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^{19}F NMR Study of Ruthenium(IV) and Osmium(IV) Fluoronitrosyl Complexes

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A ^{19}F NMR study of aqueous solutions of pentafluoro-, aquafluoro- and halogenofluoro (Cl, Br, I) nitrosylruthenates(IV) and nitrosylosmates(IV) has been reported. Fluoroligand in a trans *position to the NO-group has been shown to be inert in substitution reactions, thus they occur in the equatorial plane of $MNOF_5^{2-}$ anions. The ratio of concentrations of isomers* cis/trans-*$MNOF_a(F_e)_2X_2^{2-}$ appears to be dependent upon the nature of the ligand X and decreases from X = Cl to X = I. This tendency has been explained on the basis of ^{19}F chemical shift analysis in terms of strengthening of the F_e–M–F_e ordinate and weakening of F_e–M–X.*

Introduction

There is a great number of nitrosyl complexes of ruthenium(IV) and osmium(IV) with a very stable linear MNO moiety. Nitrosyl groups in these compounds are extremely efficient π-acceptors and weak σ-donor ligands, and according to ESCA data they possess an effective negative charge [1]. It has been found that the NO group in nitrosyl-ruthenium complexes has a very strong labilizing effect on the group in the *trans* position. As the Ru–X stretching vibration for the group *trans* to the NO in $[RuNOX_5]^{2-}$ (X = Cl, Br, I) occurred at a frequency 30–40 cm^{-1} lower than the corresponding group in the *cis* position, Durig *et al.* [2, 3] have concluded that a bond-weakening mechanism is important in the labilizing influence of nitrosyl. However, Veal and Hodgson [4, 5] on the basis of MO calculations for $Mn(CO)_5X$ (X = Cl, Br, I) [6] have suggested that the M–X bond *trans* to nitrosyl would be stronger and shorter than M–X_{cis}. This suggestion has been confirmed by the MO calculation of σ and π bond order of Ru–X_{cis} and Ru–X_{trans} in $[RuNOX_5]^n$ [7], as well as by X-ray data for $[RuNO(NH_3)_5]Cl_3$ [8] and $E_2[RuNOCl_5]$ (E = NH_4^+ [4], K^+ [5]) according to which the distance Ru–X_{trans} is 0.08 Å and 0.02 Å less than Ru–X_{cis} in the case of X = NH_3 and X = Cl, respectively. One can propose therefore that the greater lability of the group *trans* to NO is caused not by ground state but rather by a transitional state of activated complex.

Recently there have been reports on the preparation and i.r. spectra of potassium pentafluoronitrosylruthenate [9] and nitrosylosmate [10]. Our paper is devoted on the ^{19}F NMR study of aqueous solutions of pentafluoro-, aquafluoro- and halogenofluoro-nitrosylruthenates(IV) and -nitrosylosmates(IV) to find out the stereochemical features of the substitution reactions and to determine, in particular, whether the advanced lability of the axial fluoro-ligand is developing as has been shown for other halogens *trans* with respect to the NO group. Besides, it was interesting to estimate the tendencies of changes in ^{19}F chemical shifts of fluorocomplexes with d^4 electron configuration of the central atom when decreasing the symmetry of the coordination sphere from O_h for hexafluorides (RuF_6^{2-}, OsF_6^{2-} [11]; PtF_6 [12]; IrF_6^- [13]) to C_{4v} in the case of complexes $[MNOX_5]^n$ with multiply bound nitrosyl groups.

Experimental

The ^{19}F NMR spectra (75.39 MHz) of aqueous solutions of ruthenium(IV) and osmium(IV) fluoro-

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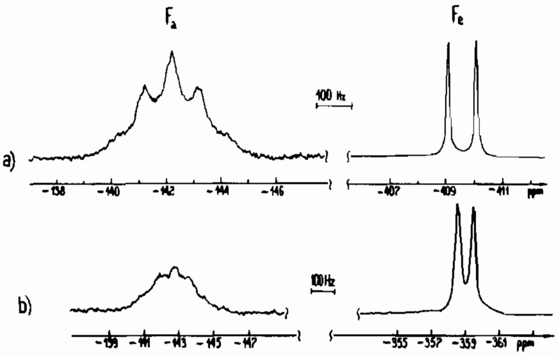


