

**SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF O-BENZOYL BENZOIC ACID AND O-BENZOYL-N-2-PYRIDYL BENZAMIDE METAL COMPLEXES.****Valli .G^{1*}**, Sankareswari. M¹¹Department of chemistry, S.F.R.College for Women, Sivakasi-626123.**ABSTRACT**

Knowing the importance of O-benzoyl Benzoic acid, its derivatives and metal complexes for their marked biological activities, we have synthesized Twenty one different mixed ligand metal complexes of O-benzoyl Benzoic acid and O-benzoyl N-2-pyridyl Benzamide. All these complexes were found to be coloured and UV-spectra of these complexes exhibited absorption in the range 210-570 nm. FT-IR spectral values of all the O-benzoyl N-2-pyridyl Benzamide of both simple and mixed ligands metal complexes indicated the presence of M-N & M-O stretching for the metal complexes. In O-benzoyl Benzoic acid mixed ligand metal complexes, the bonding linkages of -C=O and -OH of carboxylic group with metal was observed. The antibacterial activity determination leads to the conclusion that sixteen (16) of our metal complexes were found to have activities against *Escherichia coli*, *Staphylococcus species* and *Bacillus Subtilis*.

Key Word: O-benzoyl Benzoic acid, 2-aminopyridine and O-benzoyl N-2-pyridyl Benzamide.

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Nadu State, India.**Email:**mrs.valliravichandran@gmail.com**INTRODUCTION**

Metal complexes are used as a biological probe^[1], pro-drugs and also have antimicrobial activity. Metal Complexes have attracted much interest because of their wide ranging antiviral, antimicrobial^[2, 3] and anti-inflammatory activities^[4]. Various metal complexes of carboxylato ligands show antimicrobial activity^[5]. Many of the metal complexes of varied ligands were reported to have wide spectrum of antimicrobial activity. As we infer from the literature the importance of O-benzoyl Benzoic acid^[6], its benzamide derivatives^[7] and

metal complexes for their marked biological activity such as antifungal, antibacterial and genotoxic effect. In continuation of our work on O-benzoyl Benzoic acid metal complexes, we have synthesized Twenty one different mixed ligand metal complexes of O-benzoyl Benzoic acid and O-benzoyl N-2-pyridyl Benzamide.

MATERIALS AND ANALYTICAL METHODS

O-benzoyl Benzoic Acid, 2-aminopyridine, Anthranilic acid, Metal salts and solvents used for the complex synthesis were of analytical reagent

(A.R.) grade. All the melting points were determined by open capillary tube and were uncorrected.

We have recorded the electronic spectra of our transition metal complexes in HPLC grade Methanol using UV-1700 Series and FT-IR spectra in **Shimadzu spectrophotometer** by KBr pelletisation method in the range of 400-4000 cm^{-1} . The antibacterial activities of the metal complexes were carried out by Laboratory method at **Venture Institute, Pasumalai, Madurai**.

Synthesis of O-benzoyl N-2-pyridyl benzamide (B)

To an ethanolic solution of O-benzoyl Benzoic Acid (A) (2.26 g, 0.01M), 2-aminopyridine (0.94g, 0.01M) in ethanol was added. To the above mixture 5 drops of glacial acetic acid was added and the resultant mixture was stirred for 2 hours at 60 $^{\circ}$ C. The solution so obtained was reduced to nearly 30 ml volume and was kept at room temperature. The product formed was then collected by filtration as

TABLE-I Physical Properties and UV Spectral Data of O-Benzoyl Benzoic Acid Mixed Ligand Metal Complexes

S.No.	Complexes	Colour	Melting Point	% of yield	λ_{max} (nm)
1.	ACuAa	Bluish Green	210-220 $^{\circ}$ C	80	246
2.	ACuD	Black	>360 $^{\circ}$ C	65	435
3.	ACuT	DarkGreen	190-200 $^{\circ}$ C	60	206
4.	ACuPh	DarkGreen	170-180 $^{\circ}$ C	50	205-210
5.	ACuAp	Black	340-350 $^{\circ}$ C	70	244
6.	AMnAa	Pale pink	240 $^{\circ}$ C -250 $^{\circ}$ C	50	217
7.	AZnAa	Pale white	300-310 $^{\circ}$ C	70	566
8.	ANiAa	Pale Green	280-290 $^{\circ}$ C	50	208
9.	ACoAa	Pale Pink	160-170 $^{\circ}$ C	50	200-211
10.	ACdAa	Yellowish White	260 $^{\circ}$ C	65	545

A - o-benzoyl Benzoic Acid; Aa - Anthranilic acid ; D - p-Anisidine; T- Thiourea
Ph- Phenyl hydrazine and Ap - p-Aminophenol.

