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Thermal and spectroscopic studies of terbium(III) and dysprosium(III) complexes with piperidin-4-ones

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Abstract

Terbium(III) and dysprosium(III) nitrate complexes with variously substituted 2,6-diphenylpiperidin-4-ones (L^1)–(L^{10}) of general formula $[Ln(L)(NO_3)_2(H_2O)_2]NO_3$ have been synthesized. These complexes have been characterized by analytical, spectral and thermal studies. Molar conductance data show that these complexes are 1:1 electrolytes. The presence of two coordinated water molecules is confirmed by thermal and infrared spectral studies. IR spectral data indicate that piperidin-4-ones, in spite of having two coordinating sites, are monodentate, coordinating only through ring nitrogen. The IR and conductance data reveal the presence of two bidentate and one ionic nitrate groups. The nephelauxetic ratio (β), covalency factor ($b^{1/2}$) and Sinha's parameter (δ) evaluated from electronic spectral data of dysprosium(III) complexes indicate a little covalency in metal–ligand bonding.

Keywords: Piperidin-4-ones; Terbium(III) and dysprosium(III) complexes; Thermal decomposition

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1. Introduction

Lanthanide complexes containing a variety of heterocyclic compounds as ligands have been studied extensively [1–5]. Although piperidin-4-ones have been subjected to detailed kinetic and conformational studies [6–10], only a few reports are available [11–15] on the use of them as ligands in the preparation of complexes. Cockburn et al., have used *N*-benzylpiperidin-4-one as a ligand in the preparation of platinum and palladium complexes [11]. Venkappayya and co-workers have studied copper(II) complexes of piperidin-4-ones and reported that piperidin-4-ones act as bidentate ligands, coordinating through both the ring nitrogen and carbonyl group [12]. Recently, we have reported the preparation and characterization of samarium(III) [13], cobalt(II) [14] and cerium(III) [15] complexes with piperidin-4-ones in which it has been proved that only the ring nitrogen and not the carbonyl group of piperidin-4-ones coordinates with metal ions. In continuation of our earlier work, we now report the preparation, characterization and thermal studies of terbium(III) and dysprosium(III) complexes containing piperidin-4-ones.

2. Experimental

2.1. Chemicals

Terbium(III) and dysprosium(III) nitrates were prepared by evaporating a solution of the corresponding

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Table 1
Physical and analytical data of the Tb^{III} nitrate complexes

Complex		Molecular weight found[a] (calculated)	Yield (%)	Decomposition temperature (°C)	Element found (calculated)				Conductance (Ω^{-1} cm^2 mol^{-1})
Number	Formula (empirical formula)				Tb%	C%	H%	N%	
(Tb^1)	$[Tb(L^1)(NO_3)_2(H_2O)_2]NO_3$ ($C_{17}H_{21}N_4O_{12}Tb$)	630.95 (632.06)	70	325–326	25.25 (25.14)	32.00 (32.27)	3.30 (3.35)	8.50 (8.86)	60
(Tb^2)	$[Tb(L^2)(NO_3)_2(H_2O)_2]NO_3$ ($C_{18}H_{23}N_4O_{12}Tb$)	647.00 (646.07)	85	155–156	24.75 (24.60)	33.57 (33.43)	5.76 (3.59)	8.25 (8.67)	73
(Tb^3)	$[Tb(L^3)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Tb$)	662.52 (660.09)	80	160–162	24.25 (24.08)	34.50 (34.54)	3.00 (3.21)	8.75 (8.48)	63
(Tb^4)	$[Tb(L^4)(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Tb$)	676.00 (674.10)	75	139–141	23.65 (23.58)	35.76 (35.60)	4.00 (4.04)	8.20 (8.31)	75
(Tb^5)	$[Tb(L^5)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Tb$)	662.25 (660.09)	90	168–169	24.50 (24.08)	34.75 (34.54)	3.45 (3.21)	8.65 (8.48)	70
(Tb^6)	$[Tb(L^6)(NO_3)_2(H_2O)_2]NO_3$ ($C_{18}H_{23}N_4O_{12}Tb$)	648.37 (646.07)	70	>340	24.35 (24.60)	33.50 (33.43)	3.50 (3.59)	8.50 (8.67)	60
(Tb^7)	$[Tb(L^7)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Tb$)	658.59 (660.09)	75	>340	24.00 (24.08)	34.25 (34.54)	3.40 (3.21)	8.70 (8.48)	72
(Tb^8)	$[Tb(L^8)(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Tb$)	676.16 (674.10)	70	>340	23.75 (23.58)	35.00 (35.60)	4.25 (4.04)	8.65 (8.31)	64
(Tb^9)	$[Tb(L^9)(NO_3)_2(H_2O)_2]NO_3$ ($C_{21}H_{29}N_4O_{12}Tb$)	689.26 (688.12)	70	>340	23.00 (23.10)	36.50 (36.62)	4.50 (4.25)	8.00 (8.14)	70
(Tb^{10})	$[Tb(L^{10})(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Tb$)	676.23 (674.10)	70	>340	23.25 (23.58)	35.75 (35.60)	4.15 (4.04)	8.40 (8.31)	65

[a] Observed molecular weight × van't Hoff factor.

