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Complexes of Some Rare Earth Metals With 5-Acetamido-1,3,4-Thiadiazole-2-Sulphonamide And Their Biological Activity

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Abstract

Complexes of La(III),Ce(III) were synthesized by using bidentate ligand AMBT, having the general formula ML_3. The complexes were characterized by IR, UV, elemental analysis, TGA, magnetic moment, conductivity etc. The conductivity data suggests their electrolytic nature. Spectral studies and magnetic susceptibility measurements revealed an octahedral geometry for all the complexes. The ligand and it's complexes were screened for their antimicrobial activity against E. Coli, S. Aureus, A. Niger, Alternaria.

Keywords: AMBT, Conductivity, antimicrobial activity

1. 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-membered ring consists of one nitrogen and one sulfur atom in the ring.

Benzothiazole ring found to be possessing pharmacological activities such as antiviral[2], antibacterial[3], antimicrobial[4] and antifungicidal activities[5]. They are also useful as anti-allergic[6], anti-diabetic[7], antitumor[8], anti- inflammatory[9], anthelmintic[10] and anti-HIV agents. Benzothiazoles show antitumor activity, the phenyl-substituted Benzothiazoles[11-13]. Substituted 6-nitroand 6-aminobenzothiazoles show antimicrobial activity[14].

Amino methyl phenyl and carbonitrile derivatives shows selective growth inhibitory properties against human cancer cell lines[15] and proliferation of cells[16] respectively.Substituted 2-(4-aminophenyl) benzothiazoles examined *in vitro*, shows antitumor activity in ovarian, breast, lung, renal and colon carnicoma human cell line[17,18] 2-(4-Aminophenyl) benzothiazoles[19,20] consists of a novel mechanistic class of antitumor agents.

Pyrimido benzothiazole and benzothiazolo quinoline derivatives[21], imidazobenzothiazoles and polymerized benzothiazoles[22] have posses anti-tumor activity. Some Fluorinated analogues of 2-(4-aminophenyl) benzothiazoles were synthesized which block C-oxidation[23]. The 2-cyano derivatives of benzothiazole exhibit interesting *in vitro* antitumor activity.

Microbes are the causative agents for various types of diseases like pneumonia, ameobiasis, typhoid, malaria, common cough,

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cold and various infections and cause some severe diseases like tuberculosis,influenza, syphilis, and AIDS etc. 2-(substituted phenylsulfonamido)-6-substituted Benzothiazoles [24] were prepared and screened them for their anti-bacterial activity against *Bacillus subtilis*, *Salmonella typhi* and *S. dysentery*. Several benzothiazolotriazole derivatives were prepared [25] and found to possess good anti-bacterial activity against *S. aureus, E. coli* and *C.ablicans*.Some 6-fluoro-7-(substituted)-(2- *N* -p-anilinosulfonamido) benzothiazoles were synthesized and studied for their antibacterial and anti-fungal activities and all compounds showed moderate activity against *S. aureus, S. albus* and *C.ablicans* [26]. Various benzothiazolyl carboxamido pyrazoline derivatives were prepared and studied their anti-microbial activity. [27,28] . A 8-fluoro-9-substituted benzothiazolo (5, 1-b)-1, 3, 4-triazoles[29] compounds were prepared and were studied for their anthelmintic activity against earthworm, *Perituma7posthuma.* Some substituted imidazobenzothiazoles were examined *in vivo* anthelmintic activity against *H. nana* infection and were found to show good to moderate activity [30].

In the present communication we report the synthesis,spectroscopic and biocidal studies of La(III),Ce(III) complexes with AMBT ligand

2. Experimental

Materials and Method

All the chemicals used were of analytical grade. Pure ethanol and distilled water were used for preparation of the solutions. 2-amino 4-methyl benzothiazole was obtained from sigma chemical company (U.S.A) Metal chlorides were obtained from Alfa Acer company.

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 dropwise 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.

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.

Preparation of complex

The ethanolic solutions of the respective metal chloride (0.01 mol) and the Schiff base or heterocyclic ligand (0.01 mol) are refluxed for three to four hours. The pH is raised to 7.5 by adding ammonia (dissolved in alcohol). During the refluxation, the metal chelates are separated out and are filtered, washed successively with ethanol and finally dried in vaccum.

