



**SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL STUDIES OF
Ni[II], Co[II] ACETATE AND VO[II] COMPLEXES OF SCHIFF BASE
LIGAND**

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ABSTRACT:

A series of Transition metal complexes of Ni[II], Co[II] and VO[II] have been synthesized from the Schiff base ligand (HEPP) derived from dehydroacetic acid and 4-aminoantipyrine. The structural key features of Schiff base and respective metal complexes were determined from their elemental analyses (CHNS), thermogravimetric studies, molar conductivity, UV-visible, ¹H NMR, FTIR spectra, P-XRD, TGA and screened for antibacterial studies. The data shows that the complexes have composition of ML(1:1) type. The UV-VIS and P-XRD data propose monoclinic crystal system for Co(II) and Ni(II) complexes and orthorombic crystal system for VO(II) complex. Biological screening of the complexes reveals that the Schiff base transition metal complexes shows significant activity against microorganisms e.g. *S. aureus* and *E. coli*.

KEYWORDS: Schiff base, FTIR, UV-Vis, TGA, P-XRD, Metal complexes.

INTRODUCTION:

The coordination chemistry of Schiff bases having O, N donor atoms and their metal complexes have created much more interest in last decade due to its importance in medical, agricultural, analytical, biological and industrial field¹. The Schiff bases having O,N donor atoms and their metal complexes have various applications in field of catalysis, agriculture, polymer and biological sciences as antimicrobial agent, in medicinal science as anticancer, in food and dyes industry, antiseptic and antiulcer agents²⁻⁷. Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects⁸⁻¹¹, antiviral, antibacterial¹² activities and have also been used as hair colour additives and to potentiate the local anesthetic effect of lidocaine.

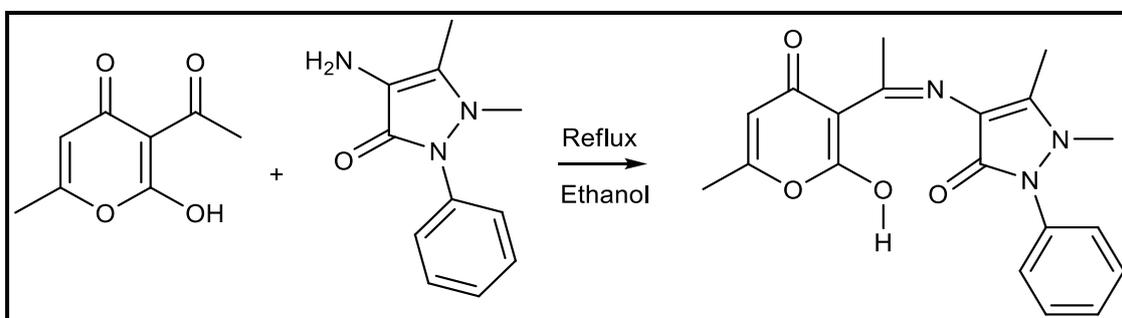
From above facts the reaction of the transition metal acetates and Schiff base ligand was carried out and structures of resulting complexes were investigated using spectroscopic data and P-XRD data. The results are discussed in this paper.

EXPERIMENTAL:

All chemicals and solvents used for the synthesis of ligand and complexes were AR grade. The CHNS analysis was performed on Elementar-Vario EL-III analyzer. FTIR spectra was recorded on Spectrum RX-I spectrophotometer using KBr pellets. ¹H NMR spectra of ligand was measured in CDCl₃ +DMSO. A mass spectrum was recorded on Bruker Esquire 3000. The TG analysis was performed on Perkin Elmer TA/SDT-2960 and P-XRD were recorded on Philips 3701. UV-visible spectra of the complexes were recorded on JascoUV-530 spectrophotometer.

Preparation of Schiff Base (Z)-4-(1-(2-hydroxy-6-methyl-4-oxo-4H-pyran-3-yl)ethylidene amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one (HEPP).

