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COMPOUNDS OF SC₆F₅ AND SCF₃ WITH PLATINUM METALS

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The chemistry of coordination compounds in which the metal atom is bonded only to fluoro-sulphurated ligands is relevant to several fields, particularly to catalysis and bioinorganics.

In this area, octahedral compounds of the type $[M(SEt_2)_3 - (SC_6F_5)_3]$ where M= Ru(III), Rh(III) and Ir(III) have been prepared and studied. The presence of the fluorinated pseudohalide diminishes the relative stability of these compounds compared with that of the chloride analogs for example, and favors the formation of the sulphur bridged polymeric compounds $[M(SC_6F_5)_3]_n$.

Square-planar complexes of Pd(II) and Pt(II) containing thio- and dithioethers with the general formula $[M(SR_2)_2(SR_f)_2]$ or $[M(RSRSR)(SR_f)_2]$ where R= CH₃, C₂H₅, C₆H₅ or C₆F₅; \underline{R} = C₂H₄, CH(CF₃)CH₂ or CH(CF₃)CH(CF₃) and R_f= CF₃ or C₆F₅, have been studied. Temperatures for inversion of configuration at sulphur centers suggest the following order of electronegativities: $CF_3S^->C1^->C_6F_5S^->Br^-$.

A different class of compounds studied are those capable to react with molecular N $_2$. Among these, $[{\rm OsCl}({\rm N}_2)({\rm SC}_6{\rm F}_5){\rm P}_3]$ P=phosphine, is the first example of a fluorinated N $_2$ -complex and one of the very few known with a metal-sulphur bond. in all cases, the nitrogen molecule is $\underline{\rm trans}$ to the halogen and every attempt to replace it ended up with loss of the N $_2$ ligand.