Synthesis and Characterization of Rare Earth Chelates (La^{3+}, Pr^{3+}, Nd^{3+}, $Eu^{3+}$and Tb^{2+}) with Salicylate (4-aminosalicylic acid, 2- acetoxybenzoic acid)

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Abstract: ***The present study deals with synthesis and characterization of chelates of Salicylates like (4-amino salicylic acid, 2-acetoxybenzoic acid) with rare earth metals like La^{3+}, Pr^{3+},Nd^{3+}, $Eu^{3+}$and Tb^{2+}. All the compounds were synthesized in different ratios 1:1, 1:2 and 1:3 under different conditions and further characterized by FTIR and XRD pattern. Thermal stability of the prepared compounds was checked by TGA/DTA and DSC method.***

Keywords: Rare Earth metals, TGA/ DTA, Salicylates, FTIR

1. Introduction

The elements which are consigning underneath the periodic table are known as f- block element of the rare earth elements. It consists of the two series named as lanthanides and actinides.

The lanthanides contain 15 elements and lanthanum (La_{57})is first element of the series on which the whole series is named upon. The lanthanides are not really rare; they are found in sands and pull out from minerals. These minerals or sand are monazite, batnasite and some other minerals and useful for different fields of study[1]. With the passage of time these lanthanide elements have become very valuable and priceless because of the utilization of these elements in several fields along with some other compounds and ligands etc. Like lanthanum is used in medical and industrial level also several fluoride, chloride and bromide compounds of this is used in communication, as luminescent, in different cameras, light projection and medically in treatment of renal and kidney failure [1-5]. Similarly praseodymium compounds are used as a color additive, in jewellary, as a luminescent and mainly in cigarette lighters. Neodymium in combination with other compounds is used in fertilizers for better growth of plants, to estimate volcanic eruption, as a magnet in different speakers, as a colorant. Major use of this element is in laser use for the treatment of bronchial cancer and for relieving pains in arthritis problem [6-9]. In addition with this europium is utilized in CRT television, as NMR shift reagent, as a phosphor and doping agent. Relating with the doping properties terbium, the member of lanthanides is employed.

Also several oxides of terbium used in TV screen, as a fluorescent and this element is a major component of Terfenol –D and several alloys [10]. A sound recognizable and chemically historic compound named as o-hydroxy benzoic acid or more commonly the salicylic acid is found naturally in slighter extent in many plants and can be synthesized commercially if large amount is required. The derivatives of this unique organic compound are known as salicylates, which have wide range of usage and applications in our routine life both biologically and medicinally. These salicylates are significant alone or in combination with some other compounds and elements. Because many of the medicine used for curing the disease for example skin diseases, allergies, irritation and inflammation problem may treated with these salicylates. Different types of medicines have diverse kinds of salicylates in them. Also some form of salicylates used in preservation of food and in cosmetic products[11]. One of the revolutionary and phenomenal drug commonly known as aspirin is an active ingredient of salicylic acid. As aspirin belongs to the salicylic acid so, this has anti-inflammatory, antirehumatic and antipyretic properties. Also it is an analgesic medicine because it shows the analgesic action on CNS and peripheral. Other than the medicinal usage of aspirin it may use as food additives, cosmetic products and for animals in foods [12].Besides this Salicylates have several side effects. Similarly another important salicylate; 4-Amino salicylic acid ASA or sometimes called as PAS, which is considered as a miraculous medicine or antibiotic for tuberculosis. Many of the medicine used for tuberculosis encloses 4-ASA in them [13].

Due to immense applications of these complexes, lanthanides become the point of interest from last few decades. The rare earth complexes with salicylates are used as an anticoagulant agent for blood. The literature survey or the previous studies shows that Lanthanides for example europium and terbium used in flour immunoassays, DNA/ RNA hybridization appraise, receptor ligands interaction and enzyme analysis cellular applications. For labeling of biomolecules or target nucleic acid lanthanides complexes are imperative. Also the chelates formation with some salicylates is useful for physical and chemical phenomenon. The best example for this replacement of lanthanum probes with calcium ions.

