X-Ray Crystal and Multinuclear N.M.R. Study of FXeN(SO₂F)₂; The First Example of a Xenon–Nitrogen Bond

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An X-ray crystallographic study has shown that $FXeN(SO_2F)_2$ contains an Xe–N bond, representing the first definitive proof for its existence; solution ^{15}N and ^{129}Xe n.m.r. studies of ^{15}N-enriched $FXeN(SO_2F)_2$ also demonstrate that this bond is present in solution.

Xenon compounds containing either xenon–fluorine or xenon–oxygen bonds have been known since the inception of noble-gas chemistry. It is only more recently, however, that the syntheses of xenon compounds containing nitrogen have been reported. Previous notes reporting compounds formulated as $FXeN(SO_2F)_2$[1] and $F[XeN(SO_2F)_2]_2^+AsF_6^-$[2] have claimed that both species contain xenon bonded to nitrogen. These claims are based primarily on ^{19}F n.m.r. results which are consistent with the proposed Xe–N bonded structures, but do not represent unique interpretations. It has been pointed out, for example, that the ^{19}F (and ^{129}Xe) solution n.m.r. spectrum of $FXeN(SO_2F)_2$ could also be interpreted in terms of a structure in which the Xe–F group undergoes a rapid intramolecular exchange over the nitrogen and/or oxygen sites.[3] Similarly, the ^{19}F n.m.r. spectrum of $F[XeN(SO_2F)_2]_2^+$ with BrF_5 as solvent suggests that the cation is partially dissociated,[2] and the ensuing chemical exchange permits neither the observation of the bridging fluorine resonance nor any definitive conclusions to be made about the xenon bonding site in the cation. In view of the fact that no clear structural evidence existed to support either Xe–N or Xe–O bonded structures for either $FXeN(SO_2F)_2$ or $F[XeN(SO_2F)_2]_2^+$, we have obtained a low temperature X-ray crystal structure of the title compound and its ^{15}N n.m.r. parameters in solution for the first time.

The synthesis of $FXeN(SO_2F)_2$ has been modified from the original procedure[1] to give larger bulk yields of pure compound in shorter periods of time.† Crystals suitable for X-ray crystallographic study were grown by dissolution of ca. 0.25 g of pure $FXeN(SO_2F)_2$ in 5 ml of SO_2ClF at room temperature. The sample was cooled to -10 °C and the temperature slowly lowered (2 to 5 °C per hour) until crystallization was complete at -40 °C. The solvent was removed *in vacuo* at -40 °C until a dry sample of single crystals was obtained. Some crystals were transferred in a dry box into a cold, dry quartz apparatus equipped with quartz capillary side tubes and manipulated at -10 °C or below. A suitable crystal was tapped into a capillary and was sealed under an atmosphere of dry nitrogen.

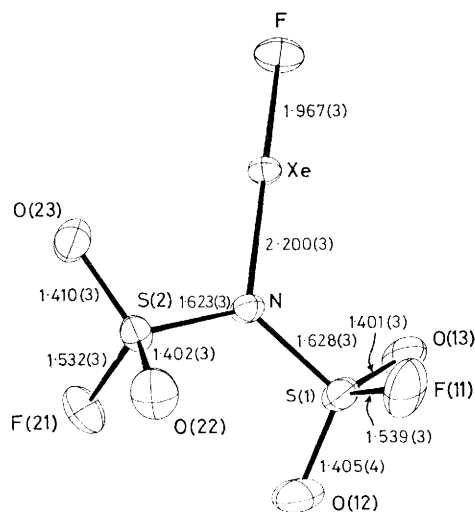*Crystal data:* $F_3NO_4S_2Xe$, $M = 330.42$, monoclinic, $a = 11.827(4)$, $b = 6.828(2)$, $c = 9.467(3)$ Å, $\beta = 112.65(2)°$,

Figure 1. The structure of $FXeN(SO_2F)_2$ with bond lengths in Å. The average bond angles (°) are: F–Xe–N, 178.1(1); Xe–N–S, 119.7(1); S–N–S, 120.5(2); O–S–O, 122.6(2); O–S–F, 106.3(2); N–S–O(13,23), 107.2(2); N–S–O(12,22), 111.2(2); N–S–F, 101.2-(2).

$U = 705.5(4)$ Å³, $D_c = 3.11$ g cm⁻³ for $Z = 4$; Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) $= 56.1$ cm⁻¹, space group $P2_1/a$.

The crystals decompose in a few hours at room temperature, so all X-ray work was performed at -55 ± 5 °C using a Syntex $P2_1$ diffractometer with an LT-1 low temperature device. Intensity data were collected on a small, approximately spherical [radius (r) = 0.1 mm, $\mu r = 0.56$] colourless crystal sealed in a quartz capillary. A total of 2517 reflections (including standards), in the quadrants (h, k, $\pm l$) with $2\theta < 60°$, were eventually collected. Lorentz, polarization, and spherical absorption corrections were applied to all data.

