carbamate) complex and a variety of tris(dithiocarbamate) complexes display similar geometries, intermediate between the trigonal prism and the pseudooctahedron. This intermediate geometry clearly cannot be ascribed to the presence of the FeS_6 core. Despite this close geometrical resemblance, tris(thiocarbamato)iron(III) and tris(dithiocarbamato)iron(III) differ in their magnetic properties, with the thiocarbamate complex showing a simple high-spin state[4] while the dithiocarbamate complex lies at the crossover between high-spin and low-spin states.[9] Whether or not the rearrangement mechanisms are also different is yet to be determined.

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Registry No. $Fe(SOCN(CH_3)_2)_3$, 61375-77-7.

Supplementary Material Available: Table II, the positions of the H atoms; Table III, the root-mean-square amplitudes of vibration; and Table IV, a listing of observed and calculated structure amplitudes (25 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of NF_4BiF_6 and Some Properties of NF_4SbF_6

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Perfluoroammonium salts are known[1] of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6{\cdot}nSbF_5^-$, BF_4^-, GeF_5^-, and GeF_6^{2-}. Very recently, the synthesis and chemistry of NF_4^+ salts have received considerable attention owing to their potential for solid propellant NF_3–F_2 gas generators for chemical DF lasers. The concept of such a gas generator was conceived[2] and to a large extent developed at Rocketdyne. Originally, the fluorine gas generators were aimed at the direct generation of F atoms by burning a highly overoxidized grain, consisting mainly of an NF_4^+ salt, with a small amount of fuel, such as Teflon powder, according to

$$NF_4MF_6 + (CF_2)_n \rightarrow CF_4 + NF_3 + MF_5 + Q$$

$$NF_4MF_6 \xrightarrow{+Q} NF_3 + F_2 + MF_5$$

$$2NF_3 + F_2 \xrightarrow{+Q} N_2 + 8F\cdot$$

The heat of reaction (Q) generated in such a system is sufficient to pyrolyze the remaining NF_4MF_6 and to dissociate most of the NF_3 and F_2 to F atoms. For an NF_3–F_2 gas generator, the underlying principle is quite similar, except for keeping the burning temperature lower since dissociation of NF_3 and F_2 to F atoms is not required.

In view of the above developments, we were interested in the synthesis of new NF_4^+ salts and in the characterization of new and known NF_4^+ salts. In this paper, we report on the synthesis of the new salt NF_4BiF_6 and on some properties of the known NF_4SbF_6. Since these two salts can be readily prepared in high yields, they are important starting materials for the syntheses of other NF_4^+ salts used in NF_3–F_2 gas generator compositions.

Experimental Section

Materials and Apparatus. The equipment and handling procedures used in this work were identical with those[1] recently described. The NF_4BF_4 starting material was prepared by low-temperature UV photolysis[1] and did not contain any detectable impurities. The α-BiF_5 was purchased from Ozark Mahoning Co. and did not contain any impurities detectable by Raman spectroscopy. The $NF_4Sb_2F_{11}$was prepared as described.[3]

Synthesis of NF_4BiF_6 by Displacement Reaction without Solvent. Pure NF_4BF_4 (10.1 mmol) and α-BiF_5 (10.1 mmol) were powdered, mixed, and placed in a prepassivated (with ClF_3) 95-mL Monel cylinder. The cylinder was heated to 180 °C for 1.5 h. Products, volatile at 20 °C, were removed by pumping and separated by fractional condensation. They consisted of 7.8 mmol of BF_3 in addition to a small amount of material noncondensable at −196 °C. The amount of BF_3 evolution was confirmed by the weight loss of the solid-containing cylinder. The conversion of NF_4BF_4 to NF_4BiF_6 was further confirmed by Raman spectroscopy of the solid. The solid was removed from the cylinder, finely powdered, returned to the cylinder, and heated to 175 °C for an additional 18 h. This resulted in the evolution of an additional 2.3 mmol of BF_3, in excellent agreement with the observed weight loss. The complete conversion of NF_4BF_4 to NF_4BiF_6 was confirmed by infrared and Raman spectroscopy and elemental analysis. Anal. Calcd for NF_4BiF_6: NF_3, 17.15; BiF_3, 64.49. Found: NF_3, 16.9; BiF_3, 60.0 An explanation for the low BiF_3 value is given below.

