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Research Article

SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL SCREENING OF Co[II], Ni[II], Cu[II] ACETATE AND Vo[II] OXYSULPHATE COMPLEXES OF SCHIFF BASE LIGAND

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ABSTRACT

Tetradentate Schiff base ligand (PBBD) and its Co[II], Ni[II], Cu[II] acetate and Vo[II] oxysulphate metal complexes have been synthesized and characterized by C,H,N & S analysis, UV–visible, ^{1}H-NMR, FTIR spectra, P-XRD, TG analysis and screened for antibacterial activity. From spectroscopic data, the stoichiometry of the metal complexes have been found to be 1:1 (M:L). The P-XRD data propose monoclinic crystal system for Co(II), Ni(II) and Vo(II) complexes, it propose orthorombic for Cu[II] complex. The ligand (PBBD) and its metal complexes were screened for antibacterial studies against *S. aureus* and *E. coli.*

Keywords: Schiff base, FTIR, UV-Vis, P-XRD, TG analysis, Metal complexes

1. 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 field [1]. 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 agents [2-7].

The tridentate and tetradentate Schiff base ligands and their metal complexes have created much more importants in various fields, Schiff bases of diamino molecules and their metal complexes have been used as biological models to study the structures of large numbers of biomolecules and their biological processes. [8] Schiff bases and their metal complexes have been well known for their synthesis, stability and wide range of applications [9-11]. The heterocyclic compound antipyrine and its derivatives having number of applications in biological field [12-13].

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.

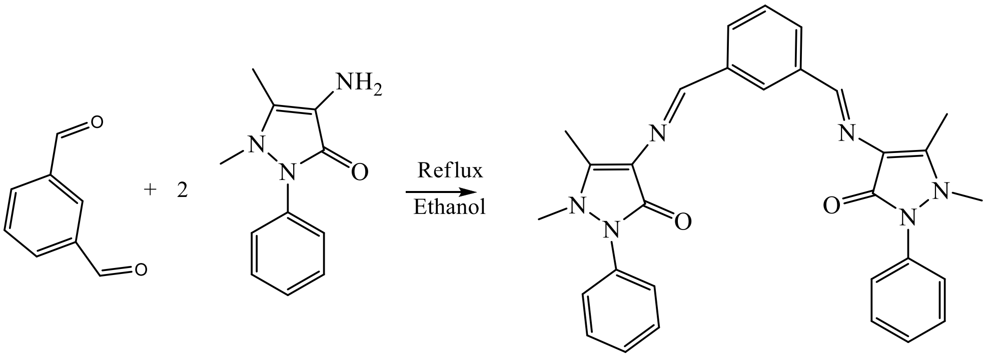
2. MATERIAL AND METHODS

2.1. Material and Physical Measurements

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. ^{1}H NMR spectra of ligand was measured in $CDCl_3$+DMSO. A mass spectrum was recorded on Bruker Esquire 3000. The TG 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 Jasco UV-530 spectrophotometer.

2.2. Preparation of Schiff Base, 4,4'-(1E,1'E)-(1,3-phenylenebis(methan-1-yl-1-ylidene))bis(azan-1-yl-1-ylidene)bis(1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one)- (PBBD)

The alcoholic solution (25ml) of Isophthalaldehyde (0.005 mol) and alcoholic solution (25 ml) of 4-aminoantipyrine (0.01 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 (Yield: 78.80%) [14].



