Steric Effects Associated with the Photolysis of $[Ru(biq)_2(dpb)](PF_6)_2$ and $[Rb(biq)_2(CH_3CN)_2](PF_6)_2$

Samuel J. Lenze, Amber Harding, Kaitlyn Wyland, Avijita Jain and Charles H. Lake
Department of Chemistry, Indiana University of Pennsylvania, Indiana, PA 15705
Email Contact: rqbw@iup.edu

This study will use ligand steric parameters to investigate the photosensitivity of the compounds $[Ru(biq)_2(dpb)]^{2+}$ and $[Ru(biq)_2(dpb)Re(CO)_4]^{2+}$ (biq = 2,2'-bipyridine and dpb = 2,3-bis(2-pyridyl)benzoquinoxaline). The former compound photocatalytically decomposes into $[Ru(biq)_2(CH_3CN)_2]^{2+}$ while the latter remains inactive. X-ray data for $[Ru(biq)_2(dpb)](PF_6)_2$ and $[Ru(biq)_2(CH_3CN)_2](PF_6)_2$ were collected at the Advanced Light Source through the SCRALS program [1]. $[Ru(biq)_2(dpb)Re(CO)_4]^{2+}$ was previously investigated by Albani et al. [2] . The solid angle (Ω), G-parameter (% metal coordination sphere shielded by the ligand) and steric congestion (Γ) will be evaluated through the use of the Solid-G program package [3].

In the complex $[Ru(biq)_2(dpb)]^{2+}$, the biq-ligands were closer to the metal center than the dpb-ligand (average Ru-N distance of 1.636 Å versus 1.661 Å, respectively) and possess larger G^x-parameters (36.28 % versus 32.61 %, respectively). The steric congestion G(Γ) associated with this complex was calculated to be 8.98 % and the unfavorable interactions associated between the ligands (V_G) was 0.27 $Å^3$. These parameters represent significant steric interactions between the ligands. Upon photolysis the complex decayed into $[Rb(biq)_2(CH_3CN)_2]^{2+}$ where V_G and steric congestion decreased to 0.11 $Å^3$ and 8.31 %, respectively, which indicate a relaxation of the steric interactions. The average Ru-N distances decreased slightly with average Ru-N distances of 1.620 Å increasing the G^x-parameters associated with the biq ligands to 36.61 %. The sterics interactions of $[Ru(biq)_2(dpb)]^{2+}$ will also be compared to the bimetallic compound $[Ru(biq)_2(dpb)Re(CO)_4]$. The coordination of the Re-moiety increases V_G to 0.39 $Å^3$, thus increasing the steric strain while lowering the overall Metal-Ligand-Charge-Transfer energy.

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