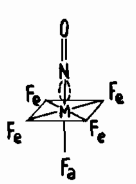
Fig. 1. ^{19}F NMR spectra (75.39 MHz) for saturated solutions of $K_2[RuNOF_5]\cdot 2H_2O$ (a) and $K_2[OsNOF_5]\cdot 2H_2O$ (b) at 10 °C (a) and 0 °C (b).

nitrosyl complexes in the temperature range 0–35 °C were recorded on a pulse radiospectrometer Bruker WP-80 with internal deuterium lock using an 'Aspect-2000' computer. Chemical shifts were measured with respect to the external standard $CFCl_3$. Negative values denote the upfield shifts.

The synthesis of fluorohalogenonitrosyl complexes of Ru(IV) and Os(IV) was carried out using the procedure of fusion of the corresponding pentahalogenonitrosyl complexes with potassium bifluoride. The 1:3 mol mixture of $E_2[MNOX_5]$ ($E = K^+, Na^+, Rb^+, Cs^+$; M = Ru, Os; $X = Cl^-, Br^-, I^-$) with KHF_2 was placed into a platinum crucible and kept at 360 °C for about 30 min in the case of ruthenium compounds, or for ~1 hr when preparing fluorohalogenonitrosylosmates. NMR samples were prepared by dissolving the melts after cooling in D_2O.

Results and Discussion

In the ^{19}F NMR spectrum of saturated solution of $K_2[RuNOF_5]\cdot 2H_2O$ in D_2O at 30 °C (Fig. 1) a quintet at −142.2 ppm and a doublet at −409.5 ppm ($^2J_{F-F} = 73.3 \pm 1$ Hz) are observed with the ratio of intensities 1:4. The analogous ^{19}F NMR spectrum is also produced by saturated aqueous solution of potassium pentafluoronitrosylosmate $K_2[OsNOF_5]\cdot 2H_2O$ (Fig. 1b) *viz.*, the quintet at −142.8 ppm and the doublet with a chemical shift of −359.1 ppm ($^2J_{F-F} = 68.3 \pm 1$ Hz). By its appearance, the spectra indicate that the anion I with C_{4v} symmetry dominates in the solution.


I

After the initial solution of $K_2[RuNOF_5]\cdot 2H_2O$ being kept at 70 °C for ~30 min, besides the main resonances from the $[RuNOF_5]^{2-}$ anion, a single line at −124.0 ppm was discovered in the ^{19}F NMR spectra, (assigned to fluoride ions), as well as multiplet signals at −148.1 ppm (triplet) and −409.9 ppm (doublet) with $^2J_{F-F} = 79 \pm 1$ Hz. The triplet/doublet intensity ratio was 1:2. It may be concluded that due to the heating there is a displacement of fluoride ions from the equatorial plane of $[RuNOF_5]^{2-}$, resulting in the complex $[RuNOF_a(F_e)_2(H_2O)_2]$; a relative content of the latter does not exceed 10%. It should be noted that heating of the pentafluoronitrosylosmate solution under the same conditions does not produce the aquafluoro-species, which agrees with a higher resistance of osmium nitrosyl complexes to hydrolysis compared with the similar ruthenium nitrosyl compounds [14]. One of the evidences indicating the participation of water molecules (but not hydroxyl ions) in the formation of coordination sphere is the fact of observation of the fluoride ion line in the spectra whereas a proton H^+ resulting from entering OH-groups will apparently bind F^- into HF which will lead the ^{19}F resonance to be detected in higher fields. Indeed, when introducing small amounts of various acids into the initial aqueous solutions of $K_2[RuNOF_5]$, a signal in the range of chemical shifts −163.7–−167.3 ppm is detected which indicates the presence of HF in the solutions.

