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Thermal and Antibacterial Studies of Novel Lanthanide–Schiff Base Complexes

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Novel lanthanide complexes with the general formula $[\text{Ln}(\text{L})(\text{ONO}_2)(\text{H}_2\text{O})_2]$ have been synthesized and characterized. {L = 5-bromosalicylidene 4-amino 3-mercapto-1,2,4-triazine-5-one (BrSAMT), Ln = La(III), Ce(III), Pr(III), Eu(III), Sm(III), Nd(III), Tb(III), Dy(III), and Y(III)}. The thermal, magnetic, molar conductance, and spectral studies confirm that the ligand coordinates through sulfur, azomethine nitrogen, and phenolic oxygen. A scheme of thermal decomposition of the complexes is also proposed. La, Eu, and Yb complexes of BrSAMT show antibacterial activity against gram negative bacteria such as *E. coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, and *Shigella flexneri*.

Keywords antibacterial studies, lanthanide complexes, thermal studies, triazines

INTRODUCTION

The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur, and/or oxygen as ligand atoms has attracted increasing attention. It is well known that the heterocyclic compounds exhibit bactericidal, fungicidal, herbicidal, and insecticidal activities in addition to their application as potential drugs. Such heterocyclic ligands, when complexes with metal ions, exhibit enhanced microbiological activities.^[1,2] The role of microelements in biochemical processes is well documented.^[3,4] 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.^[5] The chemistry of lanthanide complexes with Schiff bases has received little attention compared with the *d* block metal complexes.

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Triazole chemistry is becoming more important study due to its excellent biological activity. The triazole antifungal drugs include fluconazole, isavuconazole, itraconazole, voriconazole, pramiconazole, and posaconazole. The triazole plant protection fungicides include epoxiconazole, triadimenol, propiconazole, metconazole, cyproconazole, tebuconazole, flusilazole, and paclobutrazol.

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.^[6] The number of reports on lanthanide Schiff base complexes is very scant. However few groups have reported some Schiff bases with lanthanides.^[7–10]

In the present work synthesis and characterization of complexes of 5-bromosalicylidene 4-amino 3-mercapto-1,2,4-triazine-5-one with La(III), Ce(III), Pr(III), Eu(III), Sm(III), Nd(III), Tb(III), Dy(III), and Y(III) has been undertaken.

EXPERIMENTAL

Methods

The metal content of these complexes were estimated gravimetrically using oxalate oxide method. Infrared spectrum was recorded on ABB BOMEM (Canada) FT-IR spectrophotometer; carbon hydrogen nitrogen and sulfur were analyzed on Thermo Flash EA 112 series CHN analyzer (Italy). Magnetic susceptibilities were determined using Sherwood Scientific Magnetic Susceptibility meter (Cambridge, UK), electronic spectra of complexes in DMF on GBC model UV-visible spectrophotometer. Thermogravimetric analysis (TGA) was carried out by TG-DTA analyzer SII EXSTAR 6000 (UK) and molar conductance by Elico 32 conductivity meter (India). NMR spectra were recorded on Bruker AMX400 spectrometer (Madison, WI, USA) at Indian Institute of Science, Bangalore.

Synthesis of Ligand

The ligand was synthesized in two steps. In the first step 0.76 g of 50% glyoxylic acid was taken in 0.7 mL of water. To this a solution of 1.07 g of thiocarbonylhydrazide in 12 mL of water was

added, and refluxed for 1 h, cooled, and the resultant yellowish white precipitate of 4-amino 3-mercapto-1,2,4-triazine-5-one was filtered, dried, and recrystallized.^[11]

In the second step, to a solution of 0.1 mol of 4-amino-3-mercapto-1,2,4-triazine-5-one in 10 mL of ethanol, and 0.1 mol of 5-bromosalicylaldehyde was refluxed for 4 h, cooled, filtered, washed with water, dried, and then recrystallized from absolute alcohol. The yellow-colored 5-bromosalicylidene-4-amino-3-mercapto-1,2,4-triazine-5-one (BrSAMT) was dried in a desiccator. The ligand was characterized using elemental analysis, IR spectroscopy, and NMR spectroscopy.

