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Highly Oxidizing Excited States of Re and Tc Complexes

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The newly observed ligand-to-metal charge transfer (LMCT) excited-state of $[Tc(dmpe)_3]^{2+}$ (dmpe is bis-1,2-(dimethylphosphino)ethane) is fluorescent in solution at room temperature, as is its Re analogue.[1] Of significance to transition metal photochemistry, we have discovered that both $[M(dmpe)_3]^{2+*}$ species have extremely oxidizing excited-state potentials (ESPs)—the highest for any simple coordination complex of a transition metal. Furthermore, this potential is available using a photon of visible light. Luminescent Tc complexes have fundamental significance since direct comparisons of rate constants of radiationless and radiative processes can be made with their Mn and Re analogues[2] providing invaluable information for understanding the nature of excited-state potential surfaces and their associated reaction channels. Further practical applications of luminescent Tc complexes include the spectroelectrochemical detection in biological fluids (e.g., during drug therapy) and in the environment.[3]

Recently we have embarked on a program to discover and characterize luminescent Tc complexes by examining known complexes that possess Re analogues with room-temperature luminescence. This Communication describes the newly discovered emission behavior of $[Tc(dmpe)_3]^{2+}$ in relation to that previously reported for $[Re(dmpe)_3]^{2+}$.[3]

The complex $[Tc(dmpe)_3]^{2+}$ was prepared as previously described[4] and isolated as the purple triflate or hexafluorophosphate salt. In CH_3CN solution, the lowest energy absorption maximum occurs at 585 nm ($\epsilon = 1850$ $M^{-1}cm^{-1}$) as compared to the Re analogue at 528 nm ($\epsilon = 2110$ $M^{-1}cm^{-1}$) (Figure 1). The Tc complex emits at 660 nm with a lifetime of 8 ns compared to the Re complex at 600 nm with a lifetime of 14 ns.[5] The quantum yields are 0.023 and 0.066, respectively. Of particular note is that the excited state is not affected by the presence of air. The principal cause of the difference in ϕ and τ between Tc and Re is expressed principally in a larger nonradiative decay rate constant (1.2×10^8 s^{-1} vs 5.2×10^7 s^{-1}), which is consistent with M−P vibrations contributing as acceptor modes, since they are the only modes which are substantially perturbed by the change of metal ion. Attempts to resolve vibronic structure at 77 K (in 3:1 EtOH/MeOH) resulted only an increase in intensity and a decrease in bandwidth.

Assignment of the lowest energy transitions in both complexes to doublet−doublet processes that involve predominantly LMCT (dmpe-to-metal) in character is supported by unrestricted open-shell TDDFT calculations.[6] This is in agreement with the conclusions of Lee and Kirchhoff in their original work on $[Re(dmpe)_3]^{2+}$.[3] Our calculations for the Tc(Re) complexes predict the transition energies to be 2.46 eV (2.63) compared with the observed absorption energies of 2.12 eV (2.35). As in our previous study on *trans*-$[O_2M(L)_4]^+$ complexes,[1] the correct relative ordering of energies is predicted. The compositions of the lowest energy transition for the Tc(Re) complexes are nearly identical, that is, 86% dmpe to 79.9% Tc (83.5% dmpe to 77.4% Re), which in terms of the ligand contribution contains 52.8%(51.5%) P character. The picture of the excited-state that emerges is one in which the metal is near +1 in oxidation state owing to a hole on a dπ orbital, and where electron density has been removed from all dmpe ligands (and all P atoms). An additional, intriguing feature of the calculations is the prediction of two extremely low-lying transitions at about 0.3 V above the ground state that are intra-dπ in nature, suggesting the possibility of a competitive emission that terminates at these higher states. Multiple exponential fitting of the emission decays was not successful in resolving this issue, however (293 K).

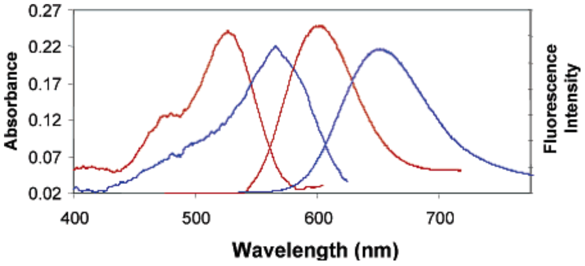

Figure 1. Absorption and emission spectra of $[M(dmpe)_3]^{2+}$ in CH_3CN (red is Re and blue is Tc).

