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SYNTHESIS AND CHARACTERISATION OF LANTHANIDE (III) CHLORIDE COMPLEXES WITH BIDENTATE DONOR 2-AMINO-4-METHYL BENZOTHIAZOLE

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ABSTRACT

The Nd(III), Sm(III) and Tb(III) complexes of 2-amino-4-methyl benzothiazole have been synthesized in alcohol and refluxed in the reaction medium (1:3, M: L ratio).The yield percentage of formed complex is ranging from 60-70%. The complexes are colored solids. The complexes were synthesized and characterized by elemental analysis, IR, electronic spectra, molar conductance, TGA and powder XRD. An IR spectrum indicates that the ligand behaves as bidentate ligand. Molar conductance studies indicates the electrolytic behaviour of these complexes. Thermal decomposition profiles are consistent with the proposed formulations. The powder XRD studies show that all the complexes are amorphous in nature. The antimicrobial activities of the ligand and their metal complexes were screened by agar diffusion method and found that the metal complexes have higher antimicrobial activity than the free ligand.

KEYWORDS: 2-amino 4-methyl benzothiazole, inner transition metals, antimicrobial activity.

INTRODUCTION

Benzothiazoles are bicyclic ring system. Benzothiazole derivatives have been studied and found to have various chemical reactivity and biological activity.[1] Benzothiazole ring made from thiazole ring fused with benzene ring. Thiazole ring is a five-member ring consists of one nitrogen and one sulfur atom in the ring.

Benzothiazole ring found to be possessing pharmacological activities such as anti-viral[2], anti-bacterial[3], anti- microbial[4] and fungicidal activities.[5] They are also useful as anti-allergic[6], anti-diabetic[7], antitumor[8], anti- inflammatory[9], anthelmintic, and anti-HIV agents. Benzothiazoles show antitumor activity, the phenyl-substituted Benzothiazoles.[10-12] Substituted 6-nitro-and 6-aminobenzothiazoles show antimicrobial activity.[13]

It's amino methyl phenyl and carbonitrile derivatives shows selective growth inhibitory properties against human cancer cell lines[14] and proliferation of cells[15] respectively. Chlorinated and fluorinated derivatives of this moiety exhibit good in vitro as well as in vivo antitumor activity. A series of potent and selective anti-tumor agents were developed. Substituted 2-(4-aminophenyl) benzothiazoles examined, in vitro, shows antitumor activity in ovarian, breast, lung, renal and colon carnicoma human cell line[16] 2-(4-Aminophenyl) benzothiazoles[17,16] consists of a novel mechanistic class of antitumor agents.

These activities are probably due to presence of the –N=C-S group.[19] Substituted benzothiazole have been reported to show diverse application as metal complexing agents[20-23] and photostabliser. The wide range of application of the ligand and its complexes are used our interest for assaying their antimicrobial activity against gram positive and gram negative micro-organism.

Hence, in the present study, 2-amino-4-methylbenzothiazole has been synthesized. Their characterization was done by spectroscopic methods. Further Anticorrosive, antibacterial and antifungal activities of these derivatives have been studied in DMSO. Thus, the aim of this research is to synthesize and characterize lanthanide (III) complexes of 2-amino-4-methyl benzothiazole as we attempted to throw light on the coordination position for 2-amino-4-methyl benzothiazole with the La(III) ion.

