Ion exchange shows that the resulting $Ru(NH_3)_4(py)_2^{2+}$ is about 70% *cis*. However, column separation of the *cis* isomer and starting material was incomplete, and further interpretation of this result should await data refinement.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF DELAWARE, NEWARK, DELAWARE 19711

The Effect of Steric Hindrance on the Bonding Mode of the Cyanate Ion in Palladium(II) Complexes

BY JOHN L. BURMEISTER AND NICHOLAS J. DESTEFANO

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The sensitivity of the bonding modes of the thiocyanate and selenocyanate ions to the steric hindrance created by both coordinated and noncoordinated groups has recently been demonstrated.[1–5] The X- → N-bonded isomerization observed[2–5] for solutions of $[Pd(Et_4dien)XCN]^+$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine; X = S, Se) has been explained in terms of the decreased interaction between the XCN^- ions and the ethyl groups of the triamine resulting from the switch to the smaller nitrogen donor atom and, concurrently, the switch from a nonlinear Pd–XCN to a linear Pd–NCX linkage. It should be noted that the parent $Pd(XCN)_4^{2-}$ and the sterically unhindered $Pd(dien)XCN^+$ complexes are stable X-bonded species. The N- → X-bonded reisomerization observed[4,5] in the solid state when the $Pd(Et_4dien)NCX^+$ ions are precipitated using a large counterion, *i.e.*, $B(C_6H_5)_4^-$, has been rationalized in terms of the steric interaction between the large X atoms and the counterion since $[Pd(Et_4dien)NCS]SCN$ is stable[2] with respect to isomerization in the solid state. It was therefore of considerable interest to ascertain whether the bonding mode of the cyanate ion (X = O) would prove to be sensitive to either of these effects, since, in this case, the angular requirements of the Pd–OCN and Pd–NCO linkages would also be expected to be different, whereas the radii of the two donor atoms are comparable.

Experimental Section

Preparation of Compounds. $[Pd(Et_4dien)NCO][B(C_6H_5)_4]$. **Method A.**—To a slurry of 5.0 mmol (0.89 g) of palladium(II) chloride in 200 ml of Spectrograde methanol was added 10 mmol each of silver cyanate (1.5 g) and sodium cyanate (0.65 g). The resulting mixture was stirred for 1.5 hr at room temperature and then filtered to remove the precipitated silver chloride and any unreacted solids. Three milliliters of 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) was added to the blood red filtrate, and the resulting solution was stirred for 1 hr at room temperature and then filtered into a solution of 5 mmol (1.75 g) of sodium tetraphenylborate dissolved in a minimum amount of methanol. The solution became cloudy after stirring for 15 min, and an off-white solid, identified as silver tetraphenylborate, was removed by filtration. *Anal.* Calcd for $AgBC_{24}H_{20}$: C, 67.4; H, 4.72; N, 0.00. Found: C, 66.93; H, 5.04; N, 0.06. The orange filtrate was allowed to stand overnight at 0°, but no crystallization of the product occurred. The volume of the solution was then reduced under a stream of dry nitrogen until a light yellow solid began to form. The solution was cooled to 0° and the product was isolated by filtration and dried *in vacuo* over calcium chloride. Several additional fractions were collected in this manner, but some were contaminated with silver tetraphenylborate. As a result, only the initial precipitate was further characterized; yield 26%; mp 154–157° dec. *Anal.* Calcd for $BC_{37}H_{49}N_4OPd$: C, 65.00; H, 7.17; N, 8.19. Found: C, 65.09; H, 7.36; N, 8.29.

Method B.—To a solution of 8.0 mmol (3.5 g) of tetraphenylarsonium cyanate dihydrate, prepared according to the method of Norbury and Sinha,[6] in 125 ml of Spectrograde acetone was added 1.0 mmol (0.18 g) of palladium(II) chloride. The mixture was stirred for 6 hr at room temperature and 2 hr at reflux temperature. After cooling the mixture to room temperature, it was filtered to remove any unreacted starting material and decomposition products. To the golden yellow filtrate was added 8.0 mmol (2.75 g) of sodium tetraphenylborate, dissolved in a minimum amount of acetone. The mixed precipitate of $[(C_6H_5)_4As][B(C_6H_5)_4]$, NaNCO, and NaCl which formed was removed by filtration. To the filtrate was added 0.6 ml of Et_4dien and, after the solution had been stirred for 15 min, 1 mmol (0.34 g) of sodium tetraphenylborate. The solution was filtered to remove the sodium cyanate precipitate, and the volume of the filtrate was reduced to *ca.* 10 ml under a stream of dry nitrogen. The yellow crystals which formed were isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate; yield 60%; mp 155–157° dec. *Anal.* Found: C, 65.47; H, 7.25; N, 8.06.

