EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 9
Issue: 1
360-364
Year: 2022

SPECTROSCOPIC STUDY OF SOME COMPLEXES OF SCHIFF-BASE DERIVED FROM β-DIKETONE AND ANTHRANILIC ACID

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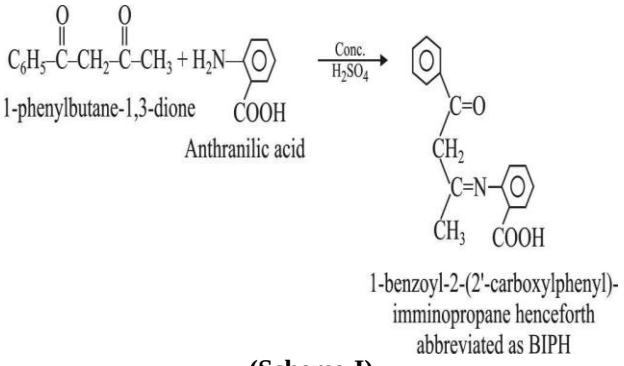
Article Received on 16/11/2021 **Article Revised on 06/12/2021** **Article Accepted on 26/12/2021**

ABSTRACT
A β-diketone viz 1-phenylbutane-1,3-dione was condensed with anthranilic acid to produce 1-benzoyl-2-(2'-carboxylphenylimminopropane) which is a potential ligand with multidonar sites, it has been used for complexation with Co(II), Ni(II) and Zn(II) metal ions using pyridine and β-picoline as secondary ligands. The low values of their molar conductivityclearly shows their non-electrolytic nature. The FTIR spectra of complexes were compared to that of free ligand which confirms the co-ordination through azomethine nitrogen and deprotonated oxygen. The electronic spectra of Co(II) complexes display three bands with v_2/v_1 ratio 2.13 to 2.34. The Racah parameter B is found to have decreased from 971 cm^{-1} in free Co(II) ion to 780-748 cm^{-1} in complexes. These crystal field parameters undoubtedly indicates the octahedral geometry of Co(II) complexes. The appearance of four bands in the electronic spectra of Ni(II) complexes and positive values of D_t are the signature of tetragonally distorted octahedral symmetry of Ni(II) complexes. The less value of Dq(z) than Dq(xy) in all the Ni(II) complexes confirms the tetragonally elongated octahedral symmetry of Ni(II) complexes. Zn(II) complexes are diamagnetic and being a d^{10}-system its complexes don't display any significant band in their electronic spectra

KEYWORDS: Anthranilic acid, distorted octahedral, *β-diketone*.

INTRODUCTION
The transition and non transition metal complexes with Schiff bases have been most extensively studied co-ordination compounds. Some co-workers.[1-3] have brought hydrazone too under the banner of Schiff bases. Recently considerable attention has been focused on the co-ordination chemistry of Schiff base because of their ease of preparation, structural varieties and varies denticities.[4-6] The co-ordination compound of Schiff base ligands shows a vast range of application such as catalyst, magnetic materials, porous materials, luminous materials, electronic and optoelectronic devices etc.[7-14] Keeping all these fact in mind the present work has been selected for spectral studies of transition metal complexes of Schiff base derived from β-diketone and anthranilic acid.

EXPERIMENTAL
The Schiff base 1-benzoyl-2-(2'-carboxylphenyl) imminopropane (BIPH) was prepared by the condensation of 1-phenylbutane-1,3-dione and anthranilic acid, these chemicals are Anal-R-grade and used as received. These both chemicals taken in equimolar ratio in ethanolic solution by refluxing in the presence of few drops of conc. H_2SO_4 for 3.5 hrs. On Cooling the solution, a dull yellow colour solid appeared which was filtered on suction pump. The solid was recrystallized in acetone whereby a bright yellow crystalline solid of 1- benzoyl-2-(2'-carboxylphenyl) imminopropane was obtained (Scheme-I) its M. P. was measured to be 234°C and yield was found about 67%. The obtained Schiff base was used for complexation with Co(II), Ni(II) and Zn(II).



(Scheme-I)

The analysis of elements of the ligand and its metal

complexes were determined by Perkin- Elmer 2400 CHN elemental analyser. Perkin-Elmer FTIR spectrometer is used for the recording of IR spectra of ligand and metal using KBr disc between 4000-400 cm^{-1}. The molar conductivity of complexes in 10^{-3} M solution in DMF solution was determine using Toshniwal CL01-06 conductivity bridge. The magnetic susceptibility of complexes was determined by Gouy balance method using mercuric tetrathiocyanatocobaltate(II) as calibrant, which is converted into magnetic moment using the expression.