Synthesis of NF_4BiF_6 by Displacement Reaction in HF. Dry HF (5 mL of liquid) was added at −78 °C to a Teflon–FEP ampule containing NF_4BF_4 and BiF_5 (9.9 mmol of each). The mixture was agitated at 20 °C for several hours and gas evolution was observed. The volatile products were pumped off at 20 °C and the HF treatment was repeated. After removal of the volatile products from the second HF treatment, 4.075 g of a white, stable solid (weight calculated for 9.9 mmol of NF_4BiF_6 4.089 g) was left behind which was shown by infrared and Raman spectroscopy to be identical with the analyzed product obtained from the above described thermal displacement reaction.

Direct Synthesis of $NF_4BiF_6{\cdot}nBiF_5$. In a typical experiment, a mixture of NF_3 (238 mmol), F_2 (238 mmol), and BiF_5 (10.06 mmol) in a prepassivated 95-mL Monel cylinder was heated for 30 h to 175 °C under an autogenous pressure of 167 atm. Unreacted NF_3 and F_2 (~463 mmol total) were pumped off at 20 °C leaving behind 3.75 g of a white, stable solid (weight calculated for 6.29 mmol of $NF_4BiF_6{\cdot}0.6BiF_5$ 3.745 g). Anal. Calcd for $NF_4BiF_6{\cdot}0.6BiF_5$: NF_3, 11.92; BiF_3, 71.60. Found: NF_3, 11.9; BiF_3, 69.00.

Pyrolysis of $NF_4BiF_6{\cdot}nBiF_5$. A sample (3.29 mmol) of $NF_4BiF_6{\cdot}1.46BiF_5$, prepared as described above expept for using a significantly shorter reaction time, was subjected to vacuum pyrolysis at 280 °C for 1.5 h. The white crystalline residue (1.13 g) was identified by vibrational spectroscopy and its x-ray diffraction powder pattern to be mainly NF_4BiF_6 (weight calculated for 3.29 mmol of NF_4BiF_6 1.36 g) corresponding to a yield of 83%.

Synthesis of NF_4SbF_6. The thermal reaction[4] of NF_3–F_2–SbF_5 at 115 °C, followed by vacuum pyrolysis at 200 °C, produces[3] a product of the approximate composition $NF_4Sb_2F_{11}$. This product can be converted to NF_4SbF_6 by vacuum pyrolysis at higher temperature; however, this SbF_5 removal is accompanied by a competing reaction, i.e., the thermal decomposition of some of the desired NF_4SbF_6. Pyrolysis at 250–260 °C for 1–1.5 h under dynamic vacuum resulted in complete conversion to NF_4SbF_6. Measurement of the NF_3 evolved during this pyrolysis showed that less than 3% of the NF_4SbF_6 had undergone decomposition. When the pyrolysis was carried out at 275–300 °C, even for relatively short periods of time, significantly higher losses of NF_4SbF_6 due to thermal decomposition occurred.

In a typical experiment, $NF_4Sb_2F_{11}$ (31.0 mmol) in a 95-mL Monel cylinder was pyrolyzed under dynamic vacuum at 255 °C for 80 min. The evolved SbF_5 was condensed in a Teflon–FEP U-trap kept at −196 °C. The white solid residue consisted of 30.4 mmol of NF_4SbF_6 (98 mol % yield based on NF_4^+). Anal. Calcd for NF_4SbF_6: NF_3, 21.80; Sb, 37.38. Found: NF_3, 21.72; Sb, 37.41; Ni, 0.08; Cu, 0.03.

