(The symbol A_{32}, for example, means $A_3 \times A_2$, the A_i values being those of eq. 4.) This equation is solved for the β values by inverting the matrix **A** and multiplying A by $\mathbf{A}^{-1}$. One manipulative detail which may be troublesome is that the matrix elements cover a wide range of values—in the work reported here, 10^{-31} to 10^{-9}—and the weights may have to be multiplied by some constant to keep the numbers within the capacity of the computer used. This constant can be factored out later.

The least-squares procedure gives not only a set of β values but also their standard deviations *if the weights are on an absolute basis, i.e.*, if the terms in eq. 9 are all known and the proper estimates of σpH and σV are used. If this is done, the standard deviations of the β values are equal to the square roots of the corresponding diagonal elements of the inverse matrix [*i.e.*, $\sigma\beta_3 = (A_{33}{}^{-1})^{1/2}$].

The last information available is the "goodness of fit," χ, described in the text. This is calculated by evaluating F (eq. 6) at each point ($\bar{n}$, [L]) using the calculated β values. These quantities are called the residuals; they would be zero if there were no errors in $\bar{n}$, [L], or the β values. The residual at each point is multiplied by the weight calculated for that point; then

$$\chi = \sqrt{\frac{\Sigma w \times (\text{residual})^2}{N}} \qquad (18)$$

where N is the number of observations (number of points) minus the number of parameters determined (3 in this case: β_1, β_2, and β_3). The interpretation of χ is described in the text.

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Difluoramine: an Infrared Study of the Complexes between Difluoramine and the Alkali Metal Fluorides

BY H. E. DUBB, R. C. GREENOUGH, AND E. C. CURTIS

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Difluoramine, HNF_2, was condensed on alkali metal fluoride optical crystals, and the infrared spectra of the resulting compounds were measured. Complex formation was observed with KF, RbF, and CsF. An analysis of the infrared spectra indicates that two compounds may be formed, one a simple hydrogen bonded complex, and the other a new species $MNF_2 \cdot HF$.

Introduction

Potassium, rubidium, and cesium fluorides form complexes with difluoramine (that dissociate reversibly) when the latter is condensed onto these materials. When the potassium and rubidium complexes are allowed to warm to room temperature they react further to form the *cis* and *trans* difluorodiazine isomers and the alkali metal bifluorides. The cesium complex explodes before reaching room temperature.[1]

It has been postulated that the explosive nature of the cesium complex as contrasted with the nonexplosive nature of the potassium and rubidium complexes might be due to the formation of difluoramide ion, NF_2^-. The present infrared study of the structures of these complexes was undertaken with the purpose of determining whether such an ion does exist.

Infrared spectra of the complexes were obtained by condensing difluoramine onto optical blanks of the alkali metal fluorides at −95° and scanning through the rock salt region with a Beckman IR-7 spectrometer. Examination of the spectra indicates that potassium and rubidium fluorides primarily form hydrogen-bonded complexes of the structure $M^+F^- \cdot HNF_2$ with possible small amounts of a difluoramide complex, $M^+ \cdot FH \cdot NF_2^-$, also present. Cesium fluoride seems at first to form a complex with two (or more) moles of difluoramine. On pumping this is converted to a mixture of $Cs^+F^-H \cdot NF_2$ and $Cs^+ \cdot FH \cdot NF_2^-$. The evidence for the existence of a difluoramide ion is strongest in the case of cesium.

Experimental

The difluoramine was prepared by the action of concentrated sulfuric acid on fluorinated urea. It was then purified by distillation under vacuum at reduced temperatures.[2] The potassium and cesium fluoride crystals were obtained from the Harshaw Chemical Co. and the rubidium fluoride from Semi-Elements, Inc.

The alkali fluoride single crystal was mounted on a copper block inside an infrared cell fitted with rock salt windows. Gaseous difluoramine was condensed onto a 1 × 1 in. optical blank of the appropriate alkali metal fluoride maintained at about −95° by a slush bath of methylcyclohexane. The copper block was in contact with the slush coolant so that the alkali fluoride plates could be kept at the proper temperature, which was meas-

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[1] E. A. Lawton, D. Pilipovich, and R. D. Wilson, U. S. Patent 3,109,711 (Nov. 5, 1963).

[2] E. A. Lawton and J. Q. Weber, *J. Am. Chem. Soc.*, **81**, 4755 (1959); E. A. Lawton and D. F. Sheehan unpublished work.

