Preparation of $AsF_4^+PtF_6^-$ containing the Tetrafluoroarsenic(v) Cation

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The AsF_4^+ cation which represents the last missing member in the series of the tetrahalogenoarsenic(v) cations has been prepared by the reaction of Pt, AsF_5 and F_2 under electrical resistance heating of the platinum wire.

All of the tetrahalogenoarsenic(v) cations, $AsCl_4^+$,[1,2] $AsBr_4^+$[3,4] and AsI_4^+,[5] have been prepared and characterized except AsF_4^+. This led naturally to the attempted synthesis of a salt of the tetrafluoroarsenic(v) cation. However, all of our systematic attempts to prepare a BF_4^- (UV photolysis of BF_3, F_2 and AsF_3 at −196 °C),[6] a BiF_6^- (reaction of BiF_5 and AsF_5 at 250 °C)[6] or a $SbCl_6^-$ salt [eqns. (1) and (2)] were unsuccessful. In fact we were surprised to find that $AsCl_4^+$ had been formed quantitatively in reactions (1) and (2).[6]

$$AsF_3 + ClF + SbCl_5 \rightarrow AsCl_4^+SbCl_2F_4^- \qquad (1)$$

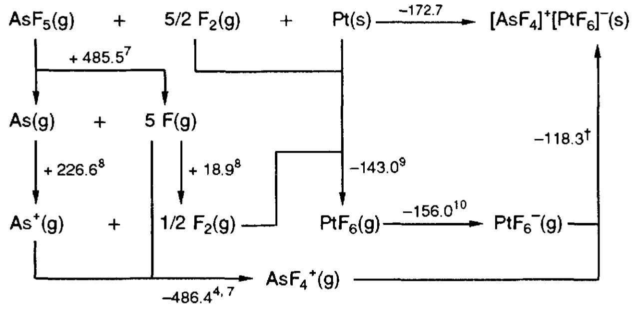
$$3\ AsF_3 + ClF_3 + Cl_2 + 3\ SbCl_5 \rightarrow 3\ AsCl_4^+SbCl_2F_4^- \qquad (2)$$

We estimated that the reaction of PtF_5 with AsF_5 (see below) and the reaction of Pt, F_2 and AsF_5 [eqn. (3)] are both

Table 1 Raman (647.09 nm, 20 °C, 20 mW) and IR (pure powder between Si discs) data of $AsF_4^+PtF_6^-$, GeF_4,[14] $AsCl_4^+SbCl_2F_4^-$,[6] $GeCl_4$[14] and PtF_6^- (XeF^+ salt)[15] (cm^{-1})

$AsF_4^+PtF_6^-$			$AsCl_4^+(SbCl_2F_4)^-$ [6,a]		$(XeF^+)PtF_6^-$ [15]	
Raman	IR	GeF_4[14]	Raman	$GeCl_4$[14]	Raman	Assignment
748 (7)		738[b]	422 (10)	397		ν_1
272 (5)		205[c]	156 (7)	125		ν_2
825 (3)	810m,br	800[d]	500 (5)	459		ν_3
287 (3)	287sh	260[e]	187 (6)	171		ν_4
656 (10)					655 (10)	ν_1
593 (2)					592 (2)	ν_2
571 (2)					580 (2)	
	570m					ν_3
	268s					ν_4
244 (2)					246 (1)	ν_5
238 (3)					230 (2)	

[a] $AsCl_4^+$ frequencies correspond to those of $AsCl_4^+$ from refs. 1, 2 and 14. [b] Raman, ν_1 = 738 (10).[16] [c] Calc. from IR combination bands, ν_2 = 205 ± 5 cm^{-1}.[16] [d] IR, ν_3 = 800vvs.[16] [e] IR, ν_4 = 260vvs.[16]



Scheme 1 Energy cycle for the formation of $AsF_4^+PtF_6^-$ (kcal mol^{-1})

thermodynamically allowed on the basis of a simple Born–Haber cycle (Scheme 1).

$$Pt + AsF_5 + 5/2\ F_2 \rightarrow AsF_4^+PtF_6^- \qquad (3)$$

Subsequently we prepared $AsF_4^+PtF_6^-$ using an apparatus as shown in Fig. 1 and identified the yellow salt by Raman and infrared spectroscopy (Table 1). In a typical reaction the Pt wire (0.200 g, 1.03 mmol) was heated to red heat and reacted with an excess of a 5:2 F_2–AsF_5 (AsF_5, 1.2 mmol; F_2, 4.2 mmol) mixture. A yellow solid formed and was transferred into the Raman capillary while all remaining volatile species were removed under dynamic vacuum.

