and so do not distinguish between inner-sphere and outer-sphere mechanisms. The rate of water exchange on Ti(III) is sufficiently large[31] that the inner-sphere mechanism cannot be excluded on the basis of arguments related to the rate of substitution. At any rate, such arguments have been shown to be insufficient for V(V) and Cr(VI) oxidations.[1-3]

With regard to $[H^+]$ dependence, it is of interest to compare the Ti(III)-V(V) reaction to the V(III)-V(V) reaction. The major paths for the latter reaction have orders of -1 and -2 in $[H^+]$,[32] in spite of the fact that overall no H^+ is consumed or released. Apparently the configurational changes accompanying electron transfer are not the sole factors determining the $[H^+]$ dependence. In other respects there is apparently little similarity between the two reactions. No evidence was found for binuclear complex formation between V(III) and V(V), although arguments were advanced for an inner-sphere configuration of the transition state.[32]

Titanium(IV) appears to have particular tendency to form binuclear complexes. Complexes are known with titanium(III)-[33] and cobalt(III)-ammine complexes[12] in SO_4^{2-} media, Ti(IV) has been reported to polymerize,[27] and we have observed complexation with V(V) and Cr(VI).[5] Considering the uncertainty in the formulation of Ti(IV) in solution as well as in that of the Ti(IV)-V(V) binuclear complex observed here, it would be presumptive to attempt to identify the reactions corresponding to each of the terms in the complexation rate law (eq 5, 6). These terms may well correspond to reactions with Ti(IV) (and/or V(V)) in different states of protonation, in which case some information could be surmised regarding the existence of such species and the magnitude of the equilibrium constants relating their concentrations. It is interesting that the formation of a complex between Ti(IV) and H_2O_2[34] follows a rate law of the same form as eq 5 and 6. The similarity extends to the magnitude of the rate constants as well, in particular that of the acid-independent term f, which has a value of 414 M^{-1} sec^{-1} for V(V) and of 120 M^{-1} sec^{-1} for H_2O_2 in perchlorate solutions of 3.0 M ionic strength.[34] Whether these similarities have any mechanistic significance must await further kinetic studies of complexation reactions of Ti(IV).

Registry No. Vanadium, 7440-62-2; titanium, 7440-32-6.

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Contribution No. 13001 from the National Research Council of Canada, Ottawa, Canada

Complex Fluoro Anions in Solution. I. Homo- and Heteropolyfluoro Anions of Niobium and Tantalum

S. BROWNSTEIN

Received July 3, 1972

The compounds $(TBA)MNF_{11}$, where TBA is tetra-*n*-butylammonium, M is tantalum or niobium, and N is tantalum, niobium, or antimony, have been prepared in solution and characterized by their fluorine resonance spectra. A comparison is made between these compounds and the corresponding ones where M and N are arsenic and antimony.

Introduction

Fluorine bridging between atoms of a transition metal in its binary fluoride or as a complex fluoro anion has been well documented by X-ray diffraction studies of crystalline compounds.[1] In solution most of the evidence for fluorine bridging is obtained from fluorine magnetic resonance spectroscopy. It has been demonstrated for antimony pentafluoride[2] and the anions $Sb_nF_{5n+1}^-$,[3] $As_2F_{11}^-$,[4,5] $AsSbF_{11}^-$,[5] and $B_2F_7^-$ [6] that it is possible to obtain information about the structure of the fluorine-bridged entity provided that fluorine exchange is not too rapid on the nuclear magnetic resonance time scale. Since fluorine bridging has been observed in the solid fluorides of niobium and tantalum, there appeared to be a distinct possibility that complex fluoro anions could be found for these elements as with $As_2F_{11}^-$ and $Sb_2F_{11}^-$. This has been realized, and details of the fluorine magnetic resonance spectra are presented. TBA will be used as an abbreviation for the tetra-*n*-butylammonium ion.

Experimental Section

All sample preparation and handling was done with standard vacuum-line techniques or by using a vacuum drybox. Solvent purification and storage were accomplished as previously described.[5] At no time was any evidence found for hydrolysis of these sensitive compounds. Fluorine resonance spectra were obtained on a Varian Associates HA 100 spectrometer operating at 94.1 MHz. Some spectra were also obtained at 25.1 MHz to distinguish with certainty between chemical shift or spin-coupling origin for certain line splittings. Chemical shifts are reported as ppm from internal $CFCl_3$. Infrared spectra of the compounds dispersed in potassium

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Table I. Chemical Shifts and Spin-Coupling Constants of Some Complex Fluoro Anions

