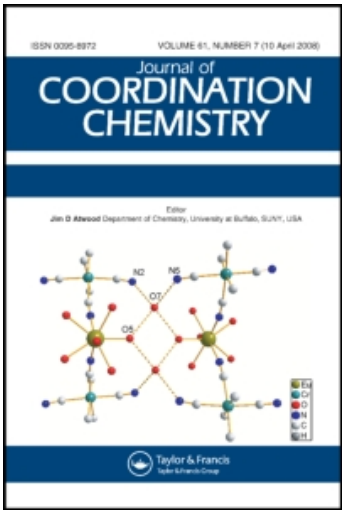

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Lanthanide complexes of D-penicillamine: formation constants, spectral and thermal properties

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Lanthanide complexes of D-penicillamine: formation constants, spectral and thermal properties

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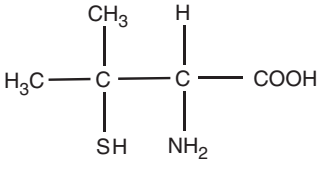
The complex-formation of lanthanide(III) elements with D-penicillamine have been investigated in acidic and neutral media. The macroscopic protonation constants of the ligand and the formation constants of $[Ln.Pen]^+$, $[Ln.Pen_2]^-$, [Ln.Pen.OH] and $[Ln.Pen.(OH)_2]^-$ complexes were determined from pH-metric data using the BEST computer program. Elemental analyses of the solid complexes indicate formation of 1 : 1 metal : ligand species. The binding sites in the complexes with the possible role of $–COO^-$, $–NH_2$ and –SH groups in the coordination have been discussed using infrared data. The complexes decompose in four steps as shown by their t.g. and d.t.a. analyses. A mechanism of decomposition is proposed which is supported by mass spectral data.

Keywords: D-penicillamine; Ln(III); Complexes; Formation constants; Spectral and thermal properties

1. Introduction

D-penicillamine is a sulfur-containing amino acid, first used as a medication for clearing the human body from excess copper in treatment of Wilson's disease [1], as a therapeutic agent in treatment of rheumatoid arthritis [2], as detoxicant (antidote) upon poisoning from heavy metals [3–5], for inhibiting HIV replication and for treatment of hepatitis [6].



D-penicillamine (H_2Pen)

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Interest in D-penicillamine as a ligand arises from several possibilities of coordination. D-penicillamine, together with its zwitterionic form, with three functional groups ($-NH_2$, $-S^{2-}$ and $-COO^-$) usually forms bidentate complexes by coordination of N and S atoms [7, 8], but formation of monodentate (S) [9, 10], tridentate (N,O,S,) or tetradentate (N,O,O,S) complexes [11, 12] cannot be ruled out. The sulfur, nitrogen or oxygen atoms could also act as a bridging ligand [13].

Complexation of some transition metal ions with D-penicillamine was studied in considerable detail including Hg(II), Cd(II) [14, 15]; Pd(II),Pt(II) [13, 16, 17]; Ni(II) [8, 18]; Cu(II) [19, 20]; Au(III),Ag(I) [21, 22]; Fe(III),Cr(III) [23, 24] and VO^{2+} [25].

The rare-earth elements are not biometals. However, because of their similarity to Ca^{2+} and Mg^{2+}, Ln^{3+} ions can replace (or supplement) these biometals in some biological processes, creating the prospect of using complexes of rare-earth elements as drugs. Data on the composition and stability of the complexes of D-penicillamine with rare-earth elements in aqueous solution as well as in the solid state are scarce. Complexation of Ln^{3+} = Pr, Nd, Gd, Ho and Yb with D-penicillamine (H_2Pen) in the pH range 3–11 was studied by computer simulation based on the data of pH-metric titration of Ln^{3+} solutions with D-penicillamine [26]. The aim of the present work is to gain better understanding of the Ln(III)-Pen formation equilibria. In addition, we synthesized and characterized the first lanthanide complexes in which the metal coordinates via the S atom, NH_2 and COO^- groups simultaneously.

2. Experimental

D-penicillamine was obtained from Fluka. Other chemicals are reagent grade and used without further purification.

2.1. *Preparation of the solid complexes*

All complexes were prepared according to the following procedure. Pen dissolved in a minimum of water is added slowly with stirring to the metal nitrate, which was also dissolved in minimum water. The pH of the mixture was increased to 5.5 by addition of dilute KOH solution dropwise with stirring. After one hour, the formed precipitate was filtered, washed with distilled water and dried under vacuum over $CaCl_2$.

2.2. *Equipment*

C, H and N content was measured using a Perkin-Elmer 2400 elemental analyzer at the Microanalytical Center of Cairo University. Infrared spectra of the ligand and its complexes were obtained on a Bruker Vector22 spectrophotometer. T.g., d.t.g. and d.t.a. analyses were recorded using a Shimadzu-50 thermal analyzer in flowing nitrogen ($30\,mL\,min^{-1}$) with heating at $10^{\circ}C\,min^{-1}$. Metal content of the complexes was obtained by titration with EDTA using xylenol orange as indicator at pH 4 using acetate buffer.

2.3. *Potentiometric titrations*

Nitrate solutions of lanthanides were prepared from A.R. grade metal nitrates (B.D.H.) and were standardized by EDTA titration. Stock solutions of HNO_3, KOH and $NaNO_3$ were prepared using A.R. grade chemicals. KOH solution was standardized against potassium hydrogen phthalate solution and carbonate content was checked using Gran's plot [27].

Measurements were carried out using a Fischer Accumet 825 MP pH Meter equipped with a Fischer combined glass electrode. The pH Meter was standardized with phthalate and phosphate buffers before titrations. Titrant solution was added with a Fischer-455 automatic burette. Sample solutions were titrated in a double-walled glass cell maintained at constant temperature using a Fischer Scientific Isotemp Refrigerated Circulating Bath under continuous flow of nitrogen. Titrations were performed over the desired pH range using 50 mL samples in a medium of a constant ionic strength (5 mL 1 M $NaNO_3$). The following solutions were titrated:

(a) 5 mL 0.1 M HNO_3 + 40 mL H_2O.
(b) 5 mL 0.06 M Pen + 5 mL 0.1 M HNO_3 + 35 mL H_2O.
(c) 5 mL 0.06 M Pen + 40 mL H_2O.
(d) 5 mL 0.02 M Pen + 5 mL 0.01 M Ln^{3+} + 5 mL 0.1 HNO_3 + 30 mL H_2O.

Equilibrium pH values were determined at every incremental addition of standard KOH to the experimental solutions. The experimental pH values were plotted as a function of m values (m is the ratio of moles of base added to moles of metal ion present). The value of $K_w([H^+][OH^-])$ used in computation was calculated from the strong base solution and was found to be 13.83 ± 0.02 at $30 \pm 0.01^\circ C$ and ionic strength of 0.1 M $NaNO_3$.