Table 2
Physical and analytical data of the Dy^{III} nitrate complexes

Complex		Molecular weight found[a] (calculated)	Yield (%)	Decomposition temperature (°C)	Element found (calculated)				Conductance (Ω^{-1} cm^2 mol^{-1})
Number	Formula (empirical formula)				Dy%	C%	H%	N%	
(Dy^1)	$[Dy(L^1)(NO_3)_2(H_2O)_2]NO_3$ ($C_{17}H_{21}N_4O_{12}Dy$)	636.50 (635.63)	65	132	25.00 (25.57)	32.50 (32.09)	3.55 (3.33)	8.50 (8.89)	65
(Dy^2)	$[Dy(L^2)(NO_3)_2(H_2O)_2]NO_3$ ($C_{18}H_{23}N_4O_{12}Dy$)	652.75 (649.64)	75	148	25.25 (25.01)	33.85 (33.25)	3.75 (3.57)	8.45 (8.62)	60
(Dy^3)	$[Dy(L^3)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Dy$)	665.00 (663.66)	70	>260	24.72 (24.49)	34.05 (34.36)	3.95 (3.80)	8.65 (8.44)	53
(Dy^4)	$[Dy(L^4)(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Dy$)	676.27 (677.67)	70	160–161	24.00 (23.98)	35.56 (35.42)	4.00 (4.02)	8.57 (8.27)	48
(Dy^5)	$[Dy(L^5)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Dy$)	664.71 (663.66)	75	174–178	24.75 (24.49)	34.55 (34.36)	3.75 (3.80)	8.50 (8.44)	50
(Dy^6)	$[Dy(L^6)(NO_3)_2(H_2O)_2]NO_3$ ($C_{18}H_{23}N_4O_{12}Dy$)	648.72 (649.64)	60	300	25.25 (25.01)	33.45 (33.25)	3.65 (3.57)	8.37 (8.62)	55
(Dy^7)	$[Dy(L^7)(NO_3)_2(H_2O)_2]NO_3$ ($C_{19}H_{25}N_4O_{12}Dy$)	665.81 (663.66)	65	>270	24.85 (24.49)	34.36 (34.36)	3.42 (3.80)	8.20 (8.44)	62
(Dy^8)	$[Dy(L^8)(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Dy$)	678.00 (677.67)	65	>300	23.75 (23.98)	35.75 (35.42)	4.25 (4.02)	8.35 (8.27)	47
(Dy^9)	$[Dy(L^9)(NO_3)_2(H_2O)_2]NO_3$ ($C_{21}H_{29}N_4O_{12}Dy$)	693.15 (691.69)	60	>300	23.00 (23.49)	36.50 (36.43)	4.55 (4.23)	8.00 (8.10)	56
(Dy^{10})	$[Dy(L^{10})(NO_3)_2(H_2O)_2]NO_3$ ($C_{20}H_{27}N_4O_{12}Dy$)	670.96 (677.67)	65	140	23.56 (23.98)	35.25 (35.42)	4.15 (4.02)	8.72 (8.27)	52

[a] Observed molecular weight × van't Hoff factor.

Table 3
Important IR absorption bands (in cm^{-1}) of the ligands and Tb^{III} nitrate complexes