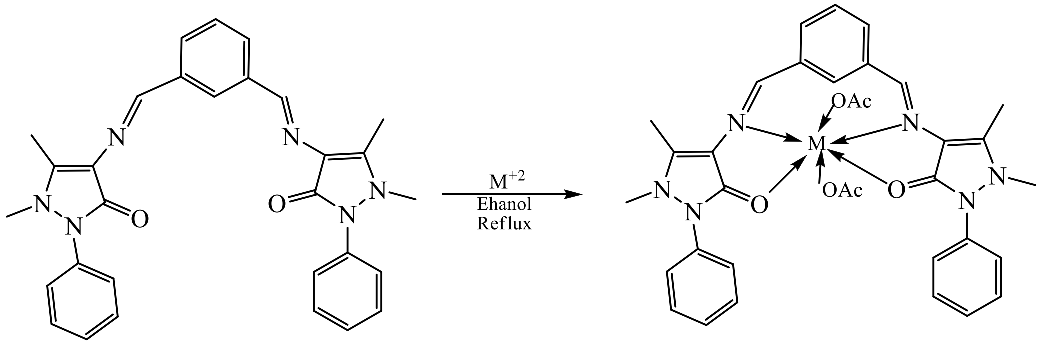
Scheme 1: Synthesis of Schiff base (PBBD

2.3. 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. (80-90ºC).On cooling ppt. was formed. It was filtered, washed thoroughly with ethanol and dried under vacuum [14].

3. RESULTS AND DISCUSSION

All the complexes have different colures, Insoluble in ethyl alcohol and methyl alcohol.



Scheme 2: Synthesis of complexes

Table 1: Physical and analytical data of ligand PBBD and metal complexes

Ligand/ Metal Complex	Colour	Yield (%)	M.P.	Elemental Analysis Found [Calc.]			
				C	H	N	M
PBBD	Yellow	78.80	192-194	71.29 [71.41]	5.43 [5.59]	16.71 [16.66]	--
[Co(II) L](oAc)$_2$	Brown	63	> 300	59.61[59.89]	4.91[4.99]	12.38[12.33]	8.59[8.65]
[Ni(II) L] (oAc)$_2$	Green	65	> 300	59.87[59.91]	4.93[4.99]	12.30[12.33]	8.66[8.61]
[Cu(II) L] (oAc)$_2$	Brown	60	> 300	59.53[59.49]	4.91[4.95]	12.28[12.24]	9.22[9.26]
[VO(II) L](SO$_4$)	Green	57	> 300	53.89[53.95]	4.16[4.19]	12.53[12.59]	7.67[7.63]

3.1. ^{1}H NMR spectra of Schiff base

^{1}H NMR (CDCl$_3$-DMSO): δ=2.4 (s, 6H, –CH$_3$), 3.2 (s, 6H,-NCH$_3$), 7.3-8.2 (m, 14H, Ar–H), 9.6 (s, 2H, -N=CH).

3.2. Mass Spectrum of Schiff base

The mass spectra of ligand PBBD shows a peak at m/z 505.23 (M+1 Peak) which confirms the formation of Schiff base (PBBD).

3.3. IR Spectra

The Infrared spectra of ligand PBBD and metal complexes were recorded and some selective bands are shown in table no.2. The spectra of ligand PBBD and metal complexes were compared to know the changes during complex formation. The peaks at 1659 cm^{-1} and 1645 cm^{-1} are due toυ [C=O] and υ [C=N] in ligand and in metal complexes, their values are decreasing it indicates than [C=O] and [C=N] form bonds with metal

[15-16]. From above discussion it is clear that Azo-methine nitrogen and carbonyl group take part in the coordination with metal ion [17-20].

The vanadium oxysulphate complex shows a band at 967 cm^{-1} assigned to V=O frequency [21].

