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THERMOCHEMICAL BEHAVIOR FOR THE MIXTURE OF HYDRATED LANTHANOID(III) CHLORIDE AND DIBENZO-18-CROWN-6 IN THE SOLID STATE

SUSUMU KOHATA *

Yatsushiro National College of Technology, Yatsushiro 866 (Japan)

SHOICHI OHTA and AKIRA OHYOSHI

Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860 (Japan)

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ABSTRACT

The thermal reaction for the solid mixture system with a 1:1 molar ratio of hydrated lanthanoid(III) chloride and dibenzo-18-crown-6 (dbc) has been investigated by TG–DTA at a nitrogen pressure of 20 mmHg. The reaction was composed of dehydration, melting, complexation, and decomposition. Three patterns for the dehydration in the six systems have been exhibited through the reaction. (1) La–dbc system: all dehydration steps completed prior to the melting–complexation step. (2) Nd–, Sm–, and Eu–dbc systems: the last dehydration took place just after the melting–complexation step. (3) Dy– and Er–dbc systems: the last water was kept until the complex initiates decomposition. Under the fusion state of dbc, about 66–87% mixture formed the complex with a 1:1 stoichiometry. Enthalpy changes for the complexation, estimated from the DTA analyses under excess amounts of the rare earth salt, decrease with the lanthanoid contraction except for the Er–dbc: 31.0, 24.9, 20.3, 15.5, 14.9 and 15.7 kJ mol^{-1} for the La, Nd, Sm, Eu, Dy, and Er systems, respectively. With the increasing order of lanthanoid(III) radius, the stability of the complex formed has enhanced. The hydrated water plays an important part in the complex formation: the water molecule seems to be kept stable in the complex when the ion size of the lanthanoid(III) decreases.

INTRODUCTION

A typical macrocyclic polyether of dibenzo-18-crown-6 (dbc) could form many complexes with various metal cations. When the solid mixture of dbc and potassium iodide was heated, it transformed into the fused state and resulted in the direct formation of the K(dbc)I complex [1]. In the thermal decomposition of the solid complex of $Ln(dbc)(SCN)_3$ (Ln = lanthanoid

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* Author to whom correspondence should be addressed.

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ion), the elimination of dbc is known to take place above its own melting point without any decomposition [2]. The enthalpy change of this reaction reveals a periodical alteration in lanthanoid series: the high thermal stability of La, Gd, and Lu complexes, with f^0, f^7, and f^{14} electronic configurations, is exhibited. From the above facts, direct preparation of the Ln(dbc)Cl_3 complex may be possible by heating the solid mixture of hydrated lanthanoid(III) chloride and dbc. The purposes of this work are: (i) to elucidate the correlation between the thermochemical behavior of the title mixture system and the lanthanoid(III) element; (ii) to estimate the heat of complex formation and clarify the stability of the formed complex by using the TG–DTA method.

EXPERIMENTAL

Materials

Twice recrystallized dibenzo-18-crown-6 (Aldrich) was used. Six kinds of $LnCl_3 \cdot nH_2O$ [Ln = La ($n = 7$); Ln = Nd, Sm, Eu, Dy, and Er ($n = 6$)], purchased from the Wako Pure Chemical Industries, were used in the mixtures. Chemical purity was confirmed by usual elemental analyses. The mixture with a 1 : 1 molar ratio of hydrated lanthanoid(III) chloride and dbc was ground by a mortar and pestle under dry-conditions, and used for the thermal reaction. According to the method of preparation of the Ln(dbc)$(NO_3)_3$ complex [3], the authentic complex La(dbc)Cl_3 was synthesized from CH_3CN solution. The complex, unfortunately, contained 7 mol of H_2O and trace quantities (0.07 mol) of uncomplexed dbc. Found: C, 33.28; H, 4.63%. Calcd. for $La(C_{20}H_{24}O_6)Cl_3(7H_2O)(0.07C_{20}H_{24}O_6)$: C, 33.92; H, 5.24%. TG analytical data (unreduced pressure) are as follows: found: H_2O, 16.75; uncomplexed dbc, 3.56%. Calcd.: H_2O, 16.64; uncomplexed dbc, 3.35%.