For Ligand, Yield: 60%; Anal. Calcd. for $C_{10}H_6BrN_4O_2S$: C, 36.4; H 2.1; N, 17.0; S 9.7. Found: C, 36.5, H, 2.1, N, 17.2, S, 9.7; IR (KBr, cm^{-1}): 1690 s ($-C=O$ stretching of $-CO$ in triazole group), 1650 ($C=N$ stretching of azomethine group), 1550, 1270, 900, and 800 cm^{-1} (thioamide bands I, II, III, and IV); 1H NMR (200 MHz, DMSO-*d*₆, δ/ppm): 11.24 (1H, s, $-SH$), 8.1 (1H, s, $CH=N$), 6.24–8.76 (3H, *m*, aromatic, $J = 7.8$ Hz).

Synthesis of Complexes

A hot solution of the ligand BrSAMT (4 mmol) in 25 mL of ethanol was added to boiling solution of lanthanide nitrate (2 mmol) in 10 mL ethanol. The resulting solution was refluxed for about 2 h. Colored solid separated was filtered and washed with ethanol followed by ether. The complex was dried in a desiccator. La(III), Ce(III), Nd(III), Eu(III), Dy(III), Y(III), Tb(III), Pr(III), and Sm(III) metal ions were used.

Biological Tests

All the complexes were screened for their *in vitro* antibacterial activity against pathogenic strains of bacteria such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Bacillus subtilis*, and *Shigella flexneri* using plate technique. The bacteria were cultured (15 mm dia) in a previously sterilized Mueller Hinton agar medium in a Petri dish and used as inoculum for the study. The components to be tested were dissolved in DMF to a final concentration of 0.5% and 1% and soaked in filter paper discs of 5 mm diameter and 1 mm thickness. These discs were placed on the previously seeded plates and incubated at $35 \pm 2^\circ C$ for 24 h. The diameter (mm) of the inhibitory zone around each disc was measured after 24 h.

RESULTS AND DISCUSSION

Analytical

The results show that the complexes of BrSAMT with La(III), Ce(III), (Pr(III) Nd(III), Sm(III), Eu(III), Tb(III), Dy(III), and Y(III) nitrates are of ML type with coordinated water molecules having the molecular formula $[Ln(L)(ONO_2)(H_2O)_2]$. All these complexes are non-hygroscopic with varying colors. Conclusive evidences for all the previous type of complexes and its geometry comes from the spectral data. Analytical data are shown in Table 1.

Magnetic Susceptibility

The magnetic susceptibility values show that all the lanthanide nitrate complexes are paramagnetic in nature except La(III) and Y(III) complexes. The results are as shown in the Table 1. The observed magnetic values were compared with that of theoretical spin-orbit coupling values (of the respective lanthanide ions and they agree each other with the exception of Sm and Eu complexes.^[12] However it is found that the experimental values of all the complexes including those of Sm and Eu agree with the theoretical values calculated from the Van Vleck formula. The discrepancies in the case of Sm and Eu complexes may be attributed to the fact that the first excited J states of Sm^{3+} and Eu^{3+} are sufficiently close to their ground states so that these states mix each other even at room temperatures causing increase in the magnetic moments. This is the reason for the breakdown of the spin-orbit coupling models for Sm and Eu complexes. The Van Vleck treatment is more refined since the method takes into account of the excited states also and leads to a closer agreement between the theoretical and experimental values. The fact is that the observed magnetic moments, from the Van Vleck values, suggest the non-participation of 4f electrons in the bond formation.

Molar Conductance

The molar conductivities of lanthanide nitrate complexes in DMF are presented in Table 1. The molar conductance values reveal that the complexes are non electrolytes.^[13] Therefore, one nitrate ion is coordinated to the metal ion and hence the nitrate complexes may be formulated as $[Ln(BrSAMT)(ONO_2)(H_2O)_2]$.

