RJC

RASĀYAN *J. Chem.*
Vol. 17 | No. 3 |964-971| July - September | 2024
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

THERMOKINETIC DIMENSIONS OF RARE EARTH COMPLEXES OF ANTIPYRALDEHYDE SCHIFF BASES

M.K. Geetha Nambiar[1], G. Rijulal[2,✉], A. Krishnakumar[3] and K. Anoop Krishnan[3]

[1]Department of Chemistry, Government College Malappuram - 676 539, Kerala, India
[2]Department of Chemistry, Government College Chittur, Chittur - 678 104, (Kerala) India
[3]National Centre of Earth Science Studies, Akkulam - 695011, Trivandrum, (Kerala) India
✉Corresponding Author: rijulalg@gmail.com

ABSTRACT

Thermogravimetric investigations of rare earth complexes $[Ln(3MPMAFA)_2(NO_3)_3]$ and $[Ln(4MPMAFA)_2(NO_3)_3]$ have been performed. All the complexes have two decomposition stages, with the formation of the respective lanthanide oxide, Ln_2O_3, as the final residue. Using the Coats-Redfern approach, the kinetic aspects for each decomposition stage were assessed from the TG data. The lowering of the steric strain of intermediate molecules is due to the higher entropy of activation of the second phase decomposition than the first stage. The entropy of activation has positive values, which means that the decomposition products have lower-ordered structures than the initial constituents, which causes the reactions to proceed more quickly than normal. Using the many mechanistic equations proposed by Satava, the mechanisms for the decomposition reactions were computed.

Keywords - Lanthanide(III) Complexes, Thermal Stability, Mechanism, Kinetic Parameters, Coats-Redfern Equation.
RASĀYAN*J. Chem.*, Vol. 17, No.3, 2024

INTRODUCTION

The numerous coordination opportunities and broad uses of Schiff bases resulting from antipyrine investigations have attracted the fascination of some researchers.[1–20] The O, N-containing ligands that comprise the Schiff bases of antipyrine carboxaldehyde and 4-amino antipyrine exhibit a diverse and extensive coordination chemistry with an extensive array of metal complexes.[8–12] Because of their broad relevance in industrial processes involving thermal decomposition reactions of solids, thermodynamic analytical methods are of great interest.[13–15] The antipyrine derivatives were used as potentiometric sensors for the detection of metal ions, and they have a variety of physiological activities.[21-24] The thermal degradation kinetics and mechanisms of each decomposition stage of lanthanum(III) complexes with Schiff base 1,2-(diimino-4'-antipyrinyl)ethane were investigated in detail.[25] The thermal properties of the ligand 4-N-(2′-furfurylidene)aminoantipyrine and lanthanide(III) nitrate complexes were studied by C.R. Vinodkumar *et al.*[26] Agarwal *et al.* synthesized and assessed the thermal properties of rare earth complexes with antipyrine derivatives.[27-34] The thermogravimetric measurement of rare earth complexes with the Schiff base 4-N-(4'-antipyrylmethylidene)aminoantipyrine implies that the thermal properties of the nitrate complexes have stability up to 220°C and the iodide complexes have stability up to 150ºC. After 800-850°C, metal oxides were obtained for lanthanide(III) nitrate complexes, and at the same time, anhydrous metal iodides were formed for iodide complexes.[35,36] The thermal aspects and kinetic characteristics of lanthanide complexes were examined in detail by Joseph *et al.*[37-41] A series of biologically active and thermally stable complexes of rare earth metal nitrates with 4-antipyrine carboxaldehyde Schiff bases were well studied.[42] Thermally stable complexes of lanthanide(III) nitrate complexes of Schiff's base derived from 4,4-methylenediantipyrine and ethylenediamine have high microbiological activity.[43] The thermal data of lanthanide(III) nitrato complexes with the 4-antipyrine carboxaldehyde Schiff bases indicate that the free ligand has three decomposition stages, while all the complexes undergo four-stage thermal degradation. The respective lanthanide oxides were obtained after complete decomposition at about 540ºC.[44] Numerous researchers have looked into the thermal behavior of lanthanide(III) complexes of antipyrine Schiff bases and in some complexes, the counter anions play a significant role in the kinetics of thermal decomposition.[25-34] Even though there are only a few thermal decomposition investigations of

http://doi.org/10.31788/RJC.2024.1738884

lanthanide(III) complexes containing antipyrine-4-carboxaldehyde Schiff bases.[35-45] This work aims to assess the thermal stabilities and the decomposition kinetics of fourteen lanthanides (III) complexes using Schiff bases developed from antipyraldehyde and methoxybenzylamines.