Species	$\delta_1{}^a$	δ_2	δ_3	δ_4	δ_5	$J_{1-2}{}^b$	J_{1-3}	J_{2-3}	J_{3-4}	J_{4-5}
TaF_5		−99.6								
TaF_6^-		−40.4								
$Ta_2F_{11}^-$	−115.1 ± 0.2	−72.0 ± 0.2	80.8 ± 0.2			23.0 ± 0.8	165 ± 4	41.8 ± 0.6		
NbF_5		−162								
NbF_6^-		−103.1								
$Nb_2F_{11}^-$	−191.0	−145.9	56.0			70	200	70		
$TaNbF_{11}^-$	−109.0	−69.1	70.8	−149.5	−196.6	25	190		70	70
$TaSbF_{11}^-$	−125.7	−78.6	99.6	117.3	134.0	23	172	43	40	90
$NbSbF_{11}^-$	−205	−156.5		118						
$TaAsF_{11}^-$	−122.3	−76.1		62.7						

[a] In ppm from internal $CFCl_3$. [b] In Hz.

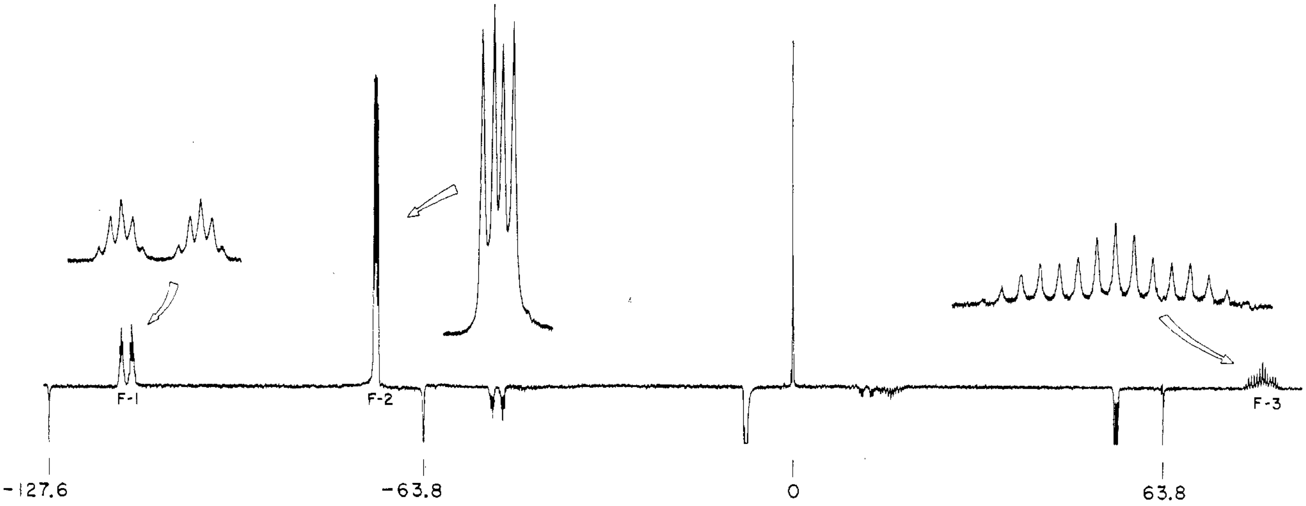


Figure 1. The fluorine resonance spectrum of $(TBA)Ta_2F_{11}$ at −100°.