2. Literature Review

Salicylates of rare earth metals have wide range of application as an antimicrobial and antibiotic these complexes may use for further treatments in human body and plants and their microbial action and mechanism were determined [14]. The effect of lanthanides and transition metals were compared on the aromatic ring of salicylic and benzoic acid [15]. The rare earth complexes with salicylates are used as an anticoagulant agent for blood [16]. Bacterial spore scan be detected with lanthanide macrocyclic complexes. Rare earth sulphosalicylates have the strong bacteriostatic effect [17].

3. Experimental

3.1 Materials

The following chemicals and reagents of analytical grade were utilized during the experimental work.

3.1.1 Metals

Lanthanum (III) nitrate, Praseodymium (III) nitrate, Neodymium (III) nitrate, Europium (III) nitrate and Terbium (III) nitrate

3.1.2 Ligands: 4-Amino salicylate (4-ASA), 2-Acetoxy benzoic acid (Aspirin).

3.2 Procedure

To 4 –Amino salicylic acid (0.0765 g; 0.02 mol) for ratio 1:1,(0.153 g; 0.04 mol) for ratio 1:2 and (0.229 g; 0.06 mol) for ratio1:3 were 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 (25 mL) slowly but with constant stirring for one hour for the preparation of 3 ratios respectively of the reaction (1). The white precipitates thus obtained were filtered off, washed several times with water. The product were dried and kept under vacuum for several hours to get white complexes of all the three ratios with percentage yields (0.1185 g; 76.79%), (0.1478 g; 30.86%), (0.1847 g; 18.97%) respectively, insoluble in any common solvent. The complexes of all the other metals with 4- amino salicylic acid and 2- acetoxy benzoic acid were prepared in the same fashion and given in the Table 1 and 2.

Table 1: Reaction of 4-Amino Salicylic acid

Reaction no.	*Complex ratios*	*Metals*	*Percentage yield*	*Colour of complexes*
1	1:1	Lanthanum (III) Nitrate	95.62%	White
	1:2	Lanthanum (III) Nitrate	63.63%	White
	1:3	Lanthanum (III) Nitrate	15.17%	White
2	1:1	Praseodymium (III) nitrate	93.66%	White
	1:2	Praseodymium (III) nitrate	32.22%	White
	1:3	Praseodymium (III) nitrate	20.64%	White
3	1:1	Neodymium (III) nitrate	96.46%	Light green
	1:2	Neodymium (III) nitrate	66.47%	Light green
	1:3	Neodymium (III) nitrate	3.88%	Light green
4	1:1	Europium (III) Nitrate	88.86%	White
	1:2	Europium (III) Nitrate	25.33%	White
	1:3	Europium (III) Nitrate	15.44%	White
5	1:1	Terbium (II) nitrate	98.11%	White
	1:2	Terbium (II) nitrate	30.89%	White
	1:3	Terbium (II) nitrate	19.69%	White

Table 2: Reaction of 2-Acetoxy benzoic acid

Reaction no.	*Complex ratios*	*Metals*	*Percentage yield*	*Colour of complexes*
	1:1	Lanthanum (III) Nitrate	96.62%	White
	1:2	Lanthanum (III) Nitrate	62.63%	White
	1:3	Lanthanum (III) Nitrate	14.17%	White
	1:1	Praseodymium (III)	93.66%	Light pink
	1:2	Praseodymium (III)	23.10%	Light pink
2	1:3	Praseodymium (III)	13.87%	Light pink
	1:1	Neodymium (III) nitrate	89.36%	Light green
	1:2	Neodymium (III) nitrate	26.42%	Light green
3	1:3	Neodymium (III) nitrate	13.55%	Light green
	1:1	Europium (III) Nitrate	84.51%	White
	1:1	Terbium (II) nitrate	86.22%	White
	1:2	Terbium (II) nitrate	28.10%	White
	1:3	Terbium (II) nitrate	13.71%	White

4. Result and Discussion

Fourier transform infrared spectra (FTIR) were measured by MIDAC Corporation USA, M-series, Model 2000. X-ray diffraction analysis (XRD) was measured by Bruker, D8 Discover, Germany. Thermal analysis was measured by TA instrument; USA, SDT 600 Model at Central Laboratory, Lahore College for Women University, Lahore, Pakistan. The FTIR analysis of the complexes and original compounds were taken by KBR pellet method formation which shows the same solid state spectra of all the rare earth complexes. The FTIR spectra of the ligands was studied and compared to those of its respective complexes.

