

¹⁹F NMR STUDY OF MIXED FLUOROHALIDE ANIONS OF NIOBIUM(V) AND TANTALUM(V) IN SOLUTION

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Summary

Anions of the type $MF_nX_{6-n}^-$ ($M = Nb^V, Ta^V$; $X = Cl^-, Br^-$), including geometric isomers, have been characterised in solution by ¹⁹F NMR spectroscopy. Thirty eight fluorine-containing complexes of tantalum of the type $TaF_xCl_yBr_z^-$ have been found from the 46 theoretically possible. The relative stability of mixed tantalum fluorochloro and fluorobromo anions of the type $TaF_nX_{6-n}^-$ has been studied.

Introduction

Nuclear magnetic resonance spectroscopy has been used previously in the study of fluorine-containing niobium and tantalum complexes in solutions [1 - 6].

Mixed fluorohalides, MF_nCl_{5-n} , of these elements were obtained by melting the pentafluoride and pentachloride and were studied by using ¹⁹F NMR spectroscopy in the solid or molten states [7]. Two resonances were observed in the spectra arising from $TaCl_2F_3$ and $TaCl_{1.7}F_{3.3}$ melts. The line which appears in the high-field part of the spectrum ($\delta = 190$ ppm relative to CF_3COOH) has been assigned to the terminal fluorines while the other line ($\delta = 20$ ppm) has been assigned to the bridge atoms. Only one signal was found in the spectra of the corresponding niobium compounds in the molten state.

Only recently has any information appeared in the literature concerning the preparation of mixed fluorohalide anions of niobium and tantalum [8,9].

We have prepared fluorochloro- and fluorobromo-niobium and -tantalum anions by the reaction of the corresponding pentahalides with anhydrous HF in CH_3CN .

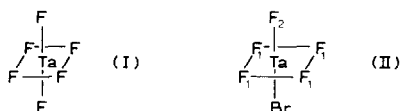
Experimental

¹⁹F NMR spectra were recorded by means of a Varian 56/60A spectrometer. ⁹³Nb NMR spectra were obtained using a broad-line spectrometer (6 MHz

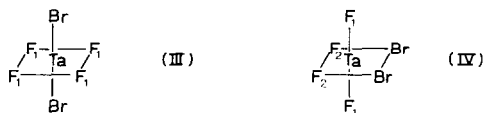
with audio-phase-sensitive detection, the resonances being recorded as the derivative of the dispersion of absorption mode. NbCl_5 , TaCl_5 , NbBr_5 were purified by sublimation. Acetonitrile was dried over P_2O_5 and distilled.

Results and discussion

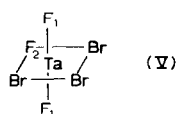
The NMR data obtained for tantalum fluorohalide complexes are recorded in Table 1. Eleven resonances were observed in the spectrum of a $\text{TaBr}_5 \cdot 3\text{HF}$ solution in CH_3CN . The signal in the highest-field part of the spectrum at 389 ppm has been assigned to the anion TaF_6^- (I) since this resonance has been observed previously [3]. A doublet and quintet in the spectrum may be attributed to a tantalum complex containing four equivalent fluorine atoms, F_1 , in the equatorial plane and one, F_2 , in a position *trans* to the bromine atom as in structure (II).



An intense sharp signal at 331.6 ppm is due to the presence of *trans*- $\text{TaF}_4\text{Br}_2^-$ (III) while two identical triplets may be attributed to *cis*- $\text{TaF}_4\text{Br}_2^-$ (IV), in which the fluorine atoms F_1 are *trans* to each other with two further fluorine atoms F_2 being *trans* to the bromine atoms, these latter fluorine atoms giving rise to a triplet at higher field strength.



The presence of a doublet and triplet with intensities in the ratio 2:1 may be accounted for by the formation of the complex *trans*- $\text{TaF}_3\text{Br}_3^-$ (V) in the solution.



