fates in fluorosulfuric acid may similarly be attributed to ion–solvent interaction. Unfortunately our measurements are not extensive enough to allow us to compare the different extents of solvation of different electrolytes as has been done in the case of sulfates in sulfuric acid.[11]

Sulfonyl Fluorides.—The results of the cryoscopic measurements are given in Table II. Methyl sulfonyl fluoride gave a freezing-point depression curve identical with that of $S_2O_6F_2$ and $S_2O_5F_2$ (Figure 2) and is clearly therefore a nonelectrolyte. 2,5-Dimethylbenzene sulfonyl fluoride gave a freezing-point depression slightly less than that of a nonelectrolyte. The reason for this is not entirely clear but it may be due to nonideality associated with the very limited solubility of this compound in fluorosulfuric acid. Neither of the sulfonyl fluorides was completely stable in solution in fluorosulfuric acid as the originally colorless solutions slowly darkened if allowed to stand at room temperature.

Nitro Compounds.—The results of the cryoscopic measurements are given in Table III. The depression produced by the first addition of trinitrobenzene was somewhat less than that expected for a nonelectrolyte; thereafter the freezing-point curve was found to have a slope slightly greater than that for an ideal nonelectrolyte that increased somewhat with increasing concentration. The reason for the initial low depression is not clear. The fact that eventually the freezing-point curve has a slope slightly greater than that for an ideal nonelectrolyte is consistent with the slight degree of ionization found previously by conductometric measurements[1] and the increasing slope with increasing concentration may be attributed to nonideal behavior such as has been previously found in sulfuric acid and which it has been supposed results largely from the large size of the solute and the consequent nonideal entropy of mixing with the solvent.[11]

2,4-Dinitrotoluene gives a depression that is greater than that for a nonelectrolyte. Values of ν calculated from the cryoscopic results are given in Table V. They indicate that this solute is extensively ionized, presumably according to the equation

$$RNO_2 + HSO_3F = RNO_2H^+ + SO_3F^- \qquad (10)$$

The equilibrium constant for this reaction calculated from the ν values is also given in Table V. The same value was obtained previously from conductometric studies.[1] This excellent agreement may be partly fortuitous as there is a difference of 115° between the temperatures at which the cryoscopic and conductometric measurements are made.

TABLE V

VALUES OF ν AND K

2,4-Dinitrotoluene

10^2m	θ, °C	ν	10^2K
2	0.117	1.49	1.0
4	0.227	1.45	1.5
6	0.329	1.40	1.6
8	0.420	1.34	1.4
10	0.512	1.30	1.5
		Mean	1.4

KF

10^2m^a	θ, °C	ν
2	0.226	2.88
4	0.453	2.88
6	0.681	2.89
8	0.923	2.94

^{a} Corrected for the KF used up initially in reaction with excess SO_3.

Acknowledgments.—We thank the Petroleum Research Fund of the American Chemical Society and the United States Air Force Office of Scientific Research for generous financial assistance. We also thank the Ontario Research Foundation for the award of a fellowship (to R. C. T.) and the National Research Council of Canada for the award of a studentship (to J. B. M.).

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CONTRIBUTION FROM THE WESTERN RESEARCH CENTER,
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Structure of the Tetrafluorochlorate(III) Anion, ClF_4^-

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Infrared and conductivity measurements show that $MClF_4$ (where M is NO, Rb, or Cs) is ionic in the solid state and in solution, respectively. A square-planar structure (point group D_{4h}) is assigned to the ClF_4^- anion in $Rb^+ClF_4^-$ and $Cs^+ClF_4^-$. For the ClF_4^- anion in $NO^+ClF_4^-$, the low-temperature infrared measurement indicates a lower symmetry.

Introduction

While the existence of $MClF_4$ (where M is NO, K, Rb, or Cs) is well known,[1–4] no reports on the ionic character of the NOF–ClF_3 adduct and on the structure of the ClF_4^- anion have been published. As-

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prey,[1] *et al.*, obtained the infrared spectrum of $KClF_4$; however, the absorptions reported by them occur at much higher frequencies than expected for the fundamental vibrations of the ClF_4^- anion. Therefore, they could have obtained only overtones and combination frequencies.

The structure of the ClF_4^- anion can be expected to be similar to that of the BrF_4^- anion since both $KClF_4$[2] and $KBrF_4$[5] crystallize in the tetragonal system and have similar unit cell dimensions. Siegel interpreted the X-ray diffraction pattern of $KBrF_4$ in terms of a tetrahedral configuration of the BrF_4^- anion. However, the pattern can be interpreted in terms of a planar BrF_4^- anion[6,7] as well. The tetrafluoroiodates(III) of potassium, rubidium, and cesium have been prepared,[8] but the structure of the anion has not been investigated. However, it was reported[8] that the X-ray powder diagrams are complex and that the IF_4^- compounds are probably not isostructural with the corresponding BrF_4^- compounds. Therefore, the evidence reported previously in the literature is insufficient to prove the structure of any of the tetrafluorohalogenate(III) anions. However, on the basis of the known square-planar structure of the ICl_4^- anion[9] and of the isoelectronic XeF_4,[10] the square-planar structure seems most likely.