The narrow bandwidths of absorption and emission coupled with the spin-allowed nature of the transition make the estimation of the excited-state potential (ESP) an easier task than for many transition-metal complexes. Using the "mirror image" relationship between absorption and emission, the determination of E_{0-0} can be made more accurately than in the case of MLCT triplet emitters, since for the latter the lowest energy singlet−triplet absorption is rarely observed without interference from the singlet manifold.[7] Indeed, the ESP values of $E_{1/2}(M^{2+*}/M^+)$ are calculated to be 2.52(2.61) V (versus SCE) using the ground state potentials of 0.48 V (Tc) and 0.40 V (Re). Previous work has identified very few highly oxidizing excited states, among them, however, $[Re(bpy)(CO)_4]^+$,[8] $[Pt(5,6\text{-}Me_2phen)(dppe)]^{2+}$,[9] uranyl ion,[10] and polyoxometalates[11] such as $\alpha\text{-}HP_3W_{12}O_{40}\cdot 6H_2O$ are prominent (bpy is 2,2-bipyridine, 5,6-Me_2phen is 5,6-dimethyl-1,10-phenanthroline and dppe is bis-1,2-(diphenylphosphino)ethane). The $[M(dmpe)_3]^{2+}$ complexes appear to have as high or higher potentials than these, and absorb strongly in the visible, making them suitable for solar energy conversion to store oxidizing equivalents. As expected from such high ESPs, quenching by aromatic hydrocarbons is observed for both complex excited states. Figure 2a shows an example of Stern−Volmer data for mesitylene quenching of $[Tc(dmpe)_3]^{2+*}$. Figure 2b shows our experimental estimation of $E_{1/2}(Re^{2+*}/Re^+)$ using a Rehm−Weller rate constant/driving force relationship[12] derived from the luminescence quenching of $[Re(dmpe)_3]^{2+*}$ by a series of substituted aromatic hydrocarbons. The fitted line corresponds to

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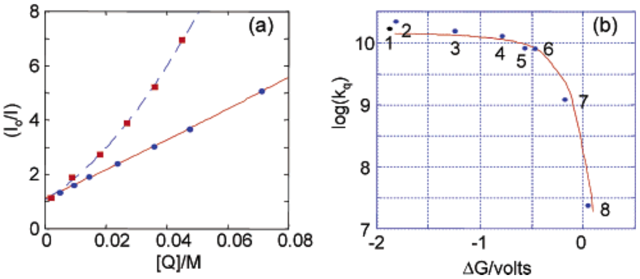

Figure 2. (a) Stern−Volmer quenching of $[M(dmpe)^3]^{2+*}$ by mesitylene (●) (M = Tc, CH_3CN) and 4-chlorophenol (■) (M = Re, H_2O);[12c] (b) Rehm−Weller plot for the Stern−Volmer quenching of $[Re(dmpe)^3]^{2+*}$ by aromatic hydrocarbons in CH_3CN solution.[12c]

the excited-state oxidation potential of +2.58 V (SCE), which is close to that calculated. Of particular note is the fact that *benzene and toluene are oxidized*. It is somewhat surprising that no direct evidence for the Marcus inverted region is found given the presumed lack of large reorganizational energies for the quenchers and the Re(II/I) redox pair.[13] Although we have not examined the $[Tc(dmpe)_3]^{2+*}$ quenching reaction in as much detail, the Stern−Volmer derived quenching rate constant for toluene, mesitylene and anisole are 3.0×10^8, 7.6×10^9, and 1.9×10^{10} $M^{-1}s^{-1}$, respectively, which compares with 8.0×10^8, 8.1×10^9, and 1.3×10^{10} $M^{-1}s^{-1}$ for the Re complex. The quenching rate constants for the former two are consistent with the slightly lower ESP of the Tc complex.

Although $[Re(dmpe)_3]^{2+*}$ is quenched by Br^-, the more interesting case is the steady-state luminescence quenching by Cl^- in acetonitrile solution. Here an upward curving Stern−Volmer (SV) plot is found, consistent with a large static quenching component for Cl^- oxidation in an ion pair, as nicely demonstrated in a recent paper on I^- quenching of $[Ru(bpy)_3]^{2+*}$.[14] Direct chloride ion quenching of transition-metal excited states is rarely reported.

A useful aspect of these highly oxidizing excited states is their ability to function under aqueous conditions. In water the lifetime of $[Re(dmpe)_3]^{2+*}$ is somewhat shorter (11.0 ns) than in acetonitrile and is unaffected by the presence of air. Photolysis in air with a 200 W quartz−halogen lamp of a 9.9×10^{-5} M solution of $[Re(dmpe)_3]^{2+}$ for 1 h showed no change in the electronic spectrum. Stern−Volmer quenching by several unusual substrates was examined. For Ce^{3+}(aq) quenching is observed but a reliable rate constant was not determined because of the quantity of substrate necessary (and consequent change in ionic strength). Interestingly, for 4-chlorophenol an upward curving S−V relationship is found (Figure 2a). The origin of this is currently under investigation.

