

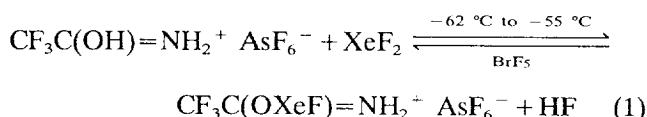
Synthesis and characterization of thermally unstable xenon(II)–nitrogen and xenon(II)–oxygen bonded cations

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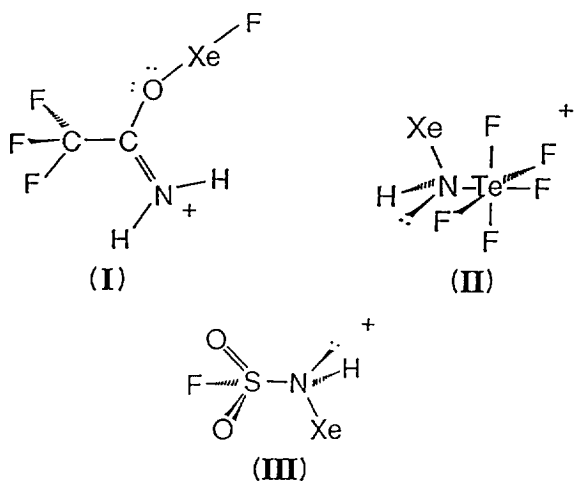
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The salt $\text{CF}_3\text{C}(\text{OH})=\text{NH}_2^+ \text{AsF}_6^-$ has been prepared from the reaction of $\text{CF}_3\text{C}(\text{O})\text{NH}_2$ with excess AsF_5 in HF solvent. In BrF_5 solvent it undergoes an HF elimination reaction with XeF_2 :



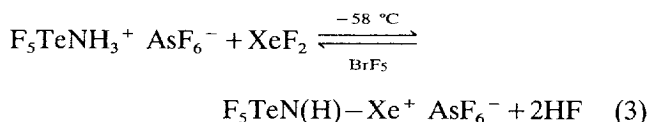
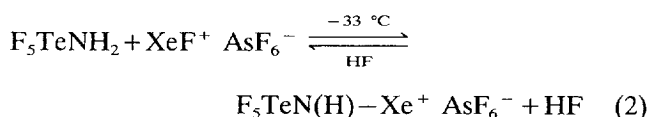
where $[\text{CF}_3\text{C}(\text{OXeF})=\text{NH}_2^+]/[\text{CF}_3\text{C}(\text{OH})=\text{NH}_2^+] = 0.32 \pm 0.03$ ($-60\text{ }^\circ\text{C}$). The ^1H , ^{19}F , ^{13}C and ^{129}Xe NMR spectra recorded in BrF_5 solvent were consistent with structure I for the $\text{CF}_3\text{C}(\text{OXeF})=\text{NH}_2^+$ cation [$\delta(^{129}\text{Xe}) = -1578$ ppm; $\delta(^{19}\text{F}) = -183.1$ (F-on-Xe^{II}) ppm; $^1J(^{129}\text{Xe}-^{19}\text{F}) = 5991$ Hz]. Hindered rotation about the C=N double bond rendered the NH_2 protons non-equivalent in the ^1H NMR spectrum.



The reaction of equimolar amounts of $\text{XeF}^+ \text{AsF}_6^-$ and $\text{CF}_3\text{C}(\text{O})\text{NH}_2$ in HF solvent followed by removal of the solvent under vacuum at $-50\text{ }^\circ\text{C}$ resulted in a white polycrystalline solid exhibiting a Raman spectrum

($-165\text{ }^\circ\text{C}$) consistent with the formulation $\text{CF}_3\text{C}(\text{OXeF})=\text{NH}_2^+ \text{AsF}_6^-$.

