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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2011, Vol. 27, No. (3):
Pg. 1185-1191

Synthesis, Characterization, Spectral & Antimicrobial Studies of Fe(III), Co(II), Zn(II), Cd(II), Y(III), and In(III) Complexes of Schiff Base Derived from L-Tryptophan

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(Received: June 20, 2011; Accepted: August 30, 2011)

ABSTRACT

In the present study 2-Amino-3-(1H-indol-3-yl)-propionic acid hydrazide (AIPAH) (1) has been prepared by reacting earlier reported compound 2-Amino-3-(1H-indol-3-yl)-propionic acid ethyl ester (AIPAEE) with hydrazine hydrate. Schiff base 3-(1H-Indol-3-yl)-2 [(4-methoxy-bezylidene)-amino]-propionic acid(4-methoxy-benzylidene)-hydrazide(IMBAPAMBH) (2) has been synthesized by reacting (1) with 4-methoxy benzaldehyde and its metal complexes with Fe(III), Co(II), Zn(II), Cd(II), Y(III), and In(III) have been prepared. The ligand and metal complexes were characterized on the basis of elemental analysis, IR, NMR spectral data, molar conductance, magnetic susceptibility measurement, thermal analysis (TGA/DTA). Fe(III), Co(II), Y(III), In (III) complexes possesses octahedral and Zn(II), Cd(II) complexes possesses tetrahedral geometry. In vitro antibacterial and antifungal activities of all compounds were tested.

Key words: Synthesis, Schiff base, Fe(III), Co(II), Zn(II), Cd(II), Y(III), and In (III) complexes, Antibacterial and antifungal activities.

INTRODUCTION

Amino acids are the building units of all proteins and enzymes[1] and associated with metal ions in biological system[2]. These acids are being converted to acid hydrazide having two amino groups, these diamine are able to form Schiff bases with condensation of aromatic aldehydes. Metal complexes prepared from Schiff bases of derivative of amino acids posses biological activities[3]. Coordination behavior of this ligand with several metal ions is found in biological systems. Preparation of heterocyclic ligands containing Carbonyl and azomethine groups with potential binding ability has drawn a lot of attention because of their antibacterial as well as fungicidal [4-6], herbicidal[7], and anti-inflammatory[8] properties.

In the present work, synthesis, characterization of asymmetric Schiff base (IMBAPAMBH)(2)derived from derivative of tryptophan and its metal complexes with some paramagnetic, diamagnetic and rare earth metal ions, their elemental analysis, IR, ^{1}HNMR spectral

data, molar conductance, magnetic susceptibility measurement, thermal analysis (TGA / DTA) is described. The Schiff base (IMBAPAMBH) (2) is prepared by refluxing 4-methoxy-benzaldehyde with Synthesis of 2-Amino-3-(1H-indol-3-yl)-proponic acid hydrazide (AIPAH) (1) in 2:1 molar ratio in ethanol. Metal complexes of Fe(III), Co(II), Zn(II), Cd(II), Y(III), and In(III) are prepared by condensation with (IMBAPAMBH)(2). The Schiff base and their metal complexes were screened for their antibactrial activity against staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis, Escherichina Coli bacteria and Aspergillus niger, Aspergillus flavus fungi. The Schiff base ligand, Zn(II), Cd(II), In(III) complexes were found to be more active and Fe(III), Co(II), Y(III) complexes were found to be moderately active against these bacteria. Schiff base ligand, Co(II), Zn(II), Cd(II), Y(III) complexes were found to be more antifungal whereas Fe(III),In(III) complexes were not shows antifungal activity against these fungi**.**

EXPERIMENTAL

Material and method

All chemicals and solvents used in present investigation were of E-Merck, Sigma - Aldrich Company and solutions were prepared in doubled distilled water, all the metal salts were used as chlorides. The melting points were recorded by capillary tube method using Toshniwal melting point apparatus and are uncorrected. The molar conductance of ligand and metal complexes was measured by digital conductometer model no. Eq-660A in DMF, 10^{-3}mol at 25°C. The magnetic susceptibility of these complexes were measured by Gouy's method at room temperature using Hg [Co (NCS)$_4$] as Celibrant. The elemental analysis were carried out on a vario EL III Elementar Carlo-Erba 1108. IR spectra were recorded using KBr disks on Perkin Elmer Spectrum RX-1 FT-IR spectrometer, in the range of 4000-400 cm^{-1} at Institute of Chemical Technology, Matunga, Mumbai. Thermal analysis (TGA /DTA) were carried out in nitrogen atmosphere with a heating rate of 10^0C/ min., using Rijaku Thermo plus TG-8120 thermoanalyser. ^{1}HNMR spectra were recorded in DMSO-d_6 using TMS as internal standard on a Jeol Japan 300 MHz FT NMR at Institute Of Science Mumbai. Purity of compounds was checked by TLC on silica gel plates (60F254) and visualized under UV light. Antibacterial and antifungal activities were screened at St. Xavier's College Mumbai.

