Synthesis, Characterization and X-Ray Diffraction Studies of Co(II), Ni(II) and Pd(II) Complexes of Schiff Base Derived from 3-Hydroxy benzaldehyde and 3-Hydroxy-2-naphthoic hydrazide

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Schiff base ligand (L) was synthesized using 3-hydroxy benzaldehyde and 3-hydroxy-2-naphthoic hydrazide. The complexes of cobalt(II), nickel(II) and palladium(II) with this bidentate ligand were synthesized having metal:ligand stoichiometry 1:2 or 1:1. The ligand and respective complexes were characterized for their analytical parameters and various spectral features. The structures of these complexes were proposed on the basis of elemental analysis, molar conductivity, IR, ^{1}H NMR, thermogravimetric method, electron absorption spectra and X-ray diffraction. The IR spectral data suggest that the ligand (L) behaves as a monobasic bidentate ligand with nitrogen and oxygen donor atoms towards metal ions. Magnetic susceptibility measurement indicates paramagnetic behaviour for Co(II), Ni(II) complexes and diamagnetic behaviour for Pd(II) complex. X-ray diffraction studies suggest orthorhombic crystal system for all the complexes.

INTRODUCTION

Schiff bases and their metal complexes have aroused considerable research interest for several decades[1]. In Schiff base, azomethine nitrogen and other donor atoms like oxygen play a vital role in coordination chemistry. Hydrazides and their Schiff bases are found to be biologically active, their metal complexes showed some degree of antibacterial[2], antifungal[3] and antitumor[4] activity. A literature survey reveals that Schiff base containing polyfunctional group can coordinate with transition metal ions. The coordination of metal to ligand depends on various parameters like temperature of solution, reagents, pH of solution, solvent media *etc.*

In the present work, Schiff base of 3-hydroxy benzaldehyde with 3-hydroxy-2-naphthoic hydrazide was synthesized, (Fig. 1) and its cobalt(II), nickel(II) and palladium(II) complexes were prepared. The metal complexes were characterized by elemental analysis, IR, UV-Vis, ^{1}H NMR, thermal and magnetic susceptibility methods. The crystal structure was determined by powder X-ray diffraction method. These metal complexes may have enhanced biological activity which may find their importance in the applied medicinal chemistry.
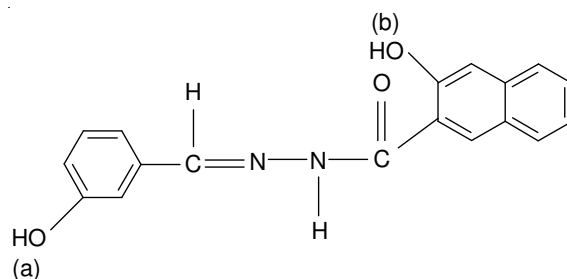
Fig. 1. Structure of Ligand (L)

EXPERIMENTAL

3-Hydroxy benzaldehyde, 3-hydroxy-2-naphthoic hydrazide and metal salts were obtained from S.D. Fine Chemicals. All reagents were analytical grade and were used without further purification.

Synthesis of Schiff base (L): The Schiff base was prepared according to the general method[5]. The ligand was synthesized by mixing equimolar quantities of aldehyde *viz.*, 3-hydroxy benzaldehyde (1.221 g, 0.01 mol) in ethanol with amine namely 3-hydroxy-2-naphthoic hydrazide (2.022 g, 0.01 mol) in ethanol and stirred vigorously for 10 min. This reaction mixture was then refluxed on water bath for 4-5 h. The solvent was concentrated to half of its volume and then poured in ice cold water. A solid precipitated out immediately which was suction filtered, washed with distilled water and cold ethanol and dried in vacuum. Recrystallization of crude product from ethanol gave the Schiff base (m.p. 260 °C) as pale white crystalline solid.

Synthesis of metal complexes: The metal chelates were prepared by mixing ethanolic solution of the respective metal(II) chlorides (1 mg/mL) and hot ethanolic solution of ligand. The pH of solution was adjusted to pH 5.5-6.5 for cobalt and nickel complexes whereas in case of palladium pH was adjusted to 1.5-2.0 by drop wise addition of alcoholic NH_3. Then it was refluxed for 2-3 h. The precipitated complexes were filtered, washed repeatedly with ethanol and dried in vacuum.

