

COMPLEXATION OF METAL IONS IN AQUEOUS SOLUTION BY
FLUORESCENT LIGANDS CONTAINING PYRIDYL GROUPS

Karen Anna Martha Oscarson

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Chair

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ABSTRACT

This research focused primarily on the induction of fluorescence by secondary ligands in solution. The Zn^{2+} ion, when complexed to fluorophoric ligands, is known to enhance the intensity of emission. With this in mind, both a fluorescence-quenching metal ion and a metal ion isoelectronic to Zn^{2+} (Ni^{2+} and In^{3+} , respectively) were utilized in this research. The high-spin Ni(II) / terpyridine (terpy) complex was studied extensively due to the tendency of the d^8 Ni^{2+} ion to quench fluorescence. Induction of fluorescence was attempted by addition of secondary ligands, primarily CN^- . Ligands were chosen that are high enough in the spectrochemical series such as to increase the energy gap by raising the energy of the e_g degenerate orbitals, giving rise to a low spin complex that could fluoresce. Although the induction of fluorescence was not achieved, the pK_1 and pK_2 of the Ni(II) / terpy hydrated complex was found by differential pulse voltammetry. X-ray crystallography further elucidated the Ni(II)/terpy /CN complex, revealing the two predominant species present, $Ni(terpy)_2$ and $[Ni(CN)_4]^{2-}$.

The In(III) / 1,10-phenanthroline (phen) complex was analyzed, and was found to fluoresce. NMR and differential pulse voltammetry were utilized for further characterization of In(III) / phen behavior in aqueous solution. $\text{Log}K_1$ for the In(III) / phen complex was found by plotting n_{bar} versus pH from the NMR data, and was also found by a Nernstian slope obtained from differential pulse voltammetry. The two binding constants obtained from the two different methodologies differed by 0.2 logarithmic units, and were comparable to the literature value.

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