The spectra of the complexes show the characteristic changes with respect to the original during complex formation in all rtios of the compounds. The major change is shown in the frequencies of COOH band in the original and COO^- band in the complexes. Because in original sample this peak is present at 1600 cm^{-1} in 4-ASA and 1607 cm^{-1} in 2- Acetoxy benzoic acid respectively and in their complexes the valency vibrations are shown 1367 – 1410 cm^{-1} and 1378 – 1416 cm^{-1} which clearly illustrate the backward shifting of about 233 – 190 cm^{-1} and mentions the very high value of splitting. The main reason for this shifting is due to the attachment of the metal during complexation with 4- ASA and 2 – Acetoxy benzoic acid. On the other hand another major change established during the chelation is to increase the aromatic ring stretch in type of complexes which also mentions the backward shifting. In the same way a narrow peak emerge in the complexes for OH group which is an evidence for the attachment of the water molecules with the chelates during chelation in both. The valency vibrations for CH stretch (aromatic) and C-O stretch appear small shifting of the peaks. The new metal – oxygen bonding materialized which substantiates the formation of the complexes or chelates in all the ratios of both types of ligands.

The qualitative X- ray diffraction analysis of the above synthesized complexes was measured by Bruker, D8 Discover, Germany. The XRD pattern acquires the same results for all the complexes and the numbers of peaks present in the complexes of both the ligands (4 –Amino salicylic acid and 2-Acetoxy benzoic acid) clearly shows that all the complexes are crystalline in nature and contains several peaks systematically.

All the complexes are insoluble in common organic solvents and do not possess the sharp melting points but decompose on heating above 500 °C. The thermal stability of the complexes was checked by the TA instrument; USA, SDT 600 Model. The TGA, DTA and DSC graphs of the rare earth complexes with 4- Amino salicylic acid shows that these complexes are stable enough. It is clear from the graphs of thermal stability that all the ratios of lanthanum with 4- ASA show 3-6% weight loss which is endothermic, in the first step this is due to the loss of water molecules from the chelation. During this change the temperature ranges 84 - 87 °C. In the next step the thermal decomposition of the complexes start in which CO and NH_2 molecule removes from the complexes. In the ratio (1:1) fusion decomposition occur in which no loss occur at this temperature range. In the last step the oxidative degradation establish which lasts at 52% weight loss in complexes here the complexes residues of reaction (1) are converted to its respective oxides and then metal is released. Similarly in reaction (2) the first is the elimination of water molecules and 3 -6% weight changeoccurs in the complexes and the change is endothermic. Then the thermal degradationin the remaining structure starts which mentions the removal of CO, $NH_{2,}$ OH and CH in both two steps and the change is continues above the temperature 450 °C in all ratio of this reaction. Finally the oxidative degradation occurs by the loss of 54% weight of the complexes.

In the reaction of neodymium with ligand or reaction (3) the ratio (1:1) is evaluated correctly than the rest ratios. In this the similar water elimination at 6% weight loss as calculated at 71 °C and the endothermic change established. Then 15% and 23% loss occur due to the thermal degradation. And an exothermic weight loss of metal from its oxide can observe in the graph.

The other two ratios patterns are in describable due to unknown changes. The same is the way as above in which the complexes of reaction (4) and (5) are decompose in which first weight loss is endothermic due to the loss of water molecules and then thermal decomposition and remains above 63% loss of the complexes from its oxides.

