Table VI. Thermodynamic Properties of $F^{35}Cl^{16}O_2$

T, K	$C_p°$, cal/(mol deg)	$(H°_T - H°_0)$, kcal/mol	$-(F°_T - H°_0)/T$, cal/(mol deg)	$S°_T$, eu
0	0	0	0	0
100	8.507	0.805	46.851	54.898
200	11.267	1.790	52.666	61.618
298.15	13.509	3.012	56.456	66.559
300	13.545	3.037	56.519	66.643
400	15.167	4.478	59.581	70.775
500	16.318	6.055	62.180	74.291
600	17.134	7.730	64.459	77.342
700	17.718	9.474	66.495	80.030
800	18.143	11.268	68.339	82.425
900	18.459	13.099	70.026	84.581
1000	18.699	14.958	71.581	86.539
1100	18.884	16.837	73.023	88.330
1200	19.030	18.733	74.368	89.979
1300	19.147	20.642	75.629	91.507
1400	19.241	22.562	76.814	92.930
1500	19.318	24.490	77.934	94.260
1600	19.382	26.425	78.993	95.509
1700	19.436	28.366	80.000	96.686
1800	19.481	30.312	80.958	97.798
1900	19.520	32.262	81.872	98.852
2000	19.554	34.216	82.747	99.854

given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator, rigid-rotor approximation.[23] These properties are given for the range 0–2000 K in Table V. Since no thermodynamic data had previously been reported for $FClO_2$, we have also computed these properties for $F^{35}Cl^{16}O_2$ (see Table VI) using the previously published frequencies[10] and geometry.[4]

Conclusion

A force field has been computed for $FBrO_2$ using gas-phase frequency values and bromine and oxygen isotopic shifts. It was shown that the most important force constants, f_{BrO} and f_{BrF}, can be determined with an accuracy of about 0.08 and 0.04 mdyn/Å, respectively. The importance of anharmonicity corrections for the oxygen shifts was demonstrated. In the absence of such anharmonicity corrections, the bromine isotopic shifts are more useful for defining the force field because of the smaller anharmonicity corrections required. The BrF bond in $FBrO_2$ (2.75 mdyn/Å) is considerably stronger than previously assumed (2.25 mdyn/Å)[5] but is still somewhat weaker than predicted by comparison with related bromine compounds. This weakening effect might be explained by assuming a polar σ bond between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical.

Acknowledgment. K.O.C. is indebted to Drs. L. R. Grant, C. J. Schack, and W. W. Wilson for helpful discussions and to the Office of Naval Research for financial support.

Registry No. $F^{79}Br^{16}O_2$, 67452-70-4; $F^{35}Cl^{16}O_2$, 35880-03-6; $FBrO_2$, 22585-64-4; $FBr^{18}O_2$, 64544-65-6; ^{18}O, 14797-71-8; ^{79}Br, 14336-94-8; ^{81}Br, 14380-59-7.

References and Notes

(1) M. Schmeisser and E. Pammer, *Angew. Chem.*, **67**, 156 (1955).
(2) M. Schmeisser and E. Pammer, *Angew. Chem.*, **69**, 781 (1957).
(3) R. J. Gillespie and P. Spekkens, *J. Chem. Soc., Chem. Commun.*, 314 (1975); *J. Chem. Soc., Dalton Trans.*, 1539 (1977); *Isr. J. Chem.*, **17**, 11 (1978).
(4) C. R. Parent and M. C. L. Gerry, *J. Mol. Spectrosc.*, **49**, 343 (1974).
(5) E. J. Baran, *Spectrosc. Lett.*, **9**, 323 (1976).
(6) E. Jacob, *Z. Anorg. Allg. Chem.*, **433**, 255 (1977).
(7) K. O. Christe, E. C. Curtis, and R. Bougon, *Inorg. Chem.*, **17**, 533 (1978).
(8) R. A. Frey, R. L. Redington, and A. L. Khidir Aljibury, *J. Chem. Phys.*, **54**, 344 (1971).
(9) K. O. Christe, E. C. Curtis, and D. Pilipovich, *Spectrochim. Acta, Part A*, **27a**, 931 (1971).
(10) D. F. Smith, G. Begun, and W. Fletcher, *Spectrochim. Acta*, **20**, 1763 (1964).
(11) R. S. McDowell, L. B. Asprey, and L. C. Hoskins, *J. Chem. Phys.*, **56**, 5712 (1972).
(12) E. C. Curtis, *Spectrochim. Acta, Part A*, **27a**, 1989 (1971).
(13) E. H. Appelman, B. Beagley, D. W. J. Cruickshank, A. Foord, S. Rustad, and V. Ulbrecht, *J. Mol. Struct.*, **35**, 139 (1976).
(14) A. H. Clark, B. Beagley, D. W. J. Cruickshank, and T. G. Hewitt, *J. Chem. Soc. A*, 872 (1970).
(15) E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).
(16) S. Siegel, B. Tani, and E. Appelman, *Inorg. Chem.*, **8**, 1190 (1969).
(17) L. C. Brown, G. M. Begun, and G. E. Boyd, *J. Am. Chem. Soc.*, **91**, 2250 (1969).
(18) H. H. Claassen and E. H. Appelman, *Inorg. Chem.*, **9**, 622 (1970).
(19) R. S. McDowell and M. Goldblatt, *Inorg. Chem.*, **10**, 625 (1971).
(20) W. Sawodny, *J. Mol. Spectrosc.*, **30**, 56 (1969).
(21) K. O. Christe, *Proc. Int. Congr. Pure Appl. Chem., 24th*, **4**, 115 (1974).
(22) K. O. Christe and C. J. Schack, *Adv. Inorg. Chem. Radiochem.*, **18**, 319 (1976).
(23) J. E. Mayer and M. G. Mayer, "Statistical Mechanics", Wiley, New York, N.Y., 1940.
(24) In a recent paper on $KBrO_2F_2$, R. Bougon, P. Joubert and G. Tantot, *J. Chem. Phys.*, **66**, 1562 (1977), also reported a force field calculation for $FBrO_2$ using the frequencies of ref 3. Their results have been included in Table III.