Synthesis of ligand (Schiff base)

2-Amino-3-(1H-indol-3-yl)-propionic acid ethyl ester was prepared by earlier reported method[9] and purity of compound was checked by TLC.

Synthesis of 2-Amino-3-(1H-indol-3-yl)-proponic acid hydrazide (AIPAH) (1)

Dissolved 2-Amino-3-(1H-indol-3-yl)-propionic acid ethyl ester (0.1 mol) was refluxed on water bath with excess of hydrazine hydrate (0.2 mol, 99%) in 25ml of ethanol for 8h. The resulting product was poured in ice-cold water and kept overnight, brown solid was crystallized out[10]. The product washed with 25 ml ice-cold alcohol and dried in air. The yield of almost pure tryptophan hydrazide was 74%, m.p. 246-248°C

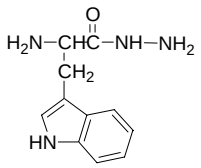
Synthesis of 3-(1H-Indol-3-yl)-2 [(4-methoxy-bezylidene)-amino]-propionic acid(4-methoxy - benzylidene) - hydrazide (IMBAPAMBH) (2)-

3-(1H-Indol-3-yl)-2 [4- ethoxy - bezylidene)- amino]- propionic acid (4- methoxy - benzylidene)-hydrazide(IMBAPAMBH) (2)was prepared by mixing an ethanoic solution (50 ml) of (1) (0.01 mol) with 4-methoxy benzaldehyde (0.02 mol) and catalytic amount of conc. H_2SO_4 in the same volume of ethanol, then the mixture was refluxed with stirring for 5-6 h. The obtained precipitate was collected by filtration through Buchner funnel, washed and recrystallized from absolute ethanol then dried at room temperature in desicator over anhydrous calcium chloride, yield was 82%, m.p. 292°C.

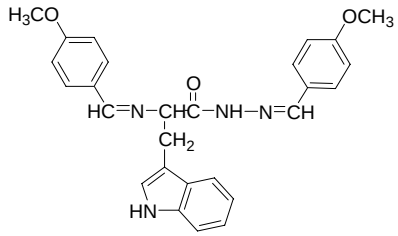
Preparation of complexes (3-a to 3-e) with Schiff base

Purified Schiff base (0.003 mol) was dissolved in ethanol (50 ml) while metal ion (0.003 mol) was dissolved in methanol (5 ml) were mixed and reflux with stirring for 5h one drop of piperidine was added as a catalyst. The solution was cooled and pH was measured by combine electrode & it was recorded as 5.3, few drops of ammonium hydroxide was added until pH 8.0 to 9.5, during which coloured complexes precipitate out, were

filtered and washed with water (15 ml x 3) & ethanol (25 ml x 3) to remove any unreactive ligand & metal ions, after that complexes dried in vacuum over anhydrous calcium chloride in a desicator. These complexes were used for further study.



(AIPAH) (1)



(IMBAPAMBH) (2)

RESULTS AND DISCUSSION

Physical properties

These complexes are air stable, colored, solids which decompose above >295°C. They are insoluble in common organic solvents but soluble in ethanol, DMSO, DMF. The molar conductance of ligand and complexes dissolved in DMF fall into the range 8-23 S cm^2mol^{-1} of 10^{-3} mol dm^{-3} solution indicating their non electrolytic nature[11] in DMF. The analytical data and magnetic moments of complexes are presented in Table -1. The magnetic moment of Fe (III) complex has value 5.80 B.M. indicating good agreement with that reported for high spin complex with d^5 system (t_2g^3 eg^2) and octahedral geometry[12]. The magnetic moment value for the Co (II) complex is 4.92B.M.expected for octahedral geometry[13] with high spin paramagnetic d^7 system ($t_2g^5eg^2$) and 3 unpaired electrons. Zn(II) and Cd(II) complexes have not ligand field stabilization effect owing to complete d-sub shell, therefore Zn(II) and Cd(II) complexes should be diamagnetic spin free tetrahedral complexes[14] with d^{10} system. Y(III) and In(III) are also diamagnetic with d^{10} system and octahedral stereochemistry[15-16]. The elemental analysis of carbon, hydrogen, nitrogen and gravimetric percentage estimation of metals indicated that Fe (III) Zn(II) Cd (II) and Y(III) complexes are 1:1 metal-ligand stoichiometry where as In(III) has 1:2 metal-ligand stoichiometry.

