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RESEARCH ARTICLE

The Corrosion Inhibition Efficiency of Isatin and Methionine Schiff Base and Structural Characterization of its Complexes

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ABSTRACT

A new class of Schiff base ligand derived from isatin and methionine (AB) and its Co(II), Cu(II), Ni(II) and Zn(II) complexes was synthesized and characterized by elemental analysis, magnetic study, molar conductance measurement and spectroscopic methods such as ¹³CNMR, FT-IR, UV, EPR, XRD and Fluorescence spectra as well as thermal studies. In all the complexes the Schiff base coordinates the metal ions in a tetradentate manner. The elemental analysis suggests the stoichiometry to be 1:1 (metal: ligand). The g values calculated for copper (II) complexes indicate the presence of the unpaired electron in the d_{x²-y²} orbital. XRD studies reveals the nano crystalline behavior of Cu(II) complex. The Corrosion inhibition activity of the ligand in acid media was also examined by weight loss experiment and optical microscopic method. The biological activity of the ligand and metal (II) complexes have been tested against few gram positive and gram negative bacterial and fungal species, and found to show more activity compared to the control. The interaction of the complexes with DNA was studied by the absorption spectra which exhibit a slight red shift with hypochromic effect.

Keywords: Schiff base, Metal Complex, EPR, Heterocyclic, Inhibition efficiency, Isatin, Methionine

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1. Introduction

Schiff base complexes, a significant part of coordination chemistry, have achieved major importance in this epoch. The extensive studies have been conducted on complexation of Schiff bases with metals due to the attractive physicochemical properties of metal complexes and broad range of consumption in diverse vicinity of science. Such types of complexes have lined the way for exploration and findings of a variety of metal complexes in current years. The data available for Schiff bases in literature embraces very wide and diversified subjects, comprising vast areas of organo-metallic compounds and numerous applications^{[1]-[5]}. An epigrammatic discussion of the major applications of Schiff base complexes can be found in many reports^{[17]-[21]}. Schiff bases with amino acids have gained importance from the inorganic view point due to their physiological and pharmacological activities. Moreover metal chelates of Schiff bases derived from isatin and amino acid are involved in a variety of biological processes^{[6]-[8], [22]}. Furthermore Schiff base complexes have an extensive importance in many fields like radio tracers, biologically active reagents, and catalysts in a large number of homogeneous and heterogeneous reactions such as oxidation, epoxidation, polymerisation and decomposition reactions. They are also considered to combine with new kinds of potential antibacterial and anticancer reagents and also play an important role as the key compounds for modeling more complicated metabolic reactions involving amino acids which are catalyzed by enzymes^{[9]-[16]}. Isatin (1 H indole 2,3,dione) and its derivatives show signs of a wide range of biological activities. Literature survey indicates that the investigations on Schiff bases derived from Isatin and amino acids are few. Keeping the importance of isatin amino acid Schiff base complexes, in this present work we have reported the synthesis of a new Schiff base ligand(AB) from Isatin (1 H indole 2,3,dione) (A) and methionine(B). The ligand has been coordinated with physiologically essential 3-d transition metal ions, viz. Co(II), Ni(II), Cu(II) and Zn(II) to form a new series of Schiff base complexes CoAB, NiAB, CuAB and ZnAB. Both the ligand and the complexes have been characterized by elemental analysis, molar conductance, magnetic measurements, FTIR, UV – visible spectra, ¹³CNMR spectra, EPR spectra, XRD studies and thermal studies.