Synthesis of metal complexes of O-benzoyl N-2-pyridyl benzamide

Simple metal complexes

A solution of Ligand (B) (0.005M, 1.5g) in aqueous ethanol (1:1,100 ml) was added to a solution of metal salts (0.0025M) in aqueous ethanol (1:1,100ml).The above solution was stirred for 5-hours and allowed to stand for overnight. The product formed was filtered off, washed with

a white solid and recrystallised from hot ethanol. The good yield of 90% was obtained and the melting point lies in the range 160-170 $^{\circ}$ C.

SYNTHESIS OF METAL COMPLEXES

Synthesis of Mixed ligand metal complexes of O-benzoyl benzoic acid.

A solution of O-benzoyl Benzoic Acid (A) (0.01M, 2.26g) in aqueous ethanol (1:1, 100 ml) and a solution of Anthranilic acid (0.01M, 1.37g) in aqueous ethanol (1:1, 100 ml) were added to a solution of metal salts (0.01M) in aqueous ethanol (1:1,100ml). The above solution was stirred for 5-hours and allowed to stand for overnight. The product formed was filtered off, washed with aqueous ethanol (1:1) and dried in air. The same method was adopted for the synthesis of metal complexes using different secondary ligands. The yield and the melting points of all complexes were noted and listed in **Table-I**

aqueous ethanol (1:1) and dried in air. The yield ranged from 50-60 % and the melting points of all complexes were recorded.

Mixed ligand metal complexes

A solution of Ligand (B) (0.005M, 1.5g) in aqueous ethanol (1:1,100ml) and a solution of secondary ligands like Anthranilic acid (0.005M, 0.66 g) in aqueous ethanol (1:1, 100ml) were added to a solution of metal salts (0.005M) in aqueous ethanol

(1:1,100ml). The above solution was stirred for 5-hours and allowed to stand for overnight. The product formed was filtered off, washed with

aqueous ethanol (1:1) and dried in air. The yield and the melting points of all mixed ligand metal complexes were noted and listed in **Table-II**

Table-II Physical Properties and UV Spectral Data of Metal Complexes Of O-Benzoyl N-2-Pyridyl Benzamide Complexes

S.No.	Complexes	Colour	Melting Point	% of yield	λ_{\max} (nm)
1.	B ₂ Cu	Green	200-210 ^o C	60	436
2.	ZnB	Pale Yellow	185-195 ^o C	65	204
3.	CoB	Blue	100-110 ^o C	55	208.5
4.	AaCuB	Pale Green	198-208 ^o C	78	201.5
5.	BCuD	Black	>360 ^o C	75	203.5
6.	BCuT	Brown	180-190 ^o C	70	237
7.	BCuPh	Brownish Green	210-220 ^o C	67	204
8.	AaMnB	Pale Pink	250-260 ^o C	55	234.5
9.	AaZnB	Pale White	230-240 ^o C	70	216.5
10.	AaNiB	Pale Green	260-270 ^o C	68	203.5
11.	AaCoB	Pink	235-245 ^o C	60	205

B- o-benzoyl N-2-pyridyl benzamide

RESULTS AND DISCUSSION

¹H NMR spectral studies

The ¹H-NMR of O-benzoyl N-2-pyridylBenzamide in DMSO-d₆ was recorded on 300MHz Bruker instrument using Tetramethylsilane as internal standard. ¹H-NMR spectra showed a singlet at 5.452(s) due to -N-H proton and a multiplet in the region 6.4-6.75 due to Aromatic protons (9H) and it showed a multiplet at 6.94 due to pyridine protons (4H).

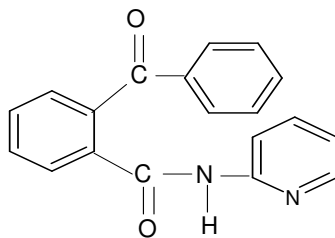
UV-visible spectral studies

All the metal complexes of O-benzoyl Benzoic Acid and O-benzoyl N-2-pyridyl benzamide have shown the UV absorption maxima in the region 210-570nm. All the above complexes were found to be colored. Physical properties and UV spectral datas were given in the **Table-I and II**.

