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MICROWAVE ASSISTED SYNTHESIS, SPECTRAL CHARACTERIZATION AND BIOLOGICAL ACTIVITIES OF Zn(II) COMPLEX WITH N,N -DONOR AND OCTANOATE ION AS LIGANDS

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ABSTRACT

A novel Zn(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, molar conductance, UV, FT-IR, and NMR spectra. The molar conductance indicates that the Zn(II) complex is a non-electrolyte. FT-IR spectra show that 2-aminobenzonitrile is coordinated to the metal ion in a bidentate(N,N-donor) and octanoate ion in monodentate manner. The nature of bonding in this diamagnetic complex was arrived from NMR spectra. The geometry of the complex is found to be tetrahedral. The antimicrobial activities of ligands and their Zn(II) complex were studied against the two Gram +ve bacteria (*staphylococcus aureus, streptococcus*), and five Gram –ve bacteria (*klebsilla, pseudomonas aeruginosa, salmonella typhi, Enterobacter*, *E.coli)* and also three fungi *(C.albicance, Aspergillus Flavus* and *Aspergillus Niger*) at different concentrations by agar- well diffusion method. The complex shows enhanced activity against the bacteria and moderate activity against the fungi compared to the free ligands. The free radical scavenging activity of metal complexes have been determined by measuring their interaction with the stable free radical DPPH and the compounds have shown encouraging antioxidant activities.

INTRODUCTION

Microwave irradiation technique in synthetic chemistry has been a very rapidly developing research area. Compared with the conventional heating, microwave heating 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 (Galema, 1997; Landry and Barron, 1993; Harpeness, R., Gedanken, 2003; Grisaru *et al*., 2003; Harpeness, 2003; Yu *et al*., 1999 and Tu *et al*., 2000). In coordination polymers, the use of polypridine, amine and carboxylate ligands is advantageous (Leong and Vittal, 2011; LaDuca, 2009; Kirrilov, 2011; Therrien, 2011; Arora and Mukherjee, 2010; Takamizawa *et al*., 2004; Barnett *et al*., 2005; Lin *et al*., 2008 and Cheng, 2002) because of the extra stability associated with metal-pyridine and metal carboxylate bonds and the greater flexibility shown by these types of ligands. Curiously, nitriles are not much explored for the construction of coordination polymers. The aromatic nitriles have a wide variety of applications in pharmaceuticals, pesticide and dye industries (Taylor *et al*., 1960). 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 (Segarra *et al*., 1998; Kabri *et al*., 2009; Patil *et al*., 2009) On the other hand, N-containing heterocyclic donors have been widespreadly used in transition metal complexes as either bridging or chelating ligands (Sun *et al*., 2009, 2010; Lin *et al*., 2006; Wang *et al*., 2006; Sun *et al*., 2010), While aminobenzonitrile ligands have attracted less attention from both theoretical and experimental points of view due to their both weak coordination sites, N_{cyano} and N_{amino} (Sun, 2011). 2-aminobenzonitrile can coordinate to a metal centre in monodentate (using either N_{amino} or N_{cyano}), bidentate or bridging fasion (using both N_{cyano} and N_{amino}

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groups) (Di Sun, 2012). The present study aims at synthesis and spectral characterization of Zn(II) complex with 2-aminobenzonitrile and octanoate ion ligands. The ligands and their complex were tested for antibacterial, antifungal and antioxidantal activities.

MATERIALS AND METHODS

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

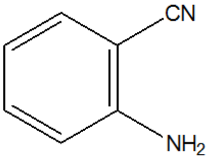
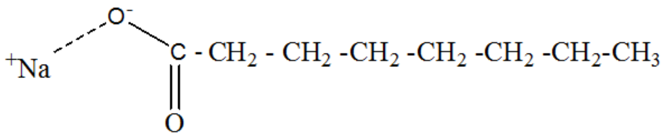


Fig. 1 . 2-aminobenzonitrile



$$^{+}Na\cdots O^{-}-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$$

Fig. 2. Sodium octanoate

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 Zn(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 for the complex and the ligands 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 was done by agar- well diffusion method.

Synthesis of metal complex

0.40g(3.36 mmol) of 2-aminobenzonitrile in ethanol and 1.11g(6.62 mmol) of sodium octanoate in ethanol were added to the zinc nitrate 1.00g (3.33 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: 63.90 %.