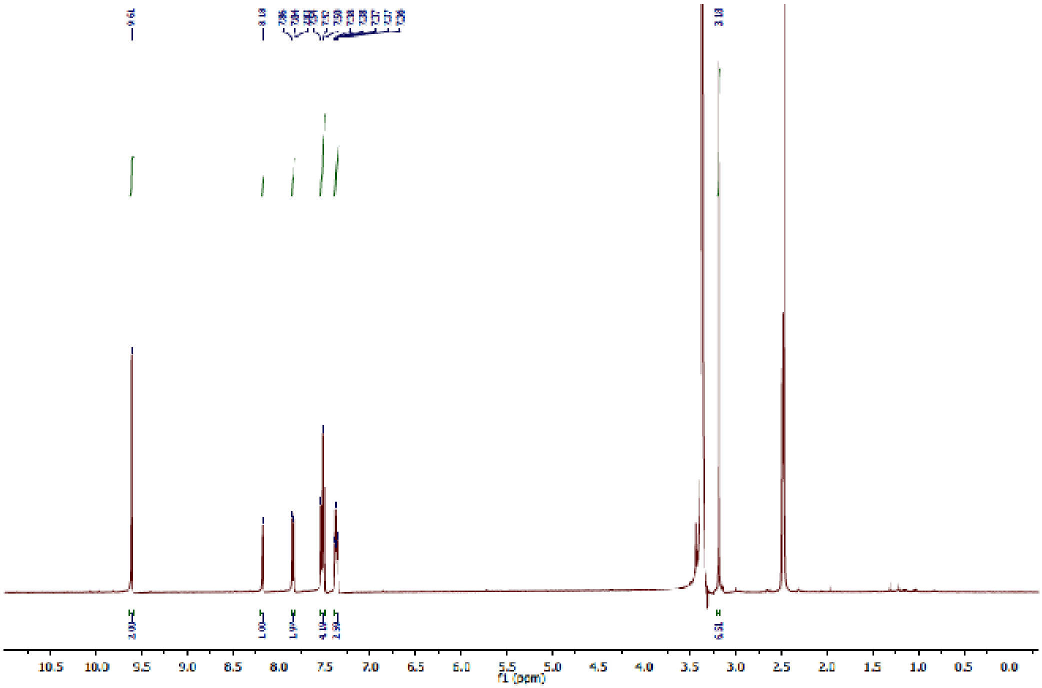


Fig.1: NMR spectrum of PBBD

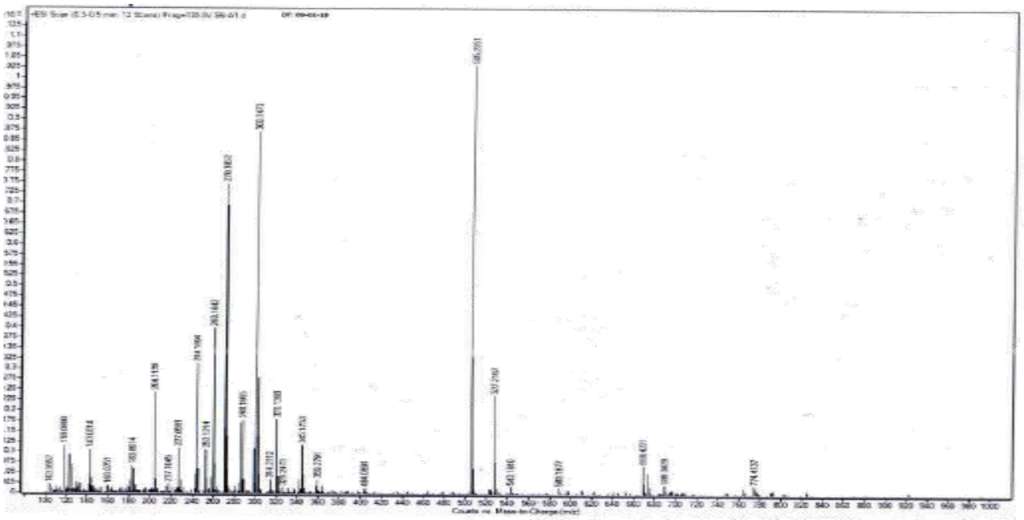


Fig. 2: Mass spectrum of PBBD

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

Code no.	υ (C=O)	υ (C=N)	υ (M-O)	υ (M-N)
PBBD	1659	1645	--	--
[Co(II) L](oAc)$_2$	1645	1562	444	482
[Ni(II) L] (oAc)$_2$	1646	1586	445	464
[Cu(II) L] (oAc)$_2$	1645	1587	446	465
[VO(II) L](SO$_4$)	1646	1587	445	465

