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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL SCREENING OF Mn[II], Co[II] ACETATE AND VO[II] SULPHATE COMPLEXES OF SCHIFF BASE LIGAND

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ABSTRACT

Transition metal complexes of O and N donor Schiff Base ligand**(**4-(2,5-dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazole-3(2H)-one)withMn[II], Co[II] and VO[II] have been prepared and characterized by CHNS analysis, ^{1}H NMR, UV–visible, FTIR spectra, P-XRD and TG analysis. From spectroscopic data, the stoichiometry of the metal complexes is 1:1 (M:L). The P-XRD data propose a monoclinic crystal system for Mn[II], Co[II] and VO[II] complexes. The ligand and its metal complexes were screened for antibacterial studies against *E. coli* and *S. aureus.*

Keywords: Schiff Base, FTIR, UV-Vis, P-XRD, TG Analysis, Metal Complexes.

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INTRODUCTION

The coordination chemistry of Schiff bases and their metal complexes has remained an important and widely admired research area due to their simple synthesis, versatility and multiple ranges of applications.[1] The metal-based Schiff bases are more potent than Schiff bases, the transition metals play an important role in pharmacology.[2] Schiff base molecules provide potential sites for bioactive compounds that are related to proton transfer equilibrium and intermolecular hydrogen bonding. Metal complexes of Schiff base ligands showed a variety of applications in the analytical, biological, clinical and industrial areas. In recent times, metal complexes of Schiff base ligands have gained remarkable attention, not only due to their applications and spectroscopic properties but also due to their significant antibacterial, antifungal and antitumor activities.[3-7]

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

EXPERIMENTAL

Material and Methods

All chemicals and solvents used for the synthesis of ligand and complexes were AR grade. The CHNS analysis was performed on the Elementar-Vario EL-III analyzer. FTIR spectra were recorded on Spectrum RX-I spectrophotometer using KBr pellets. ^{1}H NMR spectra of ligand were measured in $CDCl_3$ +DMSO. A mass spectrum was recorded on Bruker Esquire 3000. Thermal Gravimetric analysis was performed on Perkin Elmer TA/SDT-2960 and P-XRD was recorded on Philips 3701. UV–visible spectra of the complexes were recorded on a JascoUV-530 spectrophotometer.

Preparation of Schiff Base (4-(2,5-dihydroxybenzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one) (DDPP)

The alcoholic solution (25ml) of 2,4dihydroxy benzaldehyde (0.005 mol) and alcoholic solution (25 ml) of 4-amino antipyrine (0.005 mol) were mixed slowly with stirring. The above reaction mixture was

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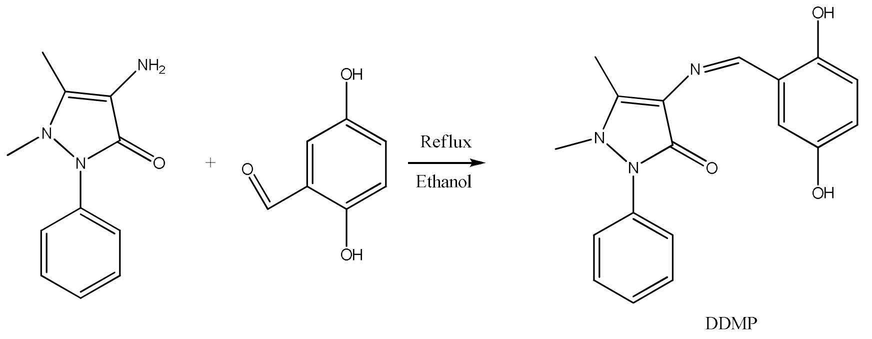
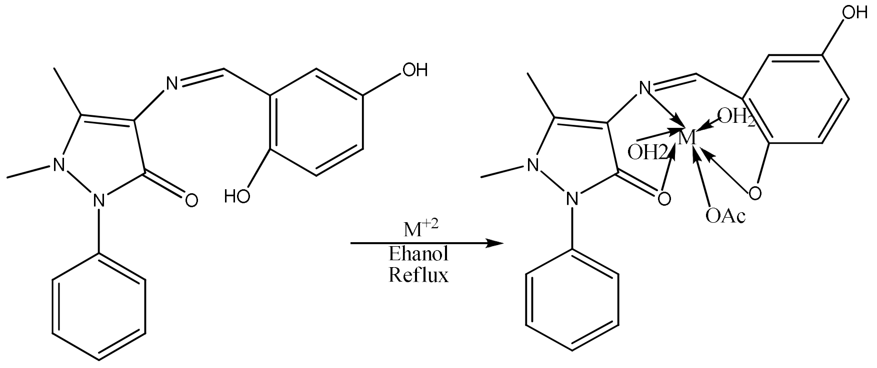
refluxed at 80-90ºC for 4–5 hrs. On cooling, the yellow color ppt. was formed, which was filtered and washed thoroughly with ethanol.[8] (Yield: 75.05%).