Procedures and apparatus

Thermal reaction was performed on a Shimadzu DTG-20 type micro-differential thermobalance under reduced presuure (N_2 atmosphere; 20 mmHg). A sample of ca. 10 mg (total amount $2.6–3.0 \times 10^{-2}$ mmol) was packed into a Pt cell and the same amount of Al_2O_3 was used as a reference material for DTA. After the system had been evacuated with a vacuum pump for 30 min, nitrogen, at 20 mmHg, was introduced into the thermobalance. Under these conditions (static atmosphere), the sample was heated at a rate of 5°C min^{-1}. IR spectra were recorded in Nujol mull with a Shimadzu IR-400 spectrophotometer. UV spectra were measured on a Shimadzu UV-200S spectrophotometer in methanol solution.

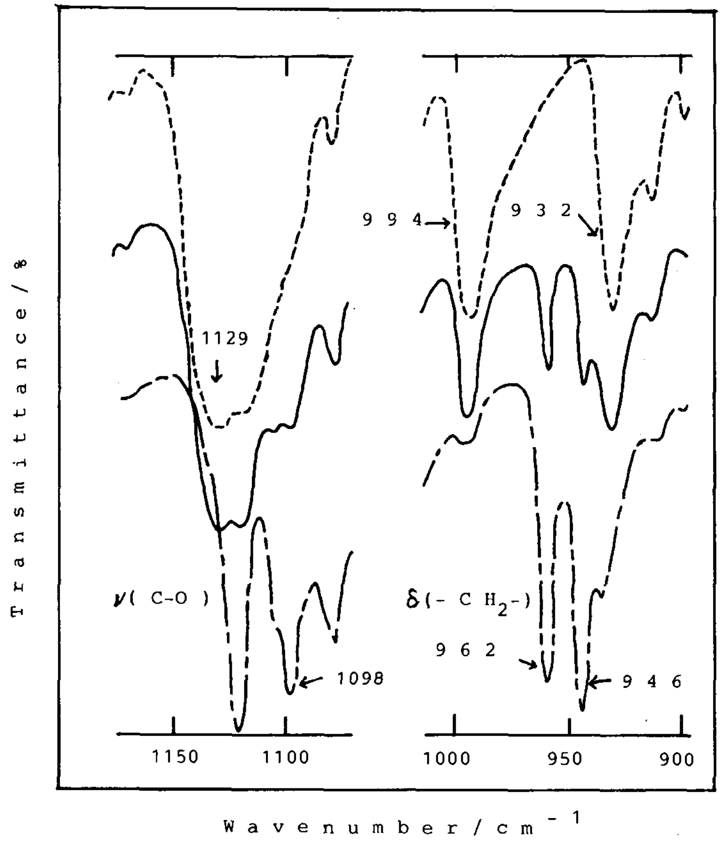

Fig. 1. Fragments of the IR spectra of: (— — —) dbc; (---) La(dbc)Cl$_3$·7H$_2$O(0.07dbc); (——·) reaction product (LaCl$_3$·7H$_2$O–dbc mixture, 170°C).

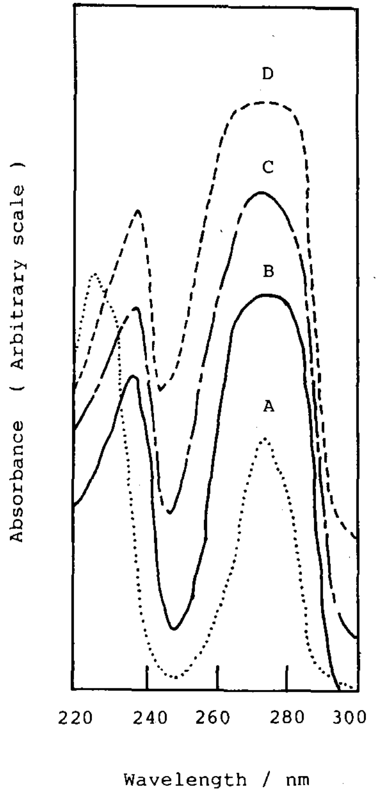

Fig. 2. UV spectra of: (A) dbc; (B) La–dbc product (180°C); (C) Sm–dbc product (180°C); (D) Er–dbc product (172°C).