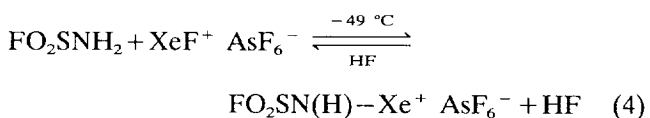
The 99% ^{15}N -enriched $\text{F}_5\text{TeN}(\text{H})-\text{Xe}^+$ cation was prepared in HF and BrF_5 solvents:



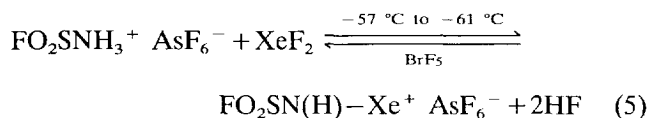
where the ratio $[\text{F}_5\text{TeN}(\text{H})-\text{Xe}^+]/[\text{F}_5\text{TeNH}_3^+]$ was 0.26 ± 0.03 ($-33\text{ }^\circ\text{C}$) and 0.87 ± 0.09 ($-57.6\text{ }^\circ\text{C}$) in HF and BrF_5 solvents, respectively. Multi-NMR spectra (^1H , ^{19}F , ^{15}N , ^{125}Te and ^{129}Xe) in both solvents were consistent with structure II [$\delta(^{129}\text{Xe}) = -2840$ ppm (HF), -2902 (BrF₅); $^1J(^{129}\text{Xe}-^{15}\text{N}) = 138$ Hz]. The orange salt $\text{F}_5\text{TeN}(\text{H})-\text{Xe}^+ \text{AsF}_6^-$ has been isolated from HF solvent at -35 to $-40\text{ }^\circ\text{C}$ and characterized by Raman spectroscopy ($-165\text{ }^\circ\text{C}$).

Decomposition of the $\text{F}_5\text{TeN}(\text{H})-\text{Xe}^+$ cation produces Xe and the novel difluoramino F_5TeNF_2 , which has been characterized by ^{19}F and ^{15}N NMR spectroscopy. Decomposition of F_5TeNF_2 was rapid at $-20\text{ }^\circ\text{C}$ in HF solvent containing AsF_5 , producing TeF_6 and $\text{FN}\equiv\text{N}^+ \text{AsF}_6^-$; this is analogous to decompositions observed for several difluoramino compounds in the presence of SbF_5 and AsF_5 [1].

The ^{15}N -enriched (99%) $\text{FO}_2\text{SN}(\text{H})-\text{Xe}^+$ cation (III) has been prepared in HF and BrF_5 solvents and characterized by ^{19}F , ^1H and ^{129}Xe NMR spectroscopy [$\delta(^{129}\text{Xe}) = -2660$ ppm, $^1J(^{129}\text{Xe}-^{15}\text{N}) = 109$ Hz; $-61\text{ }^\circ\text{C}$ in BrF_5 solvent]



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where $[\text{FO}_2\text{SN(H)-Xe}^+]/[\text{FO}_2\text{SNH}_3^+] = 0.11 \pm 0.01$ ($-60.4\text{ }^\circ\text{C}$) in BrF_5 solvent.

The ^{129}Xe NMR chemical shifts of xenon(II) compounds and the magnitudes of the $^1J(^{129}\text{Xe}-^{19}\text{F})$ coupling constants can be used to assess the covalent characters of Xe-L bonds ($\text{L} = \text{F}, \text{O}, \text{N}, \text{C}$) [2]. NMR spectroscopic data indicate that the covalent characters of the Xe-O and Xe-F bonds in the $\text{CF}_3\text{C(OXeF)=NH}_2^+$ cation are similar to those of XeF_2 . The highly shielded ^{129}Xe NMR resonances for the $\text{F}_5\text{TeN(H)-Xe}^+$ and

$\text{FO}_2\text{SN(H)-Xe}^+$ cations indicate that they contain highly covalent Xe-N bonds. The bonding and decomposition reactions of these cations are analogous to those observed for the recently prepared arylxenonium(II) cations, which contain highly covalent Xe-C bonds [3].

References

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