Infrared spectra

IR spectral data IR(KBr) (cm-1), Compound (AIPAH) (1)

3406.93 ν(>NH indole), 3360 ν(-NH2 of -NH-NH2) 3042.19 ν(-N-H strech), 1669.30 ν(-CONH-), 1606.90 ν(Benzene ring stretch),1570 ν (Aromatic ring conjugation), 1565 ν(-C-H Aromatic), 1480 ν(N-N Stretch), 1229.11n(C-N Stretch), 743.66 ν (Ar-ring).

Compound (IMBAPAMBH) (2)

3429.11 ν (>NH indole), 3240 ν (N-H Amide Stretch, Symmetric, asymmetric stretching vibration, 3005.49 ν(Ar -H), 2850 ν (-OCH_3), 1662.98 ν (-CO-NH Sec. amine),1604.95 ν (-C=N-) azomethine, 1590 n(C_6H_5 -conj.) ,3240 ν(-N-H) Amide Stretch [Sym / asymm. Str. vib], 1363.53 ν (-CH_2) , 1249.95 ν (C-N) Str., 838.15 ν (P-Sub C_6H_5).

The IR spectrum of the ligand (IMBAPAMBH) shows a band of medium intensity at 1604.95 cm^{-1} which can be assigned to ν(-CH=N-)[17-18], In the spectra of complexes this band shows a negative shift 20-64cm^{-1} and appeared in the region 1540-1585 cm^{-1} indicating the coordination of nitrogen atom of azomethine group[19] to metal ion. The coordination through azomethine nitrogen is further confirmed by the appearance of a band at 460-482 cm^{-1} in complex may be assignable[20] to ν(M-N). Other significant IR band of ligand appears at 1662.98 cm^{-1}, this band is sharp and strong may be assigned to ν(>C=O) [21-22].The position of this band in all complexes shows a negative shift 15-45 cm^{-1} and appeared at the region 1618-1648 cm^{-1}, this shift is due to coordination of oxygen atom of a carbonyl group to the metal ion. The coordination through oxygen atom is further confirmed by the appearance of the band at 525-609 cm^{-1} in the complex may be assign ν(M-O) [23]. The broad band

Table 1: Analytical Data, Molar conductance, magnetic moment of MBAPPAMBH and it's metal complexes with Fe(III), Co(II), Zn(II), Cd(II), Y(III), and In(III) ions

S. No.	Compound	Mol.Wt. Calc. (found)	Colour	% Yield	Decom position temp °C	Molar cond.S cm^2mol^{-1}	Magnetic% moment per μ_{eff} (B.M.)	Elemental Analysis			
								Metal	C	H	N
1	$C_{11}H_{14}N_4O_1$ Comp.(1)	218.26 (217.67)	Light Brown	74	246-248	08.8	_	_	60.53 (59.87)	6.47 (5.92)	25.67 (25.02)
2	$C_{27}H_{26}N_4O_3$ Comp.(2)	454.50 (453.86)	White Gray	82	292	09.2	_	_	71.28 (70.45)	5.72 (5.63)	12.32 (11.96)
3	Fe $(C_{27}H_{26}N_4O_3)$ $3H_2O$	564.50 (563.76)	Dark Brown	86	› 308	22.9	5.80	9.92 (9.77)	57.44 (57.18)	4.60 (4.62)	9.92 (9.77)
4	Co $(C_{27}H_{26}N_4O_3)$ $3H_2O$	567.43 (566.88)	Deep Green	91	› 296	20.1	4.92	10.38 (10.20)	57.14 (56.82)	4.58 (4.55)	9.87 (9.72)
5	Zn $(C_{27}H_{26}N_4O_3)$ H_2O	537.89 (537.75)	Cream	92	› 311	16.3	_	12.15 (11.94)	60.23 (59.90)	4.83 (4.78)	10.41 (10.19)
6	Cd $(C_{27}H_{26}N_4O_3)$ H_2O	584.91 (584.15)	Light Yellow	83	› 315	21.9	_	19.21 (18.94)	55.39 (55.10)	4.45 (4.43)	10.20 (10.08)
7	Y $(C_{27}H_{26}N_4O_3)$ $3H_2O$	596.90 (596.05)	Light Brown	77	› 307	19.5	_	14.89 (14.68)	54.28 (53.96)	4.35 (4.38)	9.38 (9.19)
8	In $(C_{27}H_{26}N_4O_3)_2$	1023.82 (1022.93)	Pale Yellow	89	› 321	15.7	_	11.21 (11.98)	63.29 (63.76)	5.07 (5.12)	10.93 (11.58)

Compound (1) - 2-Amino-3-(1H-indol-3-yl)-proponic acid hydrazide. (AIPAH)

Compound (2) - 3-(1H-indol-3-yl)-2[(4-methoxy-bezylidene)-amino]-propionic acid(4-methoxy-benzylidene)-hydrazide.(IMBAPAMBH)