2.4. *Calculations*

The protonation constants of the ligand and the formation constants of the complexes were computed from the titration data using the PKAS and BEST computer programs [28]. Species distribution diagrams were calculated from the formation constants and plotted using SPE and SPEPLOT computer programs [28]. The model selected was that which gave the best statistical fit to the titration data and consistent with the chemical logic. The computation of the formation constants was based on minimization of the sigma fit, however, error estimates were performed by propagation of error analysis. Hydrolysis of the lanthanides was taken into account during calculation of the formation constants of the complexes [29].

3. Results and discussion

3.1. *Solution chemistry of the D-penicillamine*

The free ligand titration curve shows three inflections (figure 1). The value of pK_1 can be ascribed unambiguously to deprotonation of the carboxylic group, but pK_2

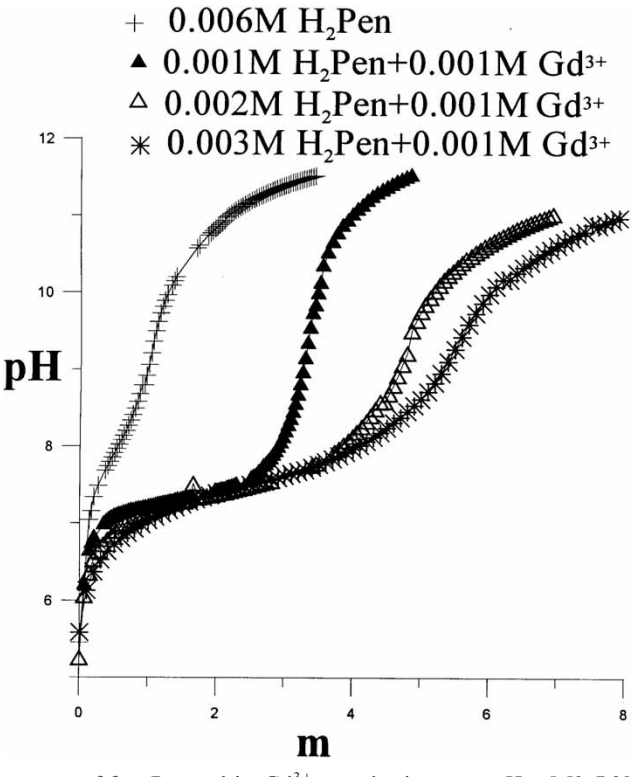


Figure 1. Titration curves of free Pen and its Gd^{3+} complex in water, pH = 5.59–7.28, [KOH] = 0.108 M, I = 0.1 M $NaNO_3$, V = 50 mL and t = 25°C.

Table 1. Macroscopic dissociation constants of D-penicillamine in water, [H_2Pen] = 0.006 M, [KOH] = 0.116 M, I = 0.1 M $NaNO_3$ at t = 25°C.

	This work						
pK_n*		n	σ	Literature			
pK_1	2.19(0.03)	109	0.007	2.94[26]	1.92[30]	1.66[31]	2.44[32]	10.99[32]
pK_2	7.91(0.06)	109	0.007	8.19[26]	8.0[30]	7.75[31]	7.97[32]	7.88[33]
pK_3	10.35(0.06)	101	0.003	10.94[26]	10.74[30]	10.64[31]	10.96[32]	10.42[33]

* Values in parenthesis are error estimates.

and pK_3 arise from a combination of: dissociation from the thiol group and the amino group [25].

The macroscopic acid dissociation constants for the triprotic acid D-penicillamine obtained in this work agree satisfactory with literature data (table 1) [26, 30–33].

3.2. *Solution chemistry of the Ln-Pen complexes*

Complexation reactions of D-penicillamine with the lanthanide ions using 1 : 1, 1 : 2 and 1 : 3 molar ratios of Ln^{3+}:H_2Pen were titrated against 0.108 M KOH. The pH-metric titrations were carried out in a restricted range of pH values from 5.59 to 7.54 since the

solutions become cloudy at higher pH values. Increasing the pH, the precipitates persist till pH = 11.5. This is contrary to the results of Atanova *et al*. [26] who studied complexation of Pr^{3+}, Nd^{3+}, Gd^{3+}, Ho^{3+} and Yb^{3+} with D-penicillamine in the pH range 5.2–11.5. They have indicated that during titration, the solution became turbid in the pH range 7–8 due to formation of slightly soluble hydroxo-complexes. On further increase of pH, the precipitate gradually dissolved. We have used dilute solutions of the lanthanide ions (0.001 M) to avoid precipitation and the possibility of formation of polynuclear or hydroxo species. Also, the calculations were restricted to data obtained at pH values before precipitation to avoid complications from hydrolysis of complex species at higher pH. Titration at low pH was used for complexation of Ln(III) with aspartic and malic acids [34].

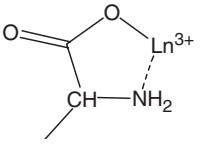
Titration curves of the Gd^{3+}:Pen complex in the pH range 5.92–7.42 are shown in figure 1 as a representative plot of the titration curves of H_2Pen with Ln^{3+}. At pH < 5, titration curves of 1 : 1, 1 : 2 and 1 : 3 Gd^{3+}:Pen overlap with the titration curve of the free Pen which indicates that the complex is not formed in this pH range. At pH = 5.92, the titration curves of the complex start to diverge from that of the free Pen indicating complex formation. Titration curves of H_2Pen with Ln(III) show a long buffer zone with a break at $m = 4$ for all systems, indicating release of four protons from the ligand for each metal ion when complexes formed. This supports the idea that 1 : 2 Ln(III):Pen complexes are predominant. The complex forming equilibria can be given as follows:

$$Ln^{3+} + H_2Pen \rightarrow [Ln.Pen]^+ + 2H^+ \qquad \beta_{[Ln.Pen]^+} = \frac{[Ln.Pen]^+.[H^+]^2}{[Ln^{3+}].[H_2Pen]}$$

$$Ln^{3+} + 2H_2Pen \rightarrow [Ln.(Pen)_2]^- + 4H^+ \qquad \beta_{[Ln.(Pen)_2]^-} = \frac{[Ln.(Pen)_2]^-.[H^+]^4}{[Ln^{3+}].[H_2Pen]^2}$$

A model was built using the BEST computer program with an algorithm which calculates p[H] directly and minimizes the sum of the weighed squares of $-\log[H^+]$ residuals [28]. The formation constants of hydroxo-complexes of the lanthanides [29] were used in calculations. The model includes H_2Pen, $HPen^-$ and Pen^{2-} with known ionization constants. The triprotic species H_3Pen^+ was excluded as a ligating species due to the expected repulsion in reaction with Ln^{3+}. Equivalent models of all the Ln^{3+}–H_2Pen systems included the complexes $Ln.Pen^+$, $Ln.Pen_2^-$, Ln.Pen.OH and $Ln.Pen.(OH)_2^-$, which are the most probable complexes of D-penicillamine. The $Ln.Hpen^{2+}$ and $Ln.H_2Pen^{3+}$ complexes were not identified by computer simulation and their concentrations were insignificant. The formation constants of the identified complexes of the lanthanide ion with D-penicillamine are given in table 2.