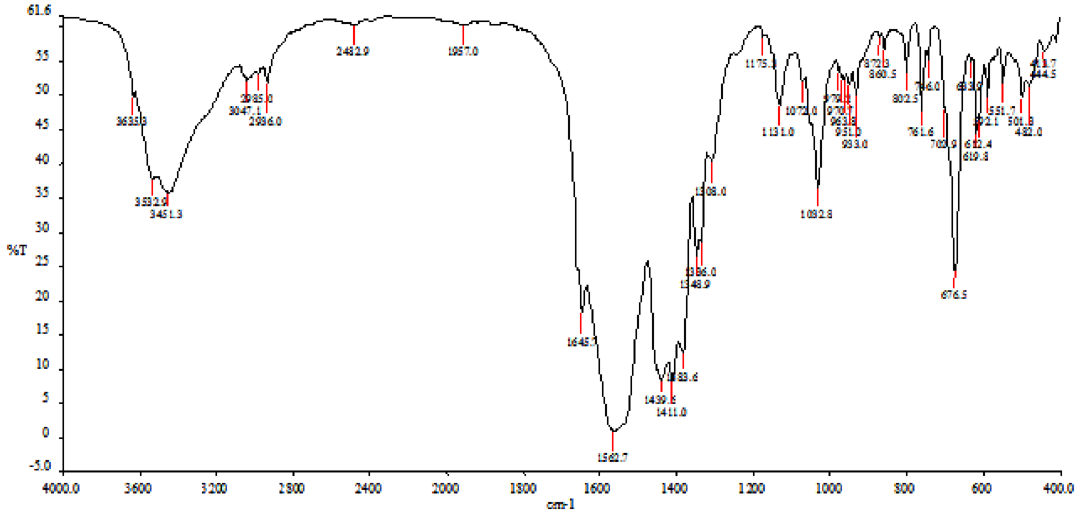


Fig. 3: IR spectra of Co(II) complex

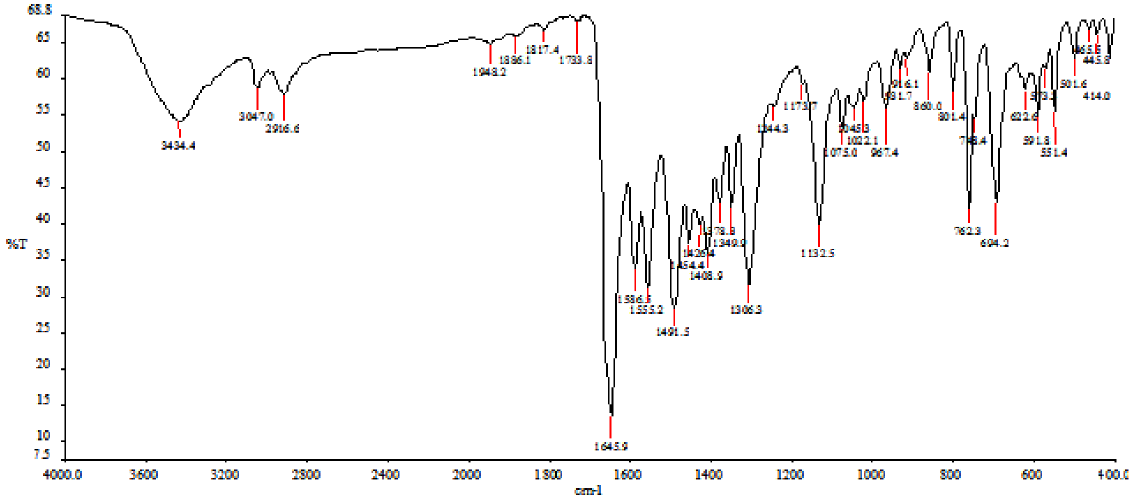


Fig.4: IR spectra of Ni (II) complex

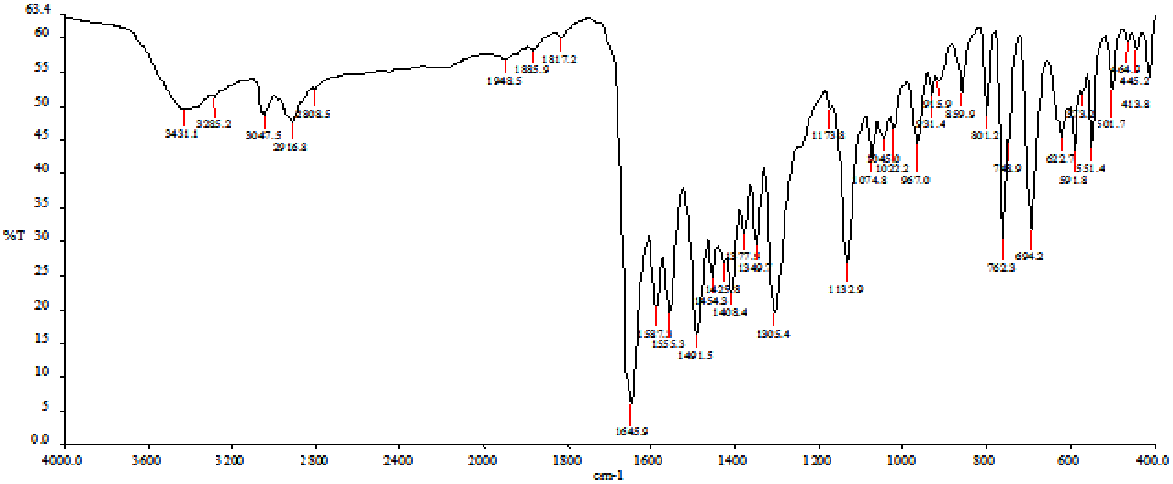


Fig. 5: IR spectra of Cu(II) complex

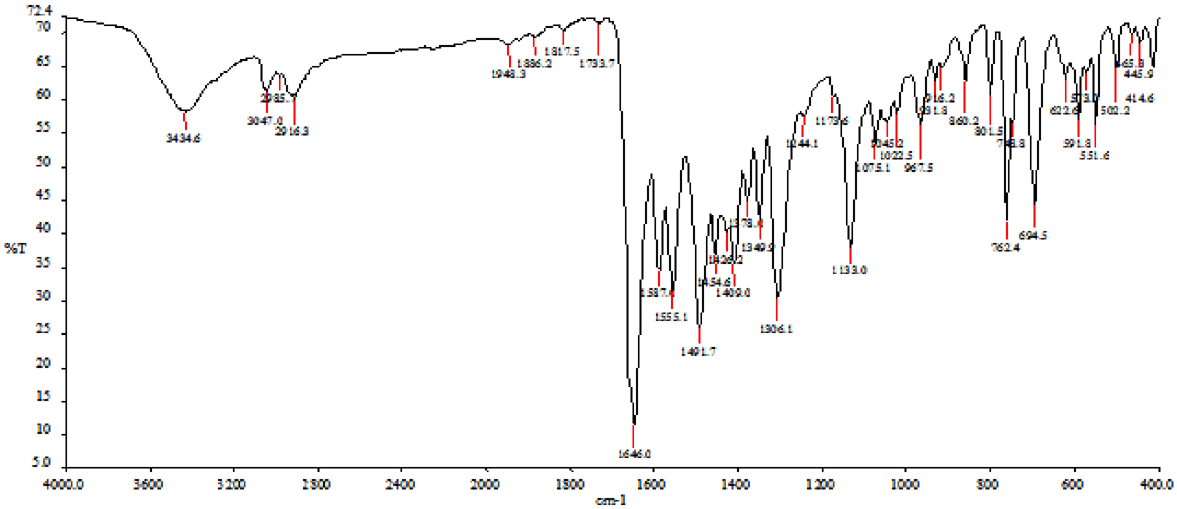


Fig. 6: IR of Vo(II) complex

3.4. Electronic spectral analysis

The electronic spectrum of ligand PBBD and metal complexes were taken in Dimethylsulfoxide($\approx 5\times10^{-4}$) Molar in range of 50000 to 16666 cm^{-1}[22-25]. Electronic spectral data of the ligand PBBD and Metal complexes are given in table no.3. The values in table no.3 are comparable with some reported metal complexes. These values are comparable with other reported complexes [26-28].

