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Communications to the Editor

Luminescent Ligand-to-Metal Charge-Transfer Excited States Based on Pentamethylcyclopentadienyl Complexes of Tantalum

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Understanding of the photochemistry and photophysics of complexes with metal-to-ligand charge-transfer (MLCT) excited states has developed rapidly over the last 20 years. In fact, it has evolved to the point that application to energy conversion processes is now a predominant focus.[1] This success can be traced directly to an understanding of the photophysics and photochemistry of complexes of the type M(bpy)$_3^{n+}$ (M is Ru, *n* is 2; M is Os, *n* is 2; M is Ir, *n* is 3)[1] and M(bpy)$_2$L$_2^{2+}$ (M is Ru and Os, and L can be variety of neutral 2-electron donor ligands),[1,2] which has reached a level of sophistication so that design of chemically stable photosensitizers with prescribed excited-state lifetimes and redox potentials can be realized by synthetic manipulation of the coordination sphere. Despite this success, there exists a whole class of complexes whose excited-state properties has been largely ignored—those containing ligand-to-metal charge-transfer (LMCT) excited states. Early examples[3] of photochemical reactions from LMCT excited states are found in the classic series Co^{III}(NH$_3$)$_5$X^{2+}, where charge transfer from halide to Co(III) results in photoreduction to Co(II) and the formation of halide radicals. However, studies of complexes containing LMCT excited states by emission spectroscopy and transient spectroscopic measurements are virtually nonexistent.[4,5]

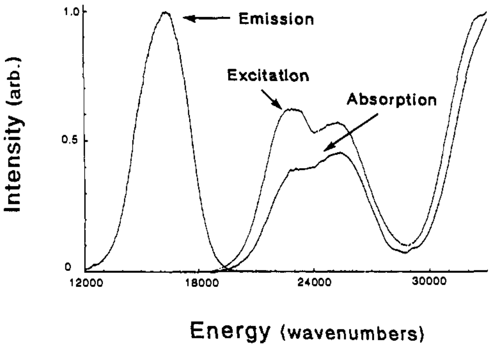

Figure 1. Absorption, excitation, and emission spectral data for Cp*TaCl$_3$(CH$_3$CO$_2$) in CH$_2$Cl$_2$ solution at room temperature (23 °C).

Our approach to the discovery of new LMCT excited states is to concentrate on those complexes that contain oxidizable donor ligands coordinated to early or middle transition metals of d^0 electron configuration, for example, Ta(V). The photochemistry and photophysics of these LMCT excited states promise to be very different than those of the MLCT excited states previously investigated, in that the coordinately unsaturated and potentially substitution-labile Ta(V) center can be the locus for many interesting, potentially catalytic reactions. It should be pointed out that such complexes will not suffer from the degradative pathways characteristic of MLCT complexes of Ru(II) where thermal activation of d–d states leads to ligand loss resulting in destruction of the useful properties of the chomophore.[6]

Here we report the excited-state properties of the complex Cp*TaCl$_4$ and the derivative Cp*TaCl$_3$(OO) (where OO is a bidentate oxygen donor such as a carboxylic or sulfonic acid),[7] which exhibit long-lived luminescence in fluid solution and can have quantum efficiencies for emission of up to 16% (23 °C).

Key to unraveling the photophysical picture is our ability to make closely related derivatives of Cp*TaCl$_4$. Substitution of Cl$^-$ can be achieved with either other halides to form Cp*TaX$_4$ or with oxygen-containing ligands such as acetylacetone, alkylphosphonic or sulfonic acids, carboxylic acids, or even electron-poor acid anions such as CF$_3$SO$_3^-$ to form the bidentate substituted complexes Cp*TaCl$_3$(OO). In addition, Cp*TaCl$_4$ recently has been shown[7] to form monodentate adducts with neutral donors such as phosphines to give complexes of the type Cp*TaCl$_4$L.[7] To support our photophysical studies, we have obtained preliminary X-ray crystal structures of formally seven-coordinate Cp*TaCl$_4$ and its formally eight-coordinate derivative Cp*TaCl$_3$(CF$_3$SO$_3$).[8] Cp*Ta^{V}Cl$_4$ has a slightly distorted "piano-stool" geometry with a Ta–Cp* separation of 2.101 Å, Ta–Cl bond lengths that vary from 2.347 to 2.363 Å, and Cp*Ta–Cl angles of ca. 100°. In contrast, the methanesulfonate derivative has a "piano stool" composed of three chlorides and a single oxygen of a bidentate CF$_3$SO$_3$ group. The Cp* ligand axis now is nearly 90° to the Cl$_3$O plane. The second oxygen of the bidentate CF$_3$SO$_3$ group occupies