Table 2: Antimicrobial activity of ligand-(IMBAPAMBH) and its complexes

Compound	Antibacterial activity								Antifungal activity			
	Gram Positive bacteria				Gram negative bacteria				Aspergillus		Candida	
	Staphylococcus aureus		*Pseudomonas aeruginosa*		*Bacillus substilis*		*Escherichia Coli*		*niger*		*albicans*	
	2.0 mg	4.0 mg	2.0 mg	4.0 mg	2.0 mg	4.0 mg	2.0 mg	4.0 mg	2.0 mg	4.0 mg	2.0 mg	4.0 mg
[IMBAPAMBH]	- -	- -	-	- -	- -	- -	- -	- -	-	- -	-	- -
[Fe(IMBAPAMBH)$(H_2O)_3$]	+	+	-	-	-	-	+	+	+	+	+	+
[Co (IMBAPAMBH)$(H_2O)_3$]	+	+	- -	-	+	+	+	+	-	- -	- -	- -
[Zn IMBAPAMBH) H_2O]	-	-	- -	- -	- -	- -	-	-	-	- -	-	- -
[Cd (IMBAPAMBH) H_2O]	-	- -	-	- -	-	- -	-	- -	- -	-	- -	-
[Y (IMBAPAMBH)$(H_2O)_3$]	+	+	-	- -	-	- -	+	+	-	-	-	-
[In (IMBAPAMBH) $_2$]	-	- -	-	- -	-	- -	-	- -	+	+	+	+

- - Very Active - Moderately active + Not active

in 3000-3300 cm^{-1} region in Fe(III),Co(II), Zn(II), Cd(II) and Y(III) complexes attributed to the presence of coordinated water molecules[24], this have also been confirmed by TGA/DTA analysis . The IR spectra of these complexes exhibited a new band in range of 3500-3550 which may be attributed to ν(OH) vibrations of coordinated water. The appearance of band around 860 (cm^{-1}) due to wagging and rocking modes of vibrations of coordinated water molecules[25].

NMR spectral data

^{1}HNMR(DMSO,300MHz, δppm), Compound (AIPAH) (1)

2.03(d,4H of $–NH_2$), 2.98(d, 2H of $–CH_2$), 3.85(t, 1H of –CH), 6.86 (s,1H of aryl), 7.23(d, 4H of aryl), 8.00 (s, 1H of –NH), 10.11(s,1H of indole).

Compound (IMBAPAMBH) (2)

2.95(d,2H of$–CH_2$), 3.72(s, 6H of $–OCH_3$), 3.95(t, 1H of –CH), 6.86-8.081 (m,13 Ar-H), 8.05 (s, 1N of –NH), 8.46(s,2H of –CH).

Biological evaluation

Antibacterial and antifungal activities of the ligand and its complexes were carried out against staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis, Escherichia Coli bacteria and Aspergillus niger, Candida albicans fungi by ditch plate method. 10-15 ml nutrient agar and sabouraud's dextrose agar is used as medium for antibacterial and antifungal activities respectively. The antimicrobial activity was estimated on the basis of size of inhibition zone and the results are shown in table-2. Antibacterial studies shows that the ligand (IMBAPAMBH), Zn(II), Cd(II), In(III) complexes were found to be more active and Fe(III), Co(II), Y(III) complexes were found to be moderately active against these bacteria. Schiff base ligand , Co(II), Zn(II), Cd(II), Y(III) complexes were found to be more antifungal whereas Fe(III),In(III) complexes did not exhibit any remarkable antifungal activity against these fungi**.**

CONCLUSION

On the basis of above studies it may be concluded that Schiff base (IMBAPAMBH)(2) has asymmetric. Fe(III), Co(II), Y(III) complexes has octahedral geometry with 1:1 metal-ligand stoichiometry,Zn(II) and Cd (II) complexes has tetrahedral stereochemistry with 1:1 metal-ligand stoichiometry and anhydrated In (III) complex has octahedral geometry with 1:1 metal-ligand stoichiometry. Antibacterial studies shows that the ligand (IMBAPAMBH), Zn(II), Cd(II), In(III) complexes were found to be more active and Fe(III), Co(II), Y(III) complexes were found to be moderately active against these bacteria. Schiff base ligand (IMBAPAMBH),Co(II), Zn(II), Cd(II), Y(III) complexes were found to be more antifungal whereas Fe(III),In(III) complexes did not exhibit any remarkable antifungal activity against these fungi**.**

ACKNOWLEDGEMENTS

The authors are grateful to the principal, St. Xavier's College, Mumbai for laboratory facilities. The authors are also grateful to Mumbai University for financial support by sanctioning M.R.P. The authors are also thankful to Mr. G.G.Joshi Liberian of Bhausaheb Nene College Pen,Raigad for providing internet and library facility and Prof.Y.S.Malge, Mr.Anirudh Patil, Shailesh Narkar , Mr. Milind More for determinations of TGA/DTA, I.R., N.M.R. spectra.

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