IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 9, Issue 5 Ver. I (May. 2016), PP 37-41
www.iosrjournals.org

Synthesis, Spectral Characterization and Biological activities of Cd(II) complex with 2-aminobenzonitrile and octanoate ion as Ligands

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Abstract: *A new cadmium(II) complex of 2-Aminobenzonitrile(ABN) and Octanoate(OC) ion was synthesized by using microwave irradiation. Microwave synthesis gives high yield of the complex within a short time. The molecular formula and the probable geometry of the complex have been deduced from elemental analysis, infrared, electronic spectra, magnetic susceptibility and electrical conductivity measurements. The molar conductance value indicates that the Cd(II) complex is a non-electrolyte. The FT-IR spectra show that 2-aminobenzonitrile is coordinated to the metal ion in a bidentate and octanoate ion in a monodentate manner. The nature of the bonding in this diamagnetic complex was arrived from the NMR spectra. The probable geometry of the complex was found to be tetrahedral. The antibacterial and antifungal activities of ligands and their Cd(II) complex were studied against the microorganisms, viz., staphylococcus aureus, streptococcus, Klebsiella, pseudomonas aeruginosa, salmonella typhi , Enterobacter, E.coli, C.albicans, Aspergillus Flavus and Aspergillus Niger by using agar- well diffusion method. The complex shows moderate activity against the bacteria and enhanced activity against the fungi as compared to the free ligands.*

Keywords: *Cadmium(II) complex, 2-Aminobenzonitrile, Octanoate ion, Antimicrobial*

I. 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 material.[4,5] The aromatic nitriles have a wide variety of applications in pharmaceuticals, pesticide and dye industries.[6] Among the aminobenzonitriles, 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] 2-aminobenzonitrile is one of the organic ligands in coordination chemistry which can coordinate to the metal ion through different modes *viz.*, monodentate, bidentate or bridging. In general, the biological activities of the metal complexes differ from those of either the ligand or the metal ion itself, and increased and/or decreased biological activities are reported for various metal complexes.[11]

On the other hand, synthesis of inorganic/organic compounds using microwave irradiation has been a very rapidly developing technique in research area.[12-18] Compared with the conventional method, microwave technique is promising due to its unique effects, such as rapid volumetric heating, higher reaction rates, higher reaction selectivity, higher yields of products, and energy saving.

The present study aims at synthesis and spectral characterization of Cd(II) complex with neutral bidentate 2-aminobenzonitrile and anionic monodentate octanoate ion as ligands. The biological activities of the ligands and their complex have also been focused in this study.

II. Experimental

2.1. Materials and Methods:

2-aminobenzonitrile, sodium octanoate and cadmium nitrate were purchased from Alfa Aaser Company and used as such. The organic solvents used, *viz.*, DMSO, DMF, methanol, ethanol which were of AnalaR grade, and used as such without further purification.

2.2. Instrumentations

CHN elemental analyses were performed using Thermo Finnegan make, Flash EA1112 Series CHNS(O) analyzer. The electrical conductivity measurements were conducted using 10^{-3} M solutions of the metal complex in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV spectrum of the Cd(II) complex was recorded on Varian, Cary 5000 model UV Spectrophotometer. Infrared

spectra for the complex and the ligands were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in KBr discs at room temperature. The Far-IR Spectrum of the complex was recorded by Bruker 3000, FT IR Spectrometer. The NMR spectra were recorded by 500 MHz (Bruker AV III). The antimicrobial and antifungal activities of the ligands 2-aminobenzonitrile, octanoate ion (using sodium octanoate) and their complex were done by agar- well diffusion method.

2.3. Synthesis of Metal Complex

0.38g(3.21mmol) of 2-aminobenzonitrile(ABN) in ethanol and 1.07g(6.46mmol) of sodium octanoate in ethanol were added to the cadmium nitrate 1.00g (3.22 mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The resulting precipitate was filtered off, washed with 1:1 ethanol: water mixture and dried under vacuum. A pale yellow colored complex was obtained with the yield of 63.8 %.