The metal contents of Co(II) in its metal complex was determined by titration with 0.01 M EDTA[6] while Ni(II) and Pd(II) in their complexes was determined by gravimetric method with dimethyl glyoxime[6]. In case of palladium(II) complexes chlorine was determined by Volhard method[6]. The Schiff base and its metal complexes were characterized by elemental analysis at IIT Mumbai. The complexes were examined for solubility by using various polar and non-polar solvents. Molar conductivity of ligand and its metal complexes was recorded using 1×10^{-3} M solution in DMSO solvent on Equiptronics conductivity meter EQ 660A at 25 °C. The electronic absorption spectra of complexes were recorded in the UV-visible region using DMSO as solvent on UV-visible 2100 spectrophotometer supplied by M/s Perkin Elmer-lambda 25. IR spectra were recorded using KBr pellet on FTIR spectrum one supplied by Perkin-Elmer instruments. The magnetic susceptibility measurements were made

on Gouy's balance. The ^{1}H NMR spectra for the ligand and its metal complexes were recorded on Bruker Advance 300 MHz spectrometer. TGA-DTA analysis was carried out for the metal complexes on Pyris Diamond TG-DTA supplied by Perkin-Elmer instruments. The crystal system was determined by X-ray powder diffraction at IIT, Mumbai.

RESULTS AND DISCUSSION

All the metal complexes are coloured, stable in air and decompose at higher temperature. The physical data of ligand and metal complexes are given in Table-1. The metal complexes are soluble in DMSO, while they are insoluble in other common organic solvents. The molar conductance values of 1×10^{-3} M solution of metal complexes in DMSO are in the range of 5.90-11.65 S cm^2 mol^{-1} (Table-2), for all the metal complexes. The low conductance values indicate the non-electrolytic nature of the complexes[7]. The magnetic behaviour of the complexes was established by determining magnetic susceptibility using Gouy's method using Hg[Co(SCN)$_4$] ($\chi_g = 16.44 \times 10^{-6}$ g cm^{-3}) as a standard[8].

TABLE-1
ELEMENTAL ANALYSIS AND PHYSICAL DATA OF
THE LIGAND AND METAL COMPLEXES

Ligand/Complex	m.w. (Colour)	m.p. (°C)	Stoichiometry	Elemental analysis (%): Found (Calcd.)				
				C	H	N	M	Cl
C$_{18}$H$_{14}$N$_2$O$_3$ (L)	306 (White)	260	-	70.39 (70.58)	5.12 (4.57)	9.64 (9.18)	-	-
Co(C$_{36}$H$_{26}$N$_4$O$_6$).(H$_2$O) CoL$_2$(H$_2$O)	686.93 (Dark brown)	239	1:2	62.18 (62.88)	4.19 (4.07)	8.26 (8.15)	8.57 (8.44)	-
Ni(C$_{36}$H$_{26}$N$_4$O$_6$).(H$_2$O) NiL$_2$(H$_2$O)	686.69 (Yellow)	>310	1:2	61.14 (62.91)	4.14 (4.07)	8.28 (8.15)	8.54 (8.38)	-
PdC$_{18}$H$_{14}$N$_2$O$_3$.H$_2$O.Cl PdL.H$_2$O.Cl	464.92 (Yellowish green)	310	1:1	45.03 (46.45)	3.41 (3.22)	6.74 (6.02)	22.88 (23.12)	7.63 (7.43)

TABLE-2
MOLAR CONDUCTIVITY, MAGNETIC SUSCEPTIBILITY AND
IR SPECTRAL DATA OF SCHIFF BASE AND METAL COMPLEXES

Ligand/ Complex	IR Spectral data (cm^{-1})						Molar cond. (S cm^2 mol^{-1})	μ_{eff} (BM)
	ν(OH)	ν(C=O)	ν(C=N)	ν(C-O)	ν(M-N)	ν(M-O)		
(L)	3403	1634	1622	1349	-	-	10.06	-
CoL$_2$(H$_2$O)	3401	1636	1608	1311	623	475	5.90	4.58
NiL$_2$(H$_2$O)	3365	1640	1601	1314	548	471	8.86	3.50
PdL.H$_2$O.Cl	3224	1639	1611	1307	583	451	11.65	Diamag.

The coordination sites of the ligand have been determined by a careful comparison of the IR spectra of the complexes with that of the parent ligand. A broad band occurring in the 3500-3100 cm^{-1} region of the spectra of the ligand as well as complexes is assigned to ν(OH) and ν(NH) bands arising from the ligand and water molecules associated with the complexes[9]. We have refrained from drawing any conclusion based on the bands appearing in the above region.