2. Materials and Methods

Reagents and instrumentation

The transition metal chlorides and all the solvents were obtained from MERCK India in pure form. The chemicals isatin and methionine were of analytical grade and purchased from High media. A CARLO ERBA 1108 elemental analyzer was employed to obtain the micro analytical data (C, H & N) of the compounds using sulphanilamide as the reference standard. FTIR spectra (4000-400 cm⁻¹) were recorded with KBr pellets on Jasco FTIR/4100 spectrophotometer annexed with ATR accessory at a resolution of 4cm⁻¹. Electronic spectra of the metal complexes were recorded on a Shimadzu UV-1601 spectrophotometer in the wave length region of 200-800 nm. ¹³CNMR spectra were recorded on a Bruker DRX-500 International Journal of Chemistry and Pharmaceutical Sciences

MHz, AVANCE spectrometer at ambient temperature in DMSO-*d*₆ using TMS as internal standard. Molar conductivity measurements were recorded on a Deep vision model 601 digital conductivity meter. Magnetic susceptibility measurements were recorded by Guoy balance at room temperature, using CuSO₄·5H₂O as the calibrant. The EPR measurements were performed on a JEOL JES TE300 spectrometer. XRD determinations were made using an X-ray diffractometer (XPERT PRO PANalytical). Thermo gravimetric (TG) studies were manipulated under a dynamic N₂ atmosphere in the 20-800 °C temperature range at a heating rate of 10 °C min⁻¹ on a Mettler Toledo star system. The fluorescence studies of Schiff base metal complexes were recorded on HITACHI F-7000 fluorescence spectrophotometer. The optical images of metal surfaces were taken by an optical microscope, Olympus-BX51M/Japan.

Synthesis of ligand and complexes

Synthesis of isatin based Schiff base L:

2 mmol of methanolic solution of isatin(A) was stirred for 2 h in a 50 ml flask using a magnetic stirrer. To the resulting methanolic suspension of isatin, 2mmol of methionine (B) was added. The mixture was allowed to react in another flask equipped with the magnetic stirrer for 24h. The obtained product, Schiff base AB, was filtered, washed with methanol followed by ether and dried at 70°C in vacuum.

Synthesis of metal complexes:

1 mmol of the purified AB was added to 1 mmol methanolic solution of CoCl₂ and refluxed under heat for 8 h. The resultant product, CoAB, was filtered and washed well with ether and dried at 70 °C in vacuum. The same procedure was employed for the synthesis of other metal complexes like NiAB, CuAB and ZnAB.

Corrosion inhibition determination

The corrosion inhibition efficiencies of the metal complexes were studied by weight loss method, using rectangular pretreated aluminium foils of size 4 cm x 3 cm x 0.01 cm. The initial weights of the polished specimens were taken. 60 ml of various concentrations of HCl was taken in 100 ml beakers and the specimens were suspended into the solution using 'V' shaped glass hooks. Care was taken to ensure the complete immersion of the specimens. The aluminium foils were exposed in acid medium for 1 hour. After the exposure period, the foils were taken out and washed with running water using a stable hair brush and then with acetone and dried. The dried specimens were then weighed. From the initial and final masses of the specimen, the loss in weight was calculated. Duplicate experiments were performed in each case and the mean values of the weight loss were calculated. The experiment was repeated with 0.2, 0.4, 0.6, 0.8 and 1 mmol concentrations of AB as inhibitor, in 1M HCl. A blank was carried out without inhibitor. The inhibition efficiency of AB was further examined by taking the optical image of aluminium foil and acid treated aluminium foil with inhibitor and without inhibitor by optical microscope.

Biological activity

Antimicrobial activity (in-vitro): The synthesized Schiff base(AB) and the CoAB, NiAB, CuAB and ZnAB complexes were tested against the gram negative bacterial

species *E. coli* and *Pseudomonas aeruginosa*, as well as fungi *T. longifusos*, *C. albicans*, by agar diffusion method. Initially the stock cultures of bacteria were revived by inoculating in broth media and grown at 37 °C for 18 hours. The agar plates of the media were prepared and the wells were made in the plate. With 18 hour old cultures each plate was inoculated and spread over the plates. The required concentration of the test sample was introduced into the respective wells. The control wells with gentamycin were also prepared. DMSO was used as negative control. The plates were incubated at 37 °C for 20 hours. Activity was determined by measuring the diameter of zones showing complete inhibition.