Complex number	ν(C=O)[a]	ν(C=O)[b]	ν(N–H)	ν(O–H)	δ(HOH)	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5	$\nu_4 - \nu_1$	$\nu_3 - \nu_5$
(Tb^{1})	1700 s	1720 s	3400 s	3200–3600 b	1630 m	1470 s	1329 s	1040 m	822 w	745 s	698 s	141	47
(Tb^{2})	1699 s	1726 s	3391 s	3200–3600 b	1638 m	1460 s	1310 s	1040 m	825 w	750 s	700 s	150	50
(Tb^{3})	1701 s	1730 s	3389 s	3200–3600 b	1624 m	1470 s	1327 s	1040 m	825 w	754 s	698 s	143	56
(Tb^{4})	1700 s	1728 s	3385 s	3200–3500 b	1627 m	1470 s	1320 s	1038 m	823 w	750 s	698 s	150	52
(Tb^{5})	1701 s	1732 s	3398 s	3200–3600 b	1624 m	1458 s	1313 s	1028 m	825 w	750 s	698 s	145	52
(Tb^{6})	1726 s	1730 s		3200–3600 b	1624 m	1480 s	1317 s	1038 m	823 w	750 s	698 s	163	52
(Tb^{7})	1722 s	1727 s		3200–3600 b	1637 m	1475 s	1307 s	1040 m	825 w	750 s	698 s	168	52
(Tb^{8})	1720 s	1725 s		3200–3600 b	1638 m	1485 s	1340 s	1038 m	825 w	750 s	698 s	145	52
(Tb^{9})	1710 s	1718 s		3200–3600 b	1638 m	1480 s	1339 s	1041 m	825 w	750 s	700 s	141	50
(Tb^{10})	1713 s	1722 s		3200–3600 b	1627 m	1480 s	1318 s	1040 m	823 w	750 s	698 s	162	52

Here, s: strong, b: broad, m: medium, w: weak.

[a] For ligands.

[b] For complexes.

oxide in concentrated HNO_3. Purified ethanol (95%) was used as a solvent.

2.2. Preparation of ligands and complexes

The various substituted 2,6-diphenylpiperidin-4-ones (L^1)–(L^{10}) were prepared following reported procedures [16,17]. The structures of the ligands are reported in our earlier papers [13–15]. All the complexes have been prepared by a general method. A mixture of lanthanide(III) nitrate (5 mmol) and piperidin-4-one (10 mmol) in ethanol (50 ml) was refluxed on a water bath for 3–4 h. Subsequently, the solvent was distilled off under reduced pressure. The residue was repeatedly washed with hot ethanol, acetone and ether anddried under vacuum over P_2O_5. All complexes are colourless amorphous solids, soluble in methanol, dimethylforamide, dimethylsulfoxide and acetonitrile and insoluble in acetone, ether, chloroform and water. They are stable in air under dry conditions.

2.3. Physico-chemical techniques

The metal content of the complexes was determined by complexometric ethylene diamine tetraacetic acid (EDTA) titration [18] using xylenol orange as an indicator at pH 6. Elemental analyses (C, H and N) were determined using a Carlo Erba 1106 microanalytical instrument. Conductance measurements were

Table 4
Important IR absorption bands (in cm^{-1}) of the ligands and Dy^{III} nitrate complexes

Complex number	ν(C=O)[a]	ν(C=O)[b]	ν(N–H)	ν(O–H)	δ(HOH)	ν_4	ν_1	ν_2	ν_6	ν_3	ν_5	$\nu_4 - \nu_1$	$\nu_3 - \nu_5$
(Dy^{1})	1700 s	1720 s	3385 s	3200–3600 b	1638 m	1480 s	1319 s	1040 m	822 w	746 s	698 s	161	48
(Dy^{2})	1699 s	1726 s	3389 s	3200–3600 b	1624 m	1470 s	1307 s	1040 m	823 w	750 s	698 s	163	52
(Dy^{3})	1701 s	1730 s	3398 s	3200–3600 b	1624 m	1470 s	1319 s	1040 m	825 w	754 s	696 s	151	58
(Dy^{4})	1700 s	1728 s	3371 s	3200–3600 b	1639 m	1470 s	1313 s	1038 m	825 w	750 s	698 s	157	52
(Dy^{5})	1701 s	1732 s	3400 s	3200–3600 b	1637 m	1470 s	1288 s	1028 m	823 w	750 s	698 s	182	52
(Dy^{6})	1726 s	1730 s		3200–3600 b	1624 m	1470 s	1316 s	1039 m	825 w	750 s	698 s	154	52
(Dy^{7})	1722 s	1727 s		3200–3600 b	1638 m	1480 s	1329 s	1040 m	825 w	748 s	698 s	151	50
(Dy^{8})	1720 s	1725 s		3200–3600 b	1627 m	1490 s	1330 s	1038 m	823 w	746 s	698 s	160	48
(Dy9)	1710 s	1718 s		3200–3600 b	1624 m	1480 s	1329 s	1030 m	826 w	758 s	700 s	150	58
(Dy^{10})	1713 s	1722 s		3200–3600 b	1624 m	1475 s	1325 s	1040 m	825 w	758 s	700 s	150	58

Here, s: strong, b: broad, m: medium, w: weak.

[a] For ligands.

