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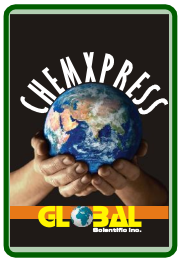

ORIGINAL ARTICLE

Synthesis, characterization and antimicrobial activity of new cobalt(II), nickel(II) and copper(II) complexes with 2-N- (1',2'- diphenyl-ethanone oxime) benzoic acid

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Abstract : Three novel complexes of type $[ML_2(H_2O)_2]$ where M = Co(II), Ni(II) and Cu(II) and L is new Schiff base ligand 2-N-(1',2'-diphenyl-ethanone oxime) benzoic acid obtained by condensation of α-benzoin oxime and 2-amino benzoic acid. The ligand and metal complexes were characterized by elemental analysis, UV-visible, IR, ^{1}H NMR spectroscopy, thermal studies and magnetic susceptibility measurement. The UV-visible and magnetic moment data revealed octahedral environment around Co(II), Ni(II) and Cu(II) ions. The ligand and metal(II) complexes were also screened for their antimicrobial activity against microorganisms *Staphylococcus aureus* and *Pseudomonas aeruginosa* and antifungal activity against the fungi *Candida albicans* and *Aspergillus niger.*

Keywords : Transition metal complexes; Schiff base; Antimicrobial activity.

INTRODUCTION

Recently there is growing interest in the coordination chemistry of oximes with transition metals[1-5] which stems from their utilization in a wide range of applications. The oximes are used as analytical reagents[6,7] and their complexes as models for biological systems[8,9]. α-benzoin oxime complex of Cu(II) is used in industry for formation of non-silver photographic images[10]. Oximes and dioximes have been used as reagent in gravimetric analysis and solvent extraction processes because of their ability to form stable complexes which are sparingly soluble in water. Oximes are widely recognized as versatile ligands that can be bound in different ways by 'O' and or 'N' atoms[11,12]. Oximes are known to be chelating ligands, frequently used in extractive and analytical chemistry. α-Benzoin oxime is a well known analytical extracting agent for Molybdenum[13], Tungsten[14] and Vanadium[15].

There is enormous interest presently in the field of coordination chemistry of transition metals with Schiff bases. Oximes have also been used as biological models[16], oxygen carriers and drugs[17]. Such an ability of Schiff bases stimulates us to study on synthesis of Schiff base and their transition metal complexes.

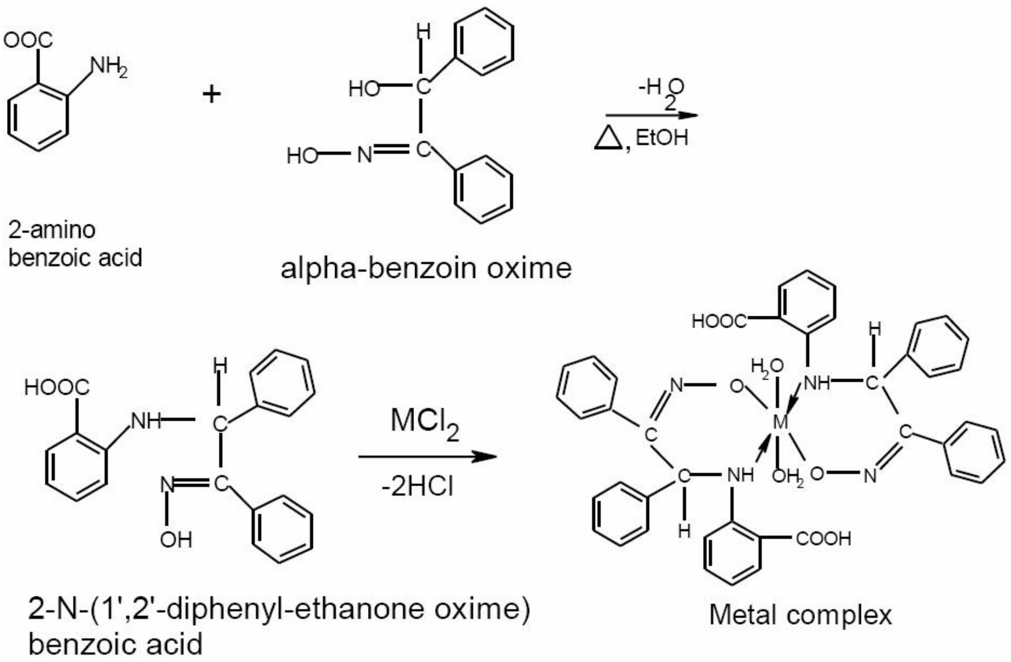
In the present paper we report the synthesis and characterization of Co(II), Ni(II) and Cu(II) complexes of Schiff base 2-N-(1’,2’-diphenyl-ethanone oxime) benzoic acid derived from condensation of α-benzoin oxime and 2-amino benzoic acid. The synthesized ligand and metal complexes were characterized by elemental analysis, UV-visible, magnetic susceptibility measurement, IR,^{1}H NMR spectroscopy and thermal studies. They were also screened for their antimicrobial activity against microorganisms *Staphylococcus aureus* and *Pseudomonas aeruginosa* and antifungal activity against the fungi *Candida albicans* and *Aspergillus niger*.

