

THERMOGRAVIMETRIC AND SPECTROSCOPIC CHARACTERIZATION OF TRIVALENT LANTHANIDE CHELATES WITH SOME SCHIFF BASES

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Abstract

Solid complexes of two derivatives of Schiff bases SAT and SAZ with Pr(III), Nd(III), Gd(III), Dy(III), Ho(III), Er(III) and Yb(III) were prepared and characterized by elemental analysis, IR spectra and TG.

The suggested formula of the obtained solid complexes is $[MLC_{12}(H_2O)_n]$ for SAT and $[MLCl(H_2O)_n]$ for SAZ where M =trivalent lanthanide ion, L =deprotonated ligand and n =2–3. The TG gives information about the coordinated water molecules, thermal stability and the coordination number of M which was found to be 6–8. A scheme of thermal decomposition of the complexes is also proposed. Comparison of the IR spectra of the ligands with those of their complexes indicate the center of chelation in SAT and SAZ which act as tridentate ligands.

Keywords: lanthanide complexes, Schiff bases, TG-DTA

Introduction

Many Schiff bases have received great attention due to their uses as chemical intermediates and perfume bases in dyes and rubber accelerators and in liquid crystals for electronics. Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure [1]. The chemistry of lanthanide complexes with Schiff bases has received little attention compared with the d -block metal complexes.

Recently, there has been a growing interest in the lanthanide-Schiff base complexes owing to the important applications of both metals and ligands. Robards and Patsalides used some lanthanide Schiff base complexes for the determination of some trace metals by liquid chromatography [2]. Hirayama *et al.* extracted the trivalent lanthanide selectively as anionic Schiff base complexes [3]. Bastida *et al.* studied the lanthanide complexes with macrocyclic Schiff base ligands and obtained complexes of 18-membered and 15-membered macrocycles [4]. Hassan determined the stability of the lanthanide Schiff base complexes and deduced the thermodynamic parameters [5]. The pK of some

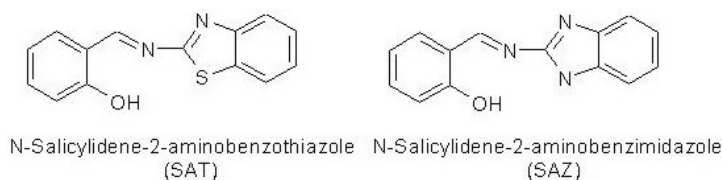
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Schiff bases and stability of their lanthanide complexes were determined potentiometrically using the Fortran program PKAS and BEST [6]. The present work describes the synthesis and characterization of some lanthanide Schiff base complexes. The TG analysis was performed on some complexes in order to obtain information about their thermal stability and to propose a scheme for their thermal decomposition.

Experimental

Synthesis of ligands

The Schiff bases SAT and SAZ were prepared by condensation of salicylaldehyde with 2-aminobenzothiazole and 2-aminobenzimidazole respectively according to the method reported by AL-Shihri [7]. The yellow product was isolated from absolute ethanol, dried and purified. The purity of the two prepared Schiff bases SAT and SAZ was confirmed by the elemental analysis. The two ligands used in the present study have the following structures:



Scheme 1

Synthesis of solid complexes

The solid complexes were prepared by mixing 10 mL portion of hot ethanol solution containing 0.001 mole of $MCl_3 \cdot nH_2O$ with a hot ethanol solution containing 0.001 mole of the Schiff base SAT or SAZ to form 1:1 (M:L) complexes where $M=Pr, Nd, Gd, Dy, Ho, Er, Yb$. The mixture was then stirred and heated for 30 min with adding few drops of NH_4OH to pH 7–8. The mixture was then allowed to stand overnight. The product was collected by filtration and washed with cold ethanol till the filtrate became colorless. It was then dried in an oven and kept in stoppered bottles. The isolated solid complexes were subjected to elemental analysis in the microanalytical center of Cairo University (Table 1).

TG measurements

The thermogravimetric analysis of some solid complexes was carried out with Shimadzu TGA-50 H thermal analyzer. The mass loss was measured from room temperature up to 600°C at a heating rate of 10°C min⁻¹. The TG and DTA curves of Ho-SAZ complex are shown in Fig. 1, and the thermal results are summarized in Table 3.

IR measurements

The IR spectra of the hydrated solid complexes M-SAT and M-SAZ and the free ligands SAT and SAZ were recorded using Pye Unicam SP-300 infrared spectrometer.