[b] For complexes.

performed on 10^{-3} mol l^{-1} solutions of the complexes in acetonitrile using a type CM-82 Elico conductivity bridge with a dip type conductivity cell fitted with a platinum electrode (cell constant = 1.0 cm^{-1}). The molecular weight determinations have been carried out by the depression of freezing point method using camphor as the solvent in which the complexes are completely soluble. The experiments were repeated thrice for each complex and the average values have been taken. The results were found to agree with the calculated values within ±2% error. The magnetic moments of complexes were determined by the Gouy method at room temperature. Electronic spectra of the complexes were recorded on a Hitachi U-2000 spectrophotometer. The IR spectra of the ligands and the complexes were recorded on a Shimadzu FT-IR 8000 spectrophotometer in the 4000–400 cm^{-1} region using the KBr disc technique. The simultaneous thermogravimetric and differential thermal analyses (TG–DTA) were carried out using a STA 1500 Shimadzu DT 40 thermal analyzer. The thermal experiments were carried out in air, using 3–5 mg samples at a heating rate of 10 °C min^{-1} in the temperature range from ambient to 800 °C using a platinum cup as the sample holder.

3. Results and discussion

The analytical and conductance data of terbium(III) and dysprosium(III) complexes are presented in Tables 1 and 2, respectively. The molar conductance data indicate that these complexes are 1:1 electrolytes [19]. The observed molecular weights of terbium(III) and dysprosium(III) complexes are found to be exactly half of the expected value, showing that the van't Hoff factor is two. Based on the analytical and conductance data, the stoichiometry of these complexes can be represented as $[Ln(L)\ (NO_3)_2(H_2O)_2]NO_3$ where, Ln: Tb and Dy, and L: piperidin-4-one.

Table 6
Bonding parameters obtained from electronic spectral data of the dysprosium(III) complexes

Complex		β	$b^{1/2}$	δ (%)
Number	Formula			
(Dy^1)	$[Dy(L^1)(NO_3)_2(H_2O)_2]NO_3$	0.9965	0.0299	0.3512
(Dy^2)	$[Dy(L^2)(NO_3)_2(H_2O)_2]NO_3$	0.9972	0.0265	0.2808
(Dy^3)	$[Dy(L^3)(NO_3)_2(H_2O)_2]NO_3$	0.9945	0.0371	0.5530
(Dy^4)	$[Dy(L^4)(NO_3)_2(H_2O)_2]NO_3$	0.9956	0.0332	0.4419
(Dy^5)	$[Dy(L^5)(NO_3)_2(H_2O)_2]NO_3$	0.9968	0.0283	0.3210
(Dy^6)	$[Dy(L^6)(NO_3)_2(H_2O)_2]NO_3$	0.9925	0.0433	0.7557
(Dy^7)	$[Dy(L^7)(NO_3)_2(H_2O)_2]NO_3$	0.9950	0.0354	0.5025
(Dy^8)	$[Dy(L^8)(NO_3)_2(H_2O)_2]NO_3$	0.9963	0.0466	0.3714
(Dy^9)	$[Dy(L^9)(NO_3)_2(H_2O)_2]NO_3$	0.9978	0.0235	0.2205
(Dy^{10})	$[Dy(L^{10})(NO_3)_2(H_2O)_2]NO_3$	0.9939	0.0390	0.6137

3.1. *Magnetic properties*

The effective magnetic moments (μ_{eff}) of terbium(III) and dysprosium(III) complexes are found between 9.39–9.51 and 10.50–10.75 BM, respectively, and do not deviate from Van Vleck values [20], revealing the non-participation of 4f-electrons in bond formation. It is also evident from the data that there is no metal–metal interaction or spin–spin coupling.

3.2. *Infrared spectra*

The IR spectra of ligands and complexes were mainly analysed for those specific frequencies which are directly involved in the complex formation and their values are recorded in Tables 3 and 4. The sharp

Table 5
Assignments of transitions in the electronic spectra of the dysprosium complexes (Dy^2) and (Dy^5)

Complexs		Absorption frequency (cm^{-1})	Log ε (max)	Assignment
Number	Formula			
(Dy^2)	$[Dy(L^2)(NO_3)_2(H_2O)_2]NO_3$	23297	3.65	$6_{H_{15/2}} \rightarrow 4_{G_{11/2}}$
		22150	3.10	$\rightarrow 4_{I_{15/2}}$
		21123	3.98	$\rightarrow 4_{F_{9/2}}$
(Dy^5)	$[Dy(L^5)(NO_3)_2(H_2O)_2]NO_3$	23257	2.98	$6_{H_{15/2}} \rightarrow 4_{G_{11/2}}$
		22165	3.35	$\rightarrow 4_{I_{15/2}}$
		21120	2.85	$\rightarrow 4_{F_{9/2}}$