Contribution from Rocketdyne,
A Division of Rockwell International, Canoga Park, California 91304

Chemistry and Structure of $N_2F_3^+$ Salts

KARL O. CHRISTE* and C. J. SCHACK

Received February 22, 1978

The novel $N_2F_3^+$ salt $N_2F_3SbF_6$ was prepared from N_2F_4 and SbF_5 in anhydrous HF solution. A metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF produced N_2F_4 and the novel salt $N_2F_3SnF_5$. It was shown that N_2F_4 and BF_3 do not form a stable adduct at temperatures as low as −78 °C. The vibrational and ^{19}F NMR spectra of the $N_2F_3^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry C_s for $N_2F_3^+$. The previously reported vibrational assignments, made on the basis of a nonplanar structure of symmetry C_1, are revised for six fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between N_2F_4 and a Lewis acid was published[1] in 1965 by Ruff. He showed[1,2] that SbF_5, when treated with an excess of N_2F_4 in AsF_3 solution, produced, depending on the pressure of N_2F_4, either the 1:2 adduct $N_2F_4{\cdot}2SbF_5$ or the 1:3 adduct $N_2F_4{\cdot}3SbF_5$. On the basis of the observed ^{19}F NMR spectrum and an incomplete infrared spectrum, he assigned to $N_2F_4{\cdot}2SbF_5$ the ionic structure $N_2F_3^+Sb_2F_{11}^-$ with hindered rotation around the N–N bond in $N_2F_3^+$. In 1967, Young and Moy published[3] the syntheses of adducts between N_2F_4 and AsF_5. At −78 °C and ambient temperature, the $AsF_5{:}N_2F_4$ combination ratios were reported to be 2.3 and 1.3 ± 0.2, respectively. In addition to an incomplete infrared spectrum and an unresolved ^{19}F NMR spectrum, the strongest lines of an X-ray powder diffraction pattern were given which was indexed on the basis of a cubic unit cell with $a = 10.8$ Å. In the same year, Lawless published[4] a better resolved infrared spectrum of $N_2F_3AsF_6$, but no assignments were offered. In 1970, Qureshi and Aubke published[5] a paper dealing with the infrared and Raman spectra of solid $N_2F_3AsF_6$ and $N_2F_3Sb_2F_{11}$. With the exception of the N–N torsional mode, they observed and tentatively assigned all fundamental vibrations of $N_2F_3^+$ proposing a nonplanar structure of symmetry C_1.

Since $N_2F_3^+$ salts are of interest as burning aids in solid propellant NF_3–F_2 gas generator formulations,[6] we have studied (i) the synthesis of $N_2F_3SbF_6$, (ii) the possibility of converting $N_2F_3SbF_6$ into "self-clinkering"[7] $N_2F_3^+$ salts by metathetical reactions,[8] and (iii) the vibrational spectra and structure of the $N_2F_3^+$ cation. The results of this study are summarized in this paper.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon–FEP U-traps and diaphragm valves. Pressures were measured with either a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%) or a Validyne Model DM 56A pressure transducer. Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride and SbF_5 (Ozark Mahoning), N_2F_4 (Air Products), and BF_3 and SO_2 (Matheson) were purified by fractional condensation prior to use. The BrF_5 (Matheson) was treated with F_2 at 200 °C and then purified by fractional condensation. HF was dried as previously described.[9] The SnF_4 (Ozark Mahoning) was used as received. The preparation of Cs_2SnF_6 has previously been described.[7]

The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgBr or AgCl disks in a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Polarization measurements for HF solutions in thin-walled KelF capillaries were carried out by method VIII, as described[10] by Claassen et al. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon–FEP sample tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard. Debye–Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper Kα radiation.

Synthesis of $N_2F_3SbF_6$. A Teflon ampule, containing a Teflon-coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox and attached to the vacuum line. Then 2 mL of anhydrous HF was condensed into the ampule at −78 °C. While the mixture was stirred and warmed to ambient temperature, the system was pressurized with N_2F_4 (~1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4. Periodic cycling to below 0 °C seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40 °C until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4. When the reaction was repeated on a larger scale with 8 mL of HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $N_2F_3SbF_6$ (weight of $N_2F_3SbF_6$ calculated for 74.0 mmol of SbF_5: 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

Synthesis of $N_2F_3AsF_6$. A 30-mL stainless steel cylinder was loaded at −196 °C with 22.8 mmol of AsF_5 and 26.8 mmol of N_2F_4. In a prechilled but empty Dewar, the cylinder was allowed to warm slowly from −196 °C to room temperature. Unreacted N_2F_4 (4.0 mmol) was recovered by pumping at ambient temperature. The weight (6.25 g) of the resulting white solid was in excellent agreement with that (6.25 g) calculated for 22.8 mmol of $N_2F_3AsF_6$. The compound, when prepared in this manner, always was slightly tacky, but hard. It was characterized by ^{19}F NMR and vibrational spectroscopy.