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(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, F.; Belser, P.; Von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193. (c) Crosby, G. A.; Highland, K. A.; Truesdell, K. A. *Coord. Chem. Rev.* **1985**, *64*, 41. (d) DeArmond, M. K.; Hanck, K. W.; Wertz, D. W. *Coord. Chem. Rev.* **1985**, *65*, 65. (e) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.

(2) (a) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587. (b) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755. (c) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *e*, 1242. (d) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

(3) See, for example: Endicott, J. F. In *Concepts of Inorganic Photochemistry*, Wiley-Interscience: New York, 1975; p 81.

(4) Room-temperature fluid solution emission from LMCT excited states is very rare. Two examples are known to us: (a) Bandy, J. A.; Cloke, G. N.; Cooper, G.; Day, J. P.; Girling, R. B.; Graham, R. G.; Green, J. C.; Grinter, R.; Perutz, R. N. *J. Am. Chem. Soc.* **1988**, *110*, 5039. (b) Pfennig, B. W.; Thompson, M. E.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1989**, *111*, 8947.

(5) Representative examples of photochemistry orginating from assigned LMCT excited states of the early transition metals are found in the following: (a) Abramson, H. B.; Brandenburg, K. L.; Lucero, B.; Martin, M. E.; Dennis, E. *Organometallics* **1984**, *3*, 1379. (b) Brubaker, C. L.; Tung, H.-S. *Inorg. Chim. Acta* **1981**, *52*, 197. (c) Aliwi, S. M.; Bamford, C. H. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 776. (d) Chamberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, *106*, 1847. (e) Van Leeuwen, P. W. N. M.; Van Der Heijden, H.; Roobeek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169. (f) Timmers, F. J.; Scheidt, W. R.; Labinger, J. A.; Baral, S. *J. Organomet. Chem.* **1982**, *240*, 153. (g) Baynham, R. F. G.; Chetwynd-Talbot, J.; Grebenik, P.; Perutz, R. N.; Powell, M. H. A. *J. Organomet. Chem.* **1985**, *284*, 229.

(6) (a) Van Houton, J.; Watts, R. J. *J. Am. Chem. Soc.* **1978**, *17*, 3381. (b) Gleria, M.; Minto, F.; Baggiato, Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1978**, 285. (c) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860. (d) Durham, B.; Pinnick, *Inorg. Chem.* **1984**, *23*, 3841. (e) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583. (f) Wacholtz, W. M.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1986**, *25*, 227.

(7) (a) Gibson, V. C.; Bercaw, J. E. *Organometallics* **1986**, *5*, 976. (b) Sanner, R. D.; Carter, S. T.; Bruton, W. J. *J. Organomet. Chem.* **1982**, *240*, 157.

(8) Preliminary X-ray crystal structure data has been supplied by the Molecular Structure Corporation. These will be discussed in depth in a forthcoming paper.

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Table I. Photophysical Parameters for $Cp^*Ta^VCl_4$ and Derivatives

