Synthesis and Luminescence Properties of \([\text{Pt}\{4-(\sigma-\text{MeC}_6\text{H}_4)\text{-pzbipy}\}\text{Cl}]\text{SbF}_6\) [pzbipy = 6-2''-pyrazinyl)-2,2'-bipyridine]

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*Z. Naturforsch. 2007, 62b, 447–452; received November 14, 2006*

This paper is dedicated to our good friend and colleague, Helgard G. Raubenheimer, on the occasion of his 65th birthday

The synthesis and characterisation of the 4-(\sigma-R-\text{C}_6\text{H}_4)pzbipy [R = H, CH\(_3\) or CF\(_3\); pzbipy = 6-(2''-pyrazinyl)-2,2'-bipyridyl] ligands are described. Reaction of the 4-(\sigma-\text{MeC}_6\text{H}_4)pzbipy ligand with [\text{Pt}(\text{PhCN})_2\text{Cl}_2] in the presence of AgSbF\(_6\) affords [\text{Pt}\{4-(\sigma-\text{MeC}_6\text{H}_4)pzbipy\}\text{Cl}]\text{SbF}_6 as a maroon-coloured microcrystalline solid. The [\text{Pt}\{4-(\sigma-\text{MeC}_6\text{H}_4)pzbipy\}\text{Cl}]\(^+\) cation exhibits low intensity photoluminescence in dichloromethane that maximises at 543 nm and which is assigned to a \(^3\)MLCT excited state (\(\tau = 20\) ns). The emission spectrum of the cation was also recorded in a frozen DME {1 : 5 : 5 (v/v) DMF / MeOH / EtOH} glass; a highly structured band is observed with vibrational spacings of ca. 1400 cm\(^{-1}\), indicating emission from an intraligand \(^3\)\(\pi\)-\(\pi^*\) state (\(\tau = 11\) \(\mu\)s). Variable temperature solid emission spectra show maxima that occur at significantly lower energies than is observed in fluid solution and that shift to the red when the temperature is lowered; specifically, \(\lambda_{(em)}\)\(_{\text{max}}\) is 674 nm at 280 K (\(\tau = 80\) ns) and 723 nm at 80 K (\(\tau = 1.3\) \(\mu\)s). Emission behaviour of this type is typical of emission from a metal-metal-ligand charge transfer (MMLCT) excited state that has its origins in \(d_{z^2}(\text{Pt})-d_{z^2}(\text{Pt})\) orbital interactions in the crystal.

Key words: Pyrazinylbipyridyl Ligand, Platinum Complex, Luminescence