cooled to 0 °C. The solution was irradiated with a broad-band UV source from a distance of 2 cm and slowly flushed with nitrogen to remove generated carbon monoxide. After 3 h, the solution had changed from orange to dark brown and an infrared spectrum showed 90% disappearance of the 2031-cm^{-1} peak and the appearance of a ν_{CO} band at 1854 cm^{-1} accompanied by a shoulder at 1950 cm^{-1}. The solution was rotary evaporated in the dark to concentrate the mixture. Attempts at crystallization of the product resulted in crystals that were contaminated by $CpW(CO)_3SPh$. A small amount of pure sample was obtained by using size-exclusion chromatography on S-X12 BioBeads resin eluting with methylene chloride, but all other chromatographic materials (e.g., alumina, Florisil, and silica) resulted in decomposition of the product on the column. The IR and ^1H NMR spectra of $[CpW(CO)_2SPh]_2$ are reported in Tables I and II.

The complex $[CpW(CO)_2STol]_2$ was prepared in exactly the same manner; however, no attempt was made to purify the sample. An infrared spectrum of the benzene reaction solution exhibited ν_{CO} peaks of 2027 (s), 1954 (sh), 1940 (s), and 1849 (m) cm^{-1}. The peaks at 2027 and 1940 cm^{-1} correspond to $CpW(CO)_3STol$, and the remaining peaks at 1954 and 1849 cm^{-1} are assigned to the compound $[CpW(CO)_2STol]_2$ (see Table I).

Removal of the solvent by rotary evaporation, followed by dissolution of the solid in $CDCl_3$, yielded a ^1H NMR spectrum with resonances at 5.67, 5.40, 2.26, 2.23, and 7.15 (broad multiplet) ppm. The peaks at 5.67 and 2.26 ppm have been previously assigned to $CpW(CO)_3STol$ (Table III), and on the basis of its similarity to $[CpW(CO)_2SPh]_2$, the compound $[CpW(CO)_2STol]_2$ is assigned the following ^1H NMR resonances in $CDCl_3$: $\delta(Cp) = 5.40$; *p*-tolyl, $\delta(Me) = 2.23$, $\delta(aryl) = 7.15$.

Synthesis of $[CpW(CO)STol]_2$. When $CpW(CO)_3STol$ was refluxed in benzene in the manner of Watkins and George[4] and monitored every 3 min by cooling the solution to room temperature and removing a small aliquot, a mixture of $[CpW(CO)_2STol]_2$ and $[CpW(CO)STol]_2$ was initially formed as evidenced by both IR and ^1H NMR spectra. Continued refluxing resulted in the formation of $[CpW(CO)STol]_2$ (^1H NMR ($CDCl_3$): $\delta(Cp) = 5.30$; *p*-tolyl, $\delta(Me) = 2.16$, $\delta(aryl) \approx 7.0$) although there was some decomposition to a tan non-carbonyl-containing precipitate. Micropore filtration of the solution removed the precipitate to yield a solution that had spectroscopic parameters similar to those of Watkins and George's[4] "$[CpW(CO)_2STol]_2$"; however, our analysis indicates it should be formulated as $[CpW(CO)STol]_2$.

Synthesis of $[CpW(CO)SPh]_2$. A nitrogen-purged toluene solution containing ~30 mg of $CpW(CO)_3SPh$ was maintained at 95 °C for 75 min by the use of a circulating bath of H_2O. A slow flow rate of N_2 *above* the solution was used to remove free CO as it was released from solution. At the end of 75 min, removal of a small aliquot and analysis by IR indicated that the solution contained a mixture of $CpW(CO)_3SPh$, $[CpW(CO)_2SPh]_2$, and a new compound that exhibited ν_{CO} bands at 1896 and 1847 cm^{-1}. Due to the similarity of these ν_{CO} bands to the carbonyl stretching frequencies of $[CpW(CO)STol]_2$, this new compound is assigned as $[CpW(CO)SPh]_2$. Rotary evaporation of the toluene in low-light conditions resulted in the isolation of a brown-black powder. A ^1H NMR spectrum of the powder dissolved in $CDCl_3$ indicated the presence of three distinct Cp resonances at 5.67, 5.43, and 5.30 ppm. The 5.67 and 5.43 ppm peaks correspond with the cyclopentadienyl resonances of $CpW(CO)_3SPh$ and $[CpW(CO)_2SPh]_2$. The third Cp resonance is therefore assigned to the complex $[CpW(CO)SPh]_2$ and is found at the same frequency as the cyclopentadienyl resonance in $[CpW(CO)STol]_2$. Analysis of the Cp intensities reveals that the products of this reaction and their relative amounts were as follows: $CpW(CO)_3SPh$, 30%; $[CpW(CO)_2SPh]_2$, 50%; $[CpW(CO)SPh]_2$, 20%.