TABLE I

ASSIGNMENTS OF INFRARED SPECTRA

Assignment	HNF_2, gas HF, solid	KF + HNF_2	RbF + HNF_2	CsF + HNF_2 complex and gas[c]	CsF + HNF_2 complex only[d]
HF stretch	3400[a]		3300?		3500?
	3100[a]				3200?
NH stretch	3193 vw[b]	2900?	2850?	2900	3000
		2850?	2600	2600?	2870
		2600	2450?	2450	2650
				2350	2350
					1660
				1510	1545
			1440		1460
NH bend (asym.)	1424 s[b]				1432
		1410			1400
NH bend (sym.)	1307 s[b]	1320			
NF stretch (sym.)	972 s[b]	965	960	942	942
					830
NF stretch (asym.)	888 vs[b]	850	850	830	840
		830			825
		700?	700?	700?	720

[a] HF frequencies taken from R. M. Adams and J. J. Katz, *J. Opt. Soc. Am.*, **46**, 895 (1956). [b] HNF_2 frequencies taken from ref. 5. [c] Spectra taken immediately after admitting HNF_2 to cold plate. Some gaseous HNF_2 was also in the cell. [d] Spectra taken after standing briefly. All gaseous and liquid HNF_2 has been pumped off. Frequencies indicated by a question mark are subject to doubt.

ured with a copper–constantan thermocouple. The apparatus will be described in detail elsewhere.[3]

There was considerable difficulty in handling the crystals since they are very hygroscopic. The crystals were polished on a felt cloth wet with a butanol solution saturated with the appropriate salt and then were mounted on the copper block and sealed into the infrared cell. All these manipulations were done inside a very carefully constructed drybox with a 97% Ar–3% H_2 atmosphere maintained at a positive pressure so that the alkali fluoride plate was not exposed to air at any time. Even with these extreme precautions taken, some water was still frozen on or in the crystals as evidenced by absorptions at 3200 and 1650 cm.$^{-1}$. The KF·HNF_2 spectrum (Figure 1) shows this clearly.

The difluoramine was admitted through a nozzle directly onto the plate. Actually, the vapor pressure of difluoramine is high enough so that a portion of the gas condensed on the copper block; however, most of it did condense on the window. The spectra of the resulting complexes were then scanned with a Beckman IR-7 spectrometer set at low resolution and high speed. At the end of the experiment the potassium and rubidium fluoride plates were allowed to warm and the spectrum of the bifluoride salt was detected on the plates by comparison with the known KHF_2 spectrum.[4] The cesium fluoride blank was destroyed at the end of the experiment by condensing methanol onto the plate to avoid an explosion and subsequent harm to the apparatus when it was warmed to room temperature.

There was some difficulty with leaks with this apparatus; even a very small amount of water on the alkali fluoride plates gives a very intense band at 3200 cm.$^{-1}$ and a weak band at 1650 cm.$^{-1}$.

Results

The spectra of HNF_2 on KF and HNF_2 on CsF are shown in Figure 1. The spectrum of HNF_2 on RbF was very similar to that on KF. An assignment of all spectra measured is given in Table I. A spectrum of liquid HNF_2 on NaCl was also measured. Bands appeared at approximately the same frequencies as the gas phase bands.

There was some air leakage into the cell during the KF and CsF experiments, raising some doubt about the exact shape and frequency of the HF band. It is felt that absorption around 3500 cm.$^{-1}$ was not due to water but was caused by a HF stretching mode. This assignment was more certain in the case of the CsF complex as less water was observed in its spectrum. The position of the HF band does not coincide with the band due to water condensed on CsF, but does overlap it to a certain extent.

Potassium fluoride and rubidium fluoride seem to form similar complexes. The N–H stretching frequency at 2600 cm.$^{-1}$ is shifted down 600 cm.$^{-1}$ from the gas phase frequency. The N–H stretching band in the complex is considerably more intense than the same band in the gas phase.[5] The other vibrational modes have approximately the same frequencies as in the gas phase spectrum. A possible speculative structure for this complex is shown in Figure 2 as form A. It is possible that some $M^+ \cdot FH \cdot NF_2^-$ complex exists also, but, if this is so, its concentration is much smaller than in the CsF case.

