Ionic Isomerism. 3. Estimation of Enthalpies of Formation of the Gaseous Tetrachlorophosphonium Ion, $\Delta_fH°(PCl_4^+,g)$, and of the Gaseous Hexachlorophosphate Ion, $\Delta_fH°(PCl_6^-,g)$. Lattice Enthalpy Calculations for Bis(tetrachlorophosphonium) Hexachlorophosphate Halides, $[PCl_4]_2[PCl_6]X$, Where X = Cl or Br. Bond Enthalpies of Phosphorus(V) Chloro Compounds

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Recent structural and synthetic work on phosphorus−halo compounds over the past 3 years has provided a means of estimating associated thermochemical data. The lattice energy of Me_4NPCl_6 and the stability criteria for the existence of $CsPCl_6$ as the only stable alkali metal hexachlorophosphate at ambient temperature are used to predict values for $\Delta_fH°(PCl_6^-,g)$ while, in parallel, the rigorous calculation of the lattice potential energy of normal PCl_5 (phase II, PCl_5 as $[PCl_4^+][PCl_6^-]$) provides a functional thermodynamic relationship between $\Delta_fH°(PCl_6^-,g)$ and $\Delta_fH°(PCl_4^+,g)$ and hence enables estimation of $\Delta_fH°(PCl_4^+,g)$. The total lattice potential energies of the $[PCl_4]_2[PCl_6]X$ (X = Cl (phase III, PCl_5) and Br) salts are computed using a rigorous computational procedure designed to model lattices possessing complex anions and cations. These calculations lead to values of 1038 ± 5 kJ mol^{-1} for the lattice potential energy of $[PCl_4]_2[PCl_6]Cl$ and 1013 ± 5 kJ mol^{-1} for $[PCl_4]_2[PCl_6]Br$ and to estimates for the enthalpies of formation of the gaseous complex ions, $\Delta_fH°(PCl_4^+,g)$ and $\Delta_fH°(PCl_6^-,g)$ of 384 ± 10 kJ mol^{-1} and -813 ± 10 kJ mol^{-1}, respectively. The above values differ from our previous estimates, which were based on speculative structures. Bond enthalpy estimates are made for phosphorus(V) chloro compounds. A brief consideration of the recent Glasser extension of the Kapustinskii equation is made with respect to these salts.

Introduction

The various types of isomerism are a well established feature of the chemistry of phosphorus halides.[1−4] Conversion of a molecular form of a complex to an isomeric ionic form upon a change of phase is well-known among the mixed chloro-fluorides. For example, the pseudo trigonal bipyramidal (Ψ-tbp) molecular liquids PCl_4F and PCl_2F_3 are, respectively, $[PCl_4]^+[PCl_4F_2]^-$ and $[PCl_4]^+[PF_6]^-$ in the solid state[4] and the molecular liquid $Cl_4P(CH_2Cl)$ transforms into an ionic solid $[Cl_3PCH_2Cl]^+[Cl_5PCH_2Cl]^-$.[5] Ionic and Ψ-tbp solid state isomers of each of the compounds, $PhPCl_4$, Ph_2PCl_3, and Ph_3PCl_2, have been isolated recently.[6] The methyl analogue of $PhPCl_4$ is ionic, existing as $[MePCl_3]^+$ and Cl^-. In the case of

the mixed chloro−bromide salts of the tetrachloroborate anion, the cations $[PCl_nBr_{4-n}]^+$, $1 \leq n \leq 3$, in salts like $[PClBr_3][BCl_4]$, $[PCl_2Br_2][BCl_4]$, and $[PCl_3Br][BCl_4]$, have been characterized[7−10] by solid state ^{31}P NMR and vibrational spectroscopic studies, although virtually no X-ray structural data are available. The existence of $[PCl_5Br]^-$ has been speculated,[11] although attempts to stabilize this anion using tetraalkylammonium cations have proved abortive.[12] The compounds PBr_4Cl and PBr_4Cl_3 exhibit no *mixed* halogeno cations containing, respectively, $[PBr_4]^+$ and Cl^- and $[PBr_4]^+$ and $[Cl_3]^-$ ions.[13,14]

Phosphorus pentachloride is clearly rather delicately balanced on the ionic−covalent borderline, existing as an ionic solid $[PCl_4]^+[PCl_6]^-$ at room temperature but with a trigonal bipy-

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ramidal (tbp) structure in the gas phase. Trapping the vapor at 15 K yields a tbp solid which transforms to the ionic form upon warming to room temperature.[15] The ionic isomerism of this system is particularly interesting, and low-temperature DSC measurements of the trapped tbp structure as it reverts to the ionic form (as one of our referees has pointed out) should be a future goal for experimentalists.

The corresponding enthalpies and entropies of these transitions produced from variable temperature equilibrium data (or other source) would be extremely interesting to have. Ionic isomerism is exemplified further by the existence of a metastable ionic species, $[PCl_4]_2[PCl_6]Cl$.[16]

The chloride salt, bis(tetrachlorophosphonium) hexachlorophosphate, $[PCl_4]_2[PCl_6]Cl$, is the metastable (phase III) form of PCl_5 (phase II) which has been known to exist for 40 years,[17] although structural details from high-resolution powder diffraction studies[18,19] have only recently been published. No single crystal of this salt could be obtained.

The solid state structure of bis(tetrachlorophosphonium) hexachlorophosphate bromide, $[PCl_4]_2[PCl_6]Br$, empirical formula $P_3Cl_{14}Br$, has, on the other hand, been solved by both single-crystal X-ray diffraction techniques and by Rietveld refinement of high-resolution powder X-ray diffraction data.[20] The salt consists of two $[PCl_4]^+$ tetrahedra of C_s symmetry, one $[PCl_6]^-$ octahedron of C_{4v} symmetry, and one Br^- ion and is structurally very similar to its chloride analogue.

Prior to 1991 we had remarkably little information concerning the structure and stability of salts containing $[PCl_4]^+$ and $[PCl_6]^-$ ions, and our previous work in this area[3] was, of necessity, based on conjecture as to the structural features of the compounds concerned. Nevertheless, the predictions we made from that work regarding the stability of hexachlorophosphate salts, for example, have proved to be valid. We are now in a position to explore the area with considerably more certainty as a result of the recent work described above concerning the structural aspects of these salts. Accordingly, this paper represents an extensive survey of all the thermodynamic evidence available and reports values for enthalpies of formation of the gaseous tetrachlorophosphonium cation, $\Delta_f H°(PCl_4^+,g)$, and the hexachlorophosphate anion, $\Delta_f H°(PCl_6^-,g)$. The lattice potential energy calculations reported on the highly complex bis(tetrachlorophosphonium) hexachlorophosphate salts represent the most sophisticated of their kind to date (having two different complex ions within the same lattice) to be carried out on any inorganic salts, and in that sense they represent pioneering studies with regard to modeling.

Prior to presenting the results of our large scale lattice potential energy calculations for these bis(tetrachlorophosphonium) hexachlorophosphates, we consider the magnitudes which emerge for the above thermochemical data from the following considerations: (i) The total lattice potential energy of normal phase II phosphorus(IV) chloride, calculated using the LATEN program of Jenkins and Pratt.[21–23] (ii) The stabilization of the

$[PCl_6]^-$ anion by the large tetramethylammonium cation.[24] (iii) The implications of the (known) existence[3,25] of only one stable alkali metal hexachlorophosphate salt, $CsPCl_6$, at ambient temperature. We shall demonstrate that the estimates produced for $\Delta_f H°(PCl_6^-,g)$ from considerations ii and iii are later borne out by the more rigorous calculational approach adopted for $[PCl_4]_2PCl_6X$ salts. Such computations rely on sophisticated lattice energy minimization procedures which present a degree of flexibility in the modeling of complex ions while employing minimization conditions which ensure that the lattice energy calculated satisfies the constraints imposed by the structural data input.

Calculations

(a) Total Lattice Potential Energy Computation for the Parent PCl5 (Phase II) Structure. 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 contains $[PCl_4]^+$ units sandwiching $[PCl_6]^-$ octahedra of C_{4v} symmetry (see Figure 16, ref 3).[26–30] The bonding is predominantly ionic and the program LATEN[21–23] was used to compute[3] the total lattice potential energy, $U_{POT}([PCl_4]^+[PCl_6]^-)$, of this salt. The electrostatic energy, U_{ELEC}, is computed following the method of Bertaut[31]

$$U_{ELEC} = \frac{Kq}{R\kappa}\sum_{j=1}^{N} n_j q_j^2 - \frac{K}{2\pi V\kappa}\sum_h\sum_k\sum_l \frac{|F_{hkl}|^2\Phi_{hkl}^2}{S_{hkl}^2} +$$

$$K\sum_{r=1}^{p}\sum_{s=1}^{p}\frac{q_r q_s}{R_{rs}} \quad (1)$$
$$r > s$$

where the variables are as previously described.[22,23] In particular q_r is the charge on the atom of type r, and F_{hkl} is given by

$$|F_{hkl}|^2 = \left(\sum_{r=1}^{N}q_r\sum_{s=1}^{n_r}\cos(ARG_{rs})\right)^2 + \left(\sum_{r=1}^{N}q_r\sum_{s=1}^{n_r}\sin(ARG_{rs})\right)^2 \quad (2)$$

where

$$ARG_{rs} = 2\pi[hx_{rs} + ky_{rs} + lz_{rs}] \quad (3)$$

where x_{rs}, y_{rs}, and z_{rs} are the fractional coordinates of the sth type of atoms of type r.

