^{19}F CHEMICAL SHIFTS AND MUTUAL INFLUENCE OF LIGANDS

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SUMMARY

By comparing the positions of ^{19}F shifts in pentafluoro
complexes of d^o transition metals and non-transition
elements in higher oxidation state complexes MF_5L and
EF_5L with the positions of corresponding MF_6 and EF_6,
the spectra of all the pentafluoro complexes can be divid-
ed into a few types which depend on the nature of L. Cor-
relation of chemical shifts with structural data and force
constants implies that the change in the bond strength of
the fluorine and the central ion has opposite effects in
the ^{19}F NMR spectra of the complexes of transition and
non-transition elements.

DISCUSSION

Replacement of a fluorine atom in the hexafluorides of
transition MF_6 and   main-group EF_6 elements, in which
all atoms are equivalent (in solution), by a ligand L makes
the five remaining F atoms inequivalent. For this reason the
first-order ^{19}F NMR spectra of the compounds MF_5L and

EF_5L show the equatorial (F_e) and axial (F_a) fluorine atoms as a doublet and a quintet whose positions do not coincide with those of signals of MF_6 and EF_6 .

$$F_a$$
$$F_e \diagdown \quad \diagup F_e$$
$$F_e \diagup \quad \diagdown F_e$$
$$L$$
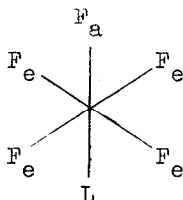
Systematization of the accumulated experimental work has clarified the major factors that affect the relative positions of the resonance signals, which can be useful in spectral inter-pretation. Because the unpaired electrons and lone pairs of the central atom affect the ^{19}F chemical shift more than does the nature of the ligand L, we have examined complexes of d^o transition metals (M) and main-group elements in higher oxidation states (E). To establish the gross tendencies go-verning the positions of the resonance lines we have referred the chemical shifts of MF_5L and EF_5L to the signal of the corresponding MF_6 and EF_6 [1]. The spectra of all the pentafluoro complexes can now be divided into a few types, which depend on the nature of L in several series of compounds of transition and main-group elements (Fig.1).

Complexes of d^o Transition Metals Introduction into the inner sphere of complexes of d^o transition metals Ti(IV) , Nb(V), Ta(V), Mo(VI), and W(VI) of ligads stronger than the fluorine atom ($L^I = S^{2-}$, NR^{2-} , O^{2-} , SR^- , NH_2^- , and OR^-) [1] that are capable of forming bonds of greater multiplicity with the central atom causes an upfield shift of the F_a and F_e resonance signals of the complexes MF_5L^I relative to MF_6 .
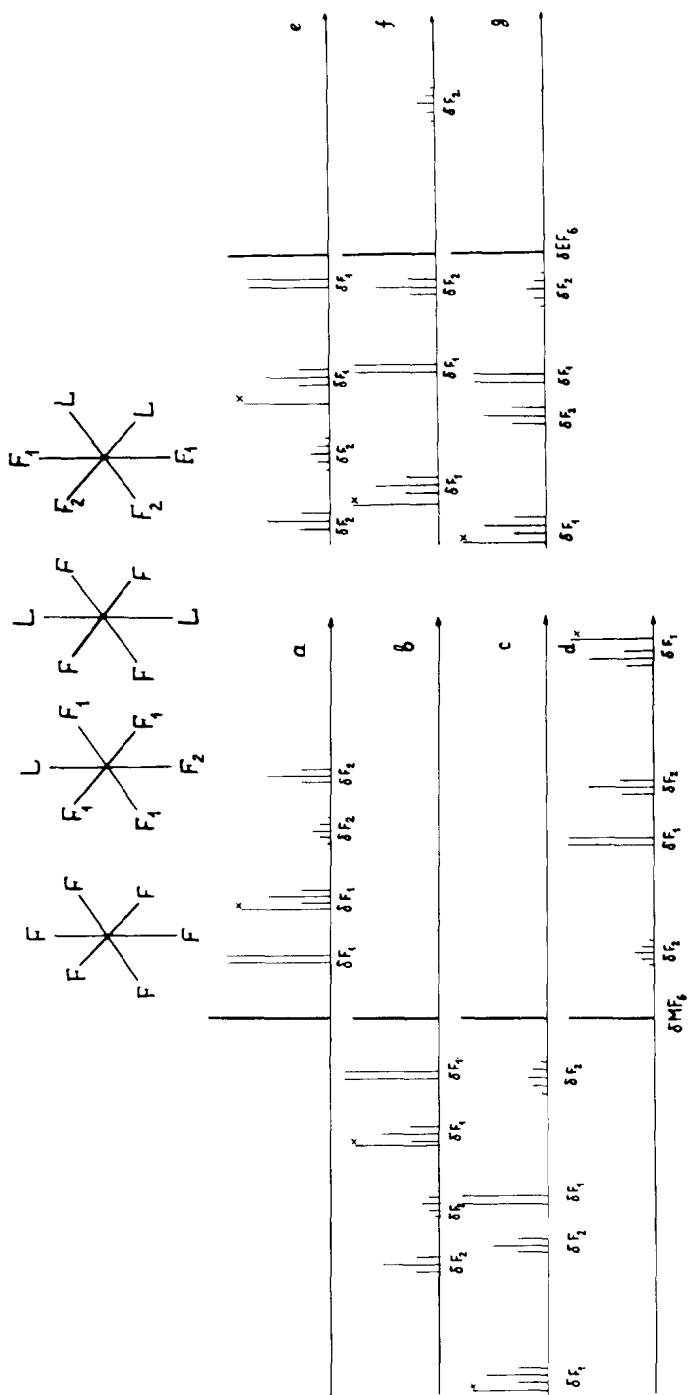
Fig.1. Types of first-order ^{19}F spectra of penta- and tetrafluoro complexes of d^0 transition MF_5L, cis-, trans- MF_4L_2 and nontransition elements in higher oxidation states EF_5L, cis- , trans- EF_4L_2 ; a,d → L^I ; b,f - L^{II}; c,g - L^{III} , d - L^{IV}.