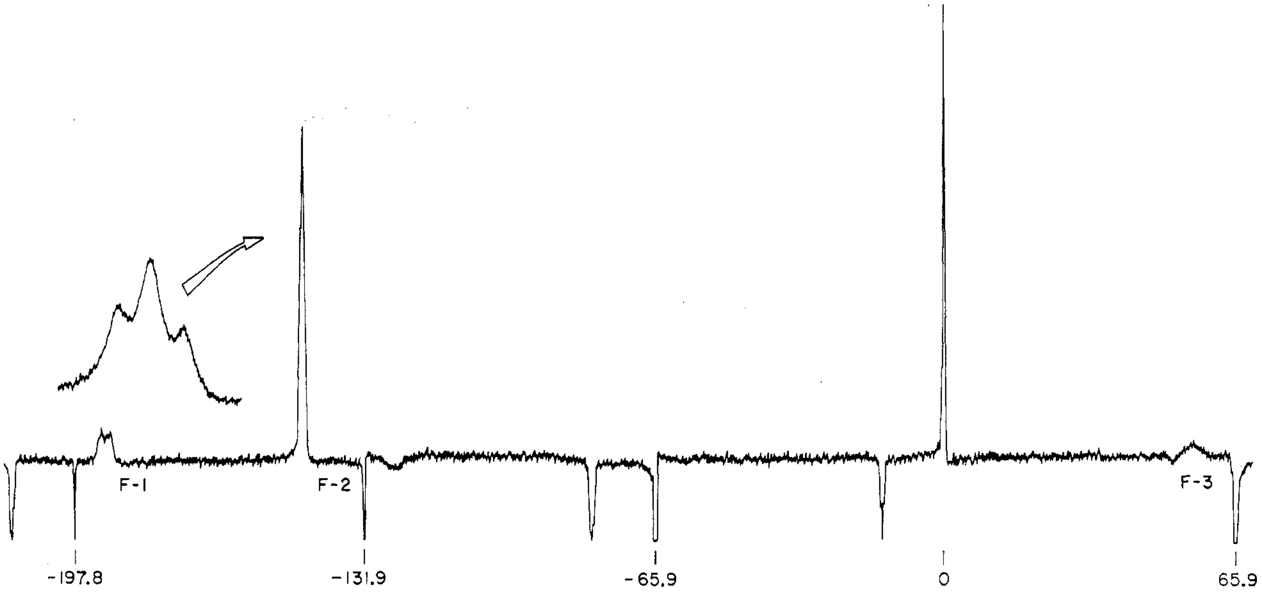


Figure 2. The fluorine resonance spectrum of $(TBA)Nb_2F_{11}$ at −100°.

bromide disks were obtained with a Perkin-Elmer 621 spectrophotometer. Tantalum and niobium pentafluorides (Research Organic/Inorganic Chemical Corp.) were used as received. Tantalum pentafluoride dissolved in methylene chloride gives a broad resonance signal, as does niobium pentafluoride in sulfur dioxide solution. Chemical shifts are listed in Table I.

Tetra-*n*-butylammonium Hexafluorotantalate. Equimolar quantities of tetra-*n*-butylammonium fluoroborate[6] and tantalum pentafluoride were dissolved in methylene chloride and mixed, and all volatile materials were removed under high vacuum. A weight loss equivalent to the boron trifluoride originally present (theory, 110 mg; found, 111 mg) was observed. The product was characterized by its infrared and fluorine resonance spectra. *Anal.* Calcd: Ta, 33.7. Found: Ta, 34.2. A single broad line is found for the fluorine resonance spectrum and is listed in Table I.

Tetra-*n*-butylammonium Hexafluoroniobate. Equimolar quantities of tetra-*n*-butylammonium fluoroborate and niobium pentafluoride were fused together at 150° in a Teflon reactor. The product was dissolved in methylene chloride and filtered, and all volatile materials were removed under high vacuum. It was characterized in the same manner as tetra-*n*-butylammonium fluorotantalate and also by its X-ray powder diffraction pattern. The hexafluoroniobate was also prepared in sulfur dioxide as solvent since niobium pentafluoride is insoluble in methylene chloride. Both preparations gave the same product. *Anal.* Calcd: Nb, 20.7. Found: Nb, 19.7. The fluorine resonance spectrum of the hexafluoroniobate ion has been extensively studied under various conditions.[7]

(TBA)Ta_2F_{11}. This compound may be prepared in solution from equimolar quantities of TaF_5 and (TBA)TaF_6. An attempt was also made to determine the possible existence of $Ta_2F_{11}^-$ in the solid state but the results are equivocal. The infrared spectrum of the solid obtained after removal, under vacuum, of the solvent from an equimolar methylene chloride solution of (TBA)TaF_6 and TaF_5 appears to absorb beyond the sum of TaF_6^- and TaF_5. A similar study, using X-ray powder diffraction, was done on the silver salt, which yields a simpler pattern than the tetra-*n*-butylammonium salt. In this case the product was found to be a mixture of $AgTaF_6$ and TaF_5, with no evidence for $AgTa_2F_{11}$.

A methylene chloride solution prepared from 0.105 mmol of TaF_5 and 0.101 mmol of (TBA)TaF_6 has at −100° the fluorine resonance spectrum shown in Figure 1.

(TBA)Nb_2F_{11}. A 0.0448-mmol sample of NbF_5 and 0.0448 mmol of (TBA)NbF_6 were dissolved in sulfur dioxide, followed by removal of the solvent under vacuum. The resultant solid was completely soluble in methylene chloride. Since it is probable that decomposition might easily occur, elemental analysis was not attempted. An X-ray powder diffraction pattern of $AgNb_2F_{11}$ prepared in the same manner shows it to be different from the starting materials. The infrared spectrum of this solid is also different from the sum of those for the starting materials.

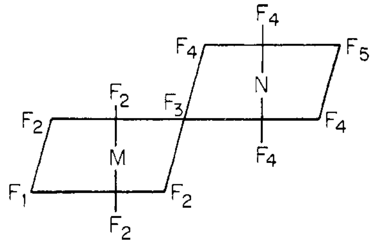
The fluorine resonance spectrum of (TBA)Nb_2F_{11} at −100° is shown in Figure 2.

In addition to the homopolyfluoro anions it is possible to obtain the heteropolyfluoro anion $TaNbF_{11}^-$. The fluorine resonance spectrum of a solution of 0.113 mmol of (TBA)NbF_6 and 0.120 mmol of TaF_5 in methylene chloride at −98° is shown in Figure 3. No single modulation frequency could satisfactorily show all the peaks without overlap with modulation side bands of opposite phase. Therefore the spectrum shown is a composite of several spectra obtained with different modulation frequencies.

