

# Synthesis, Spectral Characterization and Biological Studies of Lanthanum(III) Complexes with 3-Substituted-4-Amino-5-Mercapto-1,4-Triazoles Schiff Bases

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## ABSTRACT

Some lanthanum(III) complexes have been synthesized by reacting lanthanum(III) metal salt with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/ biacetyl/ benzyl. All these complexes are not soluble in common organic solvents. However sparingly soluble in DMF and DMSO. The chemical analysis of the complexes confirmed to the stoichiometry of the type La(III)LNO<sub>3</sub>·H<sub>2</sub>O. La(III)LCl·H<sub>2</sub>O and La(III)LNCS·H<sub>2</sub>O respectively. The chelation of the complexes has been proposed in the light of analytical, spectral studies. The measured molar conductance values indicate that, the complexes are non-electrolytes. The Schiff bases and their complexes have been screened for their antibacterial and antifungal activities. The results of these studies show the metal complexes to be more antibacterial and antifungal as compared to the uncomplexed coumarins.

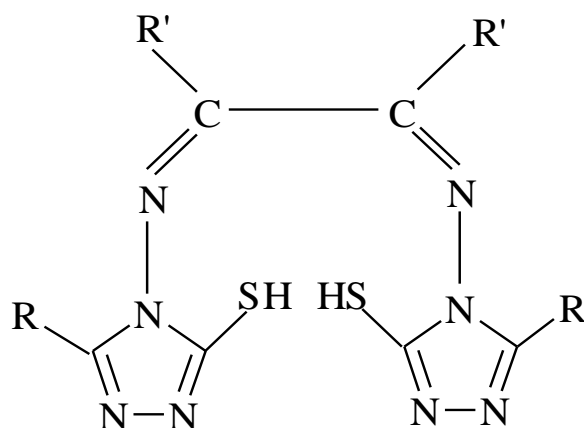
**Keywords:** lanthanum(III) complexes, Schiff, antibacterial, antifungal.

## 1. INTRODUCTION

Several complexes of various transition metals with 3-substituted-4-amino-5-mercapto-1,2,4-triazole ligands have been reported from our laboratory<sup>1-6</sup>. Metal complexes of 1,2,4-triazole derivatives have been investigated in previous reports<sup>7,8</sup>. Substituted triazoles are well known as bactericides,<sup>9</sup> pesticides<sup>10</sup>, insecticides<sup>11</sup> and potential fungicides<sup>12</sup>. Recently a number of attempts have been made to obtain Zn, Cd and Hg complexes with the Schiff base derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole<sup>13</sup>. Mishra et al, have studied the Ru(II) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole<sup>14</sup>.

In our pursuit of new ligands for metal complexes, we have synthesized a new series of Schiff bases derived by the condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole

and glyoxal/biacetyl/benzyl. These ligands have donor sites with the ONNO sequence and varied coordination abilities. The nature of ligands has attracted our attention and aroused our interest in elucidating the structures of La(III) complexes with the Schiff bases as there is scant information on these complexes of the ligands. Hence, in this paper we have report the synthesis, spectral and biological activities of La(III) complexes with the following synthesized ligands (Fig. 1).



**Fig. 1.** Structure of Schiff bases.

Schiff bases No.	R'	R
I	H	H
II	H	CH <sub>3</sub>
III	H	C <sub>2</sub> H <sub>5</sub>
IV	H	C <sub>3</sub> H <sub>7</sub>
V	CH <sub>3</sub>	H
VI	CH <sub>3</sub>	CH <sub>3</sub>
VII	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>
VIII	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>
IX	C <sub>6</sub> H <sub>5</sub>	H
X	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
XI	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>
XII	C <sub>6</sub> H <sub>5</sub>	C <sub>3</sub> H <sub>7</sub>

## 2. EXPERIMENTAL

All chemicals used were of reagent grade. Substituted salicylaldehydes were prepared as described in the literature<sup>15</sup>.

