

Synthesis and Characterization of Rare Earth Chelates (La^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} and Tb^{2+}) with salicylates (2, 4-dihydroxy benzoic acid and 2-hydroxy-5-sulpho benzoic acid)

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Abstract: *The present study deals with the synthesis, characterization, thermal stability and structural elucidation of chelates of salicylates (2, 4 dihydroxy benzoic acid and 2-hydroxy 5-sulpho salicylic acid) with rare earth metals (La^{3+} , Pr^{3+} , Nd^{3+} , Eu^{3+} and Tb^{2+}). The structural elucidation of synthetic chelates was carried out by X-ray diffractometer. The chelates were characterized by FTIR and thermal stability was checked out by TGA/DTA and DSC.*

Keywords: Chelates, Salicylates, Rare earth metals, XRD, FTIR

1. Introduction

With the advent of modern technology the use of Rare Earth metals has increased many folds. In technology these are of great importance because of the production in numerous devices [1]. Major attractions for Rare Earth metals usage in technical devices is their environment friendliness. They are also used in refractories, ceramics, abrasives, agriculture, lamps, paints, and textile and leather industry. In fact in this globalization world the uses of Rare Earth metals are immense. They are used in products which are necessary for routine life like mobile phones, plasma televisions, disk drivers etc. Other general uses of Rare Earth metals are their application in production of Rechargeable batteries, Catalytic converters, in lasers and nuclear science [2]. Salicylate has effective use in dermatology. Its use in dermatology and cosmetics is due to its ability to rapid effect as a keratolytic agent. It is used for food preservation and mild antiseptic. Salicylic compounds have been used to make analgesics and antipyretics. It is also used as flavoring agent in small quantities. It is used to give fragrance in some products. Salicylates are well known in medical science for their ability to lessen the aches, pains and fevers. Since ancient times it is being used as a cure for fever. It has also been used as an anti-inflammatory drug [3] even it has been given the study of vitamins by some scientists with the name as vitamin S [4]. due to its essence as micro nutrient in the human diet. Warts could be cured and controlled by using Salicylates [5]. Salicylate is the class of compounds, most widely used as drugs but rare earth metals enhance the biological effects of salicylates. It is evident from literature that salicylates are used as drugs [6]. The chelates of rare earth elements are useful to check out the antibacterial activity because it is having an excellent antibacterial ability for testing bacterium [7] and also used for the detection of bacterial spores [8]. These are also applicable for the

determination of grepafloxacin in human urine and serum [9]. Rare earth metal chelates are used as chemical sensors for the quantitative analysis of salicylate [10]. In the construction of bonding structures these complexes also have utility [11]. In electrochemical industries these complexes are used as the excellent material for the modification of electrodes with excellent sensitivity and recovery. Because of above mentioned applications of rare earth chelates synthesis of these compounds is of great importance. In the present study, a systematic work on the chelation of various salicylates with rare earth metals like La, Tb, Eu, Pr and Nd has been undertaken and for the characterization of complexes, FTIR spectra has been recorded and described, for the structural elucidation the patterns of x-rays diffraction of complexes has been formed and compared with starting materials and Thermo gravimetric, differential thermal and differential scanning (TGA/DTA and DSC) analysis has been used for the investigation of thermal stabilities of various prepared complexes.

2. Literature Survey

The rare earth salicylates form an interesting series of compounds, whose properties are of scientific as well as technological interest [12]. It is evident from literature that salicylates drugs are used to induce reversible tinnitus and hearing loss but it acts extracellularly, only reduced not completely blocked. Whereas complete blockage occur by addition of lanthanide in it and drug acts as intracellular [13]. Rare earth elements possess bioactivities. That's why their complexes with different ligands are important antimicrobial agents and can be utilized as antibiotics [14]. Rare earth salicylates act as anticoagulants and their amino acid complexes are used as proteins and enzymes.

Rare earth metal chelates are used as chemical sensors for the quantitative analysis of salicylurate [15]. Strong antifungal properties have been evaluated for chelates of 4-substituted salicylic acid with ligands and by rare earth complexes obtained after reactin. In electrochemical industries these complexes are used as the excellent material for the modification of electrodes with excellent sensitivity and recovery [16].

