*Asian Journal of Chemistry* Vol. 13, No. 4 (2001), 1601–1605

# Studies of Spectral and Magnetic Behaviour of Some Complexes of Co(II), Ni(II) and Cu(II) Ions with 2-(Acetylacetonato) Imino Aceto Hydroxamic Acid

S.N. THAKUR*, SHIV BRAT SINGH[1], SANJAY KUMAR[2], S.P. SINGH[3]
and ANUPMA KUMARI[4]
*Department of Chemistry, B.R.A. Bihar University, Muzaffarpur-842 001, India*

A series of complexes of the type $MLB_3$ [M = Co(II), Ni(II) and Cu(II) ions, B = $H_2O$, pyridine and γ-picoline] have been synthesised with hydroxamic acid as ligand, $H_2L$. Characterisation of the ligand and the complexes has been done on the basis of elemental analysis, spectral studies, magnetic susceptibility and electrical conductivity measurements. The ligand has been found to coordinate through two nitrogen and one oxygen atoms. Since the complexes are found to be octahedral, the remaining three coordination sites are satisfied by oxygen of $H_2O$ and nitrogen donor molecules such as pyridine and γ-picoline.

## INTRODUCTION

A large number of works on metal complexes with Schiff base ligands have been done but less work has been carried out on metal complexes with hydroxamic acid as ligand[1–6]. Therefore, in the present investigation, we report a series of complexes of Co(II), Ni(II) and Cu(II) ions of the type $MLB_3$ with hydroxamic acid as ligand, $H_2L$.

## EXPERIMENTAL

All the chemicals used in the present work (obtained from BDH) and α-amino acetic acid (obtained from Aldrich, USA) were used without further purification. For the preparation of the ligand, the procedure as reported in the literature was followed[1–6]. α-Amino aceto hydroxamic acid was prepared by Safir and Williams[1] by reacting glycine ester hydrochloride and hydroxylamine hydrochloride in equimolar proportion.

$$NH_2—CH_2—COOC_2H_5 + NH_2OH \rightarrow NH_2—CH_2—CONHOH + CH_3CH_2OH$$

---

[1] At. and P.O. Naini, Dist. Chapra, Bihar, India.

[2] Alkapuri, Bhagwanpur, Muzaffarpur, Bihar, India.

[3] Amrit Science Campus, Kathmandu, Nepal.

[4] Bakarganj, Patna-4, India.

α-Amino aceto hydroxamic acid was then dissolved in dry and cold methanol and allowed to react with the methanolic solution of acetylacetone in equimolar proportion under reflux on a water bath for several hours. The solution thus obtained on crystallisation produced a coloured solid which was then separated by filtration, washed and finally dried over KOH in a desiccator. The compound was further analysed and found to contain (%) C = 48.83, H = 6.98 and N = 16.28, which corresponds with the molecular formula $C_7H_{12}N_2O_3$.

The solution of the ligand in methanol was allowed to react with ethanolic solution of metal acetate in equimolar proportion under reflux on water bath for several hours. The resulting solution on crystallisation gave solids of different colour for different metals. The solid was then filtered, washed and dried over KOH in a desiccator. Acetates of Co(II), Ni(II) and Cu(II) ions was taken and complex of each metal was prepared separately with ligand, $H_2L$, in presence of bases like water, pyridine and γ-picoline.

Copper was estimated iodometrically. Nickel and cobalt were estimated gravimetrically as bisdimethyl glyoximato Ni(II) and $CoSO_4$ respectively. C, H and N were estimated by semimicro-combustion method.

Electrical conductivity of solutions of complexes were measured by conductivity meter bridge manufactured by Wiss-Techen Werch Stathen type-LBR at room temperature in DMF (solvent). The cell constant was measured at room temperature (30°C) using N/10 and N/100 KCl solution. 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 pellets in the range of 4000–400 $cm^{-1}$ at CDRI, Lucknow. Magnetic susceptibility of the complexes was determined by Gouy's method by using $Hg[Co(NCS)_4]$ as a calibrant.

## RESULTS AND DISCUSSION

The reaction taking place in the preparation of the ligand and its metal complexes involving acetylacetone (enolic), α-amino aceto hydroxamic acid and metal acetates can be represented as follows:

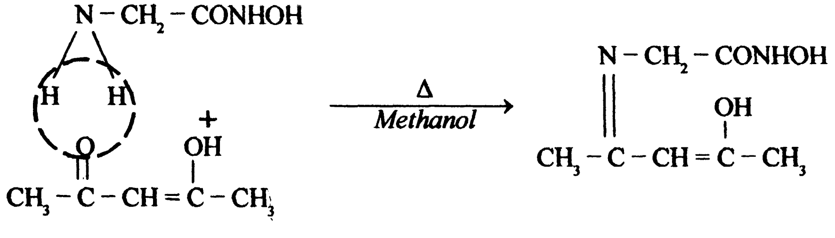
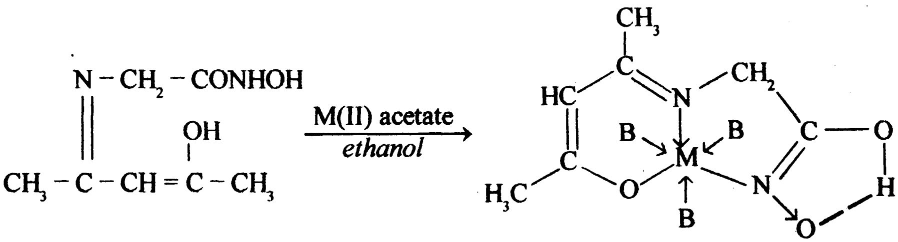