If acidified solutions ($HClO_4$; HCl; H_2SO_4; $H_2C_2O_4$) of $K_2[RuNOF_5]$ are kept for 30 min at 70 °C or for 24 hr at room temperature, their colour transforms from violet to orange. More prolonged heating is needed in the case of systems containing osmium fluoronitrosyl complexes. In the ^{19}F NMR spectra of the prepared solutions a set of signals independent on the acid used is observed, with identical chemical shifts and F–F coupling constants, indicative of the formation of aquafluorocomplexes of RuNO(III) and OsNO(III) resulting from the interaction of $[MNOF_5]^{2-}$ with acids. As an example, the ^{19}F NMR spectrum of the orange solution of $K_2[RuNOF_5]$ in 40% $HClO_4$ is shown in Fig. 2. The compositions and ^{19}F NMR parameters of the ruthenium and osmium aquafluoronitrosyl complexes formed in these systems are given in Table I. The assignment of the observed resonance lines was carried out by the type of their multiplicity, considering also the trends of changes in F–F coupling constants and chemical shifts upon variation in the number of fluoroligands and their location in the coordination sphere.

The data obtained allow us to conclude that there is a substitution of fluoroligands by water molecules

TABLE I. Composition and ^{19}F NMR Parameters of Aquafluoro-nitrosylruthenates(IV) and -nitrosylosmates(IV).

	Complex	Chemical shifts, ppm			$^{2}J_{F-F}$, Hz ± 1		
		M/F	Ru	Os	M/F–F	Ru	Os
I	$[MNOF_a(F_e)_4]^{2-}$	F_a	–142.7*	–145.0*	F_a–F_e	73.7	68.3
		F_e	–410.0*	–360.7*	$^{t}_{e}$		
II	$[MNOF_a(F_e)_3(H_2O)]^-$	F_a	–147.4	–147.9	F_a–F_e^t	75.0	72.5
		F_e^c	–392.3	–344.3	F_a–F_e^c	74.2	70.6
		F_e^t	–410.8	–366.0	F_e^c–F_e^t	7.3	9.5
III	*cis*-$[MNOF_a(F_e)_2(H_2O)_2]$	F_a	–151.9	–152.0	F_a–F_e^c	78.0	74.4
		F_e^c	–396.1	–350.0			
IV	*trans*-$[MNOF_a(F_e)_2(H_2O)_2]$	F_a	–151.9	–152.0	F_a–F_e^t	78.5	73.3
		F_e^t	–412.5	–371.3			
V	$[MNOF_aF_e(H_2O)_3]^+$	F_a	–156.6	–156.2	F_a–F_e^c	82.0	74.4
		F_e^c	–400.8	–356.1			
VI	$[MNOF_a(H_2O)_4]^{2+}$	F_a	–162.8	–			

[a] At these values of chemical shifts F_a and F_e resonances of $[MNOF_5]^{2-}$ are detected in the spectra of highly acidified solutions.

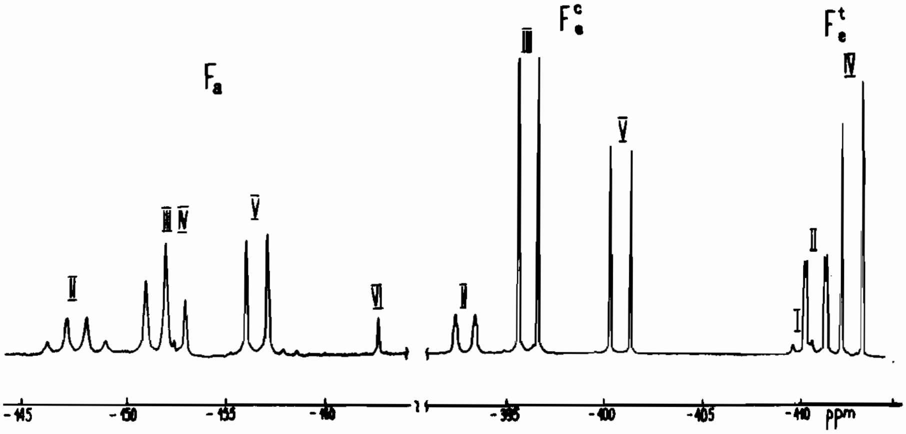
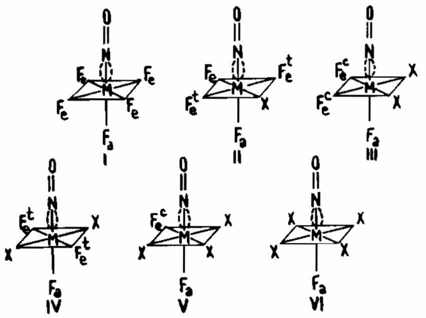


