

Synthesis, Characterization and Biological Studies on Coordination Polymers of Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) with *Bis*-Bidentate Schiff Base

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Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) polychelates with *N,N'*-*bis*-[2-hydroxy-naphthalidine]-4,4'-diaminodiphenylmethane [H_2 -NalDADPM], have been synthesized and characterized by elemental analysis, magnetic susceptibility, spectral techniques like UV-Visible, IR, NMR, Mass, ESR and thermal studies. The molar conductivity data indicates that the chelates are non-electrolytes. Analytical data supports 1:1 (M:L) stoichiometry. The electronic spectra along with the magnetic data suggest octahedral geometry for all the chelates. The IR data shows the ligand H_2 -NalDADPM function as *bis*-bidentate ligand coordinating through ON-NO donor system. The ligand and its polychelates have also been screened for their antimicrobial activity using various microorganisms and all of them have been found to be moderately active against them.

Key Words: *N,N'*-*bis*-[2-Hydroxynaphthalidine]-4,4'-diaminodiphenylmethane, *bis*-Bidentate coordination, Antimicrobial activity.

INTRODUCTION

Polymers with inorganic elements in the backbone or as pendant groups, having unique property profiles that make them different from organic polymers. They shows characteristics like strong bonds, which resists cleavage reactions, multiple valences for attachment of wide variety of ligands, high thermal stability, the ability to tailoring new and interesting structures with endless variations. The metal polychelates depending on their structures can be used as catalyst, high-temperature and flame resistant fibres, semi-conductors, ion-exchange resins and for agricultural purposes. The use of transition metals in catalysis has been known for a long time, however recently they have been considered for practical applications. The metal alone or in combination with other moiety is used as catalyst. The tendency of transition elements to acquire different oxidation states is very useful

and informative. The study of polymeric ligands and their metal complexes is useful in metal separation, as a catalyst and in bioinorganic chemistry^{1,2}. Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups, which act as a chelating group in binding polyvalent metal ions. Schiff bases have remarkable property of forming complexes and serve as excellent chelating ligands³. Synthesis of polymeric complexes using *bis*-bidentate Schiff base ligands aroused much interest in recent times particularly with a view to examine their structural diagnosis^{4,5}. The present work deals with synthesis and characterization of polymeric Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) complexes of Schiff base derived by condensation of 4,4'-diaminodiphenylmethane (DADPM) with 2-hydroxy-naphthaldehyde. The compounds have been characterized by various physicochemical methods. The antimicrobial activity of the ligand as well as its metal chelates against *S. aureus*, *E. coli*, *S. typhi* and *B. subtilis*, have also been reported.

EXPERIMENTAL

All the chemicals used were of AR grade, 4, 4'-diaminodiphenylmethane were obtained from M/s Fluka chemicals. Co(OAc)₂·4H₂O, Ni(OAc)₂·6H₂O, Cu(OAc)₂·H₂O, Mn(OAc)₂·4H₂O and Zn(OAc)₂·2H₂O and 2-Hydroxy-naphthaldehyde were purchased from Acros Organics. The solvents were purified and doubly distilled before use.

The compounds were analyzed for C, H and N while the metal contents in the complexes were estimated by standard methods. The molar conductance values at room temperature were measured in DMF (10⁻³ M) on an Elico digital direct reading conductivity meter model CM-180. Room temperature magnetic susceptibility measurements were made on solid samples, by a Gouy method using Hg[Co(SCN)₄] as a calibrate. The electronic spectra of ligand and complexes were recorded on Shimadzu 160A spectrophotometer. Reflectance spectra of the solid complexes in the UV-Visible region were recorded against BaSO₄ as reference in Jasco 560 solid state UV-Visible spectrophotometer. Infrared spectra were recorded on a Perkin Elmer FTIR Spectrophotometer model 1600 using KBr pellets. The ¹H NMR spectra were recorded on Jeol-300 MHz high resolution instrument in chloroform solvent using TMS as the internal reference. The ESR spectra of Cu(II) complexes were recorded on E-112 Varin-E line, electron spin resonance spectrometer at room temperature in polycrystalline state using TCNE marker. TG and DTA data were made on Perkin-Elmer diamond instrument by recording the potential variations on increasing the temperature from room temperature at a heating rate of 10 °C/min.