$\mu = 2.828(x_A.T)^{\frac{1}{2}}$ B.M. The electronic spectra of the metal complexes have been recorded on Shimadzu UV-visible spectrophotometer (UV-160).

RESULT AND DISCUSSION

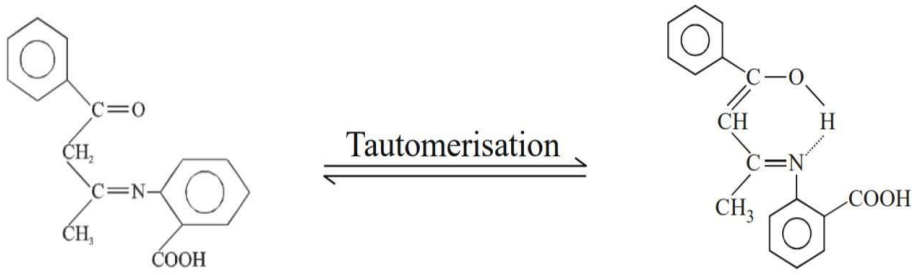
The elemental analysis colour, yield, M. P. of the ligand and complexes is shown in table-1. On the basis of percentage composition and molar conductivity the complexes have been formulated as $[ML_2X_2]$ where M = Co(II), Ni(II) and Zn(II), where L = 1-benzoyl-2-(2'-carboxylphenyl)imminopropane (BIPH) and X = Pyridine and α-picoline.

The molar conductivity value of complexes lies between 8.4 to 9.6 $\Omega^{-1}cm^2mol^{-1}$ whichindicates their non-electrolytic nature.[15,16]

Table 1- Analytical data and molar conductivity of ligand (BIPH) and complexes given in table -1.

Compounds	Color	Yield %	Melting Point	Metal	C	H	N	λ ($Ohm^{-1}cm^2mol^{-1}$)
Ligand (BIPH) $[C_{17}H_{15}O_3N]$	Yellow	67	234°C	—	72.83 (72.60)	5.16 (5.33)	4.72 (4.98)	—
$[Co(BIP)_2(Py)_2]$	Light Pink	65	289°C	7.24 (7.60)	78.41 (67.95)	4.53 (4.90)	7.00 (7.20)	8.6
$[Co(BIP)_2(\alpha\text{-pico})_2]$	pink	64	291°C	7.14 (7.32)	68.86 (68.60)	5.00 (5.21)	6.81 (6.95)	9.3
$[Ni(BIP)_2(Py)_2]$	Gree-nish	61	294°C	7.21 (7.47)	68.33 (68.04)	4.58 (4.89)	7.10 (7.21)	9.5
$[Ni(BIP)_2(\alpha\text{-pico})_2]$	green	60	297°C	7.00 (7.21)	68.82 (68.65)	5.11 (5.22)	6.78 (6.96)	9.6
$[Zn(BIP)_2(Py)_2]$	Brown	77	270.5°C	8.16 (8.30)	67.72 (67.43)	4.46 (4.85)	7.00 (7.15)	9.4
$[Zn(BIP)_2(\alpha\text{-pico})_2]$	Brown	77	274°C	7.89 (8.01)	68.32 (68.06)	4.91 (5.17)	6.69 (6.90)	8.7