EXPERIMENTAL

General Procedure

The lanthanide(III) nitrato complexes of antipyraldehyde Schiff bases were prepared by reported methods and have a common formula, $[M(L)_2(NO_3)_3]$, where M = Ln(III), Pr(III), Ne(III), Sm(III), Gd(III), Dy(III), Y(III) and L = 3MPMAFA/4MPMAFA.[47] Using the Mettler Toledo STARe thermal analysis instrument, TG, DTG, and DTA measurements of the complexes were captured. All the thermogravimetric measurements were conducted in a dynamic air environment with a flow rate of 60 mL min^{-1}, using a sample mass of about 3 mg.

RESULTS AND DISCUSSION

The TG/DTG/DTA graphs of all the complexes are disclosed in Figures-1 and 2. The key characteristics of the thermal behavior and the kinetic aspects are briefly illustrated below and are presented in Tables - to 4. Up to about 260°C and 220°C, respectively, the lanthanum nitrate complexes are stable, and after that, they break down into two phases, and the information gleaned from the TG graph for each phase as well as the estimated mass loss values indicate that one ligand molecule was eliminated at each step. The ultimate decomposition residue, La_2O_3 produced after ~530ºC. The plateau indicates that Pr(III) nitrato complexes are stable up to about 230-250°C, after which they decompose into two phases, as indicated by the DTG peaks at 386 and 478°C and at 375 and 482°C. The exothermic DTA peaks appeared in both complexes. Based on the TG curves, pyrolysis experiments, and computed values, the total mass loss (83.4%) and 82.9%) suggested that Pr_6O_{11} formed as the ultimate residue. The complexes $[Nd(3MPMAFA)_2(NO_3)_3]$ and $[Nd(4MPMAFA)_2(NO_3)_3]$ are stable up to ~250ºC and have two-stage thermal decomposition, and the thermal decompositions of both complexes were completed after 520ºC. The nitrato complexes of Sm(III) with the Schiff bases of 3MPMAFA and 4MPMAFA are stable up to ~250ºC and ~260ºC. The complexes decompose in two stages, completing at ~600ºC and ~560ºC. The DTG peaks at 391ºC, 482ºC and 391ºC and 482ºC are obtained for $[Sm(3MPMAFA)_2(NO_3)_3]$ and $[Sm(4MPMAFA)_2(NO_3)_3]$, respectively. The mass losses (82.7%) and (83.1%) from the TG and the pyrolysis experiments indicate that the end product is Sm_2O_3. Gadolinium(III) complexes are stable up to about 240°C and 250°C respectively, according to their TG curves. The DTG peaks then indicate the two stages of their subsequent decomposition. The initial degradation phase begins at 260°C and culminates at 410°C. At 420°C, the second decomposition stage begins and continues until 500°C; the final residue, Gd_2O_3 forms at about 700°C. The thermal breakdown of $[Dy(3MPMAFA)_2(NO_3)_3]$ and $[Dy(4MPMAFA)_2(NO_3)_3]$ starts after 270°C and 230°C. The DTG peaks and the matching DTA peaks indicate the two stages of thermal decomposition.

According to the computed mass loss value, TG curve, and total mass loss data, the ultimate residue is Dy_2O_3. Based on the thermogravimetric analysis, the Yttrium(III) complexes containing the Schiff bases 3MPMAFA and 4MPMAFA are stable up to about 200ºC. Both complexes have two thermal decomposition stages, with the final stage ending at about 550ºC. According to the overall mass loss percentage, the complexes decomposed to produce Y_2O_3 as the final residue. The Coats-Redfern method was used to compute the kinetic parameters for the thermal breakdown processes of the lanthanide(III) nitrato complexes, which are displayed in Tables-3 and 4.

The kinetic parameters for every step of each complex's thermal decomposition have been assessed. The thermal decomposition order parameter has values between 1.4 and 2.7. The complexes undergo thermal decomposition, with the energy of activation (E) ranging from 274.2 to 375.8 $kJmol^{-1}$ for the first stages and 320.4 to 709.8 $kJmol^{-1}$ for the second stages. For the first and second stages of decomposition, the pre-exponential factors (A) range from 2.7 x 10^{18} to 1.5 x 10^{28} and 1.4 x 10^{23} to 1.1 x 10^{48} s^{-1}. The first and second decomposition phases had entropy of activation values of 101.5-287.3 and 137.5-668.8 $JK^{-1}mol^{-1}$, respectively. The several mechanistic equations proposed by Satava were used to calculate the mechanism for the complex thermal decomposition reactions. For every decomposition reaction examined, the highest correlation coefficient values are obtained, which correspond to the Mampel equation $-\ln(1-\alpha)$.