Synthesis of $CpW(CO)_2(PPh_3)SPh$. In a manner analogous to the preparation of $[CpW(CO)_2SPh]_2$ above 0.1734 g (0.392 mmol) of $CpW(CO)_3SPh$ and 0.1208 g (0.392 mmol) of triphenylphosphine were dissolved in degassed benzene and cooled with cold-water flow. The solution was irradiated with a broad-band UV source and continuously flushed with nitrogen. After 3 h, an infrared spectrum indicated an appreciable accumulation of a new compound with ν_{CO} peaks of 1950 and 1865 cm^{-1}. After reduction of the volume to 10 mL by rotary evaporation, the solution was applied to the top of a 2.5 × 20 cm grade I neutral alumina column poured under benzene. Benzene elution removed unreacted $CpW(CO)_3SPh$ and PPh_3. A yellow-orange band eluted with a 1:1 mixture of benzene/CH_2Cl_2. Rotary evaporation of the yellow fractions gave orange crystals of $CpW(CO)_2(PPh_3)SPh$ (see Table III for spectral data).

Synthesis of $CpW(CO)_2(PPh_3)STol$. In a manner completely analogous to the method for preparation of $CpW(CO)_2(PPh_3)SPh$, 0.0870 g (0.19 mmol) of $CpW(CO)_3STol$ and 0.0571 g (0.19 mmol) of PPh_3 were dissolved in degassed toluene, cooled, and irradiated with broad-band UV light. After 1 h, an infrared spectrum of an aliquot of the reaction solution indicated that ~95% of the $CpW(CO)_3STol$ had reacted and the irradiation was terminated. The grade I alumina column was filled with toluene, and the concentrated reaction solution was stripped onto the column. Toluene elution removed the unreacted $CpW(CO)_3STol$, and a 1:1 toluene/CH_2Cl_2 mixture eluted an orange solution. Comparison of the IR and ^1H NMR spectra of the chromatographically pure product to the spectra of $CpW(CO)_2(PPh_3)SPh$ demonstrated a high degree of similarity (see Table III). A ^{31}P NMR spectrum of the crystals dissolved in $CDCl_3$ confirmed the presence of two isomers. On the basis of a comparison of the relative intensities of the Cp resonances in the ^1H NMR spectrum to the relative intensities of the ^{31}P resonances, *cis*-$CpW(CO)_2(PPh_3)STol$ is assigned as +27.1 ppm ($J_{P-W} = 242$ Hz) and *trans*-$CpW(CO)_2(PPh_3)STol$ is assigned as +34.7 ppm ($J_{P-W} = 214$ Hz).

Acknowledgment. The support of the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Exploratory work was also supported by the Research Corp.

Registry No. $CpW(CO)_3SPh$, 12110-93-9; $[CpW(CO)_3]_2$, 12091-65-5; $[CpW(CO)_2SPh]_2$, 12115-39-8; $CpW(CO)_3STol$, 58057-63-9; $[CpW(CO)_2STol]_2$, 58129-82-1; $[CpW(CO)STol]_2$, 108366-46-7; $[CpW(CO)SPh]_2$, 108366-47-8; $CpW(CO)_2(PPh_3)SPh$, 108366-48-9; $CpW(CO)_2(PPh_3)STol$, 108366-49-0; $[PhS]_2$, 882-33-7; di-*p*-tolyl disulfide, 103-19-5.

Contribution from the Institut für Anorganische Chemie
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Properties of Triazadienyl Fluoride, N_3F

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A safe preparative method has been developed for the synthesis of the very explosive N_3F in pure form. This allowed the comprehensive characterization of N_3F by means of IR, UV/vis, NMR, and mass spectroscopy as well as a determination of the melting point and vapor pressure. The usefulness of N_3F as a synthetic reagent is demonstrated.