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 salt (0.003 mol) were mixed with stirring. The pH of the reaction mixture was maintained between 7-8 by adding 10% solution of alcoholic ammonia. The reaction mixture refluxed for 2–3 hrs (80-90ºC). On cooling, ppt. was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum.[8] (Yield 68-84.19%).



Scheme-2: Synthesis of Complexes

RESULTS AND DISCUSSION

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

Table-1: Analytical and Physical Data of Ligand DDPP and its Metal Complexes

S. No.	Ligand/ Metal Complex	Colour	Yield (%)	M.P. (^{0}C)	Elemental Analysis Found[Calc.]			
					C	H	N	M
01	DDPP	Yellow	75.05	184-186	67.03 [66.86]	5.41 [5.30]	13.11 [13.00]	--
02	[Mn(II) L(H_2O)$_2$(oAc)]	Brown	68.00	> 300	50.69 [50.81]	4.92 [4.86]	8.95 [8.89]	11.58 [11.63]
03	[Co(II) L(H_2O)$_2$ (oAc)]	Green	79.13	> 300	50.46 [50.39]	4.89 [4.82]	8.77 [8.81]	12.31 [12.37]
04	[VO(II) L(H_2O) (SO_4)]	Yellow	84.19	> 300	51.39 [51.47]	4.58 [4.50]	8.89 [9.00]	10.97 [10.92]

^{1}H NMR Spectra of Schiff Base

^{1}H NMR ($CDCl_3$-DMSO): δ=2.4 (s, 3H, –CH_3), 3.2 (s,3H,-NCH_3), 6.0-7.5 (m, 8H, Ar–H), 9.5 (s, 1H,-N=CH), 9.7 (s, 1H, Ar-OH), 13.5 (s, 1H, Ar-OH)

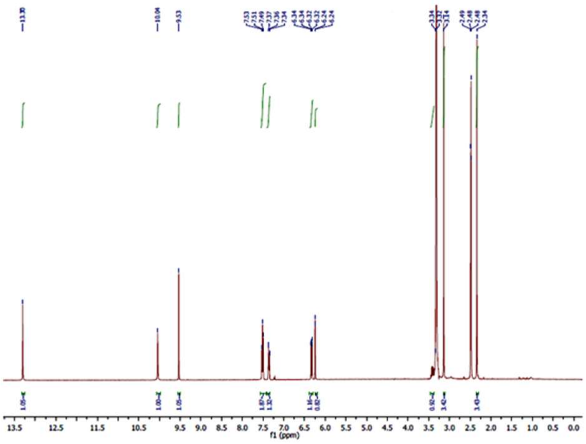


Fig.-1: NMR Spectrum of DDPP

Mass Spectrum of Schiff Base

The mass spectra of ligand DDPP shows a peak at m/z 324.1 which confirms the formation of Schiff base **(**DDPP).