Apparently, coordination of Ln^{3+} by D-penicillamine is analogous to coordination by glycine NH_3^-–CH_2–COO^-, because the affinity of Ln^{3+} for nitrogen and oxygen is higher than that for sulfur. Formation of the five-membered glycine cycle is typical of Ln^{3+} chelation [26].

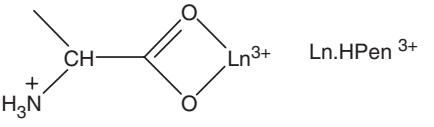


Ln.HPen $^{2+}$

Table 2. Formation constants of lanthanide-D-penicillamine complexes in water $[H_2Pen] = 0.002$ M, $[Ln^{3+}] = 0.001$ M, $[KOH] = 0.108$ M, $I = 0.1$ M $NaNO_3$, $V = 50$ mL, $t = 25°C$.

Ion	pH-range	$\log \beta_{[Ln.Pen]^+}$	$\log \beta_{[Ln.(Pen)_2]^-}$	$\log \beta_{[Ln.Pen.OH]}$	$\log \beta_{[Ln.Pen.(OH)_2]^-}$	n	σ
La^{3+}	5.66–7.54	5.72 (0.04)	10.84 (0.12)	−2.84 (0.14)	−10.34 (0.12)	40	0.01
Ce^{3+}	5.68–7.33	5.50 (0.03)	10.83 (0.02)	−3.03 (0.12)	−10.23 (0.17)	45	0.009
Pr^{3+}	5.67–7.40	5.47 (0.02)	10.63 (0.09)	−3.16 (0.08)	−10.51 (0.08)	40	0.007
Nd^{3+}	5.83–7.49	5.85 (0.02)	10.92 (0.03)	−2.60 (0.07)	−10.15 (0.09)	64	0.01
Sm^{3+}	5.93–7.31	6.07 (0.02)	11.42 (0.12)	−2.21 (0.07)	−9.59 (0.09)	50	0.01
Eu^{3+}	5.59–7.28	6.06 (0.02)	11.44 (0.1)	−1.28 (0.04)	−9.49 (0.07)	52	0.009
Gd^{3+}	5.92–7.42	6.05 (0.03)	11.26 (0.16)	−1.98 (0.07)	−9.49 (0.06)	70	0.01
Tb^{3+}	6.04–7.20	6.06 (0.02)	11.62 (0.1)	−1.25 (0.02)	−8.53 (0.03)	59	0.006
Dy^{3+}	6.41–7.50	6.07 (0.05)	11.62 (0.16)	−1.06 (0.03)	−8.60 (0.04)	58	0.009
Ho^{3+}	5.82–7.22	6.06 (0.04)	11.80 (0.2)	−1.18 (0.05)	−8.37 (0.07)	64	0.006
Er^{3+}	5.82–7.23	5.94 (0.03)	11.60 (0.08)	−1.53 (0.04)	−8.81 (0.04)	68	0.006
Tm^{3+}	5.81–7.36	5.91 (0.07)	11.78 (0.2)	−0.97 (0.05)	−8.51 (0.07)	71	0.01
Yb^{3+}	6.03–7.22	5.92 (0.08)	11.62 (0.08)	−0.74 (0.07)	−7.99 (0.1)	87	0.02
Lu^{3+}	6.04–7.38	5.93 (0.03)	11.46 (0.2)	−0.71 (0.14)	−8.08 (0.19)	98	0.02

Taking into account higher affinity for Ln^{3+} for oxygen compared to nitrogen, it may be proposed that in acid and neutral solutions, in which nitrogen is protonated, Ln^{3+} bonds to D-penicillamine through carboxyl oxygen atoms.



Choppin [35] has indicated that amino carboxylic acids, O–Ln–N with a five-membered chelate ring have high stability; however, a five-membered glycine ring is far more stable than four-membered carboxylate ring as observed for $Ln.Pen^+$.

Data on the composition and stability of complexes of D-penicillamine with lanthanides in aqueous or the solid state is scarce. Table 3 compares the data obtained in this study with that of the literature data for Ln(III)-glycine and Ln(III)-cysteine complexes. Agreement of our data with data obtained for Ln(III)-glycine complexes [36–38] confirm the formation of a glycine ring in the lanthanide-D-penicillamine complexes. On the other hand, formation constant values obtained in this work are higher than published values (table 3), perhaps due to formation of the glycine ring and participation of the SH group in bonding. Thus Ln^{3+}-Pen complexes, D-penicillamine is tridentate ligand with coordination predominantly with the oxygen atom and weakly with the nitrogen and sulfur. Because D-penicillamine is a derivative of cysteine, which contains the same donor groups, similar coordination of the lanthanides with this ligand would be expected, except that the Ln(III)-Pen complexes would be more stabile than Ln(III)-cysteine complexes because the donor properties of the glycine N atom are enhanced by inductive effects of the two CH_3 groups. Table 3 shows this for the La, Sm, Gd, Dy and Yb-cysteine complexes studied in 0.1 M KCl ionic strength [39]. Lanthanide-cysteine complexes studied in zero or 0.1 M KNO_3 ionic strength have higher formation constants compared to our results perhaps due to the supporting electrolyte.

A plot of the formation constants of the complexes against lanthanide atomic number is given in figure 2. Instead of the expected linearity from electrostatic

Table 3. Comparison of the obtained values of $\log\beta_{ML}$ and $\log\beta_{ML_2}$ of the Ln(III)-Pen complexes in the present work with those found in literature for glycine and cysteine complexes with lanthanides using glass electrode.

