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COMMUNICATION

PREPARATION AND SPECTROSCOPIC CHARACTERIZATION OF CAESIUM HEXACHLOROPHOSPHATE

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Abstract—The first alkali-metal hexachlorophosphate, $Cs^+PCl_6^-$, was prepared and characterized by elemental analysis, solid-state ^{31}P NMR, IR and Raman spectroscopies. The thermodynamic stability of alkali-metal hexachlorophosphates is briefly discussed.

The hexafluorophosphate and hexachlorophosphate anions are both well-known and have been characterized as essentially octahedral species by X-ray diffraction[1,2] and a variety of spectroscopic techniques.[3,4] However, the hexabromophosphate anion is unknown, as indeed is the trigonal bipyramidal (molecular) form of PBr_5: this presumably results from steric factors. Mixed chlorofluorophosphate anions have also been reported, as well as a variety of pseudo halogen-substituted anions: ^{31}P and ^{19}F NMR spectroscopy have proved particularly useful in identifying such species in solution.[5–10] Alkali-metal hexafluorophosphates have been known for some time[11] but until now hexachlorophosphates were only known with large polyatomic cations[4,12,13] and *none* of the related alkali-metal salts have been reported. Thermodynamic calculations for the decomposition reactions [eq. (1)] using the Kapustinskii–Yatsimirskii approach have indicated that such species are of borderline stability,[12,13] with values of $\Delta G_R^{\ominus}$ for $K^+PCl_6^-$ and $Cs^+PCl_6^-$ of *ca* -38 and -6 kJ mol^{-1}, respectively.

$$MPCl_6(c) \longrightarrow MCl(c) + PCl_5(c) \quad (M = K, Cs) \qquad (1)$$

EXPERIMENTAL

All manipulations were carried out in an atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used without further purification, although CsCl, RbCl and KCl were dried by warming to *ca* 100°C *in vacuo* for several hours. $Cs^+PCl_6^-$ was prepared typically as follows: hydrogen chloride gas (dried by passage through concentrated H_2SO_4) was condensed onto a mixture of CsCl (2.00 g, 1.20×10^{-2} mol) and $PCl_4^+PCl_6^-$ (2.50 g, 1.19×10^{-2} mol) by immersing the reaction vessel in liquid nitrogen. HCl liquefaction was achieved by warming to *ca* -95°C with a toluene/nitrogen slush-bath and the reaction mixture was agitated for 15 min. The HCl was then permitted to evaporate over $2\frac{1}{2}$ h by controlled warming. The resulting off-white solid was dried by pumping. Chlorine was analysed by potentiometric titration: Found: Cl, 56.3. $CsPCl_6$ requires: Cl, 56.5%.

Raman spectra were recorded using a Coderg PHO spectrometer with excitation at 514.5 nm provided by a Coherent Radiation Argon Ion laser; samples were contained in sealed capillaries. IR spectra were recorded using a Perkin–Elmer 983 spectrometer; CsI plates were used and samples were prepared either as Nujol mulls or as finely-ground solids. Solid-state MAS ^{31}P NMR spectra were recorded using a Bruker MSL 300 spectrometer operating at 121.5 MHz.

RESULTS AND DISCUSSION

The IR and Raman wavenumbers obtained for $Cs^+PCl_6^-$ are presented in Table 1, along with appropriate data for some previously known hex-

Table 1. IR and Raman spectroscopic data (cm^{-1}) for some hexachlorophosphates

		Modes					
Complex	Reference	$\nu_1(A_{1g})$	$\nu_2(E_g)$	$\nu_3(T_{1u})$	$\nu_4(T_{1u})$	$\nu_5(T_{2g})$	$\nu_6(T_{2u})$
$Cs^+PCl_6^-$	Current study	359(s)	268 277 (m)	440(vs)	286(w)	250 240 (m)	Inactive
$PCl_4^+PCl_6^-$	Current study	360(s)	279(m)	N.R.	N.R.	240(w)	Inactive
$Et_4N^+PCl_6^-$	4	360(s)	283(m/w)	444(vs)	285(w)	238(w)	Inactive
$pyH^+PCl_6^-$	4	357(s)	275(m)	444(vs)	285(w)	240(w)	Inactive

