

Synthesis and Spectroscopic Investigation of Schiff Base Complexes of Lanthanides(III)

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A series of La(III), Pr(III), Nd(III), Sm(III) and Tb(III) complexes have been synthesized with Schiff base (SAZ) derived from the condensation of salicylaldehyde with hydrazine. The prepared Schiff base and its lanthanide complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibilities, UV-visible, IR, ¹H NMR, thermal studies and XRD. The complexes have stoichiometry of the type [Ln(SAZ)₂·2(H₂O)]Cl₃, for Pr(III), Sm(III) and Tb(III) where as [Ln(SAZ)₂Cl₂]Cl for La(III) and Nd(III), where the ligand SAZ coordinates to the lanthanide ion through azomethine nitrogen and phenolic oxygen of azine moiety.

Keywords: Azine, Schiff base, Lanthanide complexes, Spectroscopic investigation.

INTRODUCTION

Azines are an important class of organic compounds for industrial purposes as precursors in the synthesis of various heterocyclic compounds such as purines and pyrimidines¹ and as pigment and dyes². Most importantly, azines are biologically active as antimicrobial^{3,4}, anticancer⁵⁻⁷ and herbicidal agents³. This study focuses on the synthesis, characterization and biological properties of various types of new azines as therapeutic agents.

Azines containing the N, O donor system are an important class of ligands and have found wide application in various fields⁸⁻¹⁴. Continuing earlier research¹⁵⁻¹⁷ on biologically active complexes, an attempt has now been made to synthesize azines derived from salicylaldehyde and hydrazine.

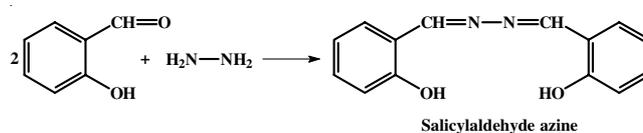
Azines (R₂C=N-N=CR₂) are 2-3-diaza analogues of 1,3-butadiene. The chemical properties of azines have been extensively investigated in the past decades because of their interesting physical and spectral properties^{18,19}. Azines are also potential ligands owing to their having 2 imine groups side by side. Therefore, they have recently been used as ligands in coordination chemistry¹⁹⁻²². The azines can be considered as models of some biological systems^{23,24}.

Although many works have been devoted to study the structure of azines, less research has been attempted concerning the complexes of the azine compounds and their bioinorganic relevance^{23,24}. Therefore, we described the synthesis and characterization of new bis(azine)s and their La (III), Pr (III), Nd(III), Tb(III) and Sm(III) complexes.

EXPERIMENTAL

All chemicals and solvents are used AR grade. All the metals were used as their chloride salts. UV spectra recorded on UV-visible spectrophotometer 119. Conductance or metal complex was determined in DMSO on conductivity meter quiptronics model NO-EQ665. Melting points were recorded on in recorded by open capillary method and are uncorrected. ¹H NMR spectra of a Schiff base and its metal complex recorded on Bruker 300 MHz spectrometer in DMSO. Elemental analysis was carried out on Eager 350 analyser. Magnetic measurement were done on solid complexes using Guoy method. Powder XRD pattern of complexes are recorded Philips Analytical XRD B.V. at CFC Shivaji University Kolhapur, India.

Synthesis of ligand: Step-I: For the synthesis of ligand, 50 mL ethanolic solution of 0.002 mol of salicylaldehyde was taken in round bottomed flask and to this 0.001 mol of hydrazine in ethanol was added slowly under stirring. The resulting mixture was refluxed for about 0.5 h. It was naturally cooled to room temperature²⁵. After cooling, the solid residue was washed with hot ethanol (yield 80 %).



Preparation of lanthanide(III) complexes: To a hot solution of ligand (0.02 mol) in alcohol (25 mL), alcoholic

solution of the corresponding lanthanide(III) chloride (0.01 mol) was added under constant stirring. The pH of the reaction mixture was adjusted to 6.8-7 by adding 10 % ethanolic ammonia solution and refluxed for about 5 h. The precipitated solid metal complex was filtered and washed with hot methanol, followed by petroleum ether, ethyl acetate and dried over CaCl₂ in vacuum desiccator (yield 65 %).

RESULTS AND DISCUSSION

All the complexes are coloured solids, air stable and are having solubility in polar solvents DMF and DMSO. The elemental analysis showed 1:2 (metal: ligand) stoichiometry for all the metal complexes. Micro analytical data and molar conductance values are given in Table-1. The metal contents in complexes were estimated by gravimetric analysis²⁶. The magnetic measurement studies suggest that the Pr(III), Nd(III), Tb(III) and Sm(III). Complexes exhibit paramagnetic whereas the La(III) show diamagnetic behaviour. Molar conductance of the synthesized ligand complexes were measured using 10⁻³ M DMSO solvent at room temperature. The conductivity values are in the range of 80-100 Ω⁻¹ mol⁻¹ cm². The obtained values were taken as a good evidence for the existence of an electrolytic nature of the complexes²⁷.

