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SYNTHESIS, SPECTRAL AND ANTIMICROBIAL STUDIES OF LANTHANIDE (III) CHLORIDE COMPLEXES WITH THE SCHIFF'S BASE DERIVED FROM 2-BENZIMIDAZOLYL MERCAPTOACETO HYDRAZIDE AND 2-ACETYL PYRIDINE

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Abstract

Few lanthanide (III) chloride complexes with Schiff's base obtained by the condensation of 2-benzimidazolyl mercaptoaceto hydrazide and 2-acetyl pyridine have been prepared and characterized on the basis of elemental analysis, molar conductance, magnetic, electronic, infrared and ¹H NMR spectral studies, IR and ¹H NMR spectra indicates coordination through azomethine nitrogen, pyridine ring nitrogen and the carbonyl oxygen of the hydrazone moiety. A coordination number eight is suggested for these complexes. The ligand and complexes were screened for their antimicrobial activity.

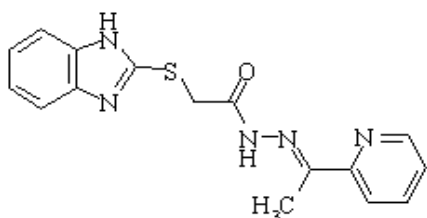
Keywords: Schiff's base; Lanthanide (III) chloride complexes; Antimicrobial activity

Introduction

The chemistry of hydrazine derivatives has been intensively investigated in the recent year owing to their coordinative capability, their pharmacological activity and their use in analytical chemistry as metal extracting agents. Bonding between lanthanides and coordinating ligands depends on the electronegativity of the donor atom in the ligand, the bonding of ligand to lanthanide is essentially electrostatic with a little if any interactions between the 4f orbitals and the ligand orbitals. The study of complexes of hydrazones is interesting from the structural point of view. It is their ability to exist in keto or enol form depending on the experimental conditions, IR spectroscopy is extensively used to study these compounds.

In present paper, we report the synthesis and structural studies of La^{III}, Pr^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, and Dy^{III} complexes of the Schiff's base derived from benzimidazolyl mercaptoaceto hydrazide, 2-acetylpyridine and henceforth abbreviated as 2-ApBzMH (Figure -1).

Fig. 1



Experimental

The chemical used were AR grade, the solvents were dried and distilled before use. 2-benzimidazolyl mercaptoaceto hydrazide was prepared by using standard method¹⁻³. The metal ions were estimated volumetrically by EDTA titration using Eriochrome Black-T as indicator, chloride was determined gravimetrically as AgCl. C, H. and N analysis were carried out on Thermo Finnegan Flash EA 1112 CHNS analyzer (IISC B'lore).

2-benzimidazolyl-mercaptoaceto hydrazide²

To an absolute ethanolic solution (100 ml) containing sodium metal (2.8g)

2-mercaptobenzimidazole (18.79) was added with stirring. The resulting mercaptide was slowly treated with ethyl chloroacetate (35.40 ml). The solution turned turbid and within a few minutes sodium chloride separated out. The mixture was refluxed on a steam bath for ~1h and then filtered. The alcoholic solution was concentrated to about 50% of its original volume and hydrazine hydrate (15ml) was added. The solution was refluxed for ~20 h on a steam bath and then cooled in ice. The separated solid was washed and crystallized from alcohol. (Yield 60%)

The hydrazone ligand 2-ApBzMH was prepared by refluxing ethanolic solution of 2-benzimidazolyl mercaptoaceto hydrazide and 2-acetylpyridine in a 1:1 mole ratio for five hours. Crystals obtained on slow cooling of the reaction mixture to the room temperature were separated by filtration, washed repeatedly with cold ethanol and dried at room temperature. The crude product was recrystallised from ethanol, found C 58.96, H 4.59, and N 21.47 calculated for C₁₆H₁₄N₅O₅S; C 59.07, H 4.61 and N 21.53 (yield 70-80%).