complex[a]	E_{em} (cm^{-1})	$\phi(296)$	$\tau(296)$ (ns)	K_r ($\times10^{-3}$)[b]	k_{nr} ($\times10^{-4}$)[c]	k_0[d]	E_a (cm^{-1})[d]	ϕ_c[e]	τ_c (ns)[e]
Cp^*TaCl_4 (**1**)	17300	0.0019	926	2.1	2.0	1.5×10^{10}	1949	0.0018	857
$Cp^*TaCl_3(PhCO_2)$ (**2**)	16520	0.1100	7039	16.0	7.0	2.6×10^{13}	4105	0.1114	6962
Cp^*TaCl_3(*p*-*t*-$BuPhCO_2$) (**3**)	16340	0.1600	5819	28.0	6.8	3.7×10^{13}	4104	0.1569	5605
$Cp^*TaCl_3(CD_3CO_2)$	16290	0.1100	7225	15.0	7.1	1.7×10^{10}	2624	0.1103	7356
$Cp^*TaCl_3(CH_3CO_2)$ (**4**)	16290	0.0570	8152	7.0	7.4	7.0×10^{9}	2469	0.0562	8023
$Cp^*TaCl_3(CH_3SO_3)$ (**5**)	16022	0.0056	945	5.9	23.0	4.5×10^{14}	4150	0.0058	964

[a] In CH_2Cl_2 solution. [b] Calculated from $k_r = \phi(296)/\tau(296)$ (in s^{-1}). [c] Calculated (in s^{-1}) from the temperature dependence of the complexes from 185 to 296 K by use of the following equation: $\phi(T) = k_r/(k_r + k_{nr} + k_0 \exp(-E_a/kT))$. [d] Pre-exponential k_0 (in s^{-1}) and activation energy E_a obtained from the fit of the temperature dependence of the complexes from 185 to 296 K by use of the equation: $\phi(T) = k_r/(k_r + k_{nr} + k_0 \exp(-E_a/kT))$. [e] Room-temperature values (296 K) calculated from $\phi(T) = k_r/(k_r + k_{nr} + k_0 \exp(-E_a/kT))$.

a position that is roughly trans to the Cp* ring, so that the structure approximates an octahedron with a Cl_3O plane and apical oxygen and Cp* substituents.

The visible absorption manifold of $Cp^*Ta^VCl_4$, which is centered at 440 nm (ϵ_{max} is 4500 ± 500 M^{-1} cm^{-1}), and the corresponding emission at 575 nm both involve states that are predominantly $Cp^{*}\cdot Ta^{IV}Cl_4$ in character. These assignments are supported by substitution studies. For example, substitution of Cp* for the more electron-donating indenyl (In) group in $(\eta^5\text{-In})Ta^VCl_4$ produces a profound red shift in the absorption spectrum (440 to 504 nm; CH_2Cl_2 at room temperature) and a similar shift in the emission maximum (581 to 707 nm; solid, 296 °C). By contrast, substitution of Br^- for Cl^- produce $Cp^*Ta^VBr_4$ results in a smaller redshift: that is, a shift in the emission spectrum from 575 to 605 nm (CH_2Cl_2).

The absorption, excitation, and emission spectral data for a carboxylic acid derivative $Cp^*TaCl_3(CH_3CO_2)$ is shown in Figure 1. Of note is the general blue shift of the absorption spectrum but the red shift of the emission maximum in the carboxylic acid derivative relative to the parent. The blue shift in the absorption spectrum is consistent with the general LMCT $Cp^* \rightarrow Ta(V)$ assignment since the 16-electron, formal eight-coordinate adduct should be less easily reduced than the 14-electron parent. The red shift of the emission maximum could be related to a greater excited-state distortion for $Cp^*TaCl_3(CH_3SO_3)$ compared to $Cp^*Ta^VCl_4$. The charge-transfer nature of the emission is also supported by the fact that a large solvent shift of E_{em} occurs. For $Cp^*TaCl_3(CH_3SO_3)$ and $Cp^*Ta^VCl_4$, E_{em} changes from 605 to 591 nm and from 575 to 559 nm, respectively, on changing the medium from CH_2Cl_2 to toluene.

Table I shows photophysical data in CH_2Cl_2 for $Cp^*Ta^VCl_4$ and five other derivatives of the chelating acid type at room temperature (23 °C) and at low temperature. In the table, E_{em}, the room-temperature quantum yield $\phi(296)$, and the room-temperature excited-state lifetime $\tau(296)$ are shown. One particularly striking feature is that the quantum yields surpass many of the more familiar MLCT ϕ values found for the $Ru^{II}(bpy)$ chromophore.[6] The lifetime of the acetato derivative is extraordinary, being an order of magnitude greater than $Ru(bpy)_3^{2+}$ under similar conditions.