Although the existence of triazadienyl fluoride (fluorine azide, N_3F) has been known since the pioneering work of Haller[1] in 1942, this interesting molecule has rarely been investigated.

Yellow gaseous N_3F is generated by the reaction of HN_3 with F_2 in the gas phase.[1] It decomposes slowly at room temperature to N_2F_2 and N_2. In the liquid and solid states N_3F is extremely explosive, and purification was impossible. Vapor density and boiling and melting points were estimated for the impure compound. Qualitative spectroscopic measurements on N_3F were made in the range 370–450 nm.[2] There are statements about

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(1) Haller, J. F. Ph.D. Dissertation, Cornell University, 1942.

(2) Gipstein, E.; Haller, J. F. *Appl. Spectrosc.* **1966**, *20*, 417.

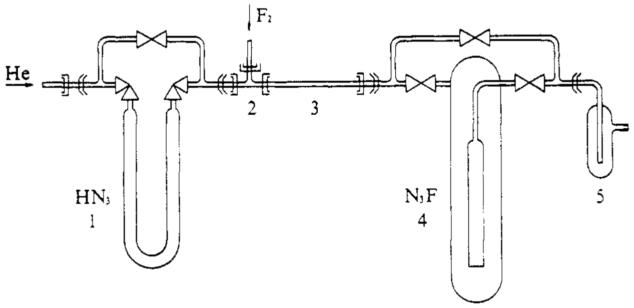

Figure 1. Apparatus for synthesis of N_3F: (1) U-trap; (2) T-fitting; (3) reaction tube (stainless steel, 6 × 0.5 mm, l = 150 mm); (4) glass trap (V = 250 mL); (5) bubble counter.

the absorption spectrum in the range 190–450 nm in a recent paper concerning ArF excimer laser photolysis of N_3F at 193 nm.[3] Some frequencies of N_3F isolated in an Ar matrix are given.[4] There are some indications of the chemistry of N_3F, but it seems doubtful that the reactions reported are relevant to N_3F, because possible impurities, such as HN_3, N_2F_2, FNO_3, and SiF_4, were not separated.[1,5,6]

Within the scope of our recent synthesis of FNCO,[7] we became interested in the properties of N_3F, which is isoelectronic with FNCO. We were able to improve the known synthesis and to purify N_3F. An extensive characterization of N_3F was carried out, and the results are summarized in this paper.

Experimental Section

Caution! Anhydrous hydrazoic acid is a dangerous compound. Triazadienyl fluoride is extremely explosive in the liquid and solid phases. HN_3 and N_3F should be handled in quantities less than 20 mg and with appropriate shielding, eye protection, and gloves.

Materials and Apparatus. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-A-10 MKS Baraton Burlington) and valves with Teflon pistons (Young, London). The vacuum line was connected directly to an IR cell (1 = 200 mm, KBr windows) by a glass tube, so it was possible to observe the effect of purifications and reactions immediately. A device described previously[8] was used for recording the low-temperature spectra. Fluorine (Kali-Chemie) was measured by *PVT* in a stainless-steel vacuum line with a diaphragm pressure gauge (ME 235-65 Medas, Laichingen, FRG). HF was removed by passing through an absorber (KF powder between SIPERM sintered Monel disks, Thyssen, Dortmund, FRG). The fluorine addition was controlled by a flow meter (Fischer & Porter, Göttingen, FRG) (Figure 1). The compounds NaN_3 (Merck), CO and He (Messer Griesheim), CF_2ClBr (Kali-Chemie), and COS and NO (Baker) were used as received.

For the spectroscopic investigations the following equipment was used: FTIR spectrometer MXS (Nicolet) 4200–400 cm^{-1}, resolution 4 cm^{-1}; UV/vis spectrometer Model 402 (Perkin Elmer) 190–670 nm, a glass cell of 100-mm path length equipped with SUPRASIL windows; NMR spectrometer WP 80 (Bruker), frequency for ^{19}F-NMR 75.39 MHz; quadrupole mass spectrometer 4021 (Finnigan).