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Preparation of the complexes

[Dichloro bis {2-acetylpyridine (2-benzimidazolyl mercaptoaceto hydrazone)} metal (III)] Chloride [Ln (2-ApBzMH)₂Cl₂]Cl, [Ln=La, Pr, Nd, Sm, Eu, Gd, Tb and Dy] were prepared by mixing together ethanolic solutions of 2-ApBzMH (2mmol) and the appropriate lanthanide chloride (1mmol) and heating under reflux for three hours the addition of acetonitrile (~10cm³) to the reaction mixture produced a solid which after decanting the supernatant solution was redissolved in ethanol and macerated with acetonitrile, successive repetitions of these process yielded crystalline complexes which were filtered washed with a mixture of acetonitrile and ethanol and dried in vacuum. Molar conductivities of the complexes were determined in DMF maintaining 10⁻³M concentration on an Elico-CM-82 conductivity bridge with a cell having cell constant 0.51cm⁻¹ at room temperature (25±2°C)

The magnetic susceptibility data at room temperature were obtained by using a Model 300 Lewis coil force magnetometer of George Associates Inc. make using a CAHN 2000 electro balance, a magnetic field of one tesla strength APD make close cycle cryostat working in the range 300-12K. The

electronic spectra of the complex were recorded on Hitachi 150-20 in the range of 800-200nm spectrophotometer. IR spectra of the ligand and the complexes were recorded in KBr matrix using Perkin Elmer 783 model IR spectrometer in the range of 4000-200 cm⁻¹. The ¹HNMR spectra were recorded in the range of 0-15 ppm in CDCl₃/DMSO solvent on a Varian 300 MHz spectrometer at room temperature using TMS as internal reference. The ligand and the complexes have been screened for antimicrobial activity.

Results and Discussion:

The complexes were synthesized starting from hydrated metal chlorides and an ethanolic solution of ligand 2-ApBzMH. Analytical data (Table-1) indicates that 2-ApBzMH reacts with lanthanum (III) chloride to form complexes of the type [Ln(2-ApBzMH)₂Cl₂]Cl. The complexes are hygroscopic and are soluble in methanol, ethanol, pyridine DMF & DMSO. The molar conductance values of the complexes in 10⁻³M DMF solution at room temperature (82.5-102.0 ohm⁻¹cm²mol⁻¹) indicate that the complexes behave as 1:1 electrolytes⁴.

Table 1: Physical and analytical data of the synthesized Complexes

Compound/ Complex	Colour	Analysis (%) Found (Calcd)					Formula Wt calcd	λ $\Omega^{-1}\text{m}^2\text{mol}^{-1}$	μ_{eff} (BM)
		M	C	H	N	Cl			
2-ApBzMH	White	-	58.96 (59.07)	4.59 (4.61)	21.47 (21.53)	-	325	-	-
[La(2-ApBzMH) ₂ Cl ₂]Cl	White	15.46 (15.53)	42.67 (42.86)	3.35 (3.37)	15.43 (15.61)	11.69 (11.86)	895.4	89.4	Diamag
[Pr (2-ApBzMH) ₂ Cl ₂]Cl	Green	15.58 (15.61)	42.39 (42.77)	3.34 (3.30)	15.69 (15.54)	11.76 (11.88)	897.4	87.2	3.77
[Nd(2-ApBzMH) ₂ Cl ₂]Cl	Blue	15.89 (16.04)	42.53 (42.60)	3.33 (3.35)	15.64 (15.50)	11.82 (11.80)	900.74	91.0	3.96
[Sm(2-ApBzMH) ₂ Cl ₂]Cl	Light Yellow	16.38 (16.56)	42.14 (42.36)	3.31 (3.33)	15.33 (15.41)	11.34 (11.72)	906.86	102.0	2.63
[Eu(2-ApBzMH) ₂ Cl ₂]Cl	Light brown	16.43 (16.75)	42.07 (42.29)	3.30 (3.32)	15.41 (15.32)	11.72 (11.64)	908.46	86.3	3.38
[Gd(2-ApBzMH) ₂ Cl ₂]Cl	Light brown	17.06 (17.22)	41.82 (42.04)	3.28 (3.26)	15.82 (15.30)	11.60 (11.67)	913.75	82.5	7.19
[Tb(2-ApBzMH) ₂ Cl ₂]Cl	Brown	17.22 (17.34)	42.01 (41.92)	3.27 (3.25)	15.19 (15.28)	11.53 (11.62)	915.42	94.6	8.56
[Dy(2-ApBzMH) ₂ Cl ₂]Cl	Brown	17.46 (17.68)	41.58 (41.75)	3.20 (3.25)	15.03 (15.20)	11.38 (11.56)	919.0	88.2	8.62

