

LEWIS ACID BEHAVIOR OF XENON(II) CATIONS AND THE SYNTHESIS AND CHARACTERIZATION OF FLUORO- AND OXOFUORO-XENON ANIONS AT THE LIMITS OF COORDINATION.

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By taking advantage of the Lewis acid properties of the XeF^+ and KrF^+ cations, it has been possible to prepare a diverse range of noble-gas adduct cations; F-Xe-L^+ , $\text{F-Kr-N}\equiv\text{CH}^+$ and $\text{F-Kr-N}\equiv\text{CR}_4^+$ ($\text{L} = \text{HC}\equiv\text{N}$, $\text{RC}\equiv\text{N}$, $\text{R}_f\text{C}\equiv\text{N}$, $\text{C}_5\text{F}_5\text{N}$, $\text{s-C}_3\text{F}_3\text{N}_3$). The adduct salts have stabilities which range from explosive at -60°C for $\text{F-Kr-N}\equiv\text{CH}^+\text{AsF}_6^-$ (the first example of a Kr-N bond), to stable at room temperature for $\text{s-C}_3\text{F}_3\text{N}_2\text{-Xe-F}^+\text{AsF}_6^-$ and have been characterized by multi-NMR spectroscopy and Raman spectroscopy. We have recently extended this work to the related noble-gas cations XeOTeF_5^+ and XeOSeF_5^+ , to yield the first examples of O-Xe-N linkages, and to the inorganic base $\text{F}_3\text{S}\equiv\text{N}$. The adduct cation $\text{F-Xe-N}\equiv\text{SF}_3^+$ undergoes successive additions of HF to the $\text{N}\equiv\text{S}$ bond in anhydrous HF to give the adduct cations F-Xe-N(H)=SF_4^+ and $\text{F-Xe-N(H}_2\text{)-SF}_5^+$. The $\text{F-Xe-N(H}_2\text{)-TeF}_5^+$ cation has also been synthesized.

The study of fluoro-anions having coordination numbers higher than six and, in particular, those involving at the same time free valence electron pairs, have recently received considerable interest. To a large extent, these studies have been greatly facilitated by the realization that anhydrous $\text{N(CH}_3)_4^+\text{F}^-$ is an excellent reagent for the preparation of novel, high-oxidation state complex fluoride or oxofluoride anions. We have recently synthesized $(\text{CH}_3)_4\text{N}^+\text{XeF}_5^-$ by the reaction of stoichiometric amounts of XeF_4 and $\text{N(CH}_3)_4^+\text{F}^-$ in dry CH_3CN . The salt was fully characterized by Raman spectroscopy, ^{19}F and ^{129}Xe NMR spectroscopy and X-ray crystallography. The XeF_5^- anion has a pentagonal planar (D_{5h}) structure with five equivalent fluorines and is of considerable significance as it represents the first example of an AX_5E_2 (E = valence electron lone pair) system.

The syntheses and structural characterization of other high-coordination number hypervalent fluoro- and oxofluoro- anions of xenon will also be discussed, i.e., XeF_5O^- , XeF_7^- , XeOF_3^- , XeO_2F_3^- .