Synthesis of N_3F. For the preparation of N_3F the apparatus shown in Figure 1 was used. After the apparatus was dried with helium, trap 4 was chilled to −160 °C with a slush of CF_2ClBr. Then fluorine was allowed to flow at a constant rate (10 mL/min) into T-fitting 2 and pure HN_3 (0.1–0.2 mmol) was slowly vaporized at −10 °C in a helium flow (30 mL/min) through U-trap 1. The gas-phase mixture of F_2/HN_3 reacted at 20–25 °C in stainless-steel tube 3 and a white solid deposited in the upper part of trap 4. N_3F is condensed as a thin film on the large surface of trap 4. After all the hydrazoic acid has been vaporized from trap 1, the excess fluorine was purged from the apparatus with a stream of nitrogen. Subsequently trap 4 was evacuated, and the product was fractionally evaporated very slowly by placing a cold Dewar vessel (dry ice) around the trap. The more volatile impurities SiF_4, N_2F_2, and N_2O were pumped away first. Then very pure N_3F was vaporized into the vacuum line and into the IR gas cell and was investigated immediately. The pure product was admitted to a flask with a stopcock (V = 500 mL). At a pressure of 10–20 mbar and a temperature of −80 °C N_3F can be stored for several months without noticeable decomposition.

Table I. Infrared Spectra of N_3F: Observed Frequencies (cm^{-1}), PR Separations (cm^{-1}), and Intensities

gas phase (300 K)		$\Delta\nu$(PR)	solid film (77 K)	assignt	
2171.5	s	16	2170	$2\nu_2$	a′
2037.0	vs	20	2052	ν_1	a′
1953.0	w	18		$\nu_2 + \nu_3$	a′
1736.0	vw	18		$2\nu_3$	a′
1090.0	m	18	1084	ν_2	a′
897.0	sh		893	$\nu_4 + \nu_5$	a′
873.5	s	17	853	ν_3	a′
658.0	m	16	649	ν_4	a′
504.0	w		505	ν_6	a″
241.0	m	20		ν_5	a′

By this method the safe preparation of about 20 mg N_3F may be accomplished. The yield of N_3F based on HN_3 was 50–70%.

Anhydrous Hydrazoic acid. A 100-mL glass ampule was cooled to −196 °C and loaded with 200 mg of NaN_3 and 3 mL of concentrated H_2SO_4. The contents warmed up very slowly and the HN_3 gas that was generated was trapped at −196 °C under dynamic vacuum. HN_3 is very soluble in concentrated H_2SO_4, and therefore the solution was heated to 80 °C at the end of the reaction. Final purification was effected by fractional condensation through traps cooled at −50, −100, and −196 °C. The fraction at −100 °C was pure anhydrous HN_3.

Results and Discussion

Synthesis and Properties of N_3F. The synthesis of pure N_3F by the method described above was repeated more than 30 times without explosion. But if N_3F is cooled to −196 °C or N_3F is vaporized faster than described, very violent explosions may occur. One drop of N_3F will pulverize any glass within a 5-cm distance.

If some water is involved in the reaction of HN_3/F_2 an impurity of FNO_3 is formed that cannot be separated by fractional evaporation. A copper tube should not be used for the reactions as previously recommended,[1] because copper or copper fluoride catalyzes the decomposition of N_3F.

The thermal decomposition of gaseous N_3F into a mixture of *cis*- and *trans*-N_2F_2 and nitrogen at different temperatures was investigated quantitatively by IR spectroscopy. Although it might be anticipated that NF molecules are formed in the primary step and that NF dimerizes rapidly to N_2F_2, the decomposition is more complex. The measured decomposition kinetics were not fully reproducible, and there was no simple law for the kinetics. It was shown that the decomposition depends strongly on temperature and pressure. If one starts from 5 mbar of N_3F at 20, 25, and 30 °C, the half-lives are 5 h, 2 h, and 20 min, respectively.

Triazadienyl fluoride is yellow in the gaseous, liquid, and solid phases. By repeated measurements, a melting point of −139 °C was determined.

Vapor pressures were measured in a small device ($V \sim 25$ mL) consisting of a capacitance pressure gauge (0–17 mbar), a glass tube (6 × 1 mm) that is connected to a thin-walled glass sphere (o.d. = 10 mm) in contact with a Pt 100 temperature sensor (inside the sphere), and a valve connecting the device with the vacuum line. For vapor pressure measurements, about 6 mg of pure N_3F was condensed at −160 °C into the glass sphere. The cooling bath was stirred and quickly warmed from one measuring temperature to the next in a range of −126 to −97 °C. The determination of vapor pressures at higher temperature was not accomplished because of the hazardous properties of N_3F and the decomposition in the gas phase. The data were fitted by a least-squares method to the following equation with a correlation coefficient of 0.985:

$$\ln p\ (\mathrm{mbar}) = -(2.683 \times 10^3)/T\ (\mathrm{K}) + 17.958$$

The extrapolated boiling point is −30 ± 5 °C.

