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Research Article

SYNTHESIS OF NOVEL SCHIFF BASED LIGANDS DERIVED FROM SUBSTITUTED DIKETONE, THEIR COMPLEXATION WITH SELECTIVE METAL IONS AND BIOLOGICAL EVALUATION.

***Mamta Ranka**
Centre for Advanced Study, Department of Chemistry,
University of Rajasthan, Jaipur-302 004 (India)
**Author for Correspondence: mmt31ran@gmail.com*

ABSTRACT
Schiff bases formed by condensation of primary amine and carbonyl compound having azomethine group (R-C=N-) have been studied extensively and their complexation behavior with transition metal ions is an important field of research. These are having a wide application in biological and pharmacological activity.

Keywords: *Azomethine, Complexation, Biological Activity*

INTRODUCTION
An attempt was made to synthesize new ligands derived from anthranilic acid and diketone or substituted diketone. The ligand act as monoanionic tridentate with potent oxygen and nitrogen as donor atoms. Further work continued to prepare Co(II) and Ni(II) complexes using above synthesized ligands. Stoichiometry revealed 1:2 metal ligand ration in metal ligand complex. The Complexes of Co(II) and Ni(II) are intensely coloured crystalline solid and stable to air.

MATERIALS AND METHODS
Double distilled water redistilled over alkaline potassium permanganate was used for preparation of solutions. All chemical used were of AR Grade and used without further purification. Melting points were determined in open capillaries and are uncorrected. Purity of all compounds were checked by using Silica Gel-G plates.

(A) SYNTHESIS OF LIGAND (PPIBA)
2-(3-phenyl pent-2-one-4-imino) benzoic acid
Equimolar ethanolic solution of 2-aminobenzoic acid and 3-phenyl pent-2-one were prepared. 5 ml of each of above solutions were poured in a round bottom flask in presence of condensing agent. Above reaction mixture is refluxed for 8 hours using water condenser at a fixed temperature 60^{o} C. After reflux the solution obtained was allowed to cool at room temperature and further cooled in refrigerator. The solid product (PPIBA) obtained was filtered, washed with alcohol and recrystallized and dried in vacuum. The purity was further checked by TLC using Silica Gel-G plates. Yield was 72%.

(B) SYNTHESIS OF COMPLEXES
A common procedure was carried out for preparation of complexes. To 20 ml Ethanolic solution of ligand (0.8 mmol) was added 20ml aqueous solution of metal acetate $M(AcO)_2 .nH_2O$ (0.4 mmol), M=Co (II), Ni(II). The resulting solution was refluxed until the reaction was complete (monitored by TLC) and further concentrated and cooled at room temperature and then in refrigerator. Solid products $M(PPIBA)_2$ obtained were filtered, washed and dried under vacuum.

All complexes are coloured, stable to air and non-hygroscopic. Ligand and metal complexes are insoluble in water but soluble in DMF. Physical and elemental analysis was carried out using conventional methods and tabulated as in Table 1. Molar conductivities in dry DMF measured and found to be in range

10-15 ohm^{-1} cm^2 mol^{-1} to indicate that the complexes are non-electrolytes. Various spectral techniques were employed to determine the presence of various functional groups, chemical environment and conjugation in different compounds. Electronic absorption spectra measurements are made on spectro scan UV-2600 double beam spectrophotometer at room temperature. IR spectra measurement recorded in KBr on a Make Bruker Model Tensor-27 spectrophotometer. IR spectra of both ligand and complexes observed and compared to elucidate molecular structure particularly the recognition of functional group and their environment. IR measurements are tabulated in Table 2.

^{1}HNMR spectra was recorded on a Hitachi Perkin Elmer Spectrometer in DMSO-d_6 using TMS as internal standard tabulated in Table 3.