The N_2F_4–BF_3 Systems. Equimolar amounts of N_2F_4 and BF_3, when combined at −78 °C in a Teflon–FEP ampule, did not form a solid. The liquid could be distilled at −78 °C to a colder trap without leaving any solid residue behind.

The N_2F_4–SnF_4 System. A suspension of SnF_4 (4.68 mmol) in 4 mL of liquid HF in a Teflon–FEP ampule was pressurized with N_2F_4 (12.7 mmol) to a pressure of 900 mm. The mixture was stirred for 5 days at room temperature. On the basis of its vibrational spectra and chemical analysis, the white solid residue obtained upon removal of all material volatile at 25 °C did not contain any $N_2F_3^+$.

Synthesis of $N_2F_3SnF_5$. Solid $N_2F_3SbF_6$ (6.48 mmol) and Cs_2SnF_6 (3.24 mmol) were placed in a previously described Teflon–FEP apparatus, and approximately 2 mL of anhydrous HF was added. After the system was stirred and shaken vigorously for 30 min at room temperature, some of the HF was removed under vacuum and the mixture was cooled to −78 °C. The solid and liquid phases were separated by pressure filtration, and the volatile products were removed by pumping at 25 °C for 15 h. The volatile material was separated by fractional condensation and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was shown by vibrational spectroscopy to contain the $N_2F_3^+$ and $(SnF_5^-)_n$ ions[1-5,7] as the main components, in addition to a small amount of SbF_6^-. The filter cake consisted mainly of $CsSbF_6$ with lesser amounts of $N_2F_3SnF_5$.

Attempts were unsuccessful to suppress N_2F_4 evolution in the above reaction by carrying out the entire metathesis at −78 °C. Again N_2F_4 evolution and $N_2F_3SnF_5$ formation were observed.

Results and Discussion

Synthesis. For the metathetical synthesis of $N_2F_3^+$ salts using the $CsSbF_6$ process,[8] $N_2F_3SbF_6$ was needed as a starting material. Although Ruff had studied[1,2] the interaction of N_2F_4 with SbF_5 in a solvent, such as AsF_3, he had obtained only the polyantimonates $N_2F_3Sb_2F_{11}$ and $N_2F_3Sb_3F_{16}$. We found that, if this reaction is carried out in HF solution using excess N_2F_4 at a pressure of about 1 atm, $N_2F_3SbF_6$ can be obtained in quantitative yield and excellent purity according to

$$N_2F_4 + SbF_5 \xrightarrow[\text{room temp}]{\text{HF soln}} N_2F_3SbF_6$$

Similarly, no difficulty was encountered in preparing a well-defined 1:1 adduct between N_2F_4 and AsF_5. In this case, no solvent was required and the yield was quantitative:

$$N_2F_4 + AsF_5 \xrightarrow{25\ °C} N_2F_3AsF_6$$

According to a previous report[3] by Young and Moy on the same system, the averaged composition of their adduct was $N_2F_4{\cdot}1.33AsF_5$ and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF_5 and AsF_5, does not form a stable adduct with N_2F_4 at temperatures as low as −78 °C. Our attempts also failed to directly synthesize an $N_2F_3^+$ salt derived from SnF_4 by treatment of a SnF_4–HF suspension with N_2F_4. No N_2F_4 uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF_4 since metathesis in HF yields stable $N_2F_3SnF_5$ (see below). A more plausible explanation is that N_2F_4 is not a strong enough Lewis base to depolymerize SnF_4.

Since the direct synthesis of an adduct between N_2F_4 and SnF_4 was not possible, a metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 was carried out in HF solution. The following reaction occurred:

$$2N_2F_3SbF_6 + Cs_2SnF_6 \xrightarrow[-78\ °C\ \text{filtration}]{\text{HF soln}} 2CsSbF_6{\downarrow} + N_2F_3SnF_5 + N_2F_4$$

The $N_2F_3SnF_5$ salt is a white solid, stable at room temperature. It is considerably more soluble in HF than $CsSbF_6$, thus making the metathesis possible. Attempts were unsuccessful to prepare $(N_2F_3)_2SnF_6$ by modification of the above reaction

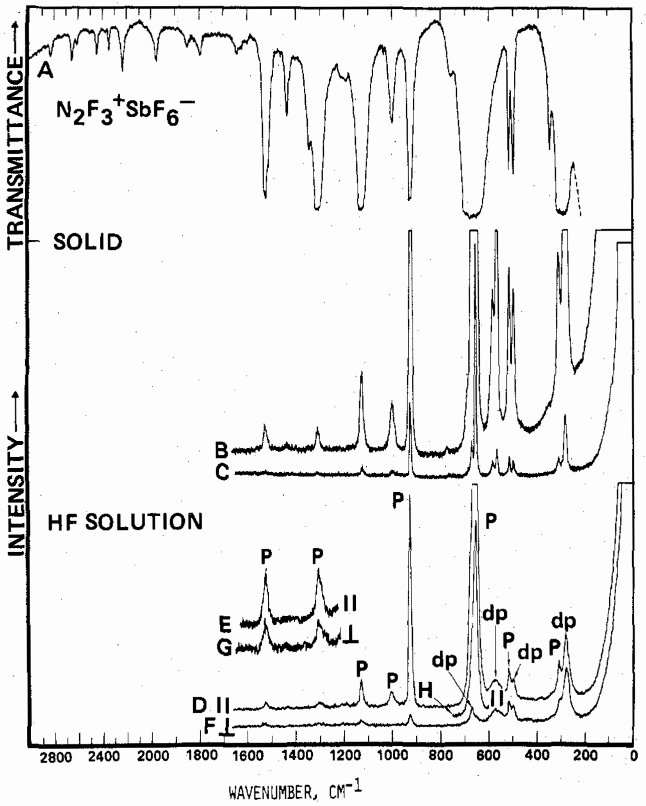
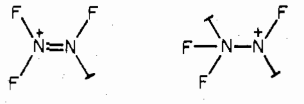


