

Ocean Optics Program A Educational Cost Sharing Award, Grant #171

Robert A. Holwerda

Department of Chemistry and Biochemistry

Texas Tech University

June 11, 2004

We propose to prepare dinuclear V(IV) and V(V) complexes containing three distinct classes of bridging group: 1) monatomic dianions: O^{2-} , S^{2-} , Se^{2-} ; 2) substituted hydroquinone dianions, i.e. $[OC_6H_{4-x}Y_xO]^{2-}$ (Y = alkyl, halogen, hydroxo or amino group); or 3) pyrazine (NC_4H_4N) and related conjugated diamine ligands. Characterization will include 1) X-ray structural studies of members from each bridging group class; 2) uv-visible and fluorescence spectroscopic investigations to identify distinctive electronic transitions associated specifically with the bridging unit; 3) infrared tracking of V=O stretching frequencies as a probe of electron density at the vanadium centers; 4) 1H and ^{13}C NMR measurements of the extent to which bonding within diamine ligands is perturbed by incorporation into a bridging unit; and 5) X-ray photoelectron spectroscopy to define occupied molecular orbital energies. Electrochemical measurements of comproportionation equilibrium constants will be used to assess the dependence of V(IV,V) complex stability on both bridging and non-bridging ligands. Finally, the availability of a complete set of related V(IV,IV), V(IV,V) and V(V,V) complexes offers a rare opportunity to compare the dynamics of one-electron and two-electron transfer processes for a particular vanadium reductant or oxidant. Research targets have been chosen to be suitable for undergraduate research students at the junior, senior level. The primary educational goal is to expose students to a broad range of inorganic instrumental techniques, with primary emphasis on both static and dynamic applications of uv-visible electronic and fluorescence spectroscopies.