Table-1: Phenomenological Data of Thermal Decomposition of Lanthanide(III) Nitrato Complexes of 3MPMAFA
(mass ~ 3mg, $\phi = 10^0$C min^{-1}, atmosphere = air)

Compounds	Stage	Plateau in TG	DTG Peak (^{0}C)	Peak width in DTG (^{0}C)	DTA Peak (^{0}C)	Mass loss (%)			Product
						TG	Pyrol*	Calc.**	
	I	Upto 260	362	270-430	381	33.9	--	33.7	$[La(3MPMAFA)(NO_3)_3]$
$[La(3MPMAFA)_2(NO_3)_3]$	II	After 530	482	440-520	486	84.2	83.9	83.6	La_2O_3
	I	Upto 230	386	260-430	394	34.1	--	33.6	$[Pr(3MPMAFA)(NO_3)_3]$
$[Pr(3MPMAFA)_2(NO_3)_3]$	II	After 650	478	440-530	478	83.4	85.2	82.9	Pr_6O_{11}
	I	Upto 250	368	270-420	366	34.3	--	33.5	$[Nd(3MPMAFA)(NO_3)_3]$
$[Nd(3MPMAFA)_2(NO_3)_3]$	II	After 600	470	440-520	472	83.1	83.6	83.2	Nd_2O_3
	I	Upto 250	375	280-400	376	32.5	--	33.3	$[Sm(3MPMAFA)(NO_3)_3]$
$[Sm(3MPMAFA)_2(NO_3)_3]$	II	After 600	468	420-500	469	83.0	83.2	82.7	Sm_2O_3
	I	Upto240	373	250-420	385	32.6	--	33.1	$[Gd(3MPMAFA)(NO_3)_3]$
$[Gd(3MPMAFA)_2(NO_3)_3]$	II	After 550	490	430-540	487	82.2	81.7	82.1	Gd_2O_3
	I	Upto 240	376	270-440	391	32.3	--	32.9	$[Dy(3MPMAFA)(NO_3)_3]$
$[Dy(3MPMAFA)_2(NO_3)_3]$	II	After 610	489	460-540	488	82.0	81.9	81.7	Dy_2O_3
	I	Upto 200	382	230-440	410	34.8	--	35.5	$[Y(3MPMAFA)(NO_3)_3]$
$[Y(3MPMAFA)_2(NO_3)_3]$	II	After 580	500	450-540	499	88.5	88.7	88.1	Y_2O_3

*Pyrolysis; **Calculated

Table-2: Phenomenological Data of Thermal Decomposition of Lanthanide(III) Nitrato Complexes of 4MPMAFA
(mass ~ 3mg, $\phi = 10^0$C min^{-1}, atmosphere = air)

Compounds	Stage	Plateau in TG	DTG Peak (^{0}C)	Peak width in DTG (^{0}C)	DTA Peak (^{0}C)	Mass loss(%)			Product
						TG	Pyrol*	Calc.**	
	I	Upto 220	368	250-420	382	33.3	--	33.7	$[La(4MPMAFA)(NO_3)_3]$
$[La(4MPMAFA)_2(NO_3)_3]$	II	After 580	486	430-530	486	84.1	83.9	83.6	La_2O_3
	I	Upto 250	375	260-400	360	34.3	--	33.6	$[Pr(4MPMAFA)(NO_3)_3]$
$[Pr(4MPMAFA)_2(NO_3)_3]$	II	After 550	482	410-500	484	83.4	84.1	82.9	Pr_6O_{11}
	I	Upto 240	370	280-410	375	34.2	--	33.5	$[Nd(4MPMAFA)(NO_3)_3]$
$[Nd(4MPMAFA)_2(NO_3)_3]$	II	After 540	483	420-510	484	82.5	84.0	83.2	Nd_2O_3
	I	Upto 260	391	270-420	380	33.2	--	33.3	$[Sm(4MPMAFA)(NO_3)_3]$
$[Sm(4MPMAFA)_2(NO_3)_3]$	II	After 560	482	430-510	483	82.9	83.1	82.7	Sm_2O_3
	I	Upto 250	382	260-410	379	33.4	--	33.1	$[Gd(4MPMAFA)(NO_3)_3]$
$[Gd(4MPMAFA)_2(NO_3)_3]$	II	After 700	488	420-500	488	82.5	82.8	82.1	Gd_2O_3
	I	Upto 230	376	280-410	373	32.3	--	32.9	$[Dy(4MPMAFA)(NO_3)_3]$
$[Dy(4MPMAFA)_2(NO_3)_3]$	II	After 550	484	420-520	485	82.0	81.5	81.7	Dy_2O_3
	I	Upto 230	369	260-440	382	35.4	--	35.5	$[Y(4MPMAFA)(NO_3)_3]$
$[Y(4MPMAFA)_2(NO_3)_3]$	II	After 590	522	450-550	522	88.2	88.7	88.1	Y_2O_3