Method C.—A solution of 2.1 mmol (0.35 g) of silver nitrate in 5 ml of water was added, with vigorous stirring, to a suspension of 1.0 mmol (0.39 g) of $[Pd(Et_4dien)Cl]Cl$, prepared according to the method of Baddley and Basolo,[7] in 50 ml of water. A white precipitate formed immediately. The solution was maintained at 40–50° for 1 hr, with continued stirring, and then cooled to 0° and filtered. A solution of 1.1 mmol (0.071 g) of sodium cyanate in 5 ml of water was added to the pale yellow filtrate, and the resulting solution was stirred for 45 min. Half of the solution was filtered into a solution containing 0.5 mmol of sodium tetraphenylborate in 10 ml of acetone. A heavy, cream-colored precipitate formed immediately which, on stirring, became more flocculent. A light yellow solid was isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate; yield 88%; mp 154–157° dec. *Anal.* Found: C, 64.91; H, 7.39; N, 7.82.

The remaining half of the reaction mixture was treated in an identical manner, except for the fact that the sodium tetraphenylborate was dissolved in 20 ml of 50% (v/v) acetone–water. A larger yield of 98% resulted; mp 156–158° dec. *Anal.* Found: C, 65.24; H, 7.35; N, 7.77.

$[Pd(dien)NCO][B(C_6H_5)_4]$.—A solution of 4.1 mmol (0.69 g) of silver nitrate in 5 ml of water was added, with stirring, to a suspension of 2.0 mmol (0.93 g) of $[Pd(dien)I]I$ (dien = diethylenetriamine), prepared according to the method of Basolo,

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TABLE I

CONDUCTIVITY DATA[a]

Compound	Λ_0, ohm^{-1} cm^2 equiv^{-1}	Slope of ($\Lambda_0 - \Lambda_e$) vs. $C^{0.5}$	Electrolyte type
$[(n\text{-}C_4H_9)_4N]Br$	89.7	130	1:1
$Na[B(C_6H_5)_4]$	87.4	190	1:1
$[Ru_2Cl_3(P(C_2H_5)_2C_6H_5)_6]ClO_4$[b]	104	288	1:1
$[Pd(Et_4dien)NCO][B(C_6H_5)_4]$	76.3	317	1:1
$[Pd(dien)NCO][B(C_6H_5)_4]$	75.0	281	1:1
$[Pd_2(P(C_6H_5)_2)_2\{(C_6H_5)_2PC_2H_4P(C_6H_5)_2\}_2][ClO_4]_2$[b]	121	552	2:1

[a] Methanol solutions at 25°. [b] Data taken from ref 9.

TABLE II

INFRARED DATA FOR THE COMPLEXES

Compound	C–O str,[a,i] ν_1(NCO), cm^{-1}	NCO bend,[a,i] ν_2(NCO), cm^{-1}	C–N str,[b] ν_3(NCO) Freq, cm^{-1}	C–N str,[b] ν_3(NCO) $10^{-4}A$,[c] M^{-1} cm^{-2}
$[Pd(Et_4dien)NCO][B(C_6H_5)_4]$	1335 m	611, 601 m	2220	17
$[Pd(dien)NCO][B(C_6H_5)_4]$	1329 m	609, 587 m	2222	15
$[(CH_3)_4N]_2[Pd(NCO)_4]$[d]	1319 m	637 vw, 613 m, 604 m, 594 s	2202	17[e]
Ionic cyanate	1300, 1205[f,g]	636, 626[f]	2158[h]	8.4[h]

