The Fluoro(hydrocyano)krypton(II) Cation $[HC{\equiv}N{-}Kr{-}F]^+$; the First Example of a Krypton–Nitrogen Bond

Gary J. Schrobilgen

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

The first example of krypton bonded to an element other than fluorine has been provided by the synthesis of the novel $[HC{\equiv}N{-}Kr{-}F]^+$ cation, prepared as its AsF_6^- salt by low-temperature reaction of $HC{\equiv}NH^+AsF_6^-$ with KrF_2 in HF or BrF_5 as solvent, and characterized by low-temperature Raman spectroscopy and ^1H, ^{13}C, ^{15}N, and ^{19}F n.m.r. spectroscopy.

Numerous examples of xenon bonded to oxygen or fluorine and of xenon bonded to other highly electronegative inorganic ligands through oxygen are now known.[1] However, it is only within the last few years that the first examples of xenon bonded to an element other than fluorine or oxygen have been fully characterized. These are provided by the xenon–nitrogen bonded derivatives of the $-N(SO_2F)_2$[2–6] and $-N(SO_2CF_3)_2$[7] groups, and two recent reports of the XeF^+ cation nitrogen-bonded to $HC{\equiv}N$ and organo-nitrogen ligands (nitriles and perfluoropyridines).[8,9] Hitherto, no examples have been reported in which krypton is bonded to an element other than fluorine.

We have recently shown that XeF^+ forms relatively stable Lewis acid–base adduct cations with $HC{\equiv}N$,[8] nitriles,[8] and several perfluoropyridines[9] which are resistant to oxidation by XeF^+ at low temperatures. On the basis of photoionization studies, $HC{\equiv}N$ is oxidatively the most resistant ligand among the pyridines and nitriles we have investigated thus far (first ionization potential 13.59 eV).[10] In view of the estimated electron affinity of XeF^+ (10.9 eV) and our previous success in forming the xenon(II) cation $[HC{\equiv}N{-}Xe{-}F]^+$ as its AsF_6^- salt, the synthesis of the krypton(II) analogue was undertaken. The estimated electron affinity for KrF^+ (13.2 eV) suggested that $HC{\equiv}N$ might have at least a marginal resistance to oxidative attack by the KrF^+ cation and that $[HC{\equiv}N{-}Kr{-}F]^+$ might have sufficient thermal stability to permit its spectroscopic characterization.

Direct interaction of $KrF^+AsF_6^-$ with $HC{\equiv}N$ solutions in HF or BrF_5 solvent [as used for the xenon(II) analogue] was not attempted owing to the strongly oxidizing character of the KrF^+ cation towards $HC{\equiv}N$ and BrF_5 as well as its tendency to undergo autoredox reactions in both solvents. Instead, the interaction of less reactve KrF_2 with $HC{\equiv}NH^+AsF_6^-$ in HF was initially investigated. At −60 °C reaction of sparingly soluble $HC{\equiv}NH^+AsF_6^-$ with KrF_2 in HF led to instantaneous deposition of a white solid which, upon warming above −50 °C, rapidly began to evolve Kr, NF_3, and CF_4 gases. This was usually followed by a violent detonation and accompanying emission of white light. When these reactions were allowed to proceed at approximately −60 °C, the mixtures could be periodically quenched to −196 °C in order to study the development of the Raman spectrum of the product. Raman spectra were recorded for the solid under HF at −196 °C with 541.5 nm excitation. ^{19}F n.m.r. spectra were obtained by briefly warming the samples to −60 °C followed by rapid acquisition of the free induction decays with a high-field pulse instrument.

The Raman spectrum is consistent with the formation of the novel $[HC{\equiv}N{-}Kr{-}F]^+$ cation. In addition to strong lines arising from unreacted KrF_2 (465 and 122 cm^{-1}), an intense line at 560 (100) cm^{-1} attributable to a new Kr–F stretching mode was observed. The higher frequency of this line relative to that of the difluoride (465 cm^{-1}) is consistent with a more covalent Kr–F bond and parallels Xe–F stretching frequency increases observed for F–Xe–L compounds in general and those of the $HC{\equiv}N$ and nitrile cations in particular.[8] Despite the lower mass of the krypton atom, the Kr–F stretching frequency of $[HC{\equiv}N{-}Kr{-}F]^+$ is only slightly lower than the factor-group-split Xe–F stretching frequency of the xenon analogue [559 (100) and 569 (94)][8] and indicates that this Kr–F bond, like those of KrF_2, KrF^+, and $Kr_2F_3^+$,[11] is substantially weaker than in the xenon analogue. Two C≡N stretching frequencies were observed, at 2116 (8) and 2158 (41) cm^{-1}. The former is assigned to unreacted $HC{\equiv}NH^+AsF_6^-$, by comparison with the Raman spectrum of the pure solid. The C≡N stretch at 2158 (41) cm^{-1} is assigned to the $[HC{\equiv}N{-}Kr{-}F]^+$ cation and is similar to that of $[HC{\equiv}N{-}Xe{-}F]^+AsF_6^-$ (2161 cm^{-1}).[8] Vibrational bands associated with $\nu(Kr{-}N)$, $\nu(H{-}C)$, and $\delta(C{\equiv}N{-}Kr)$ are expected, by analogy with $[HC{\equiv}N{-}Xe{-}F]^+AsF_6^-$, to be weak and/or

