl (PCl_6^- ions, axial Cl)	2a	0.25	0.75	0.9667
	2a	0.25	0.75	0.1133
	2a	0.25	0.75	0.3000
	2a	0.25	0.75	0.7800
Cl (free Cl^- ions)	2a	0.25	0.75	0.4466
	2a	0.25	0.75	0.6333

[a] Symmetry coordinates: 2a, $\pm(^1/_4, ^3/_4, z)$; 6e, $\pm(^1/_4, ^1/_4, 0)$, $\pm(^1/_4, ^1/_4, ^1/_3)$, $\pm(^1/_4, ^1/_4, ^2/_3)$; 8f, $\pm(x, y, z)$, $\pm(^1/_2 - x, \bar{y}, z)$, $\pm(\bar{y}, ^1/_2 + x, z)$, $\pm(^1/_2 + y, \bar{x}, z)$. [b] This structure is a preliminary one, and further work is being undertaken to ascertain the accurate coordinates.

Calculations

The tetragonal cell of normal, phase II, PCl_5 has space group $P4/n$ with $a = 9.22$ Å and $c = 7.44$ Å and comprises PCl_4^+ units sandwiching nearly octahedral PCl_6^- units.[13-16] A more recent study of PCl_5 by Preiss[17] is substantially in agreement with the earlier work, except that the plane of the four equatorial Cl atoms in the PCl_6^- units is situated slightly above and below the plane of the phosphorus atoms, the centrosymmetric nature of the cell being preserved.

Schematic diagrams of the two structures are shown in Figure 1. No crystal structure is currently available for phase III ($2PCl_4^+{\cdot}PCl_6^-{\cdot}Cl^-$), and for the purposes of the present calculations, we have modeled the phase III modification as shown in Figure 2. To obtain this model structure we have assumed that (i) ionization takes place in selected PCl_6^- ions to generate PCl_4^+ and Cl^- ions, (ii) in order to achieve the necessary stoichiometry the unit cell is extended in the c direction, such that a and b remain at 9.22 Å while $c = 22.32$ Å, and (iii) the arrangement of ions (which is not a unique choice) is shown schematically in Figure 2. The proposed parameters defining the crystal structure are listed in Table I.

On the basis of the unit cells shown in Figures 1 and 2, the

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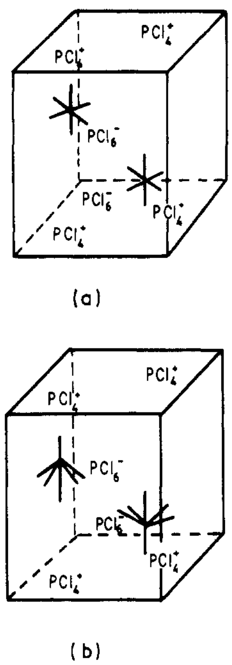

Figure 1.

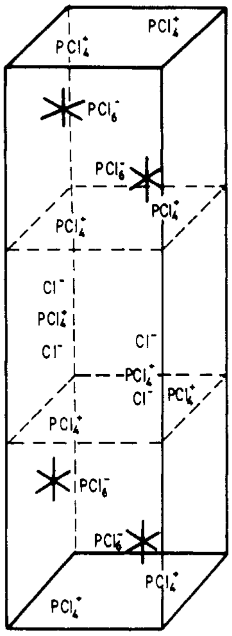

Figure 2.

lattice energies of phase II and phase III can be defined by the following processes:

$$\text{phase II (c)} \rightarrow 2\mathrm{PCl_4^+(g)} + 2\mathrm{PCl_6^-(g)}$$

$$\text{phase III (c)} \rightarrow 8\mathrm{PCl_4^+(g)} + 4\mathrm{PCl_6^-(g)} + 4\mathrm{Cl^-(g)}$$

the values calculated being dependent on the structures assumed for these phases. With use of the computational program LATEN[18] and the theory of direct minimization described and used in earlier papers,[19-22] results of calculations based on the three structures drawn in Figures 1 and 2 and also on a structure assuming that the PCl_5 crystal exists as $PCl_4^+Cl^-$ were made. For the latter calculation, we allow the PCl_6^- ions of the unit cells of Figure 1 to become PCl_4^+ ions and dissociated free axial Cl^- ions. For the calculation, a "basic" radius of 1.512 Å was assumed for free chloride ions;[19] corresponding charges and radii parameters for the PCl_4^+ ion, consistent with the minimum energy, requirement were obtained. A similar model for the PCl_4^+ ion was then retained in the calculations on phase II and phase III structures.