The resonance corresponding to the F_2 atoms in the spectra of TaF_5Br^- , *cis*- $\text{TaF}_4\text{Br}_2^-$ and *trans*- $\text{TaF}_3\text{Br}_3^-$ all occur at a higher field than those assigned to the F_1 atoms. The difference between the chemical shifts for these two types of fluorine atom, *i.e.* $\delta(\text{F}_2) - \delta(\text{F}_1)$, increases as the number of bromine atoms in the anions increases. At the same time, the signals due to the F_1 atoms shift almost linearly to a lower field (by approximately 25 ppm) as the number of bromine atoms increases. From these observations the singlet at the lowest field strength was assigned to the anion *trans*- $\text{TaF}_2\text{Br}_4^-$ (VI), in which the fluorine atoms are *trans* to each other with all the equatorial positions occupied by bromine atoms. The signal occurring at a higher field

TABLE 1

NMR data for tantalum fluorohalide complexes

Complex	Assignments ^a	Chemical shift ^b /ppm	Complex	Assignments ^a	Chemical shift ^b /ppm
TaF ₆ ⁻	(I) F ₁	389.0	<i>trans</i> -TaF ₂ Cl ₃ Br ⁻	(XVI) F ₁	300.2
TaF ₅ Cl ⁻	F ₁	366.2	<i>trans</i> -TaF ₂ Br ₄ ⁻	(VI) F ₁	287.3
	F ₂	376.4	<i>trans</i> -TaF ₂ ClBr ₃ ⁻	(XVII) F ₁	291.3
TaF ₅ Br ⁻	(II) F ₁	359.2	<i>trans</i> -TaF ₂ Cl ₂ Br ₂ ⁻	(XVIII) F ₁	295.6
	F ₂	372.7	<i>trans</i> -TaF ₂ Cl ₂ Br ₂ ⁻	(XIX) F ₁	295.6
<i>trans</i> -TaF ₄ Cl ₂ ⁻	F ₁	343.6	<i>cis</i> -TaF ₂ Cl ₃ Br ⁻	(XX) F ₂	321.0
<i>trans</i> -TaF ₄ ClBr ⁻	(X) F ₁	337.5	<i>cis</i> -TaF ₂ Cl ₄ ⁻	F ₂	324.1
<i>cis</i> -TaF ₄ Cl ₂ ⁻	F ₁	343.6	<i>cis</i> -TaF ₂ Cl ₂ Br ₂ ⁻	(XXI) F ₂	317.8
	F ₂	356.9	<i>cis</i> -TaF ₂ Br ₄ ⁻	(VIII) F ₂	319.0
<i>trans</i> -TaF ₄ Br ₂ ⁻	(III) F ₁	331.6	<i>cis</i> -TaF ₂ ClBr ₃ ⁻	(XXII) F ₂	321.6
<i>cis</i> -TaF ₄ ClBr ⁻	(XI) F ₁	337.0	<i>cis</i> -TaF ₂ Cl ₂ Br ₂ ⁻	(XXIII) F ₂	324.0
	F ₂	350.0	TaFCl ₅ ⁻	F ₂	310.5
<i>cis</i> -TaF ₄ Br ₂ ⁻	(IV) F ₁	331.2	TaFCl ₄ Br ⁻	(XXIV) F ₂	307.8
	F ₂	351.3	TaFCl ₃ Br ₂ ⁻	(XXV) F ₂	305.3
<i>trans</i> -TaF ₃ Cl ₃ ⁻	F ₁	323.0	TaFCl ₃ Br ₂ ⁻	(XXVI) F ₂	305.3
	F ₂	340.0	TaFCl ₂ Br ₃ ⁻	(XXVII) F ₂	303.0
<i>trans</i> -TaF ₃ Cl ₂ Br ⁻	(XII) F ₁	317.8	TaFClBr ₄ ⁻	(XXVIII) F ₂	300.9
	F ₂	337.4	TaFClBr ₄ ⁻	(XXIX) F ₂	308.8
<i>trans</i> -TaF ₃ Cl ₂ Br ⁻	(XIII) F ₁	317.7	TaFBr ₅ ⁻	(VII) F ₂	306.8
TaF ₃ ClBr ₂ ⁻	(XIV) F ₁	312.1	TaFCl ₂ Br ₃ ⁻	(XXX) F ₂	310.9
TaF ₃ ClBr ₂ ⁻	(XV) F ₁	312.0	TaFCl ₂ Br ₃ ⁻	(XXXI) F ₂	310.9
<i>trans</i> -TaF ₃ Br ₃ ⁻	(V) F ₁	307.0			
	F ₂	336.7			
<i>cis</i> -TaF ₃ Cl ₃ ⁻	(IX) F ₂	339.1			
<i>trans</i> -TaF ₂ Cl ₄ ⁻	F ₁	304.8			