Table 1 Elemental analysis of lanthanide complexes with SAT and SAZ

Formula	C/%	H/%	N/%
SAT(C ₁₄ H ₁₀ N ₂ SO)	65.9 (66.12)	3.9 (3.9)	12 (12.6)
Pr(SAT)Cl ₂ (H ₂ O)	34.1 (34.7)	2.8 (2.4)	5.1 (5.7)
Nd(SAT)Cl ₂ (H ₂ O)	34.0 (34.5)	2.8 (2.3)	5.3 (5.8)
Dy(SAT)Cl ₂ (H ₂ O)	33.0 (33.3)	2.6 (2.3)	5.1 (5.6)
Er(SAT)Cl ₂ (H ₂ O)	32.5 (33.0)	2.7 (2.2)	5.2 (5.5)
SAZ(C ₁₄ H ₁₁ N ₃ O)	70.7 (70.88)	4.6 (4.64)	18.8 (17.72)
Pr(SAZ) ₂ (H ₂ O)	50.2 (51.8)	4.0 (3.4)	5.8 (6.4)
Nd(SAZ)Cl(H ₂ O)	36.5 (37.3)	3.5 (3.0)	8.8 (9.3)
Gd(SAZ)Cl(H ₂ O)	36.0 (37.7)	3.0 (2.5)	8.9 (9.4)
Yb(SAZ)Cl(H ₂ O)	36.1 (36.4)	2.9 (2.5)	8.5 (9.1)

*Calculated values in parenthesis

Results and discussion*Formulation of the complexes*

The formulation of the Schiff base complexes are mostly hydrated 1:1 species as may be shown from the elemental analysis (Table 1). These analytical results can show that these complexes have the formula [MLC₁₂(H₂O)_n] for SAT and the formula [ML'Cl(H₂O)_n] for SAZ, where M=trivalent lanthanide metal ion, L=deprotonated ligand SAT, L'=deprotonated ligand SAZ and n=2–3. According to these formulae, the M ion has a coordination number 6–8 provided that SAT and SAZ are tridentate ligands. The insolubility of complexes and their very low conductivity indicate that they are non-electrolyte and that Cl⁻ ion is bound to M(III) ion inside the coordination sphere.

IR spectra of the complexes

It was necessary to measure the IR spectra of the complexes in order to determine the center of chelation in the two Schiff bases SAT and SAZ (Table 2). The IR results can be summarized as follows:

1. Upon chelation, the phenolic OH weak band disappears and a new very broad band appears near 3400 cm^{-1} which is assignable to $\nu(\text{OH})$ of H_2O molecules in the complexes. This may indicate the replacement of hydrogen of OH group by the metal ion. Another band, due to the bending variation of H_2O , was found at $849\text{--}903\text{ cm}^{-1}$ indicating that these complexes are hydrated.

In the case of SAZ, the weak NH band near 3200 cm^{-1} is overlapped with the broad $\nu(\text{OH})$ band of H_2O molecules present in the spectra of its complexes.

2. The imine $\text{C}=\text{N}$ stretching bands of the free ligands which appear near 1600 cm^{-1} shifted to higher frequencies $1635\text{--}1643\text{ cm}^{-1}$ upon complex formation. This implies the participation of the azomethine N in chelation with M ions [9, 10]. This finding is further confirmed by the appearance of $\text{M}\text{--}\text{N}$ band at $420\text{--}440\text{ cm}^{-1}$.

3. The band near 1280 cm^{-1} which is assignable to the asym $\nu(\text{C}\text{--}\text{OH})$ in the free ligands shifted to lower frequencies upon complexation.

4. The aromatic $\text{C}=\text{C}$ bands near 1500 cm^{-1} in the free ligands undergo small shifts on complex formation due to mesomeric effect with the aromatic ring in the chelates [11].

5. The $\text{C}\text{--}\text{S}$ band of the free SAT which appears at 754 cm^{-1} suffers a very little effect by complexation indicating that S atom is not involved in chelation.

6. The shift of the asym $\nu(\text{C}\text{--}\text{OH})$ in both SAT and SAZ to lower frequencies indicates that phenolic O participates as a donor atom [12]. This participation is confirmed by the appearance of new bands at $460\text{--}480\text{ cm}^{-1}$ which are attributable to $\text{M}\text{--}\text{O}$ stretching mode.

7. Two new bands with medium to weak intensities are observed in the region or $420\text{--}480\text{ cm}^{-1}$ in the complexes under study. Such bands were previously reported to be assignable to $\nu(\text{M}\text{--}\text{O})/\nu(\text{M}\text{--}\text{N})$ modes [13, 14].