Table 1. N.m.r. (^{19}F, ^{13}C, ^{15}N, and ^{1}H) parameters for the $[HC{\equiv}N{-}Kr{-}F]^+$ cation and related species.[a]

Species	δ(^{19}F)/p.p.m.[b]	δ(^{13}C)[b]	δ(^{15}N)/p.p.m.[b]	δ(^{1}H)/p.p.m.[b]	*J*/Hz[e]
$[HC{\equiv}N{-}Kr{-}F]^+$	99.4[c] (81.0)	98.5	−200.8	6.09[d]	$^{1}J(^{13}C{-}^{1}N)$ 312 $^{2}J(^{15}N{-}^{19}F)$ 26 $^{2}J(^{15}N{-}^{1}H)$ 12.2 $^{3}J(^{19}F{-}^{13}C)$ 25.0 $^{4}J(^{19}F{-}^{1}H)$ 4.2
KrF_2	63.9 (48.1)				
AsF_6^-	−62.6 (−69.1)[f]				
HF	−192.9 (−194.4)			6.71	$^{1}J(^{1}H{-}^{19}F)$ 520(519)
BrF_5	134.7[g] 271.9[h]				$^{2}J(^{19}F{-}^{19}F)$ 73

[a] Spectra were recorded in 4 mm (ext. diam.) FEP sample tubes at spectrometer frequencies (MHz): 235.36 (^{19}F), 50.70 (^{15}N), and 80.02 (^{1}H); BrF_5 solvent at −57 °C; values in parentheses are for spectra recorded with HF as solvent at −60 °C. [b] Samples were referenced externally at 24 °C with respect to the neat liquid references: $CFCl_3$ (^{19}F), $MeNO_2$ (^{15}N), and $SiMe_4$ (^{13}C, ^{1}H). A positive chemical shift denotes a resonance to high frequency of the reference. [c] Krypton isotopic shifts of 0.0138 p.p.m. per a.m.u. were observed for this resonance, corresponding to fluorine directly bonded to ^{82}Kr, ^{84}Kr, and ^{86}Kr. [d] The corresponding resonance in $HC{\equiv}NH^+$ occurs at 5.20 p.p.m. in BrF_5 as solvent at −57 °C. [e] Measured for samples containing 99.5% ^{15}N or 99.2% ^{13}C. [f] Linewidths at half-height were 1840 (HF) and 2190 Hz (BrF_5); the AsF_6^- resonance in BrF_5 exhibited the saddle-shaped structure of a partially quadrupole-collapsed 1:1:1:1 quartet arising from $^{1}J(^{75}As{-}^{19}F)$. [g] Doublet. [h] Quintet.