Electronic Spectra

The electronic spectrum of the ligand showed $n-\pi^*$ and $\pi-\pi^*$ transitions at 33333 and 37364 cm^{-1} , respectively. Complex formation with metal ions resulted in a hypsochromic shift of these bands. The absorption bands of Ln(III) in the UV and visible region appear due to transitions from the ground levels 3H_4 , $^4I_{9/2}$, and $^6H_{5/2}$, respectively, to the excited J levels of 4f configuration.^[14] The sharp bands due to *f-f* transition originating within the 4f*n* configuration of lanthanide ions are only slightly affected by the immediate surroundings of the metal ion, and this is commonly attributed to the shielded nature of the 4f orbitals by the overlying $5s^2$ and $5p^6$ orbitals. However, the shift to lower frequency region can be concluded as due to complex formation.^[15]

Infrared Spectra

The ligands shows infrared band at 2900 cm^{-1} , indicating the absorptions $\nu(C-H)$. The ligand also shows the presence of four thioamide bands, I, II, III, and IV, at 1550, 1270, 900, and 800 cm^{-1} , respectively, indicating the presence of thioamide moiety in the ligand molecule. In the spectra of lanthanum complexes, the thioamide band IV, at around 800 cm^{-1} has been shifted

TABLE 1
Analytical, molar conductance, and magnetic susceptibilities of lanthanide BrSAMT complexes

Complex	% Found (calculated)						Molar conductance μS	μ_{eff} BM (theoretical)
	Lanthanide	Carbon	Hydrogen	Nitrogen	Sulfur			
[La(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	24.5 (24.6)	21.3 (21.49)	1.6 (1.6)	12.4 (12.4)	5.6 (5.7)	9.3	Diamagnetic	
[Ce(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	24.7 (24.7)	21.2 (21.2)	1.6 (1.6)	12.2 (12.4)	5.8 (5.7)	5.10	2.59 (2.54)	
[Sm(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	26.0 (26.0)	20.8 (20.8)	1.6 (1.6)	12.3 (12.1)	5.5 (5.6)	4.47	1.85 (0.84)	
[Eu(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	26.3 (26.3)	20.7 (20.8)	1.6 (1.6)	12.1 (12.1)	5.6 (5.5)	4.22	3.48 (3.58)	
[Nd(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	25.4 (25.3)	21.0 (21.0)	1.6 (1.6)	12.5 (12.3)	5.6 (5.6)	3.82	3.60 (3.62)	
[Pr(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	24.8 (24.9)	21.3 (21.2)	1.6 (1.6)	12.3 (12.4)	5.6 (5.6)	5.18	3.63 (3.58)	
[Dy(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	27.6 (27.6)	20.3 (20.4)	1.6 (1.5)	11.8 (11.9)	5.5 (5.4)	4.22	10.79 (10.63)	
[Y(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	17.5 (17.4)	23.2 (23.4)	1.6 (1.8)	13.5 (13.7)	6.1 (6.3)	4.22	Diamagnetic	
[Tb(C ₁₀ H ₆ BrN ₄ O ₂ S)(ONO ₂)(H ₂ O) ₂]	27.2 (27.2)	20.4 (20.5)	1.6 (1.6)	11.3 (12.0)	5.4 (5.5)	4.17	9.64 (9.72)	

TABLE 2
Infrared band positions and probable assignments of BrSAMT ligand and its lanthanide nitrate complexes

Complex	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu_4(\text{NO}_3)$	$\nu_1(\text{NO}_3)$	$\nu_2(\text{NO}_3)$	$\nu(\text{Ln-O})$	$\nu(\text{C-Br})$
	water								
BrSAMT	—	1620 s	1610 m	1310 m	—	—	—	—	669 s
[La(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	480 w	668
[Ce(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	493 w	668
[Sm(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	473 w	669
[Eu(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	458 w	669
[Nd(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	465 w	669
[Pr(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	473 w	669
[Dy(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	464 w	668
[Y(BrSAMT)NO ₃ .3H ₂ O]	3500B	1620 s	1580 m	1350 m	1450 s	1320 s	1020 w	460 w	669

to lower side by 30–40 cm^{-1} , the thioamide band III at around 1180 cm^{-1} has shifted to 20–30 cm^{-1} on the higher side, and the thioamide band I at 1500 cm^{-1} and thioamide band III at 1180 cm^{-1} have less intensity compared with the ligand. These systematic shifts of bands in the IR spectra of the complexes, supports the bond formation through both nitrogen and sulfur atoms of the ligand. The lanthanum complexes exhibit a broad band at around 3500 cm^{-1} and at 890 cm^{-1} indicating that the metal ion is coordinated to water molecules. The band at 1620 cm^{-1} , corresponding to $\nu(\text{C=O})$ of the carbonyl group, in the ligand is not altered in the complexes. This shows the non-participation carbonyl group in the bonding. The bands at 1610 and 1580 cm^{-1} in the ligand and the complexes corresponds to that of $\nu(\text{C=N})$ of the azomethine linkage, and the shift in frequency to lower wave number side indicates the coordination