The ligand shows intense absorptions at 1634 and 1622 cm^{-1} which may be assigned to ν(C=O) and ν(C=N) bands, respectively. The corresponding >C=O peak in metal complexes appears in the same region indicates non-involvement of >C=O group in co-ordination with metal ion. However the band due to ν(C=N) at 1622 cm^{-1} in the free ligand shifts to negative frequency on complexation suggesting coordination *via* the azomethine group[10]. The ligand exhibits ν(C-O) stretching vibration at 1349 cm^{-1}. In the metal complexes ν(C-O) phenolic absorption band appears at 1311-1293 cm^{-1} which is 40-60 cm^{-1} lowers than the corresponding (C-O) vibration of free ligand. This indicates bonding of phenolic oxygen to the metal ion[11]. The peak at 848 cm^{-1} in case of Pd(II) complex confirms the presence of coordinated water as reported in literature[12]. The additional bands occurring in the range 623-548 and 475-451 cm^{-1} region in all the complexes are assigned to ν(M-N) and ν(M-O) stretching vibration respectively[13,14].

The proton NMR of ligand and its metal complexes were recorded using TMS as a reference in DMSO solvent. Data related to various protons is summarized in Table-3. Spectrum of ligand shows multiple signals in the range of 6.75-7.95 ppm, which are characteristic signals for aromatic ring protons[15]. The signals were integrated for 10 protons. The corresponding metal chelates also show similar multiple signals with δ value in the range of 6.54-7.99 ppm. Similarly in the spectrum of ligand signal at 9.68 ppm can be assigned to (>NH) proton[16] which was appeared in

TABLE-3
THERMAL, UV-VIS AND NMR SPECTRAL DATA OF
LIGAND AND METAL COMPLEXES

Ligand/ complex	TGA data for complexes Obs. (Calcd. %)		Electronic spectral data (cm^{-1}) (ε = dm^3 mol^{-1} cm$^{-1} \times 10^{-4}$)			^{1}H NMR chemical shift (δ ppm)			
	Organic content	Metal oxide content	Assignments for *d-d* transition			Aromatic	CH=N	OH$_{(a)}$	OH$_{(b)}$
(L)	-	-	31948 (2.6)	31364 (2.5)	38314 (2.1)	6.81-7.95	8.35	11.93	11.30
CoL$_2$(H$_2$O)	87.76 (88.80)	10.12 (10.90)	26666 (1.4)	31348 (4.4)	35211 (2.4)	6.98-7.82	8.49	-	11.32
NiL$_2$(H$_2$O)	87.75 (88.83)	10.05 (10.87)	26737 (1.3)	30120 (4.5)	34364 (3.5)	6.54-7.86	8.67	-	11.30
PdL.H$_2$O.Cl	72.61 (73.23)	25.87 (26.33)	29325 (0.5)	23809 (0.1)	20000 (0.1)	7.02-8.10	8.59	-	11.31

the same region in the corresponding chelates. The signal at 8.35 ppm can be assigned to (>CH=N). The shift of this signal in the corresponding complexes indicates coordination through azomethine nitrogen. However an important feature of the metal complexes spectrum is absence of the signal due to phenolic proton of ligand at 11.93 ppm indicating the coordination through aromatic proton after deprotonation.

Thermal behaviour and decomposition pattern of the metal complexes was established by recording TGA and DTA curves. These are reproduced in Fig. 2. It can be seen that Co(II) and Ni(II) complexes are hygroscopic in nature whereas Pd(II) complex has one water molecule coordinated to the metal. The decomposition begins around 260-360 ℃ and it is completely decomposed around 650-800 ℃. Organic matter is decomposed after the loss of water molecules. After decomposition metal oxide remain as a residue. The percentage loss at decomposition temperature is in agreement with the calculated values[17] (Table-3).

Electronic spectrum of ligand showed three high intensity bands lying at 31948, 31364 and 38314 cm^{-1} assigned to n→π*, π→π* and σ→σ* transitions respectively in ligand. The electronic absorption spectrum of Co(II) complex showing a band in the visible region at 26666 cm^{-1} is characteristic of tetrahedral geometry[18]. The spectrum also shows bands at 31348 and 35211 cm^{-1} which are attributed to the ligand to metal charge transfer transitions as observed in most of the Co(II) tetrahedral complexes[18]. This is further supported by the magnetic moment value found to be 4.58 BM.

The electronic absorption spectrum of Ni(II) complex exhibits bands at 26737 and 30120 cm^{-1} which may be assigned to the $^3T_1(F) \rightarrow {}^3T_2(P)$ transitions[12,18]. The spectrum also showed an intense sharp band at 34364 cm^{-1} which is attributed to ligand to metal charge transfer transition as observed in most of the tetrahedral complexes. The magnetic moment of Ni(II) complex is found to be 3.48 BM which supports the tetrahedral geometry.