Elemental Analyses. For the elemental analyses, a weighed amount (several mmol) of the NF_4^+ salt was placed in the bottom of a Teflon–FEP U-trap, which was closed off by valves. The trap was cooled to −196 °C and several milliliters of distilled water was frozen out in the upper section of the U-trap. The frozen water was shaken down into the cold bottom section of the U-tube and the ice and the NF_4^+ salt were mixed while being cold. This mixing procedure was found important to avoid violent reactions between solid NF_4^+ salts and isolated droplets of liquid water, which sometimes were encountered when thawing the ice in the upper part of the tube and allowing the liquid water to run down onto the NF_4^+ salt. The mixture of ice and NF_4^+ salt was warmed to 20 °C for 30 min. Upon melting of the ice, gas evolution occurred. The contents of the trap were cooled and the evolved O_2 and NF_3 were distilled off at −196 and −126 °C, respectively, and were measured volumetrically. For NF_4SbF_6, the aqueous hydrolysate was analyzed for Sb by x-ray fluorescence spectroscopy. For the BiF_5 salts, a white, water-insoluble precipitate formed on hydrolysis. This precipitate was filtered off at 0 °C, washed with a small amount of cold, distilled water, dried at 103 °C, and weighed. It was identified by its x-ray powder diffraction pattern[4] and by electron microprobe x-ray analysis as BiF_3. Anal. Calcd for BiF_3: Bi, 78.57; F, 21.43; O, 0. Found: Bi, 78.6; F, 21.3; O, 0. Although 93–97% of the BiF_3 could be isolated in this manner, the solubility of BiF_3, particularly in the presence of HF, is not low enough[5] to permit a quantitative precipitation of BiF_3.

Results and Discussion

Syntheses. The new NF_4^+ salt NF_4BiF_6 was prepared either from NF_4BF_4 and BiF_5 by the displacement reaction

$$NF_4BF_4 + BiF_5 \rightarrow NF_4BiF_6 + BF_3$$

or directly by the elevated temperature–pressure method[6] followed by vacuum pyrolysis

$$NF_3 + F_2 + (n+1)BiF_5 \xrightarrow{175\ ^\circ C} NF_4BiF_6 \cdot nBiF_5$$

$$NF_4BiF_6 \cdot nBiF_5 \xrightarrow{280\ ^\circ C} NF_4BiF_6 + nBiF_5$$

The displacement reaction can be carried out either at 25 °C in HF solution or in the absence of a solvent at elevated temperature.

The synthesis of NF_4BiF_6 is more difficult than that of NF_4SbF_6 owing to the fact that at ambient temperature α-BiF_5 is a nonvolatile, polymeric, trans-fluorine-bridged solid. Consequently, temperatures above the melting point (151.4 °C) of BiF_5 are required for both the displacement reaction and the elevated temperature–pressure method. Since removal of excess BiF_5 is inconvenient, the displacement reactions are best carried out with stoichiometric amounts of starting materials. As for SbF_5,[6] the direct synthesis of the perfluoroammonium perfluorobismuthate salt at elevated temperature and pressure tends to produce polyanions (mainly $Bi_2F_{11}^-$).[7] The feasibility of converting these salts to NF_4BiF_6 by vacuum pyrolysis was demonstrated, but no effort was made to maximize the reaction conditions.

The pyrolysis of $NF_4Sb_2F_{11}$ to NF_4SbF_6 and SbF_5 was briefly investigated, when we discovered that the reaction conditions (200 °C) previously recommended[8] for the pyrolysis were not suitable for obtaining pure NF_4SbF_6. In our experience, a significantly higher pyrolysis temperature of about 250 °C was required for the production of essentially pure NF_4SbF_6. At this temperature, little or no decomposition of the NF_4SbF_6 itself took place. On the basis of the results obtained in our laboratory, the thermal reaction between approximately equimolar amounts of NF_3, F_2, and SbF_5 at temperatures ranging from 115 to 200 °C and autogenous pressures of about 200 atm produces a product of the composition $NF_4SbF_6 \cdot nSbF_5$ with n ranging from 2.1 to 3.2 depending on the exact reaction conditions. Vacuum pyrolysis of these products at 200 °C reduces n to a level ranging from 0.8 to 1.1. Pyrolysis at 260 °C reduces the value of n to zero.

