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of Di-halide Complexes
PHOTOCHEMISTRY ~~AND CHARGE TRANSFER CHEMISTRY~~
OF THE PLATINUM GROUP ELEMENTS

Progress Report

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SUMMARY OF PROGRESS IN YEAR ONE

During the current grant period, significant progress has been achieved on the photochemistry and photophysics of dithiolate complexes of the platinum group elements. Major efforts continue to focus on square planar complexes of platinum(II) of formula $\text{PtL}_2(\text{S-S})$ where S-S is a dithiolate and L_2 represents α,α' -diimine, diphosphine or diolefin chelating ligand or pairs of monodentate $2e^-$ donors. In previous studies supported by DOE, we have established that all complexes of this type prepared to date are emissive in rigid media at 77 K and that for $\text{L}_2 = \text{bpy}$, phen and alkylated derivatives, the complexes exhibit rare solution luminescence. These studies have also shown that the diimine dithiolate complexes possess a very solvent sensitive charge transfer band, the nature of which has been determined to be a mixed metal/ligand-to-ligand charge transfer (MMLCT) by systematic ligand substitution. Despite similarities in their absorption spectra, complexes **1** and **2** have been found to possess different emissive states through low temperature emission and lifetime studies, and the conclusions were found to be in accord with semi-empirical Huckel molecular orbital calculations.

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During the current year, studies on the preparation, characterization and emission spectroscopy of $\text{PtL}_2(\text{S-S})$ where $\text{L}_2 = 1,5\text{-cyclooctadiene (COD)}$ and phosphine or diphosphine ligands have appeared or are in press. These investigations which include crystal structure determinations of several systems led to the conclusion that for all of these complexes the emissive state is of the metal-to-ligand charge transfer type (MLCT) involving a π^* orbital of the dithiolate ligand. In previous studies, it was demonstrated that complexes **1** and **2** undergo electron transfer quenching of the excited state with both donors such as dimethylaniline and acceptors such as o-nitrobenzaldehyde. The current year has witnessed completion of a study on the reductive quenching of the phen derivative **3** including an estimation of the excited state reduction potential based on a graded series of amine quenchers and a Marcus analysis of the results and on a simple thermochemical cycle using the measured reduction potential $E_{1/2}$ for the process $\mathbf{3} \longrightarrow \mathbf{3}^\bullet$ and E_{00} of the excited state. Both methods yield a value of *ca.* 1.0 v vs SCE. A paper describing this study is in press.

The range of luminescent platinum complexes was extended during the past year through the synthesis and characterization of new systems containing dithiolate ligands other than those in **1** and **2**. In one study, analogs of **1** were prepared that contained the dithiolate ligand met (**4**) which yields complexes having substantially greater solubility. Crystal structure determinations and emission spectroscopy were conducted on several representative systems. The complex $\text{Pt}(\text{Me}_2\text{bpy})(\text{met})$ was found to have a highly structured emission spectrum with a major progression of 1175 cm^{-1} consistent with emission results observed for the structurally analogous met complexes **1**. Cationic $\text{Pt}(\text{II})$ complexes in which the dithiolate was replaced by the monoanionic ligand dithiocarbamate were also synthesized, and for the complex containing Me_2bpy , solution luminescence was observed. A common MLCT ($d-\pi^*$ dithiolate) emissive state was assigned for all of the complexes that did not contain a diimine ligand. However, further studies are needed for analysis of the emissive state of the solution luminescent diimine systems. A manuscript describing this study is in press.

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Another interesting series of complexes was synthesized using quinoxaline-2,3-dithiolate (qdt), **5**. The diolefin complex $\text{Pt}(\text{COD})(\text{qdt})$ exhibits a highly structured emission in frozen glass solution with a major vibrational progression of 1370 cm^{-1} corresponding to a $\text{C}=\text{C}$ stretching frequency of the quinoxalinedithiolate backbone. Solution emissions from $(\text{TBA})_2[\text{Pt}(\text{qdt})_2]$ and $\text{Pt}(\text{phen})(\text{qdt})$ have been detected with quantum yields, Φ_{em} , of 10^{-5} and 10^{-3} respectively, although the latter is highly sensitive to solvent effects. Like other diimine dithiolate complexes, $\text{Pt}(\text{phen})(\text{qdt})$ possesses a low energy MMLCT absorption band which exhibits a high degree of negative solvatochromism. Reductive quenching of the excited state of $\text{Pt}(\text{phen})(\text{qdt})$ has been examined using aromatic amines and an excited state reduction potential of 1.2 eV (vs SCE) has

been estimated. The acid-base behavior of both the ground and excited states of $\text{Pt}(\text{qdt})_2^{2-}$ and $\text{Pt}(\text{phen})(\text{qdt})$ have been examined since the complexes exhibit pH-dependent changes in both absorption and emission spectra. For $\text{Pt}(\text{qdt})_2^{2-}$, single protonation leads to a large red-shift of the low energy $d(\text{Pt})-\pi^*(\text{qdt})$ MLCT absorption band and the emergence of a new red-shifted emission feature at 728 nm. In solutions of pH below 6, a second protonation takes place at the other qdt ligand, yielding $\text{Pt}(\text{Hqdt})_2$ which has been isolated and characterized. The ground-state acidity constants for the two qdt protonations have been determined from spectrophotometric titrations to be $\text{pK}_{a1} = 7.1$ and $\text{pK}_{a2} = 5.6$. We are currently in the process of determining the excited state pK_a^* for $\text{Pt}(\text{qdt})_2^{2-}$.

Regarding a different aspect of the light driven chemistry of dithiolate complexes of the platinum group elements, we have completed a study of the photochemistry of the Ir(III) alkyl complexes $\text{IrR}(\text{CO})\text{L}_2(\text{mnt})$ ($\text{R} = \text{Me}, \text{Et}, \text{Bz}$; $\text{L} = \text{PAr}_3$). These unusual luminescent alkyl systems have been reported to undergo M-R bond homolysis in preference to CO photodissociation as has been observed for other metal alkyl carbonyl complexes such as $\text{CpFeR}(\text{CO})_2$. In a detailed examination of the β -elimination shown as eq (1), we have determined that CO does not exchange into **6** during the course of the reaction. This result, combined with

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evidence of radical trapping in the photolysis of $\text{IrMe}(\text{CO})(\text{PPh}_3)_2(\text{mnt})$, clearly supports preferential homolysis of Ir-R over CO photodissociation. The nature of the photoactive state in $\text{IrR}(\text{CO})\text{L}_2(\text{mnt})$, however, is not unambiguously established and may be of either a $\sigma^b-\pi^*_{\text{mnt}}$ SBLCT or a $d-\pi^*_{\text{mnt}}$ MLCT type. A paper describing this study is in press to *J. Am. Chem. Soc.*

During the coming year efforts will continue to focus on the photochemistry of square planar dithiolate complexes in the context of light to chemical energy conversion and whether these systems can be employed as chromophores for the reduction of water. Additionally, efforts will move forward in the synthesis and characterization of d^7 odd electron systems that have been proposed to be effective in the activation of stable substrates such as CO and C-H bonds.

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