From the results of these calculations it is possible to (i) obtain estimates of the enthalpies of formation of the gaseous PCl_4^+ and PCl_6^- ions and (ii) predict the likely stabilities of some hexachlorophosphate salts.

Results

(1) Lattice Energies. Table II summarizes the total lattice potential energies (comprised of electrostatic, repulsive, and dispersive components) calculated for the following processes for the three types of structure considered:

$$\underset{(\mathrm{PCl_4^+Cl^-})}{\mathrm{PCl_5(c)}} \xrightarrow{U_\mathrm{I}} \mathrm{PCl_4^+(g)} + \mathrm{Cl^-(g)}$$

$$\underset{(^1/_2\mathrm{PCl_4^+}\cdot{}^1/_2\mathrm{PCl_6^-})}{\text{phase II(c)}} \xrightarrow{U_\mathrm{II}} {}^1/_2\mathrm{PCl_4^+(g)} + {}^1/_2\mathrm{PCl_6^-(g)}$$

$$\underset{(^2/_3\mathrm{PCl_4^+}\cdot{}^1/_3\mathrm{PCl_6^-}\cdot{}^1/_3\mathrm{Cl^-})}{\text{phase III(c)}} \xrightarrow{U_\mathrm{III}} {}^2/_3\mathrm{PCl_4^+(g)} + {}^1/_3\mathrm{PCl_6^-(g)} + {}^1/_3\mathrm{Cl^-(g)}$$

Minimization of the lattice energy in the calculation of U_I (for the Figure 1a structure) leads to a charge distribution q_P = 1.352 and q_Cl = −0.88, and this model for the ion (represented as four chlorine atoms) corresponds to a "basic" radius for chlorine of 1.286 Å. The corresponding calculation based on the Figure 1b structure gave an identical charge distribution on PCl_4^+ with a chlorine atom radius of 1.309 Å. For calculations on phases II and III, the above model for PCl_4^+ was adopted. Results are summarized in Table II.

(2) Derived Thermodynamic Data. The calculated lattice energies, together with the known enthalpy of transition of phase II → phase III, $\Delta H_{\mathrm{II}\rightarrow\mathrm{III}}$ (2.4 kJ mol^{-1}),[1] can now be analyzed on the basis of the cycle in Scheme I to yield various thermodynamic data. Hence, we have eq 1 and 2. Using the

$$\tfrac{1}{2}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_4^+(g)}) + \tfrac{1}{2}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_6^-(g)}) = U_\mathrm{II} + RT + \Delta H_\mathrm{f}^\ominus(\mathrm{PCl_5(c)}) \quad (1)$$

$$\tfrac{2}{3}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_4^+(g)}) + \tfrac{1}{3}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_6^-(g)}) + \tfrac{1}{3}\Delta H_\mathrm{f}^\ominus(\mathrm{Cl^-(g)}) = U_\mathrm{III} + \tfrac{5}{6}RT + \Delta H_{\mathrm{II}\rightarrow\mathrm{III}} + \Delta H_\mathrm{f}^\ominus(\mathrm{PCl_5(c)}) \quad (2)$$

calculated lattice energies U_II (based on the structure in Figure 1a for phase II) and U_III (based on the model derived from the structure in Figure 1a) and the known enthalpy of transition, $\Delta H_{\mathrm{II}\rightarrow\mathrm{III}}$, together with the enthalpies of formation of PCl_5(c) (−443.5 kJ mol^{-1})[23] and of Cl^-(g) (−246 kJ mol^{-1})[24] we obtain eq 3 and 4. Solution of eq 3 and 4 leads to the

$$\tfrac{1}{2}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_4^+(g)}) + \tfrac{1}{2}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_6^-(g)}) = -209.0\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

$$\tfrac{2}{3}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_4^+(g)}) + \tfrac{1}{3}\Delta H_\mathrm{f}^\ominus(\mathrm{PCl_6^-(g)}) = 14.8\ \mathrm{kJ\ mol^{-1}} \quad (4)$$