We calculate the derivatives such that the internal P–Cl distances in the $[PCl_4]^+$ cation and the $[PCl_6]^-$ anion are not affected by cell-length variation. We ensure this by incorporating d_a, d_b, and d_c, the resolved components of the P–Cl distances into eq 3

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$$ARG_{rs} = 2\pi\left[h\left(x_{rs} + \frac{d_a}{a}\right) + k\left(y_{rs} + \frac{d_b}{b}\right) + l\left(z_{rs} + \frac{d_c}{c}\right)\right] \quad (4)$$

$$\left(\frac{\partial|F_{hkl}|^2}{\partial i}\right)_{i=i_0,d} =$$

$$2(\sum_{r=1}^{N} q_r \sum_{s=1}^{n_r} \cos(ARG_{rs}))\left[\sum_{r=1}^{N} q_r \sum_{s=1}^{n_r}\left(\frac{2\pi m d_i}{i^2}\right)\sin(ARG_{rs})\right] -$$

$$2(\sum_{r=1}^{N} q_r \sum_{s=1}^{n_r} \sin(ARG_{rs}))\left[\sum_{s=1}^{N} q_r \sum_{s=1}^{n_r}\left(\frac{2\pi m d_i}{i^2}\right)\cos(ARG_{rs})\right] \quad (5)$$

where $m = h$ for $i = a$, $m = k$ for $i = b$, and $m = l$ for $i = c$. From eq 2 we then obtain

$$\left(\frac{\partial U_{ELEC}}{\partial i}\right) = \frac{K}{2\pi\kappa V^2}\left(\frac{\partial V}{\partial i}\right)\sum_h\sum_k\sum_l \frac{|F_{hkl}|^2\phi_{hkl}^2}{S_{hkl}^2} - \frac{K}{2\pi\kappa V}\times$$

$$\sum_h\sum_k\sum_l\left[\left(\frac{\partial|F_{hkl}|^2}{\partial i}\right)\frac{\phi_{hkl}^2}{S_{hkl}^2} + \left(\frac{\partial\phi_{hkl}^2}{\partial i}\right)\frac{|F_{hkl}|^2}{S_{hkl}^2} + \left(\frac{\partial S_{hkl}^{-2}}{\partial i}\right)|F_{hkl}|^2\phi_{hkl}^2\right]$$

$$(6)$$

In the calculation of the repulsive energy U_R we employ the Huggins and Meyer[32] procedure and use the equilibrium conditions ($i = a, b, c$)

$$\left(\frac{\partial U_R}{\partial i}\right)_0 = \left(\frac{\partial U_{ELEC}}{\partial i}\right)_0 + \left(\frac{\partial U_{dd}}{\partial i}\right)_0 + \left(\frac{\partial U_{dq}}{\partial i}\right)_0 \quad (7)$$

It is the multiplicity of these conditions (as i is variously the cell lengths a, b, or c; eq 7) that permits us to develop the complex ion models for the lattices. For phase II the results are

$$U_{POT}([PCl_4][PCl_6]) = 453 \pm 6 \text{ kJ mol}^{-1} \quad (8)$$

(i.e., 226 ± 3 kJ mol^{-1} per PCl$_5$ unit) for the process

$$[PCl_4][PCl_6](c) \xrightarrow[\Delta H_u^\circ]{U_{POT}([PCl_4][PCl_6]) + 2RT} PCl_4^+(g) + PCl_6^-(g) \quad (9)$$
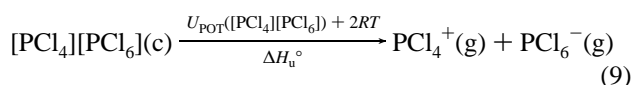
(with $U_{ELEC} = 392$ kJ mol^{-1}, $U_R = 97$ kJ mol^{-1}, $U_{dd} = 147$ kJ mol^{-1}, and $U_{qd} = 11$ kJ mol^{-1}) where

$$U_{POT}([PCl_4][PCl_6]) = U_{ELEC} - U_R + U_{dd} + U_{qd} \quad (10)$$

and U_{dd} and U_{qd} are the dipole−dipole and quadrupole−dipole dispersion energies, respectively.

In the above computation, the [PCl$_4$]$^+$ ion is represented as four spheres sited on the chlorine atom positions while the [PCl$_6$]$^-$ ion is represented as spherical envelope centered on the phosphorus atom position. The parameters used in these calculations are those that have been previously published.[3] The data file employed in the program LATEN for the above structure is available on request to the authors.

Figure 1a shows the interrelationship that exists between the various energy terms calculated, $E([PCl_4]^+)$, $E([PCl_6]^-)$, and $E([PCl_4][PCl_6])$ are the total absolute internal energies of the species involved and $U_{POT}[PCl_4][PCl_6]$ is the lattice energy calculated above.
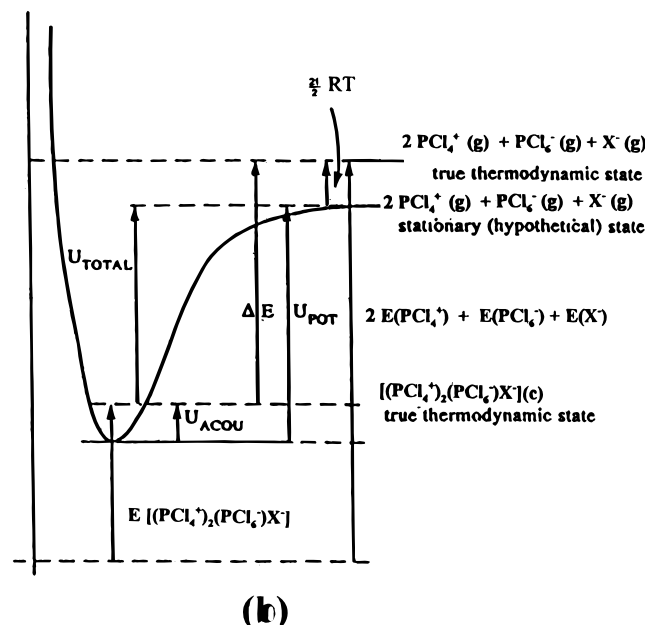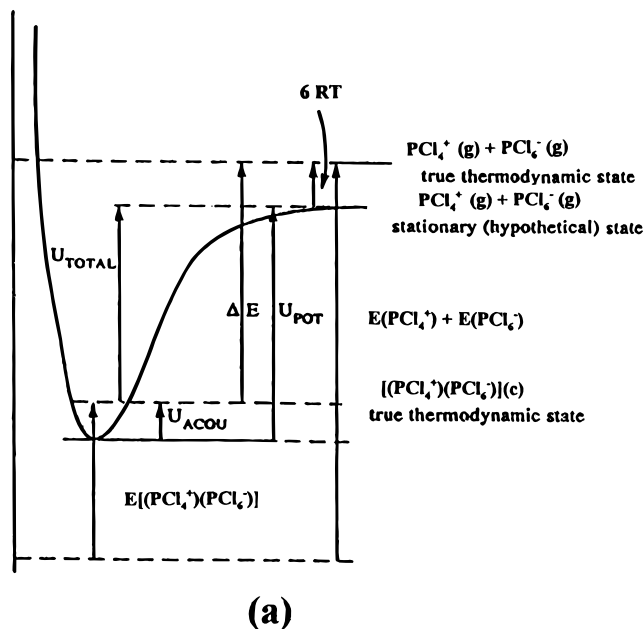
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(a)

(b)

Figure 1. Inter-relationships that exist between various energy terms and the calculated lattice potential energies of (a) [PCl$_4$][PCl$_6$] and (b) [PCl$_4$]$_2$[PCl$_6$]X, X = Cl or Br.

For the lattice enthalpy, ΔH_u°, step 9, we have for the internal energy of vaporization

$$\Delta E = E([PCl_4]^+) + E([PCl_6]^-) - E([PCl_4][PCl_6]) \quad (11)$$

For a perfect gas $E = nRT/2$ (where $n = 6$ for nonlinear polyatomic species, like [PCl$_4$]$^+$ and [PCl$_6$]$^-$), and hence

$$\Delta E = 6RT - E([PCl_4][PCl_6])$$

$$= 6RT + U_{POT}([PCl_4][PCl_6]) - U_{ACOU}([PCl_4][PCl_6]) \quad (12)$$

and the lattice enthalpy is related to ΔE by the equation

$$\Delta H_u^\circ = \Delta E + 2RT \quad (13)$$

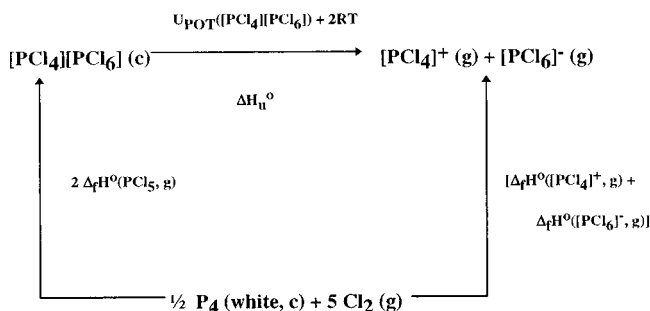We can of course calculate U_{ACOU} for a crystal lattice either

Figure 2. Thermochemical cycle for normal PCl$_5$, phase II.

from a knowledge of the specific heats as a function of temperature and from the zero point energy of the lattice or by means of either the Einstein or Debye theory of specific heats. At absolute zero $U_{ACOU} = 3NK\Theta_E$ or $9/4NK\Theta_D$, where Θ_E and Θ_D are the Einstein and Debye characteristic temperatures, and at temperatures considerably greater (298 K) than Θ_E or Θ_D, then $U_{ACOU} = 6RT$ for the alkali halides. At 298.15 K we can set U_{ACOU} for most salts equal to $3RT$ per ion, and in the absence of specific heat data for the compounds of interest this strategy is adopted. Hence

$$\Delta H_u{}^\circ = U_{POT}([PCl_4][PCl_6]) + 2RT \qquad (14)$$

as is incorporated into the thermochemical cycle of Figure 2, whereupon we have

$$\Delta_f H^\circ([PCl_4]^+,g) + \Delta_f H^\circ([PCl_6]^-,g) =$$
$$U_{POT}([PCl_4][PCl_6]) + 2RT + 2\Delta_f H^\circ(PCl_5,c) \quad (15)$$

Substituting the value for $U_{POT}([PCl_4][PCl_6])$ calculated above and the data for $\Delta_f H^\circ(PCl_5,c) = -443.5$ kJ mol^{-1} [33] leads us to the conclusion that

$$[\Delta_f H^\circ([PCl_4]^+,g) + \Delta_f H^\circ([PCl_6]^-,g)]/kJ \ mol^{-1} =$$
$$-429.0 \pm 6 \quad (16)$$

similar to an earlier result (eq 3, ref 3). We shall now use this dependence as the "anchor" relationship for our data.