The magnetic moments of the complexes show very little deviation from Van Vleck values⁵ indicating little participation of the 4f electrons in bond formation. The slightly higher value observed in case of Sm^{III} complex may presumably be due to temperature dependent magnetism on account of low *J*-*Seperation*.⁶

The electronic absorption spectra of lanthanide ions have been subject of several investigations.⁷⁻¹⁰ The ligand 2-ApBzMH show bands at 27895, 32760 and 34240 cm⁻¹, whereas in lanthanide (III) chloride complexes, the ligand bands are shifted to higher or lower frequency sides. This shift may be due to ligand to metal charge transfer transitions.¹¹⁻¹³ No absorption

band due to f-f transition of lanthanide (III) ion could be located in the visible region in the spectra of all these complexes. This is probably due to the fact that the f-f bands are weak and are obscured by the intense charge transfer bands.

Infrared spectra

The diagnostic IR frequencies of the ligand 2-ApBzMH and its complexes are given in Table 2. The ligand show bands at 3210 cm⁻¹ (NH of hydrazide), 3035 cm⁻¹ (-NH of imidazole), 1690 cm⁻¹ (C=O) and 1646 cm⁻¹ (C=N).¹⁴⁻¹⁶ In IR spectra of the lanthanide (III) complexes the bands due to $\nu(\text{NH})$ of hydrazide and $\nu(\text{NH})$ of imidazole moiety remain unaltered in their positions and intensity; particularly non shifting of $\nu(\text{NH})$ of hydrazide band clearly suggests the reaction of ligand in keto form. The band due to $\nu(\text{C=O})$ suffers a negative shift to the extent 18-24 cm⁻¹ indicating the coordination of $\nu(\text{C=O})$ group through oxygen to the metal ion. The band due to $\nu(\text{C=N})$ also suffers a negative shift by 15-20 cm⁻¹ indicating the involvement

of azomethine nitrogen in the coordination, the coordination of the pyridine ring nitrogen is suggested on the basis of the observed changes in the ring skeletal mode (ligand 975 cm⁻¹; complex 990-1005 cm⁻¹) in plane ring deformation mode (ligand 590 cm⁻¹; complex 620-635 cm⁻¹) and out of plane ring deformation mode (ligand 405 cm⁻¹; complex 440-445 cm⁻¹)¹⁷

In the farinfrared region all the complexes exhibit bands around 575-550, 430-416 and 325-312 cm⁻¹ are assigned to $\nu(\text{M-O})$, $\nu(\text{M-N})$ and $\nu(\text{M-Cl})$ modes respectively, the $\nu(\text{M-N})$ band is usually sharp and strong and the $\nu(\text{M-O})$ band is broad and strong. Since a large dipole moment change is involved in the vibrations of the M-O bond comparison to that of the M-N bond.¹⁸ Hence it is expected that the $\nu(\text{M-O})$ band should appear at a higher energy in comparison to that of the $\nu(\text{M-N})$ band.¹⁸ The M-O bond length is usually shorter than the M-N bond length¹⁹ and this also supports the occur of the $\nu(\text{M-O})$ band at a higher energy in comparison to that of the $\nu(\text{M-N})$ band.

Table 2: IR spectral data (cm⁻¹) of the ligand and complexes

Compound	$\nu(\text{NH})$ imidazole	$\nu(\text{NH})$ hydrazine	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
2-ApBzMH	3035	3210	1690	1646	-	-	-
La-complex	3034	3208	1670	1630	558	418	322
Pr-complex	3035	3212	1668	1628	565	430	320
Nd-complex	3032	3210	1666	1626	562	428	312
Sm-complex	3032	3210	1668	1628	550	416	318
Eu-complex	3035	3207	1666	1626	575	422	324
Gd-complex	3036	3212	1672	1631	572	426	325
Tb-complex	3034	3212	1670	1628	566	430	318
Dy-complex	3037	3210	1669	1630	570	428	320