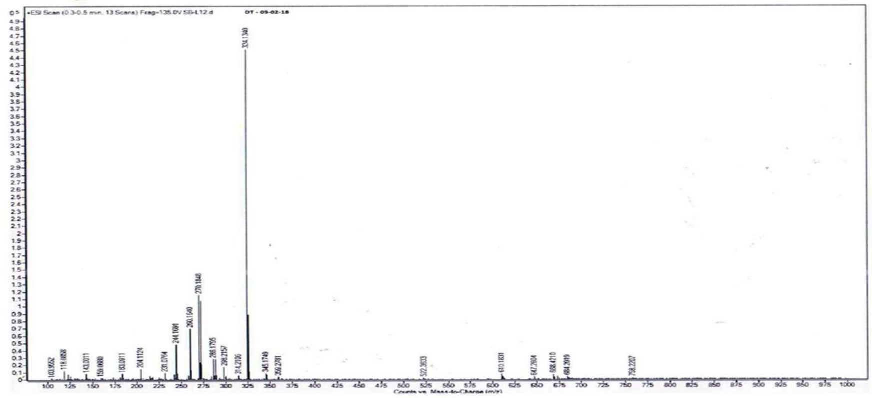


Fig.-2: Mass Spectrum of DDPP

IR Spectra

The Infrared spectra of ligand DDPP and its metal complexes were recorded and some selective bands are shown in Table-2. The spectra of ligand DDPP and metal complexes were compared to know the changes during complex formation. The peaks at 3651 cm^{-1} and 3155 cm^{-1} are due to two υ [OH] of ligand and in metal complexes, the peak at 3155 cm^{-1} is missing, it indicates that one [OH] is engaged in bonding with metal. The peaks at 1612 cm^{-1} and 1584 cm^{-1} are due to υ [C=O] and υ [C=N] in ligand respectively and in metal complexes, their values are shifting towards lower regions it indicates that [C=O] and [C=N] form bonds with metal. From the above discussion, it is clear that Azo-methine nitrogen, carbonyl and phenolic hydroxyl group take part in the coordination with metal ion.[9-13]

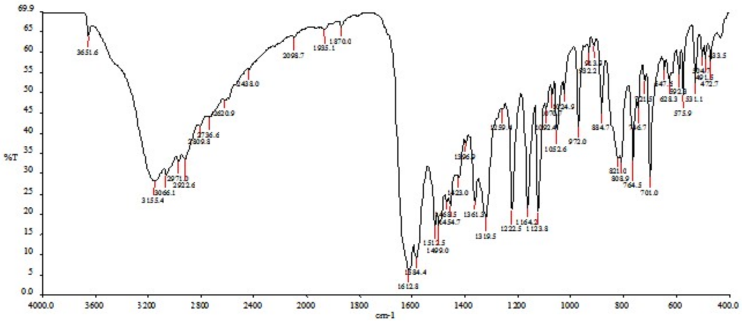


Fig.-3: IR of DDPP.

Table-2: FTIR Spectral Data of the Ligand (DDPP) and its Metal Complexes (cm^{-1}).

Code no.	υ (4-OH)	υ (2-OH)	υ (C=O)	υ (C=N)	υ (M-O)	υ (M-N)
DDPP	3651	3155	1612	1584	--	--
[Mn(II) L(H_2O)$_2$ (oAc)]	3645	--	1602	1567	530	471
[Co(II) L(H_2O)$_2$ (oAc)]	3612	--	1602	1551	516	481
[VO(II) L(H_2O) (SO_4)]	3630	--	1607	1579	512	469

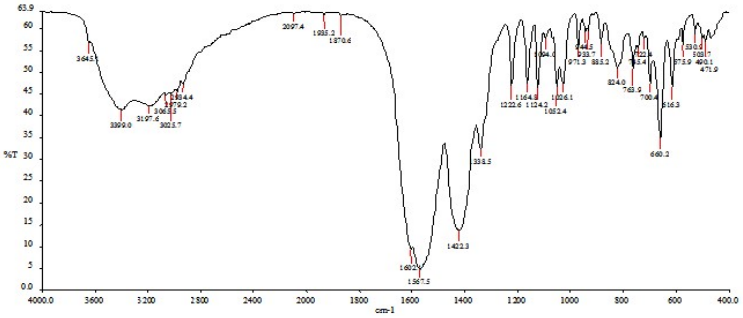


Fig.-4: IR of Mn(II) Complex

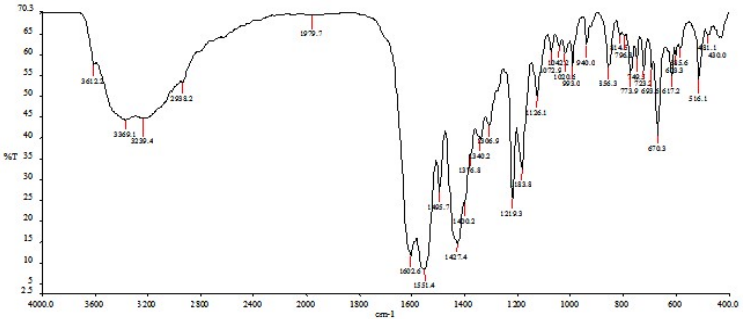


Fig.-5: IR of Co(II) Complex

Electronic Spectral Analysis

The electronic spectra of ligand DDPP and metal complexes were taken in Dimethylsulfoxide (≈5×10^{-4}) Molar in range of 50000 to 16666 cm^{-1}.[14-16] Electronic spectral data of the ligand DDPP and metal complexes are shown in Table-3.