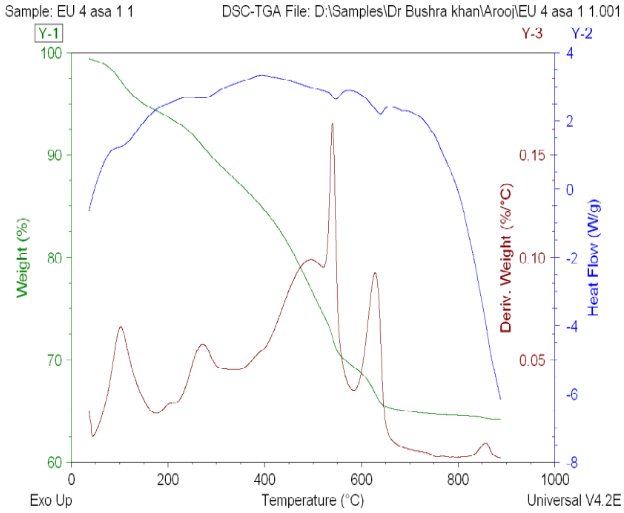

Figure 1: Reaction of Europium (III) Nitrate with 4-amino salicylicacid(1:1)

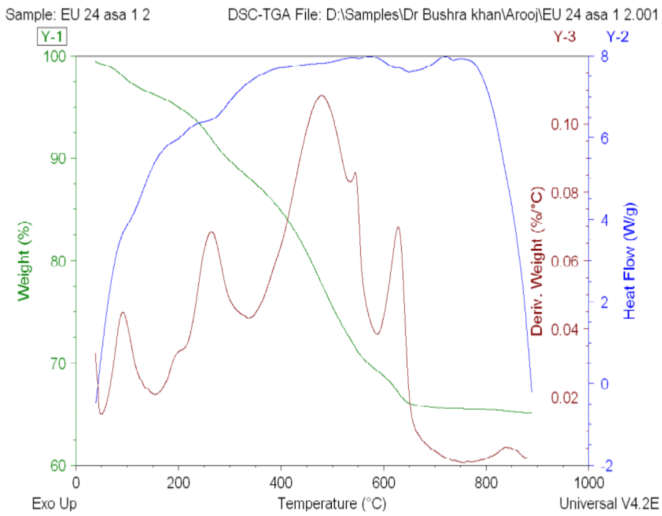

Figure 2: Reaction of Europium (III) Nitrate with 4-amino salicylic acid (1:3)

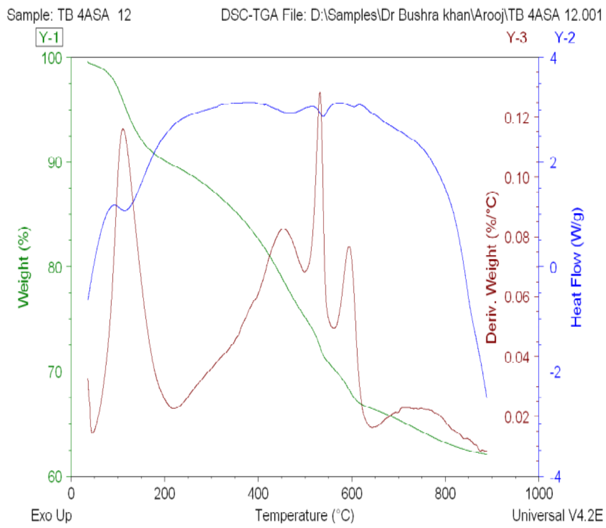

Figure 3: Reaction of Terbium (II) Nitrate with 4-amino salicylicacid(1:2)