III. Pharmacology

3.1. Antimicrobial Activity:

The cadmium(II) complex and the free ligands were tested for *in vitro* antimicrobial activity by the well diffusion method[19] using agar nutrient as the medium. The antibacterial and the antifungal activities of the ligands and their cadmium(II) complex were evaluated by well diffusion method against the strains, cultured on potato dextrose agar as medium. According to the typical procedure[20] a well was made on the agar medium inoculated with the microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated for 24 hours for bacteria and 72 hours for fungi at 35^{o}C. At the end of the period, inhibition zones formed on the medium were evaluated in millimeters(mm) diameter.

IV. Results And Discussion

4.1. Elemental analysis and metal estimation

The elemental analysis and metal estimation of the complex lead to the formula, $[MLX_2]$ where M= Cd(II) L= 2-aminobenzonitrile (ABN) and X= octanoate ion. The experimental data are in good agreement with the theoretical values.

Table-1 Analytical data of ligands and the Cd(II) Complex

S.No	Ligands/Complex	Empirical Formula	Elements found (Calc) %				Λ_m ($\Omega^{-1}cm^2 mol^{-1}$)
			C	H	N	M	
1	ABN	$C_7H_6N_2$	71.1685 (71.1672)	05.1186 (05.1188)	23.7121 (23.7125)	-	-
2	NaOC	$C_8H_{15}O_2Na$	57.8176 (57.8181)	09.0965 (09.0971)	-	-	-
3	$[Cd(ABN)(OC)_2]$	$CdC_{23}H_{36}N_2O_4$	53.4377 (53.4382)	07.0181 (07.0188)	05.4185 (05.4190)	21.7439 (21.7445)	59.84

4.2. Molar conductance

The molar conductance of 10^{-3} M solution of the dissolved complex in acetonitrile are measured at 25^{o} C. The molar conductance value of the synthesized $[Cd(ABN)(OC)_2]$ are found to be 59.84 Λ_m ($\Omega^{-1}cm^2$ mol^{-1}) indicating that the complex is a non electrolyte.[21]

The proposed structure of the Cd(II) complex

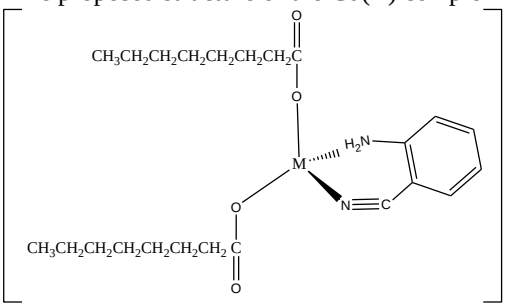

Fig.1 M= Cd (II)

4.3. Electronic Spectra:

In the Cd(II) complex, the d shell is complete, and is not available for bonding. The metal is relatively soft compared with the other transition metals, probably because the d electrons do not participate in metallic

bond. There is no ligand field stabilization effect in Cd^{2+} ions because of its complete d shell. The electronic spectra of Cd(II) complex gave CT [22] absorption at 295nm. Which suggest the tetrahedral geometry around the Cd(II) metal ion, with the formula $[Cd(ABN)(OC)_2]$.