Figure 1. Vibrational spectra of $N_2F_3SbF_6$: trace A, infrared spectrum of the solid as an AgBr disk, the broken line being due to absorption by the window material; traces B and C, Raman spectrum of the solid recorded at two different recorder voltages with spectral slit widths of 3 and 8 cm^{-1}, respectively; traces D–H, Raman spectra of an HF solution recorded at different recorder voltages and spectral slit widths (5 and 8 cm^{-1}) with incident polarization parallel and perpendicular (p and dp stand for polarized and depolarized bands, respectively).

conditions. This was somewhat unexpected in view of the fact that previously no difficulty was encountered in the preparation of the analogous $(NF_4)_2SnF_6$ salt from NF_4SbF_6 and Cs_2SnF_6 under similar reaction conditions.[7] It should be remembered, however, that the favored reaction product from the displacement reaction between NF_4BF_4 and SnF_4 in HF was NF_4SnF_5 and not $(NF_4)_2SnF_6$.[7] These results indicate that the reaction chemistry of SnF_4 and its anions in HF is rather complex and hard to predict without exact knowledge of the corresponding solvation and lattice energies of the possible products.

Vibrational Spectra. Figures 1–3 show the vibrational spectra of $N_2F_3SbF_6$, $N_2F_3AsF_6$, and $N_2F_3SnF_5$, respectively. The observed frequencies are listed in Tables I and II. The vibrational spectra of SbF_6^-,[5,6,11,12] AsF_6^-,[5,11,13,14] and $(SnF_5^-)_n$[7] are well-known and can be assigned without difficulty (see Tables I and II). The remaining bands should be due to the $N_2F_3^+$ cation.

The $N_2F_3^+$ cation could possess either a planar structure of symmetry C_s (I) or a nonplanar structure of symmetry C_1



I (C_s) II (C_1)

caused by significant contributions from resonance structure II. The assignments previously made[5] by Qureshi and Aubke for $N_2F_3^+$ were based on symmetry C_1, although structure II is energetically considerably less favorable than I (one nitrogen possesses only six valence electrons) and is in poor agreement with the published NMR data[1,2] which show hindered rotation around the N–N bond up to at least 120 °C. Symmetry C_1 had previously been chosen[4] because the highest Raman frequency observed for either solid $N_2F_3AsF_6$ or $N_2F_3Sb_2F_{11}$ occurred at about 1310 cm^{-1}. Since this frequency is considerably lower than expected[15,16] for an N=N bond, significant contributions from II were assumed.[5]

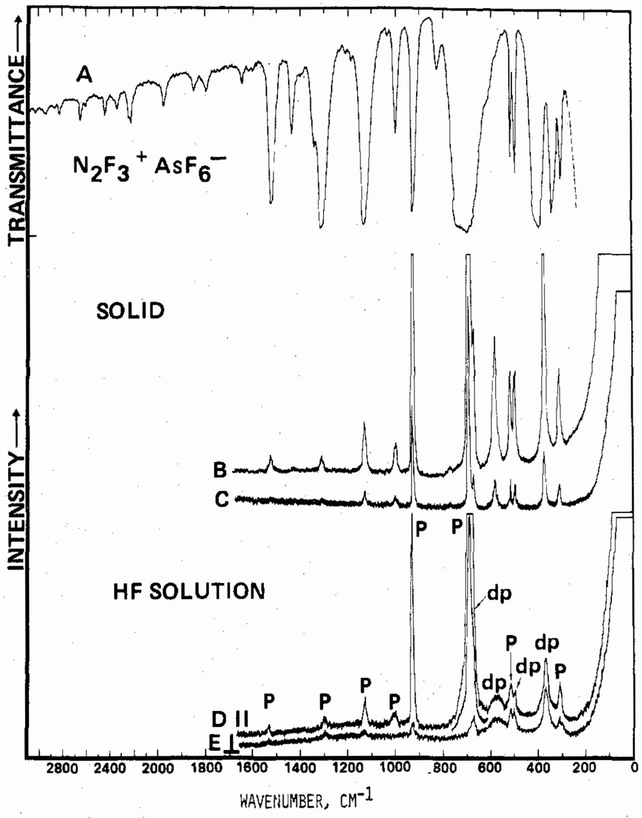


Figure 2. Vibrational spectra of $N_2F_3AsF_6$. For explanation, see caption of Figure 1.

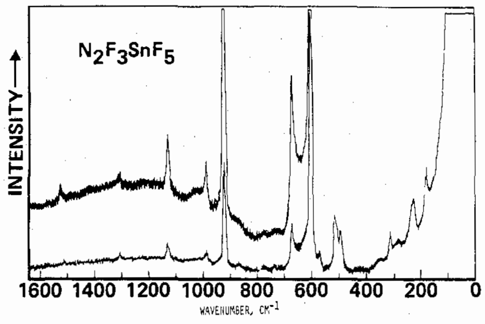


Figure 3. Raman spectrum of solid $N_2F_3SnF_5$ recorded at two different recorder voltages.