Table 3: ¹H-NMR spectral data of the ligand and La (III) complex

2- <i>ApBzMH</i>	La-Complex	Assignments
3.68(s)	4.23(s)	-CH ₂ – group protons
7.26-7.89(m)	7.21-8.07(m)	- Aromatic protons
8.62(s)	8.79(s)	-N=CH-azomethine proton
11.02(s)	11.03(s)	-NH (hydrazine) proton
12.68(s)	12.69(s)	-NH (imidazole) proton

s = singlet m = multiplet

¹H NMR spectra

The ligand 2-*ApBzMH* and its lanthanum (III) chloride complex were scanned for ¹H NMR spectra in DMSO-*d*₆ solvent in the range of 0-15 ppm downfield of TMS data along with assignment are displayed in Table-3. In the ligand 2-*ApBzMH*; 3.68s (-CH₂-group), 7.26-7.89m (Ar, H), 8.62s (N=CH azomethine proton), 11.02s (-NH hydrazine proton) and 12.68s (-NH imidazole proton) in the lanthanum (III) chloride complex: 4.23s (-CH₂- group proton), 7.21-8.07m (-aromatic protons) 8.79s (N=CH azomethine proton), 11.02s (-NH hydrazine proton), and 12.68s (-NH imidazole proton). The observed downfield shift of the iminoproton signal of hydrazide moiety in the spectrum of lanthanum (III) complex suggests coordination of the hydrazide carbonyl group and azomethine nitrogen with the metal ion. The singlets due to the -NH proton (hydrazine) as well as -NH proton (imidazole) are

unaffected in the spectra of the La^{III} complex indicates noninvolvement of -NH group in coordination.

All these information put together clearly denotes that the ligand is in keto form and it coordinated to the metal atom through the carbonyl oxygen azomethine nitrogen and pyridine nitrogen.

Biological activity

The biological and medical potency of coordination compound has been established by their antitumour²⁰, antiviral²¹ and antimalarial²² activity observed for some derivatives. The characteristic property has been related to the ability of the metal ion to form complexes²³ with ligand containing sulphur, nitrogen and oxygen donor atoms. The compounds were tested for their in vitro antibacterial activity against *Escherichia coli* and *Bacillus cirroflagellosus* and antifungal activity against *Aspergillus niger* and *Candida albicans* by the plating method²⁴ and results are given in table 4.

Table 4: Antibacterial & Antifungal activity of complexes (zone of inhibition in mm)

Sl.No.	Complex	Antibacterial		Antifungal	
		B.c	E.c	A.n	C.a
1	La-complex	13	11	14	12
2	Pr-complex	13	15	13	14
3	Nd-complex	13	16	15	14
4	Sm-complex	18	16	13	12
5	Eu-complex	13	12	15	14
6	Gd-complex	15	14	13	12
7	Tb-complex	16	14	15	13
8	Dy-complex	16	15	14	13
9	Contrimoxazole	25	22	-	-
10	Flucanazole	-	-	24	23

Bc = *Bacillus cirroflagellosus*; Ec = *Escheria coli*; An = *Aspergillus niger*; Ca = *Candida albicans*

It is evident from the bacterial and fungal screening data, the activity of the ligand has not profoundly increased on complexation with lanthanides except in some cases Sm^{III} and Gd^{III} complexes are

moderately active against *Bacillus cirroflagellosus* Pr^{III} and Nd^{III} complexes are moderately active against *Escherichia coli* and Eu^{III} complex is moderately active against *Aspergillus niger*. Overall the ligand and

complexes are less active as compared to the standard contrimoxazole and flucanazole used in the present study.

Conclusion

Based on the above analytical data and spectral studies the empirical formula $[\text{Ln}(\text{2-ApBzMH})_2\text{Cl}_2]\text{Cl}$ (Figure-2) has been tentatively proposed for the present complexes, with coordination number eight for the metal ion and ligand behaves as neutral tridentate in nature.

Figure 2: Structure of the complex

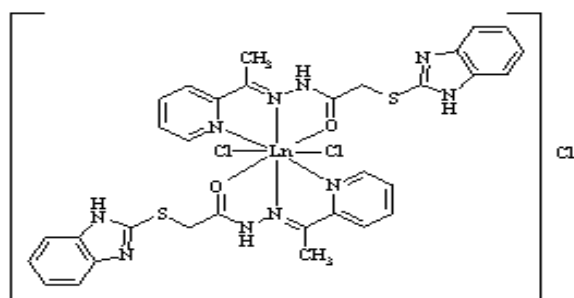


Fig 2 $[\text{Ln}(\text{2-ApBzMH})_2\text{Cl}_2]\text{Cl}$

Where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Dy

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