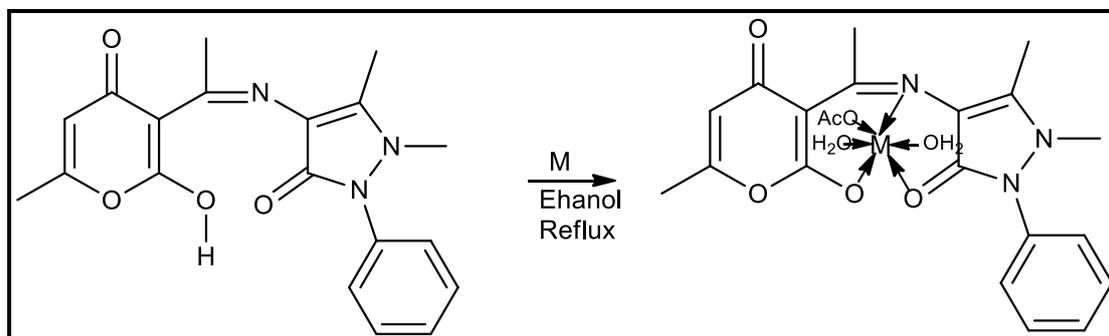
The alcoholic solution (25ml) of Dehydroacetic acid (0.005 mol) and alcoholic solution (25ml) of 4-aminoantipyrine (0.005 mol) was mixed slowly with stirring. The above reaction mixture was refluxed at 80-90°C for 4-5 hrs. On cooling, the solid yellow ppt. was formed, which was filtered and washed thoroughly with ethanol and dried.



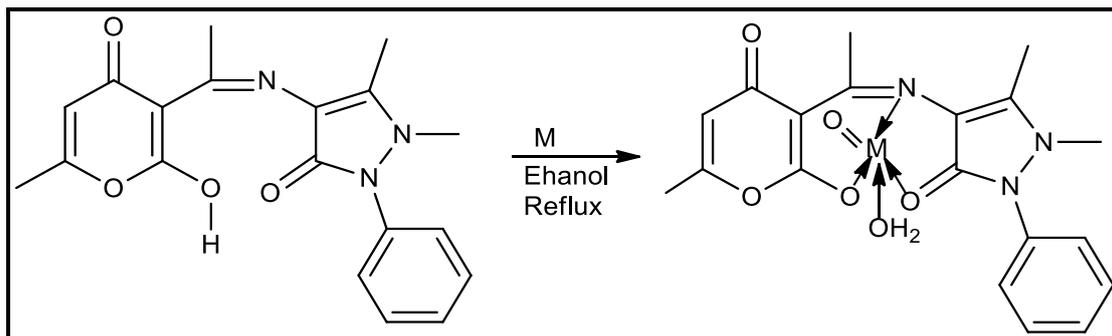
Scheme 1. Synthesis of Schiff base

Preparation of metal complexes

The alcoholic solution (25 ml) of the ligand (0.003 mol) and alcoholic solution (25 ml) of the respective metal acetate (0.003 mol) was mixed together with stirring. The pH of reaction mixture was maintained in between 7-8 by adding 10% solution of alcoholic ammonia. The reaction mixture refluxed for 2-3 hrs. (80-90°C). On cooling ppt. was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum.



Scheme 2. Synthesis of Co²⁺ and Ni²⁺ complexes



Scheme 3. Synthesis of VO(II) complexes

RESULTS AND DISCUSSION:

All complexes having different colours, Insoluble in ethyl alcohol and methyl alcohol.

Table 1. Physical and analytical data of ligand HEPP and metal complexes

Sr. No.	Ligand/Metal Complexes	Colour	Yield (%)	M.P. °C	Elemental Analysis Found[Calc.]			
					C	H	N	M
01	HEPP	Yellow	72.27	208	64.63 [64.58]	5.38 [5.42]	11.83 [11.89]	-- --
02	[Ni(II) L(H ₂ O) ₂ (oAc)]	Green	68.31	> 300	55.57 [55.46]	4.29 [4.20]	14.59 [14.70]	12.28 [12.33]
03	[Co(II) L(H ₂ O) ₂ (oAc)]	Pink	73.12	> 300	49.69 [49.78]	5.27 [5.13]	8.18 [8.29]	11.59 [11.65]
04	[VO(II) L(H ₂ O)]	Green	72.08	> 300	54.26 [54.14]	4.35 [4.28]	15.73 [15.79]	11.43 [11.50]