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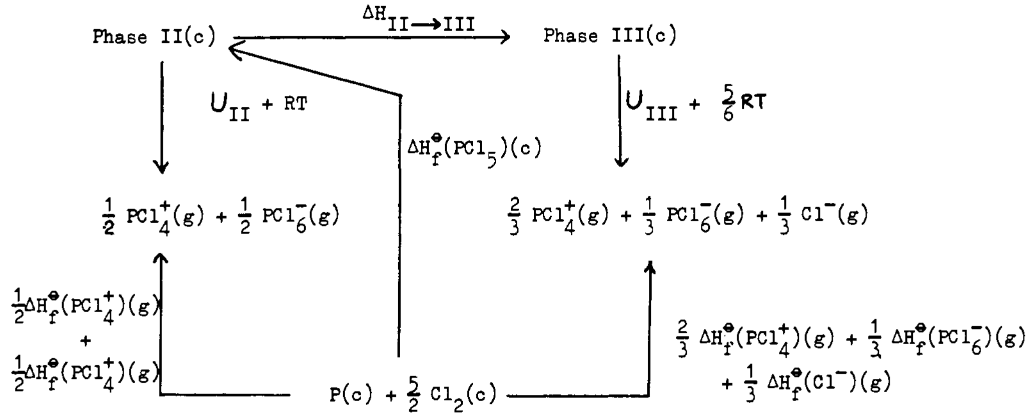
Table II. Lattice Energy Calculations for Various PCl_5 Structures[a]

structure	lattice energy components/kJ mol^{-1}: electrostatic	repulsive	dispersive	total lattice energy/kJ mol^{-1}	PCl_4^+ parameters: Cl atom radius/Å	charge distribution: q_P	q_{Cl}	PCl_6^- parameters: "basic" radius of PCl_6^- ion/Å	q_{Cl}
$PCl_4^+Cl^-$ [b]	769	−217	140	692	1.286	1.352	−0.88		
$PCl_4^+Cl^-$ [c]	729	−197	123	656	1.309	1.352	−0.86		
phase II, $PCl_4^+PCl_6^-$ [b]	195	−50	87	232				2.685	−0.53
phase II, $PCl_4^+PCl_6^-$ [c]	194	−49	80	224				2.671	−0.67
phase III[d]	378	−101	95	372				2.821	−0.95

[a] $PCl_4^+Cl^-$ structures based on the replacement of two PCl_6^- ions in Figure 1, a and b, by two PCl_4^+ ions and dissociated free coaxial Cl^- ions. [b] Figure 1a type. [c] Figure 1b type. [d] Our model, Figure 2.

Scheme I



values $\Delta H_f^\ominus(PCl_4^+(g)) = 462.4$ kJ mol^{-1} and $\Delta H_f^\ominus(PCl_6^-(g)) = -880.4$ kJ mol^{-1}. In addition, the double chloride affinity A_{2Cl^-} of PCl_4^+ in the gas phase is defined by eq 5 from which

$$PCl_4^+(g) + 2Cl^-(g) \xrightarrow{A_{2Cl^-}} PCl_6^-(g) \qquad (5)$$

$A_{2Cl^-} = \Delta H_f^\ominus(PCl_6^-(g)) - \Delta H_f^\ominus(PCl_4^+(g)) - 2\Delta H_f^\ominus(Cl^-(g))$ can be calculated as −850.8 kJ mol^{-1}. Further, using the data $\Delta H_f^\ominus(PCl_5(g)) = -374.9$ kJ mol^{-1},[23] $\Delta H_f^\ominus(PCl_3^+(g)) = +757.3$ kJ mol^{-1},[23] $\Delta H_f^\ominus(PCl_3(g)) = -287.0$ kJ mol^{-1},[23] $\Delta H_f^\ominus(PCl_3(l)) = -319.7$ kJ mol^{-1}, and $\Delta H_f^\ominus(PCl(g)) = +149.6$ kJ mol^{-1},[25] we can obtain the enthalpies for the following processes:

$$PCl_5(g) + Cl^-(g) \rightarrow PCl_6^-(g) \qquad \Delta H_1 = -259.5 \text{ kJ mol}^{-1}$$

$$PCl_5(c) + Cl^-(g) \rightarrow PCl_6^-(g) \qquad \Delta H_2 = -190.9 \text{ kJ mol}^{-1}$$

$$PCl_4^+(g) + Cl^-(g) \rightarrow PCl_5(g) \qquad \Delta H_3 = -591.3 \text{ kJ mol}^{-1}$$

(3) Thermochemical Radii. Using eq 2 of ref 26 we can estimate, on the basis of the calculations made above, a thermochemical radius for the two ions: $PCl_4^+ = 1.50$ Å and $PCl_6^- = 3.46$ Å.