DNA binding experiments:

The interaction between metal complexes and DNA were studied using electronic absorption methods. Disodium salt of calf thymus DNA was stored at 4 °C. Solution of DNA in the buffer 50 mM NaCl/ 5 mM Tris-HCl (pH 7.2) in water gave a ratio 1.9 of UV absorbance at 260 and 280 nm, A₂₆₀/A₂₈₀, indicating that the DNA was sufficiently free from protein. The concentration of DNA was measured using its extinction coefficient at 260 nm (6600 M⁻¹ cm⁻¹) after 1:100 dilutions. Stock solutions were stored at 4 °C and used for not more than 4 days. Doubly distilled water was used to prepare solutions. Concentrated stock solutions of the complexes were prepared by dissolving the complexes in DMSO and diluting suitably with the corresponding buffer to the required concentration for all of the experiments.

3. Results and Discussions

Micro Analysis and Molar Conductance Measurements

The molar conductivity of the metal complexes at room temperature was measured in DMSO. The conductance data, shown in Table 1, indicate that all the metal complexes are non ionic in nature. The micro analysis results of the synthesized Schiff base ligand and the complexes given in Table 1 suggest that Schiff base ligand is potentially tetradentate and form complexes in 1:1 ratio metal to ligand. Thus the general formula of the synthesized complexes is suggested to be [M(AB)Cl].

¹³C NMR Spectra

The ¹³C NMR spectra of AB (Fig 1) was analysed and the signals at 109 ppm, 121 ppm, 128 ppm of AB are assigned to carbons of isatin moieties. A characteristic signal for the imino carbon (C=N) appears at 155 ppm. The signal at 183 ppm represents the carboxylate carbon. The signals obtained in the region 78 – 128 ppm are assigned to aromatic carbon. The methylene carbon observed at 40 ppm indicates the coordination of Schiff base ligand. The signal appears at 15 ppm is assigned to the presence of CH₃ carbon [21]. Thus the ¹³C NMR of the ligand AB confirms the formation of Schiff base.

Infra-Red Spectra

The FT-IR spectra of AB show (Fig 2) characteristic bands at 3200 cm⁻¹ & 3500 cm⁻¹ which can be assigned to the vibration of the free -COOH group. The band observed at 1712 cm⁻¹ can be attributed to the -C=O stretching of the ligand. The strong band observed at 1625 cm⁻¹ could be assigned to -C=N stretch which further confirms the

formation of Schiff base (AB) from methionine and isatin. The absorption band of the carboxylate group (-COO) of methionine appears at 1470 cm⁻¹. The small peaks noted in the region of 2900 cm⁻¹ might be due to the axial C-H stretches. The IR spectra of the metal complexes exhibit a broad band around 3200 cm⁻¹ - 3500 cm⁻¹ assigned to ν(OH) of crystalline or coordinated water molecules associated with the complex and it is shown in figure S1 (b-e). The imino stretching frequency of the complexes appears at around 1625 cm⁻¹ to 1621 cm⁻¹, compared to 1625 cm⁻¹ of the free ligand AB. This shift to the lower energy clearly indicates the coordination of the imino nitrogen atom to the M(II) ion. Similarly, the absorption band of the carboxylate group (-COO) of methionine has been shifted from 1470 cm⁻¹ to 1466 cm⁻¹ in MAB, confirming the bonding of carboxylate ion with M(II) ion. Moreover, the absorption peak due to the amido group (present in isatin moiety) has been shifted from 1712 cm⁻¹ to 1690 cm⁻¹, which signifies its coordination with the central M(II) ion. Further, the appearance of new bands at around 520 cm⁻¹ to 530 cm⁻¹ and 490 cm⁻¹ authenticates the formation of M-N and M-O bonds respectively. Another new absorption band at 420 cm⁻¹ in the FTIR spectrum of the complex MAB can be assigned to the M-Cl bond present. Hence it has been concluded that the Schiff base coordinates to M(II) ion through the imino nitrogen atom, and the carboxylate and amido oxygen atoms. The fourth position of the possible square planar arrangement is occupied by chloride ion in CoAB, NiAB & CuAB and in ZnAB chloride ion may occupy the fourth position of the tetrahedral arrangement. This makes the complex neutral, which is confirmed by the non-electrolytic nature of the complex [24]-[27].