Preparation of the Schiff base ligand: The Schiff base was obtained by reacting the 2-hydroxynaphthaldehyde (0.2 mol, 6.9 g) and 4,4'-diamino-

diphenylmethane (0.1 mol, 3.966 g) in EtOH medium. The mixture was refluxed on a heating rotamantle for 3 h with constant stirring. The product was then filtered, repeatedly washed with EtOH and acetone and dried in air. The ligand so obtained was recrystallized from xylene as microcrystalline compounds.

Preparation of complexes: In a typical reaction the ligand (0.504 g, 0.01 M) suspended in EtOH was added to NaOH (0.02M) and CH_3COONa (0.02 M) solution. The suspension was stirred on a heating rotamantle whereupon a reddish brown solution produced. To this a hot solution of corresponding metal acetate (0.01 M) was added drop-wise. The resulting mixture was stirred for 3-5 h with heating on a heating rotamantle. The separated compound was filtered by suction, repeatedly washed with EtOH dried in vacuum.

Antimicrobial screening: The antimicrobial activity of ligand and its metal chelates have been studied by disc diffusion method⁶. The activity of the compounds was assessed by measuring the diameter of inhibited zone in millimeters (mm). The culture of *E. coli*, *S. typhi*, *S. aureus* and *B. subtilis* were used as test organism, which were grown on nutrient agar medium. Solutions of the chelates ($1 \text{ mg}/10 \text{ cm}^3$) in DMSO were used for the studies. Growth was compared with standard antibacterial compound Tetracycline. Solvent DMSO used as blank was also run to know its activity.

RESULTS AND DISCUSSION

The reaction of 4,4'-diaminodiphenylmethane with 2-hydroxynaphthaldehyde, yields Schiff base ($\text{H}_2\text{-NalDADPM}$), the formulation of which is supported by analytical (Table-1) and spectral data. The ease of synthesis and high yield in a single step reaction from commercially inexpensive reagents make this an extremely attractive ligand system. The incorporated phenyl spacer sterically can prevent the two metal binding sites from coordinating to a single metal center. The reaction of Schiff base with metal ions yielded polychelates, which were found to be quite stable in atmosphere and non-hygroscopic in nature. The analytical and spectral data indicates that the metal ligand stoichiometry is 1:1 in all the polychelates. The resultant polychelates found to be highly coloured and insoluble in water and most of the organic solvents but were sparingly soluble in DMF and DMSO. The molar conductance values ($0.007\text{-}0.029 \text{ mhos cm}^2 \text{ mol}^{-1}$) of the complexes in DMF (0.25×10^{-3} molar) at 27°C suggest their non-electrolytic nature.

The ^1H NMR spectrum of the ligand in CDCl_3 exhibits the following data (δ ppm). The multiplet signals corresponding to aromatic protons occur in the range of 6.6-8.1, while singlet resonance signal due to methylene ($-\text{CH}_2-$) protons occurs at 3.5 ppm. A doublet at resonance signal 9.3 ppm

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF LIGAND AND
ITS METAL CHELATES

Compound / Colour	m.w. / [m.p. (°C)]	Elemental analysis (%): Found (Calcd.)				Molar cond. mhos cm ² mol ⁻¹
		M	C	H	N	
H ₂ -NaIDADPM (Yellow)	506.6 [230*]	–	82.98 (83.00)	5.53 (5.60)	5.17 (5.20)	–
[Co(NaIDADPM)·2H ₂ O] _n (Orange)	563.5 [>360]	10.40 (11.38)	74.60 (74.78)	4.92 (5.00)	4.29 (4.35)	0.029
[Ni(NaIDADPM)·2H ₂ O] _n (Green)	563.4 [>360]	10.68 (10.74)	74.62 (74.65)	4.97 (5.05)	4.29 (4.38)	0.029
[Cu(NaIDADPM)·2H ₂ O] _n (Reddish brown)	568.2 [>360]	11.18 (11.89)	73.98 (74.00)	4.97 (5.00)	4.26 (4.30)	0.025
[Zn(NaIDADPM)·2H ₂ O] _n (Brown)	570.08 [>360]	9.68 (9.63)	73.14 (73.10)	4.91 (4.80)	4.59 (4.55)	0.009
[Mn(NaIDADPM)·2H ₂ O] _n (Lemon yellow)	559.63 [>360]	11.71 (11.68)	73.12 (73.00)	4.68 (4.70)	5.00 (5.00)	0.007

*Melting point

indicating that the associated hydrogen belongs to NH rather than to an OH group this supports the condition may be an equilibrium mixture of the ketoenamine and enolimine forms⁷.