band around 3300 cm^{-1} due to the N–H stretching for the ligand (L^1)–(L^5) is shifted to higher frequency (ca. 3400 cm^{-1}) and broadened [21] in the corresponding complexes (Tb^1)–(Tb^5) and (Dy^1)–(Dy^5), respectively. The ligands containing NCH_3 group (L^6)–(L^{10}) exhibit peaks in the region 3000–2800 cm^{-1} due to C–H stretching vibrations of NCH_3 group along with the Bohlmann bands. These peaks are missing in the spectra of the corresponding complexes (Tb^6)–(Tb^{10}) and (Dy^6)–(Dy^{10}). The C–H stretching absorptions may be shifted to higher frequency and merged with the broad peak [22]. The Bohlmann bands [23] which occur in the region 3000–2750 cm^{-1} in the IR spectra of the ligands are found to be missing in the spectra of the corresponding complexes. The absence of these bands reveals that there may be a conformational change of piperidinone ring due to its complexation with the metal ion through the lone pair of electrons of the ring nitrogen. All the above observations lead to the conclusion that the ring nitrogen is coordinated to Tb^{III} and Dy^{III} ions with a slight conformational change.

Table 7
Thermal analysis of the Tb^{III} nitrate complexes[a]

Complex		DTA peak temperature (°C)	Thermogravimetry		Decomposition product
Number	Formula		Temperature range (°C)	Weight loss found (calculated) %	
(Tb^2)	$[Tb(C_{18}H_{19}NO)(NO_3)_2(H_2O)_2]NO_3$	173+	170–190	5.76 (5.58)	$[Tb(C_{18}H_{19}NO)(NO_3)_2]NO_3$
		228−			
		374−	200–490	45.75 (46.62)	$Tb(NO_3)_3$
		484−			
		529−	490–575	71.75 (71.07)	Tb_4O_7
(Tb^3)	$[Tb(C_{19}H_{21}NO)(NO_3)_2(H_2O)_2]NO_3$	185+	175–200	5.50 (5.46)	$[Tb(C_{19}H_{21}NO)(NO_3)_2]NO_3$
		230−	210–450	48.00 (47.75)	$Tb(NO_3)_3$
		410+			
		525−	460–575	72.00 (71.68)	Tb_4O_7
(Tb^4)	$[Tb(C_{20}H_{23}NO)(NO_3)_2(H_2O)_2]NO_3$	174+	170–210	5.00 (5.31)	$[Tb(C_{20}H_{23}NO)(NO_3)_2]NO_3$
		230−			
		237−	220–450	49.00 (48.84)	$Tb(NO_3)_3$
		393−			
		423−			
		511−	450–550	72.00 (72.27)	Tb_4O_7
(Tb^5)	$[Tb(C_{19}H_{21}NO)(NO_3)_2(H_2O)_2]NO_3$	202+	190–210	5.00 (5.46)	$[Tb(C_{19}H_{21}NO)(NO_3)_2]NO_3$
		218−	210–400	47.00 (47.75)	$Tb(NO_3)_3$
		367−			
		511−	450–525	72.00 (71.68)	Tb_4O_7
(Tb^6)	$[Tb(C_{18}H_{19}NO)(NO_3)_2(H_2O)_2]NO_3$	174+	170–200	6.00 (5.58)	$[Tb(C_{18}H_{19}NO)(NO_3)_2]NO_3$
		223−			
		365−	210–450	46.50 (46.62)	$Tb(NO_3)_3$
		415−			
		520−	475–575	71.00(71.07)	Tb_4O_7
(Tb^7)	$[Tb(C_{19}H_{21}NO)(NO_3)_2(H_2O)_2]NO_3$	179+	180–205	5.00 (5.46)	$[Tb(C_{19}H_{21}NO)(NO_3)_2]NO_3$
		235−			
		365−	210–450	47.50 (47.75)	$Tb(NO_3)_3$
		437−			
		527−	475–575	72.00 (71.68)	Tb_4O_7
(Tb^8)	$[Tb(C_{20}H_{23}NO)(NO_3)_2(H_2O)_2]NO_3$	193+	185–210	5.00 (5.35)	$[Tb(C20H23NO)(NO_3)_2]NO_3$
		245−			
		390−	225–450	49.00 (48.84)	$Tb(NO_3)_3$
		420−			

[a] Here, (+) endothermic; (−) exothermic.

The carbonyl stretching frequency of the ligands lie around 1700 cm^{-1}. This absorption is shifted to higher frequency in the corresponding complexes. The higher frequency shift may be due to conformational changes that occur as a result of coordination of the ring nitrogen and not due to carbonyl group participation [5].