N.R. = not recorded.

achlorophosphates. The agreement is good although there are some small shifts: for an octahedral MX_6^- species three Raman active (A_{1g}, E_g, T_{2g}) and two IR (T_{1u}) modes are predicted and observed. The Raman spectrum is shown in Fig. 1 and some splittings are seen in the degenerate modes: E_g (268 and 277 cm^{-1}) and T_{2g} (250 and 240 cm^{-1}). The IR spectrum recorded as a Nujol mull showed additional bands at 588 and 336 cm^{-1} due to $POCl_3$ impurities arising from sample

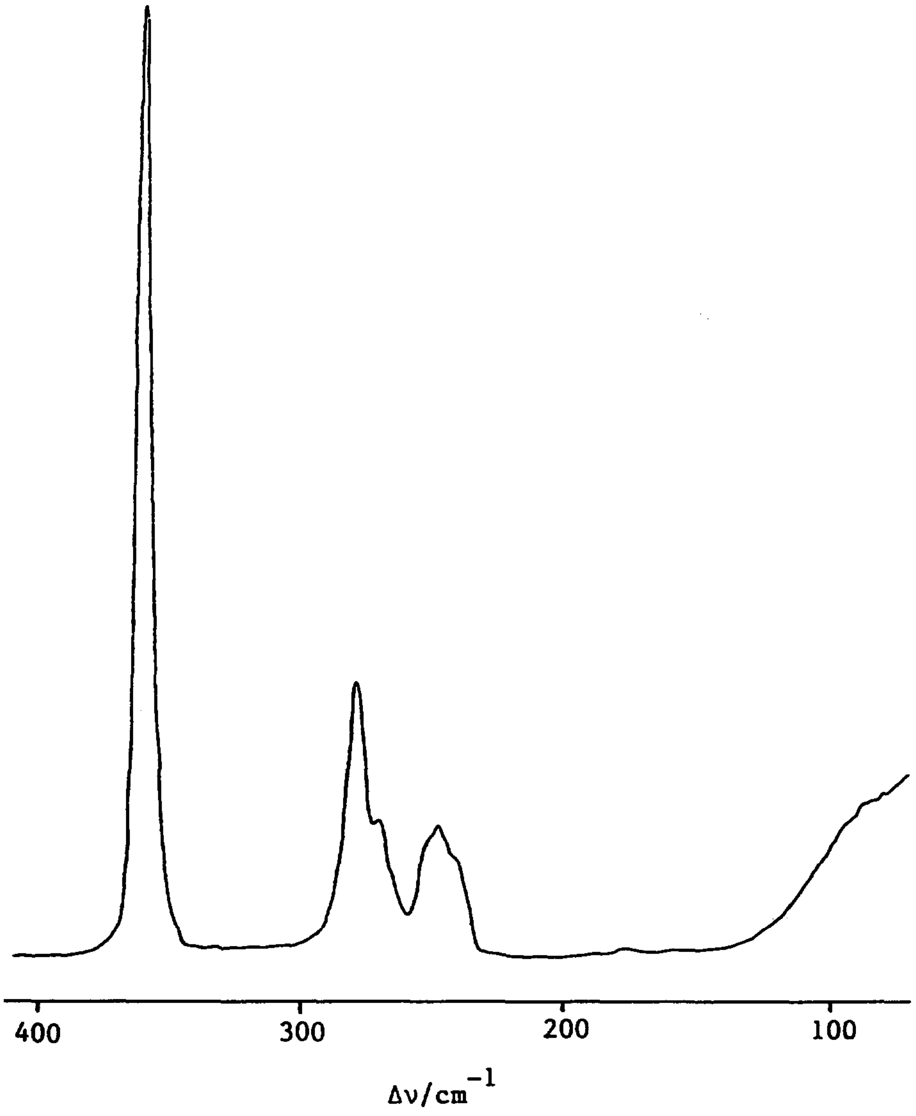

Fig. 1. Raman spectrum of $Cs^+PCl_6^-$.

decomposition, although these did not obscure the PCl_6^- modes at 440 and 286 cm^{-1}. The ^{31}P MAS NMR spectrum of $Cs^+PCl_6^-$ showed a single resonance at -294.7 ppm ($\Delta\nu_{1/2} = 30$ Hz) in accord with previous measurements of hexachlorophosphate salts.[14] The relatively narrow line width is consistent with considerable ionic motion within the system.

