RJC
http://www.rasayanjournal.com

RASĀYAN *J. Chem.*
Vol.2, No.2 (2009), 271-275
ISSN: 0974-1496
CODEN: RJCABP

# SYNTHESIS AND CHARACTERIZATION OF SOME $N_2O_2$-SCHIFF BASES AND THEIR METAL COMPLEXES

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## ABSTRACT

**The syntheses of some Ni(II), Co(II) and Cu(II) Schiff base complexes have been reported. The Schiff base ligands $H_2L^1$ ($C_{40}H_{32}N_2O_2$), $H_2L^2$ ($C_{32}H_{28}N_2O_2$) and $H_2L^3$ ($C_{22}H_{26}N_2O_2$) under were prepared by the condensation of amines namely benzidine and 1,4-phenylenediamine with benzoin, benzoylacetone and acetylacetone. A fourth ligand $H_2L^4$ ($C_{34}H_{28}N_2O_2$) was obtained by the condensation of 1,4-phenylenediamine with benzoin. Schiff base ligands and their complexes have been subjected to elemental analysis, Infrared, electronic spectral studies, molar conductivity and magnetic moment measurements. The Ni(II) and Co(II) complexes showed an octahedral and square planar geometries. In addition, the analysis exhibited a different chelation mode towards metal and ligand substitution, since a mono- and dinuclear metal complexes have been identified.**

**Keywords:** Synthesis; Benzidine; Ni(II) and Cu(II) ions; binuclear complexes.

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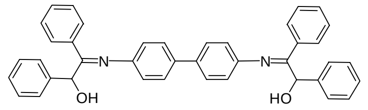
## INTRODUCTION

Recently transition metal complexes with salen ligands derived from the condensation of salicylaldhyde with a diamine, have been widely studied. Dinucleating metal complexes have been attractive area of research, in view of their significance as biomimetric catalysts in the process of oxygenation[1-5]. Discoveries of dinuclear cores at the active sites of some metalloproteins have aroused interest in the investigation of multimetallic systems.[6] Schiff bases have been widely used as ligands because of high stability of the coordination compounds and their good solubility in common solvents. The π-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions, acting as bidentate or tetradentate ligands in metal chelates involving a NO or $N_2O_2$-Schiff-base donor atom sets. These Schiff base metal derivatives have considerable interest due to their role as model complexes to biological systems, contributing to the knowledge of their structure and behavior.[7-8] Catalytic studies reveal that the metal complexes of $N_2O_2$-Schiff-base donor types of chiral metal complexes are active catalysts for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilylcyanation of aldehydes, and desymmetrization of meso-N-sulfonylaziridine.[9] We have previously reported results for the structural study of some Schiff bases derived from ß-diketones and diamines and their complexes.[10] Now we report the synthesis and structural investigation of another set of related tetradentate Schiff base ligands and their complexes with Co(II), Ni(II) and Cu(II) ions.

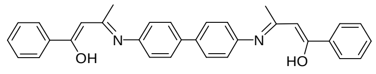
## EXPERIMENTAL

All materials and reagents used in this study were pure laboratory chemicals. The solvents and metal salts were used as they received from the supplier without further purification. The synthesis of $N_2O_2$-Schiff-base ligands and their complexes were prepared on the methods reported previously.[10-11]. A mixture of respective amines and ketons in the molar retio 1:2 was taken absolute ethanol (40 ml), to this ethanolic solution, few drops of piperidine were added as a condensing agent and refluxed for

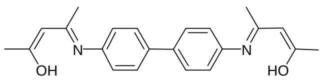
12hrs. The product formed was filtered and recrystallised from ethanol and dried over $CaCl_2$. The Schiff base ligand $H_2L^1$ ($C_{40}H_{32}N_2O_2$) was prepared by refluxing benzideine ( 9.21g, 0.05mol) and benzoin (21.22g,0.1mol) in absolute ethanol with few drops of piperidine for 12hrs. The reaction mixture was cooled to collect the product as yellow precipitate. The Schiff base complexes under investigation were synthesized as follows: The ligand dissolved in (20 ml) absolute ethanol was added to ethanolic solution (20ml) of metal chloride salt in molar ratio 1:1 or 1L:2M (L=ligand; M=metal). The mixture was refluxed for 10hrs, then the volume of the mixture was reduced to one-third. On cooling a crude product was formed, which was collected by filtration and washed several times with ethanol and dried over anhydrous $CaCl_2$.



