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Journal of Fluorine Chemistry 71 (1995) 205

JOURNAL OF FLUORINE CHEMISTRY

An excursion into phosphorus–fluoride chemistry, $N(CH_3)_4PF_4$, $[POF_2]^-$ and $M^+HPF_5^-$

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Keywords: Tetramethylammonium phosphorus tetrafluoride; X-Ray diffraction studies; Hydrolysis; Methanolysis; NMR spectroscopy; IR spectroscopy

$N(CH_3)_4^+PF_4^-$, the first example of a PF_4^- salt, has been prepared from $N(CH_3)_4F$ and PF_3 using either CH_3CN, CHF_3 or excess PF_3 as a solvent. The salt is a white, crystalline solid which is thermally stable up to 150 °C, where it decomposes to $N(CH_3)_3$, CH_3F and PF_3. It crystallizes in the tetragonal system, space group $P\bar{4}2_1m$, with two molecules in a unit cell of dimensions $a = 8.465(3)$ Å and $c = 5.674(2)$ Å with $R = 0.0564$ for 185 observed $[I \geqslant 2\sigma(I)]$ reflections. The structure can be derived from a cubic closest packing of tetrahedral $N(CH_3)_4^+$ cations and pseudo-trigonal bipyramidal PF_4^- anions. These anions possess two axial fluorine ligands and an equatorial plane which contains the remaining two fluorine ligands and one sterically active free valence electron pair. This plane is subject to a threefold disorder with unequal occupancy factors. Since the disorder involves a free valence electron pair which is shorter and more repulsive than the P–F bonds, the apparent equatorial P–F bond lengths are much too short and the apparent bond angles differ significantly from those predicted by the ab initio calculations for the free PF_4^- ion. However, good agreement between the apparent and calculated geometries can be reached by correction of the calculated geometry for the disorder effects. Hence, the geometry of the ordered, free PF_4^- ion must be very close to the calculated one. The calculated structure of ordered PF_4^- is similar to that of isoelectronic SF_4, but differs significantly from those found for the corresponding tetra-chlorides or -bromides which are deformed toward ionic $X^- \cdots MX_3$-type structures.

The hydrolysis and methanolysis of $N(CH_3)_4PF_4$ were studied by their material balances and multinuclear NMR and vibrational spectroscopy. With an equimolar amount of water in CH_3CN solution, PF_4^- forms HPO_2F^- and HPF_5^- in a 1:1 mole ratio. With an excess of water, HPO_2F^- is the sole product which was also obtained by the hydrolysis of HPF_5^-. In the presence of a large excess of F^-, the hydrolysis of PF_4^- with an equimolar amount of water produces POF_2^-. The resulting $N(CH_3)_4POF_2$ is the first known example of a stable POF_2^- salt. The geometries and vibrational spectra of POF_2^- and HPO_2F^- were calculated using local density functional theory, and normal coordinate analyses were carried out for POF_2^-, HPO_2F^- and the isoelectronic SOF_2 and HSO_2F molecules. The methanolysis of PF_4^- produces $PF_2(OCH_3)$ and $PF(OCH_3)_2$ as the main products.

The new HPF_5^- salt, $N(CH_3)_4HPF_5$, was prepared and the infrared and Raman spectra of $N(CH_3)_4HPF_5$ and $CsHPF_5$ recorded. The spectra were assigned with the help of ab initio molecular orbital and local density functional calculations, and a normal coordinate analysis was carried out. For comparison, the unknown isoelectronic molecule HSF_5 was also calculated by the same methods. The internal stretching force constants of HPF_5^- are compared to those of closely related phosphorus and sulfur fluorides and hydrides and confirm the existence of a *cis* effect in these hydrogen-substituted Main Group hexafluorides. The observed substitution effects are explained in terms of a hypervalent bonding scheme and result in a preferential weakening of the four equatorial *cis* bonds.

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SSDI 0022-1139(94)06026-6