Research Article

Preparation, Spectroscopic Characterization and Biological Activities of Co(II) and Ni(II) Complexes with 2-Aminobenzonitrile and Octanoate Ligands

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ABSTRACT

The Co(II) and Ni(II) complexes with 2-Aminobenzonitrile (ABN) and octanoate ion (OC) were prepared using microwave irradiation. The prepared complexes were characterized by elemental analysis, metal estimation (volumetric & calorimetric method), electrical conductivity, UV-Visible, IR and Far-IR spectral studies. The antibacterial and antifungal activities of both ABN and octanoate ligands and the metal complexes at various concentrations were carried out by disc diffusion method with the following microorganisms viz., *E-coli, Enterobacter, Klebsiella, Staphylococcus aureus, Streptococci, Salmonella typhi, P.aeruginosa, C.albicance, Aspergillus Flavus* and *Aspergillus niger.* From the elemental analysis and metal estimation, the formulae for the prepared complexes are $[ML_2X_2]$ (where M=Co(II) & Ni(II), L=2-Aminobenzonitrile and X=octanoate). The UV-Visible spectra lead to the probable geometry of the complexes. The UV-Visible spectral data suggest distorted octahedral geometry around Co(II) & Ni(II) complexes. Entry of the ligands into the coordination sphere was confirmed from IR spectra. The IR spectral data indicate both ABN and octanoate can coordinate to the metal ions. The Far-IR spectra of the complexes indicate the bond between metal and linked atom of the coordination group. From far-IR data the metal ions linked to $-NH_2$ & -C≡N nitrogen atom of ABN and oxygen atom of octanoate ion. The antibacterial and antifungal activities of the complexes compared with those of pure ABN and sodium octanoate. The results indicate that Co(II) & Ni(II) complexes were active against *S. aureus* and , *P.aeruginosa* compared to the pure ligands.

Keywords: *2-Aminobenzonitrile, antibacterial, antifungal, microwave, octanoate*

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INTRODUCTION

Synthesis of metal–organic ligand coordination compounds is of high interest not only due to their variety of structures but also to their potential applications in many fields such as antimicrobial [1], conductive materials [2], luminescent [3], gas storage and magnetic materials [4,5]. The aromatic nitriles have a wide variety of applications in pharmaceuticals, pesticide and dye industries [6,]. Among the aminobenzonitrile 2-Aminobenzonitrile (ABN) is used for the induction of nitrilase activity in Arthrobacter, radio protective agent and starting materials for the synthesis of biologically active compounds [7-10]. It is one of the organic ligand in coordination chemistry it can coordinate to the metal ions through different modes *viz.,* monodentate, bidentate or bridging. Microwave assisted synthesis is a fast emerging field in synthesizing compounds. It leads to the higher reaction selectivity and utilization of the expansive reagents. In addition to providing an eco-friendly "green chemistry" approach to the reaction, it is free of environmental impacts [11]. The present work aims at the microwave irradiated synthesis, analytical, spectral and biological characterization of Co(II) and Ni(II) complexes with 2-aminobenzonitrile and octanoate ion as ligands.

MATERIALS AND METHODS

2-Aminobenzonitrile and sodium octanoate were purchased from Sigma Aldrich Company. Cobalt nitrate, nickel nitrate, DMSO, DMF, methanol, ethanol were of

AnalaR grade, and used as such without further purification.

INSTRUMENTS

The elemental analysis of the complexes was carried out by using (Thermo Finnegan make, Flash EA1112 Series Instrument) CHNS(O) analyzer. The electrical conductivity measurements were conducted using 10^{-3} solutions of the metal complexes in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV-Visible spectra of Co(II) and Ni(II) complexes were recorded on Varian, Cary 5000 model UV Spectrophotometer. The IR spectra of the complexes were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in 4000-400 cm^{-1} range with KBr pellet technique. The Far-IR Spectra of the complexes were recorded by Bruker 3000, FT IR Spectrometer. The antimicrobial and antifungal activities of the ligands 2-aminobenzonitrile, octanoate and their complexes were done by disc diffusion method.

PREPARATION OF COMPLEXES

(i) Preparation of Co(II) complex

0.83g(6.93 mmol) of ABN in ethanol and1.74g (6.90 mmol) of sodium octanoate in ethanol were added to the cobalt nitrate 1.00g (3.40 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. A dark pink coloured complex was precipitated (63.8%).

(ii) Preparation of Ni(II) complex

0.83g (6.93 mmol) of ABN in ethanol and 1.14g (6.90 m mol) of sodium octanoate in ethanol were added to the nickel nitrate 1.00g (3.40 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using microwave oven. The precipitated complex was pale green in colour with the yield 63.9 %.