Discussion

(1) Comparison of Calculated Data with Other Results. At this stage it is useful to assess the credibility of the calculated thermodynamic data since no previous estimates of $\Delta H_f^\ominus(PCl_4^+(g))$ and $\Delta H_f^\ominus(PCl_6^-(g))$ have been made. A comparison of the differences between values $\Delta H_f^\ominus(MH_3(g))$, $\Delta H_f^\ominus(MH_3^+(g))$ and $\Delta H_f^\ominus(MH_4^+(g))$ (M = N, P) with the corresponding differences generated between $\Delta H_f^\ominus(PCl_3(g))$, $\Delta H_f^\ominus(PCl_3^+(g))$, and $\Delta H_f^\ominus(PCl_4^+(g))$ is given in Table III. It can be seen that the trend among the chloro species appears to be consistent with those among the analogous nitrogen and phosphorus hydride species, thus giving confidence in the calculated value of $\Delta H_f^\ominus(PCl_4^+(g))$. Insufficient literature data are available for direct comparison of the result obtained for $\Delta H_f^\ominus(PCl_6^-(g))$, but some general comments can be made. The enthalpy for the process

$$WF_5(c) + F^-(g) \rightarrow WF_6^-(g)$$

has been calculated[28] as −450 kJ mol^{-1}, from which we obtain $\Delta H_f^\ominus(WF_6^-(g)) = -2177$ kJ mol^{-1}. In addition, Peacock[29] has obtained values of the standard enthalpies of the processes

$$KF(c) + MF_5(c) \rightarrow AMF_6(c) \text{ (M = W, Mo, P, Sb)}$$

from which we calculate values for $\Delta H_f^\ominus(KMF_6(c))$ (Table IV). The value for $\Delta H_f^\ominus(KPF_6(c)) = -2337$ kJ mol^{-1} may be compared to our estimated value for $\Delta H_f^\ominus(KPCl_6(c)) = -836.9$ kJ mol (below). Such a difference in the enthalpies of formation when chlorine replaces fluorine seem reasonable when compared to values for pairs of A_2MX_6 compounds (Table V).

(2) Stability of PCl_6^- Salts. Although alkylammonium hexachlorophosphates are well-known, no alkali-metal salts, $MPCl_6$, have been reported; preliminary attempts to synthesize $CsPCl_6$ in this laboratory were not successful. Predictive calculations are hence of interest, especially for plausible decomposition reactions, e.g., $MPCl_6 \rightarrow MCl + PCl_5$. Using the Kapustinskii equation, based on the Born–Mayer equation, and assuming $r(K^+) = 1.33$ Å, we estimate the lattice energy

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Table III. Standard Enthalpies of Formation of Some Chloro and Hydrido Species of Phosphorus and Nitrogen

compd	$\Delta H_f^\ominus$/kJ mol^{-1}		ref
$NH_3(g)$	−46.1	985	23
$NH_3^+(g)$	939.4	309	23
$NH_4^+(g)$	630.0		27
$PH_3(g)$	5.4	1010	23
$PH_3^+(g)$	1015.0	350	25
$PH_4^+(g)$	665.0		25
$PCl_3(g)$	−287.0	1044	23
$PCl_3^+(g)$	757.3	295	23
$PCl_4^+(g)$	462.4		this work

Table IV. Enthalpies of Reaction, $\Delta H_R^\ominus$, for

$$KF(c) + MF_5(c) \xrightarrow{\Delta H_R^\ominus} KMF_6(c)$$

and Derived Standard Enthalpies of Formation, $\Delta H_f^\ominus(KMF_6(c))$

M	$-\Delta H_R^\ominus$/ kJ mol^{-1} [a]	$\Delta H_f^\ominus$-(KMF_6(c))/ kJ mol^{-1}
W	203	2227
Mo	118	2072
P	174	2337
Sb	183	2088

[a] Reference 29.