* Pyrolysis; **Calculated

Table-3: Kinetic Parameters of the Thermal Decomposition of Lanthanide(III) Nitrato Complexes of 3MPMAFA

Compounds	Stage	Order'n'	E (kJmol^{-1})	A (s^{-1})	ΔS (JK^{-1}mol^{-1})
$[La(3MPMAFA)_2(NO_3)_3]$	I	2.0	279.7	1.1 x 10^{21}	151.1
	II	1.5	604.0	6.8 x 10^{39}	509.1
$[Pr(3MPMAFA)_2(NO_3)_3]$	I	1.8	274.2	5.1 x 10^{19}	125.7
	II	1.8	511.1	3.6 x1033	389.7
$[Nd(3MPMAFA)_2(NO_3)_3]$	I	1.7	309.1	1.1 x 10^{23}	190.1
	II	1.4	597.5	6.5 x 10^{39}	509.7
$[Sm(3MPMAFA)_2(NO_3)_3]$	I	2.4	366.0	2.3 x 10^{27}	272.4
	II	1.4	709.8	1.1 x 10^{48}	668.8
$[Gd(3MPMAFA)_2(NO_3)_3]$	I	1.6	302.9	3.4 x 10^{22}	180.0
	II	2.7	509.0	1.4 x 10^{23}	381.7

$[Dy(3MPMAFA)_2(NO_3)_3]$	I	1.7	296.0	4.0×10^{21}	162.3
	II	1.6	604.4	2.0×10^{39}	499.8
$[Y(3MPMAFA)_2(NO_3)_3]$	I	2.0	315.6	2.3×10^{24}	215.3
	II	1.5	473.6	1.1×10^{30}	321.6

Table-4: Kinetic Parameters of the Thermal the Decomposition of Lanthanide(III) Nitrato Complexes of 4MPMAFA

Compounds	Stage	Order'n'	E ($kJmol^{-1}$)	A (s^{-1})	ΔS ($JK^{-1}mol^{-1}$)
$[La(4MPMAFA)_2(NO_3)_3]$	I	1.8	250.4	2.7×10^{18}	101.5
	II	2.0	709.4	1.4×10^{47}	649.9
$[Pr(4MPMAFA)_2(NO_3)_3]$	I	2.0	307.1	7.9×10^{22}	187.0
	II	1.5	337.5	9.0×10^{21}	167.7
$[Nd(4MPMAFA)_2(NO_3)_3]$	I	1.5	293.1	1.1×10^{22}	170.8
	II	1.5	320.4	2.4×10^{22}	137.5
$[Sm(4MPMAFA)_2(NO_3)_3]$	I	1.8	307.0	3.1×10^{22}	179.0
	II	2.1	554.1	7.3×10^{36}	453.1
$[Gd(4MPMAFA)_2(NO_3)_3]$	I	2.2	375.8	1.4×10^{28}	287.3
	II	1.7	404.6	1.2×10^{26}	246.8
$[Dy(4MPMAFA)_2(NO_3)_3]$	I	1.8	282.0	4.9×10^{20}	144.6
	II	1.4	452.5	1.4×10^{29}	305.3
$[Y(4MPMAFA)_2(NO_3)_3]$	I	1.7	258.6	1.1×10^{19}	113.3
	II	2.0	458.6	2.8×10^{28}	291.6

CONCLUSION

The phenomenological properties of the lanthanide(III) nitrato complexes with 3MPMAFA and 4MPMAFA described that all the complexes have two decomposition stages. During the initial thermal degradation phase, one of the ligand molecules from the parent compound is eliminated. The formation of the corresponding lanthanide oxide is obtained after the elimination of nitrate ions and the remaining ligand molecule. Drawing from the previously mentioned information, the complex's thermal decomposition reaction can be depicted using the subsequent equation:

$$[Ln(L)_2(NO_3)_3] \longrightarrow [Ln(L)(NO_3)_3] \longrightarrow [Ln_2O_3]$$

(In this case, Ln = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), and Y(III); L = 3MPMAFA / 4MPMAFA)

For the first and second stages of breakdown, the entropy of activation is 101.5 - 287.3 and 137.5 - 668.8 $JK^{-1}mol^{-1}$, respectively. The complexes that undergo the second step of decomposition have the highest values of entropy of activation. Less steric strain for the intermediate molecules formed during the initial stages of decomposition may be the cause of the higher values of entropy of activation for the second stage of decomposition compared to the first stage. According to the positive values of the entropy of activation, the products of the decomposition have less organized structures than the reactants, which suggests that the reactions occur more quickly than usual. With respect to the mechanism of the thermal decomposition research, the Mampel equation $-\ln(1-\alpha)$ is followed to acquire the highest correlation coefficient values for all the decomposition reactions tested. Thus, these complexes decompose randomly, with one nucleus on each particle.