The presence of water molecules in the complexes is shown by a broad absorption band in the 3600–3200 cm^{-1} region (merged with the NH absorption) due to O–H stretching vibration and a sharp medium peak at 1624 cm^{-1} due to H–O–H bending vibration [24].

The ionic nitrate group which has $D_{3}h$ symmetry, has four fundamental vibrations, three of which are IR active. Upon coordination as either a monodentate or a bidentate ligand, the symmetry becomes C_{2v}, which has six infrared active normal modes of vibrations. The characteristic frequencies of coordinating nitrate groups ν_1 to ν_6 of the complexes are in range 1290–1330, 1029–1040, 745–758, 1458–1480, 698–700 and 822–826 cm^{-1}, respectively. The magnitudes of $\nu_4 - \nu_1$ and $\nu_3 - \nu_5$ for Tb^{III} complexes are in the range 141–168 and 47–56 cm^{-1}, respectively, and for Dy^{III} complexes 151–182, 48–58 cm^{-1},

Table 8
Thermal analysis data of DyIII nitrate complexes[a]

Complex		DTA peak temperature (°C)	Thermogravimetry		Decomposition product
Number	Formula		Temperature range (°C)	Weight loss found (calculated) %	
(Dy^1)	$[Dy(C_{17}H_{17}NO)(NO_3)_2(H_2O)_2]NO_3$	172+	170–200	5.50 (5.67)	$[Dy(C_{17}H_{17}NO)(NO_3)_2]NO_3$
		225−			
		375−	220–475	40.00 (39.51)	$Dy(NO_3)_3$
		456−			
		550−	475–600	71.00 (70.66)	Dy_2O_3
(Dy^2)	$[Dy(C_{18}H_{19}NO)(NO_3)_2(H_2O)_2]NO_3$	173+	170–190	5.25 (5.55)	$[Dy(C_{18}H_{19}NO)(NO_3)_2]NO_3$
		213−			
		285−	200–475	41.00 (40.81)	$Dy(NO_3)_3$
		407−			
		450−			
		517−	475–600	71.00 (71.29)	Dy_2O_3
(Dy^3)	$[Dy(C_{19}H_{21}NO)(NO_3)_2(H_2O)_2]NO_3$	175+	170–200	5.25 (5.43)	$[Dy(C_{19}H_{21}NO)(NO_3)_2]NO_3$
		248−			
		253−	340–460	42.00 (42.06)	$Dy(NO_3)_3$
		374−			
		452−			
		515−	460–525	72.00 (71.90)	Dy_2O_3
(Dy^4)	$[Dy(C_{20}H_{23}NO)(NO_3)_2(H_2O)_2]NO_3$	180+	175–200	5.20 (5.32)	$[Dy(C_{20}H_{23}NO)(NO_3)_2]NO_3$
		215−			
		380−	200–500	43.50 (43.26)	$Dy(NO_3)_3$
		465−			
		525−	500–600	73.00 (72.48)	Dy_2O_3
(Dy^5)	$[Dy(C_{19}H_{21}NO)(NO_3)_2(H_2O)_2]NO_3$	202+	190–210	5.50 (5.43)	$[Dy(C_{19}H_{21}NO)(NO_3)_2]NO_3$
		223−			
		370−	220–475	42.00 (42.06)	$Dy(NO_3)_3$
		455−			
		528−	475–600	71.50 (71.90)	Dy_2O_3
(Dy^9)	$[Dy(C_{21}H_{25}NO)(NO_3)_2(H_2O)_2]NO_3$	195+	190–200	5.00 (5.21)	$[Dy(C_{21}H_{25}NO)(NO_3)_2]NO_3$
		245−			
		367−	210–490	44.00 (44.41)	$Dy(NO_3)_3$
		465−			
		515−	500–575	73.00 (73.04)	Dy_2O_3

[a] Here, (+) endothermic; (−) exothermic.

respectively, suggesting that the nitrate groups are coordinated as bidentate ligands [24,25]. Another band at ca. 1384 cm^{-1} due to the ionic nitrate is also present in the spectra. This observation, coupled with elemental analyses and conductance data, reveals the presence of one ionic and two bidentate nitrate groups.

Two new bands observed in the region 550–543 and 420–415 cm^{-1} are attributed to M–N and M–O bonding, respectively [26].

3.3. Electronic spectra

The electronic spectra of dysprosium(III) complexes have been recorded in methanol as solvent and are found to be similar. In the UV region, a strong band around 220 nm and a weak band around 260 nm are present which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively, of the carbonyl group of the ligand.