RESULTS AND DISCUSSION

Elemental analysis and metal estimation

The elemental analysis and metal estimation of the complexes lead to the general formulae $[ML_2X_2]$ where M= Co(II), Ni(II), L= 2-aminobenzonitrile (ABN) and X= octanoate ion. The experimental values are in good agreement with the theoretical values.

Electrical conductivity

The electrical conductivity of 10^{-3} M solution of each complex in DMSO was measured. The molar conductance values of the complexes, *viz.,* 74.58 & 68.77 $ohm^{-1}cm^2mol^{-1}$ indicates their non-electrolyte nature (1:0 type) and there is no ion outside the coordination sphere [12].

Table 1: Analytical and Electrical conductivity data of the Complexes

Sr. No.	Complex	EC ($ohm^{-1}cm^2mol^{-1}$)	%C	%H	%N	%M
1	$[Co(ABN)_2(OC)_2]$	74.58	61.95 (61.90)	7.27 (7.29)	9.65 (9.67)	10.13 (10.15)
2	$[Ni(ABN)_2(OC)_2]$	68.77	61.97 (61.93)	7.28 (7.30)	9.63 (9.60)	10.09 (10.05)

UV- Visible Spectra

The Co(II) complex exhibited three bands at 279 nm, 308 nm and 455 nm are assigned the three transitions, $^4T_{2g}(F) \leftarrow {}^4T_{1g}$, $^4A_{2g}(F) \leftarrow {}^4T_{1g}$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ (F) respectively. These indicating **distorted octahedral geometry** for the Co(II) complex [13].

The Ni(II) complex displayed three bands at 240 nm, 580 nm and 645 nm corresponding to the transitions $^3T_{1g}(P) \leftarrow {}^2A_{2g}$, $^3T_{1g}$ (F) $\leftarrow {}^3A_{2g}$ and $^3T_{2g}$ (F) $\leftarrow {}^3A_{2g}$ respectively. These observations suggest the **distorted octahedral geometry** for Ni(II) complex [14].

IR and Far-IR Spectrum

In the IR spectrum of free 2-aminobenzonitrile exhibit strong bands at 3453cm^{-1} and 3366 cm^{-1} respectively, indicating the asymmetric and symmetric stretching frequencies of NH_2 group. These bands are broadened in the complexes (3417-3367 cm^{-1}) which indicate the amino nitrogen atom as one of the coordinating groups. The ν (C≡N) stretching frequency at 2206 cm^{-1} in free ABN gets shifted to higher wave numbers, 2212 cm^{-1} and 2218 cm^{-1} in

complexes which indicate that the nitrogen atom of the (-C≡N) is another coordinating group to the metal ions. In free octanoate the ν (C-O) stretching at 1409 cm^{-1} get shifted to the frequencies 1385 cm^{-1} & 1402 cm^{-1} in complexes which indicate the monodentate coordination of the octanoate ion through oxygen atom. All above observations confirmed the entry of both 2-aminobenzonitrile and octanoate ion in to the coordination sphere of the metal ions [15,16].