[a] Nujol mull. [b] Acetone solutions. [c] Integrated absorption intensity. [d] Data taken from ref 6. [e] Calculated per mole of coordinated cyanate. [f] Data for KNCO, taken from T. C. Waddington, *J. Chem. Soc.*, 2499 (1959). [g] Doublet due to Fermi resonance between the overtone of the bending and the fundamental C–O stretching frequencies. The unperturbed C–O stretching vibration should have a value of 1254 cm^{-1}: A. Maki and J. C. Decius, *J. Chem. Phys.*, **31,** 772 (1959). [h] Data for $[(C_6H_5)_4As]NCO\cdot 2H_2O$, taken from ref 6. [i] Abbreviations: vw, very weak; m, medium; s, strong.

et al.,[8] in 100 ml of water. A pale yellow precipitate formed immediately. The solution was maintained at a temperature of 45–50° for 45 min, with continued stirring, whereupon it was cooled to 0° and filtered. A solution of 2.1 mmol (0.13 g) of sodium cyanate in 5 ml of water was added to the pale yellow filtrate. The resulting solution was stirred for 30 min at room temperature and then filtered into a solution of 2.0 mmol (0.68 g) of sodium tetraphenylborate in 10 ml of water. A heavy cream-colored precipitate formed immediately which, on stirring, became more flocculent. A light yellow solid was isolated by filtration, washed with ethyl ether, and dried *in vacuo* over calcium sulfate; yield 91%; mp 132–134° dec. *Anal.* Calcd for $BC_{29}H_{33}N_4OPd$: C, 61.04; H, 5.83; N, 9.82. Found: C, 61.25; H, 5.98; N, 9.47.

Physical Measurements.—Carbon, hydrogen, and nitrogen microanalyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, Germany, and M-H-W Laboratories, Garden City, Mich.

Equivalent conductances, at 25°, of Spectrograde methanol solutions of the cyanate complexes and selected reference compounds were measured with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge and a cell with platinized electrodes. Seven separate measurements of the conductivity of each compound were made in the concentration range 5×10^{-3}–1×10^{-3} M. Following the procedure of Feltham and Hayter,[9] the equivalent conductivity, Λ_e, was plotted graphically as a function of $C^{0.5}$, where C is the equivalent concentration. The equivalent conductivity Λ_e was then extrapolated to infinite dilution to determine Λ_0. The plots for the cyanate complexes exhibited pronounced curvature below $C = 2.5 \times 10^{-3}$ M due, presumably, to increasing per cent dissociation of the coordinated cyanate group, and their Λ_0 values were therefore determined by extrapolating the linear portions of the curves ($C > 2.5 \times 10^{-3}$ M) to infinite dilution. Finally, $\Lambda_0 - \Lambda_e$ was plotted as a function of $C^{0.5}$, again using only the data corresponding to the linear portions of the curves for the cyanate complexes. The slope of this plot is indicative[9] of the electrolyte type and, as is shown in Table I, the data obtained in this manner support the formulation of the cyanate complexes as 1:1 electrolytes. The variation in slope for electrolytes of a given class is primarily due to the change in relative ionic mobilities with size. It is of interest to note that the bulkier Et$_4$dien complex exhibits lower Λ_e values than the dien complex in the concentration range where dissociation is not appreciable, but the situation is reversed in the low concentration range, where the more extensive dissociation of the cyanate group from the more sterically crowded Et$_4$dien complex becomes the determining factor.

Infrared spectra, in the 4000–400-cm^{-1} range, of complexes held in Nujol suspension between potassium bromide plates were measured on a Perkin-Elmer Model 337 grating spectrophotometer. A Perkin-Elmer Model 421 spectrophotometer was used to record high-resolution spectra of 10^{-2} M Spectrograde acetone solutions of the complexes, using matched 0.1-mm sodium chloride cells, in the cyanate C–N stretching range (2400–2000 cm^{-1}). The integrated absorption intensities, A (M^{-1} cm^{-2}), of the C–N stretching bands of the cyanate complexes were determined by Ramsay's method of direct integration.[10] The infrared data are shown in Table II. Visible-ultraviolet spectra of DMF solutions of the cyanate complexes were recorded on a Cary 14 spectrophotometer, using matched 1-cm quartz cells. The spectra obtained are shown in Figures 1 and 2, along with those of some analogously constituted reference complexes.[11]

Discussion

With the possible exception of $(\pi\text{-}C_5H_5)_2Ti(OCN)_2$,[12] all coordination complexes of the cyanate ion previously reported[6,13–23] are believed to contain N-bonded cy-