IR Spectral Studies

O-benzoyl Benzoic Acid (A) have shown the IR spectrum of **O-H** stretching frequency at 3442

and 3242 cm⁻¹, **C=O** stretching frequencies at 1963 and 1683 & 1662 cm⁻¹, **C-O** stretching frequencies at 1282 and 1261 cm⁻¹ and **Ar-H** stretching frequencies at 763.76 and 802 cm⁻¹. The ligand (B) O-benzoyl N-2-pyridyl benzamide was prepared from O-benzoyl Benzoic Acid and 2-aminopyridine, the IR absorption frequencies were observed as the **N-H** stretching frequency at 3145 cm⁻¹, **C=O** stretching frequency at 1641 cm⁻¹, **C-O** stretching frequencies at 1282 and 1245 cm⁻¹ and **Ar-H** stretching frequencies at 767 & 727 cm⁻¹. Comparing the IR spectra O-benzoyl Benzoic Acid and the ligand (B), we have arrived that **-OH** of O-benzoyl Benzoic Acid and the amino group of 2-aminopyridine were involved in formation of amide linkages. Hence the structure of the ligand (B) is given in **Fig.1**.



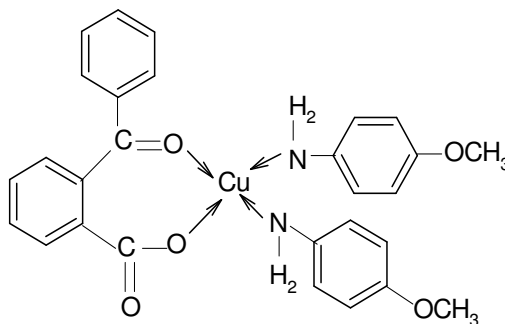
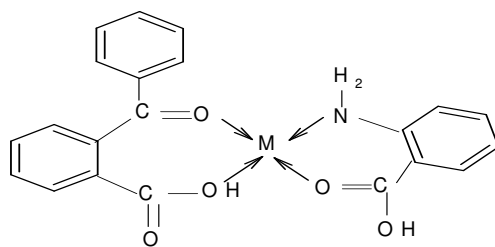
o-benzoyl -N-2-pyridyl benzamide

Fig.1 Structure of *O*-benzoyl -N-2-pyridyl-benzamide.

Mixed ligand metal complexes of *O*-benzoyl benzoic acid

The IR spectra of mixed ligand Cu (II) complexes *O*-benzoyl Benzoic Acid and *p*-Anisidine, Thiourea, Phenylhydrazine, Anthranilic Acid and *p*-Aminophenol have shown NH_2 stretching frequencies appeared in the region $3060 - 3450 \text{ cm}^{-1}$. The C=O stretching frequency of all the complexes appeared in the region around 1620 cm^{-1} and C-O stretching frequency appeared around 1280 cm^{-1} . The M-N stretching frequency of all these complexes between $490-560 \text{ cm}^{-1}$. The M-O

stretching frequency appeared around $420-500 \text{ cm}^{-1}$. The bonding involved in the *p*-Anisidine complex is given in **Fig.2**. The Cu (II) complexes of Thiourea in addition to the above spectral datas have shown M-S stretching frequency at 640.37 cm^{-1} . The IR Spectra of Mixed ligand metal complexes of *O*-benzoyl Benzoic acid and Anthranilic Acid for Cd, Mn, Ni, Zn, Co indicated that the decrease in the value of -NH_2 and C=O stretching frequencies and the appearance of M-N ($550-586 \text{ cm}^{-1}$) and M-O ($420-430 \text{ cm}^{-1}$) stretching frequencies. The bonding in the complex is given in **Fig.3**. The IR spectral datas were given in the **Table-III**.