## 2. 1. Synthesis of Schiff bases [I-XII]

The Schiff bases have been synthesized by condensation of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl in 2:1 molar proportions in EtOH for 4-5 h with an addition of 3-4 drops of concentrated hydrochloric acid. The precipitate formed were filtered, washed with cold EtOH and recrystallized from hot EtOH.

## 2. 2. Synthesis of Lanthanum(III) Complexes

A solution of lanthanum(III) nitrate / lanthanum(III) chloride / lanthanum(III) thiocyanate (0.01 mol) was treated with (0.01 mol) Schiff bases in super dry alcohol. The reaction mixture was refluxed for about 2-3 hrs. After cooling pH of the reaction mixture was adjusted to about *ca* 7 by adding dilute ammonia with constant stirring. The light yellow precipitate of complex was obtained. Then the precipitated complex was filtered, washed thoroughly with dry ethanol and ether and finally dried over fused calcium chloride in vacuum.

## 2. 3. Analysis and Physical Measurements

The lanthanum in the complex was determined by volumetric method using EDTA solution<sup>18</sup>. The nitrogen was determined by Dumas method. The results of chemical analysis and molar conductance values are listed in Table 1.

The IR spectra of the ligands and their lanthanum(III) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000-250 cm<sup>-1</sup> region in KBr disc. The electronic spectra of the complexes were recorded on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200-1100 nm.

**Table 1.** Analytical and Molar Conductance Data of Lanthanum(III) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacetyl/benzyl.

Complex. No	Empirical formula	M % Cald. Obtd.	N % Cald. Obtd.	S % Cald. Obtd.	Cl % Cald. Obtd.	Molar conductance Ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup>
1	(C <sub>6</sub> H <sub>4</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	29.49 30.68	26.75 27.85	13.59 14.10	- -	13.53
2	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	27.84 27.90	25.28 25.18	12.82 13.34	- -	12.59
3	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	26.36 26.31	23.91 24.09	12.14 12.10	- -	15.42
4	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	25.03 25.09	22.71 22.81	11.53 11.94	- -	16.92
5	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	27.84 27.90	25.25 25.32	12.82 12.32	- -	17.94
6	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	26.36 26.39	23.91 23.85	12.14 12.58	- -	20.84
7	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	25.03 25.09	22.70 22.75	11.53 11.63	- -	26.03
8	(C <sub>14</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	23.82 23.60	21.61 21.65	10.97 10.33	- -	24.84
9	(C <sub>18</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	22.29 22.18	20.23 20.31	10.28 10.59	- -	28.65
10	(C <sub>20</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	21.33 21.96	19.35 19.38	9.83 10.12	- -	14.78