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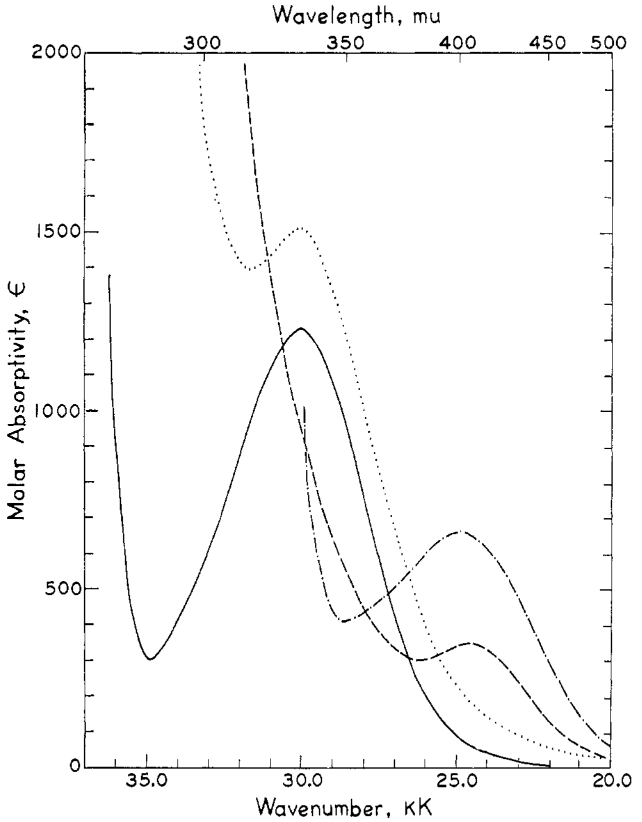

Figure 1.—Visible spectra of $[Pd(Et_4dien)L][B(C_6H_5)_4]$ complexes: $L^- = NCO^-$ (DMF solution), ———; $L^- = NCSe^-$ (DMF–H_2O, 4:1 by volume), · · · ·; $L^- = SeCN^-$ (DMF–H_2O, 4:1 by volume), - - -; $L^- = I^-$ (DMF, 0.1 *M* in $NaClO_4$), —·—·—.

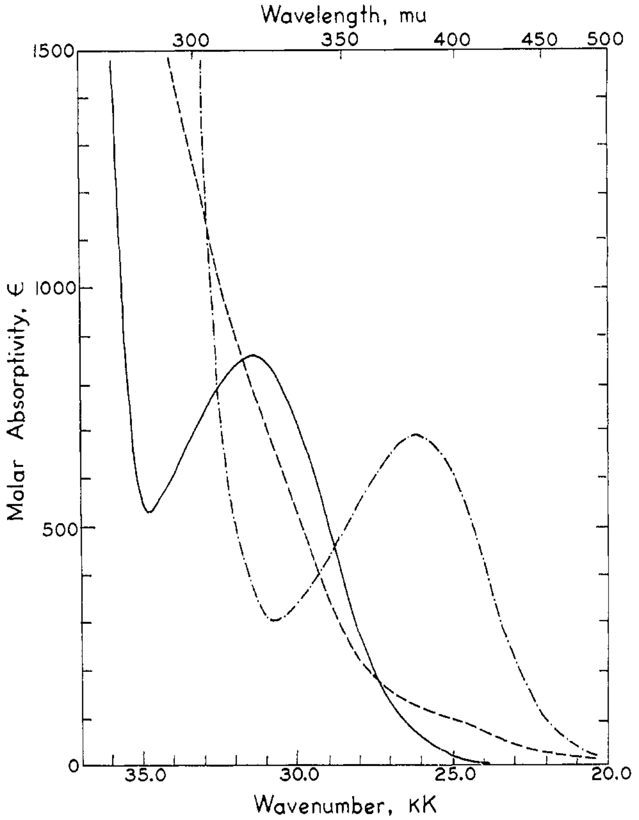

Figure 2.—Visible spectra of $[Pd(dien)L]Y$ complexes: $L^- = NCO^-$, $Y^- = B(C_6H_5)_4^-$ (DMF), ———; $L^- = SeCN^-$, $Y^- = B(C_6H_5)_4^-$ (DMF), - - -; $L^- = Y^- = I^-$ (DMF–H_2O, 4:1 by volume), -·-·-·-.