Electronic Absorption Spectra & Magnetic Moment

The UV-Vis spectra of AB (Figure 3) shows two significant absorption bands below the region 400 nm. This might be attributed to π → π* and n → π* transitions of carbonyl and azomethine groups and the π → π* transition of C=C bonds available in aromatic rings. The band appeared at around 520 nm in CoAB could be assigned to ²A_{1g} → ²B_{2g} transition and 520 nm in NiAB could be assigned to ¹A_{1g} → ¹A_{2g} transition arising due to square planar structure of the complexes. CuAB shows a broad band at 420 nm is assigned to ²B_{1g} → ²A_{1g} transition, and confirms square planar geometry for the complex. However ZnAB complex due to the completely filled d¹⁰ configuration, do not exhibit d-d transition and show no absorption above 400 nm [22]. The four coordinated ZnAB complex may be assigned a tetrahedral geometry. In all the complexes (Figure S2 (b-e)) a characteristic band centered between 285 nm and 320 nm is ascribed to an intramolecular charge transfer transition taking place in the complexed ligand [28]-[31]. The results from the magnetic moment measurement are shown in Table 1. The complexes CoAB and CuAB, with magnetic moments 2.7 BM & 1.45 BM respectively, confirm their square planar structure. The complex NiAB is diamagnetic, which authenticates dsp² hybridised square planar configuration. The ZnAB is paramagnetic due to tetrahedral structure with sp³ hybridisation [23], [37].

EPR Spectra: EPR spectral studies of transition metal (II) complexes provide information about the distribution of

unpaired electrons and the metal ion environment. The EPR spectra of the Cu(II) complex recorded in DMSO at room temperature is shown in the (Figure4). It has been observed that the g value is 2.25 and the g_{av} value is 2.1. The trend $g > g_{av} > 2.0023$ indicate that the unpaired electron is localized in the dx^2-y^2 of the Cu(II) ion and is characteristic of the axial symmetry. The g_{av} was found to be 2.17. The deviation of g_{av} from that of the free electron is due to the covalent character of the metal-ligand bond. Finally G is calculated by using the expression $G = g - 2/g - 2$. The G value indicates negligible exchange interaction between metal centers in solid complex. The EPR study also establishes square planar geometry for CuAB complex [33].

Powder XRD

Powder XRD spectra recorded for Schiff base AB, given in Fig 2a, exhibit maxima at $2\theta = 21.8373$ with d spacing 3.20299. The trend of the curve decreases from maximum to minimum intensity indicating that AB is amorphous in nature. The XRD spectra of CuAB (Fig 5), shows the maximum at $2\theta = 27.9964$ correspond to the inter-planar distance = 3.18712. The XRD patterns of the CuAB complex indicate its crystalline nature, and the complexation increases the crystallinity. It is further confirmed by calculating the grain size of CuAB using scherrer's formula $d_{xrd} = 0.9 \lambda / \cos \theta$, where d_{xrd} is the particle size, λ is the wavelength of the radiation, θ is the full – width half maximum and θ is the diffraction angle for hkl plane. CuAB is nanocrystalline with grain size 27.04 nm [28],[34]-[35].

Fluorescence studies

The Schiff base complex ZnAB in DMSO exhibit interesting fluorescence properties, with emission bands located at 438 nm. The rigidity of the molecular edifice increases and reduces the loss of energy by radiation less thermal vibrations. This may be due to the coordination of the ligand to the metal ion. The absorption spectra and emission spectra of ZnAB are shown in figure 6. The band occur at 285 nm in the absorption spectra is due to a $\pi \rightarrow \pi^*$ transition of the organic ligand and the emission is assigned to intraligand $^1(\pi \rightarrow \pi^*)$ fluorescence [38].