The IR spectra provides a valuable information regarding the nature of functional group attached to the metal atom²⁸. The important IR frequencies exhibited by the Schiff base ligands SAZ and their corresponding mixed ligand complexes are tabulated in Table-2. The ligands shows broad band at around 3535-3317 cm⁻¹ due to the phenolic hydroxyl group in free ligands, which shows shift in frequency in complexes, indicating the coordination through metal atom²⁹. The band in the range 1620 cm⁻¹ are observed due to ν(C=N) which has been shifted towards lower region at around 1610-1596 cm⁻¹ in the complexes indicating the participation of the azomethine group in the complexes formation³⁰, this shift is also due to the reduction of double bond character of carbon-nitrogen bond of azomethine group³¹. The Schiff base ligand shows a medium intensity band at around 1276 and 1388 cm⁻¹ due to phenolic ν(C-O) is remain constant indicating the coordination through the phenolic oxygen atom^{30,32} and also due to hydrogen to metal

bonded structure. The coordination through nitrogen of azomethine and oxygen of ν(C-O) of ligand are further evidenced by the appearance in the complexes of non-ligand bands around 486-422 and 565-526 cm⁻¹ are due to M-N and M-O bonds respectively^{32,33}. The spectra of Pr(III), Tb(III) and Sm(III) showed a strong band at 3600-3136 cm⁻¹ region, suggesting the presence of coordinated water in these metal complexes²⁶.

Electronic spectra: The electronic spectra of the Schiff base ligand and their complexes have been measured in DMSO solution between 200-800 nm at room temperature. The spectral data of the ligands and its complexes are tabulated in Table-3. In the spectra of the Schiff base ligands, the absorption band observed at 280 nm were assigned to a benzene π→π* transition and the band at 380 nm were assigned due to n→π* transition associated with the azomethine chromophore (-C=N)³⁴. The new bands observed near 390-450 nm can be assigned to L→M charge transfer band. The newly synthesized Schiff base gives colored complexes with metal ions that have a series of overlapping absorption bands in the UV part of the spectrum as well as in the visible part. In such cases the *d-f* transition may be completely overwhelmed and essentially impossible to observe³⁵ because of limited solubility of the complexes. Mostly *d-f* transition occurs in the region of 450-550 nm.

Thermogravimetric analysis: Thermogravimetric analysis (TGA and DTG) of metal complexes are used to (i) get information about the thermal stability of new complexes, (ii) decide whether the water molecules are inside or outside the inner co-ordination sphere of the central metal ion.

In the present investigation, heating rates were suitably controlled at 10 °C min⁻¹ under nitrogen atmosphere and the weight loss was measured from the ambient temperature upto 1000 °C. The TGA data are presented in Table-4. The TGA curve of the Nd(III) complexes showed a rapid first step decomposition around 160 °C with 4.5 % mass loss (calculated 4.8 %) indicating the loss of one lattice chloride molecules. The complex [Nd(SAZ)₂Cl₂]Cl shows a weight loss of 65.87 % at a temperature range 260 °C which corresponds to the removal of two ligand molecule. A weight loss of 9.07 % is observed in the

TABLE-1
PHYSICAL CHARACTERIZATION, ANALYTICAL AND MOLAR CONDUCTANCE DATA OF COMPOUNDS

Compound	f.w.	m.p. decom. Temp (°C)	Colour	Molar conductance (Ω cm ⁻² mol ⁻¹)	C (calcd. %)	H (calcd. %)	Cl (calcd. %)	N (calcd. %)	O (calcd. %)	M (calcd. %)
SAZ	240.26	—	Yellow	—	69.99	5.03	—	11.66	13.32	—
[La(SAZ) ₂ Cl ₂]Cl	725.78	> 270	Cream	78	46.34	3.33	14.65	7.72	8.82	19.14
[Pr(SAZ) ₂ 2H ₂ O]Cl ₃	763.42	> 270	Faint yellow	76	44.01	3.66	13.42	7.33	12.57	18.45
[Nd(SAZ) ₂ Cl ₂]Cl	731.11	> 270	Grey	72	46.00	3.31	14.55	7.66	8.75	19.73
[Tb(SAZ) ₂ 2H ₂ O]Cl ₃	781.03	> 270	Orange	81	43.01	3.61	13.60	7.17	12.28	20.33
[Sm(SAZ) ₂ 2H ₂ O]Cl ₃	773.26	> 270	Leman yellow	82	43.49	3.65	13.75	7.25	12.41	19.44