As can be seen from Figures 1–3, the highest Raman band observed for all three $N_2F_3^+$ salts occurs at about 1520 cm^{-1}, thus confirming the original assignment[1-3] of the strong 1520-cm^{-1} infrared band to the N=N stretching mode and eliminating the basis for Qureshi and Aubke's reassignment.[5] The previous failure to observe the 1520-cm^{-1} Raman band can be explained by its relatively low intensity and the low signal to noise ratio in the reported spectrum.[5]

Having established the identity of the N=N stretching mode, we can now proceed to test if the rest of the $N_2F_3^+$ spectrum is consistent with symmetry C_s. For $N_2F_3^+$ of C_s symmetry a total of nine fundamental vibrations is expected of which six belong to species A′ and three belong to A″. An approximate description of these nine modes is given in Table

Table I. Vibrational Spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$

assignments for $N_2F_3^+$ in point group C_s	obsd freq, cm^{-1}, and rel intens^a						assignments for MF_6^- in point group O_h
	$N_2F_3SbF_6$			$N_2F_3AsF_6$			
	solid		HF soln	solid		HF soln	
	IR	Raman	Raman	IR	Raman	Raman	
$\nu_1 + \nu_2$ (A′) = 2829	2825 vw			2820 vw			
$\nu_1 + \nu_3$ (A′) = 2649	2647 vw			2643 vw			
$2\nu_2$ (A′) = 2614	2608 vvw			2605 vvw			
$\nu_1 + \nu_4$ (A′) = 2447	2443 vw			2440 vw			
$\nu_2 + 2\nu_5$ (A′) = 2339	2343 vw			2340 vw			
$\nu_2 + \nu_4$ (A′) = 2232	2227 w			2223 w			
$\nu_3 + \nu_4$ (A′) = 2052	2050 sh						
$\nu_2 + \nu_7$ (A″) = 1978	1976 w			1970 w			
$2\nu_4$ (A′) = 1850	1850 vw			1846 vw			
$\nu_3 + \nu_7$ (A″) = 1798	1796 vw			1795 vw			
$\nu_3 + \nu_5$ (A′) = 1643	1642 vw			1639 vw			
$\nu_2 + \nu_6$ (A′) = 1617	1619 sh			1617 vvw			
$\nu_4 + \nu_7$ (A″) = 1596	1599 vvw			1596 vvw			
ν_1 (A′)	1522 s	1522 (0.1)	1522 (0.1) p	1519 s	1520 (0.2)	1524 (0.2) p	
$\nu_3 + \nu_6$ (A′) = 1437	1436 m	1424 (0+)	1435 (0+)	1432 m	1430 (0+)		
				1390 vw			$\nu_1 + \nu_3$ (F_{1u})
$2\nu_7$ (A′) = 1342	1343 m			1340 m			
ν_2 (A′)	1310 vs	1307 (0.1)	1306 (0.1) p	1307 vs	1305 (0.2)	1300 (0.2) p	
$\nu_5 + 2\nu_9$ (A′) = 1204	1210 vw			1206 vw			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
$\nu_5 + \nu_7$ (A″) = 1187	1189 vw			1186 vw			
ν_3 (A′)	1127 vs	1124 (0.4)	1127 (0.6) p	1128 vw	1127 (0.6)	1128 (0.7) p	
$2\nu_5$ (A′) = 1032	1033 vvw			1032 vvw			
$2\nu_8$ (A′) = 994	998 m	997 (0.2)	1000 (0.25) p	996 m	997 (0.3)	1001 (0.3) p	
ν_4 (A′)	925 s	924 (3.2)	927 (6.1) p	923 s	925 (4.7)	929 (5.9) p	
	755 mw			826 mw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
	670 vs			699 vs			ν_3 (F_{1u})
ν_7 (A″)		670 (0.9)	671 (0.8) dp		671 (0.9)	671 (0.8) dp	
		656 (10)	655 (10 p		690 (10)	689 (10) p	ν_1 (A_{1g})
				620 sh			$\nu_5 + \nu_6$ ($A_{1u} + E_u + F_{1u} + F_{2u}$)
		582 (0.4) 566 (1.1)	575 (0.4) dp		581 (1.3)	575 (0.4) dp	ν_2 (E_g)
ν_5 (A′)	515 ms	514 (0.8)	518 (1.0) p	515 ms	516 (1.2)	516 (0.9) p	
ν_8 (A″)	497 ms	496 (0.5)	499 (0.6) dp	496 ms	497 (1.1)	498 (0.5) dp	
ν_9 (A″)	345 m	348 (0+)		343 ms			
ν_6 (A′)		310 (0.5)	310 (0.6) p		310 (0.9)	310 (1.0) p	
	290 vs			392 s			ν_4 (F_{1u})
		280 (2.4)	280 (2.3) dp		374 (3.6)	371 (2.0) dp	ν_5 (F_{2g})

^{a} Uncorrected Raman intensities.

Table II. Vibrational Spectra of Solid $N_2F_3SnF_5$

obsd freq, cm^{-1}, and rel intens		assignment	
IR	Raman	$N_2F_3^+$ (C_s)	$(SnF_5^-)_n$
1518 s	1519 (0.1)	ν_1 (A′)	
1428 m		$\nu_3 + \nu_6$ (A′)	
1341 m		$2\nu_7$ (A′)	
1304 vs	1304 (0.1)	ν_2 (A′)	
1126 vs	1127 (0.5)	ν_3 (A′)	
986 m	988 (0.4)	$2\nu_8$ (A′)	
921 vs	921 (3.9)	ν_4 (A′)	
	670 (1.1)	ν_7 (A′)	
635 610 s, br	604 (10)		str modes
	572 (0.3)		
	512 (2)	ν_5 (A′)	
490–450 m, br	492 (1)	ν_8 (A″)	bridge str
	310 (0.8)	ν_6 (A′)	
	228 (1.3)		def modes
	179 (1.1)		