Table 3: Electronic Spectral data of the ligand PBBD and its Metal complexes

Ligand/ Metal Complex	Absorption Maxima cm^{-1} (nm)	Proposed assignments
PBBD	40000(250)	$\pi\rightarrow\pi^*$
	25641(390)	$n\rightarrow\pi^*$
[Co(II) L](oAc)$_2$	41666(240)	Charge Transfer
	27027(370)	Charge Transfer
	20000(500)	$^1A_1g\rightarrow{}^1B_1g$
[Ni(II) L](oAc)$_2$	41666(240)	Charge Transfer
	27027(370)	Charge Transfer
	20000(500)	$^1A_1g\rightarrow{}^1A_2g$
[Cu(II) L](oAc)$_2$	41666(240)	Charge Transfer
	27777(360)	Charge Transfer
	20408(490)	$^2B_1g\rightarrow{}^2A_1g$
[VO(II) L](SO$_4$)	41666(240)	Charge Transfer
	27777 (360)	Charge Transfer
	20000 (500)	$^2B_2\rightarrow{}^2A_1$

3.5. Powder X-ray diffraction

The P-XRD of metal complexes weres canned in range $2\theta = 20\text{-}80^{\circ}$ 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-4. The diffraction pattern shows the crystalline nature of metal complexes [29]. The data obtained is compared with some reported metal complexes [30-32].