of the nitrogen of this group with the metal ions.^[16, 17] In the complexes the band at 1300 cm^{-1} , due to the phenolic group, is shifted to higher wave number side indicating the involvement of phenolic oxygen in the coordination with the metal. The peak around 754 cm^{-1} of the ligand shifts in the complexes indicating that the sulfur atom is involved in bonding. It is also evident from the IR spectra of complexes, the presence of four bands at 1415, 1310, 1020, and 450 cm^{-1} . The first three are assigned respectively to ν_4 , ν_1 , and ν_2 vibrational modes of the coordinated nitrate ions. In fact, the ν_1 and ν_4 modes of nitrate ion are the split bands of the ν_3 mode of the uncoordinated nitrate ion. The magnitude of the separation between ν_4 and ν_1 is at 105 cm^{-1} . This type of splitting suggests that the nitrate ion is coordinated unidentately to the metal through oxygen atom. The results are tabulated in Table 2.

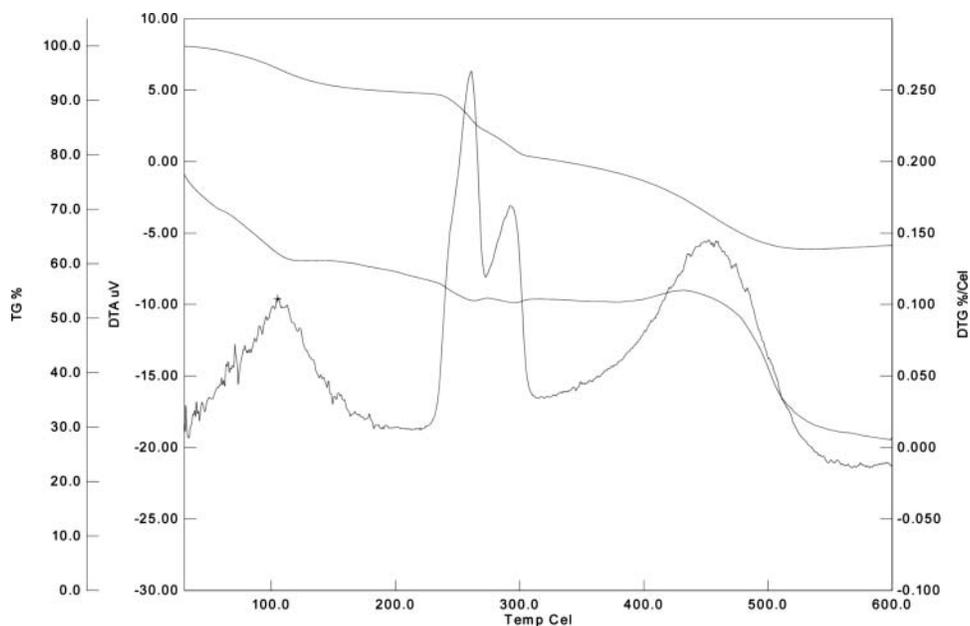


FIG. 1. TG-DTA curve of La(BrSAMT)(ONO₂)(H₂O)₂ complex.

on the normal cell process.^[24] Furthermore, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine nitrogen atom with the active centers of cell constituents, resulting in interference with the normal cell process.^[25,26]

CONCLUSIONS

On the basis of analytical, magnetic, molar conductance, and spectral data, it can be concluded that the ligand molecule coordinates to the metal ion through sulfur, phenolic oxygen, azomethine nitrogen atoms; two water molecules; and one nitrate group (Figure 2). The thermal data show that complexes are air stable up to 250°C. La, Eu, and Y complexes of Br-SAMT show antibacterial activity against pathogenic strains of gram negative bacteria such as *E. coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Bacillus subtilis*, and *Shigella flexneri*.

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