Fig. 2. ^{19}F NMR spectrum (75.39 MHz) for $K_2[RuNOF_5]\cdot 2H_2O$ solution is concentrated (~40%) $HClO_4$ at 10 °C.

taking place in the equatorial plane of $[MNOF_5]^{2-}$ anion upon interaction of the latter with acids in aqueous solutions. All of the six possible fluorocomplexes (I–VI) with the ON–M–F_a ordinate were detected in the solutions. Apparently, the fluoroligand in *trans* position to the NO group is quite firmly bound so it is replaced last, thus differing considerably from other halogenoligands lying on the ON–M–X ordinate and exhibiting an advanced lability in the substitution reactions.



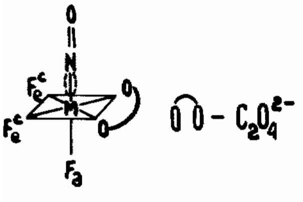
In the ^{19}F NMR spectra of $K_2[RuNOF_5]\cdot 2H_2O$ solutions in concentrated nitric acid, besides the resonances from fluoroligands of the I–VI species, a number of singlets at –170.8; –176.4; –177.6 and –184.3 ppm were also found. A nitrate ion apparently enters into the ruthenium coordination sphere and the signals observed are due to the F_a of $[RuNOF_a(H_2O)_{4-n}(NO_3)_n]^{3-n}$ complexes. By the ^{19}F spectra of H_2SO_4 acidified solutions of $K_2[RuNOF_5]\cdot 2H_2O$, it may be concluded that a sulfate ion is

TABLE II. Composition and ^{19}F NMR Parameters of Fluorohalogeno- and Fluoroaquahalogenonitrosylruthenates(IV).

	Complex	Chemical shifts, ppm				$^2J_{F-F}$, Hz ± 1			
		X/F	Cl	Br	I	X/F–F	Cl	Br	I
I	$[RuNOF_a(F_e)_4]^{2-}$	F_a	–143.2	–143.7	–142.3	F_a–F_e	73.6	74.0	74.0
		F_e	–411.1	–410.0	–408.5				
II	$[RuNOF_a(F_e)_3X]^{2-}$	F_a	–153.3	–155.6	–149.7	F_a–F_e^t	82.2	80.2	78.0
		F_e^c	–351.0	–335.4	–348.2	F_a–F_e^c	83.6	84.7	84.0
		F_e^t	–411.1	–413.5	–408.8	F_e^c–F_e^t	11.5	15.0	11.5
III	*cis*-$[RuNOF_a(F_e)_2X_2]^{2-}$	F_a	–160.8	–168.0	–167.9	F_a–F_e^c	87.8	89.0	85.0
		F_e^c	–347.1	–333.2	–344.4				
IV	*trans*-$[RuNOF_a(F_e)_2X_2]^{2-}$	F_a	–161.9	–169.4	–186.8	F_a–F_e^t	82.1	86.2	89.6
		F_e^t	–413.9	–421.0	–431.6				
V	$[RuNOF_aF_eX_3]^{2-}$	F_a	–170.8	–183.7	–197.5	F_a–F_e^c	91.6	99.0	103.0
		F_e^c	–347.9	–337.3	–369.9				
VI	$[RuNOF_aX_4]^{2-}$	F_a	–182.9	–203.6	–250.1				
	$[RuNOF_a(F_e^t)_2X(H_2O)]^-$	F_a	–	–159.1	–173.2	F_a–F_e^t	–	82.2	84.0
		F_e^t	–	–416.5	–421.9				
	$[RuNOF_aF_e^cX_2^t(H_2O)]^-$	F_a	–	–172.2	–183.0	F_a–F_e^c	–	93.5	97.0
		F_e^c	–	–334.6	–357.4				
	$[RuNOF_aX_3(H_2O)]^-$	F_a	–	–188.9	–230.9				

also capable to coordinate to RuNO(III), the fluoroligand remaining in the *trans* position to nitrosyl groups.