Since none of the substrates in Figure 2b possess excited states below that of $[Re(dmpe)_3]^{2+*}$ it is reasonable to assume that there is no energy transfer quenching, but that single electron-transfer quenching via oxidation of the hydrocarbon substrate occurs. Beside the prima facie evidence from the Rehm−Weller analysis, support for this mechanism comes from a steady-state experiment where redox products are detected directly. When a CH_3CN solution of 1.42×10^4 M $[Re(dmpe)_3]^{2+}$ containing 0.02 M 10-methylphenothiazine (MePTZ) and 0.3 M $HClO_4$ is irradiated with a 200 W quartz−halogen lamp, UV−visible spectroscopy shows the progressive production of the MePTZ radical cation.[15] After 40 min a ratio of 0.60/1 $MePTZ^{+\bullet}$/Re is found. This irreversible behavior is rationalized by the photooxidation of MePTZ by $[Re(dmpe)_3]^{2+*}$ followed by autoxidation of $[Re(dmpe)_3]^{+}$ to regenerate the starting complex.

Transition-metal complexes that absorb visible photons to produce highly oxidizing excited states are rare species but have great potential in solar energy conversion applications. Examples include photogeneration of molecular chlorine, or use in regenerative photoelectrochemical cells where the valence band oxidation of the semiconductor is utilized. Other low spin d^5 complexes are likely to exhibit similar behavior if the intervening low-lying excited states are close in energy to the ground state so that radiationless decay rate constants are minimized.

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Supporting Information Available: DFT/TDDFT calculations for the complexes and complete ref 6 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Lee, Y. F.; Kirchhoff, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 3599. (b) Kirchhoff, J. R.; Allen, M. R.; Cheesman, B. V.; Okamoto, K.; Heineman, W. R.; Deutsch, E. *Inorg. Chim. Acta* **1997**, *262*, 195.
(2) Del Negro, A. S.; Wang, Z.; Seliskar, C. J.; Heineman, W. R.; Sullivan, B. P.; Hightower, S. E.; Hubler, T. J.; Bryan, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 14978.
(3) (a) Stegemiller, M. L.; Heineman, W. R.; Seliskar, C. J.; Ridgway, T. H.; Bryan, S. A.; Hubler, T. L.; Sell, R. L. *Environ. Sci. Technol.* **2003**, *37*, 123. (b) Kaval, N.; Seliskar, C. J.; Heineman, W. R. *Anal. Chem.* **2003**, *75*, 6334.
(4) (a) Vanderheyden, J. L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roeker, L.; Motz, P.; Whittle, R.; Elder R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184. (b) Vanderheyden, J. L. *Dissertation* **1985**, University of Cincinnati.
(5) Instrumentation for fluorescence luminescence measurements is described in Wang, Z.; Hemmer, S. L.; Friedrich, D. M.; Joly, A. G. *J. Phys. Chem. A* **2001**, *105*, 6020.
(6) Electronic ground state and geometry optimization were carried out using the B3LYP approximation, followed by TDDFT calculation of the lowest excited states employing the same functional. Calculations utilized the 6−31G* basis set for the ligands and the LANL2 relativistic effective core potential (RECP) for the transition metal: Frisch, M. J.; et al. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(7) (a) Vlcek, A. A.; Dodsworth, E. S.; Pietro, W. S.; Lever, A. B. P. *Inorg. Chem.* **1995**, *34*, 1906. (b) Del Negro, A. S.; Sullivan, B. P. *The Spectrum*, **2006**, *19*, 12.
(8) Shaver, R. J.; Rillema, D. P. *Inorg. Chem.* **1992**, *31*, 4101.
(9) Wan, K.-T.; Che, C. M. *J. Chem. Soc., Chem. Commun.* **1990**, 140.
(10) Sarakha, M.; Bolte, M.; Burrows, H. D. *J. Phys. Chem. A* **2000**, *104*, 3142.
(11) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148.
(12) (a) Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259. (b) Hydrocarbon potentials were taken from Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968. (c) The hydrocarbons in Figure 2b are (1) 10-MePTZ, (2) dimethylaniline, (3) p-dimethoxybenzene, (4) anisole, (5) mesitylene, (6) p-xylene, (7) toluene, and (8) benzene.
(13) The electron transfer quenching rate constant of $Ru(bpy)_3^{2+*}$ by $Re(dmpe)_3^{+}$ is 1.5×10^9 $M^{-1}s^{-1}$, consistent with a small reorganizational energy.
(14) Marton, A.; Clark, C. C.; Srinivasan, R.; Freundlich, R. E.; Narducci, S.; Amy, A.; Meyer, G. J. *Inorg. Chem.* **2006**, *45*, 362.
(15) Electronic spectral data for 10-MePTZ is from Wagner, E.; Filipek, S.; Kalinowski, M. *Monatsh. Chem.* **1988**, *119*, 929.

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