The Raman and infrared data of the product showed $AsF_4^+PtF_6^-$ to be present (Table 1). The part of the Raman spectrum assigned to AsF_4^+ consists of four bands which are very similar in intensity and relative position to those observed for $AsCl_4^+$[1,2] and the isoelectronic GeF_4,[14] and is consistent with its possessing T_d geometry.

The heat of formation of $AsF_4^+PtF_6^-$ was estimated from the heat of reaction eqn. (2) (*cf.* Scheme 1) and the heat of the formation of AsF_5 (−295.6 kcal mol)[17] to be −468 kcal mol^{-1} (1 cal = 4.184 J). The decomposition according to eqn. (4) is therefore seen to be thermodynamically unfavourable (ΔH_4 = +42.7 kcal mol^{-1}; $\Delta_f H°$, PtF_5 (g) = −130.0 kcal mol^{-1}).[9]

$$AsF_4^+PtF_6^-(s) \rightarrow AsF_5(g) + PtF_5(g) \qquad (4)$$

Under an inert-gas atmosphere $AsF_4^+PtF_6^-$ is stable at room temperature and melts under decomposition at 108 ± 5 °C. With water, however, the compound reacts violently and hydrolyses often under the appearance of fire. The yellow solution in HSO_3F shows a rather broad absorption from 470 nm downwards with a maximum of $\lambda \leq 350$ nm. As the cut-off by the used cell was at 300 nm the expected shoulder at approximately 280 nm could not be observed (*c.f.* $KPtF_6$, λ = 400, 280 nm). In the mass spectrum (E.I., 70 eV, 80 °C) besides the very strong peaks (rel. intensity 80–100%) of PtF_n^+ (n = 0,1,...6) only signals owing to PtF_m^{2+} (m = 0,1,2,3), AsF_3^+ and AsF_2^+ (5–15%) could be detected. A qualitative magnetic measurement showed the compound to be paramagnetic, however, owing to the extreme sensitivity towards air and moisture an accurate scale had not yet been possible.

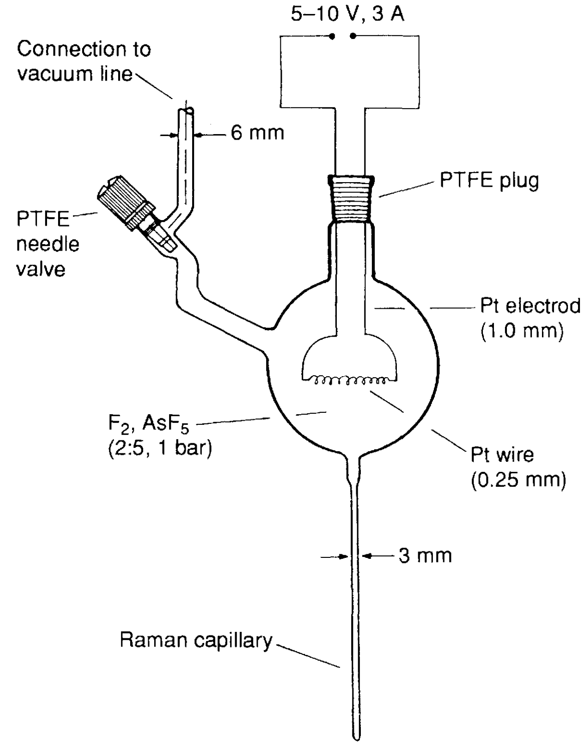


Fig. 1 Reaction vessel used for the preparation of $AsF_4^+PtF_6^-$; [PTFE = poly(tetrafluoroethylene); 1 bar = 10^5 Pa]

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† U_L calculated from the molecular volume V_M ($Å^3$) using the linear relationship: U_L (kcal mol^{-1}) = 556.3 $(V_M)^{-0.33}$ + 26.3;[11,12] $V_M(PtF_6^-)$ was taken to be equal to $V_M(PtF_6)$ = 105 $Å^3$,[10] $V_M(AsF_4^+)$ was taken to be equal to $V_M(GeF_4)$ = 116 $Å^3$ (d = 2.176 g cm^{-3}).[13] This gives U_L ($AsF_4^+PtF_6^-$) = −118.3 kcal mol.

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