^a F₁ *trans* to F, F₂ *trans* to Cl, Br.^b δ (F₂) = 0.

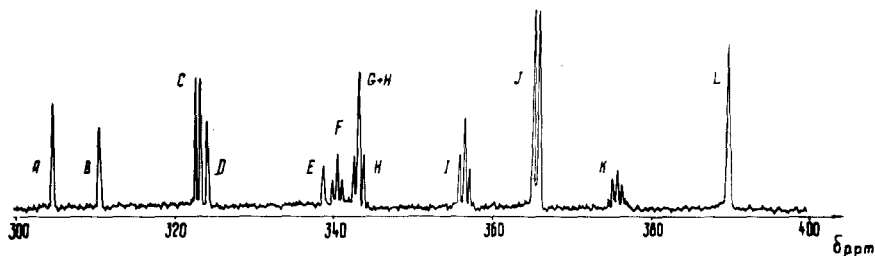
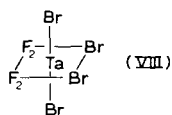
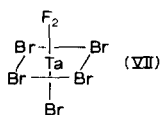
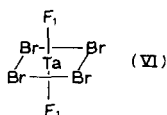
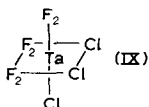


Fig. 1. The fluorine resonance spectrum of TaF_nCl_{6-n} anions at $-30^\circ C$: A, *trans*- $TaF_2Cl_4^-$; B, $TaFCl_5^-$; C, F_1 -*trans*- $TaF_3Cl_3^-$; D, *cis*- $TaF_2Cl_4^-$; E, *cis*- $TaF_3Cl_3^-$; F, F_2 -*trans*- $TaF_3Cl_3^-$; G, *trans*- $TaF_4Cl_2^-$; H, F_1 -*cis*- $TaF_4Cl_2^-$; I, F_2 -*cis*- $TaF_4Cl_2^-$; J, F_1 - TaF_5Cl^- ; K, F_2 - TaF_5Cl^- ; L, TaF_6^- .

arises from the anion $TaFBr_5^-$ (VII). The shift of this resonance with respect to that of *trans*- $TaF_2Cl_4^-$ may possibly be due to the *trans* influence of bromine. The singlet at 319 ppm has been assigned to the complex *cis*- $TaF_2Br_4^-$ (VIII).



The composition and structure of the fluorochloro anions studied are both similar to the corresponding fluorobromo anions (I) - (VIII). The ^{19}F NMR spectrum of a $TaCl_5 : 3HF$ solution in acetonitrile is shown in Fig. 1. In addition to the signals already discussed, the spectrum also contains a relatively broad signal near the F_2 resonance which has already been assigned to the anion *trans*- $TaF_3Cl_3^-$. This additional signal has been attributed to the complex *cis*- $TaF_3Cl_3^-$ (IX) in which all the fluorine atoms are in *trans* positions to chlorine.



This anion has not been observed in the case of fluorobromo anions and its signal only arises in $TaCl_5 : 3HF$ solutions where formation of complexes of the type $MF_3Cl_3^-$ is more probable.

It is of interest to point out that the spin-spin coupling constant $J(FF)$ in tantalum fluorobromo and fluorochloro complexes has a value of 36 Hz which remains unchanged as the number of fluorine atoms in the complex is changed.