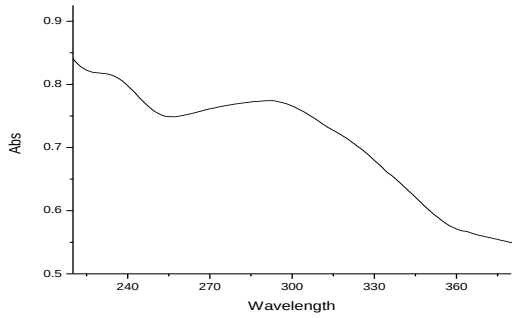

Fig. 2 UV Spectrum of $[Cd(ABN)(OC)_2]$ complex

4.4. IR and Far-IR Spectrum

In order to study the binding modes of the ligands, 2-aminobenzonitrile and octanoate ion to cadmium in the complex, IR spectra of free ligands were compared with Cd(II) complex. The 2- aminobenzonitrile shows in characteristic absorption bands in the 3453, 3366 and 2206 cm^{-1} region, assignable to asymmetric, symmetric stretching frequencies of $\nu(NH_2)$ and ν (C≡N) respectively. A small band noticed at 3076 cm^{-1} is due to ν(CH) aryl.[23] Aromatic ν(C= C) stretching vibration is seen as a sharp peak at 1563 cm^{-1}.[24] The octanoate ion shows ν(C–O) at 1207cm^{-1}. A strong band with a shoulder noticed at 1605 cm^{-1} can be attributed to ν(C=O) of the carbonyl group.[25] The band(s) are broadened at 3417-3367 cm^{-1} and the nitrile group of the ABN underwent higher frequency at 2228cm^{-1} after complexation, indicating the coordination of amino nitrogen and nitrile group to the metal atom. In free octanoate ion the ν (C-O) stretching at 1207 cm^{-1} get shifted to the frequencies of 1235 cm^{-1} in complex, which indicates the monodentate coordination of the octanoate ion through oxygen atom.

The low frequency region of the spectra revealed the presence of medium intensity bands in the region of 600-300 cm^{-1} due to ν(M-N) and ν (M-O)[26] respectively in the complex which supports the involvement of N, O[27] vibrations in Cd(II) complex which again supports complexation with the metal ion under investigation. Thus, the IR spectral data suggest that the ABN is bound to the metal ion through the amino nitrogen & cyano nitrogen and OC is bound through the oxygen donor atom.

4.5. **NMR Spectra**

The ^{1}H-NMR spectra of the ligands (ABN and OC) and their Cd(II) complex were recorded in DMSO-d^6 solvent using tetramethylsilane as internal reference. The ^{1}H NMR spectrum of the ligand, 2-aminobenzonitrile shows the following signals: phenyl protons as multiplet at 7.2 – 7.8 ppm, ortho(NH_2) protons at 4.1 ppm, and octanoate ligands shows δ(CH_2) protons at 2.4 ppm, δ(CH_2) at 1.8 ppm. The amino proton signal at 4.1ppm, in the spectrum of the Cd(II) complex is shifted to downfield as compared to the free ligand, suggesting deshielding of the amino group due to coordination with the metal ion.

The ^{13}C NMR spectra of the 2-aminobenzonitrile and octanoate ion shows the following signals: the chemical shift value of δ(C− C ≡ N) at 93.0 ppm, δ(C-NH_2)at 152.0 ppm and the octanoate shows δ (=C−O) at180.0 ppm,. These chemical shift values of δ(− C ≡ N) at 95.4 ppm and δ(=C−O) at180.7 ppm of the complex are shifted to upfeild compared to the free ligand, suggesting deshielding of the nitrile and carboxylate group due to coordination with the metal ion. There is no appreciable change in all the other signals of this complex. Comparing the spectra of the pure ligands and the cadmium complex, appreciable changes in the chemical shift values in the other signals are not noted.

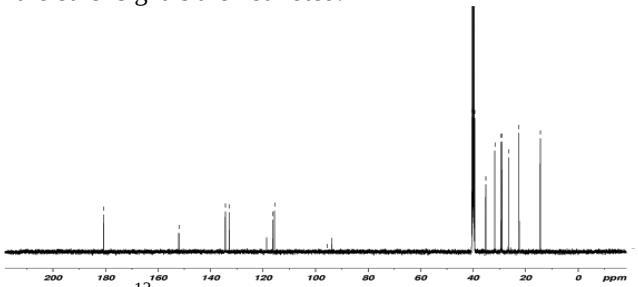

Fig.3 ^{13}C-NMR Spectrum of $[Cd(ABN)(OC)_2]$

V. Biological Activity

5.1. Antibacterial activity

The synthesized compounds and the free ligands were evaluated against the Gram +ve bacteria (*staphylococcus aureus* and *streptococcus*) and the Gram –ve bacteria (*Klebsiella, pseudomonas aeruginosa, salmonella typhi, Enterobacter* and *E .coli)* at different concentration (50 µg/ml and 100 µg/ml) using agar-well diffusion method. The complex does not show any activity against Gram +ve bacteria (*staphylococcus aureus, streptococcus*). On the other hand, the complex has moderate activity against the Gram –ve bacteria (*Klebsiella, pseudomonas aeruginosa, salmonella typhi, Enterobacter* and *E.coli).* The antibacterial activities of the free ligands and the complex are as shown in Table 2.

