



Synthesis and Antifungal Study of Mixed Ligand Complex of Ni(II) with Dibasic Tridentate Schiff Base as Primary and Naphthoic Acid as Co-ligand

MUKTI VERMA¹, MONI VERMA² and NAZIA TARANNUM^{1,*}

¹Department of Chemistry, Chaudhary Charan Singh University, Meerut-250 005, India

²Department of Chemistry, Nanak Chand Anglo Sanskrit College, Meerut-250 003, India

*Corresponding author: E-mail: naz1012@gmail.com

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The present work reports the synthesis of mixed ligand complex of Ni(II) with dibasic tridentate Schiff base derived from the condensation of thiosemicarbazides with acetoacetanilide and *o*-chloro acetoacetanilide as primary and 1-hydroxy-2-naphthoic acid as co-ligand. The complex was characterized on the basis of elemental analysis, magnetic, spectral and electrolytic conductance study. Different ligand field parameters were also calculated. The ligand and its Ni(II) complex were also screened for their antifungal activity against different fungi strains viz. *Drechlera tetramera*, *Alternaria alternate* and *Fusarium oxysporum*.

Keywords: Nickel(II) complex, Thiosemicarbazones, Naphthoic acid, Antifungal activity, *o*-Chloro acetoacetanilide, Schiff base.

INTRODUCTION

The coordination chemistry of divalent ions involving multidentate ligands have received limited attention. Amongst divalent ions, Ni(II) is known to form high spin, ($s = 5/2$), low spin ($s = 1/2$) and intermediate spin ($s = 3/2$) complexes under influence of different ligand field. Spin-crossover phenomenon is usually observed in Ni(II) compounds. Kanungo and Rahman [1] have reported five and six coordinate low-spin Ni(II) complexes. Patel and Verma [2] have reported the formation of Ni(II) chelates of N,N'-hexamethylene-bis-(2,5-di-OH-acetophenone/propionophenone/benzophenone). Complexes of nickel(II) with *p*-dimethyl aminoaniline-3-penten-2-one have been prepared and characterized by Agrawal and Chandra [3]. Complexes of Ni(II) with 1-(2'-pyridyl) benzothiazole-2-thione have been studied by Khan *et al.* [4], where spectrophotometric study of reaction between Ni(II) and 2-hydroxy-1-naphthaldoxime was carried out [5].

Kumar and Sethi [6] have reported the spectral, magnetic, Mossbauer and chemotherapeutic studies of Ni(II) complexes with various new derivatives of isonicotinic acid hydrazide. Complexes of the composition $H[M(C_{18}H_{31}NO_4)_2]$ [$M = Fe^{3+}$] with N-4-methyl-7-hydroxy-8-acetocoumarinylidene-*o*-aminophenol were prepared and characterised [7]. All these metal complexes exhibited octahedral geometry. Ni(II) complex of Schiff bases derived from salicylhydrazide and 6-methyl-4-hydroxy-3-acetyl-coumarin has also been reported in literature [8].

Various studies on stability constant [9] of Ni(II) complexes of N-(8-aceto-7-hydroxy-4-methyl coumarin)-*o*-phenylene diamine was determined at 25 °C and $\mu = 0.1M$ ($NaClO_4$) in 75 % (v/v) aqueous-dioxane medium at different M:L ratio. Synthesis and structural characterization of Ni(II) complexes with terephthalic acid hydrazide Schiff bases were carried out by Agrawal and Tutlani [10]. Octahedral complexes of Ni(II) with 2,5-dihydroxyacetophenone Schiff bases were also reported [11]. Magnetic and spectral studies of octahedral complexes of Ni(II) with β -phenylamino dihydroxy propiophenone, β -benzidiny-2:5 dihydroxy propiophenone and β -benzidiny-2,3,4-trihydroxy propiophenone were also reported [12]. Synthesis and structural determination of Ni(II) compounds with nitrogen, oxygen and sulphur ligands were studied [13]. Mossbauer studies on Ni(II) complexes with some nitrogen donor ligands were also analyzed [14].

