Studies on Co²⁺, Ni²⁺ and Cu²⁺ Complexes with Schiff Bases Derived from Benzil Monohydrazone

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The synthesis of Co²⁺, Ni²⁺ and Cu²⁺ complexes of Schiff bases derived from the condensation of ethanolic solution of benzil monophenyl hydrazone with aniline and substituted anilines (in presence of H_2O, α, β, γ picoline and pyridine), The complexes are characterized by elemental analyses, magnetic, IR, electronic, mass spectra and thermal studies. The schiff base behaves as a tridentate ligand. Spectral studies shows the dimeric nature of complexes.

Key Words: Metal, Complexes, Schiff base, Benzil mono-hydrazone.

INTRODUCTION

Benzil monophenyl hydrazone and its various derivatives have been extensively used as biologically active complexing agent and analytical reagent. The present work involves synthesis of binuclear Co²⁺, Ni²⁺ and Cu²⁺ complexes of Schiff bases (Structure I) formed by the condensation of benzil monophenyl hydrazone with analine and substituted aniline.

$M = $ Co²⁺, Ni²⁺ and Cu²⁺ ; $B = H_2O$, pyridine, α⁻, β⁻ or γ⁻-picoline; $X = H$ or Br; $Ph = $ —C_6H_5

EXPERIMENTAL

All the chemicals used during this study were of AnalaR grade. All amines were distilled or recrystallized prior to use. The solvents were dried and distilled before the use according to standard procedures.

Preparation of Schiff Base

The Schiff base was synthesized by the condensation of benzil monophenyl hydrazone and aniline in 1 : 1 molar ratio; yellow precipitate of Schiff base appeared. The compound is highly soluble in ethanol, acetone, ether, etc. The compound was analyzed and found to contain C 83.2, H 5.6, N 11.2% which corresponds with the formula $C_{26}H_{21}N_3$.

Preparation of $[M(L_1)_2B_2]$ and $[M(L_2)_2B_2]$ complexes

The acetate of a metal was dissolved in aqueous ethanolic solution. To the known weight of the metal solution was then added an ethanolic solution of (L_1H_2) and (L_2H_2) in 1 : 1 molar ratio followed by a few drops of acetic acid (pH 6). The resulting solution was then refluxed on steam bath for 0.5–1 h till the complex precipitated out. Precipitate obtained was dried over KOH pellets. The complexes of this ligand were prepared using acetates of Co^{2+}, Ni^{2+} and Cu^{2+} in aqueous medium as well as in presence of base like pyridine, α^-, β^- or γ^--picoline with each of the metals separately and the procedure carried out in each case was of similar nature with a slight variation of time of reflux. On the basis of analytical data, the complexes were found to possess the molecular formula $M(L_1)B_2$ and $M(L_2)B_2$ where M = Co(II), Ni(II) and Cu(II), B = H_2O, pyridine, α, β or γ-picoline. Electrical conductivities of solutions of complexes were measured by conductivity meter bridge manufactured by Wiss-Techenwerch Stathen type-LBR at room temperature in DMF.

The electronic absorption spectra of the complexes were recorded with Hitachi-320 spectrophotometer at CDRI, Lucknow. The infrared spectra were recorded on Perkin-Elmer-577 spectrophotometer using KBr.

RESULTS AND DISCUSSION

The ligands L_1H_2 and L_2H_2 are potential ligands to coordinate with metal ions. The weak band in the region around 530–520 cm^{-1} may be due to $\nu(M-N)$ vibration. In the case of aquo complexes separate band for coordinated H_2O is obtained around 3400 cm^{-1}. The frequency observed in the range of 800–700 cm^{-1} in aquo complexes may be attributed to rocking mode of coordinated water. The pyridine or α, β or γ-picoline complexes, however, display some extra band in finger print and in far infra red region. The pyridine ring breathing mode of vibration, located at 1020–990 cm^{-1} in complexes, has been taken to be characteristic vibrations of coordinated pyridine and picoline molecules.