11	(C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	20.45 20.40	18.56 18.61	9.42 9.70	- -	18.26
12	(C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )LaNO <sub>3</sub> ·H <sub>2</sub> O	19.64 19.63	16.82 15.82	9.05 9.10	- -	19.63
13	(C <sub>6</sub> H <sub>4</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	31.25 31.27	25.20 25.22	14.40 14.38	7.98 7.95	16.30
14	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	29.40 29.42	23.70 23.68	13.54 13.52	7.51 7.52	12.09
15	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	27.75 27.78	22.38 22.35	12.78 12.75	7.09 7.05	16.06
16	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	26.28 26.26	21.19 21.20	12.11 12.12	6.71 6.72	13.44
17	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	29.40 29.42	23.70 23.72	13.54 13.53	7.51 7.53	12.19
18	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	27.75 27.79	22.38 22.36	12.78 12.80	7.09 7.05	10.61
19	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	26.28 26.30	21.19 21.18	12.11 12.13	6.71 6.75	18.10
20	(C <sub>14</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	24.96 24.98	20.12 20.14	11.50 11.48	6.38 6.40	12.83
21	(C <sub>18</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	23.28 23.25	18.77 18.75	10.73 10.75	5.95 5.96	17.94
22	(C <sub>20</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	22.24 22.20	17.93 17.90	10.24 10.20	5.68 5.70	22.90
23	(C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	21.29 21.30	17.16 17.15	9.80 9.82	5.44 5.42	16.13
24	(C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )LaCl·H <sub>2</sub> O	20.41 20.40	16.46 16.45	9.40 9.42	5.21 5.19	19.14
25	(C <sub>6</sub> H <sub>4</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	29.74 29.75	26.98 26.95	20.56 20.58	- -	12.34
26	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	28.06 28.09	25.45 25.47	19.39 19.37	- -	19.35
27	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	26.56 26.54	24.09 24.05	18.35 18.32	- -	16.18
28	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	25.21 25.22	22.87 22.88	17.42 17.44	- -	14.93
29	(C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	28.06 28.05	25.45 25.49	19.39 19.32	- -	16.34
30	(C <sub>10</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	26.56 26.55	24.09 24.10	18.35 18.30	- -	20.18
31	(C <sub>12</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	25.21 25.33	22.80 22.83	17.42 17.45	- -	22.13
32	(C <sub>14</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	23.99 23.86	21.76 21.80	16.58 16.55	- -	17.14
33	(C <sub>18</sub> H <sub>12</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	22.44 22.45	20.35 20.38	15.51 15.53	- -	19.36
34	(C <sub>20</sub> H <sub>16</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	21.33 21.35	19.35 19.36	14.74 14.75	- -	22.34
35	(C <sub>22</sub> H <sub>20</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	20.58 20.59	18.66 18.68	14.22 14.24	- -	25.35
36	(C <sub>24</sub> H <sub>24</sub> N <sub>8</sub> S <sub>2</sub> )LaNCS·H <sub>2</sub> O	19.76 19.75	17.92 17.90	13.65 13.64	- -	13.19

### 3. RESULTS AND DISCUSSION

The Lanthanum(III) complexes are colored, stable and non-hygroscopic in nature. The elemental analyses shows that, all the Lanthanum(III) complexes have 1:1 stoichiometry of the type La(III)LNO<sub>3</sub>·H<sub>2</sub>O, La(III)LCI·H<sub>2</sub>O and La(III)NCS·H<sub>2</sub>O respectively. The molar conductance values are too low to account for any dissociation of the complexes in DMF, indicating the non-electrolytic nature of the complexes (Table 1).

In order to establish whether water molecule present in the complexes coordinated to the metal ion, weighed complexes (1) and (2) were dried over P<sub>2</sub>O<sub>5</sub> in a vacuum for *ca* 1h and then weighed again. No loss in weight was observed.

This was confirmed by heating the complexes for *ca.* 2 h at 105 °C and no weight loss was observed. These observations suggest the water molecule in the complexes is coordinated to the metal ion.

#### 3. 1. Infrared Spectra

The important diagnostic bands in the IR spectra were assigned and the bands positions are given in Table 2.

**Table 2.** Important Infrared Frequencies (in cm<sup>-1</sup>) of lanthanum(III) complexes of 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases along with their assignments.

Complex No	$\nu$ (OH)	N(CN)	Thiamide I	Thiamide II	Thiamide III	Thiamide IV	N(M-N)	N(M-S)	$\nu$ M-Cl)
1	3400br	1625s	1580s 1555s	1320m	1040m	670m	430m	230m	-
2	3400br	1620s	1590s 1530m	1325m	1040m	675m	435m	245m	-
3	3400br	1615s	1599s 1525m	1320m	1050m	670m	430m	240m	-
4	3400br	1620s	1580s 1530m	1325m	1959m	670m	440m	245m	-
5	3400br	1620s	1585s 1530s	1330m	1050m	675m	460m	250m	-
6	3400brs	1625s	1590s 1520s	1340m	1040m	670m	460m	250m	-
7	3400br	1620s	1590s 1525s	1335m	1045m	675m	445m	260m	-
8	3400br	1625s	1585s 1535s	1335m	1040m	670m	450m	265m	-
9	3400br	1620s	1590h 1555s	1330m	1045m	665m	435m	280m	-
10	3400br	1615s	1590s 1550s	1330m	1045m	670m	445m	275m	-
11	3400br	1620s	1585s 1545s	1335m	1040m	680w	460m	270m	-
12	3400br	1625s	1590s 1540s	1330m	1050m	680w	455m	265m	-
13	3400br	1620s	1580m 1535m	1345s	1040m	670w	430m	280m	245m
14	3400br	1615s	1590m 1520m	1340s	1045m	675w	435m	235m	250w
15	3400br	1610s	1595m 1525m	1320s	1040m	670m	455m	240m	245m