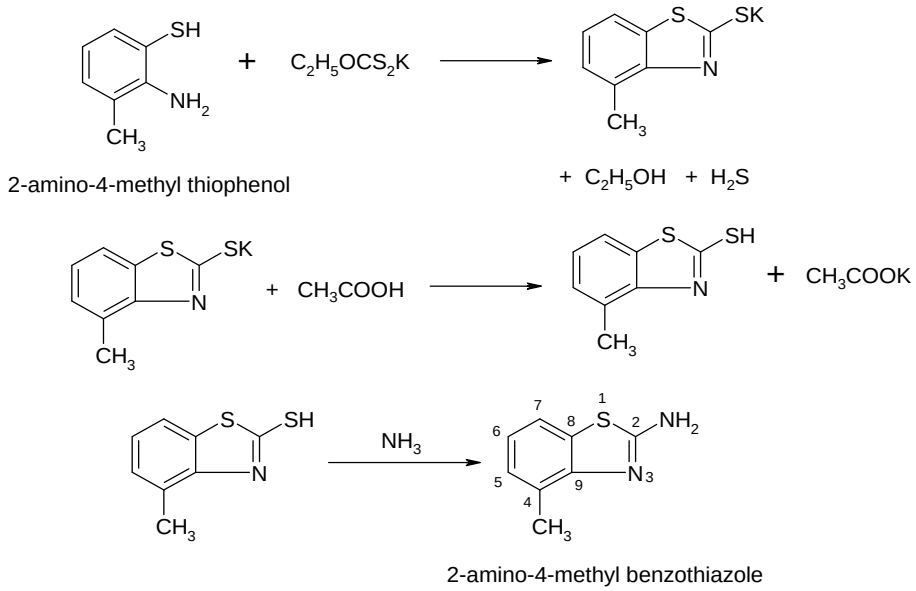
EXPERIMENTAL

a) Synthesis of 2-amino-4-methyl Benzothiazole

Synthesis of 2-amino-4 -methyl benzothiazole was carried out by the method of Rojer Adams. The method of thiocynation and bromination was adopted. (0.1M) 2-xylidine (2-methylaniline) and sodium thiocyanate (0.2M) in 100 ml glacial acetic acid are mixed together maintaining 0^0C temperature.

0.2M bromine in acetic acid (25 ml) was added to the above solution drop wise and the mixture was stirred

continuously by a mechanical stirrer till the complete addition of bromine. The temperature was maintained below 5^0C. The solid thus obtained after complete addition of bromine was filtered so as to remove excess of bromine and then dissolved in hot water.



2-amino-4-methyl thiophenol

2-amino-4-methyl benzothiazole

Again it was filtered and filtrate then treated with alkali like NaOH or KOH for the precipitation of free base. The precipitate thus obtained was filtered, washed and dried. The product was recrystallized from ethanol.

Synthesis of AMBT Lanthanide complexes

To a hot methanolic solution (30ml) of the 2-amino 4-methyl benzothiazole (0.02 mol), solution (10 ml) of methanolic solution metal (III) chlorides hydrated (0.01 mol) was added with constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 45 min. The precipitated solid metal complex cooled at room temperature and was filtered off and washed with methanol, petroleum ether and dried over calcium chloride in vacuum desiccators, light pink coloured fine crystals of complexes were obtained. Purity of sample was checked by TLC and melting point (yield= 60 %).

RESULT AND DISCUSSION

Physical and analytical parameters

Reagent grade chemicals were used without further purification. All the melting points were taken by open capillary method. All the complexes having melting point > 270^0C. The purity of the synthesized compounds was checked by Thin Layer Chromatography. The coloured Lanthanide (III) chloride complexes were found to be stable at room temperature. In complexes, metal and ligands are in 1:3 molar ratio possessing general formula [ML_3]. It was confirmed by elemental analysis. The molar conductivity in DMSO is ranges from 89-102 indicating electrolytic nature of complexes. Yeild of complexes is in range 60-65%.

Table No. 1: Physical and analytical Data

Compound	Empirical Formula	Formula Wt	Yield (%)	Color	M.P. ^{0}C	M : L ratio
AMBT	$C_8H_8N_2S$	164.23	70	White	>190^0C	-
[Nd(AMBT)$_3$2H$_2$O]3Cl	$C_{24}H_{28}N_6O_2S_3Cl_3Nd$	779.28	65	lavender	>270^0C	1 : 3
[Sm(AMBT)$_3$2H$_2$O]3Cl	$C_{24}H_{28}N_6O_2S_3Cl_3Sm$	785.4	60	cream	>270^0C	1 : 3
[Tb(AMBT)$_3$2H$_2$O]3Cl	$C_{24}H_{28}N_6O_2S_3Cl_3Tb$	793.97	60	Light orange	>270^0C	1 : 3

Table No. 2: Elemental Analysis Data

Compound	M.F.	Elemental Analysis % found (calculated)						
		C	H	N	O	S	Cl	M
AMBT	$C_8H_8N_2S$	55.89 (58.51)	5.23 (4.91)	17.83 (17.06)	- -	20.11 (19.52)	- -	- -
Nd–AMBT	$C_{24}H_{30}N_6O_2S_3Cl_3Nd$	37.46 (36.99)	4.19 (3.62)	11.42 (10.78)	4.98 (4.11)	12.84 (12.06)	14.01 (13.65)	18.95 (18.51)
Sm–AMBT	$C_{24}H_{28}N_6O_2S_3Cl_3Sm$	37.28 (36.70)	4.12 (3.59)	11.13 (10.70)	4.80 (4.07)	12.89 (12.25)	13.96 (13.54)	20.12 (19.14)
Tb–AMBT	$C_{24}H_{28}N_6O_2S_3Cl_3Tb$	36.86 (36.30)	3.90 (3.55)	11.22 (10.58)	4.79 (4.03)	12.81 (12.12)	13.88 (13.40)	20.62 (20.02)