RESULTS AND DISCUSSION

IR and UV spectra

To confirm complexation from the fused state of dbc, IR and UV spectra for the reaction products were recorded (Figs. 1 and 2). In the IR spectra of the authentic complex, the $\delta(CH_2)$ out-of-plane modes (994 and 932 cm^{-1}) clearly shifted to 962 and 946 cm^{-1} and the $\nu(CO)$ stretching mode partly separated from 1129 to 1098 cm^{-1}. These spectral changes have been observed in the metal–dbc complex [4]. In the IR spectra of the La–dbc product, which was removed at 170°C, similar shifts, inherent to complex formation, have been observed, though small amounts of unreacted dbc are left.

UV spectral changes relevant to complexation have been found to be the appearance of a shoulder around 273 nm, which is assigned to the Π–Π* transition of aromatic ether in dbc [4,5]. The reaction products, harvested after the fused state had been kept for 1 h, exhibited broadening absorption bands in the range 260–285 nm. The IR and UV spectral data indicate the formation of $Ln(dbc)Cl_3$ by ion–dipole interactions between dbc–oxygen and the Ln(III) ion.

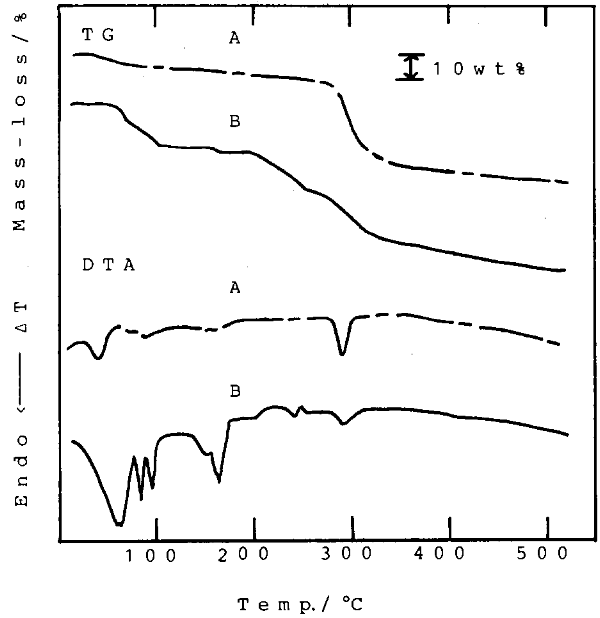

Fig. 3. TG and DTA curves of: (A) $La(dbc)Cl_3 \cdot 7H_2O(0.07dbc)$; (B) $LaCl_3 \cdot 7H_2O$–dbc mixture (under 20 mmHg).

Thermal behavior

Derivatograms for the 1 : 1 mixture systems and for the authentic complex are given in Figs. 3 and 4. Thermal reaction schemes by TG–DTA analyses for the mixture and for hydrated $LnCl_3$ are given in Table 1.