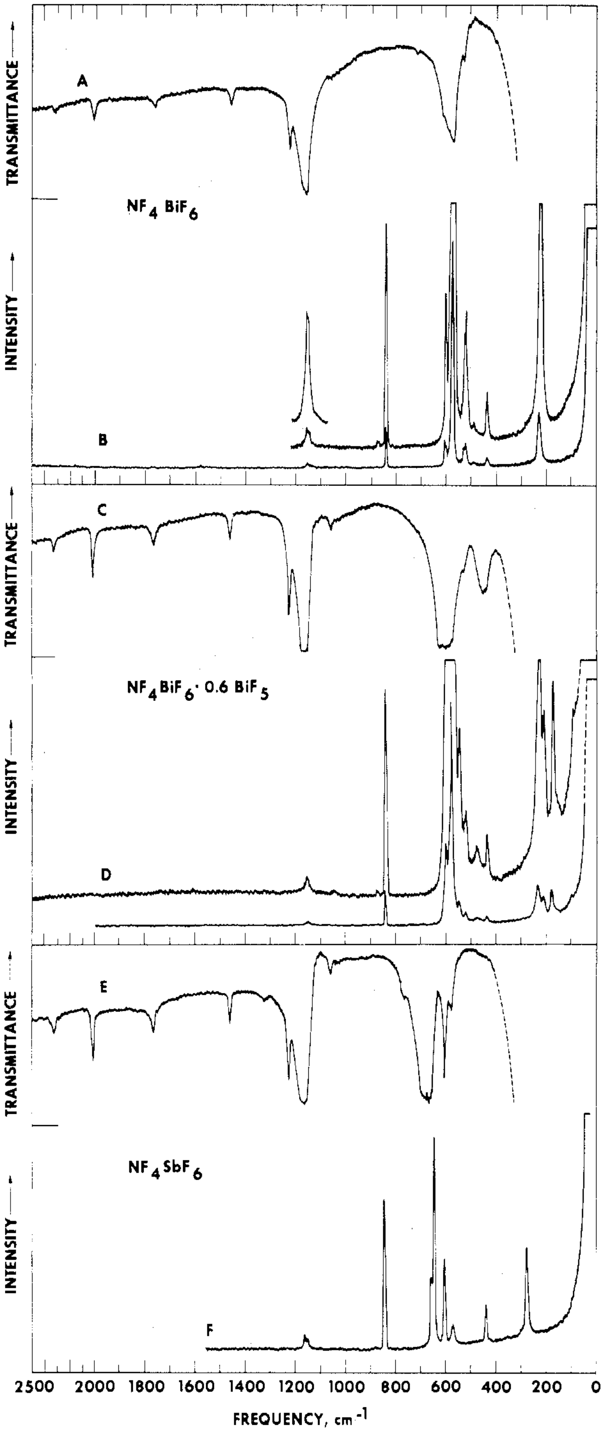

Figure 1. Vibrational spectra of NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6: traces A, C, and E, infrared spectra of the solids in silver chloride disks, the absorptions below 300 cm^{-1} (broken lines) being due to the AgCl windows; traces B, D, and F, Raman spectra of the solids recorded at different sensitivities, the spectral slit width used at the lower sensitivity levels being 2 cm^{-1}.

Properties. The composition of the NF_4^+ salts was established by both the observed material balances and elemental analyses. The NF_4BiF_6 salt is a white crystalline solid melting in a sealed glass capillary at about 341 °C. The x-ray powder diffraction pattern of the sample prepared by pyrolysis of

Table I. Crystallographic Data of NF_4SbF_6 and NF_4BiF_6 Compared to Those of NF_4PF_6 and NF_4AsF_6

	Tetragonal unit cell dimensions					
	a, Å	c, Å	V, Å^3	Z	Vol/F, Å^3	Calcd density, g/cm^3
NF_4PF_6[a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6[b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6	8.006	5.821	373.10	2	18.66	3.68

[a] Reference 1. [b] Reference 7.