The anion $TaSbF_{11}^-$ has also been identified by its fluorine resonance spectrum. The spectrum of a methylene chloride solution prepared from 0.180 mmol of (TBA)SbF_6 and 0.180 mmol of TaF_5 is shown in Figure 4.

Discussion

It is possible to explain completely the fluorine resonance spectra on the basis of structure I where M and N are from among tantalum, niobium, and antimony. The assignment for $Ta_2F_{11}^-$ can be made unambiguously on the basis of the first-order spin-coupling patterns. The chemical shifts are listed in Table I and the peak assignments are indicated on the spectra. Fluorine 1 is a doublet of quintets due to spin coupling with fluorine 3 and the four equivalent fluorine 2 atoms. Fluorine 2 is a doublet of doublets from spin coupling with fluorine 1 and fluorine 3. Fluorine 3 ought to give a triplet of nonets, or 27 lines. Since J_{1-3} is almost exactly 4 times J_{2-3}, there is considerable overlap to yield a theoretical pattern of 17 lines with relative intensities of 1:8:28:56:72:72:84:120:142:120:84:72:72:56:28:8:1. The experimental spectrum is in fact very close to this intensity ratio. As the temperature of this sample is raised, all the lines broaden in a uniform manner which suggests that



I

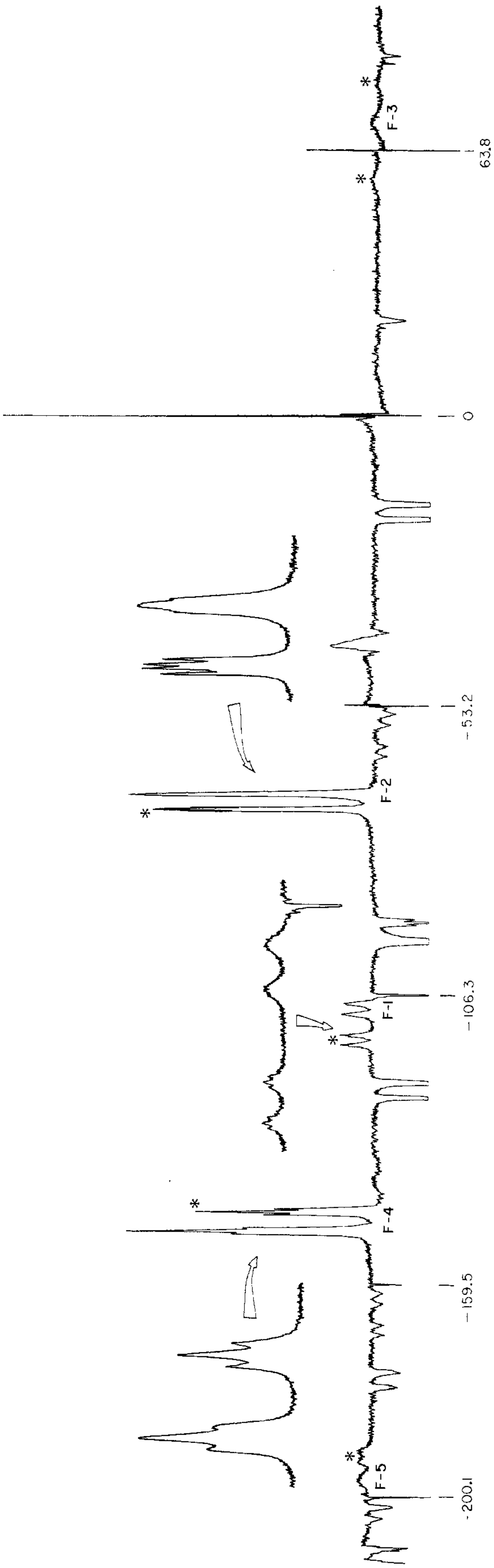


Figure 3. The fluorine resonance spectrum of an equimolar solution of (TBA)NbF_6 and TaF_5 at −98°.

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(7) D. W. Aksnes, S. M. Hutchinson, and K. J. Parker, *Mol. Phys.*, 14, 307 (1968).