In addition, Table I presents the radiationless decay rate, k_{nr}, and the radiative decay rate, k_r, which have been calculated from data obtained from a combination of room-temperature and variable-temperature quantum yield and lifetime measurements. The procedure was first to determine k_r at room temperature via determination of $\tau(296)$ and $\phi(296)$. Using this value of k_r, emission yields determined in methylene chloride over the range 296–185 K (just above the solvent's freezing point) were fit to the function

$$\phi(T) = k_r/(k_r + k_{nr} + k_0 \exp(-E_a/kT)) \quad (1)$$

in order to extract values of k_0, k_{nr}, and E_a. In eq 1, the term $k_0 \exp(-E_a/kT)$ represents an additional temperature-dependent nonradiative decay process that is responsible for the observed temperature dependence of the emission yields.[9] Table I also shows the calculated room-temperature quantum yield and lifetime values using eq 1, which agree quite well with the observed values.

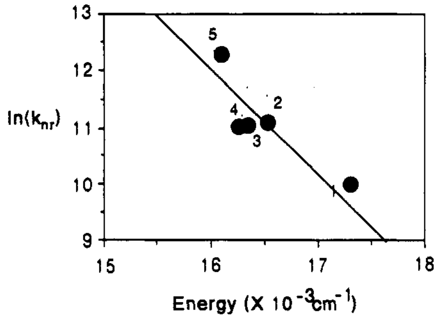

Figure 2. Energy gap law plot for Cp^*TaCl_4 and derivatives (see Table I), which follows the relation, $E_{em} = 40.55 - 14.32 \ln k_{nr}$ (in eV^{-1}).

From the values of k_{nr} shown in Table I, a correlation of E_{em} with ln (k_{nr}) can be constructed (Figure 2). With further experiments, this rough "energy gap law",[10] like that demonstrated for MLCT excited-states based on Os(II),[11] should give insight into the detailed electronic coupling and vibronic factors that are responsible for the relatively long-lived emitting states of the complexes.

Cyclic voltammetry studies of $Cp^*Ta^VCl_4$ in poorly coordinating solvents, for example, either (trifluoromethyl)benzene or CH_2Cl_2 with 0.1 M TBAH as supporting electrolyte, show a partially reversible reduction to a Ta(IV) complex (at a scan rate of 200 mV/s, the cathodic to anodic peak ratio is 0.88):

$$Cp^*Ta^VCl_4 + e^- \rightarrow [Cp^*Ta^{IV}Cl_4]^- \quad E_{1/2} \approx -0.77 \text{ V (in eq)} \quad (2)$$

Due to the sensitivity of the complex to external trace water, the potential quoted is reported vs SCE calculated from a Fc^+/Fc internal reference. No oxidation process is observed to the solvent limit, ca +1.9 V (SCE). From these observations it is clear that the excited state of $Cp^*Ta^VCl_4$ is a strong 1-electron oxidant (ca. 1.4 V). The complex is a weak reductant (>−0.3 V) if a large kinetic overpotential does not exist for the Cp*-based oxidation. Our future studies will take advantage of the potent oxidizing power of the new excited states with regard to the transformation of small molecules. For example, reductive quenching of $[Cp^*TaCl_4]^*$ will yield $[Cp^*Ta^{IV}Cl_4]^-$, which in recent studies has been implied to react with variety of substrates.[12]

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(9) Interpretation of the pre-exponential and activation energy has not been attempted. We have not attempted to screen the complexes for photosensitivity, although this is a reasonable explanation for the temperature-dependent term.

(10) (a) Henry, B. R.; Siebrand, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; London, 1973; Vol. 1, Chapter 4. (b) Avouris, P.; Gelbart, W. M.; El-Sayed, M. A. *Chem. Rev.* **1977**, *77*, 793. (c) Freed, K. F. *Acc. Chem. Res.* **1978**, *11*, 74. (d) Lin, S. H. *Radiationless Transitions*; Academic Press: New York, 1980. (e) Heller, E. J.; Brown, R. C. *J. Chem. Phys.* **1983**, *79*, 3336.

(11) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(12) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1990**, 3199.