$NF_4BiF_6{\cdot}nBiF_5$ is given as supplementary material. It could readily be indexed for a tetragonal unit cell, analogous to those of NF_4PF_6,[1] NF_4AsF_6,[9] and NF_4SbF_6 (see Table I). Several weak lines of variable intensity could not be indexed for a tetragonal unit cell, and corresponding lines had not been observed for the other isotypic NF_4MF_6 salts. Consequently, these extra lines are attributed to impurities, such as polyanion salts, and have not been included in the listing.

The NF_4SbF_6 salt melts at about 318 °C. Its x-ray powder diffraction pattern is given as supplementary material. All of the observed lines could be indexed for a tetragonal unit cell, analogous to those observed for the other NF_4MF_6 salts (see Table I). As expected, the unit cell dimensions and calculated densities increase in the order $PF_6^- < AsF_6^- < SbF_6^- < BiF_6^-$.

The hydrolyses of NF_4SbF_6 and NF_4BiF_6 showed a distinct difference as far as the amount of oxygen evolution is concerned. The NF_4SbF_6 behaved as the previously studied[1] NF_4^+ salts and generated O_2 according to

$$NF_4^+ + H_2O \rightarrow NF_3 + H_2F^+ + {}^1/_2O_2$$

This reaction, however, is not quantitative owing to a competing reaction[1] involving the formation of some H_2O_2. Thus, for NF_4SbF_6, only 0.45 mol of O_2 was observed per mole of NF_3. For NF_4BiF_6, however, 0.86 mol of O_2 was obtained per mole of NF_3. Furthermore, no evidence for the formation of brown Bi_2O_5 (generated when BiF_5 is hydrolyzed) was observed, but white BiF_3 was precipitated. This oxidation of H_2O by BiF_6^- according to

$$BiF_6^- + H_2O \rightarrow BiF_3\downarrow + HF_2^- + HF + {}^1/_2O_2$$

can account for the additional O_2 evolution, which by analogy[1] with NF_4^+ might not be quantitative owing to the formation of some H_2O_2.

The oxygen evolution during the hydrolysis of the closely related O_2^+ salts has recently been studied.[10] In agreement with our findings for NF_4^+ salts, the observed O_2 evolution was generally lower than the calculated values. However, for O_2BiF_6, no evidence for the reduction of pentavalent bismuth was reported. Furthermore, the given explanation, i.e., that the low observed O_2 values are due to samples which had undergone partial decomposition according to

$$2O_2MF_6 \rightarrow O_2M_2F_{11} + O_2 + {}^1/_2F_2$$

cannot account for the low O_2 value found for salts, such as O_2AsF_6, which contain a volatile Lewis acid and do not form a stable $M_2F_{11}^-$ anion. Therefore, some of the conclusions, such as "*all* dioxygenyl salts prepared so far are intrinsically unstable at room temperature", which are based on the low observed oxygen values, are open to question. Obviously, competing side reactions, such as those observed for the NF_4^+ salts, might play an important role and give rise to low oxygen values.

Vibrational Spectra. The vibrational spectra of NF_4BiF_6, $NF_4BiF_6{\cdot}0.6BiF_5$, and NF_4SbF_6 are shown in Figure 1. The

Table II. Vibrational Spectra of Solid NF_4BiF_6, $NF_4BiF_6{\cdot}0.6BiF_5$, and NF_4SbF_6