Antimicrobial activity:

The free ligands (ABN & OC) and the synthesized complex were tested for *in vitro* antimicrobial activity by the well diffusion method (Irobi *et al*., 1996) by using agar nutrient as the medium. The antibacterial and the antifungal activities of the ligands and the zinc (II) complex were evaluated by well diffusion method against the strains, cultured on potato dextrose agar as medium. In typical procedure (Pelczar *et al*., 1998) 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 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 as millimeters (mm) diameter.

Antioxidantal activity

Evaluation of Antioxidant Activity Stock solution (1 mg/mL) was diluted to final concentrations of 10–500 µg/mL. Ethanolic DPPH solution (1 mL, 0.3 mmol) was added to sample solutions in DMSO (3 mL) at different concentrations (10–500 µg/mL) (Chen *et al*., 1999). The mixture was shaken vigorously and allowed to stand at room temperature for 30 min. The absorbance was then measured at 517 nm in a UV-Vis Spectrophotometer. The lower absorbance of the reaction mixture indicates higher free radical scavenging activity. Ethanol was used as the solvent and ascorbic acid as the standard. The DPPH radical scavenger was calculated using the following equation:

$$\text{Scavenging effect (\%)} = \frac{A_0 - A_1}{A_0} \times 100$$

where Ao is the absorbance of the control reaction and A_1 is the absorbance in the presence of the samples or standards.

RESULTS AND DISCUSSION

Elemental analysis and metal estimation

The elemental analysis and metal estimation of the complex lead to the formula $[Zn(ABN)(OC)_2]$. The percentages of carbon, hydrogen, nitrogen and zinc in the complex were found to be 58.78(59.85), 7.72(7.85), 5.96(5.99) and 13.91(13.99) respectively. The experimental data are in good agreement with the theoretical values (given in the parentheses).

Molar conductance

Molar conductance (ΛM) measurements of the complex carried out using acetonitrile as the solvent at the concentration of 10^{-3}M, indicate non-electrolyte (Geary, 1971) behaviour of the complex and conductivity value were found to be 89.51 $\Omega^{-1}cm^{2}$ mol^{-1}. Thus the complex may be formulated as $[Zn(ABN)(OC)_2]$.

Electronic Spectra

The Zn(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 Zn^{2+} ions because of its complete d shell. The electronic spectra of Zn(II) complex gave charge transfer (Lever, 1986) absorption at 265nm. Tetrahedral geometry is proposed for the zinc complex, with the formula $[Zn(ABN)(OC)_2]$.

The proposed structure of the Zn(II) complex

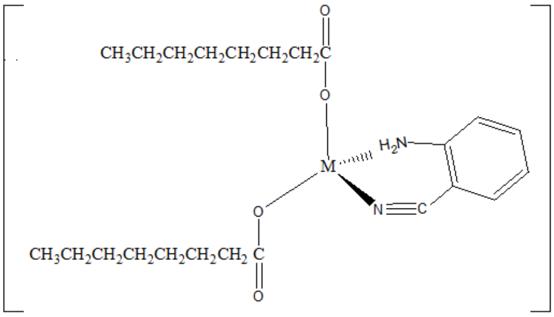


Fig. 3. M= Zn(II)

IR spectra and mode of bonding

The IR spectra of the Zn(II) complex were compared to those free ligands. The stretching vibrations of the NH_2 group and CN groups were observed near 3336 and 2218 cm^{-1}, respectively, higher than those of the corresponding free ligand 2-aminobenzonitriles (N,N-donor). This indicates that the ligands coordinate to the zinc(II) metal via nitrogen atoms of both amino and cyano groups. The trend is in agreement with previous examples reported for nitrile ligands (Nakamoto, 2009). The increase in nitrile stretching frequency has been attributed to the increase bond polarity as the electronegativity of the nitrogen of the nitrile group increases on nitrogen- metal bond formation (Coerver, 1985) On the other hand, the ν(C–O), which occur at 1207 cm^{-1} for the octanoate ligand, was moved to higher frequencies, 1262 cm^{-1} after complexation, this shift confirms the participation of carboxylic oxygen of the ligand in C–O–M bond formation (Mohamed *et al*., 2005) Conclusive evidence regarding the bonding of the non–ligand bands observed at 455–410 cm^{-1} region assigned to ν(M–N) stretch (Mohamed *et al*., 2009) Oxygen to the metal ions is provided by the occurrence of bands at 530–504 cm^{-1} region due to ν(M–O) (El–Sherif and Eldebss, 2011).