3. Experimental

Following analytical grade chemicals were used: 2,4-dihydroxy benzoic acid, 2-hydroxy-5-sulpho benzoic acid, potassium bicarbonate (E.merck). Nitrates of rare earth metals including lanthanum, terbium, europium, praseodymium and neodymium (E.merck). All the apparatus

used were washed with detergent, rinsed with tap water and then washed with deionized water for 3 times. The chemicals used for different analysis were of high purity. Complexes of 2, 4-dihydroxybenzoic acid and 2-hydroxy-5-sulphobenzoic acid with rare earth metals (La, Tb, Eu, Pr and Nd) were prepared as to 2,4-dihydroxy benzoic acid (0.077g; 0.02 mol) was dissolved in potassium bicarbonate (2.00 g; 0.02 mol) in water (25 mL) was added lanthanum (III) nitrate (0.216 g; 0.02 mol) in water (25mL) slowly but with constant stirring for one hour. The white precipitates thus obtained were filtered off, washed several times with water. The product was dried and kept under vacuum for several hours to get white complex (IA) (0.163 g; 98.5%). The same procedure is repeated for all the metals and other ligands. Details are given in Table-1 and Table-2.

Table 1: Data of chelates of rare earth metals (La, Tb, Eu, Pr and Nd) with 2,4-dihydroxy benzoic acid

Ligands	Rare Earth Metals	Metal to Ligand Ratio	Colour of Precipitates	Percentage Yield
2, 4 dihydroxy benzoic acid	Lanthanum (III) nitrate	1:1	White	98.56%
2, 4 dihydroxy benzoic acid	Lanthanum (III) nitrate	1:2	White	68.72%
2, 4 dihydroxy benzoic acid	Lanthanum (III) nitrate	1:3	White	52.45%
2, 4 dihydroxy benzoic acid	Terbium (II) nitrate	1:1	White	97.98%
2, 4 dihydroxy benzoic acid	Terbium (II) nitrate	1:2	White	96.21%
2, 4 dihydroxy benzoic acid	Terbium (II) nitrate	1:3	White	76.67%
2, 4 dihydroxy benzoic acid	Europium (III) nitrate	1:1	White	94.91%
2, 4 dihydroxy benzoic acid	Europium (III) nitrate	1:2	White	57.24%
2, 4 dihydroxy benzoic acid	Europium (III) nitrate	1:2	White	57.24%
2, 4 dihydroxy benzoic acid	Europium (III) nitrate	1:3	White	63.85%
2, 4 dihydroxy benzoic acid	Praseodymium (III) nitrate	1:1	Light pink	98.32%
2, 4 dihydroxy benzoic acid	Praseodymium (III) nitrate	1:2	Light pink	63.66%
2, 4 dihydroxy benzoic acid	Praseodymium (III) nitrate	1:3	Light pink	45.33%
2, 4 dihydroxy benzoic acid	Neodymium (III) nitrate	1:1	Light green	98.76%
2, 4 dihydroxy benzoic acid	Neodymium (III) nitrate	1:2	Light green	25.24%
2, 4 dihydroxy benzoic acid	Neodymium (III) nitrate	1:3	Light green	71.99%

Table 2: Data of chelates of rare earth metals (La, Tb, Eu, Pr and Nd) with 2-hydroxy-5-sulphobenzoic acid

Ligands	Rare Earth Metals	Metals to Ligand Ratio	Colour of Precipitate	Percentage Yields
2-hydroxy,5-sulpho benzoic acid	Lanthanum (III) nitrate	1:1	White	78.58%
2-hydroxy,5-sulpho benzoic acid	Lanthanum (III) nitrate	1:2	White	22.38%
2-hydroxy,5-sulpho benzoic acid	Lanthanum (III) nitrate	1:3	White	12.51%
2-hydroxy,5-sulpho benzoic acid	Terbium (II) nitrate	1:1	White	80.64%
2-hydroxy,5-sulpho benzoic acid	Terbium (II) nitrate	1:2	White	25.85%
2-hydroxy,5-sulpho benzoic acid	Terbium (II) nitrate	1:3	White	10.74%
2-hydroxy,5-sulpho benzoic acid	Praseodymium (III) nitrate	1:1	Light pink	69.35%
2-hydroxy,5-sulpho benzoic acid	Praseodymium (III) nitrate	1:2	Light pink	21.20%
2-hydroxy,5-sulpho benzoic acid	Praseodymium (III) nitrate	1:3	Light pink	10.29%
2-hydroxy,5-sulpho benzoic acid	Neodymium (III) nitrate	1:1	Light green	72.16%

