

NOTES

Characterization and Formation Constants of Ni(II) Complexes with Some Aryl Schiff Bases

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A series of nickel(II) complexes with aryl schiff bases have been synthesized and characterized on the basis of their elemental analysis, magnetic moment, infrared spectra and electronic spectra. The Schiff bases act as bidentate ligands coordinating through azomethine nitrogen and phenolic oxygen. The diamagnetic nature and spectral study of these complexes suggest their square-planar geometry. The potentiometric studies have been carried out to determine the metal-ligand stability constants of these complexes at 25°C 0.1 M ionic strength.

Mononuclear and binuclear copper(II) complexes with aryl Schiff bases have been reported in our earlier publication¹. The present communication details the preparation and characterisation of nickel(II) complexes with Schiff bases derived from the condensation of *ortho*-hydroxy-5 chloro acetophenone and substituted anilines.

All the chemicals used were of AR grade. The *ortho*-hydroxy acetophenone and the Schiff bases were prepared as reported earlier². The nickel(II) complexes were prepared by taking metal nitrate in ethanol and pH was adjusted to 7.0 to 8.0 by adding alcoholic ammonia. The ligand solution in hot ethanol keeping 1 : 2 metal-ligand ratio was added in it and the mixture was refluxed for 1 hr. The coloured complex was filtered, washed thoroughly with hot ethanol and dried over anhydrous CaCl₂ in vacuo. All the physico-chemical techniques were used as reported earlier².

To evaluate the metal-ligand stability constants Bjerrum-Calvin pH-metric titration technique as modified by Irving and Rossotti³⁻⁵ was used. All the required solutions were prepared in CO₂-free doubly distilled water. The titrations were carried out in 60 % (v/v) ethanol-water medium at 25°C and 0.1 M (NaClO₄) ionic strength. The method of least squares is invariably used for getting the accurate values of log K₁ and log K₂, since their difference is less than 1.41 indicating the simultaneous formation of these complexes. In all the calculations, pH correction and volume correction factors have been applied for the ethanol-water mixtures.

All the complexes are greenish-yellow in colour. The complexes could not be further recrystallized due to their insolubility in common solvents. The analytical data corresponds to the formula (ML₂) where L is the

respective ligand with the abbreviation; (5-Cl-OHA-anil), (5-Cl-OHA-p-Cl-phen-anil), (5-Cl-OHA-p-Br-phen-anil), (5-Cl-OHA-p-Cl-tolyl), (5-Cl-OHA-m-Cl-tolyl), (5-Cl-OHA-p-anisyl), (5-Cl-OHA-p-phenetyl) and (5-Cl-OHA- α -naphthil). The molar conductance values of these complexes in DMF indicate their non-electrolytic nature.

The broad weak band at $2350\text{--}2600\text{ cm}^{-1}$ in the infrared spectrum of free ligand may be due to intramolecularly H-bonded νOH . The band appearing at $1560\text{--}1570\text{ cm}^{-1}$ in the ligand show a shift to higher frequency in the complexes has been assigned to $\nu\text{C}=\text{N}$. Two strong bands at $1370\text{--}1380$ and $1285\text{--}1295\text{ cm}^{-1}$ in the ligands may be attributed to $\nu\text{C}=\text{N}$ and $\nu\text{C}-\text{O}$; these bands shifted to higher frequency (1400 and 1410 cm^{-1}) in the complexes indicating the coordination of ligands to the metal through azomethine nitrogen and phenolic oxygen^{6,7}.

All the complexes are diamagnetic, indicating the square-planar structure of the complexes^{8,9}. The electronic absorption bands observed at $16260\text{--}16950\text{ cm}^{-1}$ and $21505\text{--}21740\text{ cm}^{-1}$ which are assigned to ${}^1\text{A}_{1\text{B}} \rightarrow {}^1\text{A}_{2\text{B}}$ and ${}^1\text{A}_{1\text{B}} \rightarrow {}^1\text{B}_{1\text{B}}$ transitions¹⁰, further support the square-planar geometry of these complexes.

The metal-ligand titration curve of nickel (II) deviates from the ligand curve in the pH range 6.5 to 7.5 indicating the complexation of nickel(II) in this pH range. In all the cases studied, the values of \bar{n} were always less than 2 showing the formation of only 1 : 1 and 1 : 2 complexes. The closeness of $\log K_1$ and $\log K_2$ in all the complexes indicate that they are formed by simultaneous equilibrium. The method of least squares was therefore adopted for the accurate determination of these constants. The different stability constants, i.e., values $\log K_1$, $\log K_2$ and $\log \beta$ are in the range (4.41–5.05), (3.45–4.30) and (8.01–9.30) respectively. The relationship $\log K = a pK + b$ was used to understand the effect of substituent groups on the chelating tendencies of ligands. The $\log \beta$ values were plotted against pK_2 values of Schiff bases. The points on the graph are so much scattered that a single straight line passing through all the points is not possible. Moreover, the points of the complexes with substituted ligands show lower stabilization than the unsubstituted derivative. The lower stabilization of the complexes of substituted ligands is due to the steric hindrance of the substituted group in the ligand molecule for the incoming metal ion.

The present observations indicate that the benzene molecule attached to nitrogen is not planar, thereby the substituted group causes the steric hindrance to the incoming metal ion.

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