Thermal Analysis: The thermograms of the Schiff base AB & CuAB (7) were recorded in the range of 0 to 800°C. In the Schiff base ligand AB the first mass loss stage is due to the loss of physically adsorbed water molecules from the ligand (180-200 °C). The second and third stages may be attributed to the decomposition of methionine group and the isatin moiety around 350°C and 450°C. The residual metal oxides are obtained above 700 °C. In complex CuAB the first mass loss stage is due to the loss of water molecules (90-130 °C). The second and third stages may be attributed to the decomposition of methionine group around 220 °C, and the isatin moiety at 310 °C. The remaining material is the residual metal oxide obtained above 700 °C. According to the DTG curves of ligand AB & complex CuAB all the thermal decays involved endothermic decomposition [30],[32],[35],[36].

Corrosion inhibition studies

The application of the synthesised AB as Corrosion inhibitor was studied on aluminium foil in 1N HCl solution, by weight loss method. The results are given in Table 2.

The graphical presentation of variation of the inhibitor efficiency with concentration of AB is given in Fig 8 and that of surface coverage in Fig 8. Corrosion inhibition is ascribed to the adsorption of inhibitor on aluminium foil. The results indicate that the inhibition efficiency increases with the concentration of the inhibitor. The lone pair of electrons on N and O atoms along with the delocalized pi electrons can be the reason for high inhibition efficiency of the ligand. As inhibitor concentration increases, it covers more and more surface area and results in the reduction of corrosion rate. The maximum efficiency of 68.8 % was observed for 1 mmol concentration of AB. Further the corrosion inhibition efficiency of AB can be examined by taking the optical image of aluminium foil, optical image of acid treated aluminium foil without inhibitor and with inhibitor which are shown in figure 9. It is well clear that a smooth surface has been observed in the aluminium foil before acid treatment. But the surface has been corroded vigorously when it was treated with acid. However the corrosion tendency has been reduced well when it is treated with inhibitor AB. The inhibitor AB acquires high inhibition efficiency due to the lone pair of electrons of nitrogen and oxygen atoms along with the delocalized π -electron. The adsorption of inhibitor on the aluminium foil can occur by the interactions between the π electrons of the inhibitor and the vacant d orbitals of metal surface atoms. This is due to the ability of the ligand AB to form a passive film on the surface of the foil. Extent of film formation is more prominent in the ligand AB because of its high chemical adsorptive nature. It can be explained on the basis of the effect of chemical structure. In this respect the isatin ring, N-H, C=O and C=N of the Schiff base can form a big π bond. These bonds produce more than one centre of chemical adsorption on aluminium foil thus prevent corrosion. [39],[40].

DNA binding studies

There has been substantial interest in studying the affinity and selectivity in binding of metal complexes to DNA. Electronic absorption spectrum is one of the powerful techniques for probing interaction of metal complexes with DNA. The electronic absorption titration of the Co(II), Ni(II), Cu(II) and Zn (II) complexes of AB has been carried out at a fixed concentration of the complex in DMSO at 25 °C, varying the concentration of DNA. They are illustrated in Figure 10. The absorption spectra of all the complexes show bands in the region 270 -350 nm and are assigned to ligand to metal charge transfer (LMCT) transitions. When the amount of DNA is increased, the intensity of the charge transfer band is also changed, due to either hypochromism or hyperchromism. The complexes CoAB, NiAB, and ZnAB shows hypochromism with slight red shift in the presence of DNA characteristic of intercalation, which is attributed to the interaction between the aromatic chromophore ligand of metal complex and the base pairs of DNA [23],[28], and the complex CuAB shows hypochromism without any shift.

Biocidal activities

The antimicrobial activities of Schiff base metal complexes were tested against two bacterial and one fungal species, by disc diffusion method and is provided in Figure 11. The

inhibition zone against each organism shows that the metal complexes show more activity against each class of organism. The activity is related to the structure and nature of the complexes. Anti-bacterial activity follow the order ZnAB > CuAB > CoAB > NiAB and the antifungal activity was in the order of CoAB > ZnAB > CuAB > NiAB.