The FTIR spectra for the complexes and the spectra for 2, 4-dihydroxybenzoic acid and 2-hydroxy-5-sulphobenzoic acid were recorded as KBr discs on M-2000 spectrophotometer (range 4000-400 cm^{-1}). The X-ray diffraction patterns of the prepared chelates were taken on a D8 diffractometer using Ni-filtered Cu K α radiation. The measurements were made within the range $2\theta = 8-75$. The thermal stabilities of complexes were studied. The TGA, DTA and DSC curves were recorded with SDT M-600 derivatograph at a heating rate of 1°C min with the sensitivity of 10 mg 50 uv. The samples (60 mg) were heated to 900°C in platinum crucibles.

4. Result and discussion

2, 4-Dihydroxybenzoates of rare earth metals were obtained as solids a molar ratio of metal to ligand of 1:1, 1:2 and 1:3 with the general formula $\text{Ln}[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]_n\text{H}_2\text{O}$, $\text{Ln}[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]_2\text{H}_2\text{O}$, $\text{Ln}[\text{C}_6\text{H}_3(\text{OH})_2\text{COO}]_3\text{H}_2\text{O}$. The complexes were prepared as hydrates and all the chelates of La^{III}, Tb^{III}, Eu^{III}, Pr^{III} and Nd^{III} are crystalline in nature showed by the results of XRD and all the complexes of different ratios are isostructural. All rare earth chelates show similar solid-state FTIR given in table 3. However the characteristic frequencies related to the carbonyl group are

altered markedly in going from acid to salt. In the FTIR spectrum of 2, 4-dihydroxybenzoic acid, there is an absorption band at 3610 cm^{-1} due to the valency vibration of the OH group, the band of the COOH group at 1580 cm^{-1} and the stretched band of C-O is at 1258 cm^{-1} . In the FTIR spectra of the prepared complexes, there are bands at $1390 - 1409\text{ cm}^{-1}$ of the COO- group. Broad absorption bands with a maximum at $3380-3310\text{ cm}^{-1}$ and narrow bands at $1620-1605\text{ cm}^{-1}$, confirming the presence of lattice water, and bands of the metal-oxygen bond at $445-475\text{ cm}^{-1}$ as described in table 3. The absorption bands due to the free OH group in the FTIR spectra of the complexes are obscured by the broad

absorption band of the lattice water molecules. The absorption bands of the C-O group at 1258 cm^{-1} are shifted insignificantly relative to the absorption bands in the spectrum of the acid, which suggests that the OH groups do not play any direct part in the coordination of the metal ion. On the basis of the interpretation of the FTIR spectra, the 2, 4 dihydroxy benzoic acid ligand is monodentate, and coordinates the metal through the oxygen of the carboxylate group. Moreover, the band of the asymmetric vibration (COO-) is very strong and is not split, which suggests that all the ligands are coordinated in the same manner.

Table 3: Frequencies (cm^{-1}) of the absorption bands of COO-, O-H, C-O, M-O groups and aromatic ring stretch of 2, 4-dihydroxybenzoic acid and its chelates