16	3400br	1615s	1585m 1520m	1325s	1050m	675m	440m	255m	240w
17	3400br	1620s	1590m 1540m	1330m	1045m	670m	440m	260m	245w
18	3400br	1610s	1580m 1540m	1340s	1050m	670m	445m	275m	250m
19	3400br	1615s	1585m 1540m	1345s	1045m	680m	450m	270m	250m
20	3400br	1615s	1590m 1530m	1340s	1050m	680m	450m	265m	255m
21	3400br	1615s	1590m 1530m	1320s	1040m	670w	460m	280m	250w
22	3400br	1610s	1590m 1530m	1325s	1050m	680m	445m	270m	245m
23	3400br	1620s	1555m 1535m	1340s	1045m	680w	435m	275m	240m
24	3400br	1615s	1590m 1525m	1345s	1040m	675w	430m	260m	245m
25	3400br	1620s	1580m 1540m	1345s	1040m	670m	430m	280m	-
26	3400br	1610s	1590m 1530m	1330s	1040m	675m	440m	245m	-
27	3400br	1615s	1580m 1540m	1340s	1050m	675m	445m	245m	-
28	3400br	1610s	1590m 1530m	1345m	1050m	670m	450m	240m	-
29	3400br	1615s	1590m 1535m	1340m	1045m	680m	445m	255m	-
30	3400br	1620s	1585m 1530m	1345m	1040m	680m	450m	260m	-
31	3400br	1610s	1580m 1530m	1340m	1040m	680m	450m	280m	-
32	3400br	1610s	1580m 1540m	1340m	1040m	670w	445m	275m	-
33	3400br	1615s	1590m 1540m	1340m	1050m	675w	450m	240m	-
34	3400br	1620s	1585m 1545m	1335m	1045m	675m	440m	255m	-
35	3400br	1610s	1590m 1550m	1340m	1040m	670w	445m	275m	-
36	3400br	1620s	1585m 1530m	1345m	1045m	670w	445m	280m	-

All the complexes do not show a broad medium band in the region 3280-3140  $\text{cm}^{-1}$  nor do they show band centered around 2400  $\text{cm}^{-1}$  due to  $\nu(\text{NH})$  and  $\nu(\text{SH})$  vibrations of the ligands. The characteristic band of  $\nu(\text{C}=\text{S})$  around 740  $\text{cm}^{-1}$  in the ligands becomes weak and shifts to lower frequency i.e around 670  $\text{cm}^{-1}$ . These observations favor that, the ligand reacts with metal ion in thiol form via deprotonation. This agrees with the elimination of two of three nitrate ions originally present in the metal salt. Further this confirms the involvement of sulphur donor atom in coordination to the metal ion. The bands due to thiamides-I,II,III vibrations are located in the same region as appeared in the corresponding ligands. The another characteristic band of medium to high intensity band due to  $\nu(\text{C}=\text{N})$  occurring around 1635  $\pm 5$   $\text{cm}^{-1}$  in the ligands is observed at 1625-1610  $\text{cm}^{-1}$  in the complexes indicating that,

the C=N groups of the ligand have coordinated to the metal ion through nitrogen<sup>19</sup>. That confirms the presence of the salicylidene residue<sup>4</sup>. These observations suggest that, the ligand reacts with metal ion through all its coordinating centers.