The formation of both *cis* and *trans* isomers has been observed for all anions NbF_nCl_{6-n} of type (I) - (VIII), with the exception of *cis*- $NbF_3Cl_3^-$. Failure to observe a resonance corresponding to *cis*- $NbF_3Cl_3^-$, as well as one corresponding to *cis*- $TaF_3Br_3^-$, may be due either to the low stability of these anions resulting from the *trans* influence of chlorine and bromine, or to the strong polarity of the *cis* complexes. The NMR data obtained for niobium fluorohalide complexes are recorded in Table 2.

TABLE 2

NMR data for niobium fluorohalide complexes

Complex	Assignments ^a	Chemical shift ^b /ppm
NbF_6^-	F ₁	325.5
NbF_5Cl^-	F ₁	299.5
	F ₂	313.3
<i>trans</i> - $\text{NbF}_4\text{Cl}_2^-$	F ₁	277.5
<i>cis</i> - $\text{NbF}_4\text{Cl}_2^-$	F ₁	275.0
	F ₂	296.2
<i>trans</i> - $\text{NbF}_3\text{Cl}_3^-$	F ₁	254.7
	F ₂	285.0
<i>trans</i> - $\text{NbF}_2\text{Cl}_4^-$	F ₁	236.0
<i>cis</i> - $\text{NbF}_2\text{Cl}_4^-$	F ₂	268.0
NbFCl_5^-	F ₂	257.5
NbF_5Br^-	F ₁	292.0
	F ₂	309.5
<i>trans</i> - $\text{NbF}_4\text{Br}_2^-$	F ₁	269.0
<i>cis</i> - $\text{NbF}_4\text{Br}_2^-$	F ₁	268.0
	F ₂	230.0
<i>trans</i> - $\text{NbF}_2\text{Br}_4^-$	F ₁	222.0

^a F₁ *trans* to F, F₂ *trans* to Cl, Br. ^b $\delta(\text{F}_2) = 0$.

The relative amounts of fluorochloro and fluorobromo complexes of niobium and tantalum have been measured at different $\text{TaF}_5:\text{HF}$ ratios in solution. In many cases the value of the ratio calculated from the NMR spectra appeared to be higher than that of the prepared specimens, and on this basis it is possible that niobium and tantalum complexes which contain no fluorine atoms in the inner sphere are present in the solution. In order to confirm this suggestion, solutions of the fluorochloro complexes of niobium and a solution of NbCl_5 in CH_3CN have been studied by the use of ^{93}Nb NMR spectroscopy. The spectra of solutions of niobium fluorochloro anions contain a line at 1450 ppm [$\delta(\text{NbF}_6^-) = 0$] which has previously been assigned to the anion NbCl_6^- . The latter was also found in the spectrum of NbCl_5 solutions in CH_3CN [10].

Signals corresponding to the following anions were observed in the spectrum of the $\text{NbBr}_5:3\text{HF}$ solution: NbF_5Br^- , *trans*- $\text{NbF}_4\text{Br}_2^-$, *cis*- $\text{NbF}_4\text{Br}_2^-$ and *trans*- $\text{NbF}_2\text{Br}_4^-$. It was not possible to measure the $J(\text{FF})$ values for niobium fluorobromo complexes.

The resonances of the niobium and tantalum fluorobromo anions as well as those of the fluorochloro anions are shifted linearly to low field as the number of chlorine or bromine atoms in the complexes increases (Fig. 2).

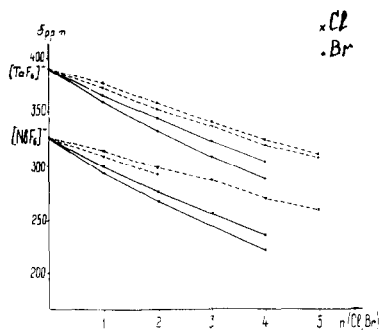
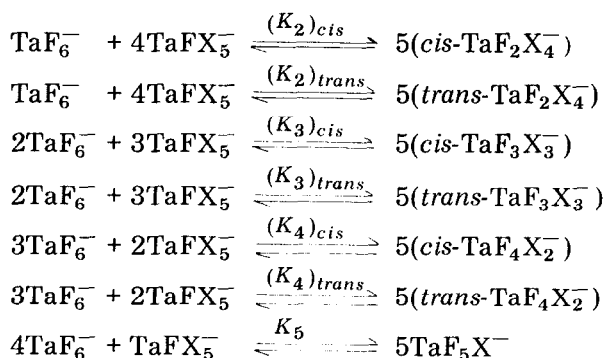


Fig. 2. $\delta(\text{F})$ value of $\text{MF}_n\text{X}_{6-n}^-$ ($\text{M} = \text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}; \text{X} = \text{Cl}^-, \text{Br}^-$) vs. the number of X atoms [— $\delta(\text{F}_1)$; - - - $\delta(\text{F}_2)$].