The structure was solved by the use of the Patterson function to locate the position of the xenon atom. Subsequent cycles of least-squares and Fourier calculations located all the remaining atoms in the structure. Least-squares refinement with all atoms having anisotropic thermal parameters converged to give the agreement index $R_1 = 0.027$ for 1888 observed reflections [$F > 2\sigma(F)$].‡

The crystal has been found to consist of $FXeN(SO_2F)_2$ molecules possessing a molecular point symmetry of C_2 in which the xenon atom of the Xe–F group is bonded to the nitrogen atom (Figure 1). This study represents the first definitive proof for the existence of a stable xenon–nitrogen bond. The Xe–N and Xe–F distances are 2.200(3) and 1.967(3) Å, respectively, and the F–Xe–N system is very nearly linear [$\angle$F–Xe–N = 178.1(1)°]. A comparison of the Xe–N

Table 1. N.m.r. parameters for $[^{15}N]FXeN(SO_2F')_2{}^a$ in BrF_5 solvent (-58 °C).

Nucleus	$\delta/\text{p.p.m.}^b$	Coupling constant/Hz
$^{129}Xe^c$	-1997.3	$^{129}Xe^{-19}F$, 5586
$^{19}F^d$	$\begin{cases} -126.1,\ F \\ 57.6,\ F' \end{cases}$	$^{129}Xe^{-19}F'$, 18.7
$^{17}O^e$	169.4	$^{129}Xe^{-15}N$, 307.4
$^{15}N^f$	109.5	$^{19}F^{-15}N$, 39.2

^{a} 30% ^{15}N enrichment. ^{b} The chemical shift convention is that outlined by the IUPAC (*Pure Appl. Chem.*, 1972, **29**, 627; 1976, **45**, 217); *i.e.*, a positive chemical shift denotes a positive frequency and *vice versa*. The following external reference substances were used. ^{c} Neat $XeOF_4$, 25 °C. ^{d} Neat $CFCl_3$, -58 °C. ^{e} H_2O, 24 °C. ^{f} Aqueous 7.1 M NH_4Cl, δ (^{15}N) (w.r.t. 90% formamide in $[^2H_6]$dimethyl sulphoxide $=\delta$ (^{15}N) (w.r.t. NH_4Cl) -90.0 p.p.m.

bond length with Xe–F and Xe–O bond lengths in XeF_2 (2.00 Å),[5] $FXeOSO_2F$ (2.16 Å),[6] $Xe(OSeF_5)_2$ (2.12 Å),[7] and $(FXe)_2SO_3F^+$ (2.21 Å)[8] shows the overall anticipated bond length increase with decreasing ligating atom electronegativity.

The $N(SO_2F)_2$ group has S–F and S–O bonds which are similar in length to those in the $[NSF_2NSO_2F]^-$ anion[9] while the bridging S–N bonds are approximately 0.1 Å shorter than in the xenon compound. The bond hybridization for nitrogen is best described as sp^2 with the sulphur atoms and xenon atom giving an arrangement about the nitrogen atom which is very close to trigonal planar (sum of the bond angles is 360.1°).

In order to record the n.m.r. data, nitrogen-15 enriched $FXeN(SO_2F)_2$ (30% ^{15}N) was prepared by the reaction of $[^{15}N](H_2N)_2CO$ with 30% oleum at 100 °C. The resulting $[^{15}N]H_2NSO_3H$ was used to synthesize $[^{15}N]HN(SO_2F)_2$ and $[^{15}N]FXeN(SO_2F)_2$ according to the procedures discussed above. The ^{15}N, ^{129}Xe, and ^{19}F n.m.r. spectra of $[^{15}N]$-$FXeN(SO_2F)_2$ were recorded with BrF_5 as solvent at -58 °C. In addition to the directly bonded $^{129}Xe^{-19}F$ coupling of the Xe–F group observed in the ^{129}Xe and ^{19}F spectra, a two-bond coupling between the fluorine of the Xe–F group and nitrogen

observed in the ^{15}N and ^{19}F spectra and a three-bond coupling between xenon and the two chemically equivalent fluorine atoms on sulphur observed in the ^{129}Xe and ^{19}F spectra, the ^{129}Xe and ^{15}N spectra both display satellites arising from a one-bond xenon–nitrogen coupling (Table 1). A comparison of the reduced coupling constant[10] for the directly bonded Xe–F interaction ($|K_{Xe-F}| = 11.84 \times 10^{22}$ N A^{-2} m^{-3}) with that for Xe–N ($|K_{Xe-N}| = 6.05 \times 10^{22}$ N A^{-2} m^{-3}) reveals that both couplings are considerably less than an order of magnitude apart ($K_{Xe-F}/K_{Xe-N} = 1.96$), and is consistent with the view that the observed $^{129}Xe^{-15}N$ coupling is due to a directly bonded interaction between xenon and nitrogen in solution.

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