			Literature data									
	Present work		Glycine coomplexes					Cysteine complexes				
Ln^{3+}	$\log\beta_{ML}$	$\log\beta_{ML_2}$	I [M]	t°C	$\log\beta_{ML}$	$\log\beta_{ML_2}$	Ref.	I [M]	t°C	$\log\beta_{ML}$	$\log\beta_{ML_2}$	Ref.
La^{3+}	5.72	10.84	0.1 KCl	30	3.23	6.15	[40]	o.1 KCl	20	4.9	–	[47]
			0.2 $NaClO_4$	25,30	5.32,3.85	–	[37],[41]	0	20	6.02	–	[46]
			0.1 NaCl	20	3.56	–	[42]	0.1 KNO_3	30	13.25	18.45	[39]
Ce^{3+}	5.5	10.83	0.1 KCl	30	3.4	6.4	[40]	0	20	6.38	12.56	[46]
			0.2 $NaClO_4$	25,30	5.38,4.45	–	[37],[41]	0				
Pr^{3+}	5.47	10.63	0.1 KCl	30	3.62	6.96	[41]	0	20	6.58	12.97	[46]
			0.2 $NaClO_4$	25,30	5.55,4.5	–	[37],[42]	0.1 KNO_3	30	13.30	18.45	[39]
			0.22 KNO_3	25	5.6	–	[36]					
			0.2 KNO_3	25	4.4,6.25	–	[43],[38]					
Nd^{3+}	5.85	10.92	0.1 KCl	30	3.71	7.01	[40]	0	20	6.85	13.52	[46]
			0.2 $NaClO_4$	25,30	5.68,4.61	–	[37],[42]	0.1 KNO_3	30	13.35	18.55	[39]
			0.15 NaClO	25	3.26	–	[44]					
			0.1 $NaClO_4$	25	4.0	–	[45]					
			0.1 $NaClO_4$	25	5.84	–	[36]					
			0.22 KNO_3	25	4.5,6.31	–	[43],[38]					
			0.2 KNO_3									
Sm^{3+}	6.07	11.42	0.2 $NaClO_4$	25	5.84	–	[37]	0.1 KCl	20	4.8	–	[47]
								0	20	7.3	7.0	[46]
Eu^{3+}	6.06	11.44	0.22 KNO_3	25	5.54	–	[36]	0	20	7.52	14.02	[46]
Gd^{3+}	6.05	11.26	0.22 KNO_3	25	5.84	–	[36]	0.1 KCl	20	4.7	–	[47]
			0.2 KNO_3	25	4.64,6.11	–	[43],[38]	0	20	7.95	15.07	[46]
Tb^{3+}	6.06	11.62	–	–	–	–	–	0	20	7.9	15.52	[46]
Dy^{3+}	6.07	11.62	0.22 KNO_3	25	6.01	–	[36]	0.1 KCl	20	5.0	–	[47]
								0	20	8.62	15.07	[46]
Ho^{3+}	6.06	11.80	0.22 KNO_3	25	5.93	–	[36]	0	20	8.02	15.82	[46]
			0.03 KNO_3	25	4.44	–	[45]					
Er^{3+}	5.94	11.60	0.03 KNO_3	25	4.45	–	[45]	0	20	8.0	15.79	[46]
Tm^{3+}	5.91	11.78						0	20	7.99	15.89	[46]
Yb^{3+}	5.92	11.62	0.22 KNO_3	25	6.08	–	[36]	0.1 KCl	20	5.2	–	[47]
			0.03 KNO_3	25	4.51	–	[45]					
Lu^{3+}	5.93	11.46	0.03 KNO_3	25	4.51	–	[45]	–	–	–	–	–

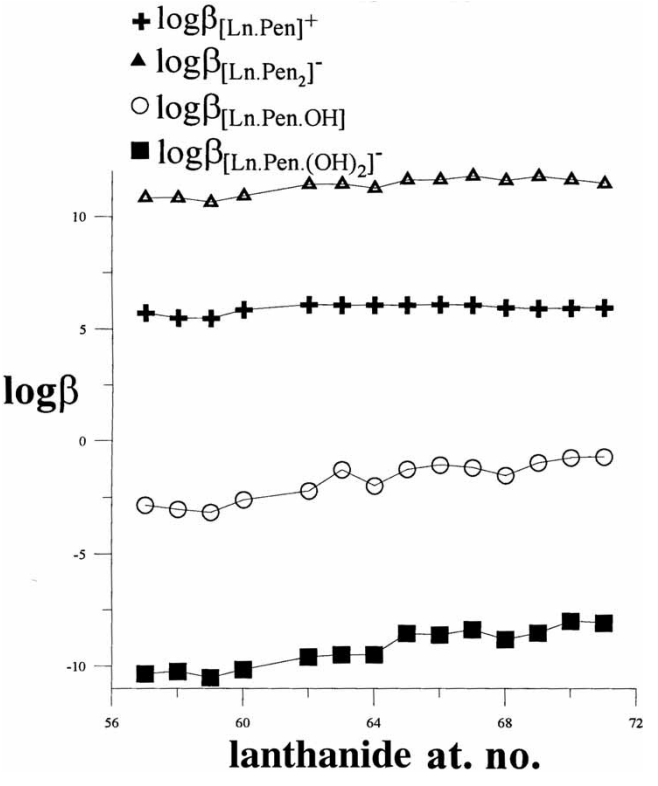


Figure 2. Variation of logβ of the Ln-Pen complexes with the lanthanide atomic number.

interaction between the lanthanide and the ligand, a curve is obtained with gradual increase between La and Eu, followed by a small decrease in Dy-Lu region. This deviation from linearity beyond Gd has been attributed to change in hydration along the series [35]. This kind of behavior has been observed for a variety of lanthanide complexes [48, 49].

Different magnitudes of the formation constants of the complexes are manifested in different concentrations of the complex species. The concentration distribution of various lanthanide D-penicill-amine complex species in solution as a function of pH are calculated and plotted using SPE and SPEPLOT computer programs [28]; an example is given in figure 3. The most probable complex species are $[Ln.Pen]^+$, $[Ln.Pen_2]^-$, [Ln.Pen.OH] and $[Ln.Pen.(OH)_2]^-$ with the percent of formation of $[Ln.Pen]^+$ reaching a maximum in the range from 36.4% ($[La.Pen]^+$) to 29% ($[Gd.Pen^+]$) at pH 7.6 to 7.8. For $[Tb.Pen]^+$, the maximum decreases to 19.8% at pH 7.2 and has the lowest value at $[Yb.Pen]^+$ and $[Lu.Pen]^+$ (6 and 6.2%) at pH 7.2. The same trend is observed for $[Ln.(Pen)_2]^-$ which has its maximum value at $[La.(Pen)_2]^-$ (26.4%) at pH 8.7 and decreases to 5.3% at $[Gd.(Pen)_2]^-$ (pH 8). This value is decreased further between $[Dy.(Pen)_2]^-$ and $[Tm.(Pen)_2]^-$ (2.5–2.9%) in the pH range 7.7–7.8. $[Yb.(Pen)_2]^-$ and $[Lu.(Pen)_2]^-$ have the lowest percent values of the complex species (0.7–0.6%) at pH 7.5.