EXPERIMENTAL

All the chemicals used were of analytical grade. Infrared and electronic spectral analysis was recorded using Shimadzu spectrophotometer in the range 400-4000 cm^{-1} and 200-1000 nm respectively. ^{1}H NMR spectra was recorded on Varian 300 MHz spectrometer. Thermal measurements were performed with instrument ‘Metler Star^{e}SW 9.01. Magnetic susceptibilities of complexes were measured by Gouy’s method at room temperature.

6.855g (0.05 moles) of 2-amino benzoic acid was dissolved in ethanol. The ethanolic solution of amino benzoic acid was added to the ethanolic solution of α-benzoin oxime (11.36 g, 0.05 moles) in equimolecular (1:1) amount. The mixture was refluxed on water bath for 4 hours (Scheme 1). The completion of reaction was checked by TLC. Then separated Schiff base was filtered with suction, washed and recrystallized from ethanol and dried under vacuum over a fused $CaCl_2$[18-22].

2.379g (0.01mole) of cobalt chloride or 2.377g (0.01mole) nickel chloride or 2.377g (0.01mole) of copper chloride was dissolved in 25ml ethanol and added to the 25ml ethanolic solution of 3.46g, (0.01mole) Schiff base. The reaction mixture was then refluxed on water bath for 4 hours (Scheme 1). The completion of reaction was checked by TLC.



Where M= Co(II), Ni(II) and Cu(II)

Scheme 1

The crystals separated were washed thoroughly and recrystallized with ethanol and finally dried in vacuum over a fused $CaCl_2$[18-22].

Ligand and all the metal complexes are colored crystalline solids. Ligand exhibit sharp melting point and stable at room temperature. All the compounds are soluble in organic solvents like alcohol, acetone, chloroform, DMF, etc. and give satisfactory C, H, N, analysis as given in TABLE 1.

RESULT AND DISCUSSION

Theoretical and experimental values of elemental analysis of compounds are in good agreement with each other confirms the stoichiometry of ligand and metal complexes. Elemental data is listed in TABLE 1. Electronic spectral analysis together with magnetic susceptibility measurement reveals that Co(II), Ni(II) and Cu(II) complexes are octahedral in nature.

TABLE 1 : Physical and elemental analysis data:

Sr no	Compound (Mol. formula)	Mol. Wt.	colour	M.P. °C	Elemental analysis			Metal% Found (cal.)
					C% Found (cal.)	H% Found (cal.)	N% Found (cal.)	
1	HL ($C_{12}H_{18}0_3N_2$)	346	Pale yellow	103	72.86 (72.83)	5.23 (5.20)	8.15 (8.20)	-
2	HL-Co Co($C_{42}H_{38}N_4O_8$)	785	Brown	>200	64.25 (64.20)	4.81 (4.84)	7.17 (7.13)	7.41 (7.50)
3	HL-Ni Ni($C_{42}H_{38}N_4O_8$)	785	Greenish brown	>200	64.30 (64.22)	4.76 (4.84)	7.15 (7.13)	7.55 (7.48)
4	HL-Cu Cu($C_{42}H_{38}N_4O_8$)	789	Yellowish brown	>200	64.11 (64.22)	4.90 (4.84)	7.16 (7.13)	7.39 (7.48)