This indicates that the covalency of the metal-fluorine bond increases which may be accounted for by a decrease in the effective charge on the central atom as a result of the entry of less electronegative ligands (Cl or Br) into the inner sphere of the complex. In all niobium and tantalum fluorochloro and fluorobromo complexes the central atom has a coordination number of 6 with the ligands arranged in an octahedral manner.

Since the chemical shifts of the transition metal fluorides (Groups IVA, VA and VIA) lie at considerably lower field values in comparison to the signals of fluorides of the corresponding B subgroups, it has been suggested that transition metals form metal-fluorine π -bonds [11,12]. Comparison of the chemical shifts for niobium and tantalum complexes of similar composition shows that the signals of the tantalum complexes lie towards higher field values by approximately 65 ppm. If account is taken of the fact that for similar elements such as niobium and tantalum the chemical shift values for species of the same composition and structure reflect changes in the nature of the metal-fluorine bond, it appears that fluorine-niobium bonds are more covalent than the corresponding fluorine-tantalum bonds. This suggestion is supported by the higher value for $J(\text{FF})$ of 54 Hz for niobium fluorochloro anions in comparison with a value of $J(\text{FF})$ of 36 Hz for tantalum fluorochloro complexes.

The formation of mixed fluorohalide complexes may be expressed by the following equilibria:



For the general case

$$K_n = \frac{[\text{TaF}_n\text{X}_{6-n}]^5}{[\text{TaF}_6]^{n-1} [\text{TaFX}_5]^{5-n+1}}$$

The random redistribution theory of Calingaert and Beatty [13] has been used to determine the expected redistribution of TaF_6^- with TaFX_5^- . In particular, the $\delta \Delta G_n$ values for the random redistribution of the ligands have been calculated, the difference in free-energy changes $\delta \Delta G_n = \Delta G_{\text{exp.}} - \Delta G_{\text{random}}$ being taken as a measure of the deviation of a particular redistribution from randomness. A similar calculation has been reported for the fluoro complexes of Si, Ge and Ti [14]. The results obtained for redistribution in the $\text{TaF}_6^- - \text{TaFCl}_5^-$ and $\text{TaF}_6^- - \text{TaFBr}_5^-$ systems are recorded in Table 3.

None of the redistributions is completely random, although the deviations from randomness are quite small in all cases. Positive values of $\delta \Delta G_n$ indicate that mixed complexes are less stable than would be expected from a random redistribution of ligands with fluorochloro anions being more stable than fluorobromo anions. Comparison of the $\delta \Delta G_n$ values for fluorochloro complexes shows that their stability decreases in the series: $\text{trans-TaF}_4\text{Cl}_2^- > \text{trans-TaF}_2\text{Cl}_4^- > \text{TaF}_5\text{Cl}^- > \text{trans-TaF}_3\text{Cl}_3^- > \text{cis-TaF}_4\text{Cl}_2^- > \text{cis-TaF}_2\text{Cl}_4^- > \text{cis-TaF}_3\text{Cl}_3^-$. The order of stability is slightly different for fluorobromo anions with $\text{trans-TaF}_2\text{Br}_4^-$ being the most stable. We may therefore conclude that mixed fluorohalide complexes of tantalum with similar ligands *trans* to each other are more stable. The stability of the complexes decreases with increasing numbers of chlorine or bromine atoms.