IR Spectra. Figure 2 shows the infrared spectrum of gaseous and solid N_3F. The observed frequencies are listed in Table I.

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(3) Patel, D.; Pritt, A. T., Jr.; Bernard, D. J. *J. Phys. Chem.* **1986**, *90*, 1931.

(4) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1964**, *40*, 2461.

(5) Lawless, E. W.; Smith, I. C. *Inorganic High-Energy Oxiders*; Marcel Dekker: New York, 1968.

(6) Gordon, J.; Surkonick, B. *U.S. Publ. Pat. Appl. B.* **1976**, *111*, 130. Gordon, J.; Surkonick, B. U.S. Pat. 3969486, 1976.

(7) Bielefeldt, D.; Gholivand, K.; Haas, A.; Willner, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1211.

(8) Schnockel, H. G.; Willner, H. *Z. Anorg. Allg. Chem.* **1974**, *408*, 247.

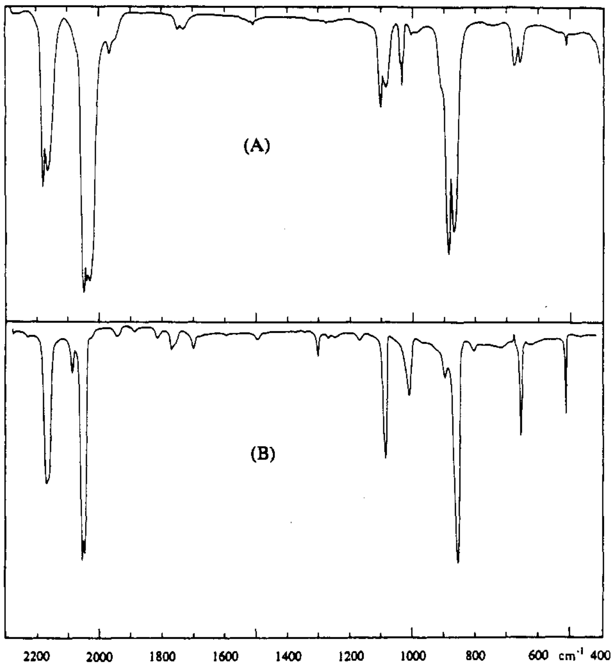


Figure 2. Infrared spectra of N_3F: (A) spectrum of the gas recorded in a 20-cm cell equipped with KBr windows at a pressure of 11.3 mbar; (B) spectrum of the solid film at 77 K.

Table II. Assignment of the Six Fundamental Vibrations (cm^{-1}) of XN_3 Molecules

assignt		approx descrpn of modes	HN_3[a]	DN_3[a]	ClN_3[b]
a′	ν_1	$\nu_{as}(N_3)$ or $\nu(N_2N_3)$	2140	2141	2075
	ν_2	$\nu_s(N_3)$ or $\nu(N_1N_2)$	1274	1184	1140
	ν_3	$\nu(XN)$	3336	2480	719
	ν_4	$\delta(N_3)$ in plane	522	498	545
	ν_5	$\delta(XNN)$	1150	955	223
a″	ν_6	$\delta(N_3)$ out of plane	672	638	522

[a] Data from ref 10. [b] Data from ref 11.

Since the N_3F molecule has C_s symmetry, five of the six fundamental modes of vibration belong to species a′ and one belongs to species a″. Assignments for the six modes are based on comparison with known spectra of XN_3 compounds (Table II), characteristic frequencies, and observed band contours. For the asymmetric top molecule N_3F, the oscillations of the dipole moment in a′ modes are not in the directions of the moments of inertia I_a and I_b. Therefore A/B hybrid band contours with PR distances of 17–20 cm^{-1} are predicted for these vibrations.[9] The dipole moment oscillates parallel to I_c during the out-of-plane vibration ν_6, and a C-type band is expected with a prominent Q-branch. Accordingly, the band at 504 cm^{-1} is assigned to ν_6. The two characteristic NN vibrations for the N_3 group are easily assigned by comparison with the corresponding vibrations of ClN_3 and HN_3. The remarkably high intensity of $2\nu_2$ arises by Fermi resonance with ν_1. Consequently the frequency of ν_1 is lowered. The NF vibration is observed at 874 cm^{-1} in the expected range. The remaining a′ modes at 658 and 241 cm^{-1} are assigned to the in-plane N_3 deformation and the FNN deformation, respectively. The extent of coupling can only be evaluated by a normal-coordinate analysis, which is not within the scope of this study. Finally, the small change of vibrational frequencies in different states shows that N_3F molecules are only slightly associated in the solid state.