The knowledge of the structure of interhalogen complexes such as the tetrafluorochlorates(III) is important for theoretical bonding considerations since a certain symmetry of a compound could rule out certain theoretical bond models. If, for example, the tetrafluorochlorate(III) anion were tetrahedral, the semiionic bond model[10] would be incorrect.

Experimental Section

The compounds examined were prepared as described in the literature.[3,4] The infrared spectra of $RbClF_4$, $CsClF_4$, and $NOClF_4$ were taken with a Beckman IR-9 spectrophotometer in the range 4000–400 cm^{-1}. The spectrum of $RbClF_4$ was also recorded on a Beckman IR-11 spectrophotometer in the range 800–33 cm^{-1}. Nujol mulls or dry powder between AgCl or polyethylene disks were employed. The low-temperature spectrum of $NOClF_4$ was taken using the same technique described earlier for $NO^-ClF_2^-$[11] and $ClF_2^+AsF_6^-$.[12] The conductivity measurements were done using the method reported earlier.[11]

Results

Conductivity.—The solubility of $NOClF_4$ in liquid ClF_3 at −23° was quite low. Table I shows the results obtained for a saturated solution of $NOClF_4$ in liquid ClF_3. Assuming complete solubility of the $NOClF_4$ in ClF_3 (not actually the case), the solution would have had a molarity of 0.079 and thus a minimum equivalent conductance, $\Lambda = 3.69 \times 10^{-3}$ ohm^{-1} cm^2.

TABLE I

CONDUCTIVITY OF $NOClF_4$ IN LIQUID ClF_3

Compd	Temp, °C.	Specific conductance, σ, ohm^{-1} cm^{-1}
ClF_3	−23	9.2×10^{-9}
NOF	−79	5.4×10^{-5}
Saturated solution of $NOClF_4$ in liquid ClF_3	−23	2.1×10^{-7}

TABLE II

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF $MClF_4$ AND VIBRATIONAL ASSIGNMENTS FOR $RbClF_4$ AND $CsClF_4$ IN THE POINT GROUP D_{4h}

$RbClF_4$	$CsClF_4$	Assignment for $RbClF_4$ and $CsClF_4$ in the point group D_{4h}	$NOClF_4$
1242 mw		$\nu_6 + \nu_7$	2298 m νNO^+
745 vs	742 vs	$\nu_6\ (E_u)$	676 ms
			541 vs
486 s	478 s	$\nu_2\ (A_{2u})$	498 m
430 m	425 m	$\nu_7\ (E_u)$	434 s
118 m		Lattice vibration	

Infrared Spectra.—Table II shows the absorption frequencies of $NOClF_4$, $RbClF_4$, and $CsClF_4$. The frequencies of the pure solid starting materials, NOF[11] and ClF_3,[12] have previously been reported. The $NOClF_4$ sample was prepared directly on a cold AgCl window using excess NOF or excess ClF_3. It was found more convenient to remove unreacted NOF from $NOClF_4$ owing to its greater volatility. Figure 1 shows the low-temperature infrared spectrum of solid $NOClF_4$.

Discussion

$NOClF_4$, Ionic Character.—Three reasonable structures for the complex are: coordination complex, $ClF_3 \cdot NOF$ (I); $ClF_2^+NOF_2^-$ (II); $NO^+ClF_4^-$ (III). Structure I should show no significant conductivity increase in ClF_3 solution and would require an infrared spectrum similar to that of ClF_3 superimposed on NOF with perhaps some shifting of absorption bands. The NO bond in structures I and II has double-bond character and should absorb at 2000–1800 cm^{-1}.[11] In structure III the NO bond has triple-bond character and should absorb at 2350–2100 cm^{-1}.[13] The solution containing the complex has an increased conductivity, and the infrared spectrum shows the NO absorption at 2298 cm^{-1} indicative of the NO^+ cation. In addition, considering only symmetry, structure II would have required a higher number of infrared-active vibrations, the position of which would have to have been quite different. Thus, structure III is assigned to the complex.

Structure of the ClF_4^- Anion.—Table III shows the point groups taken into consideration as structural possibilities for the ClF_4^- anion and the infrared-active fundamental vibrations expected for each group.