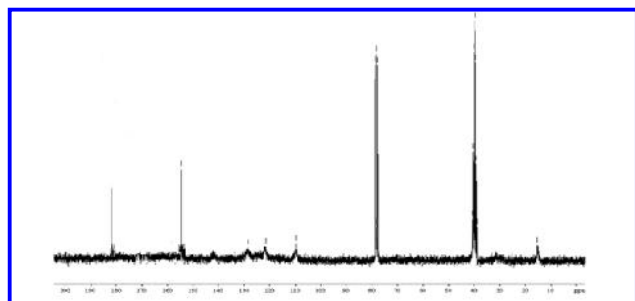


Fig 1: ¹³C NMR of the ligand AB

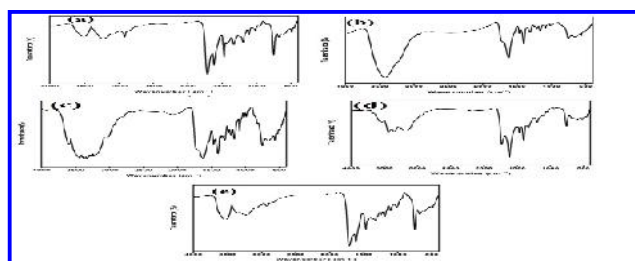


Fig 2: FT-IR spectrum of ligand AB (b) CoAB (c) NiAB (d) CuAB (e) ZnAB

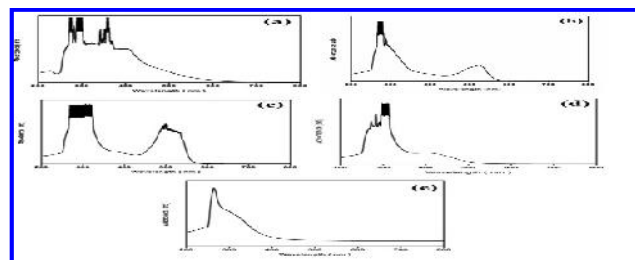


Fig 3: UV Spectra of ligand AB (b) CoAB (c) NiAB (d) CuAB (e) ZnAB

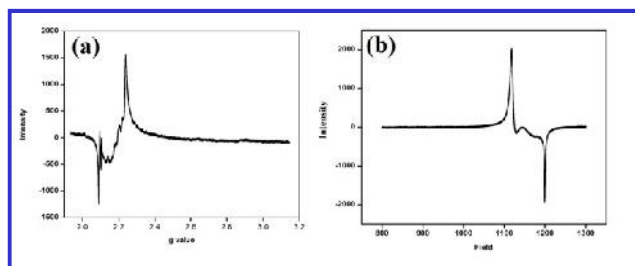


Fig 4: (a) & (b) EPR spectrum of complex CuAB

From the results it is very clear that the increasing activity of metal complexes may be explained on the basis of overtone concept and the chelation theory. According to the overtone concept, liposolubility is an important factor which controls the antimicrobial activity. On chelation the polarity of the metal ion was greatly reduced due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups [35].

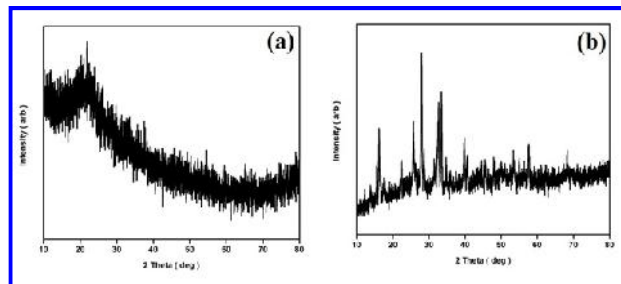


Fig 5: Power XRD pattern of Ligand AB (2b) CuAB complex

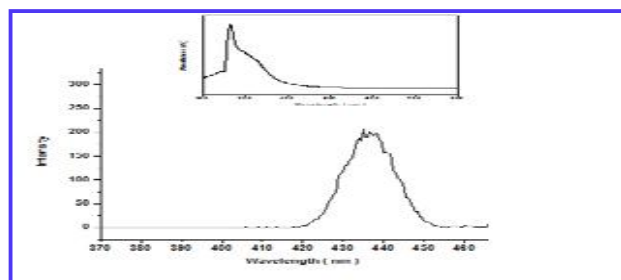


Fig 6: Emission spectra of complex ZnAB (inset: Absorption spectra of ZnAB)

