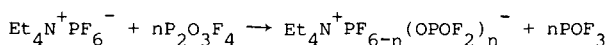


DIFLUOROPHOSPHATOFLUOROPHOSPHATES(V): SYNTHESIS AND CHARACTERISATION BY ¹⁹F AND ONE- AND TWO-DIMENSIONAL ³¹P NMR SPECTROSCOPY

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The difluorophosphate ligand -OPOF₂ exhibits a high effective group electronegativity, as demonstrated by the stability (albeit marginal) of the xenon(II) derivatives Xe(OPOF₂)₂ and FXeOPOF₂ at 22°C (M. Eisenberg and D.D. Desmarteau, *Inorg.Chem.*, 1972, 11, 1901). Yet, in spite of this, the ligand remains virtually unstudied in terms of derivative chemistry. Only recently have the first anionic species B(OPOF₂)₄⁻ (M.F.A. Dove, R.C. Hibbert and N. Logan, *J.Chem.Soc. Dalton*, 1984, 2719) and MF₅(OPOF₂)⁻, where M = P, As and Sb, (E.G. Il'in, M. Maizel, M.N. Shcherbakova, G.U. Volf and Yu.A. Buslaev, *Dokl.Akad.Nauk.*, SSSR, 1982, 266, 878), been reported. The chemistry of this interesting ligand has been extended to include other members of the octahedral PF_n(OPOF₂)_{6-n}⁻, n = 2-5, anion series. Thus, the normally 'inert' PF₆⁻ anion reacts readily with P₂O₃F₄ at room temperature according to the equation



The composition of the mixture of anions produced depends on the duration of the reaction. The anions have been characterised in solution by ³¹P and ¹⁹F NMR spectroscopy. Two-dimensional ³¹P COSY NMR experiments have been invaluable in assigning the connectivities between the -OPOF₂ ligand resonances and the six coordinate central phosphorus resonances. NMR demonstrates the existence of large proportions of the trans-isomer for PF₄(OPOF₂)₂⁻ and PF₂(OPOF₂)₄⁻ and of the mer-isomer for PF₃(OPOF₂)₃⁻. This observation is unusual since cis isomers are normally observed in mixed octahedral systems with monoatomic ligands, e.g. PF_nCl_{6-n}⁻ (Yu.A. Buslaev, E.G. Il'in and M.N. Shcherbakova, *Dokl.Akad.Nauk.*, SSSR, 1974, 217, 317). The size of the -OPOF₂ ligand and mutual repulsion between ligands may be the cause of this.