ACKNOWLEDGMENTS

The authors would like to thank the C.H. Mohammed Koya Library, University of Calicut, Kerala, India, for providing insightful recommendations for this work, as well as the National Centre of Earth Science Studies (NCESS), Akkulam, Trivandrum, Kerala, India, for enabling us to perform the analysis.

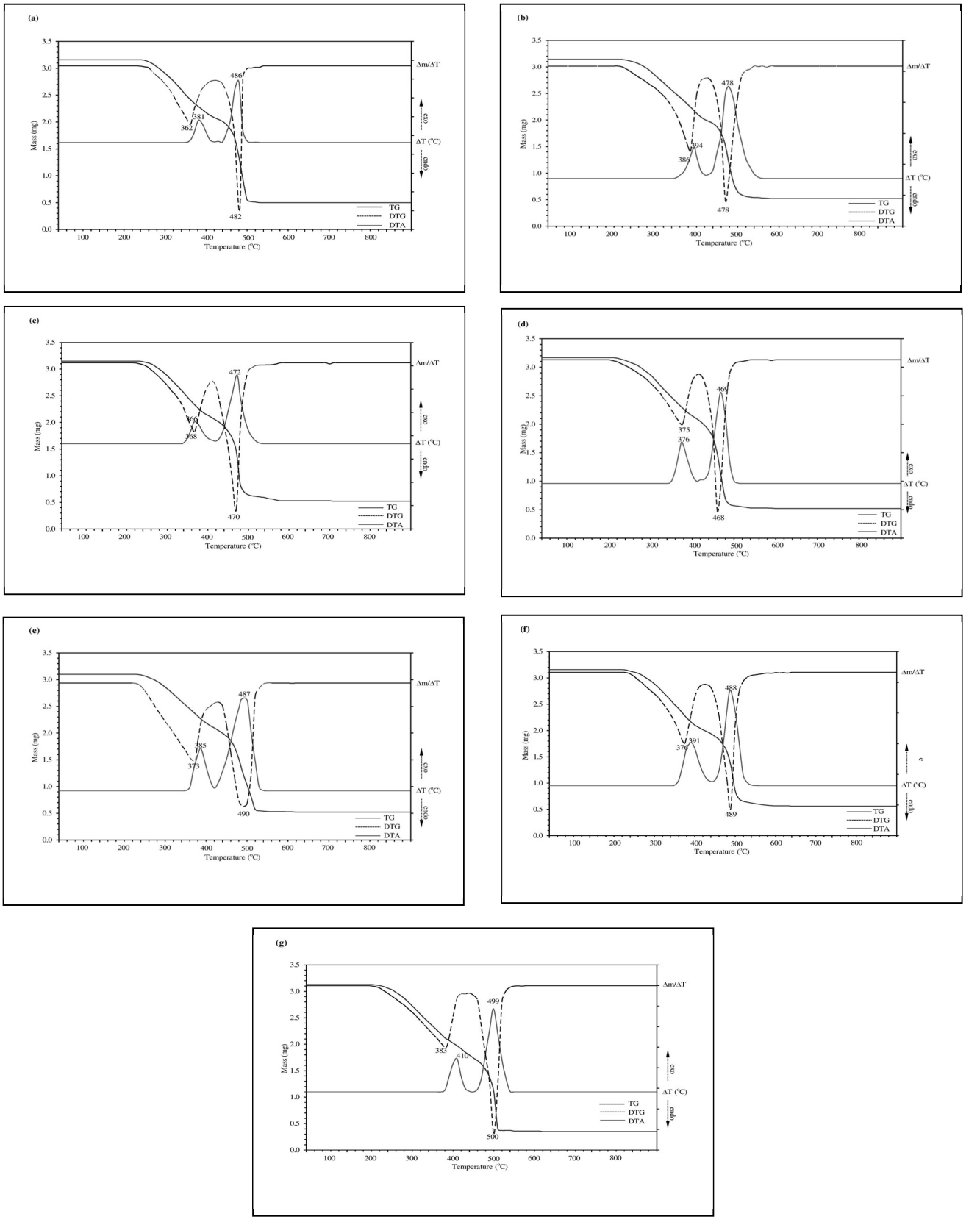