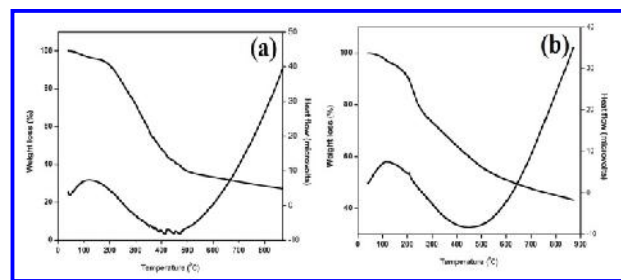


Fig 7: Thermogram of Ligand AB (4b) CuAB complex

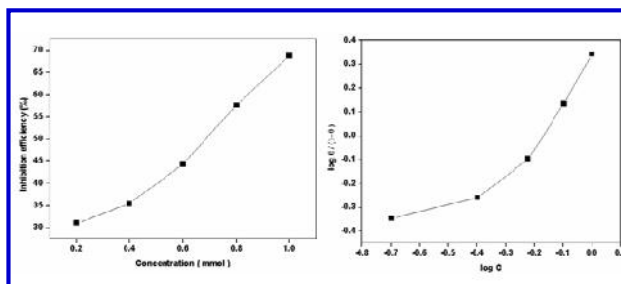


Fig 8: Inhibitor efficiency of ligand AB (5b) Surface Coverage of ligand AB

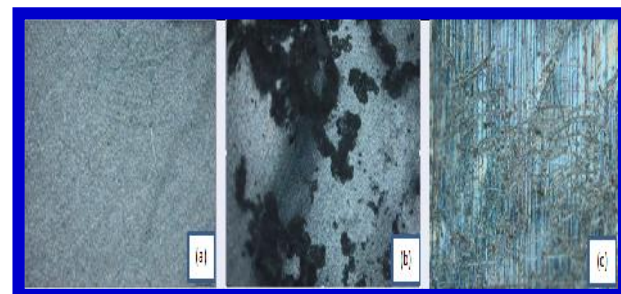


Fig 9: Optical image of aluminium sheet (b) acid treated aluminium sheet without inhibitor (c) acid treated aluminium sheet with inhibitor AB

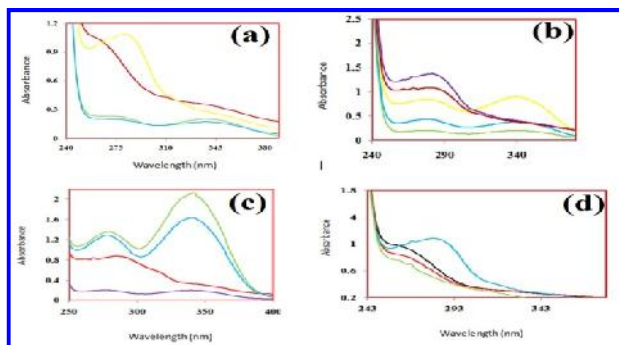


Fig 10: DNA Absorption spectra of complex (a) CoAB (b) NiAB (c) CuAB (d) ZnAB

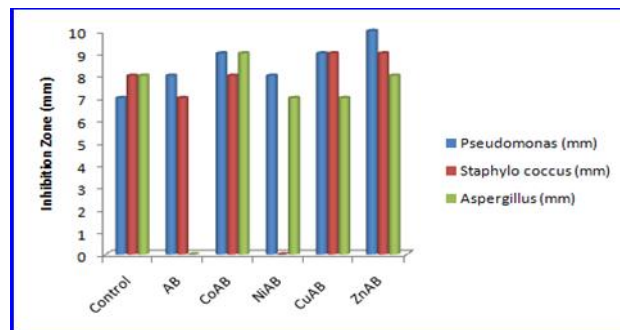


Fig 11: Biological activity of AB and its complexes CoAB, NiAB, CuAB & ZnAB

Table 1: Analytical Data of AB and its Co (II), Ni (II), Cu (II) and Zn (II) complexes