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

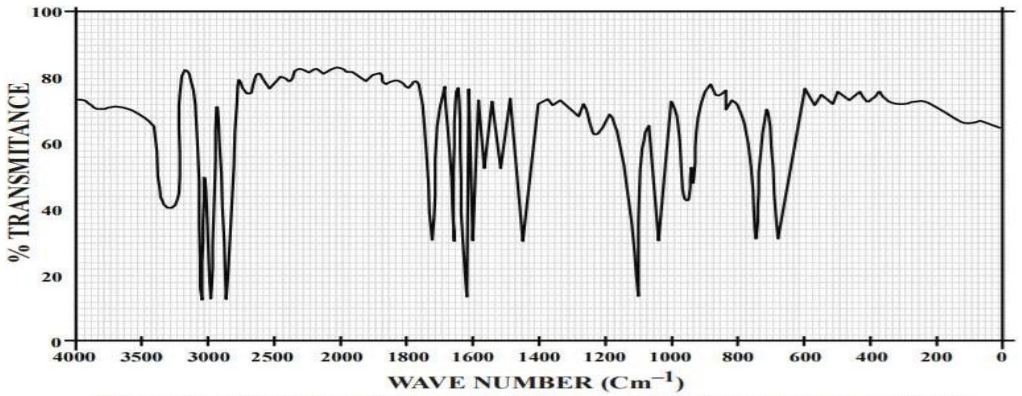


KETO FORM ENOLIC FORM

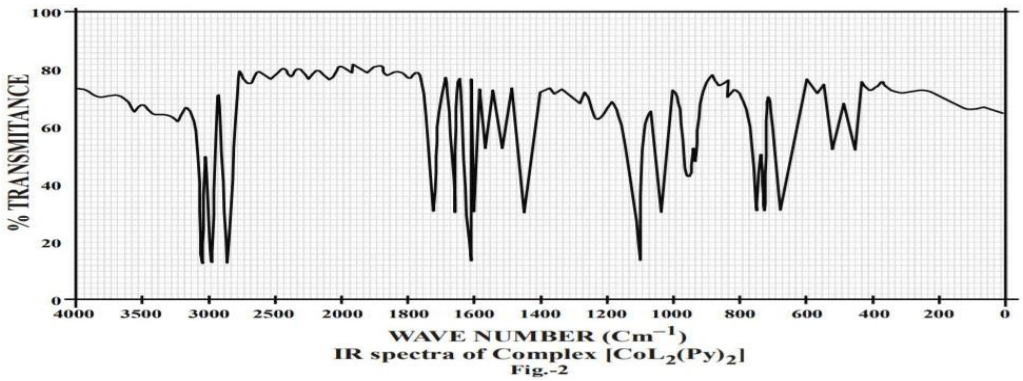
(Scheme-II)

The FTIR spectra of ligand and its metal complexes are very cumbersome as shown in fig.1-3 and hence only important band have been discussed. The broad band appearing at 3350 cm^{-1} is assigned to H-bonded OH[17-21] which shows the existance of ligand in enolic form shown in (Scheme-II), which is further confirmed by the absence of band near 1760 cm^{-1} due to ν(C=O) and appearance at a band at 1040 cm^{-1} due to ν(C–O) and another at 1655 cm^{-1} due to.[22-27] A band at 3350 cm^{-1} get disappeared in all the complexes which shows that – OH group has undergone deprotonation and co-ordination has occurred through the deprotonated oxygen. The medium band appearing at 1720 cm^{-1} is assigned for anthranilic acid,[28,29] this band remain intact, so it doesn't participate in co-ordination. A strong band at 1640 cm^{-1} in the spectra of free ligand is fairly assigned to ν(C=N), azomethine group stretching vibration.[30,31] In the spectra of all metal complexes this band get shifted 1615- 1605 cm^{-1} which shows azomethine nitrogen is involved in co-ordination to metal ion.[32,33] The co-ordination through deprotonated oxygen and azomethine nitrogen is further confirmed by the appearance of two new bands in far infrared spectra region of IR spectra of complexes. The new band at 515-510 cm^{-1} is assigned ν(M–O) while other at 450-445 cm^{-1} is assigned to ν(M–N) vibration.[34-36]

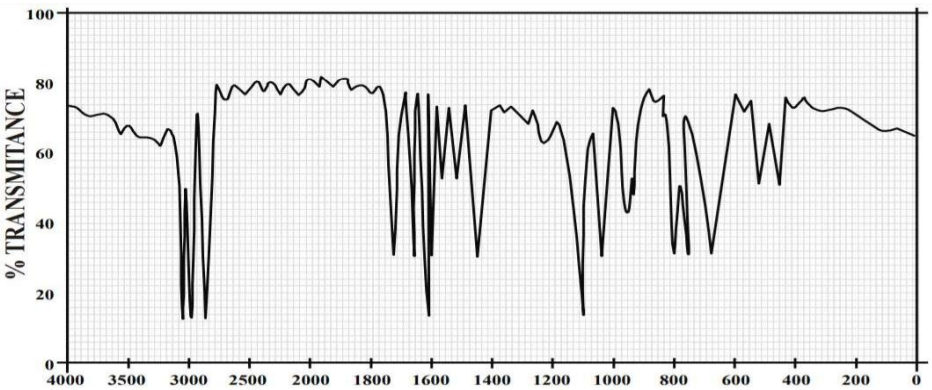
The new band appearing at 750 cm^{-1} and 800 cm^{-1} suggest the presence of co-ordinated pyridine and α-picoline respectively[37,38] in the co-ordination sphere of these complexes.