TABLE-2
IR SPECTRAL DATA FOR LIGANDS AND THEIR METAL COMPLEXES

Complex	ν(O-H)	ν(C=N)	ν(M-N)	ν(M-O)	ν(C-O)	ν(H ₂ O)
SAZ	3535-3317	1620	—	—	1276	—
[La(SAZ) ₂ Cl ₂]Cl	3154	1604	459	565	1276	—
[Pr(SAZ) ₂ 2H ₂ O]Cl ₃	3136	1596	459	549	1276	3136-3500
[Nd(SAZ) ₂ Cl ₂]Cl	3234	1608	437	455	1276	—
[Tb(SAZ) ₂ 2H ₂ O]Cl ₃	3186	1611	422	453	1276	3150-3600
[Sm(SAZ) ₂ 2H ₂ O]Cl ₃	3178	1613	486	426	1276	3145-3600

TABLE-3
ELECTRONIC SPECTRAL AND MAGNETIC MOMENT DATA FOR THE LIGANDS AND THEIR COMPLEXES

Ligand complex	Absorbance (nm)	n(cm ⁻¹)	Transition	Geometry	Magnetic moment (BM)
SAZ	—	—	—	—	—
[La(SAZ) ₂ Cl ₂]Cl	299	33444	π - π^*	Octahedral bi pyramidal	—
	352	28409	n- π^*		
	749	13351	LMCT		
[Pr(SAZ) ₂ ·2H ₂ O]Cl ₃	297	33670	π - π^*	Octahedral bi pyramidal	2.81
	353	28328	n- π^*		
	756	13227	LMCT		
[Nd(SAZ) ₂ Cl ₂]Cl	305	32786	n- π^*	Octahedral bi pyramidal	3.86
	749	13351	LMCT		
[Tb(SAZ) ₂ ·2H ₂ O]Cl ₃	297	33670	p- π^*	Octahedral bi pyramidal	7.91
	356	28089	n- π^*		
	756	13227	LMCT		
[Sm(SAZ) ₂ ·2H ₂ O]Cl ₃	297	33670	p- π^*	Octahedral bi pyramidal	5.94
	356	28089	n- π^*		

TABLE-4
THERMAL ANALYSIS DATA FOR METAL COMPLEXES

Complex	Decomposition temp. (°C)	Lost fragment	Weight loss (%)	
			Experimental	Theoretical
[Pr(SAZ) ₂ ·2H ₂ O]Cl ₃	180	Coordinated two water molecules	4.7	4.8
	180-300	Two ligand molecule	62.87	62.56
	300-800	Three lattice chloride	13.95	13.25
	800-1000	Metal oxide	21.60	21.90
[Nd(SAZ) ₂ Cl ₂]Cl	160	One lattice chloride	4.5	4.8
	160-260	Two ligand molecule	65.87	65.00
	260-500	Coordinated two chloride molecules	9.07	9.1
	500-1000	Metal oxide	21.60	21.05
[Tb(SAZ) ₂ ·2H ₂ O]Cl ₃	150	Coordinated two water molecules	4.7	4.2
	150-300	Two ligand molecule	61	60.60
	300-800	Three lattice Chloride	13.06	13
	800-1000	Metal oxide	23.40	23.60

temperature range 250-500 °C which suggests the elimination of coordinated two chloride molecules. In the Nd complex the amount of residue is 21.60 %.

The TGA curve of the Pr(III) complexes showed a rapid first step decomposition around 180 °C with 4.7 % mass loss (calculated 4.8 %) indicating the loss of two coordinated water molecules. The complex [Pr(SAZ)₂·2H₂O]Cl₃ shows a weight loss of 62.87 % at a temperature range 300 °C which corresponds to the removal of two ligand molecule. A weight loss of 13.95 % is observed in the temperature range 300-800 °C which suggests the elimination of three lattice chloride molecules. In the Pr complex the amount of residue is 21.60 %.

The TGA curve of the Tb(III) complexes showed a rapid first step decomposition around 150 °C with 4.7 % mass loss (calculated 4.8 %) indicating the loss of two coordinated water molecules. The complex [Tb(SAZ)₂·2H₂O]Cl₃ shows a weight loss of 61 % at a temperature range 300 °C which corresponds to the removal of two ligand molecule. A weight loss of 13.06 % is observed in the temperature range 300-800 °C which suggests the elimination of three lattice chloride molecules. In the Tb complex the amount of residue is 23.40 %.

