

Synthesis of platinum complexes with N[^]N- sulphonamide ligands towards fluorescence imaging applications

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Ethylenediamine has been used as the backbone to synthesize the novel Pt-N[^]N complexes. The outstanding binding ability of ethylenediamine allows it to be used in the synthesis of hydrophilic ligand systems, by substituting the terminal amine group with bulky aromatic sulphonamide fragments which would also incorporate lipophilicity as well as enhanced fluorescence. Employing such amphipathic ligand systems would be an optimal approach of synthesizing platinum coordination complexes for biological applications with improved uptake by targeted cells. In this study, two ligands (L1=N(SO₂biphenyl)ethylenediamine, L2=N(SO₂azobenzene)ethylenediamine) (Figure 1) and their corresponding novel platinum complexes (C1=PtCl₂(N(SO₂biphenyl)ethylenediamine), C2=PtCl₂(N(SO₂azobenzene)ethylenediamine)) were synthesized. UV-Visible spectra of the ligands indicate clear changes from starting material along with the presence of intra-ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, giving rise to absorption peaks around 200-400 nm. Shifts of these peaks can be observed in the UV-Visible spectra of the complexes related to MLCT transitions. The strong S-N band detected in the FTIR spectra of the ligands is found at 820 cm⁻¹ in L1 and 842 cm⁻¹ in L2 and shifts to lower wavenumbers in ethylenediamine complexes (801 in C1 and 836 cm⁻¹ in C2) due to direct donation of nitrogen lone pair to platinum. Disappearance of the -NH and -NH₂ stretching vibration frequency in the FTIR spectra of the complexes, found around 3300 cm⁻¹ in the ligands, indicates the deprotonation of the amine groups on coordination in the complex. Methylene protons of the amine moiety of the ligands can be seen to be magnetically inequivalent in L1 and L2, appearing as triplets within the 2.00 - 3.00 ppm range in ¹H NMR spectra. Complexes display slightly higher fluorescence intensity compared to the ligands, possibly due to rigidification of the ligand systems on developing the coordination complex. Structural data was obtained from single crystal X-ray diffraction of L2 and C1 which validated the formation of the ligand and complex.

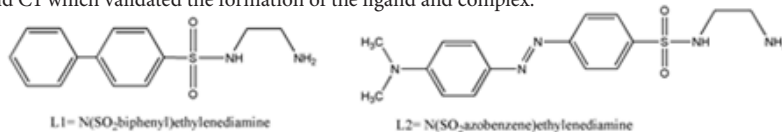


Figure 1: Line diagrams of N(SO₂R)_nen ligands

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