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Communications

Spectroscopic and Structural Properties of Binuclear Platinum–Terpyridine Complexes

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Square planar d^8 complexes show a pronounced tendency to aggregate as weakly metal–metal-bonded oligoners.[1] The most thoroughly investigated materials include infinite-chain $Pt(CN)_4^{2-}$ species[2] and several luminescent binuclear complexes (e.g., $Pt_2(P_2O_5H_2)_4^{4-}$ and $[LL'Ir(\mu\text{-pz})]_2$ (LL' = $(CO)_2$, $(CO)(PR_3)$, 1,5-cyclooctadiene; pzH = pyrazole)) that possess metal–metal-bonded $d\sigma^*(d_{z^2})p\sigma(p_z)$ excited states.[3] Mononuclear α-diimine complexes of Pt(II) (e.g., $Pt(bpy)(CN)_2$ (bpy = bipyridine)) tend to crystallize as linear chains, and the highly luminescent solid materials are more intensely colored than the monomers.[4] These complexes exhibit luminescence spectra that occur at lower energy and have much different emission profiles than those for the $Pt(CN)_4^{2-}$ chains. It has been suggested[4] that the solid-state emission of this type of complex is attributable to a $d\sigma^* \rightarrow \pi^*$-($\alpha$-diimine) excited state.

We have begun an investigation of the photophysics of $d\sigma^*\pi^*$ excited states in discrete binuclear d^8–d^8 complexes containing polypyridyl ligands. Kostic has characterized $\{[Pt(tpy)]_2(\mu\text{-can})\}(PF_6)_3$ (tpy = terpyridine; can = canaverine),[5] and we have prepared related complexes with a variety of anionic N–N bridging ligands (Table I).[6] The colors of the compounds range from light orange (**1**) to deep red (**3**, **4**). In addition to UV absorptions attributable predominantly to $\pi\pi^*$ transitions, there are new visible absorption bands that, along with emission maxima, move to lower energy with decreasing Pt–Pt separation (Figure 1).[7] The solid-state luminescence spectra at ambient temperature for all these complexes exhibit featureless bands (Figure 1) that blue-shift slightly at 77 K (Table I); the excited-state lifetimes fall between 1 and 2.5 μs. The 77 K glassy solutions of **2**–**4** show similar luminescence profiles. Terpyridine vibrations (1300–1700 cm^{-1}) are enhanced in the resonance Raman spectra of **1**–**4**,

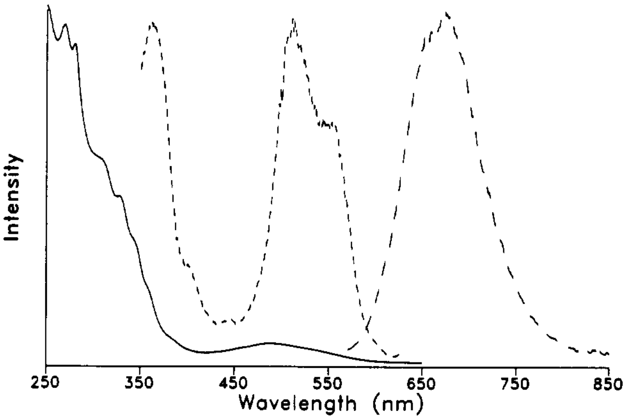

Figure 1. Electronic spectra of **3**: —, absorption at room temperature (CH_3CN solution); – –, emission at 77 K (10:10:1 MeOH:EtOH:DMF glass); - - -, excitation at 77 K (10:10:1 MeOH:EtOH:DMF glass).

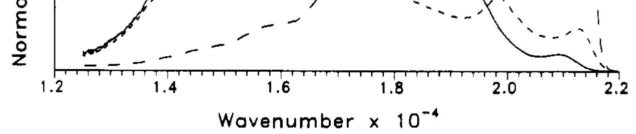

Figure 2. Emission spectra of **1** at 77 K: —, CH_3CN solution; – –, CH_3CN/1% DMF; - - -, CH_3CN/1% MeOH.

[†] Contribution No. 8696.

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(6) A related compound $\{[Pt(tpy)]_2(\mu\text{-guanidine})\}(ClO_4)_3$ (**5**) has been reported: Kip, H.-K.; Che, C.-M.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369. The relationship between the Pt–Pt separation (3.090(1), 3.071(1) Å) and the absorption spectrum (λ_{max} 483 nm) of **5** accords with our findings. Kip, Che, and co-workers have observed weak emission ($\phi = 1.27 \times 10^{-4}$) for **5** in fluid CH_3CN solution. We also have found very weak emissions from **1**–**4** in CH_3CN solutions.