In the present experiments $Ni(L_1)_2B_2$ and $Ni(L_2)_2B_2$ complexes have magnetic moments in the range 2.89–3.10 B.M. which corresponds to their octahedral geometry. The spectra of $Ni(L_1)_2B_2$ and $Ni(L_2)_2B_2$ complexes do not give the bands at lower energy which might have been impeded by the absorption bands of the ligands. However, bands near 465–470 nm in the Ni(II) complexes may be assigned due to $^3A_{2g}$, $^3T_{1g}(p)$ or C.T. band which is suggestive of their octahendral geometry.

TABLE-1
ELECTRONIC BAND POSITIONS (nm) AND THEIR ASSIGNMENTS
$M(L_1)_2(B)_2$ COMPLEXES

Complexes	π-n	n-π	π-π*	d-d	Band
$Cu(C_{26}H_{20}N_3)_2(H_2O)_2$	210	240	305	410	$^2B_{1g} \rightarrow {}^2E_g$ + C.T.
$Cu(C_{26}H_{20}N_3)_2(C_5H_5N)_2$	205	240	305	410	
$Cu(C_{26}H_{20}N_3)_2(\alpha\text{-pic})_2$	205	240	305	410	
$Cu(C_{26}H_{20}N_3)_2(\beta\text{-pic})_2$	205	240	305	410	
$Cu(C_{26}H_{20}N_3)_2(\gamma\text{-pic})_2$	205	240	305	410	
$Ni(C_{26}H_{20}N_3)_2(H_2O)_2$	225	450	370	465	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P) or C.T.
$Ni(C_{26}H_{20}N_3)_2(C_5H_5N)_2$	210	255	370	470	
$Ni(C_{26}H_{20}N_3)_2(\alpha\text{-pic})_2$	205	250	370	460	
$Ni(C_{26}H_{20}N_3)_2(\beta\text{-pic})_2$	205	250	370	460	
$Ni(C_{26}H_{21}N_3)_2(\gamma\text{-pic})_2$	205	250	370	465	
$Co(C_{21}H_{21}N_3)_2(H_2O)_2$	210	250	320	460	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Co(C_{26}H_{21}N_3)_2(C_5H_5N)_2$	250	250	320	460	
$Co(C_{26}H_{21}N_3)_2(\alpha\text{-pic})_2$	250	250	320	460	
$Co(C_{26}H_{21}N_3)_2(\beta\text{-pic})_2$	250	250	320	460	
$Co(C_{26}H_{21}N_3)_2(\gamma\text{-pic})_2$	250	250	320	460	

TABLE-2
ELECTRONIC BAND POSITIONS (nm) AND THEIR ASSIGNMENTS
$M(L_2)_2(B)_2$ complexes

Complexes	π-n	n-π*	π-π*	d-d	Bands
$Cu(C_{26}H_{20}BrN_3)_2(H_2O)_2$	210	250	300	410	$^2B_{1g} \rightarrow {}^2E_g$ + C.T.
$Cu(C_{26}H_{20}BrN_3)_2(C_5H_5N)_2$	210	250	300	410	
$Cu(C_{26}H_{20}BrN_3)_2(\alpha\text{-pic})_2$	210	250	310	410	
$Cu(C_{26}H_{20}BrN_3)_2(\beta\text{-pic})_2$	210	250	310	410	
$Cu(C_{26}H_{20}BrN_3)_2(\gamma\text{-pic})_2$	210	250	310	410	
$Ni(C_{26}H_{20}BrN_3)_2(H_2O)_2$	215	240	375	465	$^3A_{1g} \rightarrow {}^3T_{1g}(P)$
$Ni(C_{26}H_{20}BrN_3)_2(C_5H_5N)_2$	215	240	370	470	or C.T.
$Ni(C_{26}H_{20}BrN_3)_2(\alpha\text{-pic})_2$	215	240	370	460	
$Ni(C_{26}H_{20}N_3)_2(\beta\text{-pic})_2$	215	240	370	460	
$Ni(C_{26}H_{21}N_3)_2(\gamma\text{-pic})_2$	215	240	370	460	
$Co(C_{26}H_{20}BrN_3)_2(H_2O)_2$	250	250	320	460	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Co(C_{26}H_{20}BrN_3)_2(C_5H_5N)_2$	250	250	320	460	
$Co(C_{26}H_{20}N_3)_2(\alpha\text{-pic})_2$	250	250	320	460	
$Co(C_{26}H_{20}BrN_3)_2(\beta\text{-pic})_2$	250	255	320	460	
$Co(C_{26}H_{20}BrN_3)_2(\gamma\text{-pic})_2$	250	255	320	460	