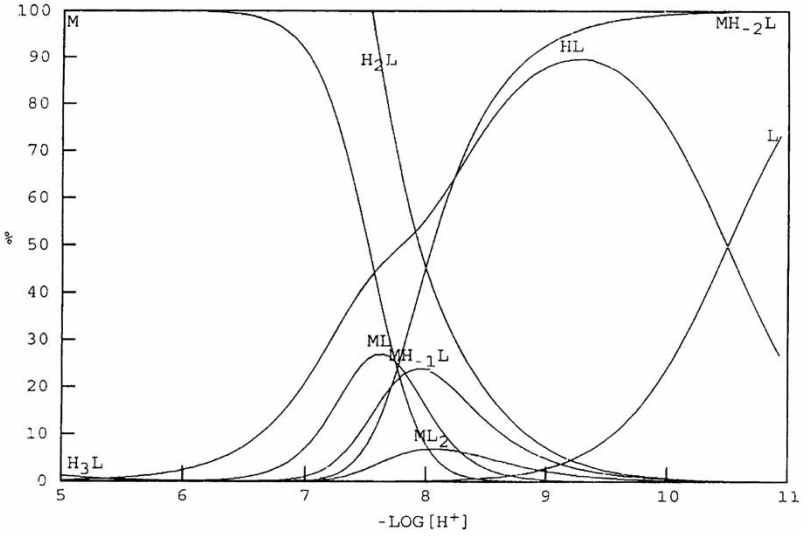


Figure 3. Species distribution diagram of the Eu^{3+}-Pen complex.

Table 4. Analytical data of the lanthanide-D-penicillamine complexes.

		Elemental analysis*			
Complex	Mol. wt.	%C	%H	%N	%M
$[Pr.Pen.NO_3] \cong 1\frac{1}{2}H_2O$	377.07	15.92 (15.55)	2.91 (3.15)	7.42 (7.52)	37.63 (37.33)
$[Gd.Pen.NO_3] \cong 2H_2O$	402.41	14.92 (14.58	3.23 (3.32)	6.95 (6.93)	39.07 (39.27)
$[Yb.Pen.NO_3] \cong H_2O$	400.21	15.00 (15.22)	2.74 (2.51)	6.99 (6.81)	43.23 (43.69)

* Calculated (found).

3.3. *Solid Ln-Pen complexes*

Isolated complexes of Sm^{3+}, Gd^{3+} and Yb^{3+} with Pen are listed in table 4. All the complexes are white solids insoluble in alcohol, acetone, diethyl ether, pyridine, and also in solvents like DMF and DMSO. Elemental analyses of the complexes show 1 : 1 metal : ligand stoichiometry. Pen is functioning as a doubly negatively charged chelating agent.

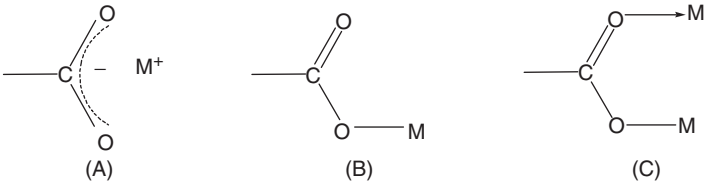
3.4. *Infrared spectra*

The infrared data of D-penicillamine and its Pr^{3+}, Gd^{3+} and Yb^{3+} complexes are shown in table 5. The most important bands in the spectra of D-penicillamine are assigned to $\upsilon_{as}(NH_3^+)$ at 3174 cm^{-1} and $\upsilon_{as}(COO^-)$ at 1594 cm^{-1} corresponding to the zwitterionic form of the amino acid. Consequently, the C=O at 1700 cm^{-1} of the protonated carboxylic group is absent. The frequencies corresponding $\delta_d(NH_3^+)$(aa-I) and $\delta_s(NH_3^+)$(aa-II) appear at 1617 and 1527 cm^{-1}, respectively. The medium intensity bands at 2609 and 2513 cm^{-1} assigned to υ(S–H) in the D-penicillamine spectrum

Table 5. Infrared spectra of D-penicillamine and its complexes.

Complex	Band assignments cm^{-1}														
	υ_{OH}	$\upsilon_{as}(NH_3^+)$	$\upsilon_{as}(NH_2)$	υ(SH)	$\delta_d(NH_3^+)$	$\delta_s(NH_3^+)$	$\upsilon_{as}COO^-$	$\delta(NH_2)$	υ_sCOO^-	$\Delta\upsilon$	$\upsilon_{NO_3^-}$	υ_5–υ_1	ρ_wCOO^-	υ_{M-O}	υ_{M-N}
D-Pen.	–	3174br.	–	2609m. 2513m.	1617s. 1527m.		1594s.	–	1393s.	201	–	–	755s.	–	–
[Pr.Pen.$(NO_3)_2$] $\cong 1\frac{1}{2}H_2O$	3425br.	–	3254sh.	–	–		1634s.	1592s.	1415s.	219	1386 1187 1023	199	736s.	566m.	474w.
[Gd.Pen.$(NO_3)_2$] $\cong 2H_2O$	3419br.	–	3253sh.	–	–		1634s.	1597s.	1418s.	216	1386 1187 1027	199	742s.	562m.	457w.
[Yb.Pen.$(NO_3)_2$] $\cong H_2O$	3427br.	–	3252sh.	–	–		1634s.	1593s.	1417s.	217	1385 1188 1030	197	751s.	566m.	474m.

disappeared in the spectra of the three complexes indicating coordination of the S atom to the metals (figure 4). This contradicts Atonva [26] who reported that complexes in which Ln^{3+} is coordinated by –SH and –S groups are unlikely. The shift of $\upsilon_{as}(NH_3^+)$ toward higher frequencies in the spectra of the complexes is typical for coordination of NH_2 [50] and the changes in the bands related with $\delta(NH_3^+)$ confirm coordination through the nitrogen atom [51]. Infrared spectra of the D-penicillamine complexes have no bands corresponding to free carboxylic group. Instead, strong bands between 1634 and 1592 cm^{-1} include $\upsilon_{as}COO^-$ resulting from the coordinated carboxylic group and $\delta(NH_2)$ are observed. Bands corresponding to $\upsilon_s(COO^-)$ appear in the 1415–1418 cm^{-1} range, giving frequency differences ($\Delta\upsilon = \upsilon_{as}COO^- - \upsilon_sCOO^-$) of 219, 216 and 217 cm^{-1} respectively, corresponding to Pr^{3+}, Gd^{3+} and Yb^{3+} complexes of D-penicillamine. It has been accepted by several authors [52–54] that as the covalent character of the M–O bond increases (structure B) the carboxyl group becomes more symmetrical, resulting in an increase in the frequency separation of the two COO^- stretching bands compared to the symmetry of the free ion (structure A). Structure (C) involves coordination of the cabonyl group and the strength of the $O \rightarrow M$ band increases, as does the symmetry of the COO^- group, and a decrease in $\Delta\upsilon$ results. In our complexes, the values of $\Delta\upsilon$ reflect the monodentate nature of the carboxylate group and indicate that $\Delta\upsilon$ follow the order $Pr^{3+} > Gd^{3+} < Yb^{3+}$ while the Ln–O bond strength shows the order $Pr^{3+} < Gd^{3+} > Yb^{3+}$ (table 5).