X-ray diffraction study: The X-ray diffractogram of a representative metal complex of Nd(III) was scanned in the range 5-100° at wavelength 1.54 Å (Fig. 1). The diffractogram and associated data depict 2 θ values for each peak, relative intensity and inter planar spacing (d-values). The diffractogram

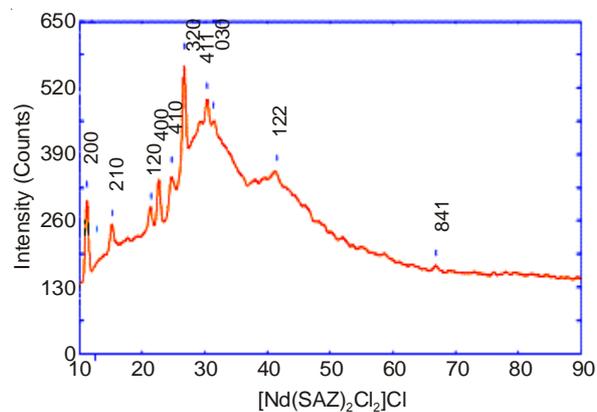


Fig. 1

of Nd(III) complex showed ten reflections with maxima at 2 θ (33.46390) corresponding to d value 1.39834 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10 % have been indexed by using computer programme³⁶. The above indexing method also yields Miller indices (hkl), unit cell parameters and volume. The unit cell of Nd(III) complex yielded values of lattice constants, a = 15.84608 Å, b = 8.55337 Å, c = 5.10553 Å and unit cell volume, V = 165.39 (Å)³. In concurrence with these cell parameters of Nd(III) complex, the condition such as a ≠ b ≠ c and $\alpha = \beta = \gamma = 90^\circ$ required for the compounds to

be orthorhombic were tested and found to be satisfactory. The above values indicate that the metal complex has orthorhombic crystal system.

The X-ray diffractogram of a representative metal complex of Pr(III) was scanned in the range 5-100° at wavelength 1.54 Å (Fig. 2). The diffractogram and associated data depict 2θ values for each peak, relative intensity and inter planar spacing (d-values). The diffractogram of Pr(III) complex showed ten reflections with maxima at 2θ (22.99709) corresponding to d value 1.97167 Å. The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10 % have been indexed by using computer programme³⁶. The above indexing method also yields miller indices (hkl), unit cell parameters and volume. The unit cell of Pr(III) complex yielded values of lattice constants, a = 23.77998 Å, b = 4.62100 Å, c = 3.56444 Å and unit cell volume, V = 165.39 (Å)³. In concurrence with these cell parameters of Pr(III) complex, the condition such as a ≠ b ≠ c and α = β = γ = 90° required for the compounds to be orthorhombic were tested and found to be satisfactory. The above values indicate that the metal complex has orthorhombic crystal system.

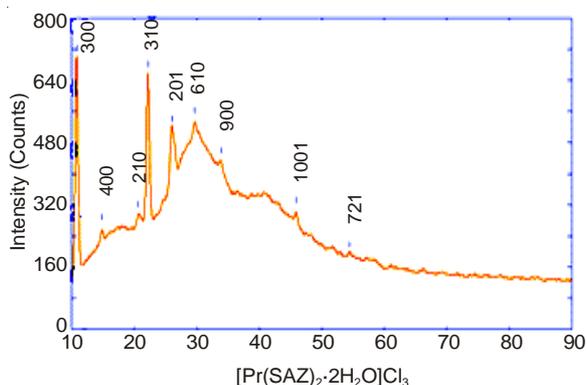
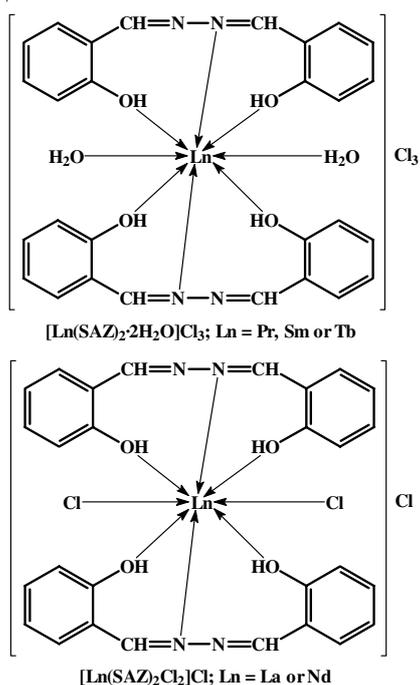


Fig. 2

Based On the above results probable structures have been proposed:



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