Table III. Fundamental Frequencies (cm^{-1}) of $N_2F_3^+$ and Their Assignment in Point Group C_s

freq	assignment		approx description of mode
1522	A′	ν_1	N=N str
1307		ν_2	asym NF_2 str
1127		ν_3	NF′ str
925		ν_4	sym NF_2 str
516		ν_5	δ(sym NF_2) in plane
310		ν_6	δ($FNNF_2$) in plane
671	A″	ν_7	δ(asym $FNNF_2$) out of plane
497		ν_8	δ(sym $FNNF_2$) out of plane
344		ν_9	N=N torsion

III. All nine modes should be infrared and Raman active, with a possible exception being the torsional mode ν_9 which is expected to be of very low Raman intensity. The three A″ modes should result in depolarized Raman bands.

As can be seen from Table III, three NF stretching modes are expected all belonging to species A′ and occurring in the frequency range 900–1300 cm^{-1}. There are three very intense infrared bands in this region (see Figures 1 and 2), all of which have Raman counterparts. Of the three predicted NF stretching modes, the symmetric NF_2 stretch (ν_4) is expected to have the highest Raman intensity and the lowest depolarization ratio and, therefore, is assigned to the band at about 925 cm^{-1}. The reverse should hold true for the antisymmetric NF_2 stretching mode ν_2 which, therefore, is assigned to the band at about 1310 cm^{-1}. This leaves the assignment of the band at about 1127 cm^{-1} to the unique NF stretching mode ν_3, the frequency of which is similar to that of the NF stretch in N_2F^+.[17]

For the assignment of the five deformation modes, the following five frequencies are available: 671, 516, 497, 344, and 310 cm^{-1}. Of these, the 516- and 310-cm^{-1} bands are clearly polarized in the Raman spectra and therefore must represent the two remaining A′ modes. By comparison with

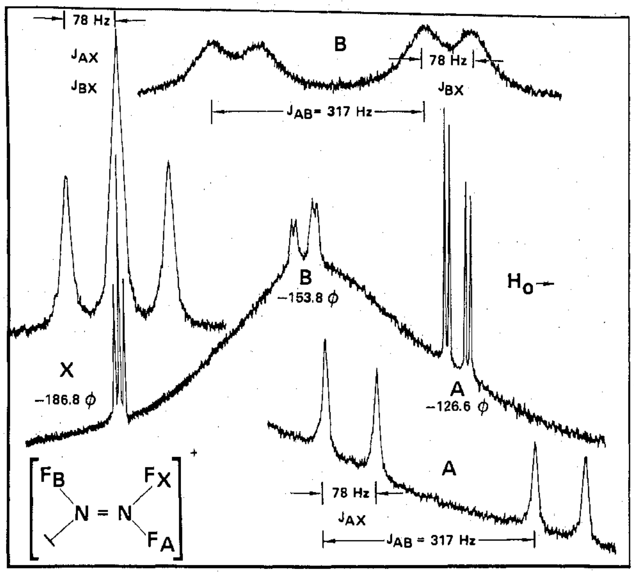


Figure 4. ^{19}F, NMR spectrum of $N_2F_3AsF_6$ in BrF_5 solution, recorded at −78 °C and 84.6 MHz using $CFCl_3$ as external standard. The very broad background signal is due to rapidly exchanging BrF_5 and AsF_6^-. The inserts show the A, B, and X signals, all recorded with tenfold scale expansion, but different recorder gain settings.

the known frequencies of the NF_2[18] and CF_2[19] radicals, the 516-cm^{-1} band is assigned to the NF_2 scissoring mode ν_5, leaving the 310-cm^{-1} band for the unique FNN in-plane deformation mode ν_6.

Of the remaining three fundamental frequencies, the 671- and 497-cm^{-1} ones exhibit reasonably intense depolarized Raman bands, whereas the 344-cm^{-1} one has been observed only in one Raman spectrum (Figure 1, trace B) as an extremely weak band. In the infrared spectra, the 344-cm^{-1} fundamental is of medium intensity. These intensity relations indentify the 344-cm^{-1} band as the N═N torsional mode. Of the two remaining frequencies, the 671-cm^{-1} fundamental is assigned to the antisymmetic and the 497-cm^{-1} fundamental to the symmetric $FNNF_2$ out-of-plane deformation. This assignment is based on that[20] of the related C_2F_4 molecule. Numerous combination bands were observed in the infrared spectra. Their assignment is given in Table I.

In summary, the vibrational spectra of the $N_2F_3^+$ ion are entirely consistent with our predictions for a planar model of symmetry C_s. All nine fundamentals were observed, with six of them being polarized and two of them being depolarized in the Raman spectra. As expected, the torsional mode is of very low Raman intensity. The double-bond character of the NN bond in $N_2F_3^+$ is confirmed by the high frequencies of the NN stretching and the torsional mode.

NMR Spectra. The ^{19}F NMR spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ were recorded at 84.6 MHz in SO_2, BrF_5, SbF_5, and HF solution. The HF solvent was acidified with either AsF_5 or SbF_5 to suppress exchange between the solvent and the cation.[20,22] In HF, BrF_5, and SbF_5 solutions, exchange between the anions and the solvent was observed; however, in SO_2 solution separate signals were observed for AsF_6^- at φ 57 and SbF_6^- at φ 111 with the appropriate area ratios.