Table-3: Electronic Spectral Data of the Ligand DDPP and Metal Complexes.

Ligand/ Metal Complex	Absorption Maxima cm^{-1}	Proposed Assignments
DDPP	34482	$\pi\rightarrow\pi*$
	25000	$n\rightarrow\pi*$
[Mn(II) L(H_2O)$_2$ (oAc)]	26315	$^{3}T_{1}g(F)\rightarrow{}^{3}T_{1}g(P)$
	25000	$^{3}T_{1}g(F)\rightarrow{}^{3}A_{2}g(F)$
	18518	$^{3}T_{1}g(F)\rightarrow{}^{3}T_{2}g(F)$
[Co(II) L(H_2O)$_2$ (oAc)]	27027	Charge Transfer
	20408	Charge Transfer
	18181	$^{2}T_{2}g(F)\rightarrow{}^{3}T_{1}g(P)$
[VO(II) L(H_2O) (SO_4)]	27027	Charge Transfer
	25641	Charge Transfer

Powder X-ray Diffraction

The P-XRD of metal complexes were scanned in the range 2θ = 20-80° at wavelength 1.540Å. The P-XRD data is useful for the information of cell parameters; lattice parameters, crystal system etc are given in Table-4. The diffraction pattern shows the crystalline nature of metal complexes.[17]

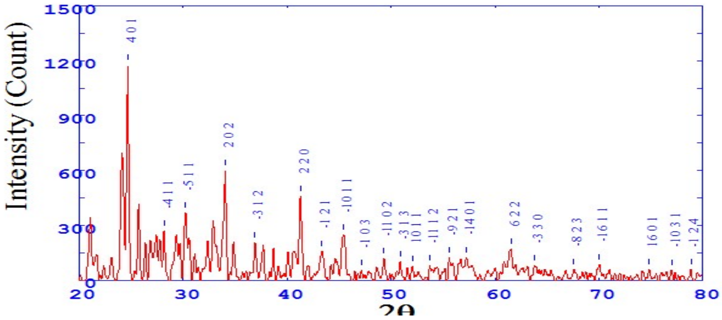


Fig.-6: X-ray Diffractograms of Mn(II) Complexes

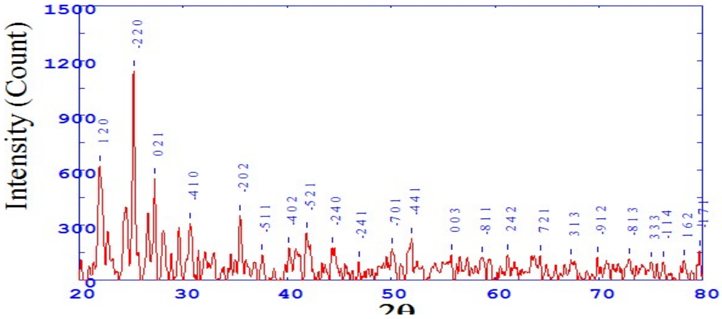


Fig.-7:X-ray Diffractograms of Co(II) Complexes

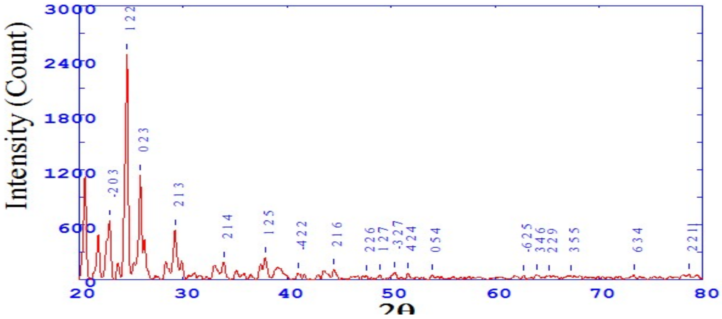


Fig.-8: X-ray Diffractograms of VO(II) Complexes

Table-4: XRD Spectral Data of Metal Complexes.

