

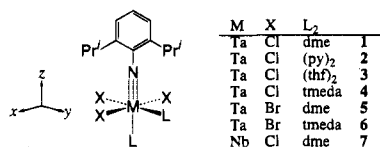
## Luminescence Properties of d<sup>0</sup> Metal–Imido Compounds

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Complexes that luminesce in fluid solution from ligand-to-metal charge-transfer (LMCT) excited states are scarce, in marked contrast to the ubiquitous metal-to-ligand charge-transfer chromophores whose emission properties have been the dominant subjects of study in inorganic photochemistry over the past two decades.<sup>1</sup> LMCT states are formally characterized by a hole in the electron shell at the ligand; complexes for which such states are long-lived in solution are therefore of interest as potential photochemical oxidants. Unfortunately, the systematic development of emissive LMCT chromophores is hindered by the fact that the few such complexes reported to luminesce in fluid solution—d<sup>5</sup>-configured ReCp\*<sub>2</sub> (Cp\* = C<sub>5</sub>-Me<sub>5</sub>)<sup>2</sup> and [Re(PMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub>]<sup>2+</sup><sup>3</sup> and d<sup>0</sup>-configured ScCp\*<sub>2</sub>X (X = Cl, NHPPh),<sup>4</sup> [Ti(NR')<sub>2</sub>{O<sub>2</sub>P(OR)<sub>2</sub>]<sub>2</sub> (R = CMe<sub>3</sub>, SiMe<sub>3</sub>; R' = CMe<sub>3</sub>, CMe<sub>2</sub>Et),<sup>5</sup> and TaCp\*X<sub>4</sub> and TaCp\*Cl<sub>3</sub>X' (X = Cl, Br; X' = O<sub>2</sub>CR, O<sub>3</sub>SMe)<sup>6</sup>—constitute too electronically disparate a class of compounds for general design principles to have been deduced from them. Herein we report the spectroscopic and photophysical properties of group V d<sup>0</sup>-configured aryl–imido compounds of the type *cis,mer*-M(≡NAr\*)X<sub>3</sub>L<sub>2</sub>,<sup>7,8</sup> which luminesce in fluid solution at room temperature, and comment on the potential generality of the emissive LMCT state they possess.



The electronic-absorption spectra of niobium and tantalum M(NAr\*)X<sub>3</sub>L<sub>2</sub> compounds in toluene solution at room temperature exhibit a weak band ( $\epsilon \approx 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a maximum in the range 19 000–22 500 cm<sup>-1</sup> (band I; Table 1) and a strong band ( $\epsilon \approx 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the range 31 000–34 000 cm<sup>-1</sup> (band II; Table 1) as the two lowest-energy features. Figure 1 shows the absorption spectrum of **1**, which is representative of those of the M(NAr\*)X<sub>3</sub>L<sub>2</sub> class. Emission from M(NAr\*)-X<sub>3</sub>L<sub>2</sub> compounds upon excitation into band I or II is observed

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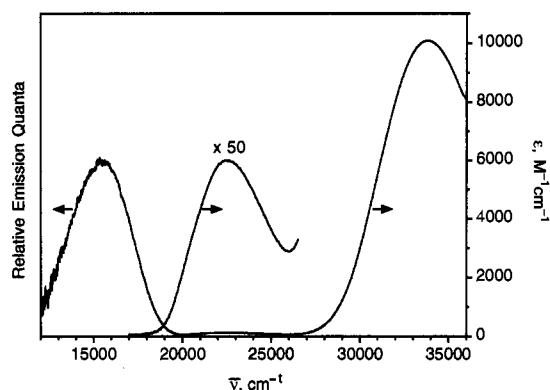
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(8) Complexes **4–7** were prepared by procedures analogous to those reported previously for **1–3** (ref 7). Elemental analyses (C, H, N) and <sup>1</sup>H-NMR spectra consistent with the formulations of **4–7** were obtained; these data are available as supporting information. Ligand abbreviations: Ar\* = 2,6-diisopropylphenyl; dme = 1,2-dimethoxyethane; py = pyridine; thf = tetrahydrofuran; tmeda = N,N,N',N'-tetramethylethylenediamine.