Bio-efficiency of both ligand and complexes were evaluated *in vitro* for growth inhibiting potential against various bacterial and fungal strains using cup-plate method. For microbial study, *in vitro* gram positive bacteria *Staphylococcus aureus* (MTCC-96), gram negative bacteria *Proteus mirabilis* (MTCC-425) and fungal strain *Aspergillus niger* (MTCC-1344) were evaluated. Nutrient agar (beef extract 1 g, yeast extract 2 g, peptones 5 g, sodium chloride 5 g, agar 15 g in 1000 ml distilled water) was employed as culture media. Sterilization of culture medias, petri dishes and other glassware done by autoclave. For antibacterial study incubation was carried out at 38± 2^o C for 48 hours. Incubation period for *Aspergillus niger* was 25± 2^o C for 72 hours. Solution of test compound (100µg/ml, 50µg/ml) were prepared by dissolving the test compounds in DMF and definite concentration is employed. Zone of inhibition (mm) was measured for different strains after incubation and results were tabulated in Table 4. Complexes were found to have remarkable microbial activity then parent ligand as shown.

RESULTS AND DISCUSSIONS

The peaks in electronic spectrum of each complexes in DMF solution was studied. The absorption spectrum of free ligand appears at 232 nm and 251 nm which is assigned to π-π^* transition but in complex to intense bands at 282 nm & 288 nm respectively observed. The shift of absorbance indicates the complexation behaviour of ligand towards metal ions. Electronic spectra of Co (II) and Ni(II) complexes show other two bands indicating the complexes with octahedral or distorted octahedral geometry.

When Schiff bases coordinates to metal ion through azomethine nitrogen, the electron density in azomethine linkage reduces and thus, lowers ν (C=N) absorption frequency. Hence, this band undergoes a shift from 1638 cm^{-1} to 1615 cm^{-1} (lower frequency) after complexation indicates coordination of azomethine nitrogen to metal. Similarly, absorption frequencies for ν (COO^-) and ν (C=O) shift to lower frequency in complexes as compared to ligand reveals the coordination through oxygen atom of acetate and ketonic group. In metal complexes absorption frequencies at 570-572 cm^{-1} and 432-438 cm^{-1} indicates the presence of newly formed (M-N) and (M-O) bonds.

^{1}HNMR spectra of synthesized compounds recorded in $CDCl_3$ and chemical shift values expressed in ppm downfield from TMS. Observed peak at δ (7.2-6.8 ppm) shows the presence of Ar-H (aromatic proton but above peak in complexes compared to ligand were found to be shifted to lower field after the complex formation takes place. However, largest shift was observed for CH=N protons due to charge transferred azomethine to metal. Methyl proton attached to C=O observed at δ 1.81 ppm. On the basis of spectroscopic (infrared, electronic, ^{1}HNMR) evidences a six coordinated behaviour is expected for complexes with no water molecules either coordinated or lattice held.

Magnetic moment measurements concide with spin only formula with slight orbital contribution. Octahedral geometry of Co(II) complex is further supported by μ_{eff} value ~ 4.89 BM. Further distorted geometry for Ni(II) complex supported μ_{eff} value ~3.17 BM.