Using the lattice potential energy calculated for $[PCl_4]^+[PCl_6]^-$ above, we can, from the Kapustinskii equation,[34,35] derive the magnitude of the sum of the thermochemical radii of the $[PCl_4]^+$ and $[PCl_6]^-$ ions, finding that

$$[r_{PCl_4^+} + r_{PCl_6^-}]/nm = 0.499 \pm 0.007 \qquad (17)$$

(b) Empirical Approach to Estimation of $\Delta_f H^\circ([PCl_6]^-,g)$: Stabilization of the $[PCl_6]^-$ Ion by the Tetramethylammonium Cation. In our previous work[3] we utilized the lattice energy calculation on a hypothetical $[PCl_4]^+Cl^-$ lattice to obtain an estimate of the thermochemical radius of $[PCl_4]^+$ (=0.150 nm), and using the calculated lattice energy for $[PCl_4]^+[PCl_6]^-$, we then obtained the thermochemical radius for $[PCl_6]^-$ (=0.346 nm) consistent with it. This procedure was not ideal in that it relied on the simulation of an *unknown* structure. In the present approach we re-examine the problem of evaluating thermochemical data from a different viewpoint. We utilize the thermochemical radii of $[PCl_6]^-$ anion and its relationship to
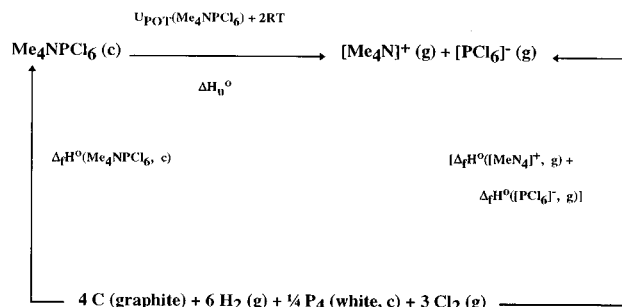

Figure 3. Thermochemical cycle for Me$_4$NPCl$_6$.

$\Delta_f H^\circ([PCl_6]^-,g)$ for the salt tetramethylammonium hexachlorophosphate, MeN$_4$PCl$_6$ (this section), in conjunction with the inequalities generated by considering the stability of rubidium and cesium hexachlorophosphates (next section) via the Kapustinskii equation (an equation which is anticipated to work reasonably well for these salts).

In the case of Me$_4$NPCl$_6$

$$U_{POT}(Me_4NPCl_6)/kJ \ mol^{-1} =$$
$$242.8[1 - (\varrho/(r_{Me_4N^+} + r_{PCl_6^-}))]/(r_{Me_4N^+} + r_{PCl_6^-}) \ (18)$$

where ρ is taken to be 0.0345 nm and the thermochemical radii are expressed in nanometers. Using the thermochemical cycle of Figure 3, the relationship (analogous to (14) above)

$$\Delta H_u{}^\circ = U_{POT}(Me_4NPCl_6) + 2RT \qquad (19)$$

exists between the lattice potential energy and the lattice enthalpy. Employing the known[24] enthalpy of formation of the salt, $\Delta_f H^\circ([Me_4NPCl_6],c) = -736 \pm 5$ kJ mol^{-1}, the value of the thermochemical radius, $r_{Me_4N^+}$, of Me$_4$N$^+$ (=0.215 nm) (taken from Jenkins and Thakur[35] as adjusted by Huheey, Keiter, and Keiter[36] to be compatible with Shannon−Prewitt crystal radii[37,38]) and the known enthalpy of formation of the tetramethylammonium ion ($\Delta_f H^\circ([Me_4N^+],g)$ (=536 kJ mol^{-1}),[39] and utilizing a combination of eqs 18 and 19, we can derive an equation (Appendix 1) for $\Delta_f H^\circ([PCl_6]^-,g)$ of the parametric form

$$\Delta_f H^\circ([PCl_6]^-,g) = f\{r_{PCl_6^-}\} \qquad (20)$$

and a plot of $r_{PCl_6^-}$ versus $\Delta_f H^\circ([PCl_6]^-,g)$ consistent with the data for Me$_4$NPCl$_6$ (Figure 4) can be made (corresponding to the broken−curve AB).

(c) Stability of Alkali Metal Hexachlorophosphates, MPCl$_6$ (M = Rb and Cs). In our previous study[3] the stability of alkali metal hexachlorophosphates was predicted as likely to be borderline with the possibility (since $\Delta G_R{}^\circ$ was estimated to be

$$MPCl_6(c) \xrightarrow{\Delta G_R{}^\circ} MCl(c) + PCl_5(c) \qquad (21)$$
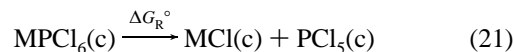
-5.6 kJ mol^{-1}) that CsPCl$_6$ might be stable at room temperature. Recently the question has been examined by Muir[41] who has reported the preparation of CsPCl$_6$ but who failed to secure the

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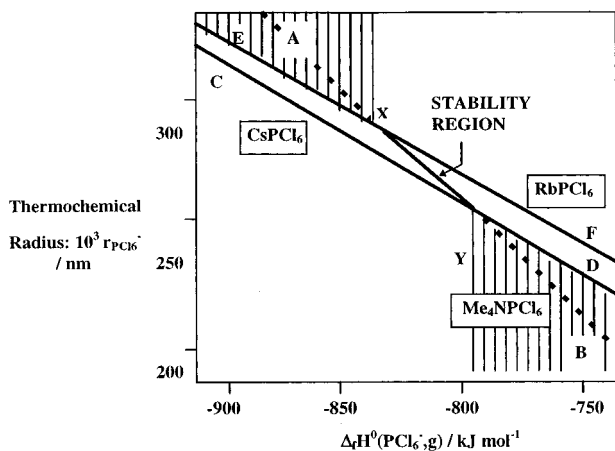(41) Muir, A. S. *Polyhedron* **1991**, *10*, 2217.

Figure 4. Limitations placed on value of $\Delta_f H°([PCl_6]^-,g)$ by virtue of information possessed concerning the stability of alkali metal hexachlorophosphates (eqs A10 and A11; Appendix III) and values of $\Delta_f H°([PCl_6]^-,g)$ for tetramethylammonium hexachlorophosphate, Me$_4$NPCl$_6$ (eq 19 in the form of eq A2; Appendix I), leading to an assignment for the enthalpy of formation of the PCl_6^- gaseous ion of $-806 \geq \Delta_f H°([PCl_6]^-,g)/kJ\ mol^{-1} \geq -835$ and of the thermochemical radius, $0.265 \leq r_{PCl_6^-}/nm \leq 0.296$.

(presumably thermodynamically unstable) RbPCl$_6$ and KPCl$_6$ salts. The decomposition route (21) is known to be appropriate for alkali metal hexachlorophosphates since when a (fully confirmed) sample of CsPCl$_6$ is induced to decompose by storage in sunlight and temperature conditions which lower the activation energy for decomposition, a diffraction pattern then obtained proves to be that for CsCl.[11] The fact that cesium hexachlorophosphate appears to be a unique example of an alkali metal salt of the anion [PCl$_6$]$^-$ enables us to make deductions about the likely magnitude of the enthalpy of formation of its anion, $\Delta_f H°([PCl_6]^-,g)$. Considering the decomposition route, eq 21, of an unstable alkali metal hexachlorophosphate, we can conclude that for M = Cs, $\Delta G_R > 0$ and for Rb (and other alkali metals salts), $\Delta G_R < 0$. ΔG_R is given by

$$\Delta G_R = \Delta_f G°(MCl,c) + \Delta_f G°(PCl_5,c) - \Delta_f G°(MPCl_6,c) \quad (22)$$

for which $\Delta_f G°(MCl,c)$ is known [CsCl = -414.53 kJ mol^{-1} [33] and RbCl = -407.80 kJ mol^{-1} [33]]. $\Delta_f G°(PCl_5,c)$ is not known although $\Delta_f H°(PCl_5,c)$ is well established[33] to be -443.5 kJ mol^{-1}. We obtain $\Delta_f S°(PCl_5,c)$ to be -432.3 J K^{-1} mol^{-1} based on the absolute entropies for phosphorus, $S°(P,white,c) = 41.09$ J K^{-1} mol^{-1}, and chlorine gas, $S°(Cl_2,g) = 223.1$ J K^{-1} mol^{-1} taken from standard tables,[33] and $S°(PCl_5,c) = 166.5$ J K^{-1} mol^{-1} [42,43] leading to $\Delta_f G°(PCl_5,c) = -314.6$ kJ mol^{-1}. ΔG_R from eq 22 is therefore

$$\Delta G_R/kJ\ mol^{-1} = -729.1 - \Delta_f G°(CsPCl_6,c) \quad (23)$$

for the cesium salt and

$$\Delta G_R/kJ\ mol^{-1} = -722.4 - \Delta_f G°(RbPCl_6,c) \quad (24)$$

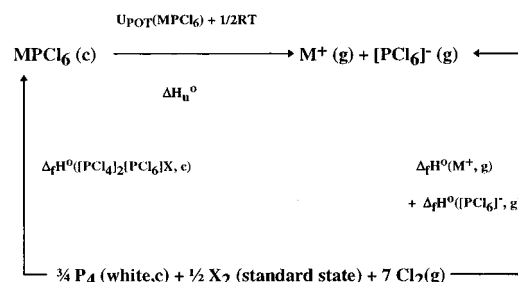for the rubidium salt. Since the former is stable and the latter

(42) Karapet'yants, M. X.; Karapet'yants, M. L. *Thermodynamic constants of Inorganic and Organic Compounds*; Humphrey Science Pub.: Ann Arbor, MI, 1970.
(43) Kelly, K. K.; King, E. G. *Contribution to the Data on Theoretical Metallurgy XIV. Entropies of the Elements and Inorganic Compounds. Bur. Mines Bull.* 1961, No. 592.