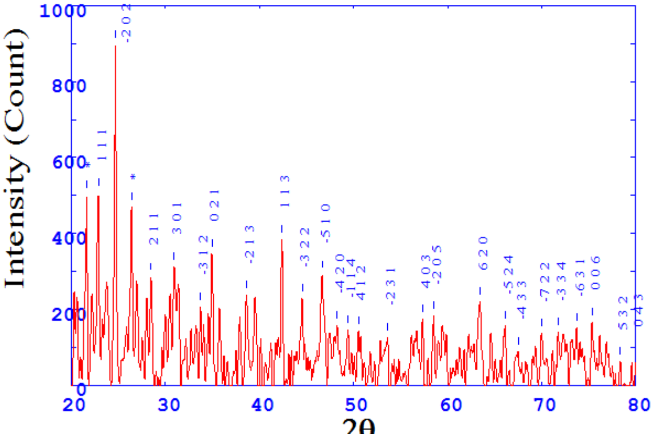


Fig. 7: X-ray diffractogram of Co(II) complexes

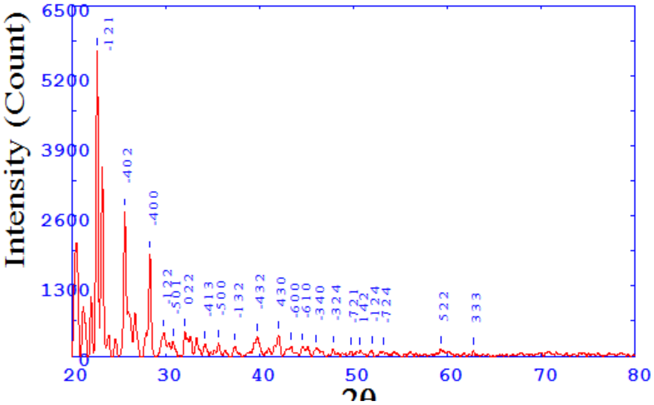


Fig. 8: X-ray diffractogram of Ni(II) complexes

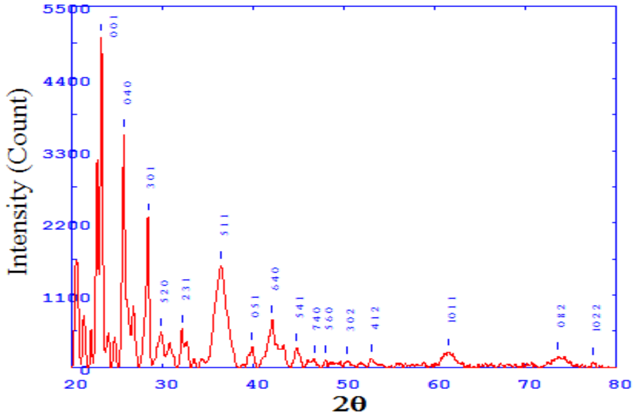


Fig. 9: X-ray diffractogram of Cu(II) complexes

3.6. Thermal analysis

The thermal stability of metal complexes of ligand PBBD were investigated by using thermal gravimetric analysis in temperature range from 50 to 800 ^{0}C. The Co[II] ,Ni[II], Cu[II] and Vn[II] complexes decompose at higher temperature which suggest the formation of metal complexes and high stability of metal complexes. The lattice water molecule and ligand loss takes place in temp. range 200-800^{0}C,and finally around 800 ^{0}C metal oxides are formed [14].

Table 4: XRD spectral data of Metal complexes

Complexes	[Co(II) L](oAc)$_2$	[Ni(II) L](oAc)$_2$	[Cu(II) L](oAc)$_2$	[VO(II) L](SO$_4$)
No. of reflection	25	21	16	23
maxima (2θ)	24.686	22.720	23.262 °	29.290°
Intensity	897.60 a.u.	5659.98 a.u.	5025.41 a.u.	874.69 a.u.
d value	3.60357 Å	3.9106 Å.	3.8207 Å.	3.0467 Å.
Lattice Type	P	P	P	P
WaveLength	1.540598	1.540598	1.540598	1.540598
lattice constants	a=10.896 Å, b = 5.450Å, c = 7.890Å	a= 14.891Å, b = 8.921Å, c=8.479Å,	a= 16.488Å, b = 13.872Å, c=3.845Å,	a= 10.377Å, b = 9.975 Å, c=15.383Å,
Unit cell volume	449.190Å^3	946.258Å^3	879.434 Å^3.	1567.236Å^3.
Axis and axis angle	a ≠b ≠ c and $\alpha = \gamma = 90^0 \neq \beta$	a ≠b ≠ c and $\alpha = \gamma = 90^0$, β=122.85^0	a ≠b ≠ c and $\alpha = \beta = \gamma = 90^0$	a ≠b ≠ c and $\alpha = \beta = \gamma = 90^0$
Partical size	380.333 Å	311.267Å	264.517Å	301.849 Å
R factor	0.00151	0.00244	0.00214	0.00099
Crystal system	Monoclinic	Monoclinic	Orthorombic	Monoclinic

Table 5: Antibacterial activity of Ligand PBBD and Metal complexes

Ligand/ Metal complex	Zone of Inhibition (mm)			
	E. coli		*S. aureus*	
	500ppm	1000ppm	500ppm	1000ppm
Ciprofloxin	14	16	11	13
PBBD	07	08	07	09
[Co(II) L](oAc)$_2$	09	10	08	09
[Ni(II) L] (oAc)$_2$	07	11	07	07
[Cu(II) L] (oAc)$_2$	06	08	07	07
[VO(II) L](SO$_4$)	08	09	08	08

3.7. Antibacterial screening

The antibacterial acticity of ligand (PBBD) and 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 shows higher inhibition than ligand [33-34]. The findings are given in Table-5.

4. CONCLUSION

The Co[II], Ni[II], Cu[II] complexes shows coordination number four and square planar geometry and Vo[II] complex shows square pyramidal 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 tetradented towards metal ion. The P-XRD data suggest that Co[II], Ni[II], Cu[II] complexes have monoclinic crystal system and Vn[II] complex have orthorhombic crystal system.

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