$RbClF_4$ and $CsClF_4$.—Since $NO^+ClF_4^-$ and the alkali metal tetrafluorochlorates(III) do not show the same number of absorption bands and do have somewhat different frequency positions, these compounds will be

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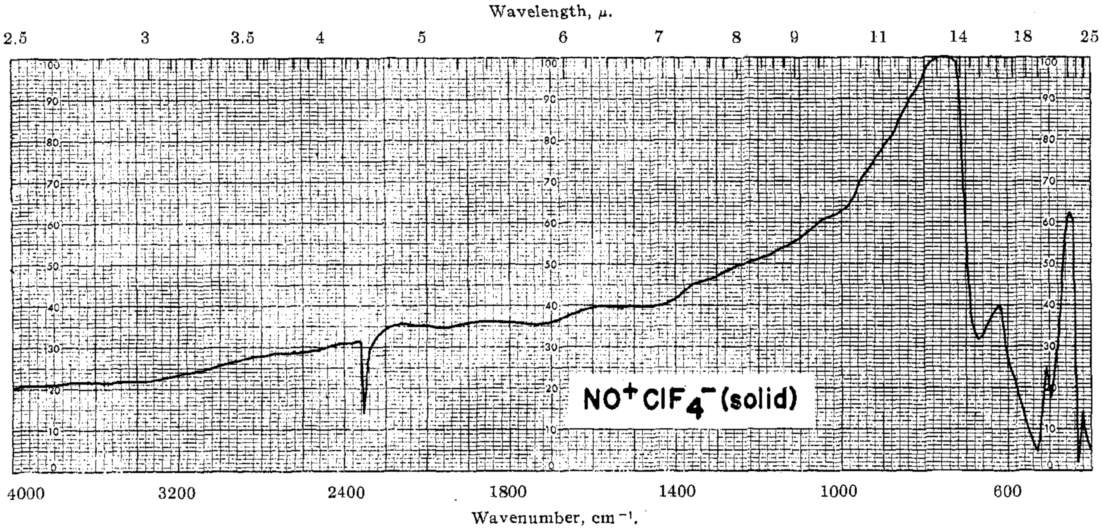

Figure 1.

TABLE III

NUMBER OF INFRARED-ACTIVE FUNDAMENTALS EXPECTED FOR THE ClF_4^- ANION IN DIFFERENT POINT GROUPS

Point group	Structure	Total no. of infrared-active fundamentals	No. of infrared-active stretching vibrations	No. of infrared-active deformation vibrations
T_d	Tetrahedral XY_4	2	1	1
D_{4h}	Square-planar XY_4	3	1	2
C_{4v}	Square-pyramidal XY_4	4	2	2
D_{2h}	Planar *trans*-XY_2Z_2	6	2	4
C_{2v}	Nonplanar XY_2Z_2	8	4	4

treated separately. The spectra of the alkali metal tetrafluorochlorates(III) show only three infrared-active fundamental vibrations. The absorption at 118 cm^{-1} in $RbClF_4$ is too low to be a fundamental vibration and, therefore, is assigned to a lattice vibration, in agreement with values found for K_2PtCl_4 and similar compounds.[14] The band at 1242 cm^{-1} occurs at too high a frequency to be a ClF fundamental and, consequently, is assigned to a combination vibration. Therefore, since only three infrared-active fundamentals were found, a square-planar structure can be assigned to the ClF_4^- anion, and the other structural possibilities can be ruled out.

A square-planar molecule of the type XY_4 has D_{4h} symmetry. The nine normal modes of vibration are classified as $A_{1g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + 2E_u$. Of these, only the E_u and A_{2u} modes will be infrared active in the isolated molecule, assuming that the selection rules in the solid are the same as they would be for the free gaseous ion.

The bands within the range of possible fundamentals in the spectrum of $RbClF_4$ occur at 745, 486, and 430 cm^{-1}. The band at 745 cm^{-1} is undoubtedly the Cl–F E_u stretching mode. Out of the two expected infrared-active deformation vibrations the in-plane vibration likely has a lower frequency than the out-of-plane vibration. Therefore, the bands at 486 and 430 cm^{-1} are assigned to the vibration of the A_{2u} species and the E_u species, respectively. Sabatini, Sacconi, and Schettino[14] and Adams and Morris[15] preferred the opposite assignment for the two deformation vibrations in $PtCl_4^{2-}$ and similar square-planar anions. Our assignment, however, is in agreement with the assignments for other square-planar AB_4-type molecules,[16,17] ClF_5,[18] and the isoelectronic XeF_4.[19] In addition, it can be assumed that the repulsion between the fluorine atoms in the ClF_4^- anion caused by the lone electron pairs is greater than the repulsion caused by the neighboring fluorine atoms. Therefore, the out-of-plane deformation vibration can be expected to show a higher frequency than the in-plane deformation vibration.