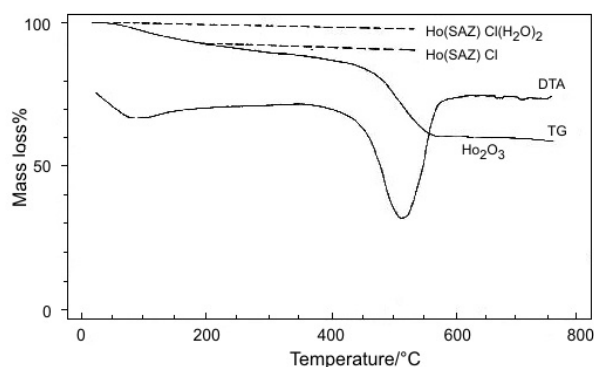


Fig. 1 TG curve of Ho-SAZ complex

Table 2 Band assignment of the IR bands of the lanthanide complexes with Schiff bases SAT and SAZ

Complexes	ν OH water	Phenolic OH	ν NH	ν C=N	Asym. C-O	γ OH water	ν C-S	ν M-O	ν M-O/ ν M-N
HSAT	-	3400w	-	1607s	1286s	-	654s	-	-
Nd: SAT	3394b	-	-	1643s	1242m	900w	760m	470m	440sh
Gd: SAT	3402b	-	-	1635s	1250m	902s	764s	470m	-
Dy: SAT	3417b	-	-	1635s	1250s	890m	764s	470w	430sh
Ho: SAT	3394b	-	-	1635s	1250s	903s	756s	470m	440w
Er: SAT	3410b	-	-	1635s	1250m	902m	756s	470w	-
Yb: SAT	3417b	-	-	1635s	1250s	903m	756s	478w	420w
H ₂ SAZ	-	3400w	3200w	1609s	1278s	-	-	-	-
Pr: SAZ	3410b	-	-	1643s	1260sh	849m	-	460sh	432m
Nd: SAZ	3395b	-	-	1643s	1250sh	849m	-	460sh	430sh
Gd: SAZ	3410b	-	-	1635s	1242m	902s	-	470m	440s
Ho: SAZ	3394b	-	-	1635s	1250m	903s	-	470m	420sh
Yb: SAZ	3395b	-	-	1635s	1250m	900m	-	480w	430sh

TG and DTA of the complexes

The TG curve of Ho-SAZ complex is shown in Fig. 1, while Table 3 lists the mass losses (found and calculated) of 4 complexes as a function of the temperature.

In the range 100–200°C, the initial mass loss is attributed to the removal of 1–3 H₂O molecules resulting in anhydrous complex.

In the DTA curves, such dehydration process appears as a small endothermic peak. The other endothermic peak at 400–500°C is attributed to the decomposition of the anhydrous complex to give the stoichiometric oxides M₂O₃ as final product [15–18]. The beginning of decomposition (Table 3) may be considered as an indication of the thermal stability of the solid complexes. Based on the above TG results, the following scheme of thermal decomposition may be proposed for the lanthanide-Schiff base complexes [19, 20].

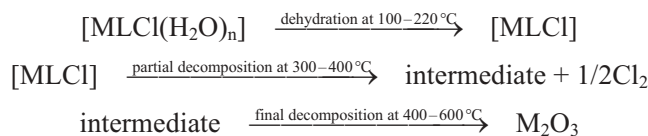
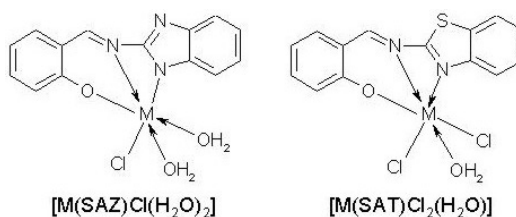


Table 3 TG results of some M(III) complexes with SAT & SAZ

Complex	Dehydration			Start of decomp./°C	Formation of M ₂ O ₃ as a solid residue		
	Temp. range/°C	H ₂ O loss			Temp./°C	calc.	found
		calc.	found				
Pr(SAT)Cl ₂ (H ₂ O)	80–220	3.6	3.2	350	500	34	35
Yb(SAT)Cl ₂ (H ₂ O) ₃	80–200	9.7	9.0	400	550	35	34
Pr(SAZ) ₂ (H ₂ O) ₂	150–170	5.6	6.0	200	350	21	20
Ho(SAZ)Cl(H ₂ O) ₂	120–200	7.6	7.3	450	560	40	41



Scheme 2

Considering that SAT is a monobasic ligand and SAZ is a dibasic ligand, we can deduce that both ligands can act as tridentate ligands [21, 22]. Moreover, coordination number 6–8 may be proposed for the trivalent lanthanide ions in these complexes, thus:

Conclusions

Based upon the above structures proposed for the SAZ and SAT Schiff base complexes, both ligands behave as tridentate ligands. The anhydrous solid complexes are thermally stable within the range 200–400°C. Furthermore, TG analysis indicates that the coordination number of the lanthanide metal ions may be 6–8 in these complexes.

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