The ligand H₂-NaIDADPM shows a medium broad band at 3041 cm⁻¹; which may be assigned to the phenolic ν(OH) stretching vibration. The observed shifts to lower frequency indicating the presence of intramolecular hydrogen bonding as part of resonating ring system⁸. This band is being disappeared in the spectra of all chelates and also confirmed by the appearance of a new low intensity band (Table-2) in the region at 656-641 cm⁻¹ in the spectra of the chelates due to ν(M-O) vibrations. A strong and sharp band at 1624 cm⁻¹ in the spectrum of the ligand is due to ν(C-N) shows a shift to lower frequency by 10-47 cm⁻¹ in the complexes; which indicates the coordination of azomethine nitrogen to the metal ion⁹. This is again supported by the appearance of new low intensity band in the region 431-410 cm⁻¹ in the polychelates are attributed to ν(M-N) vibration. Association of water molecules in the complexes is confirmed by the appearance of new band in the region 3600-3300 cm⁻¹, 1680-1600 cm⁻¹ and strong sharp band near 830 cm⁻¹ assigned¹⁰ to O-H stretching, O-H deformation and rocking mode of coordinated water molecule, respectively. Thus, the IR data suggest that the Schiff base is dibasic *bis*-bidentate in nature and its coordination to metal ions through the phenolic oxygen and azomethine nitrogen atoms^{11,12}.

TABLE-2
SELECTIVE IR BANDS (cm⁻¹) OF LIGAND AND
ITS METAL CHELATES

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{OH}\cdots\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	Coord. Water molecule $\nu(\text{OH})$
H ₂ -NaIDADPM	1624 s	1324 s	3041 b	–	–	–
[Co(NaIDADPM)·2H ₂ O] _n	1614 s	1395 s	–	655 m	410m	3423 b 1658 s 830 m
[Ni(NaIDADPM)·2H ₂ O] _n	1616 s	1393 s	–	656 m	420 m	3424 b 1689 s 826 m
[Cu(NaIDADPM)·2H ₂ O] _n	1577 s	1388 s	–	641 m	415 m	3440 b 1650 s 824 m
[Zn(NaIDADPM)·2H ₂ O] _n	1615 s	1391 s	–	645 m	431 m	3445 b 1654 s 830 m
[Mn(NaIDADPM)·2H ₂ O] _n	1617 s	1391 s	–	650 m	425 m	3420 b 1654 s 835 m

The diffuse reflectance spectrum of the Co(II) chelate exhibits three bands at 22727, 21691 and 12106 cm⁻¹ which may be assigned to ⁴T_{1g}(F) → ⁴T_{2g}(F), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions, respectively for an octahedral stereochemistry. The Co(II) chelate has magnetic moment 4.92 BM in accordance with the spin only value for three unpaired electrons¹³ corresponding to high spin octahedral Co(II) complexes. The magnetic moment of Ni(II) chelate is 3.02 BM suggesting two unpaired electrons. Ni(II) chelate shows bands at 22624, 21645 and 9372 cm⁻¹ due to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{1g}(P), respectively for an octahedral geometry¹⁴. The Cu(II) chelate possesses a magnetic moment value of 1.95 BM, which is well within the expected range of octahedral Cu(II) complexes. The Cu(II) chelate exhibit an intense broad band at 15385 cm⁻¹ which is assigned to ³E_g → ²T_{2g} transition¹⁵. The electronic spectrum of Mn(II) complex exhibit three weak bands at 25906, 22727 and 21598 cm⁻¹,

which are assigned to ${}^6A_{1g}(G) \rightarrow {}^4E_g(G)$, ${}^6A_{1g}(G) \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g}(G) \rightarrow {}^4T_{1g}(G)$ transition, respectively in accordance with high spin octahedral stereochemistry, which is further supported by magnetic moment value. The observed magnetic moment value 5.52 BM is low compared to spin only value for high spin Mn(II) complexes. This can be attributed to the spin exchange in the solid state¹⁵. The Zn(II) chelate as expected are diamagnetic in nature and their electronic spectra do not furnish any characteristic *d-d* transitions except charge transfer bands.

