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Comparison of structural, electronic, and fluorescent properties of Zn-terpyridine, Zn-1,10-phenanthroline, and Zn-hydroxyquinoline metal complexes

Lakshika W. A. I. and Wanniarachchi D. D. S. de S.*

Department of Chemistry, University of Kelaniya, Sri Lanka.
dakshikacw@kln.ac.lk*

Terpyridine is a heteronuclear, N-N-N tridentate ligand while 1,10-Phenanthroline (1,10-Phen) and 8-hydroxyquinoline (8-HQ) are N-N and N-O bidentate ligands that are commonly used for the synthesis of metal complexes. Although the $Cu^{2+,}$ $Ag^{+,}$ and Ru^{2+} complexes of these ligands have been investigated, the Zn^{2+} complexes of these ligands have not gained much attention. One-pot Kröhnke type synthesis of 4′-(4-Nitrophenyl)-2,2′:6′,2″-terpyridine ligand (Nitrotyp) and 4′-(phenyl)-2,2′:6′,2″-terpyridine ligand (Phentyp) using 2-acetylpyridine and aryl aldehyde is followed by the characterization using UV-visible, FT-IR, and H^1 NMR spectroscopy. Then Nitrotyp and Phentyp were separately coupled with Zn(II) and characterized by UV-visible and FT-IR spectroscopy. According to the UV-visible spectroscopy, after the coordination with Zn(II), both Nitrotyp and Phentyp ligands exhibit a red shift in absorption maxima (λ_{max}) from 272 nm to 284 nm and from 277 nm to 283 nm, respectively. All these electronic transitions are ligand-centered π π^* transitions. According to the FT-IR spectroscopy, the C=N stretching frequencies for the Nitrotyp and Phentyp free ligands are 1593 cm^{-1} and 1582 cm^{-1}, respectively. Compared to the FT-IR spectra of the Zn complexes of the same ligand, the stretching frequency for the C=N bond is 1601 cm^{-1} and 1552 cm^{-1}, respectively. The shift of the IR stretching frequency of the C=N bond compared to the relevant free ligand indicates the coordination of the ligands with Zn(II). In addition, commercially available 1,10-phen and 8-HQ ligands were combined with Zn(II) and characterized by UV-visible, and FT-IR spectroscopy. The formation of the Zinc complex in the 8-HQ ligand leads to a significant red shift of λ_{max} from 241 nm to 259 nm. In contrast, free 1,10-Phen exhibits a blue shift from λ_{max}= 229 nm to λ_{max}= 225 nm upon coordination with Zn. As reported by FT-IR spectroscopy, the C=N stretching frequencies for the 1,10-Phen and 8-HQ free ligand are 1582 cm^{-1} and 1576 cm^{-1}, respectively. Compared to the FT-IR spectra of the Zn complexes of these ligands the stretching frequency for the same bond is 1589 cm^{-1} and 1587 cm^{-1}, respectively. The Zn(II)-to-metal ratio of all complexes was identified as 1:1 using the job's plot method. Hence, it is concluded that the chemical formulae for the synthesized Zn(II) complexes are $[Zn(Nitrotyp)Cl]^+$, $[Zn(Phentyp)Cl]^+$ $[Zn(1,10\text{-}Phen)Cl_2]$, and $[Zn(8\text{-}HQ)Cl_2]$. According to the fluorescence spectra, all the free ligands exhibit less fluorescence intensity compared to the corresponding Zn(II) complex and, $[Zn(Nitrotyp)Cl]^+$ complexes exhibit hypsochromically (blue) shifted emission spectra, compared to the corresponding free ligand. In contrast, $[Zn(Phentyp)Cl]^+$, $[Zn(1,10\text{-}Phen)Cl_2]$, and $[Zn(8\text{-}HQ)Cl_2]$ complexes demonstrate a bathochromically (red) shifted emission spectra. Out of the four complexes, $[Zn(Phentyp)Cl]^+$ (2.4×10^{-7} M) shows a higher fluorescence intensity, even at low concentrations than other complexes. Replacing one of the pyridine rings with a phenyl group triggers the diminution of the fluorescence intensity and it is indicated by the high fluorescence intensity of the $[Zn(Phentyp)Cl]^+$ complex compared to the $[Zn(1,10\text{-}Phen)Cl_2]$ complex. These results make the $[Zn(Phentyp)Cl]^+$ complex a more promising agent for the detection of anions in a given medium, than the other three complexes.

Keywords: Fluorescence, 8-Hydroxyquinoline, 1,10-Phenanthroline, Terpyridine