Fig.-1:(a-g) TG, DTG and DTA Curves Ln(III) Nitrato Complexes of 3MBMAFA

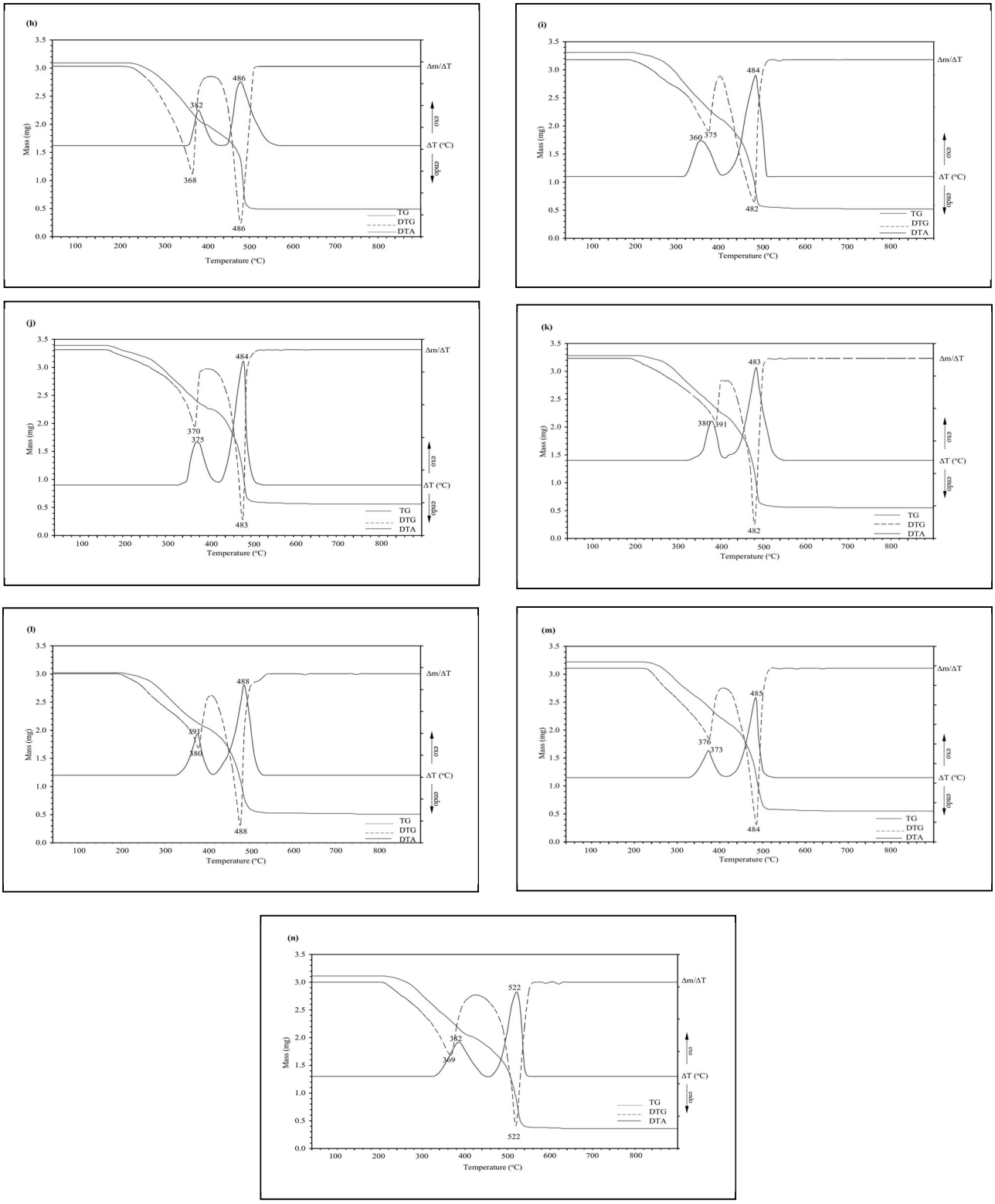

Fig.-2: (h-n) TG, DTG, and DTA curves Ln(III) Nitrato Complexes of 4MBMAFA

CONFLICT OF INTERESTS

The authors declare that none of the work reported in this study could have been influenced by any known competing financial interests or personal relationships.

