Photophysics of \([\text{Pt}\{4-(o-tolyl)isqbipy\}\text{Cl}]\text{SbF}_6\), where \(4-(o-Tolyl)isqbipy\) is the New \(4-(o-Tolyl)-6-(3''-isoquinolyl)-2,2'\)-bipyridyl Ligand

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The synthesis and characterisation of the \(4-(o-tolyl)-6-(3''-isoquinolyl)-2,2'\)-bipyridyl \([4-(o-tolyl)isqbipy]\) ligand is described. A single-crystal X-ray structure determination shows that it adopts a trans-trans conformation about the interannular bonds linking the central pyridine ring to the outer pyridine ring and the isoquinolyl moiety. The \(o\)-tolyl group is twisted by an angle of 51.7° out of the plane of the central pyridine ring. The synthesis and characterisation of the \([\text{Pt}\{4-(o-tolyl)isqbipy\}\text{Cl}]\text{SbF}_6\) complex is described. The absorption spectrum of the complex measured in acetonitrile exhibits MLCT bands at 362 and 393 nm, as well as intraligand \(\pi-\pi^*\) absorptions in the 200 – 350 nm range; the MLCT bands are shifted significantly to higher energy when compared to those recorded for the parent trpy complex, \(\text{viz.} \ [\text{Pt}\{4'-(o-tolyl)trpy\}\text{Cl}]\text{SbF}_6\), where trpy is \(2,2' : 6' , 2''\)-terpyridine. Similarly, the 3 MLCT emission measured for the \(4-(o-tolyl)isqbipy\) complex in a 1 : 1 CH\(_2\)Cl\(_2\)/CHCl\(_3\) solution is blue-shifted with respect to the emission spectrum recorded for the \(4'-(o-tolyl)trpy\) complex. We attribute the higher energy MLCT absorption and emission for the \(4-(o-tolyl)isqbipy\) complex to a significantly higher energy for its \(\pi^*-\text{LUMO}\) than for that of the \(4'-(o-tolyl)trpy\) complex. Emission spectra of the title compound have also been measured in a low-temperature 1 : 5 : 5 (v/v) DMF/methanol/ethanol (DME) glass as a function of concentration. These spectra show that aggregation of the complex occurs at rather low concentrations of 5 – 10 \(\mu\)M, probably to dimers. Variable-temperature emission spectra recorded on a solid sample of \([\text{Pt}\{4-(o-tolyl)isqbipy\}\text{Cl}]\text{SbF}_6\) comprise relatively narrow asymmetric bands whose maxima are shifted to the red as the temperature is lowered: specifically \(\lambda_{\text{em}}(\text{max})\) is 641 nm at r.t. (\(\tau = 235\) ns) and 676 nm at 77 K (\(\tau = 1.36\) \(\mu\)s). Temperature-dependent emission of this type is typical of a metal-metal-to-ligand charge transfer (MMLCT) excited state that has its origin in \(d_{z^2}(\text{Pt})-d_{z^2}(\text{Pt})\) orbital interactions in the crystal.

\textit{Key words:} Isoquinolyl-bipyridyl Ligand, Crystal Structure, Platinum Complex, Photophysics