**Fig.2-** Bonding in Copper complex of *o*-Benzoyl Benzoic Acid and *p*-Anisidine

M = Cd, Co, Ni, Zn

Fig.3- Bonding in metal complexes of *o*-Benzoyl Benzoic Acid and Anthranilic Acid

TABLE –III FT-IR SPECTRAL DATA FOR MIXED LIGAND METAL COMPLEXES OF O-BENZOYL BENZOIC ACID

S.No	Complex	$\nu_{\text{O-H}}$ Cm^{-1}	$\nu_{\text{N-H}_2}$ Cm^{-1}	$\nu_{\text{C=O}}$ Cm^{-1}	$\nu_{\text{C-O}}$ Cm^{-1}	$\nu_{\text{Ar-H}}$ Cm^{-1}	$\nu_{\text{M-N}}$ Cm^{-1}	$\nu_{\text{M-O}}$ Cm^{-1}
1.	ACuAa	---	3448.72(w) 3271.27(s) 3124.68(s)	1604.77(s) 1550.77	1280.73	871.82 810.10 717	493.78	424.34
2.	ACuD	---	3356.14(w) 3062.98(w)	1666.50(w) 1627.92(w) 1597(w)	1288.45 1249.87(w)	771 709.80 833.25	563.21	501.49
3.	ACuT	---	3309.85(b,w) 3186.40	1627.92(s,b)	1280.73(s)	771.53 709.80	640.37	493.78
4.	ACuPh	3062.96 (w,s)	3464.15(b,w)	1666.50 1627.92	1280.73	771.53 709.80	501.49(s)	416.62 (w)
5.	ACuAp	3000 - 3500(b, w)	3000 - 3500(b,w)	1512 - 1600(b)	1242.16	833.25 771.53 717.52	516.92 (V.w)	424.34 (V.w)
6.	AMnAa	3232.10 (w)	---	1589.34(s) 1543.05(s)	1327.0 1242.0	810 756 717	516.62 555.50 (w)	430(s)
7.	AZnAa	3232.70 (b)	3298.28(s) 3128.54	1616.35 1539.20	1240.23	812 750 715	514.99 (S) 586.36 (S)	430
8.	ANiAa	3302.13	3448.72 (b,s) 3124.68	1658.78 1589.34 1543.05	1265.0	802.29 756 717.52	578.64 (b,w)	424.34 (s,h)
9.	ACuPh	3062.96 (w,s)	3464.15 (b,w)	1666.50 1627.92	1280.73	771.53 709.80	501.49(s)	416.62 (w)
10.	ACuAp	3000 - 3500 (b,w)	3000 - 3500(b,w)	1512 - 1600 (b)	1242.16	833.25 771.53 717.52	516.92 (V.w)	424.34 (V.w)
11.	AMnAa	3232.10 (w)	---	1589.34(s) 1543.05(s)	1327.0 1242.0	810 756 717	516.62 555.50 (w)	430(s)
12.	AZnAa	3232.70 (b)	3298.28(s) 3128.54	1616.35 1539.20	1240.23	812 750 715	514.99 (S) 586.36 (S)	430

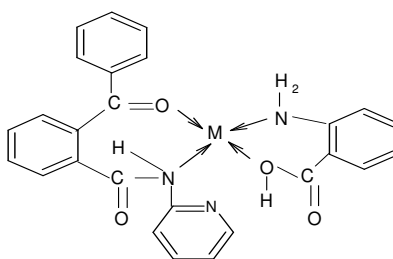
Metal complexes of O-benzoyl N-2 -pyridyl benzamide

The IR spectra of Cu, Zn, Co complexes have shown variations in stretching frequency -N-H and C=O indicated that these two groups may involved in bonding with metal atoms and further proved by the appearance of M-O (447 cm^{-1}) and M-N (480-540 cm^{-1}) stretching frequencies in the complexes. The Mixed ligand Cu(II) complexes of p-Anisidine, Thiourea and Phenylhydrazine showed the -NH₂ stretching frequency in the region 3356 - 3456 cm^{-1} , N-H stretching frequency at 3062-3233

cm^{-1} and C=O stretching frequency around 1500-1600 cm^{-1} . All these complexes were found to exhibit M-N stretching frequency at 486-550 cm^{-1} and M-O stretching frequency at 424-480 cm^{-1} . In the Thiourea Cu (II) complex in addition to the above data produced M-S stretching frequency at 640.37 cm^{-1} . The Anthranilic Acid mixed ligand complexes of Cu, Zn, Ni, Co have shown the -O-H stretching frequency at 3230-3300 cm^{-1} and -NH₂ stretching frequency at 3300-3450 cm^{-1} and N-H stretching frequency lies around 3135 cm^{-1} . The C=O stretching appeared around 1600 cm^{-1} and

the **M-N** stretching frequency at 516 cm^{-1} and **M-O** stretching frequency at 425 cm^{-1} . The structure of

the complex is given in **Fig.4**.