Analytical procedure

2-amino 4-methyl benzothiazole and rare earth metal chlorides were used as received from S.D. fine chemicals. The solvents were distilled before use an distilled water was used for the preparation and analyses. The molar conductivity at room temperature was determined in conductivity water using a dip type cell with a smooth platinum electrode. The magnetic susceptibility measurements were made by gouys method at room temperature using powedred samples of complexes.

The electronic absorption spectra of the complexes in DMSO were recorded on a Shimadzu double beam UV-visible spectrophotometer model UV 150-02. The infrared spectra of the solid samples in the 500-4000 cm^{-1} were recorded on a Shimdzu FTIR spectrophotometer and Brueker FTIR

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spectrophotometer using KBr pellets. The thermal analyses (TGA) for the complexes were recorded on a perking Elmer STA 6000 under nitrogen atmosphere at room temp to 1000^0C 5mg of the samples with the heating rate of 10^0C per min and the platinum cups as sample holders.

Table No. 1 Physical and analytical Data

3. 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%.

Compound	Empirical Formula	Formula Wt	Yield (%)	Color	M.P. ^{0}C	M : L ratio
AMBT	$C_8H_8N_2S$	164.23	70	White	190>^{0}C	-
$[La(AMBT)_3]$ $2H_2O3Cl$	$C_{24}H_{28}N_6O_2S_3Cl_3La$	773.94	65	Light pink	>270^{0}C	1 : 3
$[Ce(AMBT)_3]$ $2H_2O3Cl$	$C_{24}H_{28}N_6O_2S_3Cl_3Ce$	775.15	65	grey	>270^{0}C	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 (17.0)	- -	20.11 (19.5)	- -	- -
La – AMBT	$C_{24}H_{28}N_6O_2S_3Cl_3La$	37.79 (37.24)	4.09 (3.65)	11.12 (10.8)	4.71 (4.1)	12.84 (12.4)	14.23 (13.74)	18.43 (17.95)
Ce – AMBT	$C_{24}H_{30}N_6O_2S_3Cl_3Ce$	37.88 (37.19)	4.22 (3.64)	11.18 (10.8)	4.77 (4.1)	13.11 (12.4)	14.22 (13.74)	18.49 (17.95)

Infrared spectroscopy :

The infrared spectrum of 2-amino 4-methyl benzothiazole 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[59-61]. 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. 2-amino 4-methyl benzothiazole exhibited a strong band at 3278, 3053 cm^{-1} which are attributed to-NH_2. This band in 2-amino 4-methyl benzothiazole shifted to lower wave number 2924-2931 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 439-462 cm-1 in the spectra of the complexes which, may be assigned to ν (M-N)[62-65]. The presence of bands at 3344-3385 cm^{-1} indicates presence of H_2O molecule in complexes.

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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	-	-	-
[La(AMBT)$_3$] $2H_2O3Cl$	1496	2924	1072	457	-	3385
[Ce(AMBT)$_3$] $2H_2O3Cl$	1529	2931	1070	462	-	3385

Table No. 4 : Electronic Spectral data

Complex	Absorbance	ν / cm^{-1}	Assignment	Molar Conductance	Magnetic Moment	Geometry
AMBT	344	29069	n - π*	–	–	–
La-AMBT	256	39062	π - π*	95	Diamagnetic (–)	Octahedral
Ce-AMBT	280	35714	π - π*	99	Paramagnetic (2.33)	Octahedral

Electronic SPECTRal data :

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 280 nm and in the corresponding lanthanide complexes, bands around 255-344 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

.

Antimicrobial Activity

Above synthesized compound and the ligand have been screened against bacteria E.coli and staphalococcus aureus and fungi aspergillus Niger and alternaria. Nutrient agar as medium used for bacteria and potato dextrose Agar used for fungi. Incubation of plates with complex solution and ligand solution in well done for 48 hrs at 27^0C temperature.