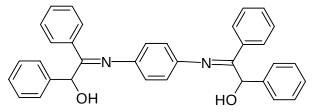
$H_2L^{1\,\yen}$($C_{40}H_{32}N_2O_2$)



$H_2L^2$ ($C_{32}H_{28}N_2O_2$)



$H_2L^3$ ($C_{22}H_{24}N_2O_2$)



$H_2L^4$ ($C_{34}H_{28}N_2O_2$)

### Measurements

The synthesized Schiff bases and their complexes were subjected to elemental analysis using Perkin_Elmer 2400 instrument. The melting points were determined using Philip Haris Shenstone-England, Serial No.B/A-211. The molar conductance values of the Schiff base complexes were measured in ($10^{-3}$M) in DMF or chloroform using CMD650 digital conductivity meter. The infrared spectra were recorded using KBr disks on BRUKER IFS-25 FTIR spectra photometer. Magnetic properties of the complexes were measured by magnetic susceptibility balance Sherwood Scientific England.

## RESULTS AND DISCUSSION

Physical characteristics and analysis of C, H and N of the compounds considered are listed in Table 1. The results of C, H and N percentage are in accordance with the composition suggested for the ligands and their complexes. The obtained analytical data indicated the formation of mono- and binuclear metal complexes.

**Table-1:** Elemental analysis, color, molar conductivity and m.p of the Schiff base complexes under investigation.

| Complex | M.Wt | color | Cond. $scm^2mol^{-1}$ | M.p C° | Found (calc.) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C% | H% | N% |
| $H_2L^1.H_2O$ | 588.70 | Yellow | - | 110C° | 81.88<br>(81.61) | 5.49<br>(5.47) | 5.28<br>(4.75) |
| $H_2L^2.H_2O$ | 490.57 | pale Yellow | - | 183C° | 77.51<br>(78.34) | 6.19<br>(6.16) | 6.93<br>(5.71) |
| $H_2L^3$ | 350.44 | pale Brown | - | 190C° | 75.42<br>(75.40) | 7.26<br>(7.47) | 8.07<br>(7.98) |
| $H_2L^4.H_2O$ | 514.59 | pale Green | - | 182C° | 79.96<br>(79.35) | 6.07<br>(5.82) | 5.89<br>(5.44) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[Co(H_2L^1)_2].H_2O$ | 1220.32 | Yellow | 0.160 | >250 | 78.53<br>(78.74) | 5.27<br>(5.29) | 4.97<br>(4.59) |
| $[Ni(H_2L^1)_2]$ | 1202.07 | Pale Green | 0.312 | 188 | 80.56<br>(79.93) | 5.58<br>(5.20) | 5.20<br>(4.66) |
| $[Co(H_2L^2)_2]$ | 1001.07 | Yellow | 0.215 | 231 | 76.95<br>(76.71) | 6.12<br>(5.43) | 6.55<br>(5.59) |
| $[(Cu\,H_2L^2)_2]2H_2O$ | 1104.24 | Green | 0.300 | 220 | 69.92<br>(69.81) | 5.48<br>(5.23) | 5.12<br>(5.01) |
| $[(NiH_2L^2)_2\,4H_2O]$ | 1130.57 | Pale Green | 0.065 | >250 | 67.50<br>(67.99) | 5.81<br>(5.35) | 4.90<br>(4.96) |
| $[Ni\,(H_2L^3)_2]$ | 753.55 | Red | 14.00 | 209 | 70.27<br>( 70.13) | 6.82<br>(6.15) | 8.45<br>(7.44) |
| $[Co\,(H_2L^4)_2\,2H_2O]$ | 1086.14 | Pale Green | 0.225 | 194 | 75.65<br>(75.20) | 5.53<br>(5.38) | 5.64<br>(5.16) |
| $[(CuH_2L^4)_2]\,3H_2O$ | 1170.3 | gray | 0.345 | >250 | 69.42<br>(69.79) | 4.90<br>(5.00) | 4.62<br>(4.79) |

## Infrared spectra

The IR stretching frequencies for the Schiff bases and their complexes are given in Table 2. The IR spectra of the Schiff base ligands exhibited bands in the region 3318-3457 cm$^{-1}$ which were due to stretching frequency of O-H groups. The bands in the region 1324-1237 and 1674-1591cm$^{-1}$ were assigned for the presence of C-O and C=N groups respectively. On complexation, it is well strategy to compare the spectra of the free ligand and its complex to account for the chelation site(s). Some positional shift have been observed for the above bands namely C=N and C=O in the complexes. New bands were emerged for the complexes which were not seen in the free ligand, these bands were assigned for M-O and M-N.