¹H NMR spectra of Schiff base

It shows singlet for 1H at $\delta=15.6$ ppm due to enolic-OH and it shows singlet for 3H of -NCH₃ at 3.6 δ ppm. It shows singlet for -CH₃ at 2.9 δ ppm, singlet for -CH₃ at 2.5 δ ppm and singlet -CH₃ at 2.3 δ ppm. The signals of six aromatic protons observed in the range of 6.0-8.0 δ ppm.

Mass Spectrum of Schiff base

The mass spectrum of ligand HEPP shows a peak at m/z 354.14 (M+1 Peak) which confirms the formation of Schiff base (HEPP).

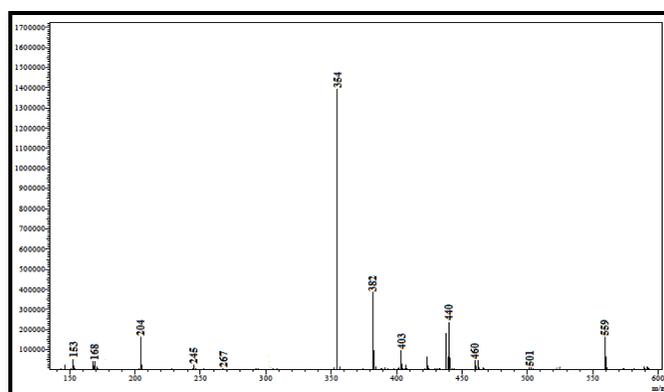


Fig.1. Mass spectrum of HEPP.

IR Spectra

The Infrared spectra of ligand HEPP and its metal complexes were recorded and table no.2 depicts some selective bands. The spectral data of ligand HEPP and metal complexes were compared to confirm the changes during formation of complexes. Various peaks are obtained and peaks at 3441 cm^{-1} is due to ν [OH] of ligand and in metal complexes the peak at 3441 cm^{-1} is missing, it indicates that [OH] is engaged in bonding with metal. The peaks at 1735 cm^{-1} and 1669 cm^{-1} are due to ν [C=O] and ν [C=N] in ligand and in metal complexes, their values are decreasing it indicates that [C=O] and [C=N] form bonds with metal. From above confirmative data it is clear that Azo-methine nitrogen, carbonyl and phenolic hydroxyl group take part in the coordination with metal ion¹³⁻¹⁴.

Table 2. FTIR spectral data of the ligand (HEPP) and its Metal complexes (cm^{-1}).

Code no.	ν (4-OH)	ν (C=O)	ν (C=N)	ν (M-O)	ν (M-N)
HEPP	3441	1735	1669	--	--
[Ni(II) L(H ₂ O) ₂ (oAc)]	--	1700	1658	527	455
[Co(II) L(H ₂ O) ₂ (oAc)]	--	1553	1439	482	439
[VO(II) L(H ₂ O)]	--	1727	1653	550	448