INFRARED SPECTROSCOPY

The infrared spectrum of AMBT exhibited a strong band at 1585 cm^{-1} which is attributed to C=N. This band value lowers in complexes indicating that the (C=N) group is involved in complex formation.[24-26] The band at 1070 cm^{-1} which is attributed C-S stretching frequencies, there is no indicable change in value of frequencies, so sulphur does not take part in complex formation. AMBT exhibited a strong band at 3278, 3053 cm^{-1} which are attributed to-NH_2. This band in AMBT shifted to lower wave number 2924-2926 cm^{-1} in the metal complexes, indicating that the $–NH_2$ group is involved in complex formation. The coordination through the nitrogen atom in (C=N) groups are further supported by the occurrences of new band around at 441-460 cm^{-1} in the spectra of the complexes which, may be assigned to ν(M-N).[27-29] The presence of bands at 3344-3385 cm^{-1} indicates presence of H_2O molecule in complexes.

Table No. 3: Infrared Spectral data

Compound	νC=N	ν-NH_2	νC -S	νM – N	νM – O	νH_2O
AMBT	1585	3278, 3053	1070	-	-	-
[Nd(AMBT)$_3$2H_2O].3Cl	1496	2924	1072	441	-	3344
[Sm(AMBT)$_3$2H_2O].3Cl	1500	2926	1070	453	-	3385
[Tb(AMBT)$_3$2H_2O].3Cl	1531	2926	1072	460	-	3383

ELECTRONIC SPECTROSCOPY

The electronic spectra of ligand and their corresponding lanthanide (III) complexes are recorded in DMSO in the region 200-800 nm. The ligand show band at 344 nm (π - π*) in the ranges 280nm and in the corresponding lanthanide complexes, bands around 270-274 nm are observed. Shifts in absorption bands and appearance of new band and increase in molar absorptivity (table-4) are indicative of involvement of metal orbital in bonding with ligand.

Table No. 4: Electronic Spectral data

Complex	Absor- bance	ν / cm^{-1}	Assignment	Molar Conduc-tance	Magnetic Moment	Geometry
AMBT	344	29069	n - π*	–	–	–
Nd-AMBT	271	36900	π - π*	89	Paramagnetic (3.63)	Octahedral
Sm-AMBT	270	37037	π - π*	90	Paramagnetic (1.45)	Octahedral
Tb-AMBT	274	36496	π - π*	101	Paramagnetic (9.23)	Octahedral

^{1}H NMR Spectroscopy

Spectra of ligand and all the complexes were recorded in DMSO-d_6 solution at 400 MHz and chemical shifts are in units of ppm relative to TMS as internal standard on the delta (δ) scale. The general ^{1}H NMR spectrum of the ligand in DMSO shows the following signals.

2 ppm a singletof 2H(-NH2) and singiet band for 3H (-CH_3) group, 6.8-7.o7 ppm a multiplet band for pyridine hydrogen. 2 ppm a singlet band for NH_2 hydrogen changes to 2-4 ppm indicating coordination through NH2 nitrogen. Two new long and sharp bands 2-4 ppm shows presence of oxygen of water molecules.

Antibacterial activity

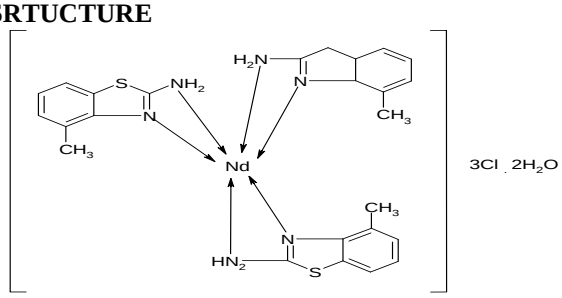
All the synthesized compounds showed significant antibacterial activity All the complexes of lanthanide metal ions with ligand shows good antibacterial activity against E.coli and Aspergillus niger.

Sr. No.	Compound	E. coli (nm)	S. Aureus (nm)
1	AMBT - Ligand	13	17
2	Nd – AMBT complex	09	11
3	Sm – AMBT complex	10	-
4	Tb – AMBT complex	09	-
5	Control	27	14

CONCLUSION

Based on the results of elemental analysis, thermal study and spectroscopic studies following structures are proposed to the complexes under study.

SRTUCTURE



Structure of Nd-AMBT complex

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