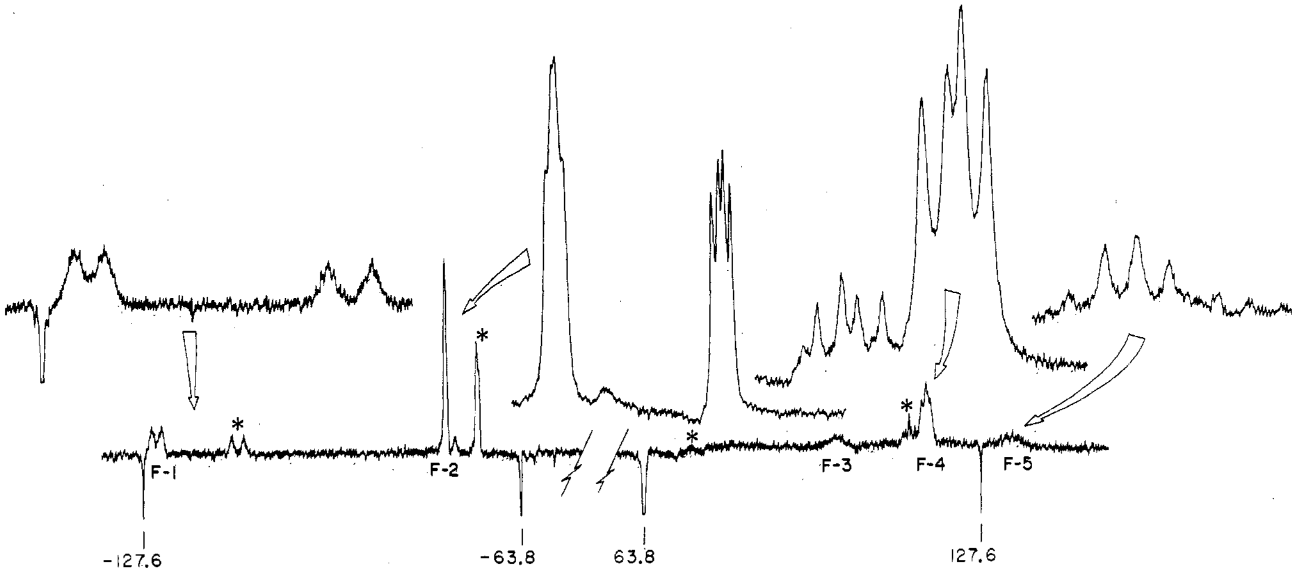

Figure 4. The fluorine resonance spectrum at − 100° of an equimolar solution of (TBA)SbF_6 and TaF_5.

magnetic averaging is occurring perhaps according to

$$Ta_2F_{11}^- \rightleftharpoons TaF_6^- + TaF_5 \qquad (1)$$

At room temperature only a single broad line is observed for the sample. The only unusual feature of the fluorine resonance spectrum of this anion is the remarkably high field location of the bridging fluorine. Upon addition of excess TaF_5 there is no evidence for ions of greater complexity. This is in contrast to the rather similar ion $Sb_2F_{11}^-$ where aggregates such as $Sb_3F_{16}^-$ and $Sb_4Fb_{21}^-$ have been found.[3]

The rather uniquely shaped spectrum of NbF_6^- has been analyzed as arising from fluorine-niobium spin coupling, rather slow niobium quadrupole relaxation, and some fluorine exchange.[7] With the particular salt, solvent, and temperatures used in the present investigation it was possible to slow down the magnetic averaging process so that the individual lines of the spin-spin multiplet are completely resolved to give a 10-line pattern with a niobium-fluorine spin-coupling constant of 330 Hz.

The assignment of the lines from the spectrum of $Nb_2F_{11}^-$ to particular fluorines is straightforward from the assignment made for $Ta_2F_{11}^-$. The chemical shifts are listed in Table I and shown in Figure 2. The coupling between fluorine 1 and fluorine 3 can just be discerned in the spectrum so that the reported value is subject to significant error. Since the signal from fluorine 2 is a poorly resolved triplet, it appears that the magnitudes of J_{1-2} and J_{2-3} are approximately equal. Here too the values of the coupling constants are not too certain because of the poorly resolved spectra. The resolution improves at lower temperature, presumably because of slower fluorine exchange between nonequivalent sites. The spectra were obtained at the lowest temperatures allowed by solubility and freezing of the solvent. A compound with the same anion, $SF_3Nb_2F_{11}$, has been prepared and its structure determined by X-ray crystallography.[8] The anion has the structure I but there is strong cation-anion interaction.

In the spectrum of Figure 3 those lines which arise from $Ta_2F_{11}^-$ and $Nb_2F_{11}^-$ are denoted by an asterisk. The remaining lines, except for a weak one from TaF_6^-, are assigned to $TaNbF_{11}^-$, structure I with M = Ta and N = Nb. These lines are assigned on the basis of the assignments for the homopolyfluoro anions of tantalum and niobium and the assignments are indicated in Figure 3 and the chemical shifts are listed in Table I. From the fine structure observed in the signal from fluorine 1 the spin-coupling constants J_{1-2} and J_{1-3} may be obtained. No spin-coupling information can be extracted from the signals of fluorines 2, 3, and 5, but the approximate triplet signal of fluorine 4 suggests equal values for J_{3-4} and J_{4-5}.

