

Dextran–Rare Earth Ion Interactions. II. Solid-State Characteristics

B. ZÜMREOĞLU-KARAN, H. MAZI, A. GÜNER

Department of Chemistry, Hacettepe University, Beytepe Campus, 06532 Ankara, Turkey

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ABSTRACT: The solid-state characteristics of dextran complexes precipitated from aqueous solutions with three different light-lanthanoid cations (La^{3+} , Ce^{3+} , and Nd^{3+}) were investigated by spectroscopic and thermal methods. Spectroscopic characterization was realized by the comparative interpretation of the FTIR spectra, and the complexes were found to involve both ligating water and dextran through its O(2) and O(3) atoms. Remarkable spectral changes were noted, particularly with La^{3+} , which parallels the previous solution studies. The order of $\text{La}^{3+} > \text{Ce}^{3+} > \text{Nd}^{3+}$ was determined to display the tendency of the Ln^{3+} ion in favor of dextran throughout the competition between water and dextran. The thermal stabilities of the complexes were examined by thermogravimetry (TG), differential TG, and DSC methods. The decomposition steps and temperatures were assigned with respect to the lanthanoid ions used. The TG and DSC results indicated that the complexes are less stable thermally than dextran itself with increasing thermal stabilities in the order of $\text{La}^{3+} < \text{Ce}^{3+} < \text{Nd}^{3+}$ in their anhydrous states. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2168–2174, 2002

Key words: dextran; light lanthanoids; complexation; FTIR spectra; thermal analysis

INTRODUCTION

The lanthanide ions form complexes with polysaccharides in the electrostatic manner of polyelectrolytes. The use of lanthanides as probes for evaluating binding sites in metal–sugar complexes has great potential. The luminescence and chirality properties of lanthanide-ion substituted polysaccharides can yield important information regarding the metal–ion binding sites of these polymers.¹ The lanthanoid complexes of some polyhydroxo species are reported by several authors with 1 : 1 stoichiometry.²

In aqueous solutions dextran interacts with several metal ions and forms solid complex compounds of therapeutic use.^{3,4} Paramagnetic particles of dextran–rare earth complexes have also been reported to be promising agents in the treatment of the AIDS virus.⁵ They have potential use in the diagnostic methods based on NMR as well.⁶ Lanthanoid nitrates $[\text{Ln}(\text{NO}_3)_3]$ form solid complexes with several poly(ethylene glycol)s and glymes.² The lanthanoid complexes of crown ethers have also been reported.^{7–10} However, data on the interaction of dextran with lanthanide ions and on the preparation and applications of these complexes are very limited and are mostly reported as patent formulations. The progress of this research requires information on the composition and structure of species containing dextran and the lanthanoid ion existing in both the solu-

Correspondence to: B. Zümreoğlu-Karan (bkaran@hacettepe.edu.tr).

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tion and solid phases and their spectral, thermodynamic, and kinetic parameters. Following the dextran-rare earth ion interaction dynamics in aqueous solutions,¹¹ here we report solid-state properties of the dextran complexes with La^{3+} , Ce^{3+} , and Nd^{3+} ions precipitated from aqueous solutions.

EXPERIMENTAL

The dextran used in this study (T500) was purchased from Pharmacia Fine Chemicals AB (Uppsala, Sweden). The molecular weight characteristics were determined by the manufacturer as the number-average and weight-average molecular weights of 191,500 and 496,000 g mol^{-1} , respectively. The dextran was dried and stored over CaCl_2 in a desiccator and used without further purification. The lanthanoid ions were supplied as laboratory-grade hydrated nitrate salts [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, BDH; $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich] and were used as received. Dextran and lanthanoid solutions were prepared in deionized, bidistilled water.

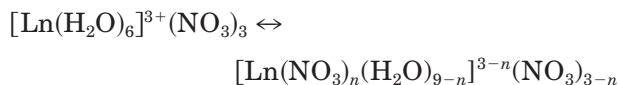
The solid complexes of La^{3+} , Ce^{3+} , and Nd^{3+} ions with dextran were precipitated by methanol. Solid dextran was introduced into 10 mL of an aqueous solution of the Ln^{3+} ions (0.005–0.3 mol L^{-1}) to obtain a final dextran concentration of 5.00 g dL^{-1} . The complexes were then deposited by the addition of 10 mL of cold methanol, filtered, dried, and weighed. Blank experiments were performed with aqueous lanthanoid nitrate solutions in the absence of dextran, and the addition of methanol did not cause any precipitation of the lanthanoid nitrate.