Complex	O-H (cm^{-1}) Stretching	COO- (cm^{-1}) vibrations	C-O (cm^{-1})	C=C-C stretch (cm^{-1})	M-O (cm^{-1})
2,4 dihydroxy benzoic acid	3100	1580	1258	1500	----
La[C ₆ H ₃ (OH) ₂ COO]-nH ₂ O	3090	1490	1220	1390	465
La[C ₆ H ₃ (OH) ₂ COO] ₂ -nH ₂ O	3090	1409	1220	1399	465
La[C ₆ H ₃ (OH) ₂ COO] ₃ -nH ₂ O	3090	1490	1310	1390	465
Tb[C ₆ H ₃ (OH) ₂ COO]-nH ₂ O	3090	1509	1320	1399	465
Tb[C ₆ H ₃ (OH) ₂ COO] ₂ -nH ₂ O	3090	1489	1290	1394	466
Tb[C ₆ H ₃ (OH) ₂ COO] ₃ -nH ₂ O	3090	1503	1210	1405	466
Eu[C ₆ H ₃ (OH) ₂ COO]-nH ₂ O	3090	1487	1220	1399	465
Eu[C ₆ H ₃ (OH) ₂ COO] ₂ -nH ₂ O	3090	1510	1220	1410	463
Eu[C ₆ H ₃ (OH) ₂ COO] ₃ -nH ₂ O	3090	1580	1220	1420	460
Pr[C ₆ H ₃ (OH) ₂ COO]-nH ₂ O	3095	1471	1280	1372	465
Pr[C ₆ H ₃ (OH) ₂ COO] ₂ -nH ₂ O	3090	1487	1320	1383	470
Pr[C ₆ H ₃ (OH) ₂ COO] ₃ -nH ₂ O	3090	1481	1320	1378	471
Nd[C ₆ H ₃ (OH) ₂ COO]-nH ₂ O	3090	1476	1320	1378	465
Nd[C ₆ H ₃ (OH) ₂ COO] ₂ -nH ₂ O	3090	1492	1320	1383	469
Nd[C ₆ H ₃ (OH) ₂ COO] ₃ -nH ₂ O	3090	1509	1210	1389	465

Table 4: Frequencies (cm^{-1}) of the absorption bands of COO-, O-H, C-O, M-O groups and aromatic ring Stretch of 2-hydroxy-5-sulphobenzoic acid and its chelates

Complex	O-H (cm^{-1}) Stretching	COO- (cm^{-1}) vibrations	C-O (cm^{-1})	C=C-C stretch (cm^{-1})	M-O (cm^{-1})
2- Hydroxy-5- sulpho benzoic acid (original)	3610	1580	1258	1500	----
La[C ₆ H ₃ (OH) ₂ (SO ₄)COO]-nH ₂ O	3613	1490	1220	1390	465
La[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₂ -nH ₂ O	3620	1409	1220	1399	465
La[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₃ -nH ₂ O	3627	1490	1310	1390	465
Tb[C ₆ H ₃ (OH) ₂ (SO ₄)COO]-nH ₂ O	3608	1509	1320	1399	465
Tb[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₂ -nH ₂ O	3607	1489	1290	1394	466
Tb[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₃ -nH ₂ O	3607	1503	1210	1405	466
Pr[C ₆ H ₃ (OH) ₂ (SO ₄)COO]-nH ₂ O	3605	1471	1280	1372	465
Pr[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₂ -nH ₂ O	3608	1487	1320	1383	470
Pr[C ₆ H ₃ (OH) ₂ (SO ₄)COO] ₃ -nH ₂ O	3610	1481	1320	1378	471
Nd[C ₆ H ₃ (OH) ₂ (SO ₄)COO]-nH ₂ O	3600	1476	1320	1378	465

In the FTIR spectrum of 2-hydroxy-5-sulpho benzoic acid, there is an absorption band at 3610 cm^{-1} due to the valency vibration of the OH group, the band of the COOH group at 1600 cm^{-1} , the stretched band of C-O is at 1290 cm^{-1} and at 668 cm^{-1} a stretched band for sulphate group is appeared. In the FTIR spectra of the prepared complexes, there are bands at $1370 - 1400\text{ cm}^{-1}$ of the COO- group. Broad absorption bands with a maximum at $3380-3310\text{ cm}^{-1}$ and narrow bands at $1620-1605\text{ cm}^{-1}$, confirming the presence of lattice water, and bands of the metal-oxygen bond at $445-475\text{ cm}^{-1}$ as given in table 4. The absorption bands due to the free OH group in the FTIR spectra of the complexes are obscured by the broad absorption band of the lattice water molecules. The absorption bands of the C-O group at 1258 cm^{-1} are

shifted insignificantly relative to the absorption bands in the spectrum of the acid, which suggests that the OH groups do not play any direct part in the coordination of the metal ion. On the basis of the interpretation of the FTIR spectra, the ligand (2-hydroxy-5-sulpho benzoic acid) is monodentate, and coordinates the metal through the oxygen of the carboxylate group. Moreover, the band

of the asymmetric vibration (COO-) is very strong and is not split, which suggests that all the ligands are coordinated in the same manner different fragments after that metal is decomposed in the form of metal oxide at high temperature ($600\text{ }^{\circ}\text{C} - 800\text{ }^{\circ}\text{C}$) Decomposition occurs exothermally in all

the chelates only in case of Eu this change occur endothermally as shown by figure.1—5