This implies increase in the ionicity of the M-F bond; more-over, the F_a quintet undergoes the greatest shift (Fig.1a). Increase in the donor ability of L^I of one type, such as OR^- [2], is accompanied by a linear upfield shift of the resonance lines.

The pentafluoro complexes with molecular ligands (L^{II}) that form donor-acceptor bonds weaker than the M-F covalent bond with the central atom, regardless of the nature of the donor atom ($L^{II} = R_3PO$, R_3PS, R_3PSe , R_2O, R_2S, NR_3, ROH, H_2O, R-py, and R-pyO) [1] , have ^{19}F NMR spectra in which the resonance signals of MF_5L^{II} lie downfield relative to MF_6 (Fig.1b). If the ligands have the same functional groups, reduction in the donor ability of L^{II}, as for example in the series $(R-Ph)_3PO$, is accompanied by a linear downfield shift of the resonance lines of MF_5L^{II} .

In the fluorohalide complexes MF_5L^{III} ($L^{III} = Cl^-$, Br^-) the F_e doublet lines are downfield relative to MF_6 and the quintet either downfield but with lower shift $\delta F_e < \delta F_a <$ δMF_6^- or else upfield $\delta F_e < \delta MF_6 < \delta F_a$ as in WF_5Cl [1].

The spectra of the fourth type has been recently observed for the complexes of tantalum pentaluoride with strong π -donors $L^{IV} = ON=CHCH_3^-$, $ON=CHPh^-$, which occupy one coordination place in the inner sphere [3].

Analysis of the experimental data shows that when passing from penta-MF_5L to cis-fluorocomplexes MF_4L_2 the relative position of the resonance lines of non-equivalent atoms F_1 and F_2 remains, the singlet of trans-MF_4L_2 being in the range of trans-fluorine atoms F_1 in cis-MF_4L_2. Thus the relative position of ligands in the octahedron equatorial plane

practically does not influence the chemical shift and conse-
quently the nature of bonding of the axial fluorine atom F_1.

F₁ and L diagram structures (two octahedral coordination diagrams showing F_1, F_2, L arrangements)
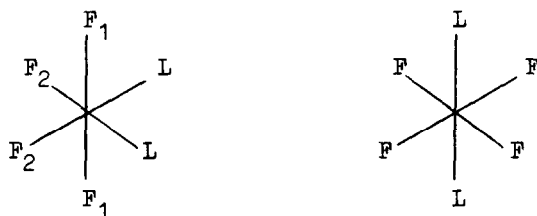
    The order of the variation in the force constants and M-F
bond lengths on going from MF_6 to MF_5L^I or MF_5L^{II}
shows that the double-bonded ligand causes weakening (lengthe-
ning) and the molecular ligand L^{II} strengthening (shortening)
of the bond to the remaining F atoms, which is apparent in the
^{19}F NMR spectra as an upfield or downfield shift respectively
of the resonance lines. Since in complexes of d^o transition
metals the trans influence is the major type of ligand inter-
action, the shift of the F_a quintet is greater in both cases,
as would be expected.