In addition to the above band all the complexes of the type LaLNO<sub>3</sub>·H<sub>2</sub>O exhibit some new bands appear around 1505, 1290, 1030, 845, 745 and 705 cm<sup>-1</sup> which are attributed to  $\nu_4$ ,  $\nu_1$ ,  $\nu_2$ ,  $\nu_6$ ,  $\nu_3$  and  $\nu_5$  vibrations of coordinated (C<sub>2v</sub>) nitrate group respectively<sup>20,21</sup>. Since the separation between  $\nu_4$ -  $\nu_1$  and  $\nu_3$ -  $\nu_5$  are in the range of 215-210 cm<sup>-1</sup> and 40-45 cm<sup>-1</sup> respectively indicating that, nitrate group is coordinated in the bidentate fashion, which is ascertained by comparing the present data with recent paper<sup>22,5</sup>.

The complexes of LaNCS·H<sub>2</sub>O exhibit the N-bonded mode of coordination of thiocyanate group which is confirmed by the appearance of the bands around 2105, 785 and 475 cm<sup>-1</sup>, which are assigned to  $\nu(\text{C}=\text{N})$  of NCS and  $\nu(\text{C}=\text{S})$  of NCS and NCS bending vibrations respectively. This is further supported by an additional band due to  $\nu(\text{La}-\text{N})$  vibration which has been found to appear around 285 cm<sup>-1</sup>. This is further supported by an additional band due to  $\nu(\text{La}-\text{N})$  vibration which has been found to appear around 285 cm<sup>-1</sup>.

The complexes of the type LaLCl·H<sub>2</sub>O show the band due to  $\nu(\text{La}-\text{Cl})$  at 250 cm<sup>-1</sup> which is assigned in view of previous reports<sup>23</sup>. Metal ligand vibrations are difficult to assign on the empirical bases since their frequencies are sensitive to the metal ligand. A comparison of IR spectra between ligand and its metal complexes fail to give clear cut assignment because some ligand vibrations activated by complex formation which may appear in the same region as metal ligand vibrations. In the far IR spectra of the complexes of the several bands observed, some of them have been assigned tentatively to  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$  vibrations<sup>24,25</sup>. All the complexes show medium intensity bands in the region 430-460 cm<sup>-1</sup> has been considered to be due to  $\nu(\text{M}-\text{N})$  and the high intensity bands found in the 280-230 cm<sup>-1</sup> region may be regarded due to  $\nu(\text{M}-\text{S})$  vibration.

### 3. 2. NMR Spectra

The NMR spectra of lanthanum(III) complexes of the ligands, the signal due to NH proton disappears suggesting that, the ligands react with the metal ion in thiol form via deprotonation. This observation supports IR inferences. The another characteristic signal due to azomethine proton in the complex of ligand I appears at 8.4 ppm indicates a downfield shift with respect to ligand I (8.2 ppm). This observation suggests the coordination of the azomethine moiety through the nitrogen to the metal ion. A further support for coordination of C=N nitrogen to the downfield shift of the aromatic proton signals appear in the range of 7.2-8.3 ppm with respect to ligand No. IX (6.9-7.9 ppm). A signal due to water proton in the complexes appears at 5.4 and 5.6 ppm respectively. The signal due to CH=N of triazole ring of the complex 9 ppm appeared at 8.44 ppm. All these observations provide support for the IR inferences.

### 3. 3. ESI-mass studies

The ESI-mass spectra of (C<sub>6</sub>H<sub>4</sub>N<sub>8</sub>S<sub>2</sub>)LaNO<sub>3</sub>·H<sub>2</sub>O complex with Schiff base I have been studied. In the spectrum of (C<sub>6</sub>H<sub>4</sub>N<sub>8</sub>S<sub>2</sub>)LaNO<sub>3</sub>·H<sub>2</sub>O complex the molecular ion peak M<sup>+</sup> is observed at m/z 471 which is equivalent to its molecular weight.

### 3. 4. Electronic Spectra

All these complexes show a very broad band around 450 nm in the visible region, which is assigned to L→M charge transfer transition.

### 3. 5. Biological activity

The biological activity of the newly synthesized Schiff base and its lanthanum(III) complexes has been studied for their antibacterial and antifungal activities by cup plate method<sup>26</sup>. The microbial results are systematized in Table 3.