Fig. 1

On the basis of elemental analysis (Table-1), the complexes were found to possess the molecular formula (Fig. 2) of the type $MLB_3$ where M = Co(II), Ni(II) and Cu(II) ions and B = $H_2O$, pyridine and γ-picoline.



M = $Co^{2+}$, $Ni^{2+}$ or $Cu^{2+}$; B = $H_2O$, pyridine or γ-picoline

Fig. 2

All the complexes having different colour are stable at room temperature. The molar conductance values in the range of 20 to 30 for the complexes using $10^{-3}$ molar solution in DMF (Table-1) show that these complexes can be represented as $[M(C_7H_{10}N_2O_3)(B)_3]$. Molecular weights of these complexes indicate the monomeric nature of the complexes.

TABLE-1
ANALYTICAL, MAGNETIC MOMENT AND ELECTRICAL CONDUCTANCE DATA OF THE COMPLEXES

| Compound | $\mu_{eff}$ (B.M.) | $\Lambda_m$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$) | % Analysis, found (calcd.) | | | |
|---|---|---|---|---|---|---|
| | | | M | C | H | N |
| $[Co(C_7H_{10}N_2O_3)(H_2O)_3]$ | 4.80 | 25 | 20.70<br>(20.82) | 29.58<br>(29.69) | 5.76<br>(5.65) | 9.98<br>(9.89) |
| $[Co(C_7H_{10}N_2O_3)(C_5H_5N)_3]$ | 4.75 | 20 | 12.50<br>(12.64) | 56.52<br>(56.66) | 5.44<br>(5.36) | 15.16<br>(15.02) |
| $[Co(C_7H_{10}N_2O_3)(C_5H_4NCH_3)_3]$ | 4.85 | 30 | 11.32<br>(11.41) | 59.20<br>(59.06) | 6.18<br>(6.10) | 13.87<br>(13.78) |
| $[Ni(C_7H_{10}N_2O_3)(H_2O)_3]$ | 2.96 | 30 | 26.74<br>(20.76) | 29.65<br>(29.71) | 5.74<br>(5.65) | 9.98<br>(9.90) |
| $[Ni(C_7H_{10}N_2O_3)(C_5H_5N)_3]$ | 2.92 | 20 | 12.50<br>(12.60) | 56.56<br>(56.68) | 5.44<br>(5.36) | 15.18<br>(15.03) |
| $[Ni(C_7H_{10}N_2O_3)(C_5H_4NCH_3)_3]$ | 2.95 | 22 | 11.44<br>(11.56) | 58.95<br>(59.09) | 6.20<br>(6.10) | 13.90<br>(13.78) |
| $[Cu(H_7N_{10}N_2O_3)(H_2O)_3]$ | 1.95 | 30 | 21.95<br>(22.08) | 29.06<br>(29.21) | 5.64<br>(5.56) | 9.80<br>(9.73) |
| $[Cu(C_7H_{10}N_2O_3)(C_5H_5N)_3]$ | 1.92 | 20 | 13.40<br>(13.49) | 56.01<br>(56.11) | 5.40<br>(5.31) | 14.96<br>(14.87) |
| $[Cu(C_7H_{10}N_2O_3)(C_5H_4NCH_3)_3]$ | 1.90 | 25 | 12.30<br>(12.39) | 58.40<br>(58.53) | 6.16<br>(6.04) | 13.74<br>(13.65) |

**IR spectra:** A sharp and strong band near 3100 $cm^{-1}$ is assigned due to combined frequencies of ν(O—H) and ν(N—H) vibrations. The ν(OH) of the enol form (—C—OH) shifts from 3500 to 3100 cm$^{-1}$ due to hydrogen bonding. So, there is always a chance of coupling ν(OH) band with ν(N—H) in the spectra of hydroxamic acid. The —C—CH$_3$ and —CH$_2$— groups present in the ligand are indicated by bands at 1830 cm$^{-1}$ and 1430 cm$^{-1}$ respectively. No specific bands for phenyl ring indicate the absence of phenyl ring in the ligand. The characteristic bands due to chelated acetylacetone ligand appear at 1575–1510 cm$^{-1}$ indicating the presence of ν(C═C) vibration in the ligand. All the complexes show a band in the range of 1640–1625 cm$^{-1}$ due to ν(C═N) vibration. In the spectra of the ligand this band appears at 1660 cm$^{-1}$. Lowering of this band in the complexes suggests participation of imine nitrogen atom in coordination. At the same time no band is obtained around 1750–1740 cm$^{-1}$ which indicates the condensation of the amine and ketone groups. The bands around 590 cm$^{-1}$ and 445 cm$^{-1}$ in all the complexes indicate ν(M—O) and ν(M—N) vibrations which further confirms the coordination of nitrogen and oxygen atoms of these groups with the metals.