It is not unreasonable to assume that complexes of tantalum containing three different types of ligand (fluorine, chlorine and bromine) in the inner sphere could be obtained as a result of halogen exchange between $\text{TaF}_n\text{Cl}_{6-n}^-$ and $\text{TaF}_n\text{Br}_{6-n}^-$. Where three different ligands (fluorine, chlorine and bromine) can co-exist, the formation of 56 octahedral complexes (including geometric isomers) is possible [15], 46 of these complexes containing fluorine [16].

The ^{19}F NMR spectrum of a solution with a $\text{TaF}_n\text{Cl}_{6-n}^- : \text{TaF}_n\text{Br}_{6-n}^-$ ratio near unity exhibits a large number of lines in addition to the signals assigned to the fluorochloro and fluorobromo anions of tantalum. On the basis that the observed chemical shift changes are proportional to the number of chlorine or bromine atoms contained in the complexes (Fig. 3), we have assumed that the existence of a narrow line equidistant from the signals of both $\text{trans-TaF}_4\text{Cl}_2^-$ and $\text{trans-TaF}_4\text{Br}_2^-$ is indicative of the formation of the anion $\text{trans-TaF}_4\text{ClBr}^-$ (X), while the two multiplets which occur in the same place demonstrate the formation of $\text{cis-TaF}_4\text{ClBr}^-$ (XI).

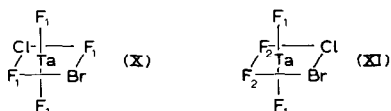


TABLE 3

Equilibrium constants and free-energy changes (in kcal mol⁻¹) for the formation of mixed tantalum fluoroalide complexes

Complex	TaF _n Cl _{6-n} ⁻ⁿ		TaF _n Br _{6-n} ⁻ⁿ				
	log K _{rand.}	ΔG _{rand.}	log K _{exp.}	ΔG _{exp.}	δΔG		
<i>cis</i> -TaF ₂ X ₄ ⁻	2.28	-0.51	-0.52 ± 0.25	0.12	0.63	0.72	1.23
<i>trans</i> -TaF ₂ X ₄ ⁻	-0.725	0.16	-1.15 ± 0.30	0.27	0.11	0.21	0.05
<i>cis</i> -TaF ₃ X ₃ ⁻	2.18	-0.48	-2.39 ± 0.30	0.54	1.02	-	-
<i>trans</i> -TaF ₃ X ₃ ⁻	3.05	-0.69	1.35 ± 0.22	-0.33	0.36	0.09	0.78
<i>cis</i> -TaF ₄ X ₂ ⁻	3.85	-0.86	1.29 ± 0.11	-0.33	0.53	0.27	1.13
<i>trans</i> -TaF ₄ X ₂ ⁻	0.83	-0.19	0.96 ± 0.03	-0.24	-0.05	-0.09	0.10
TaF ₅ X ⁻	3.11	-0.70	2.02 ± 0.02	-0.48	0.22	-0.15	0.55

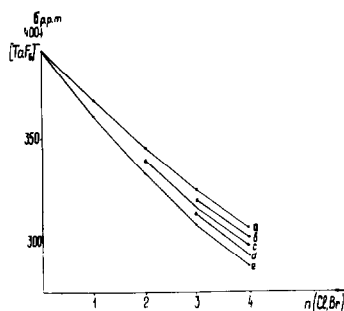
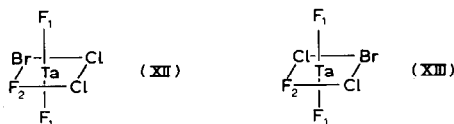
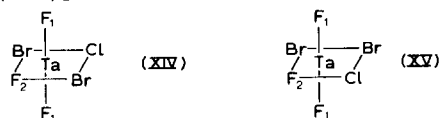


Fig. 3. $\delta(F_1)$ value of $TaF_xCl_yBr_z^-$ vs. the number of chlorine or bromine atoms: a, $TaF_{6-n}Cl_n^-$ ($n = 0 - 4$); b, $TaF_{6-n}Cl_{n-1}Br^-$ ($n = 3, 4$); c, $TaF_{6-n}Cl_{n/2}Br_{n/2}^-$ ($n = 0, 2, 4$); d, $TaF_{6-n}ClBr_{n-1}^-$ ($n = 3, 4$); e, $TaF_{6-n}Br_n^-$.