Figure 5. Thermochemical cycle for MPCl$_6$ salts.

salt is not, we conclude that

$$\Delta_f G°(CsPCl_6,c)/kJ\ mol^{-1} < -729.2 \quad (25)$$

and that

$$\Delta_f G°(RbPCl_6,c)/kJ\ mol^{-1} > -722.4 \quad (26)$$

This leads us to the conclusion (Appendix II), using Latimer's rules[44] to estimate the absolute entropy of the hexachlorophosphate salts, that in order to explain the known stability of the hexachlorophosphates:

$$\Delta_f H°(CsPCl_6,c)/kJ\ mol^{-1} < -863.0 \quad (27)$$

and

$$\Delta_f H°(RbPCl_6,c)/kJ\ mol^{-1} > -855.7 \quad (28)$$

using the cycle (Figure 5)

$$U_{POT}(MPCl_6) = \Delta_f H°(M^+,g) + \Delta_f H°(PCl_6^-,g) - \Delta_f H°(MPCl_6,c) - {}^1/_2 RT \quad (29)$$

for CsPCl$_6$, and using eq 27,

$$U_{POT}(CsPCl_6)/kJ\ mol^{-1} > \Delta_f H°(PCl_6^-,g) + 1319.7 \quad (30)$$

where $\Delta_f H°(Cs^+,g) = 457.964$ kJ mol^{-1}.[33] If we employ (analogous to eq 18) the Kapustinskii equation for the CsPCl$_6$ salt, we can again develop a relationship (Appendix III) between $r_{PCl_6^-}$, the thermodynamic radius of the [PCl$_6$]$^-$ ion, and $\Delta_f H°(PCl_6^-,g)$ of the parametric form of eq 20 which is also plotted on Figure 4 (curve labeled CD). A similar relationship is obtained using the RbPCl$_6$ instability criterion

$$U_{POT}(RbPCl_6)/kJ\ mol^{-1} < \Delta_f H°([PCl_6]^-,g) + 1344.6 \quad (31)$$

which is plotted (as curve EF) in Figure 4.

(d) Empirical Estimation of $\Delta_f H°([PCl_6]^-,g)$ and Thermochemical Radii of [PCl$_6$]$^-$ Ion, $r_{PCl_6^-}$. Figure 4 shows how the constraints placed upon the relationships in the form of inequalities 27 and 28 arising from the stability of CsPCl$_6$ and RbPCl$_6$—the associated stability of the former and instability of the latter—enables us to discard all but the range of $\Delta_f H°([PCl_6]^-,g)$ and $r_{PCl_6^-}$ values represented by the *solid portion XY* of the Me$_4$NPCl$_6$ curve. The condition 28 for RbPCl$_6$ cuts off the curve derived from Me$_4$NPCl$_6$ at $\Delta_f H°([PCl_6]^-,g)$ values greater than X on the abscissa, and the curve labeled CsPCl$_6$ cuts off the same curve at values of $\Delta_f H°([PCl_6]^-,g)$ less than Y on the abscissa. Accordingly, we are able to assign the region bounded by

(44) Latimer, W. E. *Oxidation Potentials*; Prentice Hall: Englewood Cliffs, NJ, 1961.

$$-806 \geq \Delta_f H°([PCl_6]^-,g) \text{ kJ mol}^{-1} \geq -835 \quad (32)$$

$$0.265 \leq r_{PCl_6^-}/\text{nm} \leq 0.296 \quad (33)$$

as being consistent with the relationships of the form of (20) generated from the three salts that are considered.

From eq 16 we conclude also that

$$377 \leq \Delta_f H°([PCl_4]^+,g)/\text{kJ mol}^{-1} \leq 406 \quad (34)$$

and by eq 17 that

$$0.234 \geq r_{PCl_4^+}/\text{nm} \geq 0.203 \quad (35)$$

The thermochemical radius of the $[PCl_6]^-$ ion is smaller (cf. 0.346 nm) and the $[PCl_4]^+$ ion is larger (cf. 0.150 nm) than those previously assigned,[33] the new averages being

$$r_{PCl_6^-} = 0.281 \text{ nm} \quad (36)$$

$$r_{PCl_4^+} = 0.219 \text{ nm} \quad (37)$$

The value of $\Delta_f H°([PCl_6]^-,g)$ is somewhat higher than our initial estimate[3] (based on speculative structures) and that made in a preliminary communication[45] (based on a lattice potential energy model which has since been further refined).

(e) Full Scale Calculations of $\Delta_f H°([PCl_6]^-,g)$ and $\Delta_f H°$-$([PCl_4]^+,g)$. Total Lattice Energies of the Bis(tetrachlorophosphonium) Hexachlorophosphate Halides, $[PCl_4]_2\cdot[PCl_6]X$ (X = Cl, Br). General Procedures. A similar approach to that described earlier for phase II (Figure 1b) can be used to derive the inter-relationship between the lattice enthalpy, lattice potential energy, and absolute internal energies of the species involved, and this leads us, for the salts $(PCl_4)_2PCl_6X$ (X = Cl and Br), to the relationships

$$\Delta E = 2E([PCl_4]^+) + E([PCl_6]^-) + E(X^-) -$$
$$E([PCl_4]_2[PCl_6]X) \quad (38)$$

and hence

$$\Delta E = {}^{21}/_2RT + U_{POT}([PCl_4]_2[PCl_6]X) -$$
$$U_{ACOU}([PCl_4]_2[PCl_6]X) \quad (39)$$

whereupon

$$\Delta E = U_{POT}([PCl_4]_2[PCl_6]X) - {}^3/_2RT \quad (40)$$

It follows that, in the cycle (Figure 6)

$$\Delta H_u° = U_{POT}([PCl_4]_2[PCl_6]X) + {}^1/_2RT \quad (41)$$

Also, for the thermochemical cycle itself we have

$$2\Delta_f H°([PCl_4]^+,g) + \Delta_f H°([PCl_6]^-,g) =$$
$$U_{POT}([PCl_4]_2[PCl_6]X) + {}^1/_2RT + \Delta_f H°([PCl_4]_2[PCl_6]X,c) -$$
$$\Delta_f H°(X^-,g) \quad (42)$$

(i) Total Lattice Potential Energy of Bis(tetrachlorophosphonium) Hexachlorophosphate Chloride, $[PCl_4]_2[PCl_6]Cl$: Phase III. The total lattice potential energy of bis(tetrachlorophosphonium) hexachlorophosphate chloride, phase II, U_{POT}-

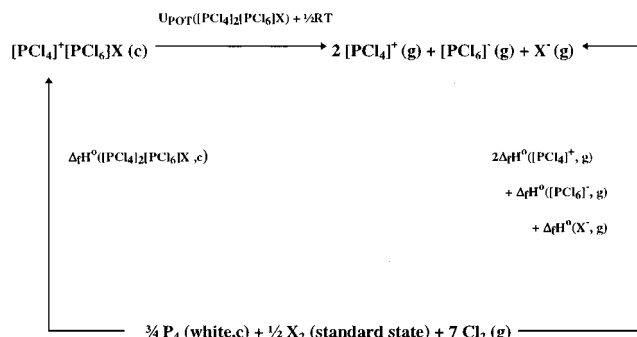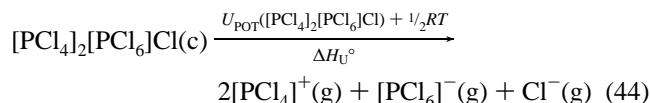(45) Jenkins, H. D. B.; Sharman, L.; Finch A.; Gates, P. N. *Polyhedron* **1994**, *13*, 1481.

Figure 6. Thermochemical cycle for bis(tetrachlorophosphonium) hexachlorophosphate halides, $[PCl_4]_2[PCl_6]X$.