ELECTRONIC SPECTRAL AND MAGNETIC SUSCEPTIBILITY MEASUREMENT

Electronic spectra of all the ligands are characterized by two bands in UV-Visible region. Bands occurring in the range 245-260 nm is due to low or medium energy $\pi \rightarrow \pi^*$ transitions within aromatic moieties. These transitions may originate due to perturbed local excitation of phenyl group[23,24]. Another intense band in lower energy region of the spectra between 340-358 nm attributed to $n \rightarrow \pi^*$ transition of azomethine group. The electronic spectra of Co(II) complex (d^7 system) display two bands at 571 and 672 nm which are due to ${}^4T_{2g}$ (P) $\leftarrow$ ${}^4T_{1g}$ (F) and ${}^4A_{2g}$ $\leftarrow$ ${}^4T_{1g}$(F) transition respectively suggesting octahedral environment around Co(II) ion[25,26]. The electronic spectra of Ni(II) complex display three bands at 956, 599 and 424 nm assignable to ${}^3T_{2g}$ (F) $\leftarrow$ ${}^3A_{2g}$ (F), ${}^3T_{1g}$ (F) $\leftarrow$ ${}^3A_{2g}$ (F) and ${}^3T_{1g}$(P) $\leftarrow$ ${}^3A_{2g}$ (F) respectively indicating that Ni(II) complex possesses a high spin octahedral configuration[27,28]. The electronic spectrum of Cu(II) complex shows band at 635 nm assigned to ${}^2T_{2g}$ $\leftarrow$ ${}^2E_g$ transition which is in conformity with octahedral geometry[29,30].

Magnetic susceptibility measurements help to give information regarding stereochemical geometry and also support the proposed structure of complexes in junction with UV-spectra[31]. The magnetic moment obtained at room temperature is as shown in TABLE 2.

Co(II) complex show the magnetic moment 4.88 BM. This value corresponds to spin only value for high spin d^7 system with three unpaired electrons. In octahedral Co(II) complexes ${}^4T_{1g}$ ground state leads to significant orbital contribution and effective magnetic moments often lie between the limits of 4.66-5.53 BM[32-35]. Usually octahedral Ni(II) complexes have magnetic moments in the range of 2.9-3.3 BM[33,36]. Observed magnetic moments for Ni(II) complex under study is 3.18 BM. Magnetic moment value for present copper (II) complex is 1.95 BM which suggests octahedral geometry[34-36].

TABLE 2

Sr No.	Complex	$\nu_{C=N}$	ν_{OH} of Oxime	ν_{N-O}	ν_{C-N} (Aromatic secondary amine)	Coordinated H_2O	ν_{OH} of -COOH	ν_{M-O}	ν_{M-N}	Mag. moment $\mu_{eff.}$
1	HL	1589	3473	1247	1300	-	2835	-	-	-
2	HL-Co	1590	-	1244	1321	3450	2833	534	493	4.88
3	HL-Ni	1588	-	1240	1323	3406	2835	524	493	3.18
4	HL-Cu	1589	-	1255	1323	3439	2831	551	482	1.95

IR SPECTRAL ANALYSIS

IR spectral data of Schiff base and metal complexes are listed in TABLE 1. The Schiff base exhibit $\nu_{C=N}$, ν_{OH} of oxime, ν_{N-O} stretching modes 1589 cm^{-1}, 3473 cm^{-1}, 1247cm^{-1} respectively[37-42]. In metal complexes $\nu_{C=N}$ remains more or less at the same position as compared to parent ligand[43] indicates C=N is not involved in bonding. ν_{N-O} changes its position as compared to parent ligand suggests bonding of ligand to metal through nitrogen[37,44]. The disappearance of ν_{OH} of oxime in complex is indicative of the coordination of ligand by oxygen of oxime group after its deprotonation. ν_{C-N} stretch for aromatic secondary amine noticed in Schiff base at 1300 cm^{-1} while in complexes this frequency is shifted to higher value suggest that bonding of ligand to metal through nitrogen of secondary amine. Schiff bases display ν_{OH} stretch for carboxylic -OH group is at 2835 cm^{-1}. This signal remains more or less at the same position as compared to the ligand suggests that –COOH group do not take part in complexation. In complexes below 600 cm^{-1} ν_{M-N} and ν_{M-O} bands are observed[45,46], indicates that M-N and M-O bonds are formed. A broad band in between 3400-3450 cm^{-1} is observed in metal complexes which indicate presence of water molecule bonded with metal ion[47].

