

Two electron transitions of Ni(II) tetrahedral complexes A. Cornacchio, F. Baril-Robert, C. Reber, Department of Chemistry, University of Montreal, Montreal, Quebec, H3C 3J7

Two electron transitions were studied using tetrahedral Ni(II) complexes: $[\text{NiX}_4]^{2-}$, $[\text{NiX}_3(\text{PPh}_3)]^-$ (where $\text{X} = \text{Cl}^-$, Br^-). These complexes are of particular interest because they exhibit both one and two electron transitions. This property allowed us to observe and compare both types of electronic transitions simultaneously. Furthermore, these complexes also allowed us to study the effects of various ligands on the energy of these electronic transitions. Raman, Infrared and UV-Visible absorption spectroscopy were used to characterize the complexes. The following metal-ligand stretch frequencies were observed in the Raman spectra: Ni-Br⁻ at 170cm^{-1} , Ni-Cl⁻ at 273cm^{-1} . The UV-Visible absorption spectra showed absorption bands between the regions of $1,500\text{nm} - 400\text{nm}$. It was determined that the most intense one electron transition (${}^3\text{T}_1 \rightarrow {}^3\text{T}_1$) has a ν_{max} of approximately $15,000\text{cm}^{-1}$ and ϵ_{max} of $150\text{M}^{-1}\text{cm}^{-1}$. The two, two electron transitions have a ν_{max} of approximately $8,000\text{cm}^{-1}$ and ϵ_{max} of $30\text{M}^{-1}\text{cm}^{-1}$ (${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$) and a ν_{max} of approximately $21,000\text{cm}^{-1}$ and ϵ_{max} of $< 10\text{M}^{-1}\text{cm}^{-1}$ (${}^3\text{T}_1 \rightarrow {}^1\text{E}$). The spectra allow a characterization of both energies and structures of these unusual excited states.