$([PCl_4]_2[PCl_6]Cl)$, was estimated[3] to be 1116 kJ mol^{-1} based on the structure proposed by us prior to the availability of the X-ray powder data which then lead us to report a preliminary value[45] of 956 kJ mol^{-1}. Refinement of the model used for this latter calculation, in the light of the studies above, led us to a revised value for the lattice potential energy of the chloride salt. Further calculations exploring alternative models for the ions lead to very consistent values of the total lattice potential energy

$$U_{POT}([PCl_4]_2[PCl_6]Cl)/\text{kJ mol}^{-1} = 1038 \pm 5 \quad (43)$$

(i.e., 346 kJ mol^{-1} per PCl$_5$ unit) with $U_{ELEC} = 936$ kJ mol^{-1}, $U_R = 177$ kJ mol^{-1}, $U_{dd} = 258$ kJ mol^{-1}, and $U_{qd} = 21$ kJ mol^{-1} for the process

$$[PCl_4]_2[PCl_6]Cl(c) \xrightarrow[\Delta H_U°]{U_{POT}([PCl_4]_2[PCl_6]Cl) + {}^1/_2RT}$$
$$2[PCl_4]^+(g) + [PCl_6]^-(g) + Cl^-(g) \quad (44)$$

The salt possesses[18,19] a regular tetrahedral $[PCl_4]^+$ unit with an octahedral $[PCl_6]^-$ unit having a small compression along the axial direction. The groups are arranged as in the antifluorite structure with the additional Cl$^-$ ion at the center of the cavity surrounded by eight cations (see Figure 2, ref 18). The monoclinic cell parameters are $a = 8.798$ Å, $b = 8.4765$ Å, and $c = 12.3683$ Å with $\beta = 92.751°$, space group $I2/m$.

The salt is modeled by adopting a four-sphere model for the $[PCl_4]^+$ cation centered on the four chlorine atoms with an overall charge on the ion of +1, and the $[PCl_6]^-$ anion is modeled as a sphere centered on phosphorus bearing a charge of -1. The chloride ion is modeled as a sphere with a basic radius of 1.506 Å. The LATEN[21−23] data file for $[PCl_4]_2[PCl_6]$-Cl is available on request.

If we take the above value of $U_{POT}([PCl_4]_2[PCl_6]Cl)$ and substitute this value together with $\Delta_f H°(Cl^-,g) = -233.13$ kJ mol^{-1} and $\Delta_f H°([PCl_4]_2[PCl_6]Cl,c) = \Delta H_{II\rightarrow III} + \Delta_f H°(PCl_5,c)$ (see ref 3) $= -1323.3$ kJ mol^{-1} into eq 42 we see that

$$[2\Delta_f H°([PCl_4]^+,g) + \Delta_f H°([PCl_6]^-,g)]/\text{kJ mol}^{-1} =$$
$$-50.9 \pm 5 \quad (45)$$

Subtracting eq 16 from eq 45 leads to the prediction that

$$370.1 \leq \Delta_f H°([PCl_4]^+,g)/\text{kJ mol}^{-1} \leq 386.1 \quad (46)$$

and hence by virtue of eq 16 that

$$-799.1 \geq \Delta_f H°([PCl_6]^-,g)/\text{kJ mol}^{-1} \geq -815.1 \quad (47)$$

The ranges, (32) and (34), derived from consideration of the Me$_4$NPCl$_6$ and MPCl$_6$ salts, are broadly in agreement with the

above values which are (more reliably) based on *accurate* structural data.

(ii) Total Lattice Potential Energy of Bis(tetrachlorophosphonium) Hexachlorophosphate Bromide, $[PCl_4]_2[PCl_6]Br$. Both powder and simple crystal X-ray[20] structural data are available for the corresponding bromide salt, and lattice energy calculations can be used to compare the structures from the two sources. The total lattice potential energy of bis(tetrachlorophosphorus) hexachlorophosphate bromide is found to be

$$U_{POT}([PCl_4]_2[PCl_6]Br) = 1012 \pm 5 \text{ kJ mol}^{-1} \quad (48)$$

(with $U_{ELEC} = 912$ kJ mol^{-1}, $U_R = 174$ kJ mol^{-1}, $U_{dd} = 254$ kJ mol^{-1}, and $U_{qd} = 20$ kJ mol^{-1}) for the process

$$[PCl_4]_2[PCl_6]Br(c) \xrightarrow[\Delta H_u^\circ]{U_{POT}([PCl_4]_2[PCl_6]Br) + 2RT} 2[PCl_4]^+(g) + [PCl_6]^-(g) + Br^-(g) \quad (49)$$
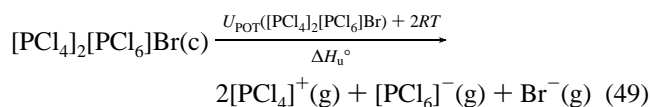
based on unpublished *powder* data[46] ($a = 8.7472$ Å, $c = 12.3281$ Å, space group $I4/m$) while taking the value

$$U_{POT}([PCl_4]_2[PCl_6]Br) = 1013 \pm 5 \text{ kJ mol}^{-1} \quad (50)$$

(with $U_{ELEC} = 908$ kJ mol^{-1}, $U_R = 172$ kJ mol^{-1}, $U_{dd} = 256$ kJ mol^{-1}, and $U_{qd} = 21$ kJ mol^{-1}) based on the published Knachel et al.[20] *single crystal* data ($a = 8.739$ Å, $c = 12.320$ Å, space group $I4$).

The consistency of these two results for the bromide salts indicates that the lattice potential energy calculated from the powder data in the case of the salt $[PCl_4]_2[PCl_6]Cl$ (which is not supported by single-crystal X-ray data) is likely also to be reliable and consequently likely to furnish satisfactory estimates of the thermodynamic parameters. The LATEN[21,23] data files used for the $[PCl_4]_2[PCl_6]Br$ calculations are available on request and are analogous to those used for the chloride salt except for modification of the Br$^-$ ion parameters.

Substitution of $\Delta_fH^\circ(Br^-,g) = -219.1$ kJ mol^{-1} into eq 42 leads to the equation (based on the single-crystal result for U_{POT})

$$[2\Delta_fH^\circ(PCl_4^+,g) + \Delta_fH^\circ(PCl_6^-,g)]/\text{kJ mol}^{-1}$$
$$= U_{POT}([PCl_4]_2[PCl_6]Br) + {}^1/_2RT +$$
$$\Delta_fH^\circ([PCl_4]_2[PCl_6]Br,c) - \Delta_fH^\circ(Br^-,g) \quad (51)$$

$$= (1233.4 \pm 5) + \Delta_fH^\circ([PCl_4]_2[PCl_6]Br,c) \quad (52)$$

Use of eq 45, derived from the results for the chloride salt, suggests that

$$\Delta_fH^\circ([PCl_4]_2[PCl_6]Br,c) = -1284.3 \pm 7 \text{ kJmol}^{-1} \quad (53)$$

Results and Discussion

(a) Thermochemical Data. We assign, after further consideration, the ranges emerging from the LATEN models for $[PCl_4]_2[PCl_6]Cl$ (inequalities 46 and 47) and the (*less reliable*) empirical estimates (inequalities 32 and 34) based on the stability criteria for alkali metal hexachlorophosphates and parameters involving teramethlyammonium hexachlorophosphate

$$-799 \geq \Delta_fH^\circ(PCl_6^-,g)/\text{kJ mol}^{-1} \geq -827 \quad (54)$$

where the range (47) is extended at the lower end to take account

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(46) Dasent, W. E. *Inorganic Energetics*, 1st ed.; Cambridge University Press: New York, 1970.

of the more empirical results. Correspondingly (eq 16)

$$370 \leq \Delta_fH^\circ(PCl_4^+,g)/\text{kJ mol}^{-1} \leq 398 \quad (55)$$

the mean values being -813 and 384 kJ mol^{-1}, respectively.

Until very recently, the precise position with regard to the stability of alkali metal hexachlorophophates was not known nor were the crystal structures of the bis(tetrachlorophosphonium) hexachlorophosphate halide salts established, and the literature estimates for the thermochemical data for the $[PCl_4]^+$ and $[PCl_6]^-$ ions were largely based on conjecture.[3] It is for this reason that comparison of the values obtained in the present study with those obtained in earlier work is hardly a valid exercise. It is probably a sufficient commentary to say (i) that the results reported here for the computational, structural, and thermochemical data appear reasonably consistent and (ii) represent the extent of our knowledge at this time and (iii) that the thermochemical data may be subject to uncertainties on the order of, at the very least, 10 kJ mol^{-1}. An appeal must be made for more structural (and attendant thermochemical) data if progress is to be made toward a full understanding of the factors which dictate the stability and thermodynamics of these fascinating compounds containing halo–phosphorus complex anions and cations.

Arising from the above estimates of $\Delta_fH^\circ(PCl_4^+,g)$ and $\Delta_fH^\circ(PCl_6^-,g)$, we can consider the strengths of the individual P–Cl bonds within the ions as described below. It should be noted however that there is a huge, and ultimately insoluble, difficulty in assigning error limits because very few of the thermochemical quantities discussed in this paper are experimental quantities. For simple salts—NaCl type—where several different, fairly independent estimates of the lattice potential energy can be made (term by term calculation, Kapustinskii equation, Glasser equation, solvation enthalpy cycle, etc.) and values can be compared, and if they agree (within reasonable limits), then it is fair to assign *probable* uncertainties. With salts containing complex ions the matter is more difficult. In the present instance we have tackled the problem in two ways: selection of alternative models for the ions of the complex salt lattices and comparison of the results and, as we shall see later, comparison of LATEN values with those derived from a recent extension of the Kapustinskii approach. On this basis we have been able to estimate errors as best as we can for the complex salt lattice potential energies.