NMR SPECTRAL ANALYSIS

NMR spectral data of Schiff base is listed in TABLE 2. ^{1}H-NMR spectral data of the Schiff base was recorded by using $CDCl_3$ solvent. A signal at 5.9 ppm and 6.22 ppm is due to –CH and –NH respectively while multiplate in between 7.1-7.9 ppm are due to phenyl protons. A peak of carboxylic –OH is not observed because of replacement with solvent $CDCl_3$. Also a broad peak of–OH of oxime is not observed due to rapid exchange with the solvent $CDCl_3$[37,38,44].

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) along with differential thermal analysis (DTA) opens up new possibilities for the investigation of metal complexes. Aim of this study is to obtain information concerning thermal stability of the various substances to understand decomposition processes and assess corresponding thermal effect. In case of metal complexes thermogravimetry proves to be more effective in determination of nature of water molecules involved in chelation to satisfy the coordination number. This study indicates not only the presence of coordinating groups in metal complexes but also suggests a general scheme for thermal decom-

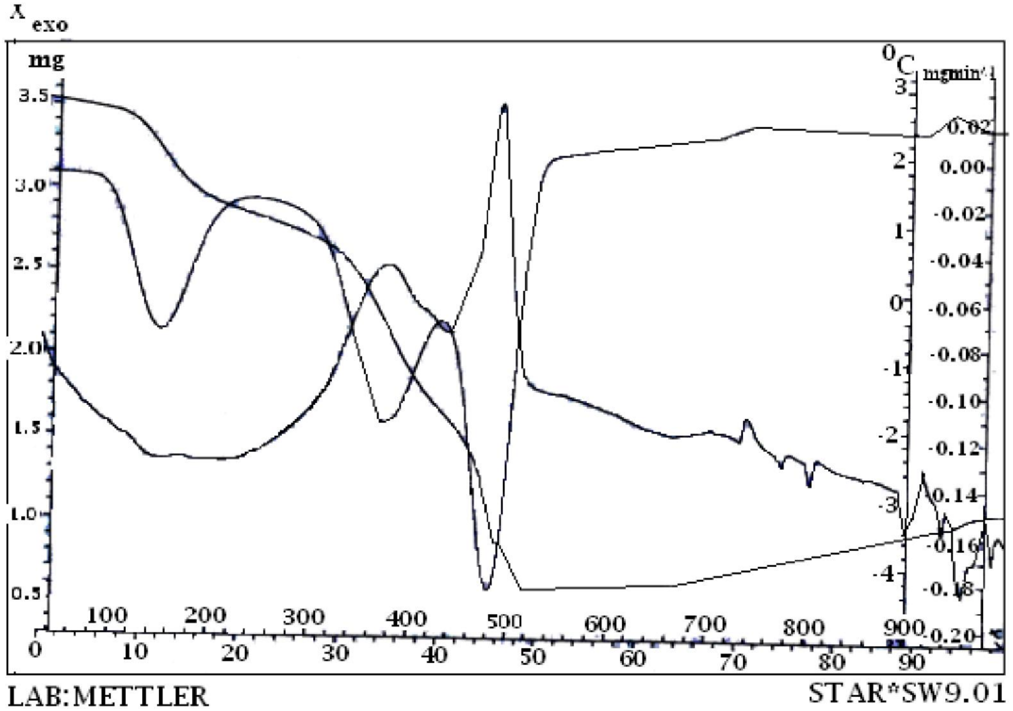


Figure 1 : Thermogram of [Ni $(L_1)_2(H_2O)_2$]

position of complexes[48,49]. To study thermal properties of metal complexes Co(II), Ni(II), Cu(II) of synthesized ligands, they were subjected to TGA and DTA. Mass loss was measured from ambient temperature up to 1000°C at the rate of 10°C/minute. The representative graph is as shown in figure 1.

Release of water molecule from complexes is an endothermic process which appears as an endothermic peak in the DTA curves of complexes. Since coordinated water molecules occupy some position in coordination sphere of the central metal ion, they are more strongly bonded to metal ion and hence are eliminated at higher temperature. Raising temperature above 200 °C the loss of mass in slow gradual manner was observed which may be caused due to decomposition of complexes by fragmentation and thermal degradation of organic part and at the end, metal oxide was formed as residue.