In the ^{19}F NMR spectra of $K_2[RuNOF_5]\cdot 2H_2O + H_2C_2O_4$ solution a doublet of low intensity with $^2J_{F-F}$ = 80 Hz at –367.2 ppm appears after their prolonged storage which cannot be assigned to the F_a signal of aquafluoro-species. Most likely, this doublet is caused by the presence in the solution of the following anion:



where $C_2O_4^{2-}$ acts as a bidentate ligand. The signal from the axial fluorine is probably masked by the F_a lines of I–VI complexes which are present in the solution in higher concentrations. Contrary to NO_3^-, SO_4^{2-} and $C_2O_4^{2-}$, both perchlorate and chloride ions do not participate in coordination to the central atom in the above systems.

The formation of aquafluorocomplexes of RuNO(III) and OsNO(III) in acidic solutions indicates that the nucleophilicity of fluoride ions decreases, due to the interaction of the latter with protons so that they let water molecules and other acidoligands into the internal sphere. On this basis it may be concluded that the treatment of any nitrosyl compounds of ruthenium and osmium by hydrofluoric acid will not lead to coordination of fluorine to the central atom. This has indeed been shown in the case of reaction of HF with ruthenium nitrosyl hydroxide [15].

The fluorohalogenonitrosyl complexes of Ru(IV) and Os(IV) were prepared as described in the experimental part. As an example, the ^{19}F NMR spectra of the solutions in D_2O of the melts of $Na_2[RuNOCl_5]$ (a), $Rb_2[RuNOBr_5]$ (b) and $K_2[OsNOBr_5]$ (c) with KHF_2 are given in Fig. 3. The compositions and ^{19}F NMR parameters of fluorohalogenonitrosylruthenates and -osmates identified in the systems studied are presented in Tables II and III. From consideration of the spectra it follows that fusion results in all of the I–VI types of complexes. Moreover, in solutions of fluorobromo- and fluoroiodo-nitrosylruthenates there are species containing water molecules in the first coordination sphere (Table II). In the nitrosylosmate systems similar aquacomplexes were not detected, which indicates a higher stability of osmium halogenonitrosyl complexes as compared with the analogous ruthenium compounds.

It should be noted that the fluorocomplexes existing in the solutions under consideration have the fluoroligand F_a in a *trans* position to the NO group. A similar phenomenon is observed as a result of re-distribution of ligands which we have performed

TABLE III. Composition and ^{19}F NMR Parameters of Fluorohalogenonitrosylosmates(IV).

	Complex	Chemical shift, ppm			$^2J_{F-F}$, Hz ± 1		
		X/F	Cl	Br	X/F–F	Cl	Br
I	$[OsNOF_a(F_e)_4]^{2-}$	F_a	−143.2	−146.7	F_a–F_e	68.7	68.5
		F_e	−358.6	−360.6			
II	$[OsNOF_a(F_e)_3X]^{2-}$	F_a	−147.5	−153.3	F_a–F_e^t	74.4	75.0
		F_e^c	−304.3	−295.6	F_a–F_e^c	84.0	85.8
		F_e^t	−359.8	−363.7	F_e^c–F_e^t	9.5	9.5
III	*cis*-$[OsNOF_a(F_e)_2X_2]^{2-}$	F_a	−153.5	−162.2	F_a–F_e^c	87.7	92.0
		F_e^c	−304.0	−296.9			
IV	*trans*-$[OsNOF_a(F_e)_2X_2]^{2-}$	F_a	−155.2	−164.6	F_a–F_e^t	78.2	80.0
		F_e^t	−362.9	−370.2			
V	$[OsNOF_aF_eX_3]^{2-}$	F_a	−162.1	−175.8	F_a–F_e^c	93.5	98.0
		F_e^c	−307.1	−304.1			
VI	$[OsNOF_aX_4]^{2-}$	F_a	−173.4	−193.4			

in the solution of $K_2[RuNOF_5]$ + $Na_2[RuNOCl_5]$, where also only complexes with the ordinate ON–Ru–F_a are formed. The data obtained show that the reactions of substitution and re-distribution of ligands in nitrosyl complexes of ruthenium and osmium occur with retaining or formation of the ON–M–F_a ordinate. Only fluoroligands in the equatorial plane of complexes take part in the substitution reactions.