**Table 1.** Electronic Spectroscopic and Photophysical Data for M(NAr\*)X<sub>3</sub>L<sub>2</sub> Compounds at Room Temperature<sup>a</sup>

compd	absorption		emission				
	band I	band II	$\bar{\nu}_{\text{max}}$ , cm <sup>-1</sup>	$\tau_{\text{em}}$ , ns <sup>b</sup>	$\phi_{\text{em}}$ ( $\times 10^3$ ) <sup>c</sup>	$k_r$ , 10 <sup>4</sup> s <sup>-1</sup>	$k_{\text{nr}}$ , 10 <sup>7</sup> s <sup>-1</sup>
1	22 450 (130)	33 800 (10 200)	15 550	135(3)	5.0(2)	3.7	0.7
2	21 100 (110)	33 900 (8 100)	14 400	51(2)	1.3(1)	2.5	2.0
3	22 400 (145)	33 500 (9 200)	14 650	74(5)	1.5(3)	2.0	1.3
4	21 175 (100)	33 350 (10 500)	14 650	71(1)	2.1(3)	3.0	1.4
5	20 750 (115)	33 700 (14 900)	14 800	57(3)	2.0(3)	3.5	1.8
6	19 275 (95)	32 300 (13 500)	13 550	<40	0.7(1) <sup>d</sup>		
7	19 450 (40)	31 350 (9 100)	~13 000	46(3)	0.7(1) <sup>d</sup>	1.5	2.2

<sup>a</sup> Electronic-absorption data are for toluene solutions; emission data are for benzene solutions. <sup>b</sup> Excitation provided by Raman-shifted (H<sub>2</sub>) pulsed Nd:YAG laser ( $\lambda_{\text{ex}} = 436 \text{ nm}$ , 7-ns pulse width, power < 0.5 mJ/pulse). Cited values are averages of a minimum of seven independent measurements; standard deviations are given in parentheses. <sup>c</sup> Relative to [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> in water (Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590) and corrected for solvent refractive index (Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 991–1024). Cited values are averages of a minimum of five independent measurements; standard deviations are given in parentheses. <sup>d</sup> The complete emission band could not be recorded due to the poor red response of our spectrofluorimeter. For **1–5**, for which full emission bands could be measured, the total area under the band was found to be 2.04–2.17 times the area between the blue-edge onset of the band and  $\bar{\nu}_{\text{max}}$ . The area under the entire emission band for **6** and **7** was estimated to be 2.12 times this area.



**Figure 1.** Electronic-absorption and corrected emission spectra of Ta(NAr\*)Cl<sub>3</sub>(dme) (**1**) in toluene and benzene solution, respectively, at room temperature.

in both the solid state and fluid solution at room temperature (Figure 1).<sup>9</sup> The overlap and mirror symmetry between the emission band and band I and the similar dependence of their energies upon the nature of ligands X and L (Table 1) suggest that the transition that gives rise to the latter directly produces the emissive state, although the possible presence of one or more weak, unresolved absorption bands at lower energy cannot be excluded. The room-temperature emission quantum yields ( $\phi_{\text{em}} = 0.7\text{--}5.0 \times 10^{-3}$ ) and lifetimes ( $\tau_{\text{em}} = 46\text{--}135 \text{ ns}$ ) indicate that the radiative rates for **1–7** are on the order of  $10^4 \text{ s}^{-1}$  (Table 1), suggesting that the emission is spin-forbidden. Consistent with this, the emission of **1** ( $E_{0-0} \geq 18 000 \text{ cm}^{-1}$ , Figure 1) is efficiently quenched by anthracene ( $E_T = 14 870 \text{ cm}^{-1}$ ;  $k_q = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).

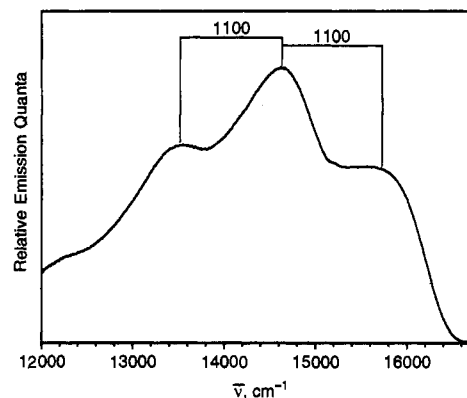
We believe that the emission of these M(NAr\*)X<sub>3</sub>L<sub>2</sub> complexes arises from the triplet state produced by a [ $\pi(\text{M}=\text{NAr}^*)$

(9) The emission–excitation spectra of **1–7** exactly match the absorption profiles of band I and the red flank of band II. The high extinction coefficient of band II ( $\epsilon \approx 10^4$ ) and the low emission quantum yields ( $\phi_{\text{em}} \approx 10^{-3}$ ) of these compounds prevented us from measuring full excitation profiles for band II at the low optical densities (OD ≤ 0.1) required for this experiment.