The zone of inhibition based upon size around the well was measured. Inhibition zone percentage are recorded in Table 3. The percentage inhibition of growth by ligand is less than 2-amino 4-methyl benzothiazole metal complex. Thus complex shows greater activity against micro-organisms as compared to ligand 2-amino 4-methyl benzothiazole. This prove that the chelation increases the antimicrobial activity. Results are presented in Table9. Above synthesized compound and the ligand have been screened against bacteria E.coli and staphalococcus aureus and fungi aspergillus Niger and alternaria. Nutrient agar as medium used for bacteria and potato dextrose Agar used for fungi. Incubation of plates with complex solution and ligand solution in well done for 48 hrs at 27^0C temperature.

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Table No. 1 : Antibacterial activity of lanthanide complexes
Medium : Nutrient Agar **Method :** Agar well method
Dose of Compound : 1% **Cup Size :** 10 mm

Sr. No.	Compound	E. Coli	S. Aureus
1.	AMBT - Ligand	13	17
2.	La – AMBT complex	10	10
3.	Ce – AMBT complex	-	-

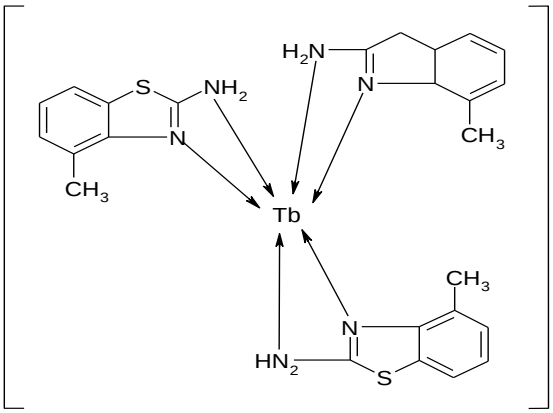
Table No. 2 : Antifungal activity of Lanthanide complexes
Medium : Potato dextrose Agar **Method :** Agar cup method
Dose of Compound : 1% **Cup Size :** 10 mm

Sr. No.	Compound	Aspergillus Niger	Alternaria
1.	AMBT - Ligand	-	-
2.	La – AMBT complex	-	-
3.	Ce – AMBT complex	-	13

The zone of inhibition based upon size around the well was measured. Inhibition zone percentage are recorded in Table 3. The percentage inhibition of growth by ligand is less than 2-amino 4-methyl benzothiazole metal complex. Thus complex shows greater activity against micro-organisms as compared to ligand 2-amino 4-methyl benzothiazole This prove that the chelation increases the antimicrobial activity. Results are presented in Table 9.

4. Conclusion

Hence on the basis of elemental analysis, IR spectra, UV, spectra, magnetic moment data, conductivity measurement and TGA data, following octahedral structure is proposed for La(III)-AMBT complex and Ce(III)-AZM complex as follows,



$3Cl \cdot 2H_2O$

5.

References

1. Bryson M., Fulton B., Benfield P. *Drugs.* **(1996);** 52: 549.
2. Akihama S., Okhude M., Mizno A., Meiji Yakka, Diagakn Kenkyu Kiyo. *Chem Abstr* **(1968);** 68: 10369v.
3. Russo F., Santagati M., Farmaco., *Ed Sci* **(1976);** 31: 41.
4. Ghoneim K.M., Basil S. El-, Osman AN, Said M.M., Megahed S.A. *Rev Roum Chim* **(1991);**