The magnetic moment values per metal ion of the present complexes are normal at room temperature indicating negligible or non-observable magnetic interactions. The binuclear complex with biphenyl moieties as bridging unit have shown that a considerable amount of antiferromagnetic interaction exist between the metal centers through the σ -overlap super exchange mechanism^{16,17}. A discontinuity in the π -delocalized electron cloud of the biphenyl moiety can be broken by the presence of tetrahedral sp^3 carbon atom between the two 1, 1' sp^2 carbons of the bridging phenyl moieties, which may lead to different magnetic interaction mechanisms.

The ESR spectrum of powdered Cu(II) chelate at room temperature (300 K) and liquid nitrogen temperature (93 K) exhibit a four-line isotropic signal ($g_{\parallel} = 2.12$, $g_{\perp} = 2.02$) which suggest the covalent nature¹⁸. The amplification and expansion show the hyperfine splitting of the band. The source of hyperfine splitting may be due to the dissimilar bonds coordinated to the metal atom. As the spectrum shows no appreciable line broadening it is possible that water molecules would occupy axial positions.

Thermogravimetric analysis of polychelates indicates that they are thermally very stable and decompose in two stages. The rate of decomposition of the ligand is faster than that of the polychelates at all temperatures. It is observed that there is no weight loss up to 120 °C indicating the absence of lattice water molecule in all chelates. The initial weight loss up to 250 °C confirms the presence of two moles of coordinated water in case of all the chelates. The order of thermal stability of the chelates is as follows Zn(II) > Mn(II) > Ni(II) \cong Cu(II) > Co(II), consistent with the observations obtained by Goodwin and Bailar¹⁹.

The free ligand shows moderate activity towards *E. coli* (10 mm) species than rest of chelates (6-7 mm). The Co(II) and Mn(II) chelate shows moderate activity towards *B. subtilis* (9 mm) than the rest of the chelates and ligand. The chelate of Ni(II), Cu(II), Zn(II) and Mn(II) shows moderate activity towards the present microorganism (Table-3). Normally the inhibition activity of the compound increases with increase in the concentration of the solution.

TABLE-3
ANTIBACTERIAL ACTIVITY OF COMPOUNDS (1 mg/10 cm³)

Compound	Antibacterial activity (% zone of inhibition) in mm			
	<i>S. aureus</i>	<i>E. coli</i>	<i>S. typhi</i>	<i>B. subtilis</i>
H ₂ -NaIDADPM	–	10.0	–	–
[Co(NaIDADPM)·2H ₂ O] _n	–	–	6.5	9.0
[Ni(NaIDADPM)·2H ₂ O] _n	5.5	6.0	–	–
[Cu(NaIDADPM)·2H ₂ O] _n	6.0	7.0	–	6.0
[Zn(NaIDADPM)·2H ₂ O] _n	5.0	6.0	–	6.0
[Mn(NaIDADPM)·2H ₂ O] _n	6.0	6.5	7.0	9.0

Conclusion

On the basis of analytical, conductivity, magnetic susceptibility, TG and DT analyses, IR, electronic and ESR Spectral data, the metal:ligand composition is 1:1 and octahedral geometry is assigned to the chelates. The insolubility and high thermal stability (> 250 °C) of the metal chelates indicates polymeric nature²⁰⁻²³ (Fig. 1). The antibacterial studies show mild antibacterial activity of the compounds against selected strains of *E. coli*, *S. typhi*, *S. aureus* and *B. subtilis* compared to standard antibacterial compound (tetracycline). The present complexes are less active against the selected strains of microorganisms.

