Synthesis and Luminescence Properties of [Pt{4-(*o*-MeC$_6$H$_4$)-pzbipy}Cl]SbF$_6$ [pzbipy = 6-2″-pyrazinyl)-2,2′-bipyridine]

John S. Field[a], Jan-André Gertenbach[a], Raymond J. Haines[a], Orde Q. Munro[a], and David R. McMillin[b]

[a] School of Chemistry, University of KwaZulu-Natal, Private Bag X01, Pietermaritzburg, 3201, South Africa
[b] Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907-1393, USA

Reprint requests to Prof. J. S. Field. E-mail: fieldj@ukzn.ac.za

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-(*o*-R-C$_6$H$_4$)pzbipy [R = H, CH$_3$ or CF$_3$; pzbipy = 6-(2″-pyrazinyl)-2,2′-bipyridyl] ligands are described. Reaction of the 4-(*o*-MeC$_6$H$_4$)pzbipy ligand with [Pt(PhCN)$_2$Cl$_2$] in the presence of AgSbF$_6$ affords [Pt{4-(*o*-MeC$_6$H$_4$)pzbipy}Cl]SbF$_6$ as a maroon-coloured microcrystalline solid. The [Pt{4-(*o*-MeC$_6$H$_4$)pzbipy}Cl]$^+$ cation exhibits low intensity photoluminescence in dichloromethane that maximises at 543 nm and which is assigned to a ^{3}MLCT excited state (τ = 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 $^3\pi$-π^* state (τ = 11 μs). 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, $\lambda(\mathrm{em})_{\max}$ is 674 nm at 280 K (τ = 80 ns) and 723 nm at 80 K (τ = 1.3 μs). 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}(Pt)-d_{z^2}(Pt) orbital interactions in the crystal.

Key words: Pyrazinylbipyridyl Ligand, Platinum Complex, Luminescence