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).

Acknowledgment.—This research was supported by the National Science Foundation (Grant No. GP-8327).

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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

Received January 17, 1969

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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[1] Based in part on work performed under the auspices of the U. S. Atomic Energy Commission.

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effected by immersing the sample in liquid nitrogen and allowing the tube to collapse by heating with a small tube oven.

The plastic sample tubes were inserted in standard 5-mm glass nmr tubes. The spectra were obtained on a Varian Associates A56-60A spectrometer equipped with a V-6040 variable-temperature controller. Neither an internal nor an external standard was employed; rather, a separate tube of CCl_3F was examined immediately before and after the samples. The post-sample standard spectra employed a variable-frequency oscillator with a counter to determine the position of the absorption peaks of the samples.

A sample of XeO_2F_2 in its Kel-F nmr tube was examined mass spectroscopically after it had been heated as high as 70° on several occasions during the nmr investigation. This sample showed only very slight decomposition to XeF_2 and the presence of low molecular weight fluorocarbons and CO_2, presumably from attacks on the Kel-F.

$XeOF_4$ containing ^{18}F was prepared by direct irradiation of $XeOF_4$ in a nickel container in the beam of a linear accelerator. A tungsten converter target was used; the preparation involves the reactions $^{19}F(\gamma,n)^{18}F$ and $^{19}F(n,2n)^{18}F$. Fluorine-18 is a positron emitter with a 110-min half-life. It is detected by means of the resulting 0.5-MeV annihilation γ radiation. The counting equipment used, a single-channel analyzer and scintillation crystal, has been described previously.[9]

The $XeOF_4$ containing ^{18}F was first purified to separate it from noncondensables by pumping on the tube at −80°. It was then distilled into a 0.25-in. Kel-F tube containing a known amount of XeO_2F_2. The tube was warmed to the exchange temperature and gently shaken to obtain a homogeneous solution. The tube was weighed to determine the amount of $XeOF_4$ distilled onto the XeO_2F_2 and kept at the exchange temperature for 1 hr. While maintaining the exchange temperature, the bulk of the $XeOF_4$ was rapidly distilled into a second 0.25-in. Kel-F tube and the remainder was pumped out of the exchange tube. The completeness of the removal of the $XeOF_4$ was ascertained by weighing both fractions. The two fractions were counted and weighed to determine specific activities. The $XeOF_4$ fraction was also examined mass spectrographically. No HF, which might have contributed to exchange, was found.

Results and Discussion

Strong, sharp nmr signals were observed for both the pure samples and the 1:1 solution. Each chemical species present produced only one main signal and a ^{129}Xe spin doublet. No significant broadening was observed for any line throughout the temperature range examined. Pure XeO_2F_2 and the 1:1 solution were examined from +16 to 70° while pure $XeOF_4$ was examined from −41 to +43°. The lower limits were imposed by the freezing points (XeO_2F_2, 30°; $XeOF_4$, −40°) while the upper ones were determined by the softening point of Kel-F. At 25° in the 1:1 solution the XeO_2F_2 line shifts upfield 0.53 ppm relative to pure XeO_2F_2 (−105.10 ppm; CCl_3F = 0). The $XeOF_4$ absorption shifts downfield 0.95 ppm relative to pure $XeOF_4$ (−100.27 ppm). The ^{129}Xe splittings for $XeOF_4$ and XeO_2F_2 are 1124 and 1178 Hz, respectively.

The difference in chemical shifts for the 1:1 solution as compared with the pure samples can be explained as being due to solution effects alone. Measurements of the bulk diamagnetic susceptibility were made according to a modification of the concentric-tube method of Li.[10] As could be expected from their chemical formula XeO_2F_2 and $XeOF_4$ differ only slightly ($-\chi_v$ = 0.86 and 0.82, respectively).

The results of the ^{18}F-exchange experiments at 29 and 0° are shown in Table I. Attempts to determine the extent of exchange at lower temperatures were inconclusive owing to experimental difficulties in obtaining complete dissolution of the solid XeO_2F_2 in the $XeOF_4$. Also, rapid separation of the two fractions after exchange was extremely difficult because of the low vapor pressure of $XeOF_4$ below 0°. Exchanges of less than 1-hr duration were not run because the time for separation would be too long a fraction of the exchange time to give meaningful results.

TABLE I

A 1-HR ^{18}F EXCHANGE IN THE SYSTEM $XeOF_4$–XeO_2F_2

Temp, °C	$XeOF_4$ mg	$XeOF_4$ mmol	$XeOF_4$ cpm (cor)	XeO_2F_2 mg	XeO_2F_2 mmol	XeO_2F_2 cpm (cor)	Fractional exchange
29	219.6	0.9834	145,000	130.1	0.6463	58,200	1.16
0	104.0	0.4657	174,000	113.3	0.5628	112,000	1.04

To ascertain that no exchange takes place between the $XeOF_4$ containing ^{18}F and the Kel-F counting tube, two samples of irradiated $XeOF_4$ (approximately 200 mg each containing about 10^6 cpm) were kept in the Kel-F counting tubes for 1.5 hr and then pumped out. Less than 0.1% of the activity remained in the tube.

Eight to ten half-times are required for the complete exchange observed at 0° in the ^{18}F experiments. Therefore it can be stated that $t_{1/2}$ for fluorine exchange in this system is less than 7 min at 0°. In order for exchange to be confirmed at 70° in the ^{19}F nmr experiments, a 2-Hz broadening of the lines would have to be observed. Since such broadening was not observed, it can be concluded that $t_{1/2}$ for the exchange is greater than 4 sec at 70°. The range of values of $t_{1/2}$ consistent with the observations is expected to become narrower when the difference in temperatures is taken into account. With this intermediate exchange rate and the experimental limitations already mentioned, a detailed kinetic study was not carried out. Therefore it is not possible to discriminate among the mechanisms proposed in the introduction.

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CONTRIBUTION FROM THE EASTERN LABORATORY,
EXPLOSIVES DEPARTMENT,
E. I. DU PONT DE NEMOURS AND COMPANY,
GIBBSTOWN, NEW JERSEY 08027

The Reaction between Diphenylchlorophosphine and Hydrazine Hydrochloride

BY E. F. MORAN AND D. P. REIDER

Received January 16, 1969

It has been reported[1] that the reaction between diphenylchlorophosphine and hydrazine monohydro-

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