The carboxyl wagging vibration appears as a strong sharp band at 755 cm^{-1} in the spectra of the free ligand. This band shifts downward to 736–751 cm^{-1} in the spectra of the complexes. The nitrate ion exhibits three NO stretching bands in the 1385–1386(υ_5), 1187–1188(υ_2) and 1023–1030(υ_1) cm^{-1} ranges as expected for C_{2v} symmetry [55]. The separation of the two highest band frequencies ($\upsilon_5 - \upsilon_1$) lies in the 197–199 cm^{-1} range, which indicates that the nitrate ion is unidentate [56].

Water of crystallization is detected by the broad bands due to –OH vibration centered at 3425, 3419 and 3427 cm^{-1}. The presence of water is also indicated by elemental analysis and t.g.a. of these complexes. In the low frequency region, two new bands for the complexes are assigned as υ(M–O) in the 562–566 cm^{-1} range and υ(M–N) cm^{-1} in the 457–474 cm^{-1} range [56], consistent with D-penicillamine losing two protons as a binegative tridentate ligand with coordination through N, S and O atoms.

3.5. *Thermal analysis of the Ln-Pen complexes*

The t.g., d.t.g. and d.t.a. curves of the Pr^{3+}, Gd^{3+} and Yb^{3+} complexes of D-penicillamine are shown in figures 5 and 6. The decomposition temperatures, the pyrolysed products, the percentage mass loss of the complexes and the percent ash are given in table 6.

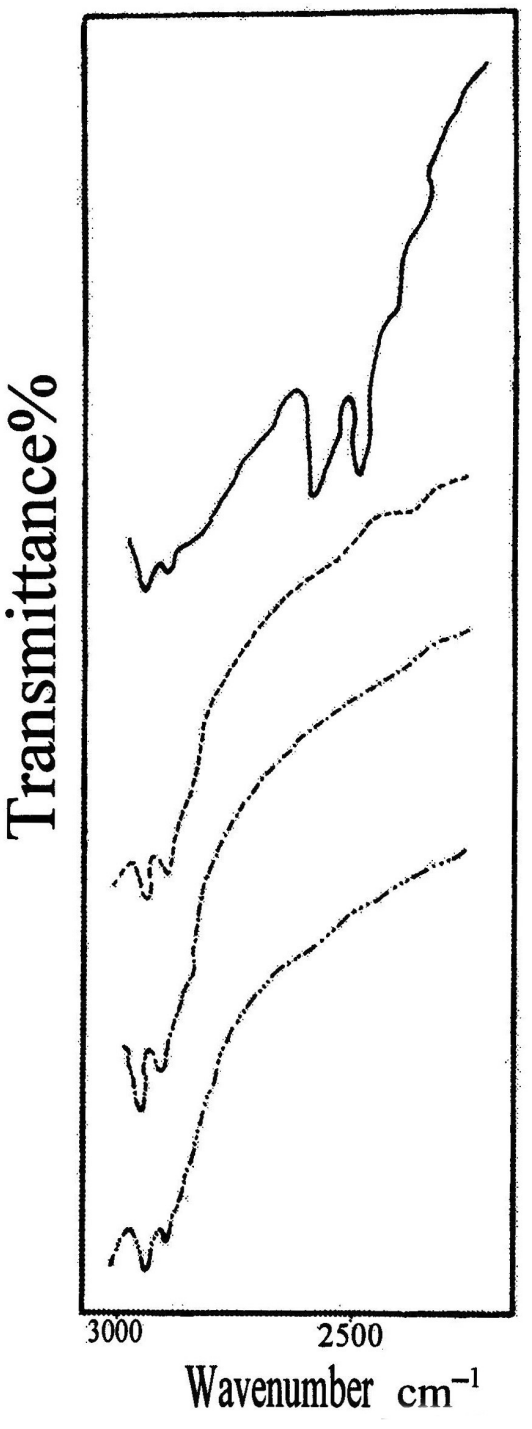


Figure 4. Infrared spectra of free Pen and its complexes ---- [Pr.Pen.NO_3] ≅ 1½H_2O, ------- [Gd.Pen.NO_3] ≅ 2H_2O ·····[Yb.Pen.NO_3] ≅ H_2O.

The complexes decompose in four steps. The first step takes place in the 33–139, 31–108 and 31–134°C ranges with d.t.g. maxima at 59, 55 and 58°C, respectively. This step has weight losses of 7.06, 8.94 and 4.49% against calculated losses of 7.15, 8.51 and 4.69%, respectively, showing the thermal liberation of crystallization water. These relatively low temperature dehydration processes support water not being coordinated. The second weight loss steps occur in the 139–307, 110–322 and 139–322°C with d.t.g. maxima at 254, 263 and 267°C, respectively, (free Pen decomposes at 215°C). This step has mass losses of 24.5, 21.48 and 22.95% against calculated losses of of 24.39, 22.71 and 22.98%, respectively, and is correlated with elimination of both the nitrate ion and the two methyl groups. The third stage transition is concerned with decomposition of D-penicillamine and loss of the carboxylate group as CH_3COOH and the amino group as NH_3. This step follows immediately the second step in the 310–557, 325–542 and 330–547°C ranges with d.t.g. maxima at 460, 426 and 457°C, respectively. During this step, the observed mass losses were 16.2, 19.44 and 20.52% against calculated losses of 16.98, 20.13 and 20.23%, respectively. Final decomposition of the complexes was observed at the temperatures of 659, 786 and 679°C respectively, with the formation of metal sulfides as final product.

The d.t.a. curves of the complexes show two endothermic and two exothermic peaks in the temperature range 30–800°C. The first endothermic peaks are assigned to the loss of crystallization water and take place in the 33–107, 31–98 and 31–82°C ranges, with maxima at 59, 53 and 58°C, respectively. The first exothermic peak takes place in the 188–370, 201–377 and 226–332°C ranges with maxima at 297, 274 and 269°C, respectively, which characterize the partial decomposition of the complexes.