^{19}F NMR Spectrum. The ^{19}F NMR spectrum of N_3F is recorded at −80 °C in CD_2Cl_2 and $(CD_3)_2O$ solution. It shows a broad signal at −113 ppm upfield from internal $CFCl_3$ in both solvents. The signal is broadened by quadrupolar coupling to ^{14}N.

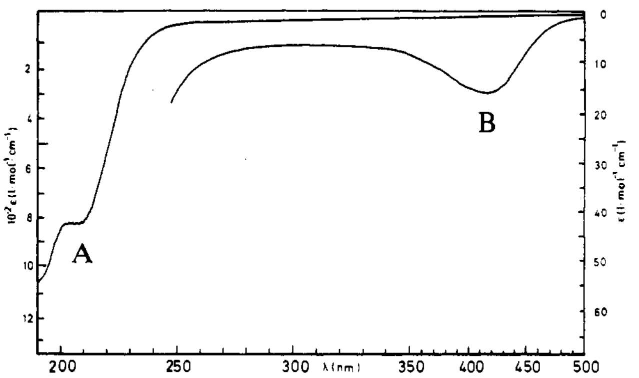
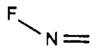
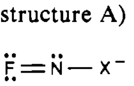


Figure 3. UV/vis absorption spectrum of gaseous N_3F: (A) 2.7 mbar; (B) 10.7 mbar.

Very few NMR data are known for molecules of the structural type



but the examples FNO, 479 ppm;[12] N_2F_2 (cis/trans), 134/94 ppm;[13] and $FNCF_2$, −67 ppm[14] show that the range of chemical shifts for FNX is very large. The unexpectedly high chemical shift for the ^{19}F NMR signal in FNO is interpreted in terms of a large paramagnetic component to the ^{19}F nuclear deshielding. The relatively strong screening of the ^{19}F nucleus in N_3F can be explained by assuming that the π-donor ability of the F atom (formation by resonance structure A) is very low in N_3F.



A

UV/vis Spectrum. The UV/vis absorption spectrum of gaseous N_3F is shown in Figure 3. The absorptions measured qualitatively in earlier studies are confirmed.[2,3] Analogous to those of other halogen azides,[15] this spectrum also shows three absorptions: λ_{max} = 414, 208, and <190 nm; ϵ_{max} = 12, 800, and >1200 L mol^{-1} cm^{-1}. The observed electronic transitions in ClN_3, BrN_3, and IN_3[15] are explained by using the MO diagram for alkyl azides.[16] On the basis of this interpretation, the influence of the halogen p orbitals on the orbital energies has been neglected. Very recent ab initio and SINDO 1 calculations on different azides led to a more detailed interpretation of the UV spectrum of N_3F.[17] It was shown that the transition energy $s_0 \rightarrow s_1$ decreases with decreasing halogen–nitrogen bond length, because the interaction of the halogen p_z orbital with the π_z orbital on N_α increases. Accordingly, the shift of the lowest energy absorption can be rationalized in the following series: IN_3, $\lambda \sim 345$ nm;[15] ClN_3, $\lambda \sim 385$ nm;[15] N_3F, $\lambda = 414$ nm.

Mass Spectrum. The mass spectrum of N_3F was measured with an ionization energy of 70 eV and an ion source temperature of 50 °C. The peak assigned to the parent ion at *m/e* 61 is surprisingly strong. In contrast to the labile N_3F the unimolecular decomposition of N_3F^+ is a process that needs high energy. The observed peaks at *m/e* 42 (N_3^+) and *m/e* 33 (NF^+) are typical for covalent azides. The intensities are as follows: N_3F^+, 100; N_3^+, 80; NF^+, 98; N_2^+, 45.