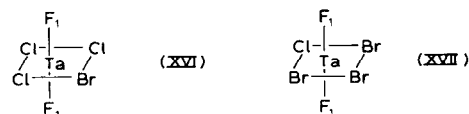
Four doublets of different intensity located between the signals corresponding to $trans-TaF_3Cl_3^-$ and $trans-TaF_3Br_3^-$ provide evidence for the presence of $trans-TaF_3Cl_nBr_{3-n}^-$ anions in the solution. The two signals at 317.7 and 317.8 ppm respectively are associated with the formation of two geometrical isomers of $trans-TaF_3Cl_2Br^-$, [(XII) and (XIII)].



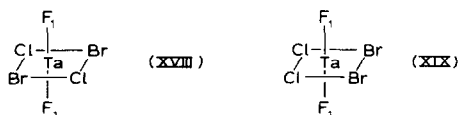
The presence of a more intense doublet and an associated triplet support the formation of isomer (XII), which may be confirmed by the observed difference in the chemical shift values, $\delta(F_2) - \delta(F_1)$. Two doublets at 312 ppm are apparently the result of the formation of isomers of $trans-TaF_3ClBr_2^-$, [(XIV) and (XV)], in solution.



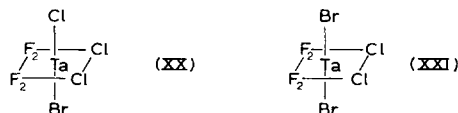
Three narrow lines located equidistant between the signals of $trans-TaF_2Cl_4^-$ and $trans-TaF_2Br_4^-$ are due to the presence of $trans-TaF_2Cl_nBr_{4-n}^-$ complexes. The complexes $trans-TaF_2Cl_3Br^-$ (XVI) and $trans-TaF_2ClBr_3^-$ (XVII) can exist in only one form.



The $trans-TaF_2Cl_2Br_2^-$ anion can exist as the two geometrical isomers (XVIII) and (XIX).

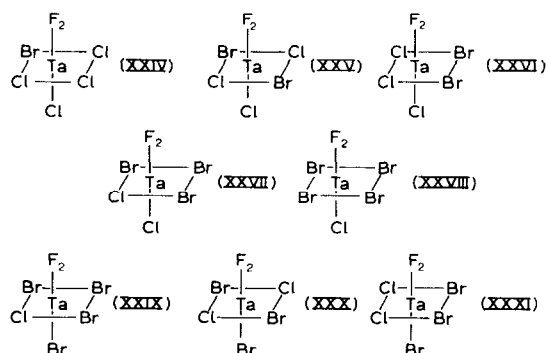


Two singlets at a lower field with respect to that of *cis*-TaF₂Cl₄⁻ are attributed to the anions *cis*-TaF₂Cl₃Br⁻ (XX) and *cis*-TaF₂Cl₂Br₂⁻ (XXI).



Two further singlets near the signal of *cis*-TaF₂Br₄⁻ at 321.6 and 324.0 ppm respectively have been taken to indicate the formation of the anions *cis*-TaF₂Br₃Cl⁻ (XXII) and *cis*-TaF₂Br₂Cl₂⁻ (XXIII), while four lines equidistant with respect to the signal of TaFCl₅⁻ at a lower field were assigned to the complexes TaFCl_nBr_{5-n}⁻ [(XXIV)-(XXVIII)] in which chlorine is *trans* to fluorine. The complex TaFCl₃Br₂⁻ may exist as two isomers in solution, i.e. (XXV) and (XXVI).

Two resonances at a higher field relative to that of TaFBr₅⁻ have been assigned to TaFBr₄Cl⁻ (XXIX) and TaFBr₃Cl₂⁻, [(XXX) and (XXXI)] in which a fluorine is *trans* to the bromine.



Hence 38 tantalum complexes have been found in solution, including seven fluorochloro anions, out of the 46 which are theoretically possible. It should however be pointed out that we have failed to observe the formation of tantalum complexes containing fluorine atoms *trans* to a chlorine or bromine atom when fluorine atoms of type F₁ are not present in the complex.

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