The fluorine resonance spectra of TaF_5, TaF_6^-, and NbF_5 show that quadrupole relaxation of the central atom is more rapid than for NbF_6^- but still slow enough that there is considerable line broadening due to residual fluorine spin coupling. In the homo- and heteropolyfluoro anions the quadrupole relaxation rate is sufficiently rapid that no evidence of fluorine-central atom spin coupling is observed. The reason for this increase in relaxation rate is not obvious. Normally a more symmetric electric environment about the central atom decreases the quadrupole relaxation rate. It would appear that the electric field gradient about the central atom ought to be at least as symmetric in the poly anions as in the parent pentafluorides or hexafluoro anions. Therefore, one may hypothesize that perhaps there is some rapid distortion of the joined octahedra or else that the fluorine bridge bond is significantly different in polarity than the other fluorine-central atom bonds. Similar line width behavior has been found previously for poly anions of arsenic and antimony[3-5] but its significance was not noted.

The reaction of MF_5 with MF_6^- to yield $M_2F_{11}^-$ appears to be essentially complete at low temperature when M is niobium or tantalum since no trace of reactants could be found in fluorine resonance spectra of these solutions. In contrast some TaF_6^- is present and some white solid, presumably NbF_5, is found in the nmr sample tube which initially contained only (TBA)NbF_6 and TaF_5. Therefore the reaction of (TBA)NbF_6 and TaF_5 can be primarily explained by (2) with some initial contribution from (3).

$$2NbF_6^- + 2TaF_5 \rightarrow 2TaNbF_{11}^- \rightleftharpoons Ta_2F_{11}^- + Nb_2F_{11}^- \qquad (2)$$

$$TaF_5 + NbF_6^- \rightarrow TaF_6^- + NbF_5\downarrow \qquad (3)$$

In the spectrum of Figure 4 those lines which arise from $Ta_2F_{11}^-$ and $Sb_2F_{11}^-$ are denoted by an asterisk. The remaining lines are assigned to $TaSbF_{11}^-$, structure I with M = Ta and N = Sb. Some of the lines of these species are

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[8] A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1494 (1970).

of such low intensity because of exchange broadening, low abundance, and high multiplicity that they cannot be found in this spectrum. However by altering the relative quantities of the two reactants it is possible to find the weaker lines due to the bridging fluorines. The lines of $TaSbF_{11}^-$ are assigned on the basis of the assignments for the homopolyfluoro anions of tantalum and antimony and these assignments are indicated in Figure 4 and the chemical shifts are listed in Table I. The value for J_{1-3} in $TaSbF_{11}^-$ may be obtained from the splittings observed in the lines for fluorine 1, while J_{1-2} and J_{2-3} may be approximated from the splitting observed in the resonance of fluorine 2. The value of J_{4-5} is found from the signals of fluorine 5 and confirmed from the peak of fluorine 4, which also yields a value for J_{3-4}.

The reaction of $(TBA)SbF_6$ with TaF_5 is consistent with eq 4 since this explains all the peaks in the fluorine resonance

$$2SbF_6^- + 2TaF_5 \rightarrow 2TaSbF_{11}^- \rightleftharpoons Ta_2F_{11}^- + Sb_2F_{11}^- \tag{4}$$

spectrum and is also analogous to the corresponding reaction with $(TBA)NbF_6$. If the equilibrium represented by (4) is completely random, one would expect an equilibrium constant of 0.25 for this reaction. By varying the relative concentrations of $(TBA)SbF_6$ and TaF_5 the relative areas of the peaks assigned to fluorine bonded to tantalum and to antimony change as shown in Table II.

It is possible to calculate the equilibrium constant for the reaction using the relative areas of the peaks arising from fluorine bonded to tantalum and to antimony in both homopoly anions and in the heteropoly anion along with the relative amounts of the two reactants. From the relative areas of the equatorial fluorines bonded to tantalum and the quantity of TaF_5 used to prepare the sample, the quantities of $TaSbF_{11}^-$ and $Ta_2F_{11}^-$ formed can be calculated. By using the quantity of $TaSbF_{11}^-$ and from the relative areas of the equatorial fluorines bonded to antimony the quantity of $Sb_2F_{11}^-$ may be calculated. If the calculations are valid, this must equal the quantity of $Ta_2F_{11}^-$ calculated in the first step of the procedure. Within experimental error the two figures were found to be equal for the samples in this study. An average equilibrium constant of 0.25 was found for reaction 4, suggesting that the distribution of Sb and Ta between the polyfluoro anions is random. The results for four samples of differing composition are presented in Table II. From the data presently available it is not possible to predict when disproportionation of MNF_{11}^- to $M_2F_{11}^-$ and $N_2F_{11}^-$ will occur. Disproportionation is found with $TaNbF_{11}^-$ and $TaSbF_{11}^-$ but not with $AsSbF_{11}^-$ [5] nor with $NbSbF_{11}^-$.[9]