The thermal properties were investigated using a DuPont 9900 thermal analyzer system (dynamic nitrogen atmosphere, $10^\circ\text{C min}^{-1}$ heating rate), and FTIR spectra were recorded with a Shimadzu DR 8001 spectrophotometer by the KBr disk method.

RESULTS AND DISCUSSION

The Ln^{3+} ions exist as aqua complexes in water with coordination numbers of 8–9. The thermodynamic, kinetic, and spectroscopic measurements concluded that different lanthanoids may have different structures for their aqua ions.¹² In addition, aqua ions with smaller coordination numbers may be present in solution, together

with the dominating aqua species. The anions, like Cl^- , NO_3^- , and SO_4^{2-} , influence the equilibrium between various aqua ions. In particular, NO_3^- was found to have a greater affinity toward Ln^{3+} than water.¹³ As a consequence, the nitrate ions may take place in the inner coordination sphere and the following equilibrium is considered:



The addition of dextran or other oxygenated ligands to the solution containing Ln^{3+} ions will result in the expulsion of some or all of the coordinated water molecules. Available data in the literature indicate that the number of water molecules remaining bound to the Ln^{3+} ion in complexes with polymeric ligands is between 1 and 4.¹⁴ However, the number of H_2O molecules displaced could be different at different sites of the macromolecule. The presence of more than one type of complex in solution, the relative proportions of which may be different for different cations, random binding of Ln^{3+} ions on the polysaccharide chain, and a large degree of asymmetry involved in the polymer lead to the presence of more than one type of complex that is also in the solid state. Water plays a part in the deposition of the complexes, and the effect of water is expected to be greater for the lanthanoid ions with greater atomic numbers and hence with greater charge densities. Cloud point and precipitation experiments showed that the associations are nearly completed at low Ln^{3+} concentrations ($<0.08 \text{ mol L}^{-1}$) from solutions.¹¹ This small number of coordinated dextran repeating units is probably due to electrostatic repulsions between the metal ions bound to the polysaccharide chain.

Optical rotatory dispersion¹³ and NMR measurements¹⁴ indicated that the OH groups bound to C_2 and C_3 atoms are capable of bidentate complex formation with dextran, as well as its low molecular weight analogue, α -methyl glucoside. In addition, the coordination of Ln^{3+} was reported to be stronger and to a much greater extent in dextran solution than that in the glucoside solution.

In view of these facts, the solids obtained by precipitating dextran with La^{3+} , Ce^{3+} , and Nd^{3+} ions were examined by IR spectroscopy and thermal studies.

Table I IR Spectral Data of Dextran and Complexes

Dextran	Dextran/La ³⁺	Dextran/Ce ³⁺	Dextran/Nd ³⁺	Assignments
3434 vs	3453 vs	3453 vs	3430 vs	O—H stretching
2924 m, sp	2926 m, sp	2926 m, sp	2928 m, sp	C—H stretching
—	1740 vw	1740 vw	—	O—H bending
1649 s, b	1645 s	1645 s	1647 s, b	O—H bending
—	1514 m	1521 w	—	ν_5 of coordinated NO ₃ ⁻
1460 w	1470 w	1470 w	1462 w	C—C stretching (ring)
—	1387 m	1387 m	—	ν_3 of free NO ₃ ⁻
1157 m	1157 m	1159 m	1157 m	C—O—C stretching (ether)
1112–1010 s	1112–1010 m	1112–1010 m	1112–1010 s	C—O stretching (alcohol)

All values are per centimeter (cm⁻¹). The spectra were recorded in KBr. vs, very strong; s, strong; m, medium; b, broad; sp, sharp; w, weak.

IR Spectra

The changes in the band positions and intensities observed from the IR spectra of parent dextran and the dextran/La³⁺, dextran/Ce³⁺, and dextran/Nd³⁺ complexes are summarized in Table I. The very strong and nearly symmetrical peak observed at 3434 cm⁻¹ in dextran is due to O—H stretching vibrations. Stable hydrogen bonds are found between the OH groups in dextran. Introduction of the Ln³⁺ ions into the dextran structure causes disruption of these hydrogen bonds and a hypsochromic shift is observed with La³⁺ and Ce³⁺ to 3453 cm⁻¹, together with many splittings on the high frequency side (Fig. 1). The broad medium intensity peak at about 1650 cm⁻¹ in dextran is due to O—H bending vibrations. This peak shows a number of splittings in the La³⁺ and Ce³⁺ complexes, and an additional weak peak is observed at 1740 cm⁻¹. Although not distinctive for the Nd³⁺ complex, this new peak may be attributed to the O—H bendings of the aqua ligands coordinated to the Ln³⁺ ions, hydrogen bonded to the groups on dextran, and/or other ligands.