The spectrum of the CsF complex is somewhat more complicated, in agreement with the fact that evidence for two complexes has been reported.[6] The bands in the early spectrum (labeled complex plus gas) are shifted even further from the gas phase frequencies than in the KF and RbF cases. The increased complexity of the NH stretching frequencies supports the existence of at least two types of complexes, but hardly permits speculation on their exact structure. On pumping the spectrum is simplified and all bands shift to the blue. A new band appears at 720 cm.$^{-1}$ and one at 3500 cm.$^{-1}$. These bands can be accounted for by a NF_2^- ion and HF. It would appear that here other types of complexes may be present. A hydrogen-bonded complex similar to the KF·HNF_2 complex,

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(3) R. E. Bell, R. C. Greenough, G. Brull, Jr., and H. E. Dubb, to be published.

(4) J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.*, **19**, 654 (1951).

(5) J. J. Comeford, N. E. Mann, L. J. Schoen, and D. R. Lide, *ibid.*, **38**, 461 (1963).

(6) E. A. Lawton, D. Pilipovich, and R. D. Wilson, *Inorg. Chem.*, **4**, 118 (1965).

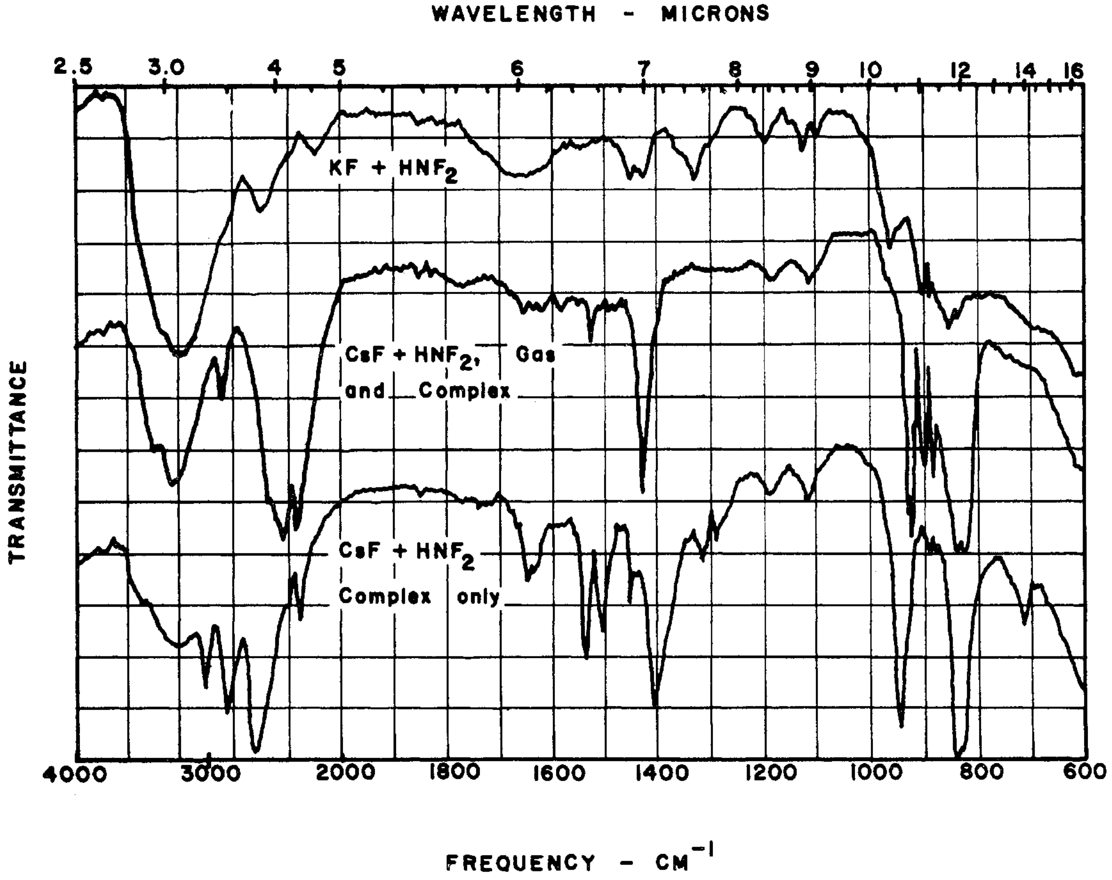

Figure 1.—Infrared spectrum of the difluoramine–alkali metal fluoride complexes.