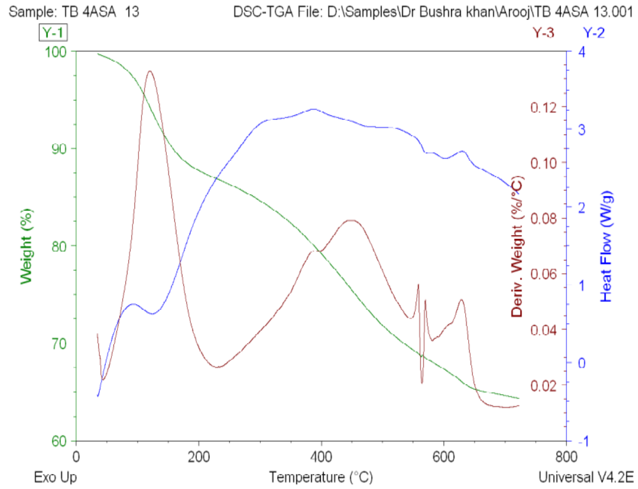

Figure 4: Reaction of Terbium (II) Nitrate with 4-amino salicylicacid(1:3)2-acetoxybenzoic acid

5. Conclusion

The reported research work is an effort towards synthesizing valuable rare earth chelates. All the complexes were obtained from good to excellent yield via purposed methodology. The characterization was carried out using FTIR, XRD, TGA, TDA and DSC. FTIR spectra provide evidence for all essential groups. All complexes were crystalline in nature. Thermal stability data was in accordance with that of expected one for these complexes.

6. Future Scope

This research methodology provides us with simple and efficient means to obtain important rare earth complexes. It can be used as a template to expand the research over other ligands to produce more varieties of complexes which may be utilized in different ways for human benefits. Variable complexes with different structural and behavioral prospective can be significant achievement by using purposed strategy which is simple and easy to carry out.

References

[1] Handbook of Chemistry and Physics, CRC press, ISBN 0849304814, 2000.
[2] “Britannica Encyclopedia: Lighting”, Retrieved, 11th edition, 2009.
[3] C. R. Hammond, Handbook of Chemistry and Physics,81st edition., CRC press, ISBN 0849304814 , 2000.
[4] B.C. Howard,Arc welding automation, CRC Press,ISBN 0824796454, pp. 139, 1995.
[5] P. F. Simon, Chemical Society Review,35, pp. 524-533,2006.
[6] K.A. Gschneidner., L. Eyring, Handbook on the Physicsand Chemistry of Rare Earths, North Holland PublishingCo., Amsterdam, 1978.
[7] Y. Wei.,X. Zhou, 10th International Repessed Congress, 1999.
[8] History of Light, subheading Timeline, 2001.
[9] Europium and the Euro, Retrieved,2009.
[10] C. Rodriguez, M. Rodriguez, I. Orue, J. Vilas, J. Barandiaran, M. Gubieda, Leon, L., “New elastomer–Terfenol-Dmagnetostrictive Composites”,SensorsAnd ActuatorsaPhysical, 149, 251, 2009.
[11] J.R. Paterson,G. Baxter,J. S. Dreyer, J. M. Halket, R.Flynn, J. R. Lawrence, Journal of Agricultural and Food Chemistry, (56), pp. 11648–11651 ,2008.
[12] D. A Mitchison, Int J Tuberc Lung Dis, (4),pp. 796–806, 2007.
[13] Y. Min. Y. Long, ActaChim. Sinica, (65), pp. 678-682,2007.
[14] C.Ai-Meil, S. QingShan, O.YouSheng, C.YiBen, T.ShaoZao, Progress in antimicrobial activity and application of Rare Earth, Microbiology, DOI:CNKI: SUN:WSWT.2009.
[15] W.Lewandowski,H.Baranska,”Comparison of the effect of lanthanides(Ln),d-transition metals and selected metals of the main groups on the aromatic system of salicylic and benzoic acids”, Journal of MolecularStructure, 174,417-21,1988.
[16] S.Yu-Min, D.Yin-Long,F.Yun-Long, “Study on synthesis and anticoagulant action of rare earth ternary complexes with warfarinanion and salicylates”, ActaChim.Sinica, 65(8),678-82,2007.
[17] P.Lun,C.Ronglian,Z.Maodong,L.Xinzhang,H.Hunzhen, “Rare Earth sulphosalicylates complexes and their bacteriostatic effect”, Journal of Jinan University, 03,20,1000-9965,1990.

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