The absorption bands observed in the visible region are due to f–f transitions. The tentative assignments of bands for the dysprosium(III) complexes (Dy^2) and (Dy^5) are given in Table 5. The spectra of the complexes show a shift of bands towards lower energy, compared with those of the aquo ions owing to the nephelauxetic effect [27]. The nephelauxetic ratio β, percentage convalency δ and the bonding parameter $b^{1/2}$ calculated [28] for these complexes are presented in Table 6. The values of β are found to be less than unity and the positive values of the bonding parameter $b^{1/2}$ and Sinha's parameter δ indicate convalency in the metal–ligand bonding [29]. The δ values are <1.0 in all of these complexes indicating weak covalent character in the metal–ligand bond. The comparatively small magnitude of $b^{1/2}$ values shows the participation of the 4f-orbitals in the metal–ligand bond to a very small extent [19]. The visible electronic spectra of terbium(III) complexes show no significant absorption.

3.4. Thermal studies

The simultaneous TG–DTA measurements of terbium(III) and dysprosium(III) complexes were carried out in air and their thermal data are given in Tables 7 and 8, respectively. The thermal studies have also been carried out for the ligand (L^5) and the thermogram is shown in Fig. 1. The thermal curves of a few complexes are given (Figs. 2 and 3). The TG–DTA curves of terbium(III) and dysprosium(III) complexes are similar. Generally, the thermal decomposition takes place in three stages. The thermal curves of all the complexes show an endothermic peak in the 170–210 °C temperature range. The mass loss at this

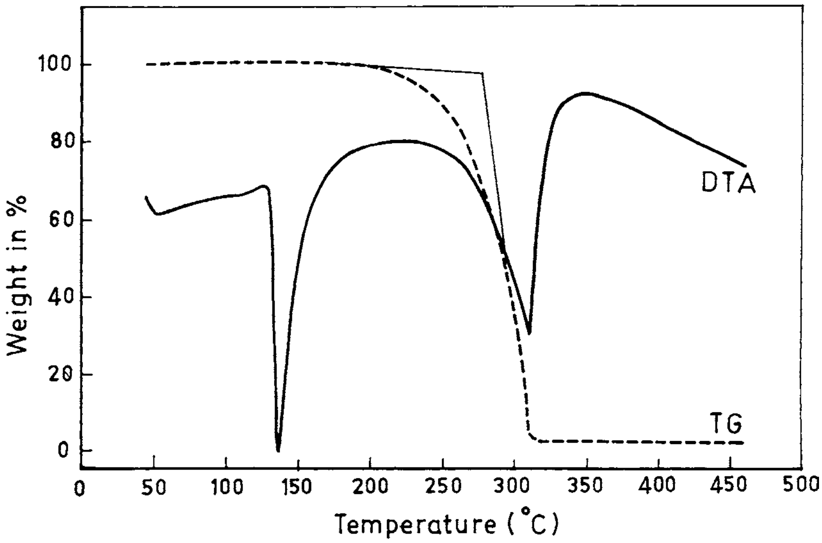


Fig. 1. TG–DTA of the ligand (L^5).

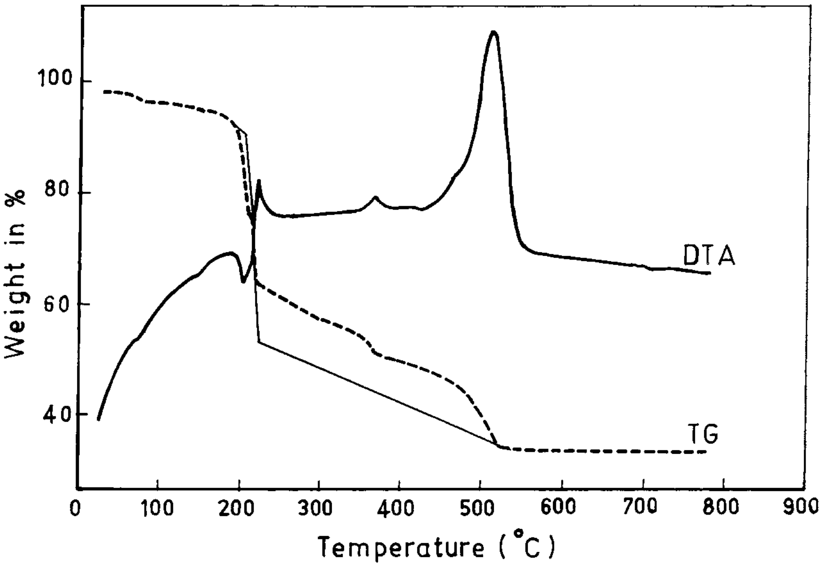


Fig. 2. TG–DTA of the complex (Tb^5).

