

**Octahedral versus trigonal prismatic rearrangements
in MoF₆ and WF₆ derivatives.**

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¹⁹F-NMR spectra on non-rigid metal complexes LMF₅

Poster presented by Prof. Dr. G. Haegele.

Australian-New Zeland Magnetic Resonance Group, ANZMAG.

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“The lowest and highest coordination numbers found in “typical” coordination compounds are 2 and 9 with the intermediate number 6 being the most important”

J. E . Huheey, 1993.

Summary

DFT calculations performed on MoF_6 and WF_6 revealed that the octahedral–trigonal prismatic–octahedral rearrangement (O_h – D_{3h} – O_h) has a relatively low energy barrier (6–10 kcal mol⁻¹). Experimental evidence using dynamic ¹⁹F NMR spectroscopy on complexes of the type $\text{F}_5\text{M–OR}$ where $\text{M} = \text{Mo}$ or W and $\text{R} = -\text{CH}_2\text{CF}_3$, $-\text{C}_6\text{F}_5$, and $-\text{C}(\text{CF}_3)_3$ confirmed these predictions. At room temperature or below these complexes present in the ¹⁹F NMR spectroscopy an AB_4 -type spectrum typically for octahedral structures. At higher temperatures the non-equivalent metal-bonded fluorine atoms undergo exchange. Experimental evidence supports the intramolecular exchange for such species. The ¹⁹F NMR spectra at different temperatures for all studied complexes were simulated successfully using the program gNMR. Two intramolecular exchange mechanisms can be used for the simulations, namely a 3:3 process (Bailar twist) and the 2:4 mechanism. Both mechanisms are experimentally undistinguishable, from theoretical calculations the preferred mechanism is the Bailar twist.

Theoretical calculations on species of the type $\text{F}_5\text{M–C}_6\text{X}_5$ ($\text{M} = \text{Mo}$ or W , $\text{X} = \text{H}$ or F) predicted in most of the cases a trigonal prismatic geometry as the ground state. Attempts to synthesize such complexes, as well as species of the type $\text{F}_5\text{M–SCF}_3$ ($\text{M} = \text{Mo}$ or W) were undertaken. From theoretical calculations on the latter even a lower energy barrier for the O_h – D_{3h} – O_h rearrangement than for the corresponding alkoxy and phenoxy derivatives is predicted. Attempts to synthesize such complexes were unsuccessful.

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