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NOBLE METAL FLUORIDES

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The present communication gives an analysis of the literature data and the recent experimental results obtained at the Institute of Inorganic Chemistry of the Siberian Branch of the USSR Academy of Sciences for the noble metal fluorides in oxidation states (II, III, IV, V) in the solid state, aqueous and non-aqueous solutions. On the basis of a comparison of X-ray structural data for solid samples and solutions of noble metal fluoro complexes and multiplicities and chemical shifts of the signals in the high and low resolution ^{19}F NMR spectra of complexes of the type $[MF_6]^{m-}$ and $[MF_{6-n}X_n]^{m-}$ (where M=Pt(IV), Rh(III), Ir(III) and X=Cl$^-$, Br$^-$, OH$^-$, H$_2$O) additional experimental evidence supporting the presence of tetragonally elongated octahedra in the crystals has been obtained and static aspect of <u>trans</u>-effect in the series of ligands $Br^- > Cl^- > OH^- > H_2O = F^-$ has been considered. The experimental characteristics of the reactions of aquation and ligand replacement by other halogens in octahedral complexes $[MF_6]^{m-}$ depending on the oxidation state of the complexes and their place in the periodic table (4d or 5d) are discussed as well as oxidation-reduction processes involving complex noble metal fluorides. The kinetic characteristics of the replacement of F$^-$ by Cl$^-$ and Br$^-$ in $[PtF_6]^{2-}$ and in $[PtF_5Cl]^{2-}$ and $[PtF_3Cl_3]^{2-}$ as possible intermediate compounds are considered and a mechanism for these consecutive reactions is proposed. It is shown that the reactions of these complexes carried out in a reducing medium give rise to corresponding aqua-complexes where the metal has a lower oxidation state. The bonding energies of the M-F bond in noble metals in different oxidation states have been compared with those of other halides which permitted us to make a conclusion about the greater bond strength in fluoro-complexes. The peculiar features of the electronic structure of hexahalogeno-complexes of noble metals are considered. The experimental results are discussed for the interaction of some noble metals with liquid bromine trifluoride and on the basis of examination of the phase diagrams and a radiospectroscopic analysis of solutions and solid phases it is concluded that the anionic fluoro-complexes of noble metals are formed both in liquid and solid states.