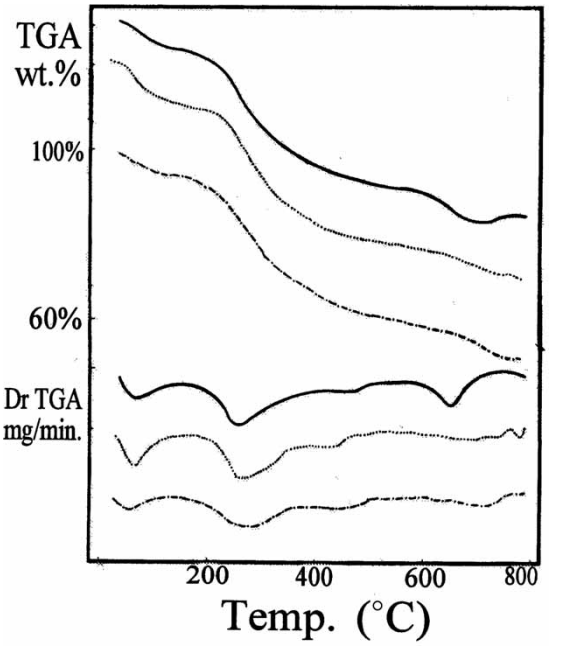


Figure 5. T.g. and d.t.g. of the Ln-Pen complexes — [Pr.Pen.NO_3] ≅ 1½H_2O, · · · [Gd.Pen.NO_3] ≅ 2H_2O and - - - - [Yb.Pen.NO_3] ≅ H_2O.

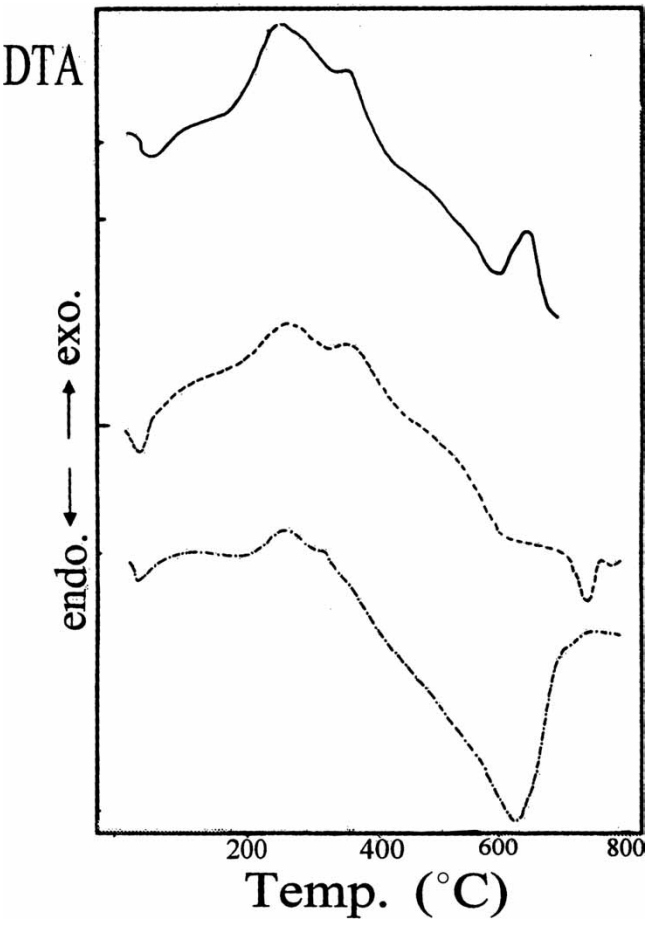


Figure 6. D.t.a. calorigrams of the Ln-Pen complexes — [Pr.Pen.NO_3] ≅ 1½H_2O, ··· [Gd.Pen.NO_3] ≅ 2H_2O and ---- [Yb.Pen.NO_3] ≅ H_2O.

Partial decomposition is continued with exothermic changes in the 355–408, 344–448 and 317–358°C ranges with d.t.a. peaks at 273, 382 and 332°C, respectively. A vigorous endothermic peak concerned with final decomposition of the complexes is observed at 607, 693 and 642°C, respectively.

To intercept intermediates in the thermal decomposition infrared spectra of heated samples of the complexes [Pr.Pen.NO_3] ≅ 1½H_2O and [Gd.Pen.NO_3] ≅ 2H_2O at 130 and 280°C were obtained. Figure 7 indicates i.r. spectral changes in shape, intensity and position of some characteristic bands. Spectra of the complexes at 130°C have no big changes in comparison with unheated complexes. Infrared spectra of the heated complexes at 280°C show the disappearance of the bands due to NO_3^- ion, indicating its decomposition. Also, the $\delta(NH_2)$ band is shifted to higher wavenumbers (1625 and 1662 cm^{-1}) while $\upsilon_{as}COO^-$ is shifted to lower wavenumber (1559 and 1563 cm^{-1}). New strong split bands with maxima at 1127, 1064 and 985 cm^{-1} for the Pr complex and at 1139, 1072 and 994 cm^{-1} for the Gd

Table 6. D.t., t.g.a. and d.t.g. data of the lanthnide-D-penicillamine complexes.

	D.t.a results					T.g.a and d.t.g. results					
								Wt. loss			
Complexes	Temp. range	t°C	ΔH (J/mol)	E_a (J/mol)	Process	Temp. range	D.t.g.°C	Found	Calcd.	Type of loss	Residue
[Pr.Pen.NO_3] ≅ 1 ½H_2O	33–107	59 endo.	168	48	Dehydration	33–139	59	7.06	7.15	1 ½H_2O	
	188–370	297 exo.	−307	50	Partial decomposition	139–307	254	24.5	25.19	$HNO_3 + 2CH_4$	
	355–408	273 exo.	−349	69	Partial decomposition	310–557	460	16.2	20.42	CH_3COOH	Pr_2S_3
	554–645	607 endo.	1460	198	Final decomposition	557–800	659	51.8	50.38		
[Gd.Pen.NO_3] ≅ 2H_2O	31–98	53 endo.	183	59	Dehydration	31–108	55	8.51	8.94	2H_2O	
	201–377	274 exo.	−306	64	Partial decomposition	110–322	263	21.48	23.6	$HNO_3 + 2CH_4$	
	344–448	382 exo.	−372	79	Partial decomposition	325–542	426	19.44	19.13	$CH_3COOH + NH_3$	Gd_2S_3
	720–767	693 endo.	1368	172	Final decomposition	545–779	786	50.13	51.02		
[Yb.Pen.NO_3] ≅ H_2O	31–82	58 endo.	195	82	Dehydration	31–134	58	4.69	4.49	H_2O	
	226–332	269 exo.	−314	105	Partial decomposition	139–322	267	22.95	23.73	$HNO_3 + 2CH_4$	
	317–358	332 exo.	−340	83	Partial decomposition	330–547	457	20.52	19.23	$CH_3COOH + NH_3$	Yb_2S_3
	485–704	642 endo.	1280	131	Final decomposition	547–800	679	53.05	55.25		