BIOLOGICALACTIVITY

Ligand and their metal complexes were screened for their antibacterial and antifungal activities. The antibacterial activity of Schiff bases and their metal complexes were tested by Agar well diffusion method[50,51]. Antifungal activity of all ligands and their metal complexes were tested by agar ditch method. Antimicrobial activities of all ligands and their metal complexes were tested against *Pseudomonas aeroginosa* and *Staphylococcus aureus*. Antifungal activity of all ligands and their metal complexes were tested against *Aspergillus niger* and *Candida albicans*. DMF was used as a solvent[52]. The concentration of stock solution was 4mg/ml. This stock solution was used to prepare concentration 0.8, 1.6, 2.4, 3.2 and 4.0 mg/ml. A measured quantity (20ml) of the sterilized nutrient agar / Sabouraud's agar is poured in the petriplates (100mm diameter) so as to maintain suitable depth of the agar. A lawn of microorganism (*Pseudomonas aeruginosa* and *Staphylococcus aureus*) and fungal culture (*Aspergillus niger* and *Candida albicans*) was seeded on the surface of the sterile nutrient agar plate and sterile Sabouraud's agar plate respectively by spread plate technique with the help of sterile glass spreader. The wells of definite

TABLE 3 : Biological activity data of compounds

Name of compound	Conc. g/lit	*Staphylococcus aureus*	*Pseudomonas aeroginosa*	*Aspergilus Niger*	*Candida Albicans*
HL	0.8	Inactive	Inactive	Inactive	Inactive
	1.6	Inactive	Inactive	Inactive	Inactive
	2.4	Weakly active	Inactive	Inactive	Inactive
	3.2	Inactive	Inactive	Inactive	Inactive
	4.0	Inactive	Inactive	Inactive	Inactive
HL-Co	0.8	Weakly active	Weakly active	Inactive	Inactive
	1.6	Weakly active	Inactive	Inactive	Inactive
	2.4	Weakly active	Weakly active	Inactive	Inactive
	3.2	Moderately active	Weakly active	Inactive	Inactive
	4.0	Moderately active	Moderately active	Inactive	Inactive
HL-Ni	0.8	Weakly active	Inactive	Inactive	Inactive
	1.6	Moderately active	Inactive	Inactive	Inactive
	2.4	Moderately active	Inactive	Inactive	Inactive
	3.2	Moderately active	Inactive	Inactive	Inactive
	4.0	Highly active	Inactive	Inactive	Inactive
HL-Cu	0.8	Weakly active	Inactive	Inactive	Inactive
	1.6	Weakly active	Inactive	Inactive	Inactive
	2.4	Weakly active	Weakly active	Inactive	Inactive
	3.2	Moderately active	Weakly active	Inactive	Inactive
	4.0	Highly active	Moderately active	Inactive	Inactive

Inhibition: Less than 1.3 cm – Inactive; 1.3 – 1.6cm – Weakly active; 1.7 – 2.0cm – Moderately active; 2.1 - 2.7cm – Highly active

dimensions (8mm) were made with the help of cork borer. The wells are separated by 15-30 mm from edge of the plate. A fixed volume of antimicrobial was poured into the wells. DMF was used as the solvent[53-56]. The inoculated plates were incubated at 37°C for 18-24 hours for antibacterial study and at 27°C for 72-76 hours for antifungal study. After incubation the zones of inhibition were measured. TABLE 3 represents biological activity data. The zones of inhibition exhibited by the ligands were compared with that displayed by the known antibiotics, Ciproflaxin (Antibacterial activity) and Nistatin (Antifungal activity) taken as standard at the same concentration.

Ligand and all complexes exhibit pronounced antibacterial activity as compared to parent ligands according to chelation theory[57]. On chelation the polarity of metal ion will reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups[58,59]. Further it increases the delocalization of π electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocking of the metal binding sites in the enzymes of microorganisms[60]. These complexes also disturb the respiration process of the cell and the block synthesis of protein in cell and restricts further growth of organisms[61]. It is observed that all above mentioned ligands and complexes does not show any antifungal activity

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