The IR spectra of La³⁺ and Ce³⁺ complexes are similar to each other. Remarkable differences were observed between the complexes and pure dextran in the 1112–1010 cm⁻¹ region (Fig. 1). The intensity loss observed in this region for the complexes indicates a weakening of the alcoholic C—O stretching vibrations and strongly suggests the participation of alcoholic oxygens in complexation. On the other hand, no change was observed that characterized the ether group at 1157 cm⁻¹, supporting the previous reports that coordination to the metal is through the O(2) and O(3) atoms not through the etheric oxygen.^{14,15} The spectra of

the complexes displayed two new peaks at about 1500 and 1387 cm⁻¹. The appearance of these peaks demonstrates that coordinated nitrate ions, as well as free nitrate ions, exist in the complexes.

On the basis of our IR results and considering the literature data on related complexes, the following structure for the complexes may be proposed to provide the 1:1 stoichiometry,² complete coordination of the lanthanoid ion,¹² and the number of water molecules remaining bound to the lanthanoid ion between 1 and 4¹⁴:

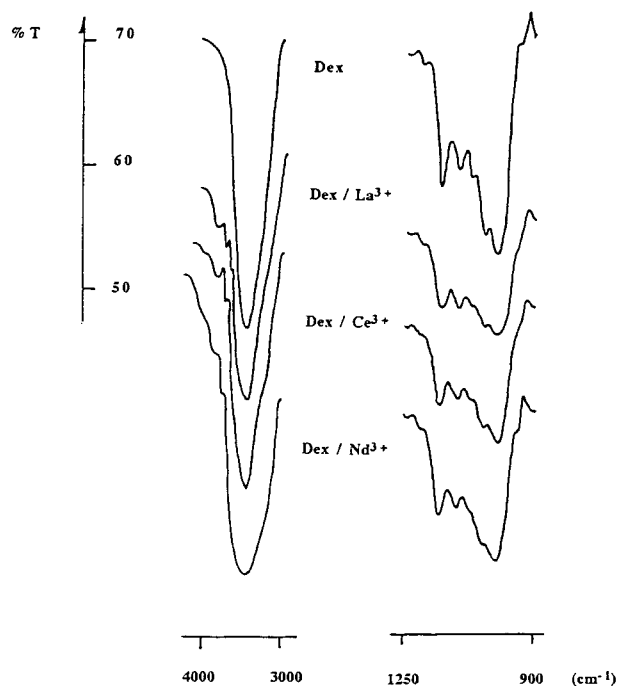


Figure 1 IR spectra of dextran and dextran/Ln³⁺ complexes.