    We can use the chemical shift difference $\Delta\delta = \delta F_e - \delta F_a$
as an index of the inequivalence of F_a and F_e in the inner
sphere of the complexes [1]. In this case a negative $\Delta\delta$ in-
dicates increased ionicity while a positive sign denotes
relative strengthening of F_a by comparison with F_e. We can
rank the trans-activity of the ligands in complexes of d^o
transition metals in terms of $\Delta\delta$ as: $S^{2-} > O^{2-} > NR^{2-} >$
$SR^- > OR^- > O_{br}^{2-} > Br^- > Cl^- > F^- > NR_3 > RCOO^- > RCOOR >$
$NCO^- > R-pyO > H_2O > ROH \geqslant R_3PO > R_2O > F_{br} > R_3PS >$
R_3PSe. Ligands to the left of the F atom in this series
cause mainly weakening of F_a and those to the right a relative
trans-strengthening.

These differences are not always detectable from changes in the interatomic distances in the crystalline state but can be traced from solution NMR of the complexes. Our trans-activity series cannot be identical to the donor ability series of ligands that differ in functional groups, since the donor ability involves the total of the σ - and π -contribution and steric factors, which will be different for different functional groups as consequently will be their effect on the F_a end F_e atoms (trans- and cis-influence). For a comparative estimate of the overall effect of ligand L on F_a and F_e on going from MF_6 to MF_5L we suggest the use of the total chemical shifts, $\sum \delta_{(MF_6)} = 4[\delta MF_6 - \delta F_e] + [\delta MF_6 - \delta F_a]$ Comparison of $\sum \delta_{MF_6}$ for the complexes WSF_5^-, WOF_5^-, and $W(NR)F_5^-$ reveals that the bonding of the F atoms is weakened mostly by the NBu^- group, which strongly affects the F_a and F_e atoms, whereas the sulfur atom mainly weakens the F_a bonding. This also applies to the halogen series, $F^- > Cl^- > Br^-$

<u>Complexes of Main-Group Elements</u> Replacement of F in EF_6 $[E = Si(IV), Ge(IV), Sn (IV), P(V), As(V), Sb(V), S(VI), Se(VI), and Te (VI)]$ by double-bonded O^{2-} atom or other strong acido ligands $L^I = NR_2^-$, OR^-, or OH^- [3-5] causes a downfield shift of the resonance signals of EF_5L^I relative to EF_6 ; the quintet is downfield $(\delta F_a < \delta F_e < \delta MF_6)$.

Complexes of main-group elements with molecular ligands $L^{II} = R_2O$, R_2S, SO_2, SO_2FCl, RCN, NR_3, R-quinO, NH_nR_{3-n}, ROH, and H_2O [4,6] have ^{19}F NMR spectra in which the F_e signal lies downfield and the F_a quintet upfield relative

to EF_6 , i.e., in contrast to L^I, replacement of a fluorine
atom in the hexafluoride by L^{II} causes contrary changes in
the F_a and F_e shielding constants. Increase in the donor
ability of L^{II} is accompanied by reduction in the chemical
shift differences $\Delta \delta = \delta F_e - \delta F_a$ [6].

^{19}F and ^1H NMR studies of the complexes formed by non-transi-
tion element pentafluorides EF_5 (E=P,As,Sb) with molecular donor
ligands L^{II} containing mobile hydrogen atoms (EtOH, Et_2NH) sho-
wed that the shift up to 23 ppm to the weak field of the ^{19}F re-
sonance signal of the axial fluorine F_2 in EF_5L^{II} spectra was
proportional to the excess of the ligands. This shift might be
caused by the increase in basicity of the ligand donor centre.
The position of the equatorial F_1 fluorines signal did not change.
The shift in the low field of the resonance ^{19}F signal of the
axial fluorine atom must be caused by the increase of basicity of
the donor atom which is a result of the hydrogen bond formation.
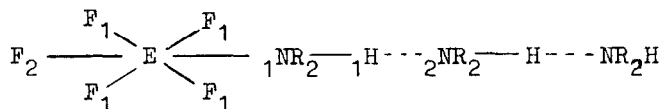
Displacement of the electron density of the coordinated ligand
$_1N(O) -- {}_1H$ bond in the direction of N (O) donor atom which chan-
ges its basic properties is a result of polarisation of the
$_1N(O) --_1H$ bond under the influence of the proton acceptor, i.e.
the N (O) atom of free ligand. Continuous (in the NMR scale)
change in basicity of the donor centre of the ligands $L^{II}H$ in
the inner sphere of the complex as the basicity of the solution
changes is known as 'continuum donor capacity'[7-9] .