Reactions with N_3F. The chemical reactions of N_3F in the gas phase were studied in a glass flask or in an infrared cell. In each

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(9) Seth-Paul, W. A. *J. Mol. Struct.* **1968**, *3*, 403.
(10) Dows, D. A.; Pimentel, G. C. *J. Chem. Phys.* **1955**, *23*, 1258.
(11) Kolitsch, K. Ph.D. Dissertation, Universität Marburg, W. Germany, 1974.
(12) Holmes, J. R.; Steward, B. B.; Mc Kenzie, J. S. *J. Chem. Phys.* **1962**, *37*, 2728.
(13) Noggle, J. H.; Baldeschwieler, J. D.; Colburn, C. B. *J. Chem. Phys.* **1962**, *37*, 182.
(14) Dybvig, D. H. *Inorg. Chem.* **1966**, *5*, 1795.
(15) Dehnicke, K.; Ruschke, P. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 750.
(16) Closson, W. D.; Gray, H. B. *J. Am. Chem. Soc.* **1963**, *85*, 290.
(17) Jug, K., private communication. Jug, K.; Nanda, D. N. *Theor. Chim. Acta* **1980**, *57*, 95.

case 1–5 mbar of pure N_3F was mixed with excess reagent and allowed to stand at room temperature. No reaction occurred with H_2O, O_2, XeF_2, OF_2, and Me_3SiN_3. Reactions with NO, CO, and COS led to products that can be interpreted as arising from the formation of NF as an intermediate.

$$N_3F \rightarrow [NF] + N_2 \rightarrow N_2F_2 \text{ (cis/trans)}$$

$$[NF] + NO \rightarrow [?] \rightarrow FNO + N_2O$$

$$\begin{aligned} [NF] + CO \rightarrow [FNCO]^{18} &\xrightarrow{\text{dim.}} NF_2C(O)NCO \\ &\xrightarrow{F_2} NF_2C(O)F \\ &\xrightarrow{CO} FC(O)NCO \end{aligned}$$

$$[NF] + COS \rightarrow [FNS] + CO \rightarrow FSN$$

These few examples show clearly that the chemistry of N_3F is significantly different from the chemistry of other halogen azides.[19]

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. N_3F, 14986-60-8; HN_3, 7782-79-8; F_2, 7782-41-4; NaN_3, 26628-22-8; H_2SO_4, 7664-93-9; NO, 10102-43-9; CO, 630-08-0; COS, 463-58-1.

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(18) Gholivand, K.; Willner, H. *Z. Anorg. Allg. Chem.*, in press.
(19) Dehnicke, K. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 169.

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Electrochemistry and Spectroelectrochemistry of the Hexachloroiridate(III) and -(IV) Complexes in the Basic Aluminum Chloride–1-Methyl-3-ethylimidazolium Chloride Room-Temperature Ionic Liquid

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In contrast to its behavior in aqueous solution, the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system exhibits classical reversible, uncomplicated electrochemical behavior at glassy-carbon electrodes in the basic aluminum chloride–1-methyl-3-ethylimidazolium chloride room-temperature ionic liquid. The formal potential of this redox system in the 49.0/51.0 mol % melt was found to be 0.370 V vs. Al in the 66.7/33.3 mol % melt. Diffusion coefficients for $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ in the former melt were 4.3×10^{-7} and 3.0×10^{-7} $cm^2\ s^{-1}$, respectively, at 40.0 °C. The Stokes–Einstein product for $[IrCl_6]^{2-}$ in the ionic liquid was remarkably close to its value in aqueous solution.

Introduction

Room-temperature chloroaluminate ionic liquids[1] are obtained when aluminum chloride is combined with certain organic chloride salts. Two examples of such mixtures are aluminum chloride–1-methyl-3-ethylimidazolium chloride ($AlCl_3$–MeEtimCl) and aluminum chloride–1-(1-butyl)pyridinium chloride ($AlCl_3$–BupyCl). Both ionic liquids can be made to exhibit a wide range of Lewis acidities and solvation characteristics at room temperature simply by varying the relative amounts of $AlCl_3$ and organic salt. The acid–base properties of these solvents have been reported;[2] mixtures that contain a molar excess of $AlCl_3$ are designated as "acidic", while those containing a molar excess of the organic salt are denoted as "basic".