anate groups. Although the available data are not as extensive as that reported for the thiocyanate and selenocyanate ions,[24] shifts in the fundamental infrared frequencies of the cyanate group upon coordination have also proved[6,12,14,15,17,19–23] to be of considerable utility in diagnosing the bond type. In this context, the shifts (Table II) of the C–O stretching bands to higher frequencies, relative to that of the free ion, in the spectra of both the Et_4dien and the dien complexes are indicative of N-bonded groups. The C–N stretching and NCO bending frequencies and the integrated absorption intensities of the C–N stretching bands also fall within the range of values cited by Norbury and Sinha[6] for a series of isocyanatopalladium(II) complexes. The integrated absorption intensity values are also in excellent agreement with those reported[12] by Burmeister, *et al.*, for a series of isocyanato complexes of the type $M(NCO)_4^{2-}$ and with those values which have been determined[25] for organic isocyanates.

Further support for this conclusion is found in the results of the visible–ultraviolet spectral measurements. As shown in Figure 1, the spectra of the Et_4dien–isoselenocyanato[5] and –isocyanato complexes are quite similar [A_{max} (ϵ_{max}) values of, respectively, 30.1 kK (1500 M^{-1} cm^{-1}) and 30.0 kK (1200 M^{-1} cm^{-1})]. If the cyanate group were O bonded, the cyanate complex would be expected to exhibit a d–d absorption band of lower energy,[26] since the ligand field strength of the OCN^- group would be anticipated to be comparable to that of the oxalate or formate ions. Earlier work by Basolo and coworkers[7,27] has shown that the energy of the lowest frequency absorption band in the visible–ultraviolet spectra of aqueous solutions of $Pd(Et_4dien)$-Y^{n+} species follows the order which would be predicted on the basis of the ligand field strength (kK) of the Y ligand: I^-, 25.8; Br^-, 28.0; Cl^-, 28.9; OH_2, 30.4; NCS^-, 30.8; N_3^-, 31.2. Much the same observations pertain to the spectrum of the dien–isocyanato complex shown in Figure 2, although the band is shifted to higher energy (31.5 kK) and is less intense (ϵ_{max} 866 M^{-1} cm^{-1}). An analogous correlation can also be made[28] for the $Pd(dien)Y^{n+}$ complexes (aqueous solutions) (Y, lowest energy bands in kK): Br^-, 29.2; Cl^-, 29.8; OH^-, 32.2; NH_3, 33.8. The values observed for the isocyanato complexes should not be compared directly with those resulting from aqueous solution measurements, since the use of DMF as solvent results in a frequency lowering, *e.g.*, 0.9 kK for the Et_4dien–iodo complex. Parenthetically, it is of interest to note that, in both cases, the spectra indicate that the ligand field strength of Se-coordinated selenocyanate[5] is even less than that of the iodide ion [A_{max} (ϵ_{max}) values of, respectively, 24.5 kK (341 M^{-1} cm^{-1})

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vs. 24.9 kK (659 M^{-1} cm^{-1}) for the Et$_4$dien complexes and 24.7 kK (98 M^{-1} cm^{-1}) *vs.* 26.1 kK (690 M^{-1} cm^{-1}) for the dien complexes].

The Et$_4$dien cyanate complex resulting from the reaction of $Pd(NCO)_4^{2-}$ with Et$_4$dien (methods A and B) was found to be identical with that obtained from the reaction of $Pd(Et_4dien)OH_2^{2+}$ with NCO^- (method C). The complex does not isomerize upon heating, nor were any significant spectral changes observed after the complex had been stored for a period of 6 months in the solid state at room temperature. This observation offers further support for the hypothesis that it is the relatively larger size of the sulfur and selenium atoms which leads to their N- → X-bonded isomerizations in the solid state.

This paper completes a series of studies by this and other laboratories on the electronic and steric effects of other ligands on the bonding modes of the NCX^- (X = O, S, Se) pseudohalides in palladium(II) complexes. However structurally similar the free ions may be, they have been found to exhibit marked differences in their bonding patterns in these complexes.

As has been noted, the bonding modes of only the thiocyanate[1,2,4] and selenocyanate[3-5] ions have been found to be affected by the steric requirements of other groups, both coordinated and noncoordinated. With regard to the electronic influence of other ligands, only the bonding mode of the thiocyanate ion has been found[29] to exhibit a sensitivity to the electronic character of other coordinated groups, the cyanate ion exhibiting[6] only the N-bonded mode and the selenocyanate ion[30] only the Se-bonded mode (in sterically noncrowded complexes).