For $CsClF_4$ slightly lower frequencies were obtained for these modes. Table II contains the vibrational assignments of the observed frequencies in the point group D_{4h} for both compounds.

$NO^+ClF_4^-$.—The low-temperature infrared spectrum of $NO^+ClF_4^-$ shows one more band in the observed range than that of the alkali metal tetrafluorochlorates(III). In addition, the positions of the higher frequency band differ somewhat. The number of observed bands rules out the tetrahedral (T_d point group) structure. The square-planar (D_{4h} point group) structure should show one vibration less. However, since

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we are dealing with spectra of solids at low temperature, in which the anion does not necessarily behave ideally, it is possible that the symmetric stretching vibration of ClF_4^- might have become infrared active. The presence of this vibration may be due to either distortion of the square-planar ClF_4^- anion (thus lowering the symmetry from D_{4h} to C_{4v}) or to a crystal lattice effect. Then the assignments could be made in analogy to the vibrations of the square-planar ClF_4 part of the ClF_5 molecule.[18] However, the found intensities do not agree so well with this assignment. The planar *trans*-XY_2Z_2 structure is also possible. In this case, the band at 498 cm^{-1} would be a deformation vibration. However, the band at 541 cm^{-1} is asymmetric, and most infrared spectra of $NO^+ClF_4^-$ showed a very weak shoulder at 570 cm^{-1}. On the basis of this and the fact that the position of the band at 498 cm^{-1} does not exclude its interpretation as a stretching vibration, the possibility of assigning the ClF_4^- anion in $NO^+ClF_4^-$ to the point group C_{2v} cannot be eliminated. Regardless, the symmetry of the ClF_4^- anion in $NO^+ClF_4^-$ at low temperature appears to be lower than D_{4h} (found for $RbClF_4$ and $CsClF_4$).

Conclusion

(i) The ionic structure, $NO^+ClF_4^-$, is assigned to the 1:1 adduct formed from NOF and ClF_3. (ii) The tetrafluorochlorate(III) anion in $RbClF_4$ and $CsClF_4$ has square-planar (symmetry D_{4h}). (iii) The tetrafluorochlorate(III) anion in $NOClF_4$ at low temperature has lower symmetry than D_{4h}. (iv) The square-planar structure found for the ClF_4^- anion in $RbClF_4$ and $CsClF_4$ is in agreement with either the semiempirical molecular orbital model, assuming semiionic bonds, or the sp^3d^2-hybridization model. (v) Since $KClF_4$ and $KBrF_4$ are isostructural according to their X-ray data, the interpretation of $KBrF_4$ in terms of a planar rather than a tetrahedral BrF_4^- anion seems more likely.

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Contribution from the Department of Chemistry,
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The Structure of the Octacyanomolybdate(V) and -tungstate(V) Ions from Electron Spin Resonance[1]

By B. R. McGarvey

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The anisotropic spin Hamiltonian parameters of the $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions have been determined from the esr spectra of frozen glycerine solutions. The results can be interpreted as showing that the ions possess the Archimedean antiprism structure in solutions. The *g* values for ions in the duodecahedral configuration have also been obtained from esr spectra of the ions trapped in the crystal lattice of $K_4Mo(CN)_8$ and $K_4W(CN)_8$. The magnitude of the spin Hamiltonian parameters shows that there is considerable covalency in the metal–cyanide bonds.

Introduction

The structure of eight-coordinated ions has been of interest for some time. On the basis of X-ray diffraction studies, Hoard and Nordsieck[2] found the structure of $Mo(CN)_8^{4-}$ to be duodecahedral in the crystal $K_4Mo(CN)_8 \cdot 2H_2O$. Stammreich and Sala[3] found, however, that Raman and infrared data support an Archimedean antisprism structure for the same ion when in solution. There have been no determinations of the structure of the paramagnetic ions $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$. The optical spectra of octacyanide complexes of Mo(IV), Mo(V), W(IV), and W(V) have been determined[4–7] but have been of little value in determining structure. In fact they have been interpreted theoretically in terms of both the duodecahedral structure[4] and the antiprism structure.[7,8] The esr of powders of $K_3Mo(CN)_8$, $K_3W(CN)_8$, $Ag_3Mo(CN)_8$, and $Ag_3W(CN)_8$ have been determined[8,9] as well as the esr of aqueous solutions[10,11] of the $Mo(CN)_8^{3-}$ and $W(CN)_8^{3-}$ ions. However there have been no reports on the anisotropic components of the spin Hamiltonian.

Experimental Section

The compounds $K_4Mo(CN)_8$ and $K_4W(CN)_8$ were prepared using procedures given in *Inorganic Syntheses*.[12] Aqueous solu-

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