Complexes	[Mn(II) L(H_2O)$_2$ (oAc)]	[Co(II) L(H_2O)$_2$ (oAc)]	[VO(II) L(H_2O) (SO_4)]
No. of reflection	22	23	19
maxima (2θ)	24.669	25.254	24.604
Intensity	1177.33 a.u.	1142.5 a.u.	2467.8 a.u.
d value	3.6059 Å	3.5238Å.	3.6152Å.
Lattice Type	P	P	P
WaveLength	1.540598	1.540598	1.540598
lattice constants	a=22.54 Å, b = 4.465 Å, c = 5.868Å	a= 12.820Å, b = 8.644 Å, c= 5.120Å,	a= 9.980Å, b = 9.520 Å, c= 15.230Å,
Unit cell volume	574.958 Å^3	547.529 Å^3	1424.216 Å^3
Axis and axis angle	a ≠b ≠ c and $\alpha = \gamma = 90^0$, $\beta = 103.20\ ^0$	a ≠b ≠ c and $\alpha = \gamma = 90^0$, $\beta = 105.20^0$	a ≠b ≠ c and $\alpha = \gamma = 90^0$, $\beta = 100.18^0$
Partical size	359.154Å	307.071 Å	261.338 Å
R factor	0.00154	0.00191	0.00090
Crystal system	Monoclinic	Monoclinic	Monoclinic

Thermal Analysis

The thermal stability of metal complexes of ligand DDPP was investigated by using thermal gravimetric analysis in the temperature range from 50 to 800 ^{0}C. The Co[II] and VO[II] complexes decompose at a higher temperature which suggests the formation of metal complexes and high stability of metal complexes.[18] The absence of weight loss upto 200^{o}C shows the lattice water molecule is absent.[19] The coordinated water molecule, acetate/sulphate molecule and ligand loss in temp. range 200-800^{0}C, and finally around 800 ^{0}C metal oxides are formed.[8]

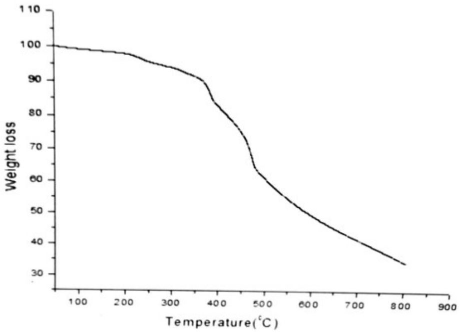


Fig.-9: TGA Graph of Mn(II) Complex

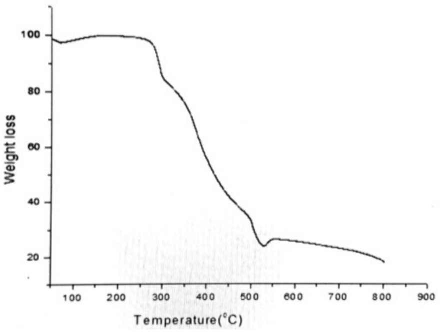


Fig.-10: TGA Graph of Co(II) Complex

Antibacterial Screening

The antibacterial activity of ligand (DDPP) and its metal complexes were screened against Gram-positive (*S.aureus*) and Gram-negative (*E.coli*) at 500 ppm and 1000 ppm by paper disc plate method. The results were compared with antibiotic ciprofloxin, from findings it is clear that some metal complexes show higher inhibition than ligand.[20-21] The findings are given in Table-5.

Table-5: Antibacterial Activity of Ligand DDPP and its Metal Complexes

Ligand/ Metal Complex	Zone of inhibition (mm)			
	E. coli		S.aureus	
	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	13	15	10	12
DDMP	07	08	08	09
[Mn(II) L$(H_2O)_2$ (oAc)]	09	10	09	09
[Co(II) L$(H_2O)_2$ (oAc)]	07	11	07	09
[VO(II) L(H_2O) (SO_4)]	08	09	08	10

CONCLUSION

The Mn[II], Co[II] and VO[II] complexes show coordination number six and octahedral geometry based on spectral and P-XRD data. 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 ions. The P-XRD data suggest that these complexes have a monoclinic crystal system.

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