For a complex with the composition $[MNOF_a(F_e)_2X_2]$ two geometric isomers are formed *viz.*, III-*cis* and IV-*trans*. The *cis/trans* ratio of isomer concentrations changes depending on the nature of ligand X and it is equal to 5.5, 2.3, <0.1 and 1.1 for X = Cl, Br, I and H_2O, respectively, in the case of ruthenium compounds. The *cis/trans* ratio for osmium complexes is higher than for the ruthenium isomers and it is equal to 10, 7 and 3 for X = Cl, Br and H_2O, respectively. The observed tendency of the stability of the *cis*-isomer to decrease on the transition from fluorochloro- to fluorobromo- and fluoroiodo-nitrosyl complexes as compared with its *trans* modification is probably related to the interligand interactions realised through the central atom. The domination of the *trans*-species over the *cis*-species for such different size ligands as I^- and H_2O indicates that the effect of steric factors (interligand repulsion) on the isomer stability is insignificant.

The change of the M–F bond character upon formation of different isomers may be evaluated by analysis of ^{19}F chemical shifts. It is thus necessary to consider in more detail the range of chemical shifts of ruthenium and osmium nitrosyl complexes which have some specific features. The ^{19}F NMR chemical shifts of fluoro-complexes of polyvalent elements form a certain scale where one can distinguish partially overlapped regions owing to fluorocomplexes with d^0, d^4, d^6 and d^{10} electronic configurations of the central atom. The range from F_2 molecule with chemical shift accepted to be zero (and corresponding to covalent bonding of fluorine atom) to free fluoride ion F^- with the chemical shift of −713 ppm [13] appears to be most 'densely populated'. This value of chemical shift of F^- is entirely determined by diamagnetic shielding of the nucleus from all ten electrons and corresponds to utmost ionic bonding of fluorine. The fluorocomplexes with d^0 and d^{10} configuration fall into the region from F_2 to F^- (−200–−600 ppm), so the correlation of chemical shift with the M–F distance seems to be quite applicable for them *i.e.*, a downfield shift of the signal is caused by shortening of the bond while an upfield shift is indicative of the lengthening of the M–F bond. ^{19}F chemical shifts for d^4 hexafluorocomplexes exceed the bounds of this scale and are observed at very low field with respect to F_2 *viz.*, 4808 ppm for $[RuF_6]^{2-}$ [11], 1553 ppm for $[OsF_6]^{2-}$ [11], 3545 ppm for PtF_6 [12] and 1580 ppm for $[IrF_6]^-$ [13]. Such enormous downfield shifts of the resonance lines for d^4-complexes are related to the strong spin–orbital interaction splitting the t_{2g}^4 level. A large constant orbital momentum resulting from mixing of sublevels formed [16] leads to a considerable downfield shift of the NMR resonance. The shift value is proportional to the magnetic momentum of d^4 ions or inversely proportional to the spin–orbital interaction constant [13].

The presence of nitrosyl groups in the coordination sphere of Ru(IV) and Os(IV) causes very large upfield displacement of the ^{19}F NMR signal. The change in the shift for equatorial fluoroligands in