TABLE-2

ELECTRONIC AND IR SPECTRAL BANDS (cm$^{-1}$) OF THE METAL COMPLEXES

| Compound | Colour | IR spectral bands (cm$^{-1}$) | | | Electronic spectral data (cm$^{-1}$) |
|---|---|---|---|---|---|
| | | ν(C═N) | ν(M—N) | ν(M—O) | |
| [Co(C$_7$H$_{10}$N$_2$O$_3$)(H$_2$O)$_3$] | Golden brown | 1640 | 450 | 595 | 17200–22400 |
| [Co(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_5$N)$_3$] | Yellowish brown | 1630 | 445 | 600 | 16500–21200 |
| [Co(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_4$NCH$_3$)$_3$] | Yellowish brown | 1625 | 440 | 580 | 16700–22000 |
| [Ni(C$_7$H$_{10}$N$_2$O$_3$)(H$_2$O)$_3$] | Greenish brown | 1640 | 445 | 590 | 17100–22000 |
| [Ni(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_5$N)$_3$] | Greenish brown | 1625 | 440 | 585 | 9500–20500 |
| [Ni(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_4$NCH$_3$)$_3$] | Greenish brown | 1630 | 435 | 575 | 8700–19200 |
| [Cu(C$_7$H$_{10}$N$_2$O$_3$)(H$_2$O)$_3$] | Parrot green | 1635 | 430 | 580 | 9800–14200 |
| [Cu(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_5$N)$_3$] | Light green | 1625 | 435 | 560 | 9600–13700 |
| [Cu(C$_7$H$_{10}$N$_2$O$_3$)(C$_5$H$_4$NCH$_3$)$_3$] | Light green | 1630 | 445 | 575 | 9500–13500 |

**NMR spectrum:** The presence of δ value for —OH corresponds to three protons in the case of the ligand whereas the δ value for —OH corresponds to one proton in the case of the metal complexes. This suggests that the protonation of two —OH protons (one from the —OH of oximino group and the other from the —OH of the acetylacetonato moeity) has occurred in the complex formation indicating participation of O and N atoms in the bonding with the metal atom.

**Electronic spectra and Magnetic Moment:** The values of magnetic moment of Co(II) complexes (Table-1) in the range of 4.75–4.90 BM indicate that Co(II) complexes should be octahedral in nature. In case of Co(II) complexes a weak band due to $^4T_{1g} \rightarrow {}^4T_{2g}$ at 8200 $cm^{-1}$ and an another broad and unsymmetrical band due to $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) in the region of 22000–17000 $cm^{-1}$ indicating octahedral arrangement of the ligands around the meal Co(II) ion.

In case of Ni(II) complexes the values of magnetic moment obtained in the range of 2.80–3.00 BM indicates octahedral nature of the complexes. The complexes of Ni(II) ion show three bands due to the spin allowed transitions from the $^3A_{2g}$ ground term to the three excited triplet terms [$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ = 8400 $cm^{-1}$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ = 15,500 $cm^{-1}$ and $^3A_{2g}(P) \rightarrow {}^3T_{1g}(P)$ = 19,400 $cm^{-1}$ indicating the octahedral nature of the complexes.

In case of Cu(II) complexes the values of magnetic moment obtained in the range of 1.90–1.95 BM indicate octahedral arrangmeent of the ligand around the metal. In Cu(II) complexes a broad and unsymmetrical band is obtained in the range of 10,00–14,000 $cm^{-1}$ due to $^2E_g \rightarrow {}^2T_{2g}$ transitions supporting octahedral or tetragonal field for the complexes.

## ACKNOWLEDGEMENTS

The authors are thankful to Dr. J. Thakur, Head of the Department of Chemistry, BRA Bihar University, Muzaffarpur for providing available library and laboratory facilities and giving invaluable suggestions from time to time during the course of carrying out the experimental work. Further one of the authors (Dr. S.N. Thakur) is thankful to his colleagues of Chemistry Department and Dr. H.C. Rai of L.S. College, Muzaffarpur for their kind cooperation and encouragement.

## REFERENCES

1. S.K. Safir and J.M. Williams, *J. Org. Chem.*, **17,** 1298 (1952).
2. H.C. Rai, Ashwini Kumar and Anuradha Kumari, *Asian J. Chem.*, **12,** 557 (2000).
3. Shiv Brat Singh and Shiva Nath Thakur, *Asian J. Chem.*, **13,** 328 (2001).
4. A.K. Chakrabutry, J. Xavier and R. Ray, *Science and Culture (Ind.)*, **20,** 146 (1954).
5. A.W. Scott and B.L. Wood, Jr., *J. Org. Chem.*, **7,** 508 (1942).
6. V.C. Bess and J.H. Yoe, *Talanta*, **13,** 735 (1968).

(*Received*: 21 June 2001; *Accepted*: 30 August 2001) AJC-2421