Ionic Isomerism in Phosphorus(v) Chloride

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Summary A facile chemical preparation of the PCl_5(c) modification, *viz* $2PCl_4^+.PCl_6^-.Cl^-$, is described; the significance of lattice single-halide ions in this and other phosphorus(v) species is noted.

Very recently, Whalley *et al.*[1–3] reported that, under high pressure, phosphorus(v) chloride can exist as $2PCl_4^+.PCl_6^-.Cl^-$ (phase III), in distinction from the normal, and abundantly confirmed, $PCl_4^+.PCl_6^-$ (phase II). They speculated that this example of a complex halide → single halide dissociation, *viz* $PCl_6^- \rightarrow PCl_4^+ + 2Cl^-$, may not be unique, but representative of a general class of solid-state reactions, with important implications for inorganic chemistry. Here we (i) present evidence for a facile synthesis of phase III by chemical means, *without* application of high pressure, (ii) cite differential scanning calorimetric evidence for the phase III → phase II conversion, (iii) comment on other phosphorus(v) halogen compounds in which the existence of single halide ions is a necessary assumption, and (iv) report the results of preliminary lattice energy calculations on different forms of PCl_5.

(i) We have observed the production of phase III when PCl_5 is recrystallized from dichloromethane solutions containing Br_2 (but not Cl_2) or SCl_2; chemical analyses confirm the stoicheiometry as PCl_5. Raman spectra of samples of phase III (Figure) are identical to those obtained elsewhere using samples produced *via* high pressure[1–3] or sublimation methods.[4–7] The main characteristic of the phase III spectrum is the large reduction in intensity of the PCl_6^- bands, relative to those from PCl_4^+, qualitatively

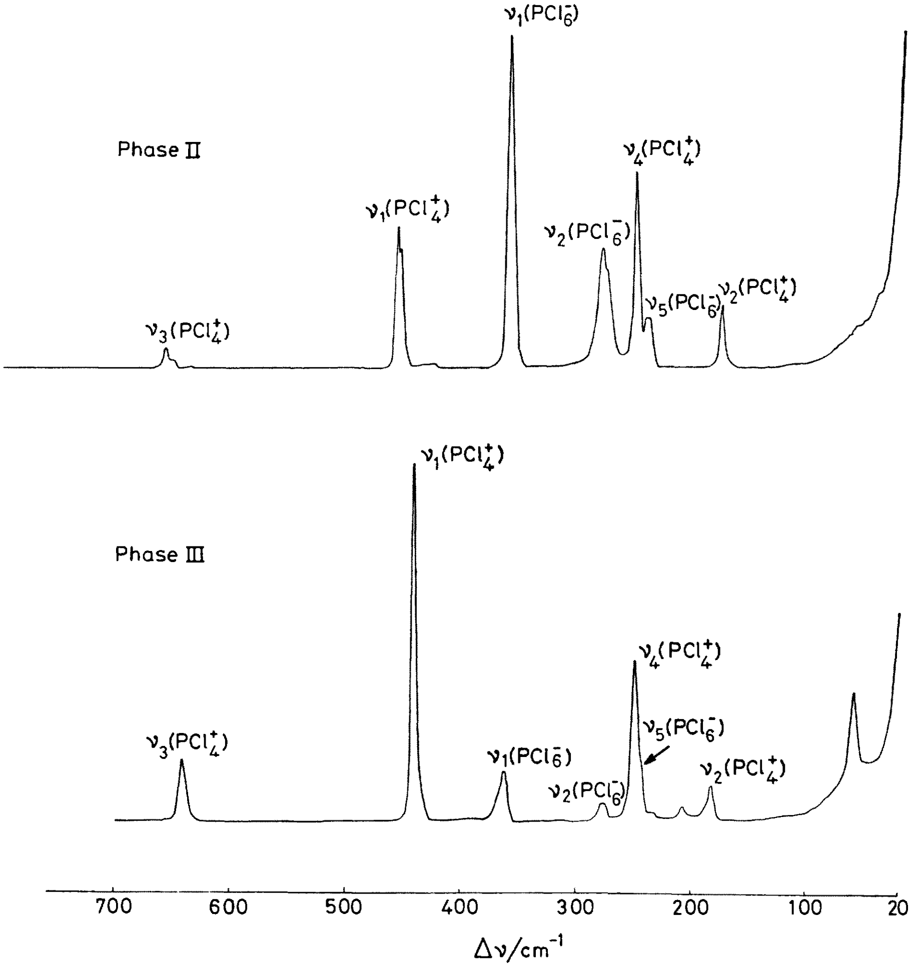

Figure. Raman spectra of PCl_5: phase II and phase III.

consistent with the ratio $PCl_4^+ : PCl_6^-$ 2:1 suggested by solid state ^{31}P n m r spectroscopic measurements [1] Furthermore, significant (*ca* 20 cm^{-1}) low-frequency shifts of the ν_1 (a_1) and the ν_3 (t_2) cation modes, compared with those of phase II, are evident