It is reported that Pd(II) generally coordinates with square planar stereochemistry with ligands and exhibits three absorption bands which are due to allowed *d-d* transition as follows[19]:

$$^1A_{1g} \rightarrow {}^1B_{1g}\ (\nu_1) \qquad\qquad {}^1A_{1g} \rightarrow {}^1E_{1g}\ (\nu_2) \qquad\qquad {}^1A_{1g} \rightarrow {}^1A_{2g}\ (\nu_3)$$

The spectra of Pd(II) complexes show presence of *d-d* bands in the range 18000-22000 cm^{-1} which are assignable to ν_1 transition while ν_2 transitions can be assigned to band appearing in the range 22200-24500 cm^{-1}. It is reported that $^1A_{1g} \rightarrow {}^1B_{1g}\ (\nu_3)$ generally appears around 29200-31000 cm^{-1}. The spectra of Pd(II) complex exhibit bands at 29325, 23809 and 20000 cm^{-1} which are in fairly good agreement and suggest that Pd(II) complexes have square planar environment of ligands[20]. This is further supported by diamagnetic behaviour of Pd(II).

The crystal lattice parameters of the complexes of Co(II), Ni(II) and Pd(II) were measured by recording X-ray diffractogram (Figs. 3-5) in the range 5º to 120º 2θ value. The major refluxes were measured and the corresponding d-values were obtained. An independent indexing for each of these refluxes was carried out by
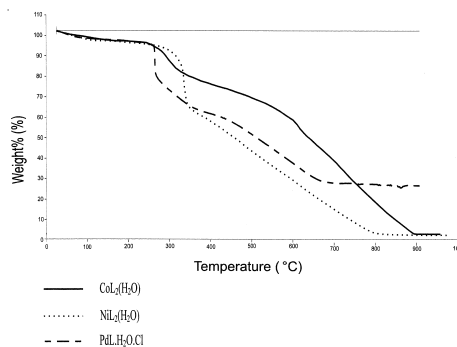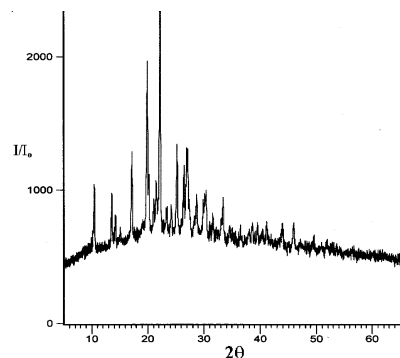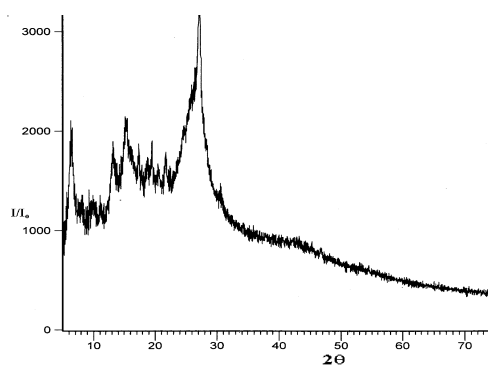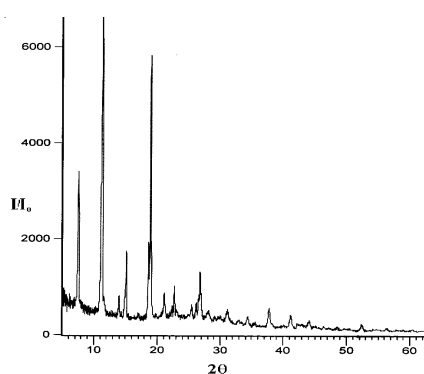
Fig. 2.   TGA traces for metal complexes

Fig. 3. X-ray spectrum of $CoL_2(H_2O)$

Fig. 4.   X-ray spectrum of $NiL_2(H_2O)$

Fig. 5. X-ray spectrum of $PdL.H_2O.Cl$

least square method. The Miller indices (hkl) were calculated and refined using Back-cal program by computational method and data has been summarized in Table-4. The data indicates the orthorhombic crystal system for all the complexes[21].