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$\rightarrow d_{xy}$ ] orbital transition, based on simple molecular-orbital considerations and on the trends in the emission band energy among these complexes. The LUMO of  $d^0$ -configured axially compressed complexes such as these is the metal-centered  $d_{xy}$  level, which is  $\pi^*(M-X)$  in character and nonbonding with respect to the imido ligand, whereas the HOMO is ligand based, with the possible candidates being  $\sigma(M-L)$ ,  $\pi(X)$ , or  $\pi(M\equiv NAr^*)$  orbitals. An emission band arising from a transition terminating in  $\sigma(M-L)$  or  $\pi(X)$  orbitals would be expected to shift in energy among these compounds approximately according to the ionization energies of L and X, respectively, given the metal-localized character of the LUMO. This is not observed for compounds 1–7. Specifically, the differences between the emission energies of the dme and tmeda derivatives of Ta( $NAr^*$ )Cl<sub>3</sub>L<sub>2</sub> (1 and 4,  $\Delta\bar{\nu}_{max} = 900\text{ cm}^{-1}$ ) and of Ta( $NAr^*$ )-Br<sub>3</sub>L<sub>2</sub> (5 and 6,  $\Delta\bar{\nu}_{max} = 1250\text{ cm}^{-1}$ ) are roughly 1 order of magnitude smaller than the difference between the ionization energies of dme and tmeda ( $11\,600\text{ cm}^{-1}$ ).<sup>11</sup> Similarly, the red shift in the emission band that arises from substitution of bromide for chloride in the pairs of Ta( $NAr^*$ )X<sub>3</sub>(dme) derivatives (1 and 5,  $\Delta\bar{\nu}_{max} = 750\text{ cm}^{-1}$ ) and of Ta( $NAr^*$ )X<sub>3</sub>(tmeda) derivatives (4 and 6,  $\Delta\bar{\nu}_{max} = 1100\text{ cm}^{-1}$ ) is substantially smaller than the difference between the ionization energies of chlorine and bromine ( $9300\text{ cm}^{-1}$ ).<sup>12</sup> The modest sensitivity of the emission band energy to the nature of L and X suggests that these ligands contribute relatively little to the parentage of the HOMO. This implies that the HOMO is  $\pi(M\equiv NAr^*)$  and, thus, that the transition giving rise to the emission band is  $[\pi(M\equiv NAr^*) \leftarrow d_{xy}]$ . As expected for an LMCT state, the emission band of Nb( $NAr^*$ )Cl<sub>3</sub>(dme) is red shifted from that of Ta( $NAr^*$ )Cl<sub>3</sub>(dme) ( $2550\text{ cm}^{-1}$ ).

Support for the assignment of the emission of  $M(NAr^*)X_3L_2$  compounds as arising from the  $[\pi(M\equiv NAr^*) \leftarrow d_{xy}]$  transition is provided by the vibronic structure observed in the emission bands at 13 K. A high-frequency ( $\nu > 1000\text{ cm}^{-1}$ ) progression is resolved for all compounds, though most clearly for 6 (Figure 2). The vibrational spectra of aryl-imido metal complexes typically exhibit bands in the  $900\text{--}1350\text{-cm}^{-1}$  region attributable to nominal " $\nu(M\equiv N)$ " modes, which contain contributions from the  $M\equiv N$  and from N–R-derived coordinates.<sup>13,14</sup> The observation of such a progression in the emission spectrum is a manifestation of a significant bond-distance change along  $[M\equiv NAr^*]$  coordinates in the emissive state, which arises



**Figure 2.** Corrected emission spectrum of microcrystalline Ta( $NAr^*$ )-Br<sub>3</sub>(tmeda) (6) at 13 K. Vibronic spacings are given in  $\text{cm}^{-1}$ .

because the formal  $M\equiv N$  bond order is reduced from 3 to  $2\frac{1}{2}$  as a result of the  $[\pi(M\equiv NAr^*) \rightarrow d_{xy}]$  orbital transition.

In closing, we note an analogy between the nature of the emissive state of the  $d^0$ -configured  $M(\equiv NAr^*)X_3L_2$  complexes described herein and those of  $d^2$ -configured *trans*- $[M(\equiv O)_2L_n]$  and  $[M(\equiv E)L_n]$  ( $E = O, N, CR$ ) complexes that may be of importance in formulating initial bonding/luminescence relationships for LMCT chromophores. The  $d^2$  complexes luminesce from  $[d_{xy} \rightarrow \pi^*(O=M=O)]$  and  $[d_{xy} \rightarrow \pi^*(M\equiv E)]$  states,<sup>15</sup> respectively, which, although they are  $d-d$  in character as opposed to the  $[\pi(M\equiv NAr^*) \rightarrow d_{xy}]$  LMCT excited state described here, have in common with the latter an electronic transition that involves the metal-centered  $d_{xy}$  orbital and a  $\pi$ -symmetry orbital associated with the metal–ligand multiple bond, such that the order of the multiple bond is reduced by  $\frac{1}{2}$  in the excited state. Other  $d^0$  analogues of emissive,  $d^2$ -configured, multiply metal–ligand bonded complexes should share these characteristics and are thus logical candidates for expanding the small class of emissive LMCT chromophores.

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**Supporting Information Available:** <sup>1</sup>H-NMR spectroscopic and elemental analysis data for 4–7 (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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