

The SiF_5^- Ion and Evidence for the Existence of GeF_5^-

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WE have recently mentioned¹ the stabilization of the SiF_5^- ion by the large cation *trans*-(Et_3P)₂- $\text{PtCl}(\text{CO})^+$. It is now clear that this anion can easily be obtained, and it is most surprising that it has not been obtained sooner. Reaction of a 1:1 molar mixture of Ph_4AsCl and SiO_2 in aqueous methanolic HF results in the formation of tetraphenylarsonium pentafluorosilicate. The compound is characterized by elemental analyses (totalling 100% composition) and by its infrared spectrum (4000—300 cm^{-1}) which in addition to bands due to the Ph_4As^+ cation, has absorptions at 925w, 915vw, 875b, vs, 790 vs, 770 vs, and 445s cm^{-1} . The 480 cm^{-1} region is obscured by cation absorptions in the arsonium salt but the spectra of Et_4NSiF_5 , obtained in an impure form by a similar method, and of *trans*-(Et_3P)₂- $\text{PtCl}(\text{CO})\text{SiF}_5$ ¹ indicate that the SiF_5^- ion has another absorption at 480 cm^{-1} . This spectrum is quite unlike that of the more usual SiF_6^{2-} ion which has strong absorptions at about 740 and 480 cm^{-1} . The exact frequencies of these SiF_6^{2-} absorptions are dependent on the cation and they are sometimes split by the symmetry effects² but such effects are too small to

account for the spectrum attributed above to SiF_5^- .

A 10^{-3}M -solution of $\text{Ph}_4\text{AsSiF}_5$ in nitromethane at 25° has a conductivity of 82 ohms⁻¹ cm.² which may be compared with 90 ohms⁻¹ cm.² for Ph_4AsBF_4 under the same conditions.

A similar reaction using GeO_2 instead of SiO_2 results in formation of a compound for which elemental analyses (totalling 100% composition) give the atomic ratio Ge:F = 1.04:5.00. The infrared spectrum (4000—300 cm^{-1}) of this material has, in addition to bands due to the Ph_4As^+ cation, absorptions at 650s, 635s, 575s, 560s, and 325s. This spectrum is similar to that attributed to SiF_5^- and is quite unlike the spectrum² of GeF_6^{2-} which has strong absorptions at about 600 and 350 cm^{-1} . The evidence indicates that GeF_5^- may be present.

The results do not unambiguously exclude the possibility of polymeric, fluorine-bridged species in the solid state but a single-crystal X-ray study of $\text{Ph}_4\text{AsSiF}_5$ at present in progress under the direction of Dr. J. A. Ibers at Northwestern University, Illinois, should resolve this point.

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¹ H. C. Clark, P. W. R. Corfield, K. R. Dixon, and James A. Ibers, *J. Amer. Chem. Soc.*, in the press.

² D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1967, 100.