When $(TBA)SbF_6$ and NbF_5 are fused together in a Teflon reactor and the product is dissolved in methylene chloride, the fluorine resonance spectrum of this solution indicates that only the mixed anion $NbSbF_{11}^-$ is formed and no evidence is found for the presence of the homopolyfluoro anions. The fusion procedure is necessary since NbF_5 is not soluble in methylene chloride and $(TBA)SbF_6$ is not very soluble in sulfur dioxide, the two solvents used in this study. The ion $NbSbF_{11}^-$ has previously been prepared in another manner and its Raman and fluorine resonance spectra were discussed.[9] The chemical shift values, which are listed in Table I for the equatorial fluorines bonded to niobium and to antimony, are in excellent agreement with those previously reported. In addition the peak for the terminal fluorine bonded to niobium was found in this study although it was not observed before. However the bridging fluorine and the terminal fluorine on antimony could not be resolved under the conditions used in this investigation.

Table II. Equilibrium Concentrations in Solutions of $(TBA)SbF_6$ and TaF_5

	Relative areas				
	Ta species		Sb species		
$SbF_6^-:TaF_5$	Hetero	Homo	Hetero	Homo	K
1.315	0.75	0.25	0.85	0.15	0.3
1.000	0.74	0.26	0.90	0.10	0.2
0.500	0.59	0.41	Not well resolved		
0.468	0.56	0.44	Not well resolved		

The fluorine resonance spectrum of a solution prepared from 0.189 mmol of $(TBA)AsF_6$ and 0.181 mmol of TaF_5 has two peaks in the region where equatorial fluorines on tantalum are found and also two peaks in the region of terminal fluorines on tantalum, similar to the corresponding antimony-containing solutions. The lines are not too well resolved especially in the fluorine bonded to arsenic region of the spectrum, probably due to rapid fluorine exchange between different environments. From the similarity with the antimony system it is possible to assign some of the fluorine chemical shifts for $TaAsF_{11}^-$ as listed in Table II.

The chemical shift behavior of the group Va and Vb elements is different both in the binary fluorides and in the polyfluoro anions. There is only a small shift difference between the pentafluoride and hexafluoro anion for group Va elements but one of about 60 ppm for tantalum and niobium. All the comparisons are listed in Table III. The terminal fluorines appear at higher field than equatorial fluorines which are at higher field than the bridging fluorine in the homopolyfluoro anions of arsenic and antimony. Exactly the reverse trend is found for the compounds of tantalum and niobium. In fact the bridging fluorines in the polyfluoro anions of these elements are found at remarkably high field in comparison with the chemical shifts of the other fluorines bonded to niobium and tantalum. The spin-coupling constants are also in the opposite order between the Va and Vb homopolyfluoro anions. J_{1-2} is greater than J_{2-3} while J_{1-3} is zero for the Va compounds while J_{1-3} is largest in the Vb compounds.

On a more subtle level one can consider the effect of the second central atom (N) on the chemical shifts of the terminal and equatorial fluorines bonded to M. In the adduct of NbF_5 and SbF_5 it has been shown that the bridging fluorine is more strongly attracted to antimony.[10] If one assumes the same behavior in $NbSbF_{11}^-$ one can say that a more strongly fluorine-attracting element shifts the equatorial and terminal fluorines on niobium to lower magnetic field, by about 10 ppm, than in the homopolyfluoro anion. A similar shift, but of only 5 ppm, is found for the fluorines on niobium when tantalum is the other central atom. The chemical shift changes for the fluorines on tantalum are also consistent with this hypothesis. The equatorial and terminal fluorines on tantalum appear at higher field with more weakly fluorine-attracting niobium as the other central atom compared with the homopolyfluoro anion. On the other hand, these fluorines are shifted to lower field when the strongly fluorine-attracting antimony is the other central atom.

Registry No. TaF_5, 7783-71-3; $(TBA)TaF_6$, 37534-33-1;

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(9) P. A. W. Dean and R. J. Gillespie, *Can. J. Chem.*, 49, 1736 (1971).

(10) A. J. Edwards, *Chem. Commun.*, 820 (1970).

Table III. Average Fluorine Chemical Shifts and Spin-Coupling Constants of Group V Fluoride Species[a]

Element	$\delta(MF_5)$	$\delta(MF_6^-)$	$\Delta\delta$	MNF_{11}^-					
				δ_1	δ_2	δ_3	J_{1-2}	J_{1-3}	J_{2-3}
P	65.8^5	71.0^5	5.2						
As	57.0^5	61.7^5	4.7	89^5	56^5	21.1^4	127^5	0^5	49^5
Sb	106.7^3	117.9^3	11.2	143^5	115^5	92^3	96^5	0^5	57^5
Nb	−162	−104	58	−192	−147	56	41	179	41
Ta	−99.6	−40.4	59.2	−116	−73	81	23	171	43

[a] δ values in ppm; J values in Hz.