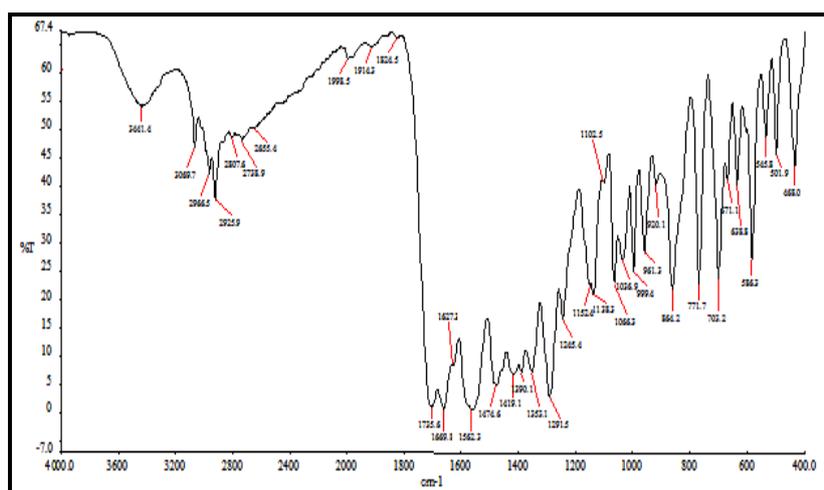


Fig.2. IR spectrum of ligand HEPP

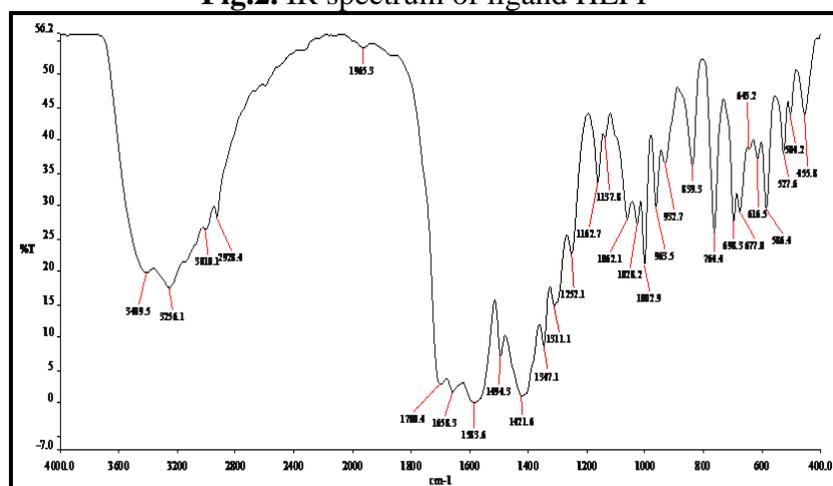


Fig.3. IR spectrum of Ni(II) complex.

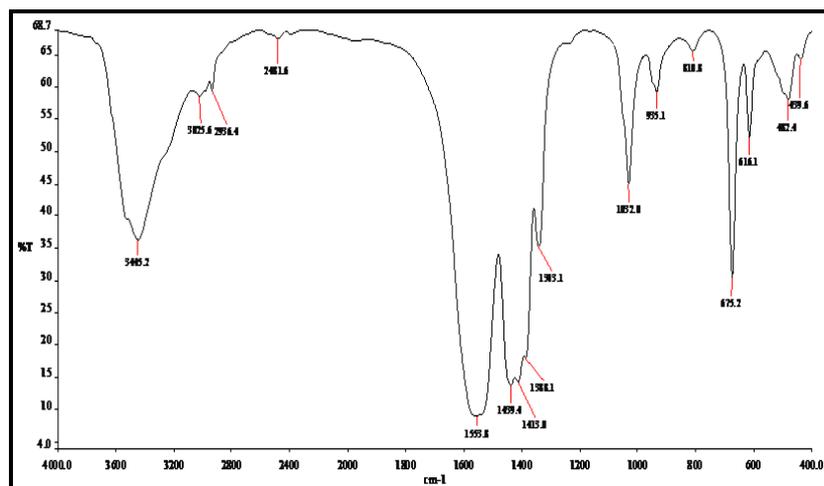


Fig.4. IR spectrum of Co(II) complex.

Electronic spectral analysis

The electronic spectrum of ligand HEPP and metal complexes were taken in Dimethylsulfoxide ($\approx 5 \times 10^{-4}$) Molar in range of 50000 to 16666 cm^{-1} ¹⁵⁻¹⁸. Electronic spectral data of the ligand HEPP and Metal complexes are given in table no.3.

Table 3. Electronic Spectral data of the ligand HEPP and its Metal complexes.