(b) Bond Energies. (i) P–Cl Bond Energy in $[PCl_6]^-$. The mean thermochemical bond energies, $EH_m^\circ(P-X, \text{homolytic})$ of P–X bonds in the simple phosphorus halides, PX_3, have long been established[40,46] for the series $EH_m^\circ(P-F \text{ in } PF_3) = 490$,[46] 503 kJ mol^{-1};[40] $EH_m^\circ(P-Cl \text{ in } PCl_3) = 319$,[46] 308 kJ mol^{-1};[40] $EH_m^\circ(P-Br \text{ in } PBr_3) = 263$,[40] 264 kJ mol^{-1};[13] $EH_m^\circ(P-I \text{ in } PI_3) = 184$ kJ mol^{-1} [46] and provide measures of bond strengths in *neutral* molecules. In this sense they cannot be applied to molecules which have a charge, e.g., complex ions. Bond strengths of the latter can be estimated in two ways according to the mode of fission considered for the bonds. Thus, bonds in $[PCl_6]^-$, for example, can be envisaged as undergoing homolytic fission to give atoms:

$$[PCl_6]^-(g) - e \rightarrow P(g) + 6Cl(g) \quad (56)$$
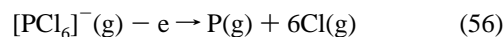
The corresponding average bond enthalpies $EH_m^\circ(P-Cl)/\text{kJ mol}^{-1}$ are given by the relationships:

$$EH_m^\circ(P-Cl,\text{homolytic})/\text{kJ mol}^{-1} =$$
$${}^1/_6[\Delta_fH^\circ(P,g) + 6\Delta_fH^\circ(Cl,g) - \Delta_fH^\circ([PCl_6]^-,g)] \quad (57)$$

Using standard thermochemical data[33] and the enthalpy of formation for gaseous $[PCl_6]^-$ obtained above enables us to estimate that:

$$EH_m°(P-Cl,homolytic,[PCl_6]^-) = 310 \pm 5 \text{ kJ mol}^{-1} \quad (58)$$

Historically there are four determinations for $\Delta_f H°(P,g)$ in the literature which agree to within 22 kJ mol^{-1} and seven determinations of $\Delta_f H°(Cl,g)$ which agree to 3 kJ mol^{-1}, and our estimated error in $\Delta_f H°(PCl_6^-,g)$ is 14 kJ mol^{-1}. Accordingly we assign the error limit in eq 58.

The typical bond lengths[4,47] for compounds containing P−Cl bonds are as follows: 1.97 Å $[PCl_4]^+$,[4] 1.98 Å in $[PCl_4]^+[ICl_2]^-$,[47] 1.99 Å in PCl_2FO and PCl_3O,[47] 2.01 Å in $PClF_2O$,[47] 2.02 Å in PCl_2F,[47] 2.03 Å in PCl_3S,[47] 2.04, 2.02 (*equatorial*), and 2.19 Å,[47] 2.14 Å (*axial*) in *gaseous* PCl_5, 2.043 Å in PCl_3,[47] 2.05 Å in PCl_2F_3,[48] 2.07 Å (*average of axial and equatorial*) in $[PCl_4]^+[PCl_6]^-$,[47] and 2.08 Å in $[PCl_6]^-$.[4] Considering these figures, we see that by and large $[PCl_4]^+$ and $[PCl_6]^-$ moieties represent the two extremities of the longest and shortest bond lengths encountered in the species listed above. In this sense, therefore, the bond enthalpy, $EH_m°(P-Cl)$ might be expected to differ for the P−Cl bond within these two ions. The fact that the P−Cl bond length in $[PCl_6]^-$ is close to that exhibited in PCl_3 correlates with the similarity in homolytic bond energies found in these two compounds (313 kJ mol^{-1} (*average*) compared to 310 kJ mol^{-1}).

(ii) P−Cl Bond Energy in $[PCl_4]^+$. Applying similar considerations for the ion $[PCl_4]^+$, we have for homolytic fission:

$$[PCl_4]^+(g) \rightarrow P^+(g) + 4Cl(g) \quad (59)$$
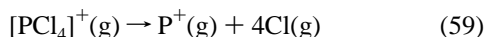
$$EH_m°(P-Cl,homolytic, [PCl_4]^+) =$$
$$\tfrac{1}{4}[\Delta_f H°(P^+,g) + 4\Delta_f H°(Cl,g) - \Delta_f H°([PCl_4]^+,g)] \quad (60)$$

Using standard thermochemical data[33] and the value for $\Delta_f H°([PCl_4]^+,g)$ predicted in this paper (inequality 55), we find a value

$$EH_m°(P-Cl,homolytic,[PCl_4]^+) = 359 \pm 5 \text{ kJ mol}^{-1} \quad (61)$$

indicating a stronger P−Cl bond by some 49 kJ mol^{-1} in this ion compared to that in $[PCl_6]^-$.

Historically the value of $\Delta_f H°(P^+,g)$ has changed by some 45 kJ mol^{-1} over the last 20 years, while recent estimates for this thermochemical magnitude differ only by 1.8 kJ mol^{-1}. For $\Delta_f H°(PCl_5,g)$, extreme values cited in the literature differ by some 32 kJ mol^{-1}, although agreement between the most recent of the cited values is 5.3 kJ mol^{-1}. Accordingly, in eq 60, taking the worst case scenario the error is 13.9 kJ mol^{-1} while in the more likely situation, the error in $EH_m°(P-Cl,homolytic,[PCl_4^+])$ is 2.1 kJ mol^{-1}, and so the cited value of 5 kJ mol^{-1} seems to us reasonable.

The above result for $EH_m°(P-Cl,homolytic,[PCl_4]^+)$ is easily rationalizable with the very *short* P−Cl bond found in $[PCl_4]^+$ (1.97 Å) compared to that of $[PCl_6]^-$ (2.08 Å). A recent study[48] of the corresponding P−Br bond in $[PBr_4]^+$ leads to a value:

$$EH_m°(P-Br,homolytic,[PBr_4]^+) = 326 \pm 5 \text{ kJ mol}^{-1} \quad (62)$$

(47) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Sutton, L. E., Ed.; Chem. Soc. Special Publication 11; Chem. Soc.: London, 1958.
(48) Jenkins, H. D. B. *Polyhedron* **1996**, *15*, 2831.

(iii) Dependence of Bond Energy on Stereochemistry. We can also consider the dependence of bond enthalpy on stereochemistry since the change in bond enthalpy for the P−Cl bond found in $[PCl_4]^+$, when compared to that in $[PCl_6]^-$, suggests that the stereochemistry understandably influences the P−Cl bond strength. We approach the question by reference to a number of bond formation reactions.

Considering the reaction

$$PCl_3(g) + 2Cl(g) \xrightarrow{\Delta H_1} PCl_5(g) \quad (63)$$
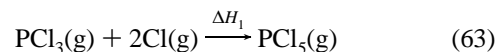
for which we can write

$$\Delta H_1 = \Delta_f H°([PCl_5],g) - \Delta_f H°([PCl_3],g) -$$
$$2\Delta_f H°(Cl,g) \quad (64)$$

then taking into account the stereochemical environment of the various P−Cl bonds we have

$$\Delta H_1 = 3EH_m°(P-Cl,pyr,PCl_3) - 2EH_m° \times$$
$$(P-Cl,tbp,ax,PCl_5) - 3EH_m°(P-Cl,tbp,eq,PCl_5) \quad (65)$$

$$= -331.3 \pm 7.0 \text{ kJ mol}^{-1}$$

using standard thermochemical data.[33] The cited values of the enthalpy of formation of gaseous PCl_3 have varied in the literature over the years by 78 kJ mol^{-1}, but the two most recent determinations differ by only 1.6 kJ mol^{-1}. The worst case error in ΔH_1 is therefore 115 kJ mol^{-1}, but this clearly includes some extremely poor and some very old measurements as well as assuming that the "true" value lies at the extreme of the entire range cited in the literature. The latter is not usually the case, it is more likely that the true value will lie near the mid-range of the spread of values so that the uncertainty is then greatly reduced. The more likely value of the error is the 7 kJ mol^{-1} we have cited.

ΔH_1 represents the enthalpy released on conversion of three P−Cl bonds in a regular pyramidal arrangement (pyr) as found in gaseous PCl_3 to three trigonal bipyramidal equatorial (tbp,eq) and two trigonal bipyramidal axial (tbp,ax) P−Cl bonds as found in PCl_5. Since the P−Cl bond length for the bond (P−Cl, pyr) in PCl_3 (estimated to have length between 2.02 and 2.04 Å) is similar in length to the P−Cl bond (P−Cl,tbp,eq) in PCl_5 (with a length = 2.02 Å), we can make the assumption that the bond enthalpies are similar, i.e.,

$$EH_m°(P-Cl,tbp,eq,PCl_5) \approx EH_m°(P-Cl,pyr,PCl_3) \quad (66)$$

and hence

$$EH_m°(P-Cl,tbp,ax,PCl_5) = -\tfrac{1}{2}[\Delta H_1] =$$
$$165.6 \pm 3.5 \text{ kJ mol}^{-1} \quad (67)$$

Thus the axial bonds in PCl_5 are found to be much weaker than the equatorial bonds (and this may indirectly be related to the phenomenon of ionic isomerization). The observation is also in accordance with the greater length of these axial bonds (2.14 Å) when compared to the equatorial bonds (2.02 Å). Weak axial bonds also occur in the compound $AsCl_5$. The preparation of this latter compound proved extremely elusive and although finally prepared[49] by ultraviolet irradiation of $AsCl_3$ in liquid Cl_2 at −105 °C, the two extra axial As−Cl bonds over and above those in $AsCl_3$ are so weak that their enthalpy appears to be insufficient to outweigh the enthalpy absorbed in the

(49) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 377.

atomization of Cl_2, with the result that $AsCl_5$ has, at most, borderline stability with respect to $AsCl_3$ and Cl_2.