Obsd freq, cm^{-1}, and rel intens[a]						Assignments (point group)		
NF_4BiF_6		$NF_4BiF_6{\cdot}0.6BiF_5$		NF_4SbF_6				
IR	Raman	IR	Raman	IR	Raman	NF_4^+ (T_d)	MF_6^- (O_h)	$M_2F_{11}^-$
2320 vw		2320 vw		2320 vw		$2\nu_3$ ($A_1 + E + F_2$)		
2010 w		2010 w		2010 w		$\nu_1 + \nu_3$ (F_2)		
1768 vw		1768 vw		1768 vw		$\nu_3 + \nu_4$ ($A_1 + E + F_2$)		
1462 vw		1462 vw		1460 vw		$\nu_1 + \nu_4$ (F_2)		
1228 mw		1228 mw		1227 mw		$2\nu_4$ ($A_1 + E + F_2$)		
1175 sh				1177 sh		ν_3 (F_2)		
1160 vs	1159 (0.15)	1160 vs	1156 (0.13)	1162 vs	1160 (0.6)			
1145 sh	1150 sh	1145 sh		1145 sh	1150 (0.2)			
				1323 vw			$\nu_1 + \nu_3$ (F_{1u})	
1056 vw		1056 vw		1056 vw		$\nu_2 + \nu_4$ ($F_1 + F_2$)		
	878 (0+)		875 (0+)		878 (0.2)	$2\nu_2$ ($A_1 + A_2 + E$)		
	844 (1.8)		844 (1.5)		843 (7.0)	ν_1 (A_1)		
				763 vw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)	
730 vw							$\nu_2 + \nu_4$ ($F_{1u} + F_{2u}$)	
		600 vs	602 (2)					BiF str
		618 m				ν_4 (F_2)		
610 m	608 (1)			609 m	604 (3.9)			
			602 (2)					
	580 (10)		580 (10)		648 (10)		ν_1 (A_{1g})	
				675 vs			ν_3 (F_{1u})	
576 vs		575 sh		665 vs				
				655 sh	655 (1)			
			548 (0.5)					BiF str
529 w	529 sh	531 sh		576 w			ν_2 (E_g)	
	521 (0.8)		521 (0.25)		569 (0.9)			
			475 (0.13)					BiFBi str
		452 m						
	438 (0.35)		436 (0.25)		437 (1.5)	ν_2 (E)		
	228 (2.1)		230 (1.4)		275 (3.8)		ν_5 (F_{2g})	
			211 (0.4)					Def
			175 (0.9)					
			150 sh					
	115 (0+) br		95 (0.1)			Lattice vib		

[a] Uncorrected Raman intensities.

observed frequencies and their assignments are summarized in Table II. The spectra are in excellent agreement with those previously reported for the NF_4^+ cation[1] and the BiF_6^- [7,11,12] and SbF_6^- [7,12-15] anions, thus confirming the ionic nature of these adducts. By analogy with the previously studied[1] NF_4^+ salts, the degeneracy of some of the modes is lifted and crystal field splittings are observed. For example, the antisymmetric NF_4^+ stretching mode ν_3 (F_2) is split into three components, and the ν_3 (F_{1u}) and the ν_2 (E_g) modes of SbF_6^- show a splitting into three and two components, respectively. The presence of polyanions, such as $Bi_2F_{11}^-$,[7] in the $NF_4BiF_6 \cdot nBiF_5$ adducts is apparent from the appearance of a medium intense infrared band at 452 cm^{-1}, which is attributed to the stretching mode of the Bi–F–Bi bridge. Furthermore, additional bands were observed in the region of the BiF stretching and deformation modes. The maximum of the most intense BiF stretching infrared band was found to vary somewhat from sample to sample and varied from 575 to 605 cm^{-1}. In addition, some of the pyrolysis products showed weak infrared bands at 475 and 400 cm^{-1}. A comparison of the spectra of NF_4BiF_6 and $NF_4BiF_6 \cdot nBiF_5$ with those of NF_4SbF_6 and $NF_4Sb_2F_{11}$[1] shows a similar pattern for both when going from MF_6^- to $M_2F_{11}^-$.

Summary

The new NF_4^+ salt NF_4BiF_6 was prepared by the reaction between equimolar amounts of NF_4BF_4 and BiF_5 either at 180 °C without solvent or at 20 °C in HF solution. A salt of the composition $NF_4BiF_6 \cdot nBiF_5$ (n = 0.6–1.5) was prepared directly from NF_3, F_2, and BiF_5 at elevated temperature and pressure. It was converted to NF_4BiF_6 by vacuum pyrolysis at 280 °C. The salts were characterized by elemental analyses and vibrational spectroscopy, and their hydrolyses were studied. The pyrolysis of $NF_4SbF_6 \cdot nSbF_5$ to NF_4SbF_6 was briefly investigated, and the vibrational spectrum and x-ray powder pattern of NF_4SbF_6 are reported.