AUTHOR CONTRIBUTIONS

Each author made a substantial contribution to the work, took part in its review and editing, and gave their approval for the manuscript to be published in its final form. The authors' ORCID IDs, which are listed below, can be used to verify their research profile.

M.K. Geetha Nambiar https://orcid.org/0009-0005-8658-2674
G. Rijulal https://orcid.org/0000-0001-9722-7786
A. Krishnakumar https://orcid.org/0000-0001-9142-4797
K. Anoop Krishnan https://orcid.org/0000-0003-4435-8410

REFERENCES

1. D. Paderni, L. Giorgi, V. Fusi, M. Formica, G. Ambrosi, and M. Micheloni, *Coordination Chemistry Reviews*, **429**, 213639(2021), https://doi.org/10.1016/j.ccr.2020.213639
2. N.S. Chundawat, S. Jadoun, P. Zarrintaj and N.P.S. Chauhan, *Polyhedron*, **207**, 7578(2021), https://doi.org/10.1016/j.poly.2021.115387
3. N.M. Aljamali, S.A. Aati, N.H. Obaid and F.A. Wannas, *American International Journal of Sciences and Engineering Research*, **2(1)**, 9(2019), https://doi.org/10.46545/aijser.v2i1.41
4. D.A. Atwood, The Rare Earth Elements: Fundamentals and Applications, John Wiley & Sons, Hoboken, New Jersey, US (2013).
5. S. Alghool, M.S. Zoromba and H.F. Abd El-Halim, 2013, *Journal of Rare Earths*, **31(7)**, 715(2013), https://doi.org/10.1016/S1002-0721(12)60347-0
6. C. Remes, A. Paun, I. Zarafu, M. Tudose, M.T. Caproiu, G. Ionita, C. Bleotu , L. Matei, and P. Ionita, *Bioorganic Chemistry*, **41-42**, 6(2012), https://doi.org/10.1016/j.bioorg.2011.12.003
7. K.B. Gudasi, V.C. Havanur, S.A. Patil and B.R. Patil, *Metal Based Drugs*, Article ID 037348(2007), https://doi.org/10.1155/2007/37348
8. R.K. Agarwal, L. Singh, D. Sharma and H. Agarwal, *Reviews in Inorganic Chemistry*, **27(1)**, 35(2007), https://doi.org/10.1515/REVIC.2007.27.1.35
9. N.T. Madhu, P.K. Radhakrishnan, M. Grunert, P. Weinberger, and W. Linert, *Reviews in Inorganic Chemistry*, **3(1)**, 1(2003), https://doi.org/10.1515/REVIC.2003.23.1.1
10. N.P. Ebosie, M.O. Ogwuegbu, G.O. Onyedika and F.C. Onwumere, *Journal of the Iranian Chemical Society*, **18(12)**, 3145(2021), https://doi.org/10.1007/s13738-021-02265-1
11. N.C. Martinez-Gomez, H.N. Vu, and E. Skovran, *Inorganic Chemistry*, **55(20)**, 10083(2016), https://doi.org/10.1021/acs.inorgchem.6b00919
12. K. C. Raju & P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **33(8)**, 1307(2003), https://doi.org/10.1081/SIM-120024311
13. A.G. Souza, M.M. Oliveira, I.M.G. Santos, M.M. Conceição, L.M. Nunes and J.C. Machado, *Journal of Thermal Analysis and Calorimetry*, **67**, 359(2002), https://doi.org/10.1023/A:1013971031425
14. H.R.C. Ouriques, M.F.S. Trindade, M.M. Conceição, S. Prasad, P.F.A. Filho and A.G. Souza, *Journal of Thermal Analysis and Calorimetry*, **75**, 569(2004), https://doi.org/10.1023/B:JTAN.0000027147.33054.8b
15. J.G. Santos, M.M. Conceição, M.F. Trindade, A.S. Araújo, V.J. Fernandes Jr. and A.G. Souza, *Journal of Thermal Analysis and Calorimetry*, **75**, 591(2004), https://doi.org/10.1023/B:JTAN.0000027150.30994.48
16. T.I. Kostelnik and C. Orvig, *Chemical Reviews*, **119(2)**, 902(2019), https://doi.org/10.1021/acs.chemrev.8b00294
17. M.M. Bomgardner, Chemical & Engineering News, **93(30)**, 36(2015).
18. G.B. Haxel, J.B. Hedrick and G.J. Orris, *Rare earth elements - Critical resources for high technology*. U.S.G.S. Fact Sheet 087-02 (2002), https://doi.org/10.3133/fs08702
19. X.J. Yang, A. Lin, X.-L. Li, Y. Wu, W. Zhou and Z. Chen, *Environmental Development*, **8**, 131(2013), https://doi.org/10.1016/j.envdev.2013.03.006
20. C.H. Evans, Biochemistry of the Lanthanides; Plenum Press: New York, (1990).