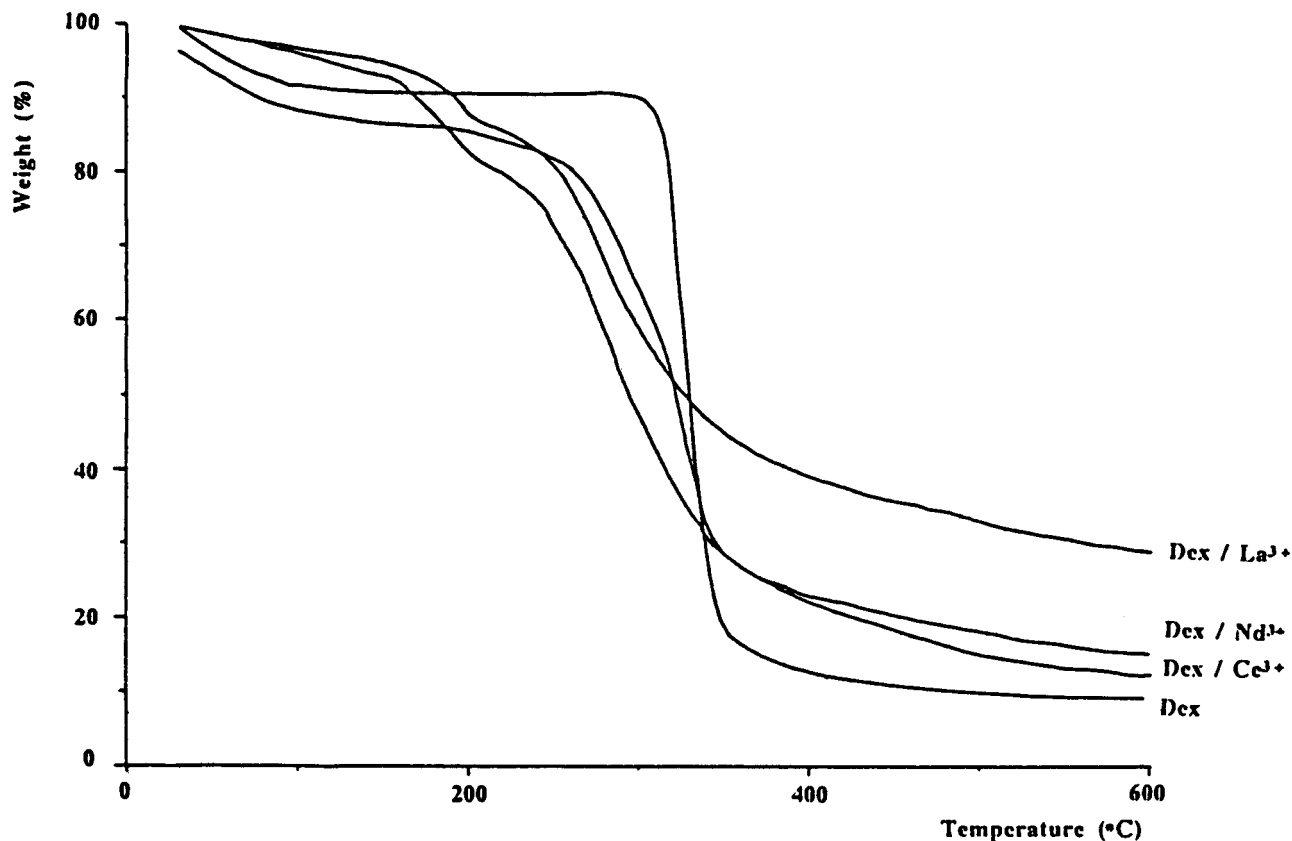
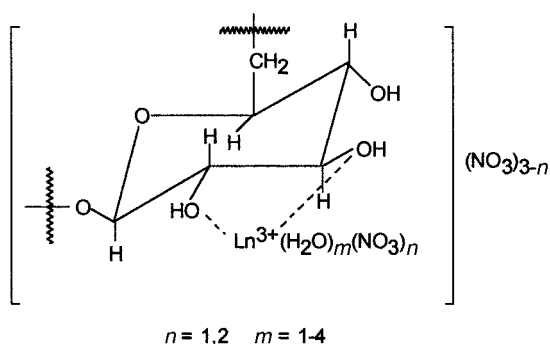


Figure 2 Thermal analyses of dextran and dextran/Ln³⁺ complexes by thermogravimetry (TG).



The IR spectrum of the Nd³⁺ complex resembles that of pure dextran, showing no remarkable spectral changes as noted with the La³⁺ and Ce³⁺ ions. Parallel to our previous solution phase studies,¹¹ the Nd³⁺ ion has a lower affinity toward complexation with dextran in competition with water. A similar result was reported for the lanthanoid complexes of poly(ethylene glycol)s in which the structure with the Nd³⁺ ion was exceptionally different from the others.¹⁶

Thermal Studies

The thermogravimetry (TG) and DSC measurements were performed to establish the thermal behavior of the complexes. Figures 2, 3, and 4 show the respective TG, differential TG (DTG), and DSC curves of dextran and its complexes with La³⁺, Ce³⁺, and Nd³⁺. Dextran undergoes a single-step decomposition in the temperature range of 314–348°C with a DTG peak temperature of 330°C. However, the complexes showed a multi-step decomposition in the range of 100–400°C. The temperatures of the thermal changes are given in Table II. Dehydration occurs in the first stage of thermogravimetric decomposition (up to 200°C). The loss of surface water, trapped water between the polymer segments, and coordinated water from various modifications of aqua complexes present in the structure take place and several steps are observed. In the second stage (200–400°C), in which the essential mass loss is observed, the decomposition and/or further dehydration of the most stable complex structure pro-