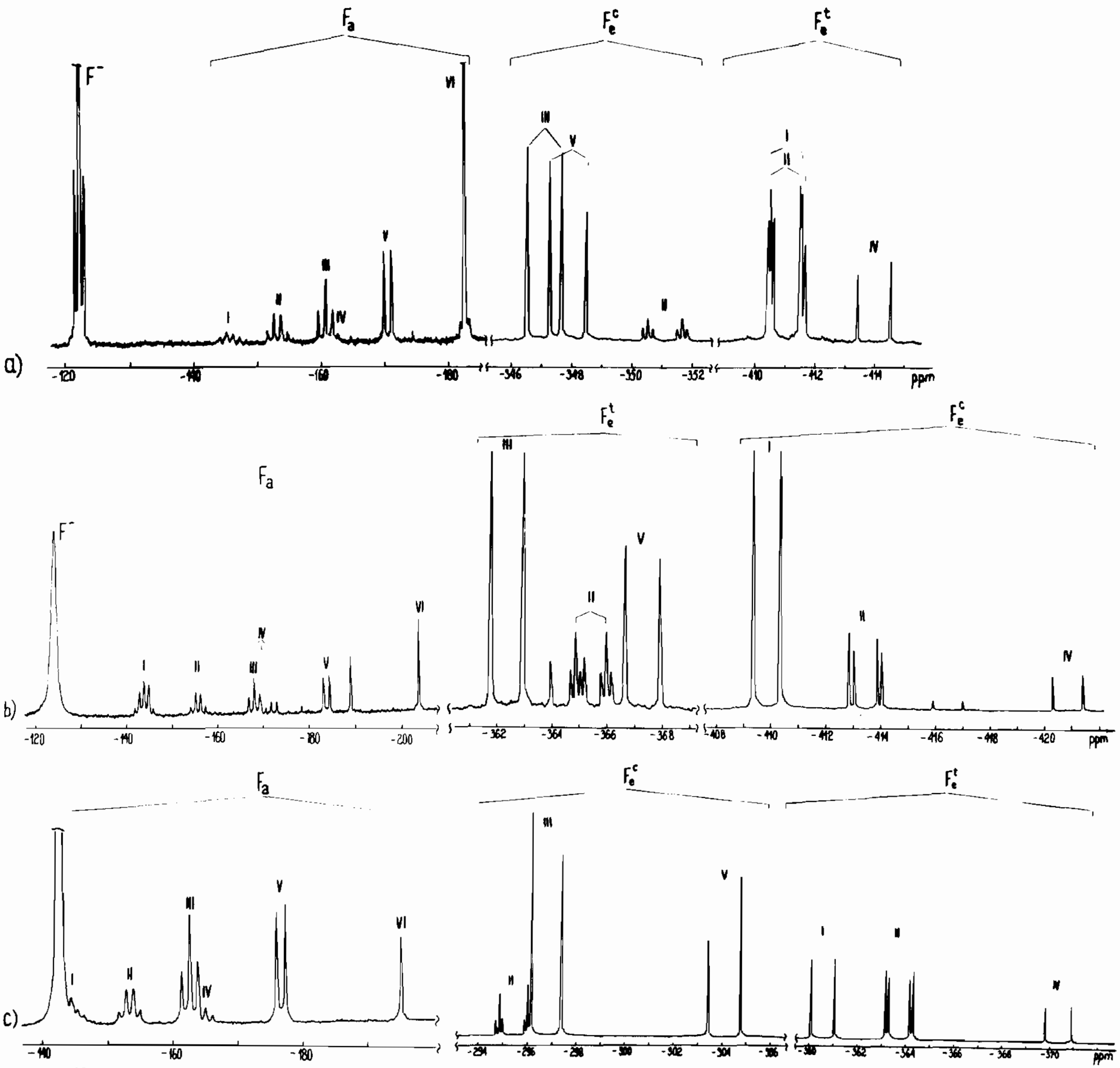


Fig. 3. ^{19}F NMR spectra (75.39 MHz) for D_2O solutions of $Na_2[RuNOCl_5]$ (a), $Rb_2[RuNOBr_5]$ (b) and $K_2[OsNOBr_5]$ (c) melts with KHF_2 at temperature 10 ℃.

$[RuNOF_5]^{2-}$ and $[OsNOF_5]^{2-}$ is ~5650 and ~2350 ppm comparing with $[RuF_6]^{2-}$ and $[OsF_6]^{2-}$, respectively, the value of chemical shift F_e exceeding the value for free fluoride ion. The reason of the observed upfield shift of the ^{19}F NMR lines (beyond the limits of F^- chemical shift) is probably connected with antiparamagnetic currents induced on the fluorine-19 nuclei due to the change in the arrangement of electronic levels upon transition from O_h to C_{4v} molecular symmetry, and because of the introduction of NO groups.

A specific feature of nitrosyl groups is that $2\pi^*$ antibonding MO is close to antibonding orbitals of the central atom, resulting in mixing [17]. Due to such interaction the lower levels (of almost pure metallic nature) become completely occuppied, so nitrosyl complexes of ruthenium(IV) and osmium(IV) may be considered as complexes with 'quasi'-d^6 electronic configurations. Under the magnetic field the transitions between occupied and vacant antibonding levels become possible. A simplified scheme for the induction of circulation of electronic orbital currents upon mixing of these levels is given in Fig. 4. The transitions between bonding and antibonding states determine the downfield shift of the ^{19}F NMR lines. As shown, the induced circulation resulting from the $t_{2g} \rightarrow e_g^*$ transition has the same direction for both fluorine and the central atom while these directions are opposite in the case of mixing of t_{2g}^* states. Since the complex as a whole