TABLE-4
CRYSTAL LATTICE PARAMETERS OF METAL COMPLEXES

Complex	a (Å)	b (Å)	c (Å)	$D_{obs.}$ (g/cm³)	$D_{cal.}$ (g/cm³)	Vol. (Å)³	SD (%)	Porosity (%)
$CoL_2.H_2O$	23.15325 ± 0.12074	20.66385 ± 0.12840	29.05994 ± 0.62507	1.2679	1.3122	13903.30	1.92	3.33
$NiL_2.H_2O$	20.79978 ± 0.09542	27.32586 ± 0.22738	30.65171 ± 0.24479	1.0490	1.0972	17385.53	1.75	4.37
$Pd.H_2O.Cl$	22.07701 ± 0.15066	23.34693 ± 0.10847	27.58395 ± 0.32458	1.7110	1.7370	14217.60	1.58	1.49

Conclusively this work describes the synthesis, characterization and X-ray diffraction studies of Schiff base and its Co(II), Ni(II) and Pd(II) complexes. On the basis of magnetic susceptibility measurements, crystal lattice parameters, analytical and

spectral data Co(II), Ni(II) complexes exhibit tetrahedral structure Fig. 6 whereas Pd(II) complex exhibits square planar structure Fig. 7. X-ray diffraction studies suggest orthorhombic crystal system for all the metal complexes. It is expected that these complexes may have better value towards biological activity.
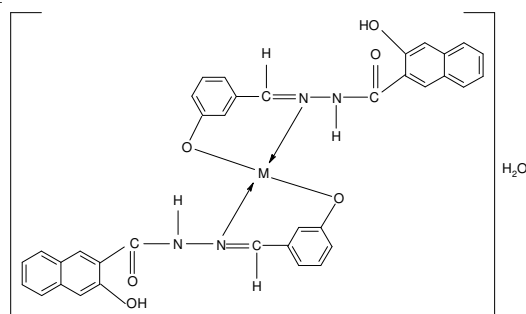
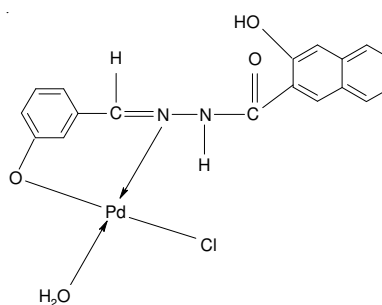where M = Co(II) or Ni(II)

Fig. 6.   Fig. 7.

ACKNOWLEDGEMENTS

REFERENCES

1. K.K. Narang and R.A. Lal, *Indian J. Chem.*, **14A**, 442 (1976).
2. L.K.W. Henri, J. Tagenine and B.M. Gupta, *Indian J. Chem.*, **40A**, 999 (2001).
3. N.K. Singh and S.K. Kushawaha, *Indian J. Chem.*, **39A**, 1070 (2000).
4. M.H. El-Tabl, A. Fathy, El-Saied and M.I. Ayad, *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.*, **32**, 1245 (2002).
5. S.D. Kolwalkar and B.H. Mehta, *Asian J. Chem.*, **8**, 410 (1996).
6. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS-Longman, London, edn. 5 (1989).
7. S. Chandra and U. Kumar, *Spectrochim. Acta*, **61A**, 219 (2005).
8. R.L. Dutta and A. Syamal, Elements of Magnetochemistry, Affiliated East-West Press Pvt. Ltd, New Delhi, India, edn. 2, p. 153 (1993).
9. T.R. Rao, M. Sahay and R.C. Aggarwal, *Indian J. Chem.*, **24A**, 649 (1985).
10. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1969).
11. B.H. Mehta and P.S. More, *Asian J. Chem.*, **19**, 3581 (2007).
12. B.H. Mehta and A.S. Salunke, *Asian J. Chem.*, **17**, 1103 (2005).
13. B.H. Mehta and Y.A. Swar, *J. Indian Chem. Soc.*, **79**, 1103 (2005).
14. C.N.R. Rao and J.R. Ferraro, Spectroscopy in Inorganic Chemistry, Academic Press, New York, Vol. 10 (1970).
15. R.M. Silverstine, G.C. Bassler and T.C. Morill, Spectrometric Identification of Organic Compounds, John Wiley and Sons, New York, edn. 5 (1991).

16. P.S. Kalsi, Spectroscopy of Organic Compounds, New Age International (P) Limited, Publishers, New Delhi, edn. 5 (2002).
17. B.H. Mehta and D.S. Joishar, *Asian J. Chem.*, **16**, 910 (2004).
18. B.H. Mehta and P.S. More, *Asian J. Chem.*, **19**, 4719 (2007).
19. S. Dagaonkar and B.H. Mehta, *Asian J. Chem.*, **7**, 611 (1995).
20. S. Chandra and R. Singh, *Indian J. Chem.*, **27A**, 417 (1988).
21. F.M. Norman and K. Lonsdale, International Tables for X-ray Crystallography, McGraw Hill Book Co., New York (1968).

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