When a sample of $Cs^+PCl_6^-$ sealed in a long (6 cm) capillary tube was heated to *ca* 220°C for 1 h in a melting point apparatus, a sublimate was observed at the cool end of the tube: the Raman spectrum of this showed bands at 178, 242, 253, 279, 359, 457 and 656 cm^{-1} indicative of phosphorus pentachloride[15] as confirmed by comparison with the spectrum of an authentic sample of $PCl_4^+PCl_6^-$. No Raman signals were obtained from the residue; thus, the decomposition in Eq. (2) may be predicted.

$$Cs^+PCl_6^-(c) \xrightarrow{\Delta} \underset{\text{residue}}{CsCl(c)} + [PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)] \longrightarrow \underset{\text{sublimate}}{PCl_4^+PCl_6^-(c)} \quad (2)$$

However, all attempts to prepare the analogous $K^+PCl_6^-$ and $Rb^+PCl_6^-$ salts by a similar process involving anhydrous HCl failed, yielding only the starting materials, although a similar reaction between CsF and PCl_2F_3 in acetonitrile at ambient temperature has been shown[6] to yield the salt $Cs^+PCl_4F_2^-$ in admixture with $Cs^+PF_6^-$. This reflects the calculated borderline thermodynamic stability for the alkali-metal hexachlorophosphates and suggests that the stability of $Cs^+PCl_6^-$ derives from kinetic factors. Moreover, on the basis of cation size, the failure to isolate either a potassium or rubidium salt indicates that the title compound is probably unique as a metallic hexachlorophosphate.

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REFERENCES

1. H. Bode and H. Clausen, *Z. Anorg. Allg. Chem.* 1951, **265**, 229.
2. H. Preiss, *Z. Anorg. Allg. Chem.* 1971, **380**, 51.
3. G. M. Begun and A. C. Rutenberg, *Inorg. Chem.* 1967, **6**, 2212.
4. I. R. Beattie, T. Gilson, K. Livingston, V. Fawcett and G. A. Ozin, *J. Chem. Soc. A* 1967, 712.
5. K. B. Dillon, R. J. Lynch, R. N. Reeve and T. C. Waddington, *J. Inorg. Nucl. Chem.* 1974, **36**, 815 and refs therein.
6. H. W. Roesky, *Angew. Chem. Int. Edn* 1967, **6**, 363.
7. Y. A. Buslaev, E. G. Il'in and M. N. Shcherbakova, *Dokl. Akad. Nauk S.S.S.R. Ser Khim.* 1984, **219**, 1154 and refs therein.
8. L. Kolditz, I. Beierlein, W. Wieker and A. R. Grimmer, *Z. Chem.* 1968, **8**, 226.
9. K. B. Dillon and A. W. G. Platt, *J. Chem. Soc., Dalton Trans.* 1983, 1159 and refs therein.
10. K. B. Dillon and A. W. G. Platt, *J. Chem. Soc., Chem. Commun.* 1983, 1089.
11. D. E. C. Corbridge, *Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, 2nd edn., Elsevier, Amsterdam (1980).
12. H. D. B. Jenkins, K. P. Thakur, A. Finch and P. N. Gates, *Inorg. Chem.* 1982, **21**, 423.
13. A. Finch, P. N. Gates, S. I. Nwankwo and M. Stephens, *Thermochim. Acta* 1980, **41**, 387.
14. K. B. Dillon, P. N. Gates, R. K. Harris, A. S. Muir and A. Root, *Spectrochim. Acta A* 1991, **47**, 831.
15. A. Finch, P. N. Gates, H. D. B. Jenkins and K. P. Thakur, *J. Chem. Soc., Chem. Commun.* 1980, 579.