**Table-2**: Infrared band assignments (cm$^{-1}$) of the Schiff bases and their complexes.

| **The complex** | **ν(C=N) cm$^{-1}$** | **ν( C-O) cm$^{-1}$** | **ν(OH) cm$^{-1}$** | **ν(M-O) cm$^{-1}$** | **ν( M-N) cm$^{-1}$** |
|---|---|---|---|---|---|
| $H_2L^1$ | 1673 | 1239 | 3379 | - | - |
| $H_2L^2$ | 1594 | 1318 | 3379 | - | - |
| $H_2L^3$ | 1628 | 1268 | 3457 | - | - |
| $H_2L^4$ | 1600 | 1261 | 3373 | - | - |
| $[Co\,(H_2L^1)_2]\,H_2O$ | 1674 | 1243 | 3377 | 569 | 445 |
| $[Ni\,(\,H_2L^1)_2]$ | 1679 | 1243 | 3379 | 638 | 486 |
| $[Co\,(H_2L^2)_2]$ | 1591 | 1317 | — | 521 | 446 |
| $[(Cu\,H_2L^2)_2]2H_2O$ | 1591 | 1317 | 3360 | 520 | 444 |
| $[(Ni(H_2L^2)_2\,4H_2O]$ | 1615 | 1324 | 3318 | 666 | 485 |
| $[Ni\,(H_2L^3)_2]$ | 1632 | 1272 | 3350 | 625 | 480 |
| $[Co(H_2L^4)_2\,2H_2O]$ | 1600 | 1299 | 3377 | 652 | 483 |
| $[(CuH_2L^4)_2]\,3H_2O$ | 1597 | 1297 | 3379 | 627 | 466 |

The molar conductance has been demonstrated to be a very useful tool in the investigation of geometrical structure of inorganic compounds. The molar conductance for the complexes is measured in 10$^{-3}$M solution in DMF and chloroform as solvents at room temperature (25-30C°). The molar conductivity was applied to investigate the existence of anions outside the coordination sphere for the complexes. The molar conductivity values are given in Table 1. The complexes showed a lower molar conductivity values in the range between 0.065 and 14.0 Scm$^2$mol$^{-1}$ which indicated their non-electrolytic behavior. Our results are in good agreement with those reported earlier[12]. The electronic spectra of the complexes in the range 200-800 nm were obtained using ($10^{-3}$M) DMF and Chloroform as solvents. The electronic spectra and magnetic moment values are useful in the evaluation of results provided by the other techniques of the structural investigation. The geometry assessment of the complexes around the metal ions was supported further from the results of electronic spectra and magnetic moment. The electronic spectra and magnetic moment results are given in Table 3. The obtained electronic spectra and magnetic moment results are in conformity with those reported previously[11-12].

The electronic spectra of the $[Co(L^1)_2].H_2O$ complex showed a band at 16393 $cm^{-1}$ which was assigned to $A_1g \rightarrow B_1g$ transition. Another band at 23094 $cm^{-1}$ was assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic ring or azomethine group. The magnetic moment susceptibility value of (1.76 B.M) supported the square planer geometry of the complex. The electronic spectra of the $[Co(L^2)_2]$ complex showed a band at 16949 $cm^{-1}$ which was assigned to $A_1g \rightarrow B_1g$ transition. Another band at 27397 $cm^{-1}$ was assigned to $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group. The magnetic moment susceptibility value of (1.80 B.M) supported the square planer geometry of the complex. The electronic spectra of the $[Co(L^4)_2(H_2O)_2]$ complex showed two bands at 17699 and 20618 $cm^{-1}$ which were assigned to ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$, ${}^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions. These transitions were supported the octahedral geometry. A band at 28248 $cm^{-1}$ was assigned to $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group. The magnetic moment susceptibility value of 3.8 B.M supported the octahedral geometry of the complex.