The coordination chemistry of transition metals and their derivatives have attracted the researchers due to their biological importance [15-17]. The metal thiosemicarbazones compounds are emerging as a new experimental anticancerous chemotherapeutic agent [18], which shows activity against most of the cancers by inhibiting an enzyme required for DNA biosynthesis and cell division [19,20]. The nickel complex also plays a crucial role in photochemical reaction as well [21]. Nitrogen, oxygen and sulphur donor ligands possess a range of biological applications such as antitumour [22], antiviral [23], antibacterial [24], antimalarial [25] and antifungal activities [26].

The mixed ligand complexes of Ni(II) with dibasic tridentate Schiff bases derived by the condensation of thiosemicarbazides with acetoacetanilide and *o*-chloro acetoacetanilide as primary and 1-hydroxy-2-naphthoic acid as co-ligand were not been being studied so far. The synthesized complex was characterized by elemental analysis, magnetic, spectral and electrolytic conductance study. Different ligand field parameters have also been calculated. These complexes were also screened for their fungicidal activity against *Drechslera tetramera*, *Fusarium oxysporum* and *Alternaria alternata* at different concentrations.

EXPERIMENTAL

Ni(II) chloride, thiosemicarbazide, acetoacetanilide, *o*-chloro acetoacetanilide, 1-hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid, dimethyl formamide (DMF) and alcohol were purchased from Fischer Scientific, India. All the reagents used were of analytical reagent grade. Solvents were purified and dried before use. The elemental analysis was performed at Central Drug Research Institute, Lucknow, India. Conductance of the metal complexes were measured in nitromethane at 25 °C on Toshniwal conductivity bridge CL01/01 using dip type cell. The following accepted range of molar conductivity for water at concentration equal to M/1000 and temperature 25 °C were taken to determine the number of ions present in solution. The standard range of molar conductivity in mhos of univalent electrolyte is 215-273 mhos.

Infrared spectra of ligand and its Ni(II) complex were recorded on Beckmann IR 120 Spectrophotometer and Perkin Elmer improved 137 spectrophotometer in Nujol mull and KBr in the range 200 to 400 cm⁻¹ and 4000-400 cm⁻¹ at room temperature. The electronic spectra of the complexes were recorded in ethanol at room temperature on CZ-specord UV-visible spectrophotometer provided with an automatic recorder. The magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for diamagnetism.

Ligand field splitting energy (10 Dq): The values of 10 Dq for different complexes exhibiting various geometries have been calculated using equations given by Ballhausen [27] and Figgis [28] while the distorted parameters were evaluated using Lever equation [29].

Ligand field stabilization energy (LFSE): LFSE can be calculated with help of known unpaired electrons of Ni(II). The calculated value of μ (μ_{cal}) was found to be 2.84 B.M. and the experimental value μ_{exp} was 3.32 B.M.

Preparation of primary ligand: Schiff base was prepared by refluxing thiosemicarbazide with acetoacetanilide/*o*-chloro acetoacetanilide in 1:1 molar ratio in alcohol for 1 h. After refluxing, it was concentrated on water bath upto half of its volume. The precipitate obtained after condensation was filtered and dried.

Preparation of co-ligands: 2-Naphthonitrile (12 g), NaOH (7.5 g) and 55 mL of alcohol were mixed and heated in a sealed tube to 160 °C for 6 h. The mixture in the tube is diluted with water and acidified using hydrochloric acid. 2-Naphthoic acid formed is filtered, washed with water and recrystallized with alcohol. Further, nitration of 2-naphthoic was carried out at room temperature resulting in the formation of 1-nitro-2-

naphthoic acid which on reduction with Fe/HCl formed 1-amino-2-naphthoic acid. The hydrolysis of 1-amino-2-naphthoic acid in acidic medium gave 1-hydroxy-2-naphthoic acid which was washed, filtered and recrystallized.