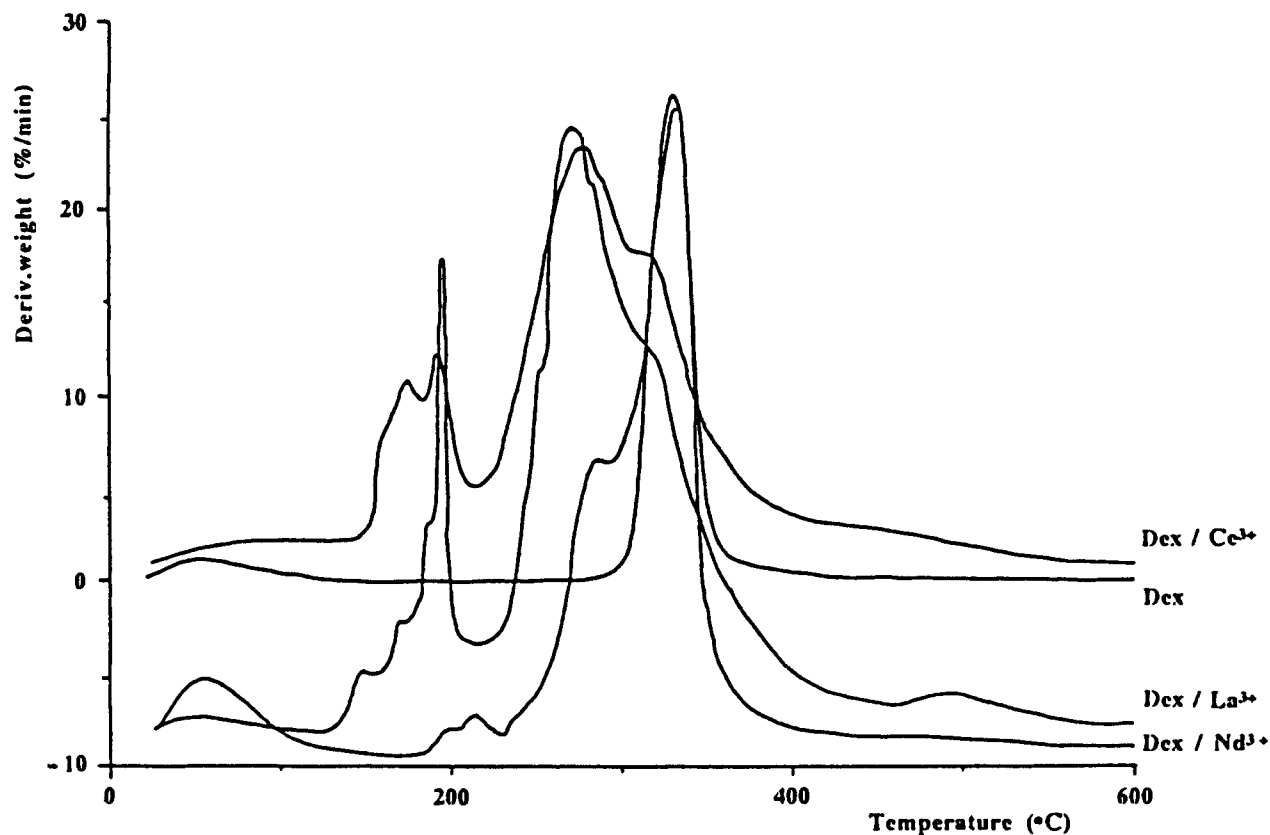


Figure 3 Thermal analyses of dextran and dextran/Ln³⁺ complexes by differential thermogravimetry (DTG).

ceed simultaneously, and the contiguous decomposition of the unaffected fraction of dextran is at 330°C. A strictly horizontal level and a weight value corresponding to the expected final composition of Ln₂O₃ were not observed. A residue contaminated with some carbonaceous material was obtained at 600°C and therefore no back calculations could have been done for the estimation of the lanthanoid contents. Nevertheless, based on the assumption of the oxide, rough calculations indicated that 10% of the initial Ln³⁺ (less for Nd³⁺) are involved in the complexes. Literature data¹⁴ and solution studies¹¹ also suggest that the interactions are favorable at low Ln³⁺ concentrations.

