

Acknowledgment. We thank Dr. D. M. Cox of Exxon Research for helpful conversations and for relating preliminary experimental results on the CID of Mn^{2+} . Financial support was provided in part by Research Corp. P.B.A. gratefully acknowledges a Dreyfus Fellowship.

Electron-Transfer Reactions and Luminescent Quantum Yield of the Triplet Excited State of Tetrakis[λ -diphosphito(2-)-P,P']diplatinate(II)

William B. Heuer, Mark D. Totten, Gary S. Rodman, Eric J. Hebert, Henry J. Tracy, and Jeffrey K. Nagle*

Department of Chemistry, Bowdoin College
Brunswick, Maine 04011

Received September 28, 1983

In the short period following the isolation and crystal structure determination^{2,3} of $Pt_2(P_2O_5H_2)_4$ ($Pt_2(pop)_4^{4-}$), many studies have focused on its intense luminescence⁴⁻¹⁵ and the related possibility of metal-metal bonding.⁵⁻⁶⁻⁸⁻¹¹⁻¹⁵ Although much is now known concerning the detailed nature of the lowest luminescent excited state, only a brief report⁶ has appeared describing its photoredox properties. Here we report the results of excited-state electron-transfer quenching studies of $Pt_2(pop)_4^{4-}$ in methanol and also its luminescent quantum yield in aqueous solution. It is demonstrated that the triplet excited state of $Pt_2(pop)_4^{4-}$ is reduced to $Pt_2(pop)_4^{5-}$ by a series of aromatic amine quenchers and shows great promise as a photoredox catalyst.

Quenching studies were performed by standard techniques¹⁶ and analyzed using the Stern-Volmer equation¹⁷ to yield values of k_{icq} , the second-order quenching rate constant. These values are presented in Table I. To correct for diffusion and encounter effects,¹⁸ values of k_{icq} were converted to first-order electron-transfer rate constants k_a by $k_{icq} = [K(k_f' / k_{ed} + 1)]^{-1}$, where k_d is the diffusion rate constant for formation of the encounter complex with equilibrium constant A .¹⁸

(1) Sperline, R. P.; Dickson, J. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* 1977, 62-63.

(2) Filomena Dos Remedios Pinto, J. A.;

the hypothesis of electron-transfer quenching. Observation of separated redox products by flash photolysis would be unlikely in view of the Coulombic forces involved. A plot of $(RT/F) \ln k_a$ vs. amine ϵ_{ly-2} values is shown in Figure 1.

A value of 1.1 ± 0.2 V for $E^{\circ}(\text{Pt}2(\text{pop})44^{+/5-})$ is obtained by fitting the data in Table I to the equation

$$(RT/F) \ln k_{tt} = ((RT/F) \ln n_{6t}) \cdot (X(I + AG/X)^{2/4}) \quad (1)$$

where $AG = E^{\circ}(\text{NR}3+^{\circ}) - E^{\circ}(\text{Pt}2(\text{pop})44^{+/5-}) + w_p - w_r$, and w_r are Coulombic work terms¹⁶ and ν_{cl} is the frequency and X the reorganization energy for electron transfer.²⁰ This value is larger than the corresponding values of 0.8 V