

Photodisproportionation of (1,5-Cyclooctadiene)copper(I) Hexafluoroacetylacetonate Induced by Metal-to-Ligand Charge Transfer Excitation

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The complex $\text{Cu}^{\text{I}}(\text{COD})(\text{hfac})$ with $\text{COD} = 1,5\text{-cyclooctadiene}$ and $\text{hfac} = \text{hexafluoroacetyl-acetonate}$ shows two long-wavelength absorptions at $\lambda_{\text{max}} = 308$ and 241 nm which are assigned to hfac intraligand (IL) and $\text{Cu}^{\text{I}} \rightarrow \text{COD}$ metal-to-ligand charge transfer (MLCT) transitions, respectively. The photolysis of $\text{Cu}^{\text{I}}(\text{COD})(\text{hfac})$ in hexane leads to the release of the olefin and the subsequent disproportionation of $\text{Cu}^{\text{I}}(\text{hfac})$ to elemental copper and $\text{Cu}^{\text{II}}(\text{hfac})_2$ with the quantum yields $\phi = 10^{-3}$ at $\lambda_{\text{irr}} = 313$ nm and $\phi = 3 \times 10^{-3}$ at $\lambda_{\text{irr}} = 254$ nm. It is suggested that the reactive excited state is of the MLCT type.

Key words: Electronic Spectra, Photochemistry, Copper Complexes, Olefin Complexes