NUCLEAR MAGNETIC RESONANCE IN AQUEOUS SOLUTIONS
OF FLUORINE COMPLEXES
V. OXOPEROXOFLUOROMOLYBDATES

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The state of fluorine complexes in aqueous solutions has been investigated by \(^{19}F\) nuclear magnetic resonance with a view to determining the spin–spin coupling constants \(J_{F-F}\) in the \([\text{MoO}_2\text{F}_4]^{2-}\) anion and investigating the reactions of the salt \((\text{NH}_4)_2\text{MoO}_2\text{F}_4\) and the oxofluoride \(\text{MoO}_2\text{F}_2\) with hydrogen peroxide. In the oxotetrafluoro anion, \(J_{F-F} = 62\) Hz. Reaction with hydrogen peroxide gives a series of oxoperoxofluoro complexes, for which the chemical shifts and \(J_{F-F}\) values were determined. It was shown that when the hydrogen peroxide concentration in the solution is increased all forms are converted into \([\text{MoO(O}_2\text{F}_2\text{H}_2\text{O}]^-\) with the formation of hydrogen fluoride.

Salts with the oxotetrafluoro anion \([\text{MoO}_2\text{F}_4]^{2-}\) have been investigated by IR spectroscopy [1], \(^{19}F\) NMR spectroscopy [2], and x-ray diffraction analysis [3]. It was shown that in the solid state and in solution the \([\text{MoO}_2\text{F}_4]^{2-}\) ion has an octahedral configuration with a nonlinear arrangement of the oxygen atoms in the \(\text{MoO}_2\text{F}_4^{2-}\) group.

In [2] it was found that there were two nonequivalent groups of fluorine atoms in the cis and trans positions with respect to the oxygen atoms of the \([\text{MoO}_2\text{F}_4]^{2-}\) ion, but owing to rapid exchange the spin–spin coupling constant \(J_{F-F}\) was not determined.

The oxotetrafluoro anion \([\text{MoO}_2\text{F}_4]^{2-}\) readily reacts with hydrogen peroxide. Salts containing the complex ions \([\text{MoO(O}_2\text{F}_4]^{2-}\) and \([\text{MoO(O}_2\text{F}_2]^{2-}\) have been isolated in the solid form. Investigation of the structure of the peroxy salt \(K_2[H_2\text{MoO(O}_2\text{F}_4] \cdot \text{H}_2\text{O}\) has shown [4] that the complex anion has the form of a pentagonal bipyramid. (See scheme on next page.)

In [5] an aqueous solution of the salt \(K_2\text{MoO(O}_2\text{F}_4\) was investigated by the \(^{19}F\) NMR method. Two signals with chemical shifts of 558.7 and 565.7 ppm with respect to \(F_2\) were found in the spectrum. The authors attributed these signals to two nonequivalent positions of the fluorine atoms in the complex. An attempt by Evans [5] to record the spectrum of an aqueous solution of \(K_2\text{MoO(O}_2\text{F}_4\) proved unsuccessful, owing to the low solubility of this salt.

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In the present work we have continued our investigations into the state of fluorine complexes in aqueous solutions by the $^{19}$F NMR method with a view to determining the $J_{F-F}$ coupling constants in the $[\text{MoO}_2F_4]^{2-}$ anion and investigating the reactions of the salt $(\text{NH}_4)\text{MoO}_2F_4$ and the oxofluoride $\text{MoO}_2F_2$ with hydrogen peroxide.

The $^{19}$F NMR spectra were recorded on a Varian spectrometer (56.4 MHz) at temperatures between 40 and $-40^\circ$C. Trichlorofluoromethane was used as external standard, and the chemical shifts were then converted to $F_2$. The error amounted to $\pm 0.5$ ppm in the determination of the chemical shifts and $\pm 1$ Hz in the determination of $J_{F-F}$. The concentrations of the compounds in the solution were determined to within $\pm 2\%$ from the ratio of the integral intensities of the $^{19}$F NMR signals. Before filling, the ampoules (external diameter 5 mm) were cooled with liquid nitrogen in order to avoid reaction between the fluorides and the glass. When the control spectra were being recorded the specimen was placed in a polyethylene ampoule. The solutions placed in glass and polyethylene ampoules gave identical spectra.

Figure 1a shows the spectrum of a 60% solution of $(\text{NH}_4)\text{MoO}_2F_4$ at $0^\circ$C. The spectrum contains two lines: a comparatively broad line at 542.8 ppm from $F_C$ and a narrow line at 507.6 ppm from $F_B$. The positions and forms of the lines vary little over the range of temperatures between 35 and $-40^\circ$C. Earlier we suggested [6] that exchange of fluorine atoms in oxofluoro anions of transition elements had a dissociation character, and it seemed possible to retard the exchange by the introduction of fluoride ions. When ammonium fluoride was added to the solution (beginning with 5% ammonium fluoride) the $F_B$ and $F_C$ signals changed into two triplets of equal intensity at $J_{F-F} = 62$ Hz. It should be noted that the temperature at which the fine structure of the spectrum appeared increased with increase in the ammonium fluoride concentration (Fig. 1b). This spectrum can be attributed to the