**Table 3.** Biological Results of 3-Substituted-4-amino-5-mercapto-1,2,4 triazole Schiff bases and lanthanum(III) complexes.

Ligand No	R	R'	Activity Against*			
			Bacteria B. cirrafigellosus	Bacteria E. coli	Fungi C. albicans	Fungi A. niger
I	H	H	13	12	18	13
II	CH <sub>3</sub>	H	15	13	20	13
III	C <sub>2</sub> H <sub>5</sub>	H	15	13	16	13
IV	C <sub>3</sub> H <sub>7</sub>	H	14	14	19	12
V	H	CH <sub>3</sub>	15	17	13	17
VI	CH <sub>3</sub>	CH <sub>3</sub>	14	13	14	21
VII	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	16	14	16	19
VIII	C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	17	15	18	19

Metal complexes of lanthanum(III) complexes LaLNO<sub>3</sub>·H<sub>2</sub>O

Ligand No	Complex No	Activity Against*			
		Bacteria B. cirrafigellosus	Bacteria E. coli	Fungi C. albicans	Fungi A. niger
I	1	17	18	13	20
II	2	22	19	12	18
III	3	18	11	10	20
IV	4	21	12	14	16
V	5	12	14	13	15
VI	6	13	19	17	12
VII	7	10	20	18	19

Metal complexes of lanthanum(III) complexes LaLCl·H<sub>2</sub>O

Ligand No	Complex No	Activity Against*			
		Bacteria B. cirrafigellosus	Bacteria E. coli	Fungi C. albicans	Fungi A. niger
I	1	21	12	14	16
II	2	17	18	13	17
III	3	19	20	21	14
V	5	12	17	16	20
VI	6	16	18	14	15
VII	7	18	16	13	15

\*Zone of inhibition in mm



DMF 0.1 ml solvent control	11	11	11	11
Sulphomethoxazole (20 mcg)	20	20	-	-
Gentamycin (10 mcg)	24	24	-	-
Nystatin (50 IU)	-	-	23	25

Key for interpretation

Less than 13 = Inactive, 13-16 = weakly active, 17-20 = moderately active, > 25 highly active.

The Schiff bases and their metal complexes were evaluated for antimicrobial activity. The results of the bactericidal study of the synthesized compounds are displayed in Table 3, the compound VIII is moderately active whereas rest of the compounds are weakly active against *B. cirrafigellosus*. The compound I is inactive, the compounds II,III,IV,VI,VII and VII are weakly active and compound is moderately active against *E. coli*.

Amongst these compounds, III,V,VI and VII are weakly active against *C. albicans* whereas compounds I,II,IV and VIII exhibit moderate activity against the same organism. Amongst these, compound II exhibits high activity than the other compounds. Of all the ligands (Table 3) only three ( viz, I, II and III) are weakly active against the *A.niger*, whereas V,VII and VIII are moderately active against the same organism. The compound VI exhibits highest activity (21mm) than the remaining compounds against *A. niger*.

Of the lanthanum(III) complexes of the type  $\text{LaLNO}_3 \cdot \text{H}_2\text{O}$ , 1 and 3 have shown moderate activity, 2 and 4 exhibit high activity, 6 has shown weak activity and the remaining complexes are inactive to *B. cirrafigellosus*. The complexes 1,2,6 and 7 are moderately active, 3 and 4 are inactive whereas, 5 is weakly active against *E. coli*. These complexes are either inactive or weakly active against *C. albicans* except 6 and 7, which are moderately active to the same organism. Of these 1,2,3 and 7 are moderately active whereas, 4 and 5 are weakly active to the *A. niger*. Complex 6 is inactive to same organism. In case of complexes of the type  $\text{LaLCl} \cdot \text{H}_2\text{O}$ , 1 is highly active, 2,3 and 7 are moderately active, 6 is weakly active and 5 is inactive to *B. cirrafigellosus*, 1 is inactive and 7 is weakly active to *E. coli*. The remaining compounds are moderately active towards the same organism. In the study of antifungal activity only complex 3 is highly active (21 mm) and remaining compounds are weakly active against *C. albicans*. The complexes 2 and 5 are moderately active and the remaining compounds are weakly active to *A. niger*.