Table 1. Infrared wave numbers (cm^{-1}) and its tentative band assignments for the ligands and the metal complexes

S.No	Ligand/ Complex	N (NH_2)	N (C≡N)	ν (C-H)	ν (C=C)	ν (C=O)	ν (C-O)	ν (C-H)
1	ABN	3366	2206	3076	1570	-	-	-
2	Octanoate	-	-	-	-	1705	1207	2926
3	$[Zn(ABN)(OC)_2]$	3396	2221	3074	1544	1700	1262	2925

NMR Spectra

The ^{1}H-NMR spectra of the ligands and their Zn(II) complex were recorded in DMSO-d6 solvent using tetramethylsilane as internal reference. The ^{1}H NMR spectrum of the ligand, 2-aminobenzonitrile shows the following signals: aromatic protons at 7.2 – 7.8 ppm , ortho(NH_2) protons at 4.1ppm, meta(C-H) proton at 7.3 ppm, and octanoate shows δ(CH_2) protons at 2.4ppm, δ(CH_2) at 2.4 ppm. The amino proton signal at 3.3 ppm, in the spectrum of the Zn(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.

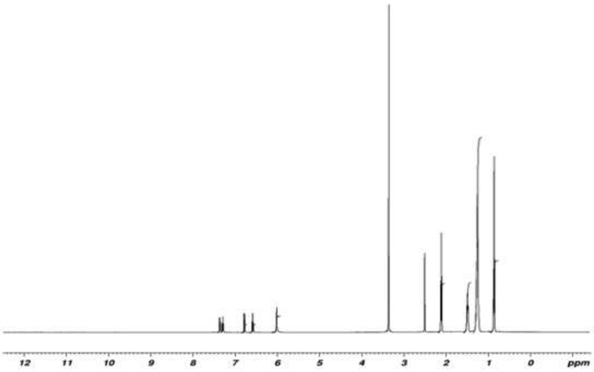


Fig. 4. ^{1}H-NMR Spectrum of $[Zn(ABN)(OC)_2]$

The ^{13}C NMR spectra of the 2-aminobenzonitrile and octanoate shows the following signals: the chemical shift value of δ (C C ≡ N) at 115.6 ppm, (C-NH_2) at 151.0 ppm and the octanoate shows δ (=C O) at181.0 ppm,. These chemical shift values of δ (C C ≡ N) at 115.7 ppm and δ(=C O) at181.7 ppm of the complex is 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 zinc complex, appreciable changes in the chemical shift values in the other signals are not noted.

Biological activity

Antibacterial activity

The synthesized complex and the ligands 2-aminobenzonitrile and sodium octanoate were tested against the two Gram +ve bacteria (*staphylococcus aureus* and *streptococcus*) and five Gram –ve bacteria (*klebsilla ,pseudomonas aeruginosa, salmonella typhi , Enterobacter* and *E.coli)* at different concentration (50 µg/ml and 100 µg/ml) by agar-well diffusion method in vitro conditions.

The complex does not show activity against Gram +ve bacteria *staphylococcus aureus* and moderate activity against the *streptococcus*. On the other hand, the complex has less activity against the Gram –ve bacteria (*klebsilla*, *Enterobacter* and *E.coli),* and enhanced activity against the *(pseudomonas aeruginosa* and *salmonella typhi*). The antibacterial activities of the free ligands and the complex are shown in Fig.5

Antifungal activity

The antifungal activity of the synthesized complex and the ligands 2-aminobenzonitrile and sodium octanoate were assayed using agar -well diffusion method at different concentration (50 µg/ml & 100 µg/ml). The zinc(II) complex has moderate activity against the fungi (*C.albicance*, *Aspergillus Flavus* and *Aspergillus niger*) in both concentration compared to that for 2-aminobenzonitrile and sodium octanoate ligands.