36: 1355.
5. Singh S.P., Seghal S. *Indian J. Chem.* **(1988);** 27 B: 941.
6. Musser J.H., Brown RE, Love B, Baily K, Jones H, Kahen R, et al. *J. Med. Chem.* **(1984);** 27: 121.
7. Pattan S.R., Suresh C., Pujar V.D., Reddy VVK, Rasal V.P., Kotti BC. *Indian J. Chem.* **(2005);** 4B: 2404.
8. Yoshida M, Hayakawa I, Hyashi N, Agatsuma T, Oda Y, Tanzawa F et al. *Bioorg. Med. Chem. Letters.* **(2005);** 15: 3328.
9. Sawhney S.N., Bansal O.P., *Indian J Chem* **(1977);** 15B: 121.
10. Brown HD. *Chem Abstr* 65: 18593.
11. Bradshaw T.D., Bibby M. C., Double J.A., Fichtner I., Cooper P.A., Alley M.C., Donohue S., Stinson S.F., Donohue S., Stinson S.F., Tomaszewjski, J. E., Sausville, E.A. and Stevens, M.F.G., *Mol. Cancer. Therapeutics*, **(2002),** 1, 239.
12. Donohue S., Stinson S.F., Tomaszewjski J.E., Sausville E.A. and Stevens, M.F.G., *Mol. Cancer. Therapeutics*, **(2002),** 1, 239.
13. Hutchinson I., Jennings S.A., Vishnuvajjala B. R., Westwell A.D. and Stevens, M.F.G., *J. Med. Chem.*, **(2002),** 45, 744.
14. El-Sherbeny, M.A., *Arzeneim-Forsch.*, **(2000),** 50, 843.
15. Racane L., Tralic-Kulenovic, V., Fiser-Jakic L., Boykin D.W. and Karminski-Zamola G., *Heterocycles*, **(2001),** 55, 2085.
16. Mahmood-ul-Hasan, Chohan Z.H. and Supuran C.T., Main Group *Met. Chem.*, **(2002),** 25, 291
17. Brien SEO, Browne H.L., Bradshaw T.D., Westwell A.D., Stevens MFG, Laughton C.A., *Org. Biomol. Chem.* **(2003);** 1: 493.
18. Trapani V., Patel V., Leong C.O., Ciolino H. P., Yeh G.C., Hose C., Trepel J.B., Steven M.F.G., Stausvill E.A., Loaiza-Perez A. I., *Brit. J. Cancer.* **(2003);** 88:, 599.
19. El-Sherbeny M.A., *Arzneim-Forsch*, **(2000),** 50, 843.
20. Trapani G., Franco M., Latrofa A., Reho A. and Liso G., *Eur. J. Pharm. Sci.*, **(2001),** 14, 209.
21. Srimanth K., Rao V.R. and Krishna D.R., *Arzneim Forsch*, **(2002),** 52, 388.
22. Watson K. J., Anderson D.R. and Nguyen S.T., *Macromolecules*, **(2001),** 34, 3507.
23. Hutchinson I., Chua M.S., Browne H.L., Trapani V., Bradshaw T.D., Westwell AD et al. *J Med Chem* **(2001);** 44: 1446.
24. Bhusari S.R., Pawar R.P., and Vibute Y.B., *Indian J. Heterocycl. Chem.*, **(2001),** 11, 79.
25. Sreenivasa M.V., Nagappa A.N. and Nargund L.V.G., *Indian J. Heterocycl. Chem.*, **(1998),** 8, 23.
26. Gopkumar P., Shivakumar B., Jayachandran E., Nagappa A.N., Nargund, L.V.G., and Gurupadaiah B.M., *Indian J. Heterocycl. Chem.*, **(2001),** 11, 39.
27. Ojha K.G., Jaisinghani N. and Tahiliani H., *J. Indian Chem. Soc.*, **(2002),** 79, 191.
28. Ghoneim K.M., Essawi M.YH., Mohamed M.S., and Kamal A. M., *Indian J. Chem.*, **(1998),** 37B, 904.
29. Nargund, L.V.G., *Indian Drugs*, **(1999),** 36, 137.
30. K. L. L., Shukla, R. K., **(1981),** 58, 115.
31. A.P. Mishra and M. Khare *Journal of the Indian Chemical Society*. **(2000)**; 77(8):367–370.
32. Basavaraj M. Kalshetty, Shambuling S, Karabasannavar, Ramesh S. ani and Mallikarjun B. Kalashetti. *Drug invention today* 5 (**2013**) 105- 112.
33. C. C. Addison and N. Logan "*Advance in inorganic Chemistry and Radiochemistry Academic press* New York Vol.**6 (1964)**.
34. Praveen K. Singh and B. Singh *Ind, J chem*. **37**A **(1998)** 331.
35. N. Chkaku and K. Nakamoto *Inorg, Chem* **10 (1971)** 768.
36. M. Alaudeen and C.P. Prabhakaran *Indian J. Chem*. **35**A **(1996)** 517.