The decomposition temperatures observed in the second step slightly increase in the order of La³⁺ < Ce³⁺ < Nd³⁺. At first sight this order seems to be normal because the stabilities of most lanthanoid complexes mainly depend on the charge density of the lanthanoid ion and accordingly increase with a decrease in the ionic radius (*r*) in the order of $r_{\text{La}^{3+}}^{3+} > r_{\text{Ce}^{3+}}^{3+} > r_{\text{Nd}^{3+}}^{3+}$. On the other hand, the IR spectrum and the TG curve of the dextran/Nd³⁺ complex show

that most of the original dextran structure is retained upon interaction with the Nd³⁺ ion. Solution studies also indicated the order of interaction as La³⁺ > Ce³⁺ > Nd³⁺.

The DSC curves show modifications through interaction with lanthanoids. Pure dextran gives a symmetrical endothermic peak in the temperature range of 35–140°C, corresponding to the rupture of the H-bonded network. This peak is broadened by the entrance of the Ln³⁺ ions into the dextran structure. The extent of broadening is in the order of La³⁺ > Ce³⁺ > Nd³⁺, which shows the effectiveness of the La³⁺ ion in interacting with dextran. The nonsymmetrical shape of this peak and the shoulders are due to the overlap of a number of endotherms arising from a bench of hydrogen-bond breakage and dehydration processes. The lanthanoid ions participate in more effective interactions with dextran segments after the removal of competing water molecules, and the exotherms following dehydration possibly correspond to a transition to a more stable phase. This transition occurs at lower temperatures with Nd³⁺ because of its smaller radius and high