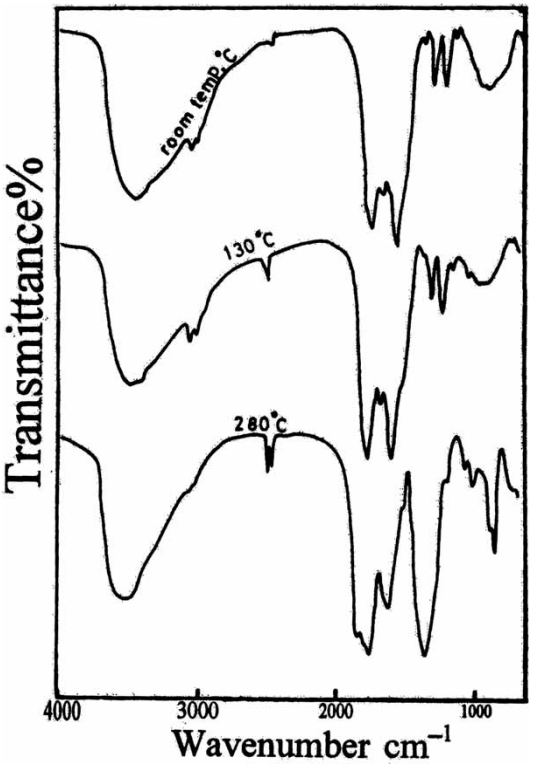


Figure 7. Infrared spectra of heated samples of [Gd.Pen.NO_3] $\cong 2H_2O$.

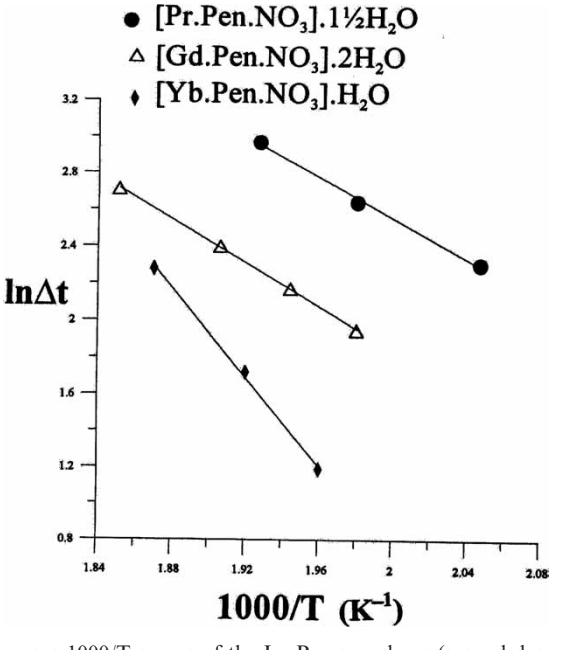


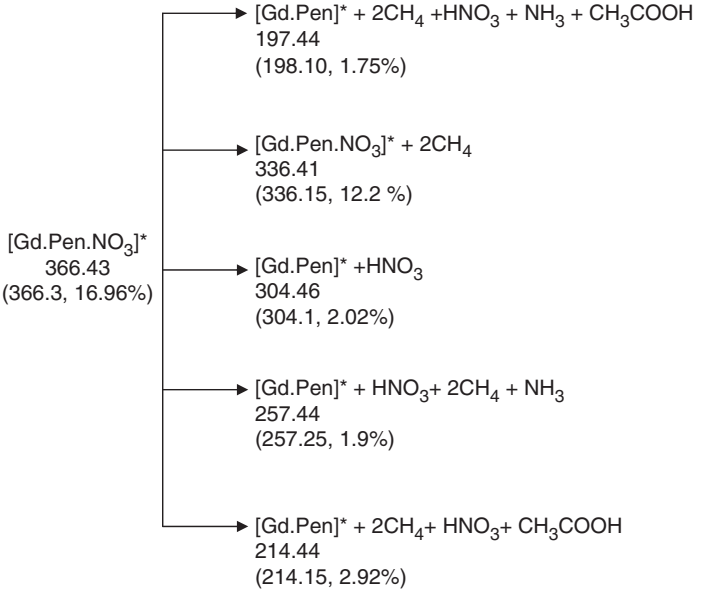
Figure 8. InΔt versus 1000/T curves of the Ln-Pen complexes (second decomposition step).

complex were observed. This band may be attributed to S-bonded coordination [56–58].

Based on the above thermal data, the following decomposition mechanism was proposed for Ln-Pen:

$$[\mathrm{Gd.Pen.NO_3}] \cong 2\mathrm{H_2O} - 55^{\circ}\mathrm{C} \rightarrow [\mathrm{Gd.Pen.NO_3}] + 2\mathrm{H_2O}$$
$$[\mathrm{Gd.Pen.NO_3}] - 263^{\circ}\mathrm{C} \rightarrow [\mathrm{Gd.Pen}] + \mathrm{HNO_3} + 2\mathrm{CH_4}$$
$$[\mathrm{Gd.Pen}] - 426^{\circ}\mathrm{C} \rightarrow [\mathrm{Gd.(0.28\%Pen)}] + \mathrm{CH_3COOH} + \mathrm{NH_3}$$
$$[\mathrm{Gd.(0.28\%Pen)}] - 786^{\circ}\mathrm{C} \rightarrow \mathrm{Gd_2S_3} + 0.28\%\mathrm{Pen}$$

The molar masses in every step were found to match with mass spectral fragments of the same value indicating the reliability of the decomposition scheme proposed.



The activation energies of the decomposition reactions were determined from d.t.a. calorigrams. The plots of $\ln \Delta t$ versus $1000/T$ are given in figure 8, and the activation energy values, E_a, obtained by the Piloyan method [59] are shown in table 6. The activation energies of Pr(III), Gd(III) and Yb(III) complexes are expected to increase proportionally to the decrease in their atomic radii. E_a values for the first and second decomposition steps have the following sequences:

First decomposition step:

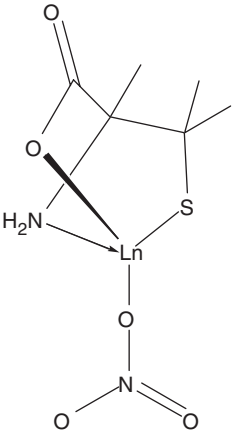
$$E_a^{Yb} = 195(r_{Yb} = 0.848\,\mathrm{A}^{\circ}) > E_a^{Gd} = 183(r_{Gd} = 0.938\mathrm{A}^{\circ}) > E_a^{Pr} = 168(r_{Yb} = 1.013\mathrm{A}^{\circ})$$

Second decomposition step:

$$E_a^{Yb} = 105 > E_a^{Gd} = 64 > E_a^{Pr} = 48$$

The shorter the radius of metal ion, metal-ligand interactions become stronger, detachment of the ligand becomes more difficult and E_a values increase [60, 61].

Based on the above analytical data and physicochemical properties, the following structure is proposed in which the metal ion is coordinated through $-NH_2$, $-COO^-$ and $-S^-$.



Ln= Pr^{3+}, Gd^{3+}, Yb^{3+}

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