Preparation of mixed ligand complex: To a warm absolute ethanolic solution of anhydrous Ni(II) chloride, hot ethanolic solution of Schiff base (primary ligand) was added dropwise. The reaction mixture was thoroughly stirred and refluxed at 70-80 °C for 2 h on water bath. Crystalline complex separated out on cooling at room temperature. The complex was filtered and washed with ethanol and ether and dried in oven over tetraphosphorus decoxide.

The mixed ligand complex was prepared by treating the ethanolic solution of binary complexes with ethanolic solution of 1-hydroxy-2-naphthoic acid. The reaction mixture was refluxed over water bath for about 4 h in each case and the reaction mixture was kept overnight at room temperature. The precipitated compounds were filtered, washed with acetonitrile and dry ether to remove unreacted ligand, if any. They were recrystallized from ethanol chloroform mixture. The crystalline complexes were dried in vacuum (yield 70 %). Elemental analysis calc. (found): C 51.4 (51.5), H 4.2 (4.1), N 10.9 (10.7), S 6.2 (6.1), Ni 11.4 (11.3).

Antifungal activity: The fungicidal activity of ligands as well as their complex was determined using the growth method [30]. The activity was determined against various fungi *i.e.* *Drechslera tetramera*, *Fusarium oxysporum* and *Aternaria alternata* at different concentrations. The testing samples were incorporated in warm Czapeck's Dox agar medium so as to give different concentration *viz.*, 100, 200 and 500 ppm. The test samples and the medium were autoclaved at 15 lbs for 15 min and then shaken well to give uniform dispersal of the chemical. The samples were poured into sterilized petri dishes keeping three replications of each treatments and a check without chemicals. Then the plates were inoculated centrally with a mycelia disc from 7 days old culture of the fungi towards complex. The linear mycelia growth rates in the presences of test samples and untreated controls were carried out and the data was statistically analyzed according to the following formula:

$$\text{Inhibition (\%)} = \frac{C - T}{C} \times 100$$

where C = diameter of fungus colony in control plates after 96 h, T = diameter of fungus colony in treated plates after 96 h.

RESULTS AND DISCUSSION

Analytical data of mixed ligand complex suggested 1:1:1 stoichiometry of isolated mixed ligand complex. Complex is stable upto 150 °C and showed non-electrolytic and non-hygroscopic nature. The complex is soluble in common organic solvents.

Infrared spectra: The comparison of infrared spectra of free ligands and mixed ligand complex showed the coordination of thiosemicarbazone and naphthoic acid to Ni(II) ions. Infrared spectra of free thiosemicarbazone ligands showed two bands at about 3450 and 3300 cm⁻¹. $\nu(\text{C}=\text{N})$ of free ligand absorbed in the region 1620 cm⁻¹ undergoes a negative shift (5-15

cm^{-1}) in the spectra of complex indicated the coordination of azomethine nitrogen to nickel. The bands of strong intensities in the spectra of the primary ligand around 1650 cm^{-1} are due to carbonyl group. In the spectra of complex, C=O group band is observed around 1620 cm^{-1} which may be present due to enolization and coordination through the deprotonated oxygen atom of $-\text{CH}_2-\text{C}=\text{O}$ group. The band due to C=S which appeared around 830 cm^{-1} in free primary ligand disappeared on complexation and a new band appears around $750\text{--}720 \text{ cm}^{-1}$. These observations may be due to thioenolization of $-\text{NH}-\text{C}=\text{S}$ group and subsequent coordination through the deprotonated sulphur [31]. Thus, it is concluded that thiosemicarbazones are potentially dibasic tridentate ligands and the coordination sites are β -nitrogen and thiolato sulphur and oxygen after deprotonation. The possibility of α -nitrogen coordination is ruled out because of considerable strain [32]. FTIR spectrum of mixed metal ligand complex is shown in Fig. 1.