$(TBA)Ta_2F_{11}$, 37534-34-2; NbF_5, 7783-68-8; $(TBA)NbF_6$, 37477-93-3; $(TBA)Nb_2F_{11}$, 37477-94-4; $(TBA)TaNbF_{11}$, 37534-35-3; $(TBA)TaSbF_{11}$, 37477-95-5; $(TBA)NbSbF_{11}$, 37477-96-6; $(TBA)TaAsF_{11}$, 37477-97-7.

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Contribution from the Inorganic Chemistry Laboratory,
University of Amsterdam, Amsterdam, The Netherlands

Semiempirical Molecular Orbital Calculation of Symmetrical Trihalide Ions

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The $\sigma_u^* \leftarrow \sigma_g$ electronic transitions of symmetrical trihalide ions (I_3^-, IBr_2^-, ICl_2^-, Br_3^-, and $BrCl_2^-$) are calculated in a molecular orbital approximation. The MO's are formed from linear combinations of $np\sigma$ halogen orbitals. For the zero-order calculations a modified Huckel theory is used. The calculations of the electronic transitions in the σ system are refined by configuration interaction with complete neglect of differential overlap. The parameters β for the σ bonds are based on the experimental electronic transitions of Br_2, Cl_2, and I_2. The method is applied to one transition of the I_3^- ion (4.25 eV) in order to obtain an equation for β. The agreement between the calculated values and the experimentally observed transitions appears to be a good one. A table of calculated charges and bond orders is also presented.

Introduction

For trihalide ions the bonding scheme of Pimentel[1] is generally accepted.[2-7] The bonds are formed from overlap of the $np\sigma$ orbitals of the constituting atoms (Figure 1). Molecular orbitals for the σ system can be formed from linear combinations of these $np\sigma$ halogen orbitals

$$\phi_i = \sum_\mu c_{\mu i}\chi_\mu \quad (\phi_i, \phi_j\text{: MO}; \ \chi_\mu, \chi_\nu\text{: AO})$$

Three MO's result from this combination, two of which are doubly occupied. In a Huckel-type calculation these orbitals are bonding and formally nonbonding, respectively (Figure 2). The p_X and p_Y orbitals of all atoms are each occupied by two electrons. The ns orbitals at each atom, which are much lower in energy than the np orbitals,[1,6] are also occupied by two electrons. In this way the total of valence electrons is 22. The only empty orbital is an antibonding one and has the σ_u symmetry (Figure 2). The p_X and p_Y orbitals are regarded as nonbonding, although in practice there will be a splitting in slightly bonding, nonbonding, and slightly antibonding orbitals, due to some interaction. The total energy of the σ electrons in a Huckel-type calculation is

$$E_{\text{tot}} = 2\sum_i^{\text{occ}}\sum_\mu\sum_\nu c_{\mu i}{}^* c_{\nu i} \int \chi_\mu{}^*(1)\hat{H}_{\text{eff}}(1)\chi_\nu(1)\,d\tau = \sum_\mu P_{\mu\mu}H_{\mu\mu} + 2\sum_{\mu>\nu} P_{\mu\nu}H_{\mu\nu} \qquad (1)$$

in which Σ_i^{occ} denotes the summation over the occupied molecular orbitals, $P_{\mu\nu} = 2\Sigma_i c_{\mu i}{}^* c_{\nu i}$ is the bond order, and H_{eff} is the one-electron Huckel Hamiltonian operator.

Wiebenga and Kracht[4] replaced the term $\Sigma_\mu P_{\mu\mu}H_{\mu\mu}$ by $\Sigma_A E_A + \Sigma_{A>B} Q_A Q_B/R_{AB}$, in which $\Sigma_A E_A$ denotes the self-energy of the atoms in the trihalide ions ($\Sigma_A E_A$ is a summation over the atoms) and $\Sigma_{A>B} Q_A Q_B/R_{AB}$ denotes the Coulomb repulsions between the net charges on the atoms; Q_A is the net charge on atom A and R_{AB} is the intraionic distance between atoms A and B in the trihalide ion.

E_A can be deduced from the ionization potential (I_A) and the electron affinity (A_A) of atom A. The ion A^- has the energy $-A_A$, A^+ has the energy $+I_A$, and the neutral atom has the energy zero. Between these values the energy can be approximated by a parabolic function (Figure 3).[4] In order to get the zero-order MO's, the total energy, modified in this way, must be minimized. In the present case, with only one basis function per atom, and neglecting differential overlap, the matrix elements that occur are

$$\begin{aligned} F_{\mu\mu} &= -{}^1\!/_2(I_A + A_A) - (I_A - A_A)Q_A - \sum_{B \neq A}\frac{Q_B}{R_{AB}} \quad \mu \in A \\ F_{\mu\nu} &= H_{\mu\nu} = \beta \end{aligned} \qquad (2)$$

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