(ii) Phase III is, in all preparations, metastable with respect to phase II, as is shown by the gradual reversion of the Raman spectra, which is slow on standing and faster on heating Additional evidence was obtained by differential scanning calorimetry using sealed pans (Perkin Elmer D S C, Model 1B) Within the range 40 to 165 °C two transitions were observed during a first scan of samples of phase III a reversible endotherm near 111 °C, resembling a similar endotherm noted in samples of phase II,[8] and an irreversible exotherm near 130 °C Re-running of such samples through a similar temperature range reproduced the lower, endothermic scan, but not the exothermic, hence it is reasonable to associate the latter with the phase III → phase II transition The general absence of exotherms at this stage, and at all stages with phase II, is good evidence for the general integrity of the system, since attack of the aluminium pans by combined or free chlorine or by hydrogen chloride from adventitious moisture, would lead to observable exotherms However, experimental difficulties are severe Measurements are further complicated by continuous sublimation and also by dissociation into phosphorus(III) chloride and chlorine The absence of unequivocal evidence either for complete conversion or for the purity of phase II makes quantification impossible

(iii) The frequency shifts noted in (i) are important We have previously observed similar shifts in other phosphorus-(v) halogen systems, *e g* the series $PCl_nBr_{4-n}^+$ $(0 \leqslant n \leqslant 3)$[9] and the compound P_2Cl_9Br [10] For the latter, available evidence indicates a face-centred cubic lattice structure involving PCl_4^+, PCl_3Br^+, and PCl_6^- ions, tentatively formulated as $6PCl_4^+\ 2PCl_3Br^+\ 4PCl_6^-\ 4Br^-$, *i e* with the ratios $PX_4^+ : PCl_6^- : Cl^-$ 2:1:1,[10] analogous to that suggested for phase II More importantly, the patterns of shifts in the frequencies of the Raman bands of both PCl_3Br^+ and PCl_4^+ in P_2Cl_9Br are analogous to that observed in phase III [10] The shifts thus appear to be associated with the presence of single halide ions in the lattice, other examples are known[9] and it is clear that the phenomenon is not rare

(iv) Using a recently developed potential energy minimisation procedure,[11-13] calculations of the lattice energies of phase II and phase III, U_{II} and U_{III}, respectively, have given estimates of *ca* 232 and *ca* 370·4 kJ mol^{-1}, respectively Equations (1) and (2) may be derived and, since

$$\tfrac{1}{2}\Delta H_f^\ominus(PCl_4^+)(g) + \tfrac{1}{2}\Delta H_f^\ominus(PCl_6^-(g) = U_{II} + RT + \Delta H_f^\ominus(PCl_5)(c) \qquad (1)$$

$$\tfrac{2}{3}\Delta H_f^\ominus(PCl_4^+)(g) + \tfrac{1}{3}\Delta H_f^\ominus(PCl_6^-)(g) + \tfrac{1}{3}\Delta H_f^\ominus(Cl^-)(g) = U_{III} + \tfrac{5}{6}RT + \Delta H^{II\rightarrow III}_{transition} + \Delta H_f^\ominus(PCl_5)(c) \qquad (2)$$

$\Delta H^{II\rightarrow III}_{transition} = 2{\cdot}4$ kJ mol^{-1},[2] values of $\Delta H_f^\ominus(PCl_4^+)(g)$ and $\Delta H_f^\ominus(PCl_6^-)(g)$ may be computed These values are key data in the thermodynamic description of the numerous salts containing the tetrachlorophosphonium and hexachlorophosphate ions Such calculations are in progress, and will be reported elsewhere

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[1] J A Ripmeester, P T T Wong, D W Davidson, and E Whalley, *J Chem Phys* , 1979, **70**, 5545

[2] R Cahay and E Whalley, *J Chem Phys* , 1979, **70**, 5534

[3] R Cahay, P T T Wong, and E Whalley, *J Chem Phys* , 1979, **70**, 5539

[4] A I Popov, D H Geske, and N C Baenziger, *J Am Chem Soc* , 1956, **78**, 1793

[5] H Chihara, M Nakamura, and K Masukane, *Bull Soc Chem Jpn* , 1967, **40**, 50

[6] S G Shore and H Knachel, personal communication

[7] R Baumgartner, W Sawodny, and J Goubeau, *Z Anorg Chem* , 1966, **333**, 171

[8] H Moureu, M Magat, and G Wetroff, *C R Acad Sci* , 1937, **205**, 545

[9] A Finch, P N Gates, F J Ryan, and F F Bentley, *J Chem Soc* , *Dalton Trans* , 1973, 1863

[10] F F Bentley, A Finch, P N Gates, F J Ryan, and K B Dillon, *J Inorg Nucl Chem* , 1974, **36**, 457.

[11] H D B Jenkins and K F Pratt, *Comput Phys Commun* , to be published

[12] H D B Jenkins and K F Pratt, *Proc R Soc London, Ser A*, 1977, **356**, 115

[13] H D B Jenkins and K F Pratt, *J Chem Soc* , *Faraday Trans* 2, 1978, 968