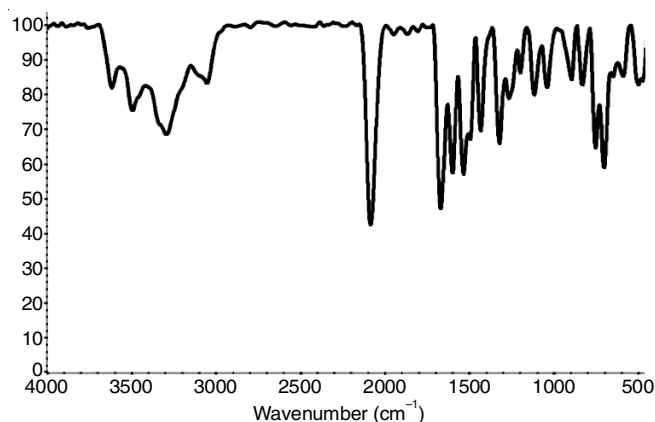


Fig. 1. FTIR of Ni(II) metal ligand complex

The νOH ($-\text{COOH}$ group) observed as a broad intense band at 2650 cm^{-1} in naphthoic acid is not traceable in the spectra of the mixed ligand complexes indicated that carboxylic proton is removed on complexation. The symmetrical and asymmetrical stretching vibrations of COO of free ligand observed at 1630 and 1410 cm^{-1} , respectively shifted to $1450\text{--}1440$ and $1580\text{--}1570 \text{ cm}^{-1}$ in the complex indicating the coordination of carboxylate oxygen to metal ion. The broad band centred at 2960 cm^{-1} in the spectra of complexes indicated the non-participation of phenolic $-\text{OH}$ present in naphthoic acid.

Magnetic moment and electronic spectral studies: The magnetic moment value of Ni(II) complex lies in the range $5.92\text{--}5.99 \text{ B.M.}$. These values are in the range usually found for high spin octahedral Ni(II) complexes. These values of magnetic moment correspond to five unpaired electrons and suggest six coordinated high, spin stereochemistry to these

complexes. The electronic spectra of Ni(II) complex show bands in the range $16700\text{--}17000$, $21700\text{--}22000$ and $24750\text{--}25150 \text{ cm}^{-1}$. These absorption bands may be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$.

The bands observed at 27900 cm^{-1} is expected to be charge transfer band (L–M). The band observed around 17600 and 29700 cm^{-1} may be due to splitting of ${}^4\text{T}_{1g}$ and thus the complex has distorted octahedral stereochemistry. The bands observed at 27900 cm^{-1} is expected to be charge transfer band (L–M). The band observed around 17600 and 29700 cm^{-1} may be due to splitting of ${}^4\text{T}_{1g}$ and thus the metal complex posed distorted octahedral stereochemistry. Six coordinated Ni(II) ions having $3d^8$ electronic configuration should exhibit a magnetic moment higher than expected for two unpaired electrons in octahedral ($2.98\text{--}3.22 \text{ B.M.}$) and tetrahedral ($3.40\text{--}4.21 \text{ B.M.}$) complexes, whereas its square planar complexes would be diamagnetic. This increase in magnetic moment value from that of spin only value has been considered due to some mixing in upper state via spin orbit coupling. The paramagnetic moment value observed for present complexes is 2.98 B.M. at room temperature which is consistent with octahedral symmetry.

In a cubic field, ${}^3\text{F}$ ground state of Ni(II) ion splits into three levels orbit singlet ${}^3\text{A}_2$ and the orbit triplet ${}^3\text{T}_1$ and ${}^3\text{T}_2$. The first excited term of the free Ni(II) ion ${}^3\text{P}$ transforms ${}^3\text{T}_{1g}$ under cubic symmetry.