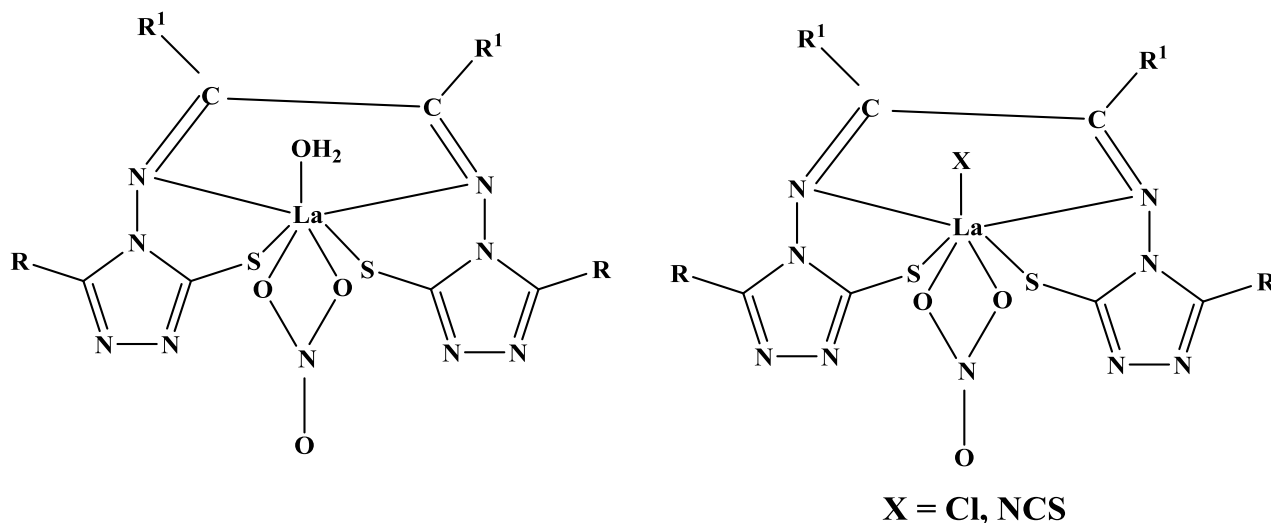
The antibacterial and antifungal studies suggested that, all the Schiff bases were found to be biologically active and some of their metal complexes showed significantly enhanced antibacterial and antifungal activity. It is, however, known that, chelating tends to make the Schiff bases act as more powerful and potent bacteriostatic agents, thus inhibiting the growth of bacteria and fungi more than the parent Schiff bases. It is suspected that, factors such as solubility, conductivity, dipole moment and cell permeability mechanism (influenced by the presence of metal ions) may be the possible reasons for the increase in activity.

#### 4. CONCLUSION

The analytical data and general behavior of the complexes suggest the empirical formula of the complexes as  $\text{LaLNO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{LaLCl} \cdot \text{H}_2\text{O}$  and  $\text{LaLNCS} \cdot \text{H}_2\text{O}$ . The molar values suggest non-electrolytic behavior of the complexes. The IR and NMR spectra suggest dibasic

tetradentate behavior of the ligands coordinating through the azomethine nitrogen and through the sulphur atom in thiol form of the ligand. IR spectral data indicate the coordination of nitrate, chloride and thiocyanate to the metal ion.

Antibacterial and antifungal study reveals that Schiff bases and some metal complexes of lanthanum(III) complexes were found to be highly active against antibacterial and antifungal activity. All these observations taken together suggest that, a seven coordination around lanthanum(III) in the complexes of the type  $\text{LaLNO}_3 \cdot \text{H}_2\text{O}$  and lanthanum(III) ion exhibits coordination number six in the complexes of the type  $\text{LaLCl} \cdot \text{H}_2\text{O}$  and  $\text{LaLNCS} \cdot \text{H}_2\text{O}$ .



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