

Hello and welcome my name is Thy Nguyen. I am an undergraduate student at the Indiana university – Purdue university at Indianapolis, working under doctor Partha Basu. This study focuses on characterizing cobalt dithione complexes and the donor-acceptor relationship between ligands and metal in the complexes. Dithiolene ligands are redox-active and can participate in charge transfer processes. Dithiolene can cycle between two redox extremes, a fully reduce dithiolate (Dt^{2-}) and a fully oxidized dithione (Dt^0). Its fully oxidized state, Dt^0 , are relatively electron deficient and may act as an electron acceptor in charge transfer processes. The non-innocent nature of Dt^0 ligand allows for metallodithiolene complexes to access more redox states. In this work, two Cobalt(III) (**1**, **2**) complexes with Dt^0 ligands ($Me_2Dt^0 = N,N'$ -dimethylpiperazine-2,3-dithione and $^iPr_2Dt^0 = N,N'$ -diisopropylpiperazine-2,3-dithione) have been thoroughly characterized utilizing elemental analysis, mass spectroscopy, IR, UV-Vis, NMR, and density functional theory (DFT). The excited state transitions of **1** and **2** were determined with TD-DFT calculations and visualized using electronic density difference maps (EDDMs). Low energy charge transfers for **1** and **2** are determined to be MLCT, while higher energy transitions are assigned as Dt^0 -based $p \rightarrow p^*$ LL'CT. The synthesis of two complexes **1** and **2** were done using 0.366 milimolar Cobalt chloride hexahydrate with 1.21 milimolar dithione ligand and 1.46 milimolar sodium hexafluorophosphate. Synthesis reaction of compound **1** has a yield of 80% while compound **2** has a yield of 78%. Elemental analysis of both compounds showed great results, correlated well with the theoretical values. Molar conductivity of compound **1** was found to be 530 molar absorptivity while it is 500 molar absorptivity for compound **2**. H one NMR also showed great correlation of hydrogens on ligands and that the metal center is diamagnetic. For compound **1** two singlet peaks were found, one at 3.98 ppm representing CH₂ and the other is at 3.59 representing CH₃. For compound **2**, a multiplet was found at 5.16 ppm representing CH groups, two triplet representing CH₂ groups were found at 3.87 ppm and 3.83 ppm with spin multiplicity of 11Hz, and two doublets representing CH₃ groups were found at 1.40 ppm and 1.36 ppm with spin multiplicity of 6.6Hz. Mass spectra data indicated successful synthesis of the complexes with good correlation between theoretical mass over charge value and fragmented ions found. UV-Vis spectra indicated an intense ligand to ligand charge transfer at 24500 to 50000 cm^{-1} facilitated by cobalt with some metal-ligand activity at approximately 21000 cm^{-1} . Different pulse voltammetry was done in acetonitrile at room temperature with a platinum working electrode, a platinum counter electrode and silver/silver reference electrode and a step size of 2 milivolt per second. Each complex exhibited 2 couples per ligand. Electronic excited states of the compounds were modeled using TD-DFT with Polarizable Continuum Model to reproduce experimental spectra recorded in acetonitrile. Their electronic structure was calculated, the resulted geometries were optimized, then a series of electronic spectra were generated using B3LYP/3-21G and 6-31G* level of theory for light atoms and LANL2DZ pseudopotential for metal atoms. Frontier molecular orbitals analysis were generated to show a series of molecular orbitals that helps visualize the atomic contribution of molecular orbitals. By analyzing the collected molecular orbitals, we found that LUMO, or the accepting orbital, of the compounds have electrons focus on their dithione ligands. On the other hand, the HOMO, or the donating orbital, of cobalt(III) compounds have electrons focusing on their sulfur atoms. The calculated excited state transitions of these compounds were superimposed onto the experimental data in order to better understand their charge transfer. Upon comparison, the calculated UV-Vis spectrum of compounds one showed an intense metal to ligand charge transfer (MLCT) in the 22,000 reciprocal centimeter and above region with the existence of a less intense ligand to metal charge transfer in the

15,000-22,000 reciprocal centimeter region. The electron difference density maps were also generated to visualize orbitals participated in these charge transfer processes. On these transitions, blue signifies accepting orbitals, while purple signify donating orbitals. On cobalt(III) compounds, electrons were being donated from ligands to ligands. The differences in charge transfer were determined to stem from a difference in donating orbitals. So we were able to come to several conclusions. The first thing is that mass spectra indicated successful synthesis of complexes with dithione ligands and cobalt. Conductivity indicated that metal center is cobalt three plus in both complexes. Different pulse voltammetry indicated that there are 6 ligand based redox couples. NMR indicated that there are low spin cobalt 3 plus metal center. UV showed an intense ligand-based charge transfer with some metal-ligand activity. Cobalt 3 complexes preferred octahedral geometries and that cobalt facilitated ligand to ligand charge transfer to redox active pi star orbitals.