If we consider the enthalpy change, ΔH_2, for the reaction

$$[PCl_4]^+(g) + 2Cl^-(g) \xrightarrow{\Delta H_2} [PCl_6]^-(g) \qquad (68)$$
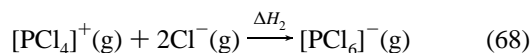
we can write

$$\Delta H_2 = \Delta_f H°([PCl_6]^-,g) - \Delta_f H°([PCl_4]^+,g) - 2\Delta_f H°(Cl^-,g) \quad (69)$$

Then taking into account the stereochemical environment of the various P–Cl bonds we have

$$\Delta H_2 = 4EH_m°(P-Cl,tet,[PCl_4]^+) -$$
$$2EH_m°(P-Cl,oct,ax,[PCl_6]^-) -$$
$$4EH_m°(P-Cl,oct,eq,[PCl_6]^-) + \Delta_f H°(P,g) +$$
$$2\Delta_f H°(Cl,g) - \Delta_f H°(P^+,g) - 2\Delta_f H°(Cl^-,g)$$
$$= -731 \pm 24 \text{ kJ mol}^{-1} \qquad (70)$$

using standard thermochemical data[33] and our assignments for the enthalpies of formation of the $[PCl_4]^+$ and $[PCl_6]^-$ ions. Historically, $\Delta_f H°(Cl^-,g)$ has varied by some 15.5 kJ mol^{-1}, although more recent determinations agree to 12.9 kJ mol^{-1}. Thus, the most extreme magnitude of the error for ΔH_2 is 29.5 kJ mol^{-1} while a more realistic error might be 24 kJ mol^{-1}.

From eq 70

$$4EH_m°(P-Cl,tet,[PCl_4]^+) -$$
$$2EH_m°(P-Cl,oct,ax,[PCl_6]^-) -$$
$$4EH_m°(P-Cl,oct,eq,[PCl_6]^-) = -420 \pm 35 \text{ kJ mol}^{-1} \quad (71)$$

Taking the value of $EH_m°(P-Cl,tet,[PCl_4]^+) = 359 \pm 5$ kJ mol^{-1} from eq 61 we find

$$2EH_m°(P-Cl,oct,ax,[PCl_6]^-) +$$
$$4EH_m°(P-Cl,oct,eq,[PCl_6]^-) = 1856.0 \pm 35 \text{ kJ mol}^{-1} \quad (72)$$

noting that this corresponds to an average P–Cl bond enthalpy in $[PCl_6]^-$ of $1856/6 = 309 \pm 6$ kJ mol^{-1}, consistent with the value predicted in eq 58. This further suggests that the thermochemical assignments made in this paper, not only for the $[PCl_6]^-$ ion but also for the $[PCl_4]^+$ ion, are reliable.

Considering now the enthalpy change ΔH_3, for the reaction

$$PCl_5(g) + Cl^-(g) \xrightarrow{\Delta H_3} [PCl_6]^-(g) \qquad (73)$$
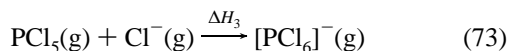
we have

$$\Delta H_3 = \Delta_f H°([PCl_6]^-,g) - \Delta_f H°([PCl_5],g) - \Delta_f H°(Cl^-,g) \quad (74)$$

Taking account of the stereochemical environment of the various P–Cl bonds we can write

$$\Delta H_3 = 2EH_m°(P-Cl,tbp,ax,[PCl_5]) +$$
$$3EH_m°(P-Cl,tbp,eq,[PCl_5]) -$$
$$2EH_m°(P-Cl,oct,ax,[PCl_6]^-) -$$
$$4EH_m°(P-Cl,oct,eq,[PCl_6]^-) + \Delta_f H°(Cl,g) - \Delta_f H°(Cl^-,g)$$
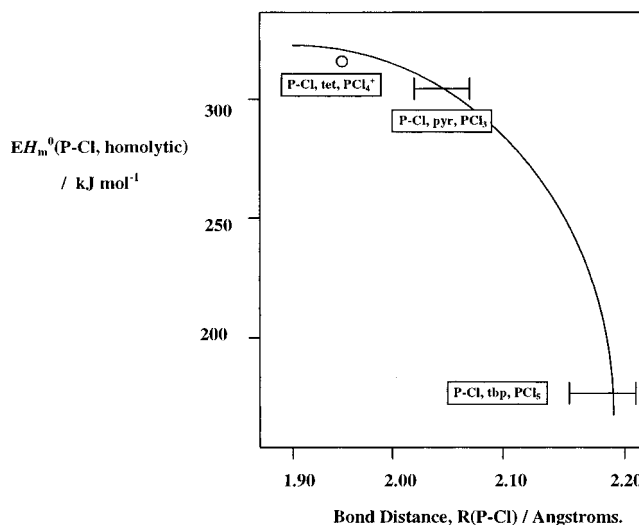$$= -205 \pm 20 \text{ kJ mol}^{-1} \qquad (75)$$

Figure 7. Bond energy $EH_m(P-Cl,\text{homolytic})$/kJ mol^{-1} as function of P–Cl distance/Å.

and using standard thermochemical data[33] and our value for $\Delta_f H°([PCl_6]^-,g)$ we find

$$2EH_m°(P-Cl,tbp,ax,[PCl_5]) +$$
$$3EH_m°(P-Cl,tbp,eq,[PCl_5]) -$$
$$2EH_m°(P-Cl,oct,ax,[PCl_6]^-) -$$
$$4EH_m°(P-Cl,oct,eq,[PCl_6]^-) = -559.8 \pm 7 \text{ kJ mol}^{-1} \quad (76)$$

Since $EH_m°(P-Cl,tbp,ax,[PCl_5]) = 165.6$ kJ mol^{-1} from eq 67 and also using the relationship that $[2EH_m°(P-Cl,oct,ax,[PCl_6]^-) + 4EH_m°(P-Cl,oct,eq,[PCl_6]^-)] = 1856.0$ kJ mol^{-1} from eq 72 we estimate that

$$EH_m°(P-Cl,tbp,eq,[PCl_5]) = 322 \pm 21 \text{ kJ mol}^{-1} \quad (77)$$

and by virtue of the relationship (66) that

$$EH_m°(P-Cl,pyr,PCl_3) = 322 \pm 21 \text{ kJ mol}^{-1} \qquad (78)$$

If we compare the predicted bond enthalpies with the corresponding bond lengths in typical structures, we find the relationship depicted in Figure 7, which shows $EH_m°(P-Cl,\text{homolytic})$/kJ mol^{-1} plotted versus the P–Cl bond distance/(Å).

In an attempt to assign values for the bond enthalpies of $EH_m°(P-Cl,oct,ax,[PCl_6]^-)$ and $EH_m°(P-Cl,oct,eq,[PCl_6]^-)$ separately, we can examine the variation of P–Cl in the crystal structures discussed in this paper. The axial and equatorial bond lengths in the $[PCl_6]^-$ ion, as they occur in the lattice ($[PCl_4]_2[PCl_6]Cl$), are found to be 2.114 Å for the two axial and 2.143 Å for the four equatorial P–Cl bonds with similar lengths being encountered in the ($[PCl_4]_2[PCl_6]Br$) lattice (2.077 and 2.132 Å being typical).

If we partition the bond enthalpies in accordance with eq 70 and pay some regard to Figure 7 and our perceived correlation between bond strengths and bond lengths, we can estimate that

$$EH_m°(P-Cl,oct,ax,[PCl_6]^-) \approx 280 \pm 30 \text{ kJ mol}^{-1} \quad (79)$$

and

$$EH_m°(P-Cl,oct,eq,[PCl_6]^-) \approx 220 \pm 30 \text{ kJ mol}^{-1} \quad (80)$$

Table 1. Calculation of Weighted Anion−Cation Separations for Use in the Glasser Extension of the Kapustinskii Equation

interaction type	number	separation
$[PCl_4]^+ - [PCl_6]^-$	2	$r_{PCl_4^+} + r_{PCl_6^-}$
$[PCl_4]^+ - Cl^-$	2	$r_{PCl_4^+} + r_{Cl^-}$
$[PCl_6]^- - Cl^-$	1	$r_{PCl_6^-} + r_{Cl^-}$
total	5	$4r_{PCl_4^+} + 3r_{PCl_6^+} + 3r_{Cl^-}$

although the latter two values must be regarded as having much more uncertainty than the other estimates made in this paper.

(c) Covalent Contributions to the Bonding. A lattice energy generated from a Born−Fajans−Haber cycle can be regarded as an "experimental" lattice energy and is not dependent on the nature of the assumptions made concerning the bonding in the crystal. The theoretical computations of lattice energy reported here *assume* the bonding in the crystal to be ionic in nature. In cases where there is an appreciable nonionic contribution to the bonding, the cycle lattice energies are usually systematically higher than computed ones. Our initial calculations involving the Kapustinskii equation involved alkali metal hexachlorophosphates and tetramethylammonium hexachlorophosphate salts which are anticipated to be *predominately* ionic in nature and whose anticipated crystal structures should render these salts ones for which the Kapustinskii approach should work well. The associated estimates of the standard enthalpy of formation of the $[PCl_4]^+$ and $[PCl_6]^+$ gaseous ions (eqs 32 and 34) should therefore be approximately correct. The broad agreement between these estimates (eqs 46 and 47) and those stemming from the more rigorous calculations we have made suggest that the ionic models used in the LATEN calculations (despite the probable proximity of the ionic−covalent borderline) are likely to be valid and that the predominant contribution to the bonding in the $[PCl_4]_2[PCl_6]X$ salts is strongly ionic. This conclusion appears to be borne out by spectroscopic evidence.[20] The magnitude of any covalent contribution to the lattice potential energies could be checked were it possible to devise a combination of thermochemical cycles such that the hybrid cycle has as its only unknown the lattice potential energy step. Unfortunately this is not possible. For example, consideration of the difference obtained by combination of equations of the type (42) for X = Cl and Br giving

$$U_{POT}([PCl_4]_2[PCl_6]Cl) - U_{POT}([PCl_4]_2[PCl_6]Br) =$$
$$\Delta_f H°(Cl^-,g) - \Delta_f H°(Br^-,g) + \Delta_f H°([PCl_4]_2[PCl_6]Br,c) - \Delta_f H°([PCl_4]_2[PCl_6]Cl,c) \quad (81)$$

provides little information on this point since any small covalent contribution there might be to the lattice energy is likely to be of similar magnitude for both halide salts and would cancel in eq 81. In any event, we are unable to use this equation in any case since we do not currently possess an independent value of the enthalpy of formation of the bromide salt which we regard as reliable.