For $N_2F_3^+$, a typical ABX pattern with an area ratio of 1:1:1 was observed at about φ −127, −154, and −187, respectively. The chemical shifts of these signals exhibited only little solvent and temperature dependence. Even at 150 °C (SbF_5 solution), no averaging of the NF resonances was noticeable, indicating strongly hindered rotation about the N–N axis, as expected for a N═N. These findings are in excellent agreement with the previous report by Ruff for $N_2F_3Sb_2F_{11}$ in SO_2 solution and the melt.

Our low-temperature spectra (−70 to −90 °C) in either BrF_5 (see Figure 4) or acidified HF solutions were much better resolved than those obtainable for the SO_2 solution and thus permitted a more accurate determination of the three coupling constants. The A signal consisted of a sharp doublet of doublets with J_{AB} = 317 Hz, J_{AX} = 78 Hz, and a line width of about 8 Hz. The B signal was again a doublet of doublets with J_{AB} = 317 HZ and $J_{BX} \approx$ 78 Hz, but with significantly broader lines (line width of about 60 Hz). The X signal was a sharp 1:2:1 (J = 78 Hz) triplet indicating very similar values of J_{AX} and J_{BX}. Our observed coupling constants significantly differ from those (J_{AB} = 379 Hz, J_{AX} = 81 Hz, J_{BX} = 45 Hz) previously reported[2] for a poorly resolved spectrum.

Assignment of ABX to the three fluorines in $N_2F_3^+$ can be made based on the following arguments. The two nitrogen atoms in $N_2F_3^+$ are not equivalent. The one possessing only one fluorine ligand is centered in an electrically less symmetric field thus making ^{14}N quadrupole relaxation more effective and causing line broadening. Consequently, the broadened B signal is assigned to the unique fluorine. Since for the related FN═NF, CF_2═NF, and substituted fluoroethylenes the cis coupling constants were found to be always significantly smaller than the trans ones,[23] A (J_{AB} = 317 Hz) should be trans and X (J_{BX} = 78 Hz) should be cis with respect to B. The resulting structure is shown in Figure 4. The observed coupling constants are similar to those observed for cis FN═NF (J = 99 Hz) and trans FN═NF (J = 322 Hz).[23]

X-ray Powder Data. The X-ray powder patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ are given as supplementary material. Young and Moy have reported[3] the three strongest lines for $N_2F_3AsF_6$ and stated that the pattern can be indexed for a cubic unit cell with a = 10.8 Å. Although our data confirm the three previously reported lines,[3] our observed pattern cannot be indexed based on the previously given unit-cell dimensions. In view of the nonspherical geometry of $N_2F_3^+$, a relatively small cubic unit cell would be very surprising for $N_2F_3AsF_6$.

Acknowledgment. We are indebted to Drs. L. R. Grant and W. W. Wilson for helpful discussions and to Mr. R. D. Wilson for experimental help. This work was supported in part by the Office of Naval Research and the U.S. Army Research Office.

Registry No. $N_2F_3SbF_6$, 67328-70-5; $N_2F_3SnF_5$, 67328-71-6; $N_2F_3AsF_6$, 12254-91-0; N_2F_4, 10036-47-2; SbF_5, 7783-70-2.

Supplementary Material Available: Table IV, listing the observed X-ray powder diffraction patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) J. K. Ruff, *J. Am. Chem. Soc.*, **87**, 1140 (1965).
(2) J. K. Ruff, *Inorg. Chem.*, **5**, 1791 (1966).
(3) A. R. Young and D. Moy, *Inorg. Chem.* **6**, 178 (1967).
(4) E. W. Lawless, *Anal. Lett.* **1**, 153 (1967).
(5) A. M. Qureshi and F. Aubke, *Can. J. Chem.*, **48**, 3117 (1970).
(6) K. O. Christe, R. D. Wilson, and C. J. Schack, *Inorg. Chem.*, **16**, 937 (1977), and references cited therein.
(7) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **16**, 849 (1977).
(8) K. O. Christe, W. W. Wilson, and C. J. Schack, *J. Fluorine Chem.*, **11**, 71 (1978), and references cited therein.
(9) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **14**, 2224 (1975).
(10) H. H. Claassen, H. Selig, and J. Shamir, *Appl. Spectros.*, **23**, 8 (1969).
(11) G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967).
(12) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **9**, 2296 (1970).
(13) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967); K. O. Christe, *ibid*, **9**, 2801 (1970).
(14) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **15**, 1275 (1976).
(15) D. J. Millen, C. N. Polydoropoulos, and D. Watson, *J. Chem. Soc.*, 687 (1960).
(16) S. T. King and J. Overend, *Spectrochim. Acta*, **22**, 689 (1966).
(17) K. O. Christe, R. D. Wilson, and W. Sawodny, *J. Mol. Struct.*, **8**, 245 (1971), and references cited therein.

(18) M. D. Harmony and R. J. Myers, *J. Chem. Phys.*, **37**, 636 (1962).
(19) D. E. Milligan, D. E. Mann, and M. E. Jacox, *J. Chem. Phys.*, **41**, 1199 (1964).
(20) T. Shimamouchi, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **39**, 75 (1972).
(21) M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, **47**, 4159 (1969).
(22) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, **12**, 84 (1973).
(23) J. W. Emsley, L. Phillips, and V. Wray, "Fluorine Coupling Constants", Pergamon Press, Oxford, England, 1977.