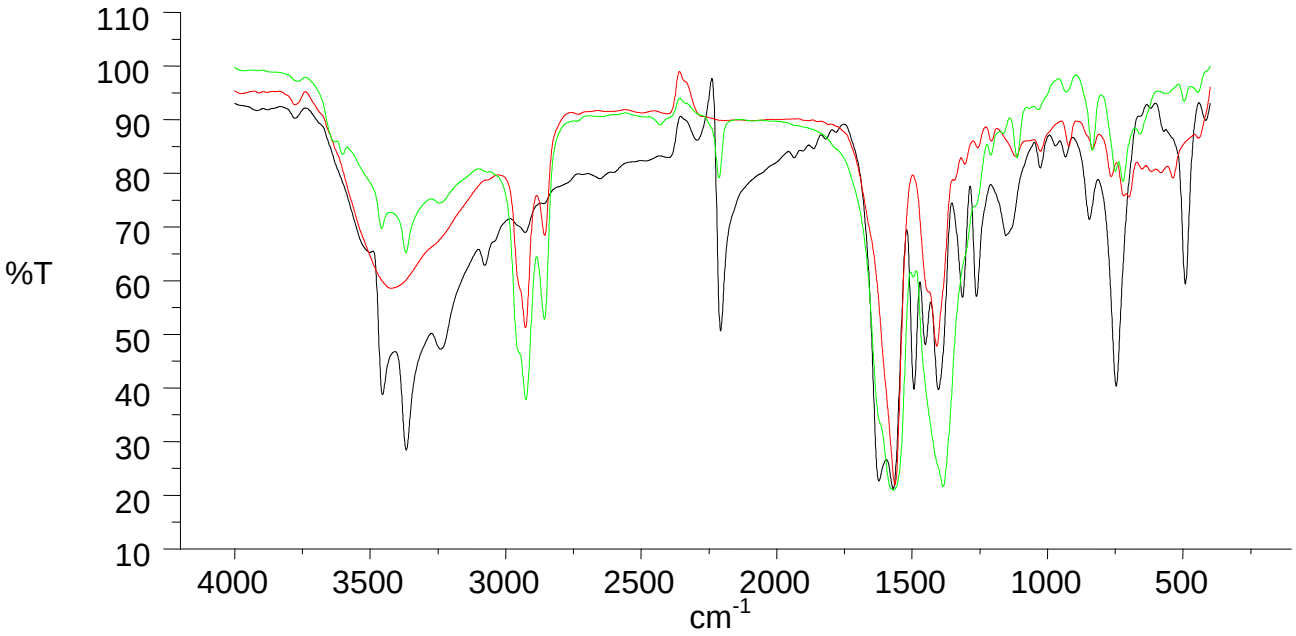


Figure 1: IR Spectra of 2-aminobenzonitrile, sodium octanoate and $[Co(ABN)_2(OC)_2]$

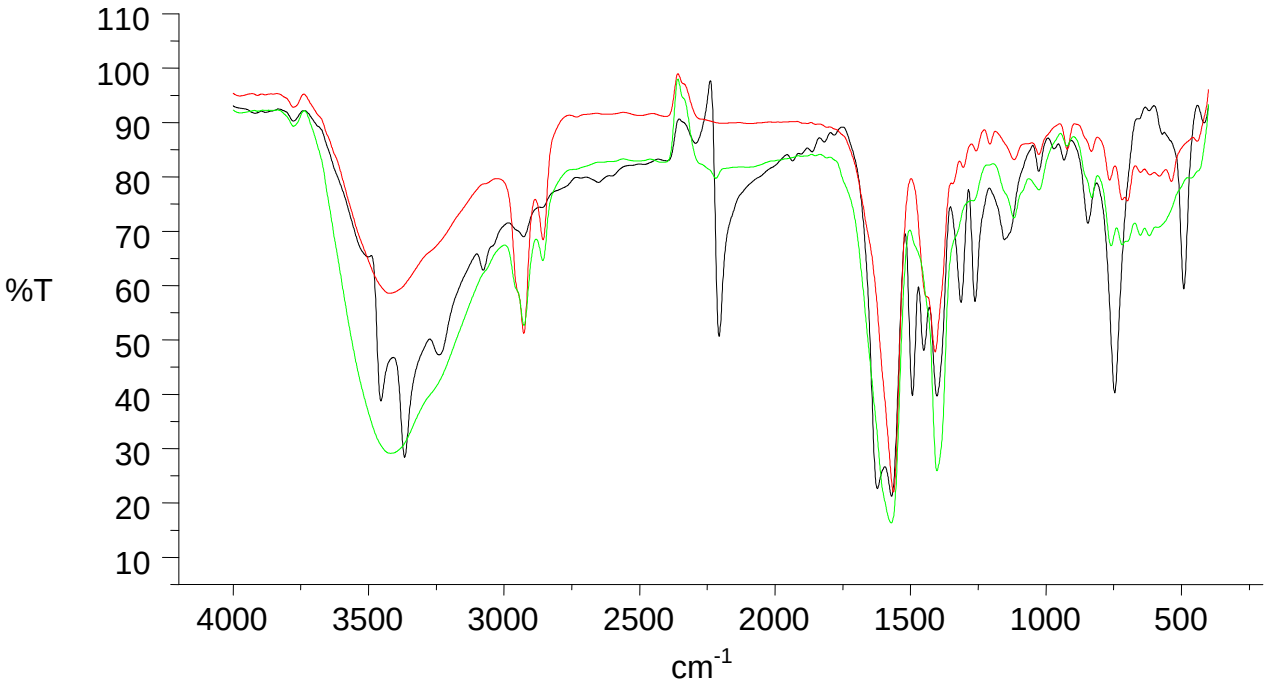


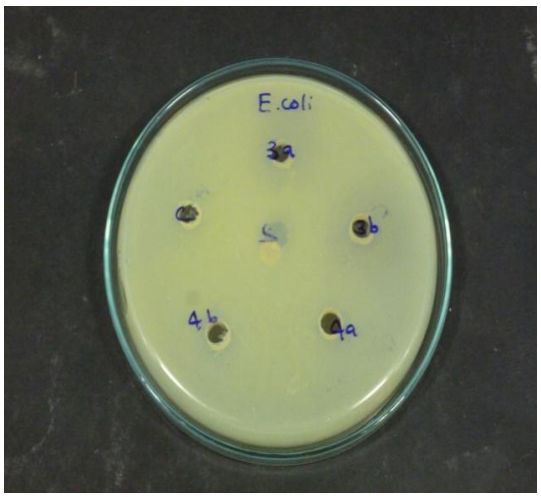
Figure 2: IR Spectra of 2-aminobenzonitrile, sodium octanoate, $[Ni(ABN)_2(OC)_2]$

From far–IR spectra, the metal-ligating atom linkage may be assigned. In Ni(II) complex, the bands at 243cm^{-1}, 494 cm^{-1} and 445 cm^{-1} correspond to δ(M-CN), δ(M-N) and δ(M-O) coordination respectively. Similarly, in Co(II) complex δ(M-CN) at 233 cm^{-1}, δ(M-N) at 495 cm^{-1} and δ(M-O) at 450 cm^{-1} indicate the bidentate nature of 2-aminobenzonitrile and the monodentate nature of octanoate ion [17].