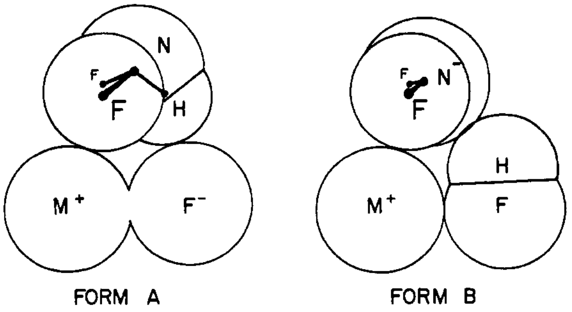

Figure 2.—Possible structures of the CsF·NHF$_2$ complex.

in addition to the complex containing the difluoramide ion, Cs$^+$·FH·NF$_2^-$ (Figure 2, form B), and a complex in which a second HNF$_2$ molecule is intimately attached to the Cs$^+$·FH·NF$_2^-$ cannot be ruled out.

An attempt was also made to find the bending mode of the NF$_2^-$ ion, which should be shifted well to the blue from the 500 cm.$^{-1}$ frequency in HNF$_2$. This would have proved the existence of a NF$_2^-$ ion, but unfortunately the CsF plate was opaque in this region and an attempt to deposit CsF powder on a AgCl window was unsuccessful, as there was too much light scattering from the powder.

Discussion

These data, while hardly conclusive, provide possibly the best evidence to date for the existence of a NF$_2^-$ ion. In the case of KF·HNF$_2$ and RbF·HNF$_2$ the difluoramine seems to form only a strong hydrogen-bonded complex, probably with the structure shown in Figure 2, form A. In the case of the CsF·HNF$_2$ complex there seem to be several different types of complexes, as evidenced in particular by the complexity of the NH stretching region. When gaseous (and presumably liquid) HNF$_2$ was in contact with the CsF, no evidence was found for a NF$_2^-$ ion. When all the gaseous HNF$_2$ was pumped off the HF stretching region significantly changed shape and a band appeared at 720 cm.$^{-1}$ which we feel can only be accounted for by a complex of the type Cs$^+$·FH·NF$_2^-$, probably having a structure not too different from that shown in Figure 2, form B.

The existence of an NF$_2^-$ ion is no great surprise in view of the stability of a number of isoelectronic species such as NH$_2$ and OF$_2$.[7] In the case studied here conditions are optimum for its formation because of the high driving force provided by formation of a HF bond and the optimum positioning of the constituent ions as shown in Figure 2. We are pessimistic, however, of attempts to find the ion in most other situations because of the explosive nature of the CsF·HNF$_2$ complex. We cannot of course be sure as to whether the explosive nature of the complex is due to instability of the NF$_2^-$ ion, or perhaps to HNF$_2$ complexed in a different fashion on the CsF.

Acknowledgments.—We wish to thank Drs. E. A.

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[7] We want to thank a referee for pointing out this fact.

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CONTRIBUTION FROM UNION CARBIDE CORPORATION,[1a]
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Trifluorophosphine Complexes of Nickel

BY R. J. CLARK[1b] AND E. O. BRIMM[1c]

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Mixtures of the $Ni(CO)_x(PF_3)_{4-x}$ compounds can best be prepared by either the interaction of $Ni(CO)_4$ and $Ni(PF_3)_4$ at about 70° or the reaction between PF_3 and $Ni(CO)_4$ at 100° in a pressure vessel. The presence of finely divided nickel metal in the latter approach increases the yield. The composition of the mixtures represents a nearly random arrangement of ligands among the various species. The pure compounds, isolated by means of vapor phase chromatography, have physical properties quite similar to those of the parent compounds and infrared and nuclear magnetic resonance studies clearly pointout the very great similarity between CO and PF_3 as ligands.