temperature corresponds to the dehydration of two water molecules. The loss of water molecules in this temperature range also indicate that they are coordinated with the metal ion [30]. This is followed by the decomposition of organic ligand in the temperature range 200–450 °C (shown by an exothermic peak) leading to the formation of lanthanide(III) nitrate. The second stage of decomposition is supported by the observation list the free ligand also undergoes decomposition the same temperature range (Fig. 1). The final residue corresponds to Tb_4O_7 and Dy_2O_3 for Tb^{III} and Dy^{III} complexes [31], respectively.The thermal decomposition sequences of terbium(III) and dyprosium(III) complexes are given in the following

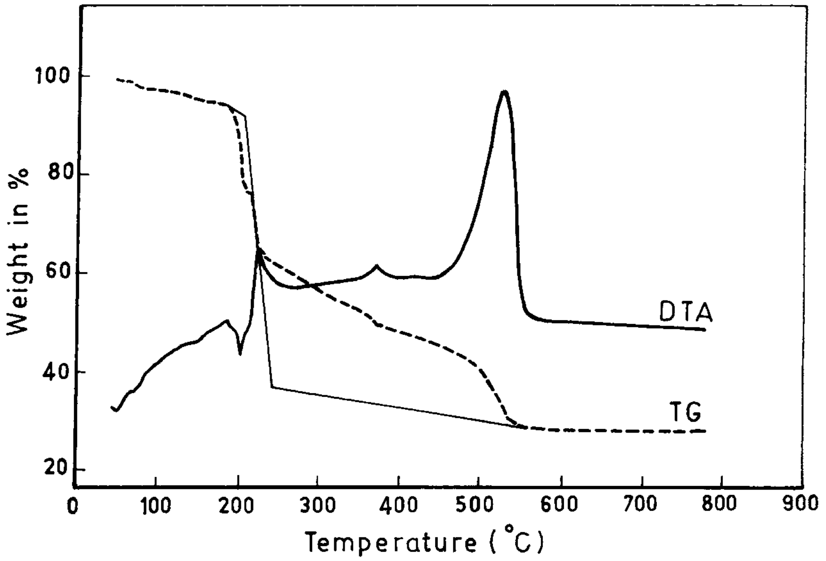


Fig. 3. TG–DTA of the complex (Dy^5).

equations.

$$[\mathrm{Tb(L)(NO_3)_2(H_2O)]NO_3} \xrightarrow[-2\mathrm{H_2O}]{170\text{–}210\,^{\circ}\mathrm{C}} [\mathrm{Tb(L)(NO_3)_2]NO_3}$$

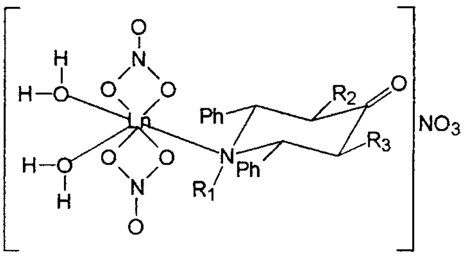
$$\xrightarrow[-\mathrm{L}]{200\text{–}450\,^{\circ}\mathrm{C}} \mathrm{Tb(NO_3)_3} \xrightarrow{475\text{–}575\,^{\circ}\mathrm{C}} \mathrm{Tb_4O_7}$$

$$[\mathrm{Dy(L)(NO_3)_2(H_2O)_2]NO_3} \xrightarrow[-2\mathrm{H_2O}]{170\text{–}210\,^{\circ}\mathrm{C}} [\mathrm{Dy(L)(NO_3)_2]NO_3}$$

$$\xrightarrow[-\mathrm{L}]{300\text{–}450\,^{\circ}\mathrm{C}} \mathrm{Dy(NO_3)_3} \xrightarrow{475\text{–}600\,^{\circ}\mathrm{C}} \mathrm{Dy_2O_3}$$

4. Conclusion

The molar conductance studies and molecular weight determinations of terbium(III) and dysprosium(III) complexes indicate the 1:1 electrolytic nature of the complexes. IR spectral and conductance studies reveal that two of the three nitrate groups coordinate to the metal ion in a bidentate fashion and the third one remains ionic. The IR spectral data also show the presence of water molecules and the thermal studies confirm the coordination of two water molecules. Although the ligands, piperidin-4-ones, contain two potential coordinating sites, namely, the ring nitrogen and the carbonyl group, they are found to coordinate only through ring nitrogen atom, thereby indicating the unidentate nature of these ligands. Thus, all the observed facts lead to the conclusion that the coordination number of terbium(III) and dysprosium(III) is seven in these complexes. The following probable structure may be assigned for the complexes.



where Ln: Tb and Dy.

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