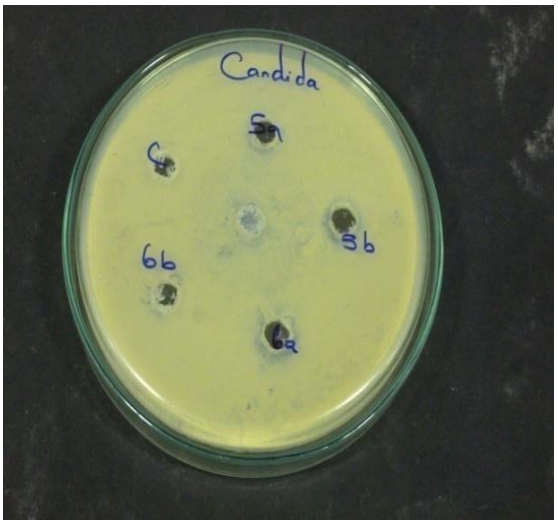
Antimicrobial Activities

The antibacterial and antifungal activities of the compounds 2-aminobenzonitrile, sodium octanoate and the complexes were determined by disc diffusion method using following microorganisms *viz., E-coli, Enterobacter, Klebsiella, Staphylococcus aureus, Streptococci, Salmonella typhi, P.aeruginosa, C.albicance, Aspergillus Flavus* and *Aspergillus niger*. Most of the microorganisms are resistant towards the complexes; except *S.aureus, P.aeruiginosa* is highly sensitive for complexes as compared to the free ligands at various concentrations. Such increase in activity may be due to the nature of ligands and structure of the complexes [18].

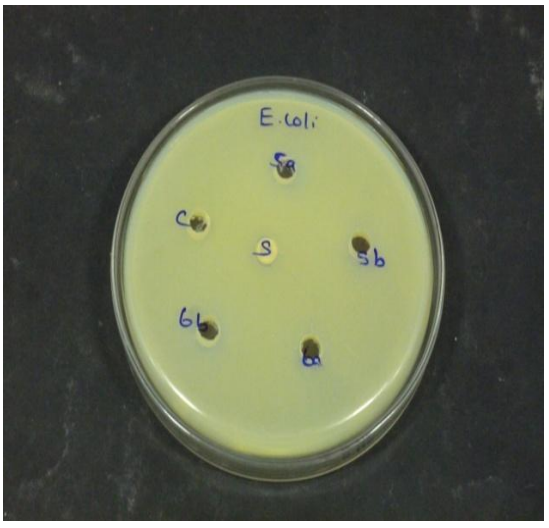
***Staphylo coccei* for Co(II) Complex**



***E.coli* for Co(II) Complex**



***C.albicance* for Ni(II) Complex**



***E.coli* for Ni(II) Complex**

Figure 3: Zone of inhibition of Co(II) and Ni(II) Complexes

Table 2: Antimicrobial Data for ABN, NaOC and their Complexes

Ligand/ Complex	Conc. (µl)	*E.coli*	*Enterobacter*	*Klebsiela*	*S.aureus*	*Strept ococci*	*Salmonella typhi*	*P. aeruginosa*	*C.albicance*	*A. Flavus*	*A. Niger*
ABN	50	04	05	11	14	10	11	06	05	04	03
	100	09	12	16	21	16	18	11	07	05	15
NaOC	50	04	05	04	11	03	05	05	04	03	04
	100	05	05	05	17	04	09	07	05	05	05
Co(II) complex	50	04	05	04	07	04	03	04	03	04	03
	100	05	09	05	16	05	05	05	05	05	04
Ni(II) complex	50	03	04	04	03	04	05	09	04	03	04
	100	05	06	09	04	07	08	14	05	05	05

CONCLUSION

In this paper, the microwave assisted synthesis of 2- aminobenzonitrile and octanoate ion complexes of Co(II) & Ni(II) is given. The structural features of the complexes are confirmed by elemental analysis, metal estimation, electrical conductivity and spectral studies. All the complexes are non-electrolytes and the antibacterial and antifungal activities of the complexes are slightly higher than those of the free ligands *viz.,* 2-aminobenzonitrile and octanoate.

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