Introduction

Nickel complexes of phosphorus trifluoride were first prepared by two different groups of workers. Irvine and Wilkinson[2] prepared $Ni(PF_3)_4$ from PF_3 and $Ni(PCl_3)_4$, with this latter compound being prepared from $Ni(CO)_4$ and PCl_3. Nearly simultaneously Chatt and Williams[3] attempted to prepare $Ni(PF_3)_4$ by the direct replacement of carbonyl groups from $Ni(CO)_4$ by PF_3. Although they did not obtain the desired compound, they did succeed in preparing materials having the composition of a di- to trisubstituted nickel carbonyl. No information was obtained to show whether these materials were mixtures of $Ni(CO)_4$ and $Ni(PF_3)_4$ or mixtures of intermediate compounds that can be formulated as $Ni(CO)_x(PF_3)_{4-x}$. $Ni(PF_3)_4$ was also prepared later by the fluorination of $Ni(PCl_3)_4$ with potassium fluorosulfinate.[4]

In this article, the preparation, isolation, and characterization of the compounds intermediate between $Ni(CO)_4$ and $Ni(PF_3)_4$ will be described.

Experimental

Some of the general techniques are reported in an earlier publication.[5]

Preparation of $Ni(PF_3)_4$.—The procedure differed from that used by Irvine and Wilkinson[2] only in the use of a reaction temperature of 75° to give a slight improvement in yield and in the use of a stainless steel pressure vessel for greater safety. Their procedure for separating the products PCl_3 and $Ni(PF_3)_4$ was changed by hydrolyzing the PCl_3 with cold water, which does not affect $Ni(PF_3)_4$. The $Ni(PF_3)_4$ was separated from excess H_2O by distilling the product *in vacuo* through a bed of Linde 4A Molecular Sieves. The $Ni(PF_3)_4$ is too large to be adsorbed in the internal pore structure, but the water is not.

Tetrakis(trifluorophosphine)nickel(0) of better than 90% purity could be prepared by the direct reaction of $Ni(CO)_4$ and PF_3 in a pressure vessel. About 2 g. of $Ni(CO)_4$ and sufficient PF_3 to create a pressure of 200 p.s.i. at room temperature were heated to 150° in a 150-ml. pressure vessel for 12 hr. The vessel was next cooled to $-195°$ and the evolved carbon monoxide pumped out. The heating, cooling, and evacuation was continued through a total of five cycles. The final product contained better than 90% tetraphosphine with the triphosphine being the only other product.

Preparation of $Ni(CO)_x(PF_3)_{4-x}$ Mixture.—Two procedures were developed for the preparation of these mixtures. The first was similar to the reaction used by Chatt and Williams.[3] $Ni(CO)_4$ (1–2 ml.) was condensed into a 300-ml. capacity stainless steel pressure vessel at $-195°$ followed by enough PF_3 to make a pressure of 200–400 p.s.i., at room temperature. Heating at 100° for several hours caused extensive reaction. The presence of several grams of active nickel prepared from nickel formate considerably increased the yield by reacting with most of the CO evolved on substitution.

Another procedure utilized the reaction between $Ni(CO)_4$ and $Ni(PF_3)_4$. These two materials were sealed in evacuated Pyrex tubes and heated to 75° for 24 to 48 hr. A very small amount of a nonvolatile, nonferromagnetic residue was formed during the process.

Ligand Redistribution.—This study was made by the second of the preparative techniques described above. Mixtures of $Ni(CO)_4$–$Ni(PF_3)_4$, varying in mole fraction by 0.125 increments, were equilibrated at 75°, and the products were analyzed by two different techniques.

One approach was vapor phase chromatography. The injection of small quantities of any of these mixtures onto a 2.5 m. × 5 mm. column of DC-710 silicone oil on Celite at room temperature resulted in five peaks in the chromatogram. The last component to elute had the same retention time as $Ni(CO)_4$. In the other approach, the F^{19} n.m.r. spectra of the mixtures were measured. There were four sets of peaks whose relative height varied with the starting composition, but only the main peak for each species was considered in the interpretation. A typical set of spectra containing only the low-field half is shown in Figure 1.

Isolation of $Ni(CO)_x(PF_3)_{4-x}$ Intermediates.—These compounds were isolated by vapor phase chromatography on a

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[1] (a) Most of the work was done at the former address. (b) Department of Chemistry, Florida State University, Tallahassee, Fla. (c) Union Carbide Europa, S.A., 40 Rue de Rhone, Geneva, Switzerland.

[2] J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, *J. Am. Chem. Soc.*, **73**, 5501 (1951).

[3] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[4] F. Seel, K. Ballreich, and R. Schmutzler, *Chem. Ber.*, **94**, 1173 (1961).

[5] R. J. Clark, *Inorg. Chem.*, **3**, 1395 (1964).