The electronic spectra of the $[Ni(L^1)_2]$ complex showed three bands at 18691, 22831 and 27397 $cm^{-1}$ which were assigned to ${}^1A_1g(P) \rightarrow {}^1A_2g$, ${}^1A_1g(P) \rightarrow {}^1B_2g$ and $\pi \rightarrow \pi^*$ transitions respectively. The magnetic moment susceptibility value is not recorded since the complex is diamagnetic and possessed square planer geometry. The electronic spectra of the $[(NiL^2)_2(H_2O)_4]$ complex showed two bands at 19607 and 14925 $cm^{-1}$ which were assigned to ${}^3A_2g \rightarrow {}^3T_1g$ (F) and ${}^3A_2g \rightarrow {}^3T_2g$ (F) transitions. A band at 27027 $cm^{-1}$ was assigned to $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group. The magnetic moment value of this complex is 2.3B.M which is lower than 2.8B.M due to anti-ferromagnetic interaction between Ni(II) ions. This indicated the formation of binuclear complex. The electronic spectra of the $[Ni(L^3)_2]$ complex showed two bands at 21739 and 23809 $cm^{-1}$ which were assigned to ${}^1A_1g(P) \rightarrow {}^1A_2g$ and ${}^1A_1g \rightarrow {}^1B_2g$ transitions. Another band at 26667 $cm^{-1}$ was assigned to $\pi \rightarrow \pi^*$ transition of the aromatic ring or azomethine group. The magnetic moment susceptibility value is not recorded since the complex is diamagnetic.

The electronic spectra of the $[(CuL^2)_2].2H_2O$ complex showed three bands at 15384, 23255 and 27397 $cm^{-1}$ which were assigned to ${}^1A_1g(P) \rightarrow {}^1A_2g$, ${}^1A_1g(P) \rightarrow {}^1B_2g$ and $\pi \rightarrow \pi^*$ transitions respectively. The magnetic moment value at room temperature of this complex is 1.3B.M which is lower than 1.7B.M due to anti-ferromagnetic interaction between two Cu ions, which confirmed the binuclear nature of the complex. The electronic spectra of the $[(CuL^4)_2].3H_2O$ complex showed three bands at 21739, 15960 and 29411 $cm^{-1}$ which were assigned to ${}^2B_1g \rightarrow {}^2A_1g$, ${}^2B_1g \rightarrow {}^2Eg$ and $\pi \rightarrow \pi^*$ transitions respectively. The first two transitions supported the square planar geometry around two metal ions. The magnetic moment value at 1.1B.M was attributed to anti-ferromagnetic interaction between two Cu ions, which confirmed the binuclear nature of the complex.

## ACKNOWLEDGEMENTS

The authors appreciatively acknowledge Mr. Omar Ahshad and Mr. Othman Al Sosee, Department of Chemistry, University, Musrata, for their immense support during this work.

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**Table-3**: Electronic Spectra, molar conductivity, magnetic moment and the geometries of the Schiff base complexes.

| **The complex** | $\lambda$ **nm** | $\varepsilon$ **Lmol$^{-1}$cm$^{-1}$** | **ν cm$^{-1}$** | **$\mu_{eff}$ B.M** | **Geometry** |
|---|---|---|---|---|---|
| [Co (H$_2$L$^1$) $_2$] H$_2$O | 433<br>610 | 2.367<br>2.053 | 23094<br>16393 | 1.76 | square planar |
| [Ni (H$_2$L$^1$)$_2$] | 438<br>535<br>365 | 2.685<br>2.108<br>1.826 | 22831<br>18691<br>27397 | Diamagnetic | square planar |
| [Co(H$_2$L$^2$)$_2$] | 590<br>365 | 3.2452.276 | 16949<br>27397 | 1.8 | square planar |
| [(CuH$_2$L$^2$)$_2$]2 H$_2$O | 650<br>430<br>365 | 2.923<br>2.499<br>1.853 | 15384<br>23255<br>27397 | 1.3 | square planar |
| [(NiH$_2$L$^2$) $_2$ .4H$_2$O] | 510<br>370<br>670 | 2.153<br>0.956<br>1.085 | 17857<br>27027<br>14925 | 2.3 | octahedral |
| [Ni (H$_2$L$^3$)$_2$] | 420<br>460<br>375 | 3.085<br>1.235<br>2.292 | 23809<br>21739<br>26666 | Diamagnetic | square planar |
| [Co(H$_2$L$^4$)$_2$ .2H$_2$O] | 566<br>485 | 2.509<br>1.303 | 17699<br>20618 | 3.8 | octahedral |
| [(CuH$_2$L$^4$) $_2$].3H$_2$O | 630<br>460<br>340 | 1.023<br>2.685<br>1.909 | 15873<br>21739<br>29411 | 1.1 | square planar |

(Received: 6 April 2009 Accepted: 17 April 2009 RJC-369)