Table V. Comparison of the Standard Enthalpies of Formation of Some Hexachloro and Hexafluoro Compounds

compd	$-\Delta H_f^\ominus$(c)/ kJ mol^{-1}	ref	compd	$-\Delta H_f^\ominus$(c)/ kJ mol^{-1}	ref
KPF_6	2337	29	K_2TiCl_6	1747	21
$KPCl_6$	836.9	this work	K_2GeF_6	2600	31
K_2TiF_6	2910	30	Rb_2GeCl_6	1464	31

of $KPCl_6$ (U_{POT}) as 470.7 kJ mol^{-1}. It may be shown that

$$\Delta H_f^\ominus(KPCl_6(c)) = \Delta H_f^\ominus(K^+(g)) + \Delta H_f^\ominus(PCl_6^-(g)) - U_{POT}(KPCl_6(c)) \quad (6)$$

and hence, putting $\Delta H_f^\ominus(K^+(g))$ = 514.2 kJ mol^{-1},[32] we calculate $\Delta H_f^\ominus(KPCl_6(c))$ = −836.9 kJ mol^{-1}. $\Delta G_f^\ominus(KPCl_6(c))$ may then be estimated via the standard entropy of formation, $\Delta S_f^\ominus(KPCl_6(c))$; following Latimer,[33] a value of the absolute entropy of $KPCl_6$, $S_{298}°(KPCl_6)$ = 250.8 J K^{-1} mol^{-1}, can be calculated from $S°_{K+}$ = 38.5 J K^{-1} mol^{-1}, $S°_P$ = 38.9 J K^{-1} mol^{-1} (estimated from Latimer's equations),[34] and $S°_{Cl}$ = 28.9 J K^{-1} mol^{-1} (assuming the case where the average cation charge is 3+). From this, a value of $\Delta S_f°(KPCl_6(c))$ = −0.52 kJ mol^{-1} K^{-1} is estimated on the basis of

$$\Delta S_f°(KPCl_6(c)) = S_{298}°(KPCl_6) - S_{298}°(K) - S_{298}°(P) - 3S_{298}°(Cl_2)$$

where $S_{298}°(K)$, $S_{298}°(P)$ at $S_{298}°(Cl_2)$ are the absolute entropies of the elements in their standard states. Hence $\Delta G_f^\ominus(KPCl_6(c)) \simeq -682$ kJ mol^{-1} at ambient temperatures. A similar calculation yields $\Delta G_f^\ominus(CsPCl_6(c)) \simeq -706$ kJ mol^{-1}. Thus for the decomposition reaction

$$MPCl_6(c) \xrightarrow{\Delta G_R^\ominus} MCl(c) + PCl_5(c)$$

$$\Delta G_R = \Delta G_f^\ominus(MCl(c)) + \Delta G_f^\ominus(PCl_5(c)) - \Delta G_f^\ominus(MPCl_6(c))$$

leading to values of $\Delta G_R^\ominus$ of −37.5 and −5.6 kJ mol^{-1} for the potassium and cesium salts, respectively. Hence, the stabilities of such alkali-metal hexachlorophosphates must be considered as borderline.

(3) Stability of a $PCl_4^+Cl^-$ Structure. Phosphorus(V) bromide is known to have a $PBr_4^+Br^-$ formulation,[13] and hence the stability of an analogous chloride structure is of interest. The enthalpy difference between the normal (phase II) and this hypothetical form of PCl_5 may be written as

$$\Delta H^\ominus_{II\to hyp} = (U_{II} - U_{hyp}) + \tfrac{1}{2}RT - \tfrac{1}{2}A_{2Cl^-}$$

where U_{hyp} and U_{II} are the lattice energies of the hypothetical PCl_4Cl and (normal) PCl_4PCl_6, respectively, and A_{2Cl^-} is the double halide affinity of PCl_4^+, discussed earlier. Calculations using the structure in Figure 1a led to a value of $U_{II} - U_{hyp} \simeq -460$ kJ mol^{-1}; calculations based on Figure 1b led to a corresponding value of $\simeq$−432 kJ mol^{-1}, hence a mean value of $\Delta H_{II\to hyp}$ of approximately −19 kJ mol^{-1} is reasonable. Thus if the entropy change is $\Delta S^\ominus_{II\to hyp} \geq -60$ J K^{-1} mol^{-1}, there should be no obvious thermodynamic barrier to the formation of $PCl_4^+Cl^-$ although a significant activation barrier would be expected for dissociation of the PCl_6^- ion.

Registry No. $2PCl_4^+ \cdot PCl_6^- \cdot Cl^-$, 75324-31-1; $PCl_4^+ \cdot Cl^-$, 60951-36-2; $PCl_4^+ \cdot PCl_6^-$, 19453-01-1; PCl_4^+, 15169-50-3; $KPCl_6$, 79593-28-5; PCl_6^-, 16920-87-9; $CsPCl_6$, 79593-29-6.

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