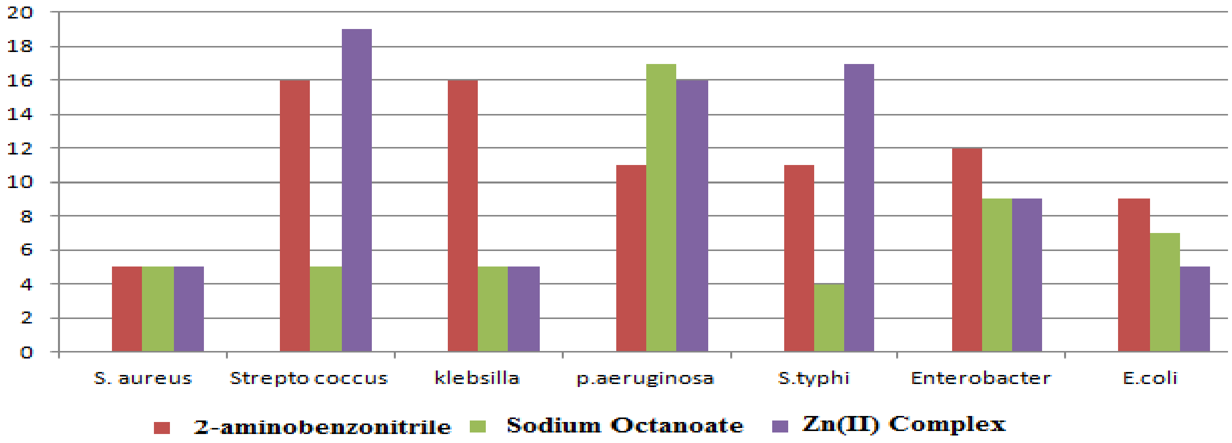


Fig. 5. Zone of inhibition (in mm) Antibacterial activities of the ABN, NaOC and [Zn(ABN)(OC)$_2$]

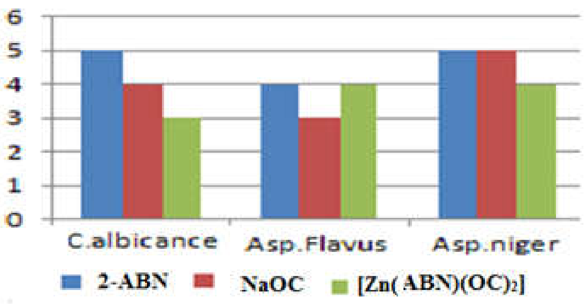


Fig.6. Zone of inhibition (in mm) Antifungal effects of the ligands and their metal complex

Antioxidantal activity (Radical Scavenging Activity)

The 2,2″-diphenyl-1-picrylhydrazyl (DPPH) radical assay provides an easy and rapid way to evaluate the antiradical activities of antioxidants. Determination of the reaction kinetic types DPPHH is a product of the reaction between DPPH• and an antioxidant.

(AH): DPPH$^{•}$ + AH → DPPHH + A$^{•}$

The reversibility of the reaction is evaluated by adding DPPHH at the end of the reaction. If there is an increase in the percentage of remaining DPPH$^{•}$ at the plateau, the reaction is reversible, otherwise it is a complete reaction. DPPH was used as stable free radical electron accepts or hydrogen radical to become a stable diamagnetic molecule (Soares *et al*., 1997). DPPH is a stable free radical containing an odd electron in its structure and usually used for detection of the radical scavenging activity in chemical analysis (Duh *et al*., 1999). The reduction capability of DPPH radicals was determined by decrease in its absorbance at 517 nm induced by antioxidants (Matthaus *et al*., 2002). The graph was plotted with percentage % inhibition on the y-axis and concentration (µg/mL.) on the x-axis. The scavenging ability of the metal complexes was compared with ascorbic acid as a standard. The metal complexes showed enhance activities as a radical scavenger compared with ascorbic acid, Fig.7. These results were in good agreement with previous metal complexes studies where the ligand has the antioxidant activity and it is expected that the metal moiety will increase its activity (Bukhari *et al*., 2009; and Gabrielska *et al*., 2006).

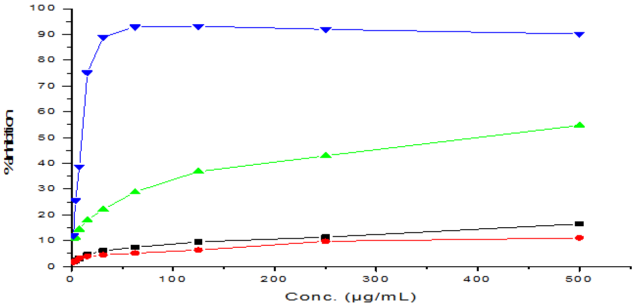


Fig.7 Scavenging effect of free ligands, Zn(II) complex, and ascorbic acid at different concentrations (10, 30, 45, 60, 80,100 and 500 µg/mL)

Conclusion

In the present study, our efforts were to synthesize and characterize a new Zn(II) metal complex with 2-aminobenzonitrile and octanoate ion as ligands. The new complex was synthesized using microwave irradiation. The 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 for the Zn(II) complex. The synthesized complexes were tested for antimicrobial and antioxidant activities. The Zn(II) complex were significant antimicrobial activities as compared to the free ligands. In addition the Zn(II) complex is also found to be a superior antioxidant as compared to ascorbic acid.

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