M = Co, Zn, Ni, Cu

Fig.4- Bonding in metal complexes of *O*-benzoyl - *N*-2-pyridyl-benzamide and Anthranilic Acid frequency at 3302 cm^{-1} , **M-N** stretching frequency around 510 cm^{-1} , **M-O** stretching frequency around 425 cm^{-1} . The IR spectral data were given in the **Table-IV** and **V**.

TABLE- IV FT-IR SPECTRAL DATA FOR SIMPLE METAL COMPLEXES OF *O*-BENZOYL *N*-2-PYRIDYL BENZAMIDE COMPLEXES

S.No.	Complex	$\nu_{\text{N-H}_2}$ Cm^{-1}	$\nu_{\text{C=O}}$ Cm^{-1}	$\nu_{\text{C-O}}$ Cm^{-1}	$\nu_{\text{Ar-H}}$ Cm^{-1}	$\nu_{\text{M-N}}$ Cm^{-1}	$\nu_{\text{M-O}}$ Cm^{-1}
1.	CuB ₂	3456.44(s) 3356.14(s)	1620.21(b,s)	1280.73(s)	702.09 752.23	486.06(s)	447.49(w)
2.	ZnB	3425.90(s) 3340.71(m)	1643.35(b,s)	1280.73	771.53 752.23	524.64(w)	470.63(s)
3.	CoB	3147.8(b,w)	1674.21(s)	1280.73(s)	763.81 694.37	547.78(s)	447.49(s)

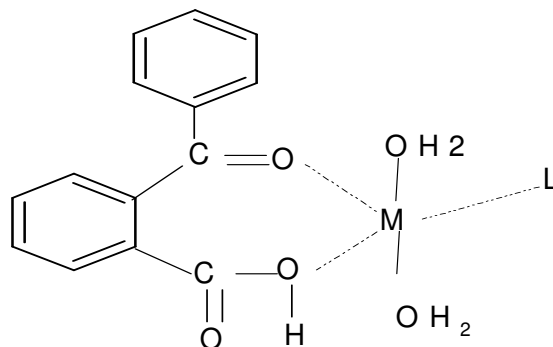
TABLE –V FT-IR SPECTRAL DATA FOR MIXED LIGAND METAL COMPLEXES OF *O*-BENZOYL *N*-2-PYRIDYL BENZAMIDE COMPLEXES

S.No.	Complex	$\nu_{\text{O-H}}$ Cm^{-1}	$\nu_{\text{N-H}_2}$ Cm^{-1}	ν_{NH} Cm^{-1}	$\nu_{\text{C=O}}$ Cm^{-1}	$\nu_{\text{C-O}}$ Cm^{-1}	$\nu_{\text{Ar-H}}$ Cm^{-1}	$\nu_{\text{M-N}}$ Cm^{-1}	$\nu_{\text{M-O}}$ Cm^{-1}
1.	AaCuB	3278.99 (s)	3456.44(s) 3356.14(w)	3124.68 (s)	1604.77 1550.57	---	756.10(s) 717.52(s)	486.06 (s)	424.34 (s)
2.	BCuD	---	3456.44(s) 3356.14(s)	3062.96 (w)	1600(b,w) 1496.76(s)	1280.73(s) 1242.16 (m)	771.53(s) 717.52 (b)	563.21 525(w)	470(w)
3.	BCuT	---	3456.44(w) 3356.14(w)	---	1635.64(b) 1496.76 (s,w)	1280.73(s)	771.53(s) 702.09 (b)	547.78 640.37	486.06
4.	BCuPh	---	3456.44 3356.14	3232.7 (b,w) 3062.96 (b,w)	1620.21 (b,s)	1280.73	771.53(s) 725.23(s)	550(v,w)	486.06 (s)
5.	BMnAa	3302.13 (s)	---	3140.11	1674.21 1589.34 1543.05	1337.03 1242.16 1280.73	756.10 717.52	425(s) 509.21	425 555.50 (m)
6.	BZnAa	3232.74 (w)	3302(s)	3132.40	1597.06(b,s) 1543.05(b,s)	---	756.10 717.52	516.12(m)	425(s)
7.	BNiAa	---	3448.72 (b,w) 3302.13(s)	3124.68 3224.98	1658.78(w) 1597.06(s) 1543.05(s)	1280.73 (b,w)	756.10 717.52	570.93 (b,w)	424.34 (s)
8.	BCoAa	3309.85 (s)	3448.72(b) 3224.98(w)	3140.11	1658.78(w) 1589.34(s) 1543.05(s)	1265.30 (b,m)	756.10(s) 717.52 810.10	516.92(s) 586.36 (b,w)	425(s)

ESR Spectral Studies

ESR Spectra of metal (II) complexes were recorded at room temperature using chloroform solution. The g_{iso} values were lies in the range 2.10-2.14 and their magnetic moment value was 1.82-1.85.