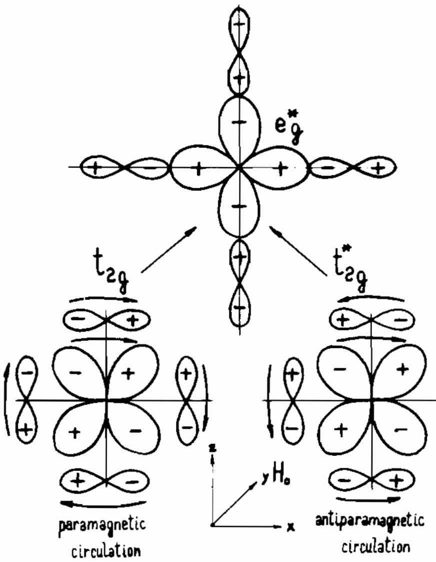


Fig. 4. Schematic representation for the circulation of electron orbital currents under magnetic field [13].

possesses Van Vleck paramagnetism, the summarized direction of the circulation of currents corresponds to the paramagnetic (clockwise) one. Such a direction of currents upon mixing of t_{2g}^* and e_g^* states under H_0 is related with the fact that the coefficients at the atomic orbitals of fluoroligands in MO (t_{2g}^*) are considerably less than for the orbitals of the central ion. So the central ion determines the excitation of currents and governs the direction of their circulation. The antiparamagnetic circulation of currents in the vicinity of fluorine nuclei will result in an upfield shift of ^{19}F NMR signals, even stronger than for F^-. Similar consideration of the 'abnormality' of ^{19}F chemical shifts was made within the limits of Cornwell's theory [18] for octahedral anions $[PtF_6]^{2-}$ and $[RhF_6]^{3-}$ [13] both possessing d^6-configuration and completed t_{2g}^* level.

Thus, strong shielding of fluorine nuclei observed for the fluoronitrosyl complexes of ruthenium and osmium with 'quasi' d^6-configuration is caused by antiparamagnetic currents induced upon mixing of occupied and vacant antibonding states. Since these currents depend on distance and the degree of covalency by the same law as paramagnetic currents (r^{-3}), the upfield shifts corresponds to lengthening (weakening) of the bond. With this assumption one may estimate by ^{19}F chemical shifts a relative strength of the M–F bond depending on the nature of the substituent X (Cl, Br, I, H_2O) and its arrangement in the coordination sphere (*cis-trans* isomerism). A numerical correlation between the ^{19}F chemical shift and the bond distance, assuming the antiparamagnetic currents to determine δ ^{19}F, may be roughly evaluated from consideration of the structure and ^{19}F chemical shifts of ClF_3 molecule *viz.*, the change in chemical shift by 1 ppm corresponds to the change in the bond length by 9×10^{-4} Å [13].

It should be noted that such an approach to the estimation of relative bond distances suffers a number of restrictions, and perhaps it is not quite correct to make a conclusion on the change in the M–F_a and M–F_e bond distances by the difference in ^{19}F chemical shifts of F_a and F_e signals where the mixing of excited states is different. Taking into consideration the numerical correlation, for *cis*-isomers III the M–F_e^c bond lengthens with respect to M–F_e in $[MNOF_5]^{2-}$ by 0.057–0.07 Å in the case of RuNO(III) fluorohalogenocomplexes and by 0.05–0.057 Å in the similar OsNO(III) anions whereas the M–F_e^t bond in the *trans* species IV, on the contrary, shortens by 0.01–0.02 Å for Ru(IV) and by 0.004–0.009 Å for Os(IV). This is an indication of greater stability of the F–M–F ordinate compared with F–M–X, the stability of the former increasing upon transition from X = Cl to X = Br and I and decreasing when Ru(IV) is changed by Os(IV). Apparently this result sufficiently explains the decreasing *cis*/*trans* ratio of isomers in the sequence Cl > Br > I and the increase in the *cis*/*trans* ratio on the transition from ruthenium nitrosyl complexes to similar osmium compounds.

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