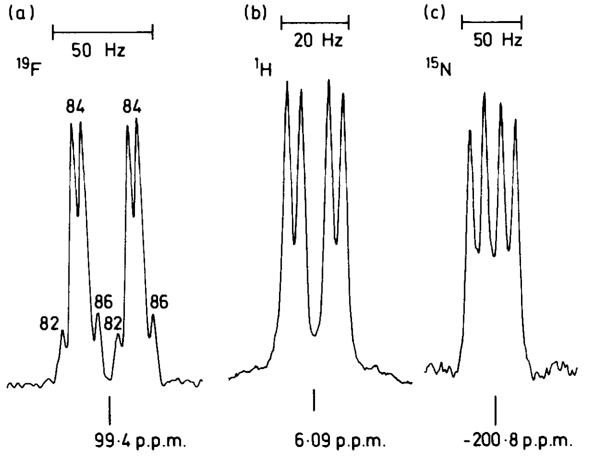

Figure 1. N.m.r. spectra of the $[HC{\equiv}N{-}Kr{-}F]^+$ cation enriched to 99.5% with ^{15}N, in BrF_5 as solvent at −57 °C. (a) ^{19}F Spectrum (235.36 MHz) depicting $^{2}J(^{19}F{-}^{15}N)$ and $^{4}J(^{19}F{-}^{1}H)$ and krypton isotope shifts. Lines assigned to fluorine bonded to ^{82}Kr (11.56%), ^{84}Kr (56.90%), and ^{86}Kr (17.37%) are denoted by the krypton mass number. The innermost lines of the ^{82}Kr and ^{86}Kr doublets overlap their corresponding ^{84}Kr doublets. The isotopic shift arising from ^{83}Kr (11.53%) is not resolved; those of ^{78}Kr (0.35%) and ^{80}Kr (2.27%) are too weak to be observed. (b) ^{1}H Spectrum (80.02 MHz) depicting $^{2}J(^{15}N{-}^{1}H)$ and $^{4}J(^{19}F{-}^{1}H)$. (c) ^{15}N Spectrum (50.70 MHz) depicting $^{2}J(^{19}F{-}^{15}N)$ and $^{2}J(^{15}N{-}^{1}H)$.

broad and cannot yet be assigned with certainty. The doubly degenerate bending mode, δ(F–Kr–N), is expected to be intense but is presumably obscured by the intense KrF_2 line at 122 cm^{-1}. Frequencies associated with the octahedral anion AsF_6^- were observed at 684 (36) [$\nu_1(a_{1g})$], 587 (16) [$\nu_2(e_g)$], and 370 (13) cm^{-1} [$\nu_5(t_{2g})$] (ν_2 and ν_5 overlap with the corresponding frequencies of unreacted $HC{\equiv}NH^+AsF_6^-$).

The interaction of $HC{\equiv}NH^+AsF_6^-$ and KrF_2 in BrF_5 led to a soluble product which was stable to at least −55 °C in BrF_5 with only slight decomposition. The ^{19}F n.m.r. spectra of these solutions at −58 °C and in HF at −60 °C (Table 1) are consistent with equation (1). A new resonance in the fluorine-on-krypton(II) region [81.0 (HF) and 99.4 (BrF_5)] occurs to high frequency of unreacted KrF_2 [48.1 (HF) and 63.9 (BrF_5)] in both solvents. In BrF_5 this resonance is split into a doublet (4.2 Hz) attributable to the four-bond coupling $^{4}J(^{19}F{-}^{1}H)$ [*cf.* $^{4}J(^{19}F{-}^{1}H)$ 2.6 Hz for $[HC{\equiv}N{-}Xe{-}F]^+$ in HF solvent]. Like the terminal fluorine resonance of $Kr_2F_3^+$ [δ 73.6 p.p.m. (BrF_5)][11] the fluorine-on-krypton resonance of $[HC{\equiv}N{-}Kr{-}F]^+$ lies to high frequency of the parent fluoride resonance. The chemical shift trend suggests that the Kr–N bond is more ionic than the Kr–F bridge bond of $Kr_2F_3^+$. The ^{1}H spectrum recorded in BrF_5 solvent is also consistent with the formation of the $[HC{\equiv}N{-}Kr{-}F]^+$ cation. In addition to the doublet arising from HF in equation (1), a doublet (4.2 Hz) attributed to $^{4}J(^{19}F{-}^{1}H)$ was observed at δ 6.09, to high frequency of the proton-on-carbon resonance of the $HC{\equiv}NH^+$ cation [δ 5.20 (BrF_5)].

$$KrF_2 + HC{\equiv}NH^+AsF_6^- \rightarrow [HC{\equiv}N{-}Kr{-}F]^+AsF_6^- + HF \quad (1)$$

The structure of the $[HC{\equiv}N{-}Kr{-}F]^+$ cation in solution has been confirmed by repetition of the reaction in BrF_5 with 99.5% ^{15}N-enriched $HC{\equiv}NH^+AsF_6^-$. The ^{19}F and ^{1}H resonances exhibit new doublet splittings attributed to ^{15}N coupling [Figure 1(a)]. The new splitting (26 Hz) of the ^{19}F resonance is attributed to the two-bond spin–spin coupling $^{2}J(^{19}F{-}^{15}N)$ and is similar in magnitude to previously reported values for $F{-}Xe{-}N(SO_2F)_2$ [$^{2}J(^{19}F{-}^{15}N)$ 39.2 Hz] and $[MeC{\equiv}N{-}Xe{-}F]^+$ [$^{2}J(^{19}F{-}^{14}N)$ 18 Hz; $^{2}J(^{19}F{-}^{15}N)$ 25 Hz (calc.)]. Krypton isotopic shifts arising from ^{82}Kr (11.56%), ^{84}Kr (56.90%), and ^{86}Kr (17.37%) are well resolved on the ^{19}F resonance (0.0138 p.p.m. per a.m.u.). The value compared favourably with that measured for KrF_2 in BrF_5 solvent (0.0104 p.p.m. per a.m.u.)[12] and serves as an added confirmation that the fluorine resonance arises from fluorine directly bonded to krypton. The new doublet fine structure (12.2 Hz) on the ^{1}H resonance of the ^{15}N-enriched cation [Figure 1(b)] is attributed to $^{2}J(^{15}N{-}^{1}H)$ [*cf.* $^{2}J(^{15}N{-}^{1}H)$ 19.0 Hz for $HC{\equiv}NH^+$ in HF solvent]. The ^{15}N n.m.r. spectrum consists of a well resolved doublet of doublets [Figure 1(c)] arising from $^{2}J(^{19}F{-}^{15}N)$ and $^{2}J(^{15}N{-}^{1}H)$, which simplifies to a doublet (26 Hz) upon broad-band ^{1}H decoupling, confirming the aforementioned coupling constant assignments. A 99.2% ^{13}C enriched sample resulted in additional doublet splittings in the ^{1}H and ^{13}C spectra arising from $^1J(^{13}C-^1H)$ 312 Hz and $^3J(^{19}F-^{13}C)$ 25.0 Hz.