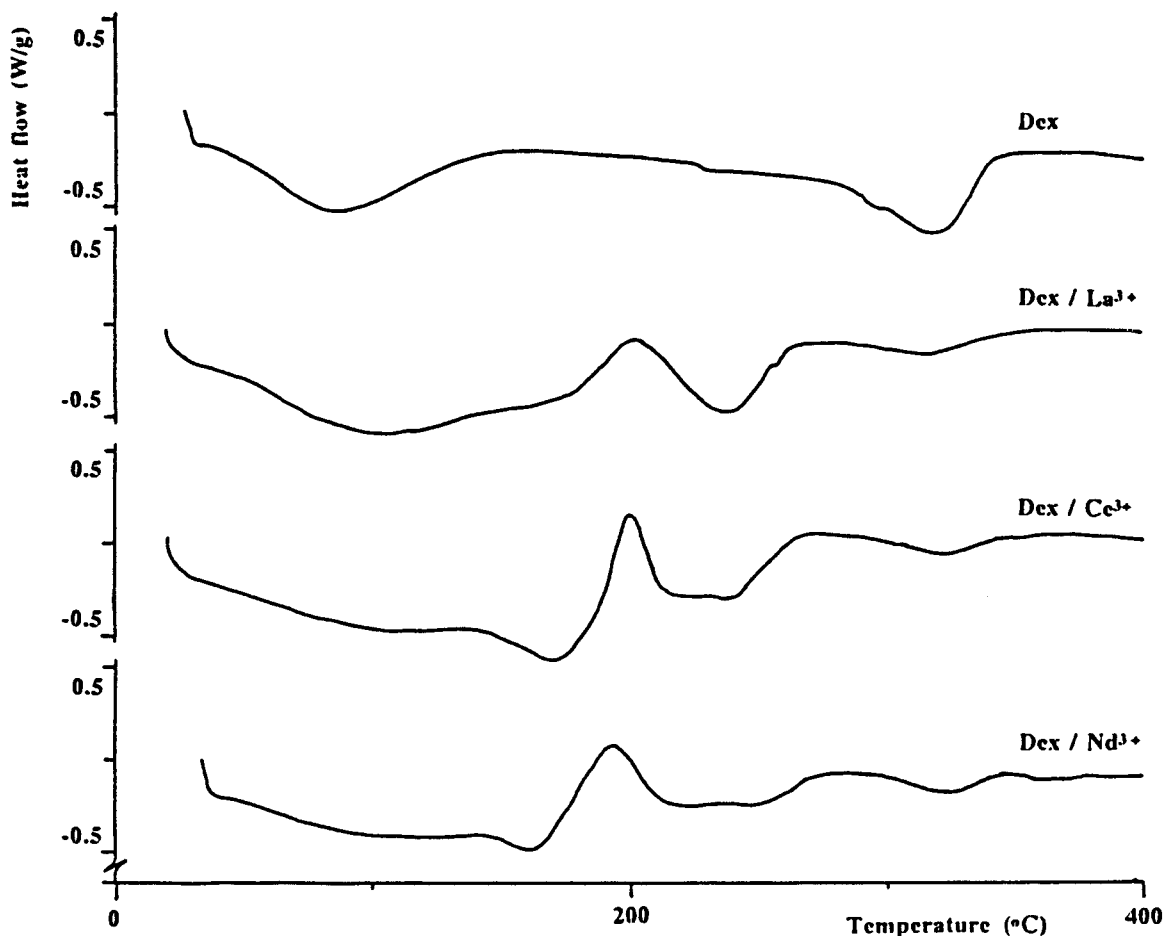


Figure 4 Thermal analyses of dextran and dextran/Ln³⁺ complexes by differential scanning calorimetry (DSC).

charge density; consequently, the exothermic peak temperatures shift to lower values from La³⁺ to Nd³⁺. Pure dextran exhibited an endotherm in the range of 290–342°C, conforming with its chemical decomposition, subsequent to the glass-transition temperature (T_g) at 230°C. The complexes were found to be thermally less stable and no T_g values could have been distinguished from their DSC curves. The temperature range of the nonsymmetrical endotherms above 200°C, which corresponds to the decomposition of the complexes, increases in the order of La³⁺ < Ce³⁺ < Nd³⁺, reflecting the effect of Nd³⁺ on the thermal stability of the anhydrous phase.

The relative order of the ions determined by thermal studies and those found by solution studies and IR spectra do not in fact conflict with each other. The lanthanoids exhibit a greater affinity toward H₂O with increasing atomic number. Consequently, a competition between the coordination of H₂O and

dextran ligands to Nd³⁺ results in favor of water. However, coordination with dextran is also realized to some extent and the dextran/Nd³⁺ complex fragments formed on random sites of the polymer show higher thermal stabilities in comparison with the complexes of La³⁺ and Ce³⁺.

CONCLUSION

The Ln³⁺ ions interact with dextran in aqueous solutions and the addition of methanol into these solutions results in the precipitation of dextran/Ln³⁺ complexes. Solution phase studies previously showed that the interaction of the lanthanoid ions with dextran is in the La³⁺ > Ce³⁺ > Nd³⁺ order. Neodymium ions have greater tendencies toward aqua ligands than dextran. The solid complexes were characterized by IR spectroscopy and thermal measurements and were

Table II Thermal Analyses of Dextran and Dextran/Ln³⁺ Complexes

Sample	TG _a (°C)	DSC (°C)	Thermal Change
Dextran		35–140 230	H-bond rupture Glass transition
Dextran/La ³⁺	314–348 (330) 35–200	290–342 35–190 (endo) 204 (exo)	Decomposition Dehydration Phase transition
	200–400 (272)	212–263 (endo) ($\Delta T = 263-204 = 59$) ^b ~ 315 (vw endo) ^c	Further dehydration and decomposition of complex Decomposition of dextran
Dextran/Ce ³⁺	35–200	35–185 (endo) 200 (exo)	Dehydration Phase transition
	200–400 (278)	212–267 (endo) ($\Delta T = 267-200 = 67$) ^b ~ 315 (vw endo) ^c	Further dehydration and decomposition of complex Decomposition of dextran
Dextran/Nd ³⁺	35–200	35–180 (endo) 196 (exo)	Dehydration Phase transition
	200–400 (330)	210–267 (endo) ($\Delta T = 267-196 = 71$) ^b ~ 315 (w endo) ^c	Further dehydration and decomposition of complex Decomposition of dextran

w, weak; vw, very weak.

^a The numbers in parentheses refer to the most intense DTG peak temperatures.

^b Range of the nonsymmetrical endotherm relative to the exothermic peak temperature.

found to contain not only dextran as a ligand but also water molecules. The IR spectroscopy provided information about the binding sites of dextran to Ln³⁺ ions. The spectral changes indicated that dextran coordinates the lanthanoid ions through its alcoholic oxygens rather than the etheric oxygen. In accord with the solution studies, the La³⁺ ion was shown to have the strongest interaction with dextran.

The thermal behavior of the complexes was followed by TG and DSC methods. The complexes undergo a multistep decomposition when compared with the single-step decomposition of dextran. Complex structures show variations in their decomposition temperatures, depending on the type of lanthanoid ion. They are thermally less stable than dextran; however, the relative order of stabilities of the anhydrous phases increases as La³⁺ < Ce³⁺ < Nd³⁺ that is due to the high charge density of the Nd³⁺ ion.

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