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Registry No. NF_4BiF_6, 61587-71-1; NF_4SbF_6, 16871-76-4; α-BiF_5, 7787-62-4; $NF_4Sb_2F_{11}$, 58702-89-9.

Supplementary Material Available: Tables III and IV, listing the observed x-ray powder diffraction patterns of NF_4BiF_6 and NF_4SbF_6 (2 pages). Ordering information is given on any current masthead page.

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Reactions of Cyanogen with Zerovalent Nickel Complexes

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Earlier[2a] we reported the reactions of HCN with NiL_4 complexes (L = phosphorus ligand) by eq 1. We now wish

$$HCN + NiL_4 \rightleftharpoons HNiL_3CN + L \tag{1}$$

to report the results of an analogous study of cyanogen reactions (eq 2), where C–C rather than C–H bond cleavage

$$NCCN + NiL_4 \rightleftharpoons NiL_3(CN)_2 + L \tag{2}$$

is the major reaction.

There appear to be only four reports[2b-5] in the literature on the reactions of cyanogen with transition metal complexes, with two brief reports involving Ni(0).[4,5] Nickel dicyanide complexes are of course well-known, though they have usually been prepared from $Ni(CN)_2$. They have been extensively studied[6-10] (usually by VIS–UV spectroscopy) mainly in order to define the factors which control equilibrium 3. No ^{31}P

$$NiL_3(CN)_2 \overset{K_3}{\rightleftharpoons} NiL_2(CN)_2 + L \tag{3}$$

NMR studies and only scattered IR data on nickel dicyanide complexes can be found in the literature. We began this study in order to see how changing the electronic[11] and steric[12] properties of L would affect the rates and products of the cyanogen reactions, for comparison with the HCN results.[2a] By following IR and $^{31}P\{^1H\}$ NMR spectra with time we have also been able in some cases to observe unstable (NCCN)-NiL_3[13] complexes.

In a typical reaction, 0.2 mmol of $Ni[P(OEt)_3]_4$ in 1.8 mL of toluene was allowed to react with 0.4 mmol of cyanogen in a 10-mm NMR tube. The solution gradually became yellow and the IR spectrum showed a new band growing in at 2115 cm^{-1}, assigned to ν_{CN} in *trans*-$Ni[P(OEt)_3]_3(CN)_2$. $^{31}P\{^1H\}$ spectra showed a decline of the $Ni[P(OEt)_3]_4$ resonance at −159.1 ppm and the appearance of a new broader resonance at −121.5 ppm, assigned the exchange average of free $P(OEt)_3$ and $Ni[P(OEt)_3]_3(CN)_2$. Figure 1a shows that cooling to −59 °C causes the product resonance to split into two in the expected 1:3 intensity ratio. Addition of free $P(OEt)_3$ simply enhances the intensity of the −136.6-ppm resonance in the −59 °C spectrum. The fact that the width (~90 Hz) of the −120-ppm resonance in the −28 °C spectrum is unaffected by the addition shows that the exchange goes by dissociation of a ligand from $NiL_3(CN)_2$ (eq 3), rather than by association.[14]

Though $Ni[P(OEt)_3]_2(CN)_2$ provides a pathway for ligand exchange, it is not present in solution to a spectroscopically significant extent. Thus the position of the average resonance at 25 °C before L addition (Table I) is in good agreement with that calculated from eq 4, where δ_1 and δ_3 are the chemical

$$\bar{\delta}_{\text{calcd}} = {}^1/_4[\delta_1 + 3\delta_3] \tag{4}$$

shifts (in the low-temperature limit spectrum) of free L and $NiL_3(CN)_2$. The IR spectrum shows only bands of unreacted cyanogen (2150 cm^{-1}) and $Ni[P(OEt)_3]_3(CN)_2$.

Rapid exchange of free L with ligand in $NiL_3(CN)_2$ is observed in nearly all cases; Table I gives ^{31}P chemical shifts

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