It is noteworthy that the resonances of both solvents displayed well resolved spin–spin couplings (Table 1) indicating that fluorine exchange is slow under the stated conditions. This, coupled with the low concentration of NF_4^+ decomposition products in freshly prepared BrF_5 samples (<1%), has allowed reliable integrations of the ^{1}H and ^{19}F resonances. The following relative intensities were obtained and further support the cation structure and equation (1): ^{19}F, $[HC\equiv N-Kr-F]^+ : HF : AsF_6^-$ 1 : 1 : 6; ^{1}H, $[HC\equiv N-Kr-F]^+ : HF$ 1 : 1.

Solutions of $[HC\equiv N-Kr-F]^+AsF_6^-$ in BrF_5 have withstood temperatures of −58 to −55 °C for several hours with little sign of additional decomposition. Monitoring the ^{19}F spectra has shown that subsequent brief warmings of these solutions above −50 °C lead to rapid formation of NF_4^+ [δ 218.9 p.p.m., $^1J(^{19}F-^{14}N)$ 229 Hz, $^1J(^{19}F-^{15}N)$ 320 Hz], CF_4 (−63.1 p.p.m.), and CF_3H (−79.3 p.p.m., $^2J(^{19}F-^1H)$ 79 Hz] and exchange-broadening of both HF and AsF_6^- resonances arising from AsF_5 formation. The HF samples also displayed weak ^{19}F resonances attributable to NF_4^+ [δ 218.9 p.p.m., $^1J(^{19}F-^{14}N)$ 229 Hz], NF_3 [142.9 p.p.m., $^1J(^{19}F-^{14}N)$ 140 Hz], CF_3H [−81.5 p.p.m., $^2J(^{19}F-^1H)$ 79 Hz], and CF_4 (−64.9 p.p.m.) as decomposition products.

Additional examples of inorganic and perfluoro-organic nitrogen bases are under investigation in this laboratory as potential electron-pair donors towards KrF^+.

This research was sponsored by the United States Air Force Astronautics Laboratory, Edwards Air Force Base, California (Contract F49620-87-C-0049) and a Natural Sciences and Engineering Research Council of Canada operating grant.

Received, 1st March 1988; Com. 8/00838H

References

1 (a) N. Bartlett and F. O. Sladky, 'Comprehensive Inorganic Chemistry,' Pergamon, New York, 1973, vol. 1, ch. 6, pp. 213—330; (b) K. Seppelt and D. Lentz, *Progr. Inorg. Chem.*, 1982, **29**, 167.
2 D. D. DesMarteau, *J. Am. Chem. Soc.*, 1978, **100**, 6270.
3 D. D. DesMarteau, R. D. LeBlond, S. F. Hossain, and D. Nothe, *J. Am. Chem. Soc.*, 1981, **103**, 7734.
4 J. F. Sawyer, G. J. Schrobilgen, and S. J. Sutherland, *Inorg. Chem.*, 1982, **21**, 4064.
5 G. A. Schumacher and G. J. Schrobilgen, *Inorg. Chem.*, 1983, **22**, 2178.
6 R. Faggiani, D. K. Kennepohl, C. J. L. Lock, and G. J. Schrobilgen, *Inorg. Chem.*, 1986, **25**, 563.
7 J. Foropoulos, Jr., and D. D. DesMarteau, *J. Am. Chem. Soc.*, 1982, **104**, 4260.
8 A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1987, 1646.
9 A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1988, 257.
10 V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, 1968, **48**, 4765.
11 R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, 22.
12 J. C. P. Sanders and G. J. Schrobilgen, unpublished work.