IR spectra of Free ligand 1-benzoyl-2(2'-carboxyl phenyl) imminopropane [BIPH]
Fig.-1



IR spectra of Complex $[CoL_2(Py)_2]$
Fig.-2



IR spectra of Complex $[ZnL_2(\alpha\text{-pico})_2]$
Fig.-3

Magnetic Moment and Electronic Spectra of Complexes

Co(II) Complexes

Magnetic moment value are 5.1-5.2 BM, showing spin free octahedral complexes having three unpaired electron, however the value is greater than that 3.872 BM, (corresponding to three unpaired electrons) which may be due to ground state cubic field term. ^4T1g which contributes significantly to the magnetic moment of octahedral Co(II) complexes. The electronic spectra of Co(II) complexes display three bands, which may be assigned the following spin allowed transition, shown in table-2.

Table – 2

Complexes	**$\nu_1(cm^{-1})$**	**$\nu_2(cm^{-1})$**	**$\nu_3(cm^{-1})$**
$[CoL_2(Py)_2]$	8270	17620	18607
$[CoL_2(\alpha\text{-pico})_2]$	8265	17640	18870
assignment	$^4T1g(F)\rightarrow{}^4T2g$	$^4T1g(F)\rightarrow{}^4A2g$	$^4T1g(F)\rightarrow{}^4T1g(P)$

The different crystal field parameters derived from these spectral bands are given in table–3.

Table – 3

Complexes	$\frac{\nu_2}{\nu_1}$	$\frac{\nu_3}{\nu_1}$	$\frac{\nu_3}{\nu_2}$	**10Dq (cm^{-1})**	$\nu_2-\nu_1=10Dq$ **(cm^{-1})**	**B (cm^{-1})**	β_{35}
$[CoL_2(Py)_2]$	2.13	2.25	1.05	9446.2	9350	755.70	0.7782
$[CoL_2(\alpha\text{-pico})_2]$	2.134	2.283	1.069	9365	9375	780	0.803

The values are in good agreement for the values reported for octahedral complexes of Co(II).[39-41]

Ni(II) Complexes

Magnetic moment values are 3.0-3.1 BM, which is slightly higher value corresponds to two unpaired electron of d^8-system which is due to spin orbit coupling effect.[42] The electronic spectra of Ni(II) display four bands as given below in table–4.[43,44]

Table – 4

Complexes	**$\nu_1(cm^{-1})$**	**$\nu_2(cm^{-1})$**	**$\nu_3(cm^{-1})$**	**$\nu_4(cm^{-1})$**
$[NiL_2(Py)_2]$	9750	11760	15740	17390
$[NiL_2(\alpha\text{-pico})_2]$	9720	11725	15745	17385
assignment	$^3B_1g\rightarrow{}^3Eg(a)$	$^3B_1g\rightarrow{}^3B_2g$	$^3B_1g\rightarrow{}^3A_2g(a)$	$^3B_1g\rightarrow{}^3Eg(b)$

The various crystal field parameters have been derived from these spectral bands which have presented in table – 5.

Table – 5

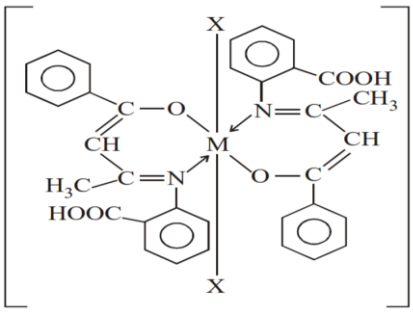
Complexes	**Dq(xy)**	**Dq(z)**	**D_s**	**D_t**
$[NiL_2(Py)_2]$	1176	774	322.85	229.71
$[NiL_2(\alpha\text{-pico})_2]$	1172.5	771.5	321.07	229.14

These values are indicative of distorted octahedral symmetry D_{4h} for Ni(II) complexes.[45,46]

Zn (II) Complexes

These complexes are diamagnetic which is in consistent with their d^{10} configuration, so they don't display any d-d transition band in their electronic spectra. However, on the basis of percentage composition and the mode of co-ordination of the ligand they have been assigned octahedral geometry. [47-50]

Tentative structure of the complexes may be given as –



Where, M = Zn(II) or Cd(II), X = pyridine and □-picoline.

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