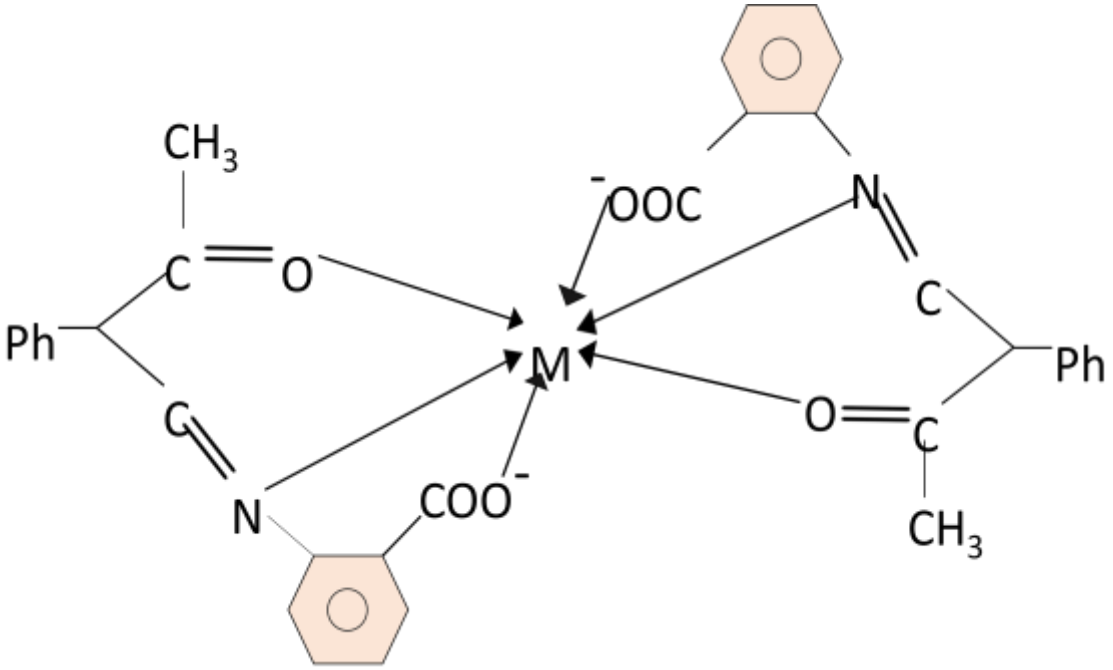

Figure 1: Proposed Structure of Complexes Molecular Formula : $M(C_{17}H_{15}O_3N)_2$

Table 1: Physical Proprieties and Elemental Analysis of Synthesized Compounds

Ligand/ complex	Colour/ M.P.	Formula Weight	% Elemental Analysis found (Cal) C	H	O	N	M	Molar cond. (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM) Appr.
PPIBA (ligand)	Yellowish White/ 194 ^{O}C	282.3	72.2 (72.3)	5.1 (5.7)	17.1 (17.0)	4.3 (4.9)	-	NA	-
Co $(PPIBA)_2$	Brownish Black/ 283 ^{O}C	621.5	65.3 (65.7)	4.9 (4.8)	15.0 (15.4)	4.7 (4.5)	9.2 (9.4)	11.2	4.89
Ni $(PPIBA)_2$	Yellowish Greenish 287 ^{O}C	621.3	65.1 (65.7)	4.4 (4.8)	15.2 (15.4)	4.4 (4.5)	9.1 (9.4)	12.4	3.17

Table 2: Selected spectral data (cm^{-1}) of ligand and complexes

Ligand/complex	ν (C=N)	ν (COO^-)	ν (C=O)	ν (M-N)	M-O
PPIBA (ligand)	1638	1442	1660	-	-
Co $(PPIBA)_2.nH_2O$	1615	1420	1635	572	438
Ni $(PPIBA)_2.nH_2O$	1619	1402	1622	570	432

Table 3: Important ^{1}HNMR spectral data (δ ppm) of ligand and complexes

Ligand/complex	Ar-H	CH=N	CH_3
PPIBA (ligand)	7.5	0.40	1.80
Co $(PPIBA)_2.nH_2O$	7.9	0.53	2.20
Ni $(PPIBA)_2.nH_2O$	8.0	0.52	2.25

Table 4: Antimicrobial Activity of Synthesized Compound using Cup-Plate Method

Ligand/ complex	Conc. (µg/ml)	Zone of inhibition (mm) Antibacterial Activity		Antifungal Activity
		S.aureus	***P.mirabilis***	***A.niger***
PPIBA (ligand)	100	22	24	18
	50	18	19	20
Co $(PPIBA)_2$	100	32	28	24
	50	21	26	17
Ni $(PPIBA)_2$	100	38	39	26
	50	25	28	22
Standard (for antibacterial)	50	22	18	NT
Standard (for antifungal)	50	NT	NT	19

CONCLUSION

The present work that involves synthesis, characterization and biological activity of ligand and metal chelates reveals that efficiency of metal ions in biological system is increased on complexation with biologically active ligands. The compounds may act either by killing the microbe or by blocking their active sites. Further, nature of microorganism plays important role to decide the potency of test compounds. The complexes were found to exhibit remarkable antibacterial and antifungal activity as compared to respective ligand.

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