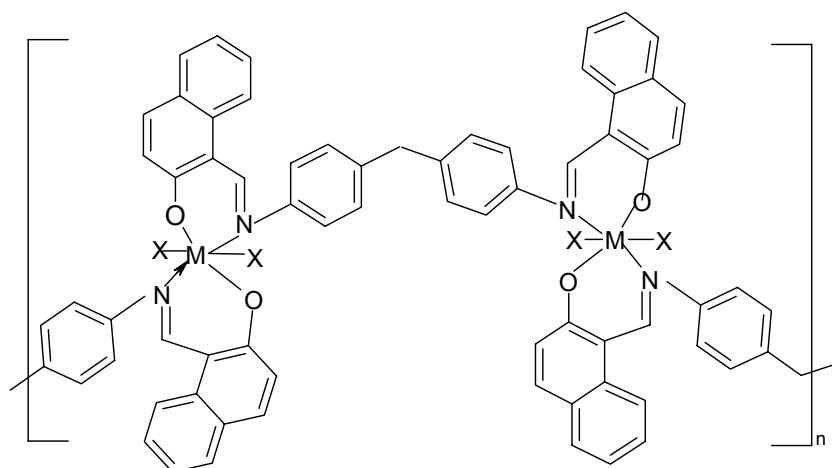


Fig. 1. Proposed structure of the polychelates
[M = Co(II), Ni(II), Cu(II), Zn(II), Mn(II) and X = H₂O]

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REFERENCES

1. A. Warshawsky, *Polymeric Ligands in Hydrometallurgy, Synthesis and Separation using Functional Polymers*, Wiley, New York, p. 327 (1998).
2. A. Alelah and A. Moet, *Functionalized Polymers and Applications*, Chapman and Hall, London, p. 93 (1990).
3. M. Bonilla-Alvarez, M. Palmeri, D. Davis and J.S. Fritz, *Talanta*, **34**, 473 (1987).
4. S.R. Aswale, P.R. Mandlik and A.S. Aswar, *Indian J. Chem.*, **42A**, 322 (2003).
5. A.S. Aswar, S.R. Aswale and P.R. Mandlik, *Indian J. Chem.*, **43A**, 1892 (2004).
6. P.K. Mukherjee, K. Saha, S.M. Giri and B.P. Saha, *Indian J. Microbiol.*, **35**, 327 (1995).
7. A.S. Al-Tai, D.M. Hall and A.R. Mears, *J. Chem. Soc. Perkin Trans. II*, 133 (1976).
8. M.R. Maurya, D.P. Singh and S.K. Verma, *Synth. React. Inorg. Met-Org. Chem.*, **19**, 929 (1989).
9. M.R. Maurya and C. Gopinathan, *Indian J. Chem.*, **35A**, 701 (1996).
10. S.I. Mostafa, T.H. Rakha and M.M. El-Egez, *Indian J. Chem.*, **39A**, 1301 (2000).
11. C.N.R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, p. 187 (1963).
12. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, New York (1970).
13. M.B.H. Howalder, M.S. Islam and M.R. Karim, *Indian J. Chem.*, **39A**, 407 (2000).
14. P.P. Hankare, K.M. Garadkar and A.H. Jagtap, *Indian J. Chem.*, **39A**, 1145 (2000).
15. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37, 210 (1964).
16. K. Nonoyama, H. Olima and M. Nonoyama, *Inorg. Chim. Acta*, **17**, 275 (1982).
17. P. S. Zacharias and A. Ramachandraiah, *Polyhedron*, **4**, 1013 (1985).
18. I. Fidon and K.W.H. Stevan, *Proc. Phys. Soc. (London)*, **73**, 116 (1959).
19. H.A. Goodwin and J.C. Bailar (Jr), *J. Am. Chem. Soc.*, **83**, 2467 (1961).
20. P.L. Maurya, B.V. Agrawala and A.K. Dey, *J. Indian Chem. Soc.*, **57**, 275 (1980).
21. P.L. Maurya, B.V. Agrawala and A.K. Dey, *Macromol. Chem. Lett.*, **183**, 511 (1982).
22. J.K. Verma, *Curr. Sci.*, **56**, 22, 1168 (1987).
23. R.M. Patil, P.T. Maskar and M.M. Shaikh, *Asian J. Chem.*, **19**, 4563 (2007).

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