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Synthesis and characterization of Zn (II)LCl_2 complexes with eight membered chelate rings

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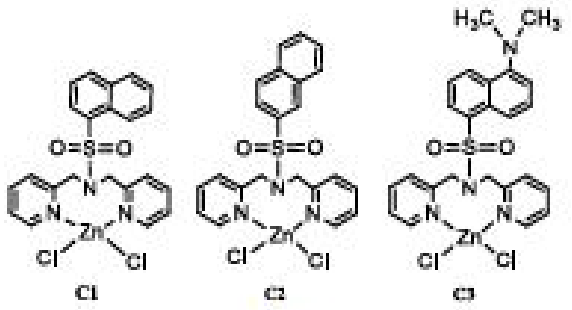
In the field of metalopharmaceutical chemistry, zinc based compounds have been identified as potential agents in biological applications such as fluorescent sensors and therapeutic agents. In this study, three novel Zn(II) complexes $[ZnL1Cl_2]$ (C1), $[ZnL2Cl_2]$ (C2) and $[ZnL3Cl_2]$ (C3) where L1 = *N*(SO_2)(1-nap)dpa, L2 = *N*(SO_2)(2-nap)dpa and L3 = *N*(SO_2Me_2Nnap)dpa were synthesized (Figure) and characterized using UV-Visible, FTIR and ^{1}H NMR spectroscopies. X-ray diffraction studies performed for C2 and C3 revealed that L2 and L3 serve as bidentate ligands. The central N of the sulfonamide group remains uncoordinated to the Zn(II) atom resulting in a rare eight membered chelate ring. The zinc centres in C2 and C3 acquire a distorted tetrahedron geometry and are four coordinated by the two pyridyl nitrogens of the respective ligand and two chlorine atoms. Formation of the complexes was further supported by ^{1}H NMR studies carried out in CD_2Cl_2. In the free ligands, the signal for the methylene hydrogens (CH_2) appears as a narrow singlet. However, in the complexes a more downfield, broad singlet peak is observed for the CH_2 groups. In the spectrum of C3 in CD_2Cl_2, broad peaks were observed for the pyridyl protons and the methylene protons. In a variable temperature study of C3 in CD_2Cl_2, the H6/6' protons were resolved at 233.2 K to give a doublet (8.96 ppm). The peaks observed for C3 in the region of 7-8 ppm at 300 K were resolved and had upfield shifts at 233.2 K. In a spectrum of C2 obtained in $CDCl_3$ at room temperature, broad peaks were observed for the pyridyl protons and the methylene protons. UV-maxima of the complexes could be observed in the region of 200-250 nm due to π-π* intraligand transitions. The compounds were excited with UV-light and emission spectra were obtained in methanol with λ_{max} = 334, 344 and 537 nm for C1, C2 and C3 complexes, respectively. C3 complex has a broad emission band in the visible region. Further studies are being carried out to investigate the behavior of the complexes in solution and their fluorescent properties.



C1 C2 C3

Figure. Zn(II) complexes used in the study: [Zn(*N*(SO_2)(1-nap)dpa)Cl_2] (**C1**), [Zn(*N*(SO_2)(2-nap)dpa)Cl_2] (**C2**), [Zn(*N*(SO_2Me_2Nnap)dpa)Cl_2] (**C3**).

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