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Table I. Structural and Spectroscopic Data for $[Pt(tpy)]_2(\mu\text{-}L)^{3+}$ Complexes

N–N	*d*(Pt–Pt) (Å)	abs λ_{max} (nm)[a,b]	emission λ_{max} (nm)	lifetime τ (μs)	excitation λ_{max} (nm)[b,c]	Raman $\Delta\nu$ (cm^{-1})[d]
μ-pyrazole (μ-pz) (**1**)	3.432(3)[e]	430 (2520)	630,[f] 630[g]			1338
			592[h]	1.1[h]		1480
			472,[i] 513[i]		410[i]	
			542,[i] 585[i]			
μ-azaindole (μ-az) (**2**)	3.13(2)[j]	460 (2050)	690[f]		497[i]	1338
			678[g]			1481
			639[i]	2.50[i]		1570
						1606
μ-diphenylformamidine (μ-dpf) (**3**)	3.049(3)[j]	490 (3390)	712[f]		515[i]	1338
			710[g]			1482
			670[i]	2.51[i]		1572
						1606
μ-arginine (μ-can) (**4**)	2.998(2)[k]	488 (3700)	730[f]	<0.02[f]	520[i]	1338
			715[g]	1.4[l]		1486
			690[i]	2.34[i]		1572
						1606

[a] DMF solutions (CH_3CN solution for **3**) at room temperature. Molar absorptivity in parentheses. [b] Lowest energy feature. [c] Monitor lowest energy emission. [d] DMSO solution at room temperature; 442-nm He/Cd laser. [e] Reference 7a. [f] Solid at room temperature. [g] Solid at 77 K. [h] CH_3CN solution at 77 K. [i] 10:10:1 MeOH:EtOH:DMF glass at 77 K. [j] Reference 7b. [k] Reference 5. [l] Solid at 10 K.

thereby confirming that a tpy orbital is involved in the low-energy electronic transition.[8]

The emission spectra of the pyrazolyl-bridged complex (**1**) in a frozen acetonitrile solution and in the solid state are similar in appearance (λ_{max} 592 nm); however, in frozen DMF or CH_3CN/1% DMF (DMF = dimethylformamide) solution or a 10:10:1 EtOH:MeOH:DMF glass, the emission blue-shifts and is highly structured (Figure 2). Since similarly structured emission bands are observed for $Pt(tpy)(NH_3)^{2+}$,[9] $Zn(tpy)Cl_2$,[10] $Ir(tpy)_2^{3+}$,[11] $[Pt(bpy)en](ClO_4)_2$ (bpy = bipyridine; en = ethylenediamine),[4] and terpyridine[9] itself, this feature is attributed to a tpy-localized $^3(\pi\pi^*)$ transition. The striking result is that very small changes in solvent composition can cause the observed emission to change from the broad, poorly structured $^3(d\sigma^*\pi^*)$ to the highly structured $^3(\pi\pi^*)$ system. Apparently, the energy of the $^3(d\sigma^*\pi^*)$ state depends strongly on the nature of the solvent, as expected for a state with MLCT character.

The fluid solutions of these new complexes in EtOH/MeOH/DMF do not show any significant emission intensity at room temperature,[6] and there is essentially complete quenching of otherwise highly emissive glassy solutions when they are warmed through their glass transition temperature. This constitutes yet another distinction from the $d\sigma^*p\sigma$ excited states of complexes such as $Pt_2(P_2O_5H_2)_4^{4-}$, which are relatively long-lived in fluid solution.[3a]

It is apparent that the orbital configuration of the lowest energy electronic excited state in complexes **1**–**4** depends on the metal–metal separation. For shorter Pt–Pt distances, the lowest state is $^3(d\sigma^*\pi^*)$; as the distance between the platinum atoms increases, the $^3(d\sigma^*\pi^*)$ energy increases. At sufficiently large Pt–Pt separations, the $^3(d\sigma^*\pi^*)$ state will move above $^3(\pi\pi^*)$. Interestingly, the μ-pyrazolyl complex **1**, which displays both $d\sigma^*\pi^*$ and $\pi\pi^*$ emission spectra, is very near this crossover.

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(8) Attempts to determine $\nu(Pt_2)$ (expected to be well below 100 cm^{-1}) have thus far been unsuccessful.

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