The room temperature magnetic moment values of the Cu(II) complexes $Cu(L_1)_2B_2$ and $Cu(L_2)_2B_2$ are around 1.91 B.M. which corresponds to their distorted octahedral geometry as explained by John-Teller effect. The ground state of Cu(II) in octahedral geometry is ^2E_g. The moment from mixing in an excited state is given by

$$\mu_{eff}(Eg) = u_s\left(\frac{1-2}{10\,Dq}\right) + \frac{4NB^2}{10\,Dq}$$

This adds to about 5% to the spin only value. The magnetic values suggest that the complex $Cu(L_1)_2B_2$ and $Cu(L_2)_2B_2$ are having octahedral arrangement of ligand around it. The reflectance spectra of the complexes $Cu(L_1)_2B_2$ and $Cu(L_2)_2B_2$ show a broad asymmetric band appearing around 410 nm which is attributed to C.T. $+\,^2B_{1g} \rightarrow\,^2E_g$ transition similar to distorted octahedral Cu(II) complexes.

The magnetic values obtained for $Co(L_1)_2B_2$ and $Co(L_2)_2B_2$ complexes are in the range of 4.83 to 5.15 B.M. which suggests the high spin six-coordinated octahedral arrangement of ligand molecules around the metal ion. The reflectance spectra of Co(II) complexes show the band near 460 nm may be assigned due to $^4T_{1g}(F) \rightarrow\,^4T_{1g}(P)$ transition. In some of the complexes, the 3 band is split into two components one near 410 nm and the other at 460 nm. The splitting of 3 band into two or more components may be due to the presence of low symmetry components in the ligand field. The lowering in the symmetry being due to the presence of mixed ligand field and the different bases acting as ligand. Thus electronic spectra of the Co(II) complexes suggest their octahedral nature.

Thus on the basis of analysis, magnetic moment measurement and spectral studies, it is suggested that the ligands form octahedral complexes with Cu^{2+}, Ni^{2+} and Co^{2+} in the presence of base like water, pyridine and α, β or γ-picolines.

REFERENCES

1. K.Ito and J.Ito, *Aust. J. Chem.*, **2**, 406 (1958).
2. L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 276 (1964).
3. C.K. Jorgensen, *Acta Chem. Scand.*, **9**, 1362 (1955); **10**, 885 (1956).
4. D.M.L. Goodgame, and F.A. Catton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).
5. A.D. Idchr, *J. Phys. Chem.*, **67**, 1214 (1963).
6. L.E. Orget, and J.D. Dunit, *Nature*, 179, 462 (1957).
7. D. Poldar, *Phys.*, **9**, 709 (1942).
8. C.J. Ballhausen, *Kgd.Danskervidenskah, Mat-fys. Medd.*, **29** (1954).
9. R.L. Belford, M. Calvin and G. Belford, *J. Chem., Phys.*, **26**, 1165 (1975).
10. J.B. Bjerrum, C.J. Ballhausen and C.K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).
11. C.K. Jorgensen, *Acta Chem. Scand.*, **10**, 887 (1956).
12. E Foster, and D.M.L Goodgame, *J. Chem. Soc.*, 2790 (1964).