60. Outer Sphere Perturbation of Delocalized Mixed-Valence Complexes
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[\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu-\text{adpc})][\text{PF}_6]_2 \quad \text{and} \quad [\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu-\text{dicyd})][\text{PF}_6]_2
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\(\text{ttp} = 4\text{-tolyl}-2,2':6',2''\text{-terpyridine}, \text{bpy} = 2,2'\text{-bipyridine}, \text{adpc}^2 = \text{azodi(phenylcyanamide)}, \text{and} \ \text{dicyd}^2 = 1,4\text{-dicyanamidobenzene}\) were prepd. and characterized by IR and NIR, visible spectroelectrochem., and cyclic voltammetry. The crystal structure of the complex, \([\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu-\text{adpc})][\text{PF}_6]_2\cdot6\text{DMF}\), revealed a planar bridging \text{adpc}^2 ligand with the cyanamide groups adopting an anti configuration. IR and comproportionation data are consistent with delocalized mixed-valence complexes, and a spectroscopic anal. assuming \(C_2\text{h}\) microsymmetry leads to a prediction of multiple MMCT transitions with the lowest energy transition equal to the resonance exchange integral for the mixing of Ru donor and acceptor orbitals with a bridging ligand orbital (the preferred superexchange pathway). The solvent dependence of the MMCT band energy that is seen for \([\{\text{Ru}(\text{ttp})(\text{bpy})\}_2(\mu-\text{adpc})]\text{PF}_6\) is due to a ground state weakening of metal-metal coupling because of solvent donor interactions with the acceptor azo group of the bridging ligand.