Ligand/ Metal Complexes	Absorption Maxima (cm^{-1})	Proposed assignments
HEPP	33333	$\pi \rightarrow \pi^*$
	25641	$n \rightarrow \pi^*$
[Ni(II) L(H ₂ O) ₂ (oAc)]	27727	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	25641	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	31250	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[Co(II) L(H ₂ O) ₂ (oAc)]	25000	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	28571	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	35714	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
[VO(II) L(H ₂ O)]	19607	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	20833	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	27777	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$

Powder X-ray diffraction

The P-XRD of metal complexes were scanned in range $2\theta = 20-80^\circ$ at wave length 1.540Å. The P-XRD data is useful for the information of cell parameters; lattice parameters, crystal system etc. are given in table no.4. The diffraction pattern shows the crystalline nature of metal complexes¹⁹.

Table 4. XRD spectral data of Metal complexes.

Complexes	[Ni(II) L(H ₂ O) ₂ (oAc)]	[Co(II) L(H ₂ O) ₂ (oAc)]	[VO(II) L(H ₂ O)]
No. of reflection	16	13	15
maxima (2θ)	7.595°	7.379°	20.364°

Intensity	6278.79 a.u.	14594.19a.u.	6988.21a.u.
d value	11.6313 Å	11.97051Å.	4.35746 Å.
Lattice constants	a =15.624 Å, b = 8.562Å, c = 12.256 Å	a= 17.31Å, b = 17.31Å, c=4.61Å,	a= 14.527Å, b = 9.239Å, c=7.8545,
Unit cell volume	1351.16 Å ³	1381.32 Å ³	1052.91 Å ³ .
Axis and axis angle	a ≠ b ≠ c and α = γ = 90° ≠ β	a ≠ b ≠ c and α = β = γ = 90°	a ≠ b ≠ c and α = β = γ = 90°
Crystal system	Monoclinic	Monoclinic	Orthorhombic

Thermal analysis

The thermal stability of metal complexes of ligand HEPP were investigated by using thermal gravimetric analysis in temperature range from 50 to 800 °C. The Co²⁺ and Ni²⁺ complexes decomposes in three steps, coordinated water molecules eliminate first, then acetate loss takes place and finally ligand loss takes place and stable metal oxides are formed. The VO²⁺ complex decomposes in two steps, coordinated water molecule eliminate first, and finally ligand loss takes place and stable metal oxides are formed. The absence of weight loss up to 200°C shows the lattice water molecule is absent²⁰. The coordinated water molecule, acetate molecule and ligand loss in temp. range 200-800°C and finally around 600°C metal oxides are formed¹⁴.

Antibacterial screening

The antibacterial activity of ligand (HEPP) and metal complexes were screened against Gram positive (*S. aureus*, *K. pneumoniae*) and Gram negative (*E.coli*, *P. aeruginosa*). The results were compared with antibiotic Ciprofloxacin, from findings it is clear that all metal complexes shows higher inhibition than ligand²¹ except Co²⁺ against *P. aeruginosa*. The findings are given in table no.5.

Table 5. Results of Antibacterial activity of HEPP series

Ligand / Metal complexes	Area of inhibition in (mm)			
	Gram +ve		Gram -ve	
	<i>S.aureus</i>	<i>K. pneumoniae</i>	<i>E.coli</i>	<i>P. aeruginosa</i>
HEPP	17	16	19	20
Co(II) Complex	20	19	20	17
Ni(II) Complex	18	21	24	20
VO(II) Complex	22	21	23	22
Ciprofloxacin*	31	32	32	29
DMSO	7	6	6	7

CONCLUSION:

The Ni[II] and Co[II] complexes shows coordination number six and octahedral geometry, VO[II] complex shows square pyramidal geometry. Bacterial study of these complexes shows that some complexes show better activity than ligand. The FTIR data suggest that the ligand behaves as tridentate towards metal ion. P-XRD data suggest monoclinic crystal system for Co[II] and Ni[II] metal complexes and orthorhombic crystal system for VO[II] complex.

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CONFLICT OF INTEREST:

The author(s) declare that there is no conflict of interests regarding the publication of this article.

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