Therefore, three spin viz., ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, allowed transition have been observed in the present octahedral Ni(II) complexes which appear at 8180 , 14200 and 23950 cm^{-1} , respectively and established for the majority of octahedral Ni(II) complexes. These bands at 8500 and 15900 cm^{-1} are due to the geometrical distortion and non-identical donor atom from octahedral symmetry. However, the observed spin allowed transition agree well with those predicted by Liehr and Ballhausen energy level diagram for Ni(II) ion in a ligand field of octahedral stereochemistry. The value of B (Racah Parameter) for the complex was calculated from ν_1 , ν_2 and ν_3 bond energies and using the diagram sum rule. The value of ν_2/ν_1 for the present complex found to be 1.69 , which confirmed the octahedral symmetry for mixed ligand Ni(II) complex.

Antifungal activity: The results (Table-1) shows that the ligand and complex inhibited the growth of fungi to a greater extent as the concentration increased. The enhanced activity of mixed ligand complex may be ascribed due to increased lipophilic nature due to chelation [33].

Conclusion

The synthesis of mixed ligands complex of Ni(II) from Schiff base derived by the condensation of thiosemicarbazides

TABLE-1
FUNGICIDAL TESTING OF LIGAND (PRIMARY + SECONDARY) AND ITS METAL COMPLEX

Test sample	Average % inhibition after 96 h								
	<i>Drechslera tetramera</i>			<i>Alternaria alternata</i>			<i>Fusarium oxysporum</i>		
	500 ppm	200 ppm	100 ppm	500 ppm	200 ppm	100 ppm	500 ppm	200 ppm	100 ppm
Ligand (Primary + Secondary)	70.0	50.1	30.4	68.8	49.8	28.9	69.4	48.8	30.2
Ni complex	50.6	43.6	20.2	50.8	42.8	20.4	57.2	43.4	20.3

*Growth responses of *Drechslera tetramera*, *Alternaria alternata* and *Fusarium oxysporum* (after 96 h at $26 \pm 1^\circ \text{C}$ on Czapek's dox agar medium) at different concentrations (ppm) in relation to the ligand and its metal complex.

with *o*-chloro acetoacetanilide as primary ligand and 1-hydroxy-2-naphthoic acid as co-ligand. These mixed ligands complex was prepared and characterized by their elemental analysis IR, UV-visible and magnetic studies. Ligands and its Ni(II) complex were also screened for their antifungal activity against different fungi using the growth method at different concentrations. Antifungal activity of the free ligand and their complexes were determined against *Drechslera tetramera*, *Fusarium oxysporum* and *Aternaria alternata*. The result indicates the growth of test fungi in untreated control whereas the growth was inhibited well by metal complex. It may be concluded that the ligands possess good fungicidal activity against all the three fungi as the NH₂ group plays a significant role in toxicity possibly by serving ligands in chelate formation. Based on magnetic moment and electronic spectral studies, it may be concluded that the metal complex posed distorted octahedral stereochemistry.