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CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS 60439,
AND THE CHEMISTRY DEPARTMENT, LOYOLA UNIVERSITY,
CHICAGO, ILLINOIS 60626

Fluorine Exchange in the System Xenon Dioxide Difluoride–Xenon Oxide Tetrafluoride. Fluorine-19 Nuclear Magnetic Resonance and Fluorine-18 Radiotracer Investigations[1]

BY H. D. FRAME, J. L. HUSTON, AND IRVING SHEFT

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The preparation and isolation of XeO_2F_2 and $XeOF_4$ have been described previously.[2,3] Structures involving molecular species have been proposed for the two compounds. Infrared analyses indicate that $XeOF_4$ is a square pyramid with the oxygen at the apex,[4] and XeO_2F_2 is a trigonal bipyramid with the two oxygen atoms and the lone pair occupying the equatorial positions.[5]

One synthesis of XeO_2F_2 involves $XeOF_4$ as an initial material:[2] $XeOF_4 + XeO_3 \rightarrow 2XeO_2F_2$. Further, the reaction $XeO_2F_2 + XeF_6 \rightarrow 2XeOF_4$ is known to take place. If either of these reactions is reversible, then fluorine exchange should take place in the system XeO_2F_2–$XeOF_4$, provided traces of XeO_3 and/or XeF_6 are present.

It has been suggested[6] that XeO_2F_2 might polymerize by formation of "oxo" bonds between xenon atoms. It is possible that such bonds are formed between $XeOF_4$ and XeO_2F_2. A more likely source of fluorine exchange in the system would be fluorine bridges similar to those proposed for XeF_6.[7]

Experimental Section

Samples of XeO_2F_2 were prepared in Kel-F apparatus by a modification of the procedure described previously.[2] Solid XeO_3 was visually titrated by distilling small increments of XeF_6 into the container and allowing each increment to react overnight: $2XeO_3 + XeF_6 \rightarrow 3XeO_2F_2$. This cycle was repeated until all the XeO_3 had been consumed. The end point was confirmed by detecting the presence of $XeOF_4$ mass spectrographically: $XeO_2F_2 + XeF_6 \rightarrow 2XeOF_4$. The $XeOF_4$ was pumped away to leave pure XeO_2F_2.

XeF_2 contamination of XeO_2F_2, which has been noted previously,[2] can be attributed to the presence of XeF_4 impurity in XeF_6, for it has been found that fluorination of XeO_3 by XeF_4 produces a mixture of XeO_2F_2 and XeF_2. Presumably the reactions involved are

$$XeO_3 + XeF_4 \longrightarrow XeOF_2 + XeO_2F_2$$

$$XeOF_2 \longrightarrow XeF_2 + 0.5O_2$$

Reports in the literature indicate that $XeOF_2$ is unstable.[8] In an attempt to minimize the amount of XeF_4 contamination in XeF_6, the preparation of XeF_6 was carried out in a small, high-pressure reactor (pressure ~500 atm). The infrared spectrum of the XeF_6 was examined to ensure the absence of labile impurities, especially HF, which might offer an additional path for exchange. This XeF_6, free from lower fluorides and HF, was then used in the XeO_2F_2 preparation. The mass spectrum and the melting point of the XeO_2F_2 verified the absence of impurities.

A sample consisting of a homogeneous mixture of XeO_2F_2 and $XeOF_4$ was made by distilling into the nmr tube a quantity of $XeOF_4$ approximately equal to the amount of XeO_2F_2 already present. (We thank G. McDonald for the $XeOF_4$ sample.) The infrared spectrum of the $XeOF_4$ had been previously examined. No HF or other impurity was found. This source of $XeOF_4$ was then used for both the nmr and ^{18}F-exchange studies.

Nmr tubes were made of Kel-F tubing, of 3.3- or 3.6-mm o.d. The tubes were sealed at the bottom by pressing them into a dimple drilled in the surface of an electric hot plate. These tubes can be flared to fit a $^1/_8$-in. flare fitting (Kel-F on a Kel-F valve). After sample preparation, a final vacuum-tight seal is

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