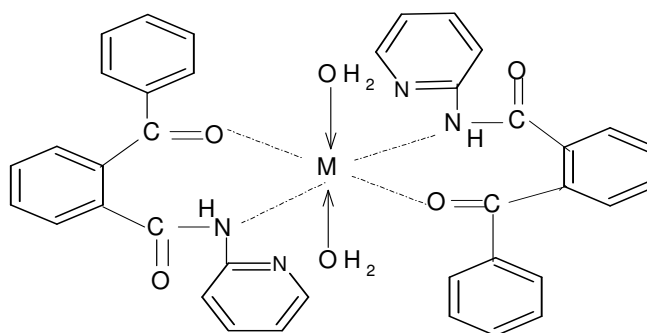
From all the above spectral data, the mixed ligand metal complexes of O-benzoyl Benzoic Acid may have the following structure



M- Cu, Mn, Zn, Ni, Co, Cd L- Aa, D, T, Ph, Ap

Fig.5 - Structure of metal complexes of o-Benzoyl Benzoic Acid and Ligands(L)

From all the above spectral data, the simple metal complexes of O-benzoyl N-2-pyridyl Benzamide may have the following structure



M = Co, Zn, Cu

Fig.6- Structure of metal complexes of O-benzoyl - N-2-pyridyl-benzamide

Biological Activity of Metal Complexes

The bacterial pathogens selected in the present investigation are *Proteus vulgaris*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Escherichiacoli*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Pseudomonas fluorescense*. We have used the Disc diffusion method to study the anti microbial

activities of our metal complexes and their activities are listed in the **Table VI and VII**.

We observed that some of the metal (II) complexes of O-benzoyl N-2-pyridyl benzamide and mixed ligand metal(II) complexes of O-benzoyl Benzoic acid were found to exhibit their activities against *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus*.

TABLE-VI ANTIBACTERIAL ACTIVITY OF O-BENZOYL BENZOIC ACID MIXED LIGAND METAL COMPLEXES

S.No	Metal complexes	Escherichia coli	Staphylococcus Aureus	S.No	Metal complexes	Escherichia coli	Staphylococcus Aureus
1.	ACuAa	A	A	5.	ANiAa	A	NA
2.	ACuD	A	A	6.	ACoAa	NA	A
3.	AMnAa	NA	A	7.	ACdAa	NA	A
4.	AZnAa	A	NA				

TABLE-VII ANTIBACTERIAL ACTIVITY OF O-BENZOYL N-2-PYRIDYL BENZAMIDE METAL COMPLEXES

S.No	Metal complexes	Escherichia coli	Bacillus Subtilis	S.No	Metal complexes	Escherichia coli	Bacillus Subtilis
1.	B ₂ Cu	NA	NA	6.	AaNiB	NA	NA
2.	ZnB	NA	NA	7.	BCuT	NA	A
3.	CoB	NA	NA	8.	BCuPh	A	NA
4.	AaCuB	A	A	9.	AaZnB	NA	NA
5.	BCuD	A	A	10.	AaCoB	A	A

NA- Non active A-Active

CONCLUSION

We have synthesized various mixed ligand metal complexes of O-benzoyl Benzoic acid and O-benzoyl N-2-pyridyl-benzamide. All the above complexes yield, melting point, UV absorption and FT-IR and ESR spectral studies were recorded. All the complexes are well colored and have shown UV absorption in the range 210-570 nm. In O-benzoyl Benzoic acid mixed ligand metal complexes, the bonding linkages of C=O and -OH of carboxylic group with metal was observed. FT-IR spectral values of all the metal complexes of O-benzoyl N-2-pyridyl-benzamide of both simple and mixed ligands indicated the presence of M-O stretching in simple metal complexes and M-N & M-O stretching in mixed ligand complexes.

Zone of inhibition studies for antibacterial activity determination leads to the conclusion that some of metal complexes were found to have activities

against *Bacillus subtilis*, *Escherichia coli* and *Staphylococcus aureus*.

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