(d) Estimation of Lattice Energies Using the Glasser Equation for Bis(tetrachlorophosphonium) Hexachlorophosphate Halides. Traditionally the Kapustinskii equation[34,35] has provided a means of estimating the lattice energy of ionic salts, provided that thermochemical radii for the ions involved are known. For the more complex compounds or salts where there is more than one type of complex anion or cation in the lattice this equation in its usual form is not suitable. Recently however Glasser[50] has devised and reported a new equation which we believe is of considerable utility in that it extends the range of

(50) Glasser, L. *Inorg. Chem.* **1995**, *34*, 4935.

compounds for which estimates of lattice energy can be made. We have used his approach to estimate the lattice energy of the $[PCl_4]_2[PCl_6]X$ salts. Consideration is given to the interaction terms involved between the component anions and cations: $[PCl_4]^+ - [PCl_6]^-$, $[PCl_4]^+ - X^-$, and $[PCl_6]^- - X^-$ and used to compute an average weighted anion−cation distance, $\langle r \rangle$. The weighted distance is derived from the final row of Table 1 and is equal to

$$\langle r \rangle = [4r_{PCl_4^+} + 3r_{PCl_6^-} + 3r_{Cl^-}]/5 \quad (82)$$

Taking $r_{PCl_4^+} = 0.219 \pm 0.014$ nm (eq 37) and $r_{PCl_6^-} = 0.280 \pm 0.015$ nm (eq 36) and the Goldschmidt radius of $r_{Cl^-} = 0.181$ nm, it is found to be

$$\langle r \rangle/nm = 0.452 \pm 0.021 \quad (83)$$

Using Glasser's equation we estimate

$$U_{POT}([PCl_4]_2[PCl_6]Cl)/kJ\ mol^{-1}$$
$$= (121.4/\langle r \rangle)[1 - \varrho/\langle r \rangle]\sum n_k z_k^2 \quad (84)$$
$$= 992 \pm 43\ kJ\ mol^{-1} \quad (85)$$

where $\sum n_k z_k^2$ is the summation of the number of types of ions in the lattice bearing a charge z_k (=4 for the above salts). The corresponding calculation for the bromide salt, $[PCl_4]_2[PCl_6]$-Br, leads to

$$\langle r \rangle/nm = 0.460 \pm 0.021 \quad (86)$$

and hence to (using $r_{Br^-} = 0.196$ nm)[40]

$$U_{POT}([PCl_4]_2[PCl_6]Br)/kJ\ mol^{-1} = 975 \pm 43 \quad (87)$$

The actual LATEN computational results for both salts (eqs 43, 48, and 50) lie near the higher end of the above predicted ranges (eqs 85 and 87), the errors for the mean values are approximately 4%. The Glasser equation is therefore of considerable use and importance.

Acknowledgment. The helpful comments and suggestions made by referees who took trouble to study this work and in particular encouraged us to pay attention to error estimates are gratefully acknowledged. A number of their suggestions have been incorporated in the presentation of this work.

Appendix 1. Explicit Form of Eq 20 Used To Obtain the Plot for Tetramethylammonium Hexachlorophosphate, Me₄NPCl₆, in Figure 4

For the cycle in Figure 3 we have

$$\Delta_f H°([Me_4N]^+,g) + \Delta_f H°([PCl_6]^-,g) =$$
$$U_{POT}(Me_4NPCl_6) + {}^1/_2RT + \Delta_f H°(Me_4NPCl_6,c) \quad (A1)$$

Substitution of eq 18 for $U_{POT}(Me_4NPCl_6)$ and using $r_{Me_4N^+} = 0.215$ nm,[35] $\Delta_f H°([Me_4N]^+,g) = 546$ kJ mol⁻¹,[39] and $\Delta_f H°(Me_4NPCl_6,c) = -736 \pm 5$ kJ mol⁻¹ [24] into eq A1 reduces to

$$\Delta_f H°([PCl_6]^-,g) = 242.8/(r_a + r_c)[1 - (0.0345/(r_a + r_c))] - (1280.8 \pm 5) \quad (A2)$$

where $(r_a + r_c) = r_{PCl_6^-} + 0.215$ nm and the value of $\Delta_f H°([PCl_6]^-,g)$ is in kJ mol⁻¹. Equation A2 represents the explicit form of eq 20, which is required to obtain Figure 4.

Appendix 2. Calculation of $\Delta_f S°(MPCl_6,c)$

In terms of absolute entropies:

$$\Delta_f S°(MPCl_6,c) = S°(MPCl_6,c) - S°(M,c) -$$
$$\frac{1}{4}S°(P_4,white) - 3S°(Cl_2,g) \quad (A3)$$

While the value of $S°(MPCl_6,c)$ is not known, the values for $S°(Rb,c)$ = 76.78 J K^{-1} mol^{-1}, $S°(Cs,c)$ = 85.23 J K^{-1} mol^{-1}, $\frac{1}{4}S°(P_4,white)$ = 41.09 J K^{-1} mol^{-1}, and $S°(Cl_2,g)$ = 223.066 J K^{-1} mol^{-1} are available in standard tables.[33] Latimer's rules [44] can be employed to estimate $S°(MPCl_6,c)$ for the two salts. Using the Latimer entropy contribution for Cs and Rb (Table 87, ref 44) corresponding to $S°_{Cs}$ = 56.9 J K^{-1} mol^{-1} and $S°_{Rb}$ = 49.8 J K^{-1} mol^{-1} with $S°_P$ calculated from $[\frac{3}{2}R \ln$-(atomic weight) $- 3.93]$ (equation 1 Appendix III in units of J K^{-1} mol^{-1}, ref 44) and equal to 38.9 J K^{-1} mol^{-1}, and taking the values of $S°_{Cl}$ corresponding to a charge of +1 on the cation of the salt (Cs or Rb) = 41.84 J K^{-1} mol^{-1} we find

$$S°(CsPCl_6) = S°_{Cs} + S°_P + 6S°_{Cl} = 346.8 \text{ J K}^{-1} \text{ mol}^{-1} \quad (A4)$$

and

$$S°(RbPCl_6) = S°_{Rb} + S°_P + 6S°_{Cl} = 339.7 \text{ J K}^{-1} \text{ mol}^{-1} \quad (A5)$$

and therefore we estimate

$$\Delta_f S°(CsPCl_6,c) = -448.7 \text{ J K}^{-1} \text{ mol}^{-1} \quad (A6)$$

$$\Delta_f S°(RbPCl_6,c) = -447.4 \text{ J K}^{-1} \text{ mol}^{-1} \quad (A7)$$

Since

$$\Delta_f G°(MPCl_6,c) = \Delta_f H°(MPCl_6,c) - T\Delta_f S°(MPCl_6,c) \quad (A8)$$

and $\Delta_f G°(CsPCl_6,c) < -729.2$ kJ mol^{-1} (eq 25) we calculate that

$$\Delta_f H°(CsPCl_6,c) < -863.0 \text{ kJ mol}^{-1} \quad (27)$$

also since $\Delta_f G°(RbPCl_6,c) < -722.4$ kJ mol^{-1} (eq 26) we calculate that

$$\Delta_f H°(RbPCl_6,c) = -855.8 \text{ kJ mol}^{-1} \quad (28)$$

Appendix 3. Explicit Form of Eq 20 Used To Obtain the Plots for Cesium and Rubidium Hexachlorophosphates (Figure 5)

Rearranging eq 29 we have

$$\Delta_f H°(M^+,g) + \Delta_f H°([PCl_6]^-,g) =$$
$$U_{POT}(MPCl_6) + \frac{1}{2}RT + \Delta_f H°(MPCl_6,g) \quad (A9)$$

Substitution into the Kapustinskii equation (analogous to eq 18) for $U_{POT}(MPCl_6)$ and using the thermochemical radii r_{Cs^+} = 0.165 nm[40] and r_{Rb^+} = 0.149 nm,[40] we can obtain the lattice energies of CsPCl$_6$ and RbPCl$_6$ as parametric functions of the unknown thermochemical radius of PCl$_6^-$. Using the data for $\Delta_f H°(Cs^+,g)$ = 457.964 kJ mol^{-1} [33] and for $\Delta_f H°(Rb^+,g)$ = 490.101 kJ mol^{-1} [33] within eqs 30 and 31 leads to the condition

$$\Delta_f H([PCl_6]^-,g)/\text{kJ mol}^{-1} <$$
$$\{242.8[1 - (0.0345/(r_a + r_c))](r_a + r_c)\} - 1319.7 \quad (A10)$$

where $(r_a + r_c)/\text{nm} = [0.165 + r_{PCl_6^-}]$ for the Cs salt and the condition

$$\Delta_f H°([PCl_6]^-,g)/\text{kJ mol}^{-1} >$$
$$[242.8[1 - (0.0345/(r_a - r_c))]/(r_a + r_c)] - 1344.6 \quad (A11)$$

where $(r_a + r_c)/\text{nm} = [0.149 + r_{PCl_6^-}]$ for the Rb salt where $\Delta_f H°([PCl_6]^-,g)$ is in kJ mol^{-1}.