Compound	Molecular Weight	Colour	Elemental analysis					Molar cond Smol ⁻¹ cm ²	Magnetic moment (B.M.)	Molecular Formula
			C	H	N	M	Cl			
AB	278.33	Light brown	55.93 (56.1)	5.09 (5.07)	9.49 (10.06)	-	-	-	-	C ₁₃ H ₁₄ N ₂ O ₃ S
CoAB	372.7	Purple	40.93 (41.89)	3.25 (3.79)	7.04 (7.52)	15.41 (15.81)	10.43 (9.51)	21.46	2.7	C ₁₃ H ₁₄ N ₂ O ₃ S CoCl
NiAB	372.47	Purple	41.27 (41.91)	3.40 (3.79)	7.09 (7.52)	15.32 (15.76)	10.09 (9.52)	13.73	0	C ₁₃ H ₁₄ N ₂ O ₃ S NiCl
CuAB	337.33	Light brown	40.05 (41.38)	3.58 (3.74)	7.97 (7.42)	16.12 (16.84)	9.21 (9.40)	14.95	1.45	C ₁₃ H ₁₄ N ₂ O ₃ S CuCl
ZnAB	379.17	Orange	40.28 (41.18)	2.93 (3.72)	7.09 (7.39)	18.09 (17.25)	9.89 (9.35)	24.8	0	C ₁₃ H ₁₄ N ₂ O ₃ S ZnCl

Table 2: Corrosion inhibition of aluminium foil by AB

S.No	Conc (m mol)	Weight loss (g)	Inhibition Efficiency (%)	Surface Coverage ()	log C	log (/1-)
1	Blank	0.00045	-	-	-	-
2	0.2	0.00031	31.1%	0.311	-0.6989	-0.3454
3	0.4	0.00029	35.5%	0.355	-0.3979	-0.2593
4	0.6	0.00025	44.4%	0.444	-0.2218	-0.0976
5	0.8	0.00019	57.7%	0.577	-0.0969	0.1348
6	1	0.00014	68.8%	0.688	0	0.3434

4. Conclusion

A new class of Schiff base ligand (AB) has been synthesized from isatin and methionine by condensation. Its complexes with Co(II), Ni(II), Cu(II) and Zn(II) have also been synthesized and characterized by various spectro analytical data. The Schiff base coordinates to M(II) ion through the imino nitrogen atom, and the carboxylato and amido oxygen atoms. The fourth position of the possible square planar arrangement is occupied by chloride ion in CoAB, NiAB & CuAB and in ZnAB chloride ion may occupy the fourth position of the tetrahedral arrangement. This makes the complex neutral, which is confirmed by the non-electrolytic nature of the complex. Square planar

geometry was assigned to the complexes CoAB, NiAB and CuAB and tetrahedral geometry was assigned to ZnAB by electronic spectral evidences which were also supported by EPR spectra. The XRD study clearly reveals that the Schiff base ligand is amorphous in nature and the CuAB complex is nanocrystalline. The TG/DTG analysis indicates that both the ligand and the metal complex have good thermal stability. The corrosion inhibition studies clearly reveal that the ligand AB possess greater activity. The antibacterial and antifungal studies reveal that the ligand and the metal complexes show greater activity when compared to the control. The DNA electronic absorption studies of CoAB,

NiAB & ZnAB shows hypochromism with slight red shift in the presence of DNA characteristic of intercalation between the aromatic chromophore ligand of metal complex and the base pairs of DNA.

5. Acknowledgement

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