2, 4 dihydroxy benzoate hydrates of rare earth elements are stable in air and can be stored for several months without changes. These chelates decompose on heating to the oxides

of rare earth metals. First of all dehydration occurs at lower temperature in the range of 50 °C to 100 °C then ligand is decomposed into

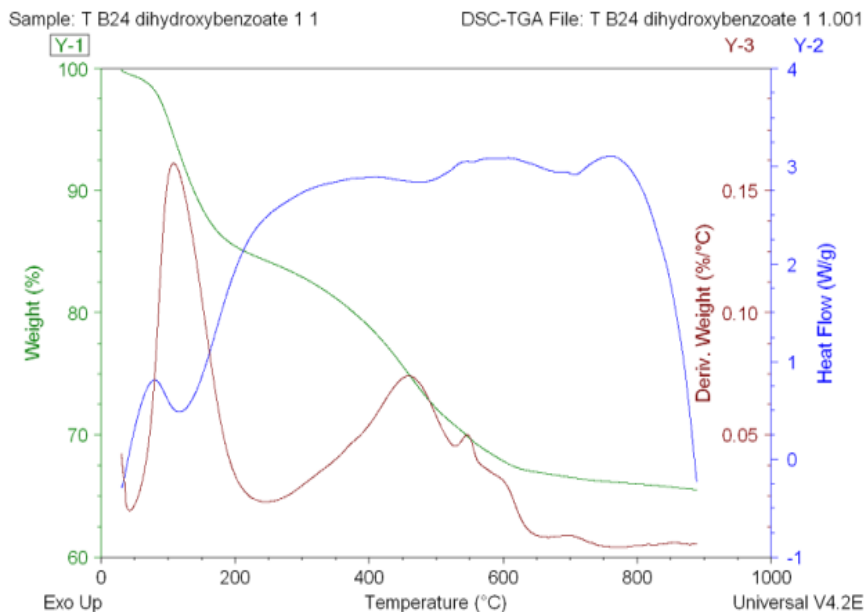


Figure 1: Chelation of 2, 4 dihydroxy benzoic acid withLanthanum in 1:1 ratio

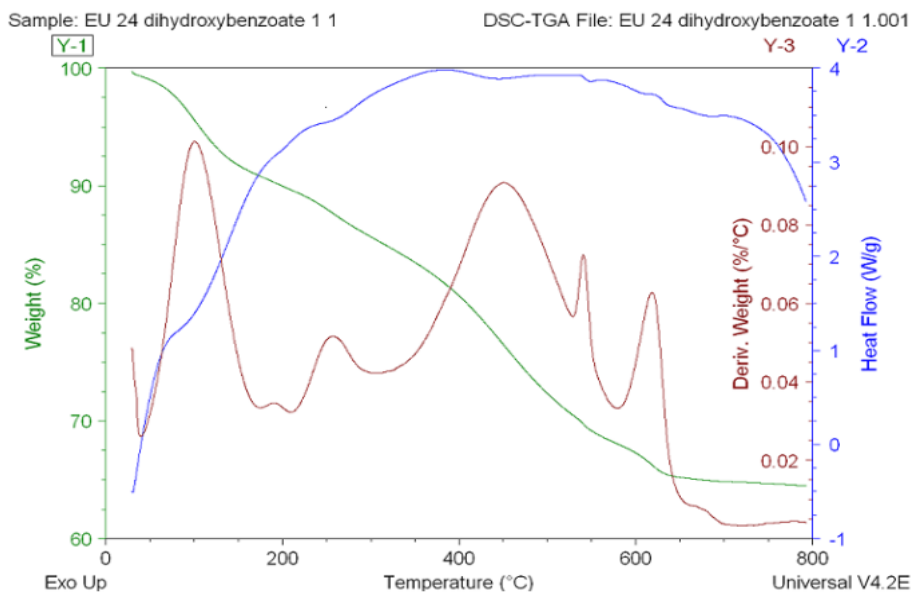


Figure 3: Chelation of 2, 4 dihydroxy benzoic acid withEuropium in 1:1 ratio

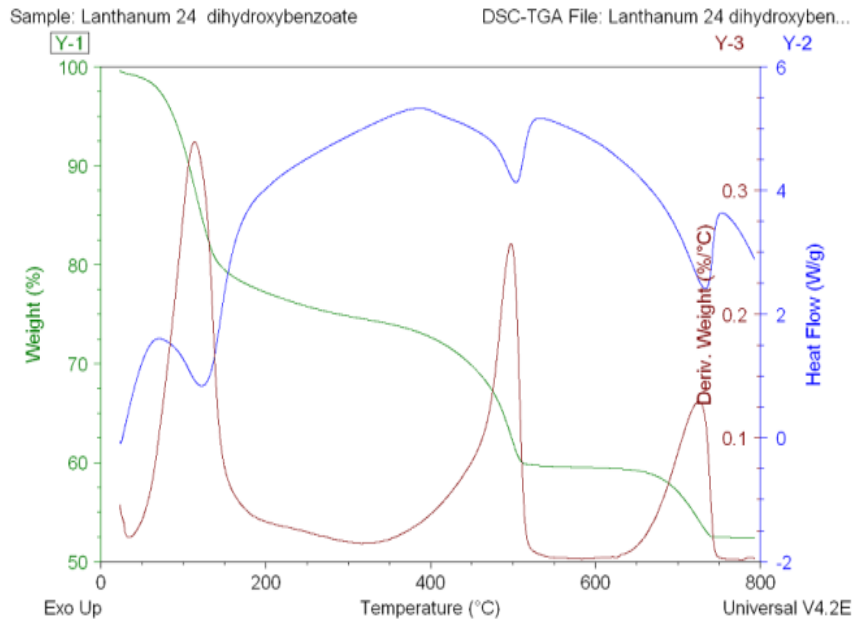


Figure 2: Chelation of 2, 4 dihydroxy benzoic acid withTerbium in 1:1 ratio

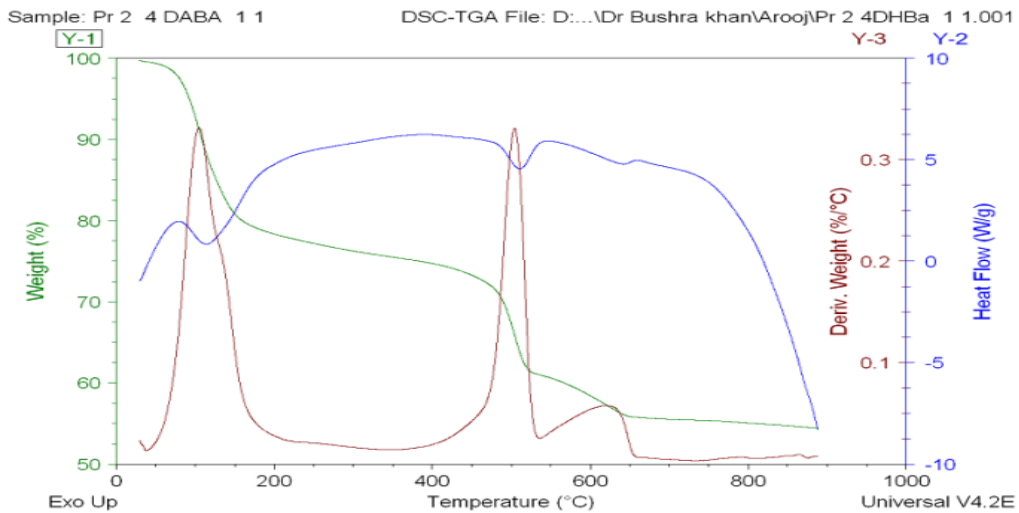


Figure 4:Chelation of 2,4 dihydroxy benzoic acid withPraseodymium in 1:1 ratio

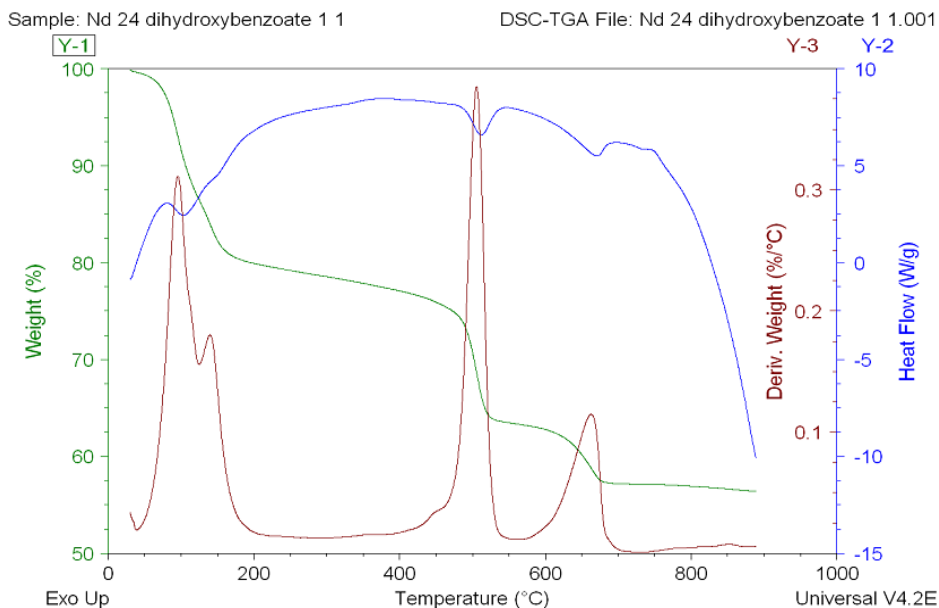


Figure 5: Chelation of 2, 4 dihydroxy benzoic acid withNeodymium in 1:1 ratio

5. Conclusion

The present study was firstly deal with the preparation of rare earth metal derivatives of different salicylates. In this investigation, 2, 4 dihydroxy benzoic acid and 2- hydroxy -5- sulpho benzoic acid were treated with different rare earth metals (La^{III} , Tb^{III} , Eu^{III} , Pr^{III} , Nd^{III}) in different metal – ligand ratios (1:1, 1:2, 1:3). The percentage yield of the synthesized chelates was calculated and their characterizations were investigated by different analytical techniques.

FTIR analysis gives the information that various peaks were shifted and their intensities were changed. Spectra exhibited some new band and also show the disappearance of some absorption this is due to the formation of new bonds by chelation. The information resulted by XRD data is evident that new complexes were formed by chelation of different salicylates with rare earth metal cations. TGA/DTA and DSC gave approval of formation of new chelates. As for as yield is concerned the greatest percentage yield is given by metal-ligand in 1:1, So it is concluded that because of greater binding capacities of above mentioned ligands with rare earth metals give good percentage yield whereas, in case of 1:2 and 1:3 steric hindrance may reduced the binding capacities and decreased the practical yield as expected in the theoretical calculation.

New synthesis, characterization of their compounds with FTIR, structure elucidation with XRD and thermal stability with TGA/DTA and DSC gave conclusion that chelation of rare earth metals with 2, 4 dihydroxy benzoic acid is more favorable as compared to the 2- hydroxy -5- sulpho benzoic acid because 2, 4 dihydroxy benzoic acid contains electron donating group so it provides the electron density to the reaction center whereas 2- hydroxy -5- sulfo benzoic acid having electron withdrawing group that draws the electron away from the center of reaction which is not favored for complexation. So the chelates of 2, 4 dihydroxy benzoic acid give more percentage yield as compared to the 2- hydroxy -5- sulpho benzoic acid.

6. Future Scope

This research methodology provides a simple and an efficient means to synthesize important rare earth metal complexes. It can be used as a template to expand the research over other ligands to produce new library of complexes which may be utilized in different ways for human benefits.

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