Basic $AlCl_3$–BupyCl and $AlCl_3$–MeEtimCl are excellent solvents in which to study the solution chemistry of transition-metal chloride complexes at room temperature since the solvation and solvolysis reactions commonly associated with these complexes in aqueous solution are absent in the melts.[3] A number of first-row transition-metal chloride complexes have been investigated in room-temperature chloroaluminate melts, including cobalt(II),[4] copper(I) and copper(II),[5] iron(II) and iron(III),[6] nickel(II),[6a,7] and titanium(III) and titanium(IV),[8] while studies with second- and third-row transition-metal ions have been limited to silver(I),[9] molybdenum(III) and molybdenum(IV),[10] ruthenium(III) and ruthenium(IV),[11] and tungsten(III) through tungsten(V).[12]

The iridium(III) chloride complex, $[IrCl_6]^{3-}$, is known to undergo aquation readily in aqueous solution to form species of the type $[IrCl_{6-x}(OH_2)_x]^{x-3}$.[13] Moreover, a recent spectroscopic study of the iridium(IV) chloride complex, $[IrCl_6]^{2-}$, in the $AlCl_3$–MeEtimCl melt suggested that much of the classical spectroscopic data reported for this species in aqueous solution (even at high chloride ion activity) was actually obtained for a mixture of chloride and aquated chloride species.[3] In addition, $[IrCl_6]^{2-}$ is reported to undergo spontaneous reduction to $[IrCl_6]^{3-}$ in neutral or basic aqueous solutions with the evolution of oxygen.[14] The formal potential of the $[IrCl_6]^{2-}/[IrCl_6]^{3-}$ system has been determined by using potentiometry in aqueous solution, and diffi-

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(1) For reviews see: (a) Chum, H. L.; Osteryoung, R. A. In *Ionic Liquids*, Inman, D., Lovering, D. G., Eds.; Plenum: New York, 1981; pp 407–423. (b) Hussey, C. L. *Adv. Molten Salt Chem.* **1983**, *5*, 185–230. (c) Gale, R. J.; Osteryoung, R. A. In *Molten Salt Techniques*; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. 1, pp 55–78.
(2) (a) Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603. (b) Schoebrechts, J. P.; Gilbert, B. P. *J. Electrochem. Soc.* **1981**, *128*, 2679. (c) Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem.* **1984**, *23*, 1491. (d) Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem.* **1985**, *24*, 2259. (e) Heerman, L.; D'Olieslager, W. *Inorg. Chem.* **1985**, *24*, 4704. (f) Hussey, C. L.; Scheffler, T. B.; Wilkes, J. S.; Fannin, A. A., Jr. *J. Electrochem. Soc.* **1986**, *133*, 1389.
(3) Appleby, D.; Hussey, C. L.; Seddon, K. R.; Turp, J. E. *Nature (London)* **1986**, *323*, 614.
(4) Hussey, C. L.; Laher, T. M. *Inorg. Chem.* **1981**, *20*, 4201.
(5) (a) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1983**, *22*, 3247. (b) Nanjundiah, C.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1312.
(6) (a) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 4079. (b) Nanjundiah, C.; Shimizu, K.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474.
(7) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 2723.
(8) (a) Linga, H.; Stojek, Z.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 3754. (b) Stojek, Z.; Linga, H.; Osteryoung, R. A. *J. Electroanal. Chem.* **1981**, *119*, 365.
(9) Laher, T. M.; Hussey, C. L. *Inorg. Chem.* **1983**, *22*, 1279.
(10) Scheffler, T. B.; Hussey, C. L.; Seddon, K. R.; Kear, C. M.; Armitage, P. D. *Inorg. Chem.* **1983**, *22*, 2099.
(11) Hussey, C. L.; Appleby, D.; Hitchcock, P. B.; Seddon, K. R.; Zora, J. A.; Crisp, R. I., submitted for publication in *Inorg. Chem.*
(12) Scheffler, T. B.; Hussey, C. L. *Inorg. Chem.* **1984**, *23*, 1926.
(13) (a) Jørgensen, C. K. *Acta Chem. Scand.* **1956**, *10*, 500. (b) Poulsen, I. A.; Garner, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 2032. (c) Chang, J. C.; Garner, C. S. *Inorg. Chem.* **1965**, *4*, 209.
(14) Fine, D. A. *Inorg. Chem.* **1969**, *8*, 1014.

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