REFERENCES

1. P.B. Kanungo and R.D.V. Raman, *J. Indian Chem. Soc.*, **63**, 243 (1986).
2. R.B. Patel and J.K. Verma, *J. Indian Chem. Soc.*, **60**, 1094 (1983).
3. S.K. Agrawal and R. Chandra, *Proc. Nat. Acad. Sci. India*, **55A**, 180 (1985).
4. A. Khan, S. Tabrez and S.A.A. Zaidi, *Indian J. Chem.*, **36A**, 153 (1997).
5. L.K.S. Santha, N.R. Raghava and V.R. Krishnan, *J. Indian Chem. Soc.*, **62**, 79 (1985).
6. K. Yogendra and P.D. Sethi, *J. Indian Chem. Soc.*, **67**, 796 (1990).
7. G.P. Pokhariyal, *J. Indian Chem. Soc.*, **60**, 1089 (1983).
8. S.L. Nalanda, M.C. Ganorkar and N.R. Rao, *J. Indian Chem. Soc.*, **72**, 439 (1995).
9. G.P. Phokariyal and S.K. Agarwal, *J. Inst. Chemists (India)*, **63**, 147 (1991).
10. S.K. Agarwal, R. Gupta, R. Chandra and D.R. Tutlani, *Rev. Roum. Chim.*, **33**, 533 (1988).
11. P.S. Reddy, P.V. Ananthalakshmi and V. Jayatyagaraju, *E-J. Chem.*, **8**, 415 (2011); <https://doi.org/10.1155/2011/536269>.
12. S.K. Agarwal, R. Gupta, R. Chandra and D.R. Tutlani, *J. Inst. Chemist (India)*, **59**, 186 (1987).
13. S.K. Agarwal, D.R. Tutlani, P. Gupta and S.K. Hajela, *Bull. Pure Appl. Sci.*, **4C**, 48 (1985).
14. S.K. Agarwal and V.K. Tyagi, *Orient. J. Chem.*, **5**, 98 (1989).
15. N. Raman and S. Ravichandra, *Asian J. Chem.*, **15**, 255 (2003).
16. A. Bansal and R.V. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 381 (2001); <https://doi.org/10.1081/SIM-100002226>.
17. J.B. Gandhi and N.D. Kulkarni, *Polyhedron*, **18**, 1735 (1999); [https://doi.org/10.1016/S0277-5387\(99\)00041-8](https://doi.org/10.1016/S0277-5387(99)00041-8).
18. J. Patole, S. Pandhye, S. Pandhye, C.J. Newton, C. Anson and A.K. Powell, *Indian J. Chem.*, **43A**, 1654 (2004).
19. A. Murugkar, B. Unnikrishnan, S. Padhye, R. Bhonde, E. Triantafillou, S. Teat and E. Sinn, *Met. Based Drugs*, **6**, 177 (1999); <https://doi.org/10.1155/MBD.1999.177>.
20. A. Murugkar, S. Padhye, S. Guha-Roy and U. Wagh, *Inorg. Chem. Commun.*, **2**, 545 (1999); [https://doi.org/10.1016/S1387-7003\(99\)00152-5](https://doi.org/10.1016/S1387-7003(99)00152-5).
21. E. Yousif, R. Haddad, G.A. El-Hiti and R.M. Yusop, *J. Taibah Univ. Sci.*, **11**, 997 (2017); <https://doi.org/10.1016/j.jtusc.2017.03.002>.
22. S.K.S. Gupta, O.P. Pandey, A. Bhatt, A. Srivastava and K.N. Mishra, *Indian J. Chem.*, **41A**, 1421 (2002).
23. K.M. Ibrahim, S.I. Mostafa, N. Nawar and Z.A. Younis, *Indian J. Chem.*, **43A**, 2294 (2004).
24. R.C. Maurya, A. Pandey and D. Sutradhar, *Indian J. Chem.*, **43A**, 763 (2004).
25. S. Dave, A. Chaudhary, M. Agrawal, S.C. Joshi and R.V. Singh, *Indian J. Chem.*, **42A**, 268 (2003).
26. K. Dey, B.B. Bhaumik and S. Sarkar, *Indian J. Chem.*, **43A**, 773 (2004).
27. C.J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw Hill, New York (1996).
28. B.N. Figgis and J. Lewis, *Techniques of Inorganic Chemistry*, Interscience, New York, vol. 4 (1965).
29. A.B.P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817 (1971); <https://doi.org/10.1021/ic50098a031>.
30. R.K. Verma, S.C. Vyas, P.P. Shastri and A.C. Jain, *Indian Phytopathol.*, **32**, 394 (1979).
31. S.K. Dutta, D.B. McConville, W.J. Youngs and M. Chaudhury, *Inorg. Chem.*, **36**, 2517 (1997); <https://doi.org/10.1021/ic960670z>.
32. M.S. El-Shahawi and A.F. Shoaib, *Spectrochim. Acta A*, **60**, 121 (2004); [https://doi.org/10.1016/S1386-1425\(03\)00191-4](https://doi.org/10.1016/S1386-1425(03)00191-4).
33. J. Chakrabarti and B. Sahoo, *Indian J. Chem.*, **20A**, 931 (1981).