Table 2: Antibacterial results of the synthesized and tested compounds

Ligands/ Compounds	Conc. µg/ml	Zone of Inhibition (in mm)						
		Gram +ve		Gram –ve				
		S. aureus	*Streptococcus*	*Klebsiella*	*P.aeruginosa*	*S.typhi*	*Enterobacter*	*E.coli*
ABN	50	04	05	11	14	10	11	06
	100	09	12	16	21	16	18	11
NaOC	50	04	05	04	11	03	05	05
	100	05	05	05	17	04	09	07
$[Cd(ABN)(OC)_2]$	50	04	05	04	05	10	10	09
	100	05	07	05	05	17	20	13

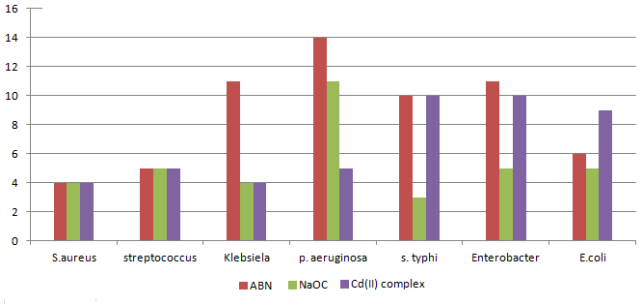

Fig.4 Zone of inhibition (in mm)
Antibacterial activities of the ABN, NaOC and $[Cd(ABN)(OC)_2]$

5.2. Antifungal activity

The antifungal sensitivity testing of the synthesized compound and the free ligands were assayed using agar-well diffusion method at different concentration (50 µg/ml & 100 µg/ml) and they are shown in Table 2. The *Cd*(II) complex has enhanced activity against the fungi (*C.albicans*, *Aspergillus Flavus* and *Aspergillus niger*) compared to that of 2-aminobenzonitrile and sodium octanoate ligands and cadmium complex.

Table 3. Antifungal results of the ligands and cadmium complex

Ligands/ Complex	Conc. µg/ml	Zone of Inhibition (in mm)		
		C.albicans	*Asp. Flavus*	*Asp. Niger*
ABN	50	05	04	03
	100	07	05	15
NaOC	50	04	03	04
	100	05	05	05
$[Cd(ABN)(OC)_2]$	50	12	12	04
	100	20	20	05

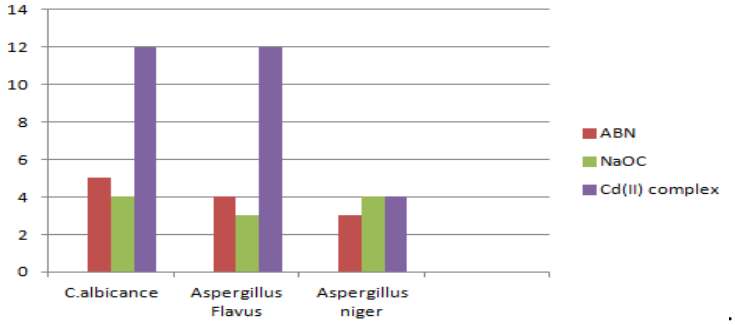

Fig.5 Zone of inhibition (in mm)
Antifungal effects of the ligands and their metal complex

However, the Cd (II) complex is effective against the bacterium and fungus.

VI. Conclusion

In the present study, our efforts were to synthesize and characterize a new Cd(II) metal complex with 2-aminobenzonitrile and octanoate ion as ligands. The new complex was synthesized using microwave irradiation (Green synthesis). These synthesized compounds were characterized by various chemical and spectral analyses. Based on the analytical, electrical conductance, spectral and magnetic moments data, tetrahedral geometry has been suggested probably for the Cd(II) complex. The antibacterial and the antifungal activities of the ligands were compared with the Cd(II) complex. The complex shows enhanced activity against the fungus.

Acknowledgement

The authors wish to thank the Principal for providing the infrastructural facilities in the Department of Chemistry, Government Arts College, Ariyalur, Tamil Nadu, India. They also thank to the Head and Staff members of STIC, Cochin University, SAIF,IIT, Mumbai and SAIF,IIT, Chennai for providing instrumental data.

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