21. V. Gupta, A. Singh, S. Mehtab and B.A. Gupta, *Analytica Chimica Acta*, **566(1)**, 5(2006), https://doi.org/10.1016/j.aca.2006.02.038
22. A.G. Gilman, L.S. Goodman and A. Gilman The Pharmacological Basis of Therapeutics, Macmillan Publishing Co., New York, (1980).
23. S.J. Wadher, M.P. Puranik, N.A. Karande and P.G Yeole, International Journal of Pharm Tech Research, **1(1)**, 22(2009).
24. M. Rudrapal and B. De, International Research Journal of Pure and Applied Chemistry **3**, 232(2013), https://doi.org/10.9734/IRJPAC/2013/3996
25. M.K.M. Nair and P.K. Radhakrishnan, *Journal of Thermal Analysis and Calorimetry*, **52**, 475(1998), https://doi.org/10.1023/A:1010182514633
26. C.R. Vinodkumar, M.K.M. Nair, and P.K. Radhakrishnan, *Journal of Thermal Analysis and Calorimetry*, **61**, 143(2000), https://doi.org/10.1023/A:1010120909987
27. R.K. Agarwal, I. Chakraborti and N. K. Sharma, *Oriental Journal of Chemistry*, **19(1)**, 4(2003), http://www.orientjchem.org/?p=17580
28. R.K. Agarwal, I. Chakraborti, *Oriental Journal of Chemistry*, **19(2)**, 13(2003), http://www.orientjchem.org/?p=17738
29. R.K. Agarwal, I. Chakraborti and H. Agarwal, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **34(8)**, 1431(2004), https://doi.org/10.1081/SIM-200026274
30. R.K. Agarwal, I. Chakraborti and H. Agarwal, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **34(8)**, 1453(2004), https://doi.org/10.1081/SIM-200026288
31. R.K. Agarwal, S. Prasad, and N. Goel, *Turkish Journal of Chemistry*, **28**, 405(2004), https://journals.tubitak.gov.tr/chem/vol28/iss4/2
32. R.K. Agarwal, R. Garg and S.K. Sindhu, *The Bulletin of the Chemical Society of Ethiopia*, **19**, 185(2005), https://doi.org/10.4314/bcse.v19i2.21124
33. R.K. Agarwal and S. Prasad, *Turkish Journal of Chemistry*, **30**, 553(2006), https://journals.tubitak.gov.tr/chem/vol30/iss5/3
34. R.K. Agarwal, B. Prakash, V. Kumar and A.A. Khan, *Journal of the Iranian Chemical Society*, **4**, 114(2007), https://doi.org/10.1007/BF03245809
35. M.K.M. Nair and P. K. Radhakrishnan, *Polyhedron*, **12**, 1227(1993), https://doi.org/10.1016/S0277-5387(00)88215-7
36. M. K. M. Nair and P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **26(3)**, 529(1996), https://doi.org/10.1080/00945719608005122
37. S. Joseph, M. K. M. Nair and P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **27(7)**, 1025(1997), https://doi.org/10.1080/00945719708000244
38. S. Joseph and P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **28(3)**, 423(1998), https://doi.org/10.1080/00945719809349366
39. S. Joseph and P. K. Radhakrishnan, *Polyhedron*, **18,** 1881(1999), https://doi.org/10.1016/S0277-5387(98)00432-X
40. S. Joseph and P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **29(6)**, 1077(1999), https://doi.org/10.1080/00945719909349512
41. S. Joseph and P. K. Radhakrishnan, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **29(7)**, 1219(1999), https://doi.org/10.1080/00945719909349523
42. E.M. JINCY and M.K.M. NAIR, *Asian Journal of Chemistry*, **30(5)**, 1037(2018), https://doi.org/10.14233/ajchem.2018.21151
43. K.A. Hussein and N. Shaalan, *Indonesian Journal of Chemistry*, **22(5)**, 1365(2022), https://doi.org/10.22146/ijc.74214
44. K.A. Hussein, S. Mahdi and N. Shaalan, *Baghdad Science Journal*, **20(2)**, 469(2023), http://dx.doi.org/10.21123/bsj.2022.7088
45. G. Rijulal, A. Krishnakumar, K.A. Krishnan and M.K.G. Nambiar, *Asian Journal of Chemistry* **36(6)**, 1245(2024), https://doi.org/10.14233/ajchem.2024.31337

[RJC-8884/2024]