Contribution from the Inorganic Chemistry Laboratory, Oxford, OX1 3QR, England,
and Exxon Research and Engineering Company, Linden, New Jersey 07036

Organometallic Intercalates of the Layered Transition-Metal Dichalcogenides TaS_2 and ZrS_2

RENE P. CLEMENT, WARWICK B. DAVIES, KEITH A. FORD, MALCOLM L. H. GREEN, and ALLAN J. JACOBSON*

Received March 23, 1978

Substituted cobaltocenes $(RC_5H_4)_2Co$ (R = Me, *i*-Pr, and *n*-Bu) have been intercalated into the layered dichalcogenides TaS_2 and ZrS_2 by direct reaction of toluene solutions of the organometallic compounds and the solid disulfides. Intercalates of TaS_2 have also been prepared by ion exchange of the hydrated sodium intercalate with organometallic cations in aqueous solution. Lattice expansions of the host disulfides on intercalation have been determined by powder X-ray diffraction and are discussed in relation to the orientation of the organometallic cation between the layers. Some chemical reactions of the intercalates and some ion-exchange experiments in nonaqueous solvents are described.

Introduction

Layered transition-metal dichalcogenides may act as host lattices and react with a variety of guest atoms or molecules to give intercalation compounds in which the guest is inserted between the host layers.[1,2] Interest in these materials has arisen for such diverse reasons as the observation that the superconducting transition temperature of some hosts increases on intercalation of amines[3] and the use of alkali metal intercalation reactions such as Li/TiS_2 in secondary battery systems.[4] Chemical applications of intercalates of other layered materials have been demonstrated. Graphite/bromine and graphite/bisulfate are useful reagents in organic syntheses[5] and the catalytic hydrogenation properties of $Rh(PPh_3)_x^+$ are modified on intercalation into silicates.[6]

The observation by Dines[7] that cobaltocene and chromocene could be directly intercalated into most layered dichalcogenides to give compounds such as $\{[(\eta\text{-}C_5H_5)_2Co]_{1/4}TaS_2\}$ prompted us to examine more generally the synthesis and potential applications of such organometallic intercalated systems as models for heterogeneous catalysis. In a preliminary report[8] we described the synthesis of several new intercalation compounds of organometallic compounds and the host ZrS_2. These data are summarized in Table I. All of the intercalates were prepared by direct reaction of ZrS_2 and the neutral organometallic molecule in toluene solution. On the basis of this study three preliminary criteria for direct intercalation were established. All of the organometallic compounds which were successfully intercalated have sandwich structures with parallel carbocyclic rings, have first ionization potentials less than 6.2 eV, and form cations which are stable to isolation. Experimental details of this work not given in the preliminary communication are included in the Experimental Section.

In this paper, we report an extension of this work to other layered dichalcogenide host lattices and organometallic compounds. In particular, we have examined in more detail steric effects associated with the organometallic compound on the direct intercalation reaction and on the orientation of the guest molecule between the layers. We have also investigated ion-exchange reactions as a more general synthetic route to new intercalation compounds.

Table I. Organometallic Intercalates of ZrS_2

guest	stoichiometry $(x)^a$	c, Å	lattice expansion, Å
$(\eta\text{-}C_6H_6)_2Mo$	0.16	34.93 (2)	5.81 (1)
$(\eta\text{-}C_6H_5CH_3)_2Mo$	0.13	34.90 (4)	5.80 (2)
$(\eta\text{-}C_6H_3(CH_3)_3)_2Mo$	0.08	34.83 (4)	5.78 (2)
$(\eta\text{-}C_6H_6)_2Cr$	0.16	35.20 (2)	5.90 (1)
$(\eta\text{-}C_5H_5)_2Cr$	0.25	34.31 (2)	5.61 (1)
$(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)Cr$	0.24	35.70 (2)	6.07 (1)
$(\eta\text{-}C_7H_7)(\eta\text{-}C_5H_5)Cr$	0.25	36.0 (2)	6.17 (7)
$(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)Ti$	0.23	36.69 (1)	6.40 (1)

[a] x in $(\text{guest})_xZrS_2$.

Experimental Section

Powder X-ray diffraction data were obtained using a Philips wide-angle goniometer and Cu Kα radiation. Lattice parameters were obtained by least-squares analysis of the peak positions. The compounds $M(\eta\text{-}C_6H_6)_2$, M = Cr, Mo,[9,10] $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]PF_6$,[11] and $Co(\eta\text{-}MeC_5H_4)_2$[12] were prepared as described previously. The compounds $Co(\eta\text{-}RC_5H_4)_2$, R = *i*-Pr or *n*-Bu, were prepared as described below.

Synthesis of Metal Dichalcogenides. Most of the dichalcogenides were synthesized from the elements. The metals were obtained "Specpure" from Johnson Matthey Chemicals and sulfur and selenium from BDH. The metal (typically 10 g) and the chalcogen (1% excess over the stoichiometric amount) were placed in a silica tube (ca. 25–50 cm^3) and sealed under vacuum. The silica tubes were baked out at 900 °C prior to use. Reaction conditions for the various preparations are given in Table II. Excess chalcogen was removed by vacuum sublimation. Sample purity was checked by X-ray diffraction and thermogravimetric analysis.

Direct Synthesis of Intercalates. A typical reaction is described. The pure transition-metal dichalcogenide was ground and sieved to 200 mesh and placed in a dry Pyrex ampule. A solution of the sandwich compound in dry toluene was added under nitrogen and the ampule sealed under vacuum. The ampule was heated at 130 °C for 3 days and opened under nitrogen, and the solid separated. The solid was washed several times with dry degassed toluene and dried under vacuum. The reaction was assumed complete when no lines due to starting material were observed in the X-ray powder diffraction pattern.

---

*To whom correspondence should be addressed at Exxon Research and Engineering Co.

0020-1669/78/1317-2754$01.00/0