The pentafluoro complexes with medium-strength acido ligands L^{III} = Cl^-, Br^-, I^- or $RCOO^-$ [4,10] have spectra in which the F_e resonance signal lies far downfield relative to EF_6 while the quintet lies close to the signal of EF_6 : $\delta F_a > \delta F_e \lesssim \delta\ EF_6$. In the series of the pentafluorides of a certain element when passing from EF_5Cl to EF_5Br / E = Sn(IV), S(VI), Se(VI), and Te(VI) and SnF_5I^{2-}/ a considerable downfield shift of the F_e doublets is observed, whereas the F_a chemical shifts vary only slightly, i.e., the substitution by the ligand L^{III} affects mainly the fluorine atoms cis to L^{III}.

The experimental reduction of the E-F bond constants on going from EF_6 (E = S, Se, Te, I) to EOF_5 demonstrates that in compound of non-transition elements replacement of an F atom by double-bonded O^{2-} weakens the bonding of the remaining fluorine atoms [11-

Comparison of the relative position of the resonance lines of the hexafluorides and oxopentafluorides (Fig.1 e) reveals that replacement of F by a double-bonded ligand causes an upfield shift of the resonance lines in the case of d^o transition metals but a downfield shift in complexes of main-group elements.

The experimental results regarding the differences between F_a and F_e in EF_5L^I even in the case of ligands L which are very dissimilar to fluorine, such as O^{2-}, are contradictory. In $SeOF_5^-$ and $TeOF_5^-$ the force constants of the $E-F_e$ bonds are higher than those of the axial $E-F_a$ bonds [3,6], whereas the contrary applies to SOF_5^- and IOF_5 12 . Recently combined electron-diffraction-microwave work has shown that in IOF_5, whose NMR spectrum also has the F_a signal downfield of F_e, the $I-F_a$ bond is slightly longer than the $I-F_e$ bonds [13].

In compounds of the type EF_5L^{II} , such as PF_5py [14]
and SbF_5SO_2 [15], the $E-F_a$ distances lie within the $E-F_e$
range, but in both cases they are slightly shorter than
$(E-F_e)_{av}$, which is supported by the downfield position of
the F_e doublet.

Comparison of the relative positions of the resonance lines
of the nonequivalent fluorines in the complexes MF_5L^I , MF_5L^{II}
EF_5L^I , and EF_5L^{II} suggests that the longest bonds corre-
late with signals lying further downfield in complexes of main-
group elements but further upfield in compounds of d^o transi-
tion metals.

This situation is also exemplified by the dimeric anions
M_2F_{11} (M= Ti, Nb, Ta) and $E_2F_{11}^-$ (E= As, Sb), in whose ^{19}F
NMR spectra [16] the relative positions of the F_1 , F_2, and F_3
lines also vary in the opposite sense in compounds of transition
and main-group elements, whereas in all the complexes the bridge
bonds are the longest while the shortest bonds are trans to the
bridging fluorine [17,18].
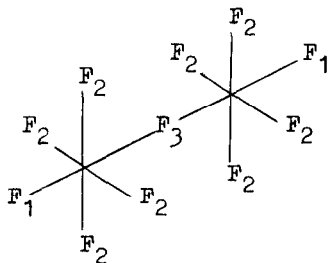
It can also be seen when comparing the ^{19}F NMR data for cristalline salts of hexafluoride anions $TiF_6{}^{2-}$, $ZrF_6{}^{2-}$, $TaF_6{}^{-}$, $NbF_6{}^{-}$ and $PF_6{}^{-}$ with structural data. In cases of d^0 transition metals the axial fluorine signals are in a low field and the $M-F_a$ distance is shorter than $M-F_e$. For the hexafluorophosphate anion $PF_6{}^{-}$ the F_a line is also in the low field, but the octahedron is distorted, the F_a-F_a distance being elongated [19 -22].

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