

Syntheses, Spectroscopic and Electrochemical Analysis of Tungsten(VI) Complexes with π -Expanded Ligands

(Graduate School of Science, Tokyo Metropolitan University) Omd. Wahidul Islam Ratul, Tohru Nishinaga, Ken-ichi Sugiura

Keywords: Tungsten, π -Expanded Ligands, Cyclic Voltammetry, LMCT.

Development of inorganic-organic hybrid system have been attracting much attention to obtain novel advanced materials. To obtain the specific properties attributable to inorganic and organic materials, strong electronic perturbations are needed. However, instabilities of such materials prevent the progress of the chemistry. Considering this background, we focused on tungsten (W^{6+}) phenolatos because of the stabilized coordination bond between W^{6+} , hard acid, and oxygen, hard base. In this study, we introduced π -expanded phenolato ligands shown in the Scheme with a hope obtaining the strong electronic communications with the metal.

The target complexes were obtained by the direct substitution reaction, *i.e.*, WCl_6 with aryl alcoholate ligands in boiling chlorobenzene solution. The isolated products were characterized by NMR and mass spectroscopic analysis. Two important properties are found, first, the complexes show ligand-to-metal charge transfer band in visible region. The energies are shifted to lower energy region depending on the expansion of the π -system. Second, two reversible reduction processes were observed in cyclic voltammetry which the processes were attributable to W^{6+} to W^{5+} and W^{5+} to W^{4+} redox. The potentials were also shifted to negative region depending on the π -expansion of the ligands.

