

CHELATED I(V) ALCOHOLATE FLUORIDES

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The behavior of IF_5 towards nucleophilic exchange of fluoride against mono- and polyfunctional alcoholates in aprotic media was investigated using silylated alcohols as educts.

In a series of homologous bifunctional alcoholates $^-\text{O}(\text{CH}_2)_n\text{O}^-$ ($n = 2, 3, 4, 5, 6, 12$) systems with short CH_2 -chains ($n < 4$) form short lived species $\text{IF}_4[\text{O}(\text{CH}_2)_n\text{O}]\text{X}$ ($\text{X} = \text{SiMe}_3, \text{IF}_4$) which rearrange to mononuclear chelates $\text{IF}_3[\text{O}(\text{CH}_2)_n\text{O}]$ of high stability. Dialcoholates with long CH_2 -chains ($n > 4$) behave as bridging ligands forming multinuclear compounds $\text{IF}_4[\text{O}(\text{CH}_2)_n\text{O}]\text{IF}_4$ and $\{\text{IF}_3[\text{O}(\text{CH}_2)_n\text{O}]\}_m$ ($m \geq 2$).

In a series of α, β -ethandiolates with increasing number of CH_3 -groups in α - and β -positions short lived intermediates and stable chelates $\text{IF}_3[\text{OC}_2\text{H}_{4-n}(\text{CH}_3)_n\text{O}]$ and $\text{IF}[\text{OC}_2\text{H}_{4-n}(\text{CH}_3)_n\text{O}]_2$ ($n = 0-4$) are observed and characterized.

Time and temperature dependence of ^{19}F -NMR-spectra in relation to degree of methylation, arrangement and stereo-chemistry are discussed. Reactions of IF_5 with a geminal dialcoholate $\text{CCl}_3\text{CH}(\text{O}^-)_2$ and a trifunctional alcoholate $\text{CH}_3\text{C}(\text{CH}_2\text{O}^-)_3$ are reported.