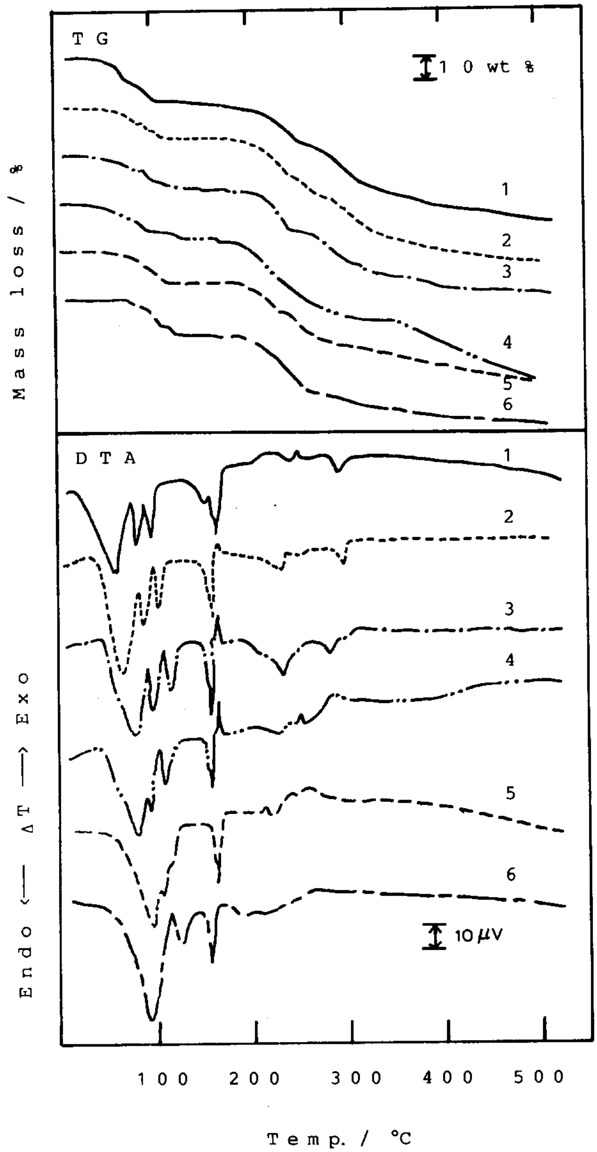

Fig. 4. TG and DTA curves of the mixtures under 20 mmHg: (1) La–dbc; (2) Nd–dbc; (3) Sm–dbc; (4) Eu–dbc; (5) Dy–dbc; (6) Er–dbc.

TABLE 1

Thermal reaction schemes [a] for the hydrated $LnCl_3$ and its mixture with dibenzo-18-crown-6 under reduced pressure (20 mmHg)

$LaCl_3 \cdot 7H_2O$

$$LaCl_37H_2O \xrightarrow[-2H_2O]{\text{reduced pressure}} LaCl_3 \cdot 5H_2O \xrightarrow[-2H_2O]{51°C} LaCl_3 \cdot 3H_2O \xrightarrow[-H_2O]{80°C} LaCl_3 \cdot 2H_2O$$

$$\xrightarrow[-H_2O]{95°C} LaCl_3 \cdot H_2O \xrightarrow[-H_2O]{148°C} LaCl_3 \xrightarrow{>368°C\ ^{b}} \text{decomposition}$$

$LaCl_3 \cdot 7H_2O$–dbc mixture

$$(LaCl_3 \cdot 7H_2O, \text{dbc}) \xrightarrow[-3.5H_2O]{57°C} (LaCl_3 \cdot 3.5H_2O, \text{dbc}) \xrightarrow[-H_2O]{81°C} (LaCl_3 \cdot 2.5H_2O, \text{dbc})$$

$$\xrightarrow[-1.5H_2O]{95°C} (LaCl_3 \cdot H_2O, \text{dbc}) \xrightarrow[-H_2O]{150°C} (LaCl_3, \text{dbc})$$

$$\xrightarrow[\text{melt} \rightarrow \text{complexing}]{163°C} 0.66La(\text{dbc})Cl_3, 0.34LaCl_3, 0.34\text{dbc}$$

$$\xrightarrow[-0.34\text{dbc}]{240°C} 0.66La(\text{dbc})Cl_3, 0.34LaCl_3$$

$$\xrightarrow[\text{melt} \rightarrow \text{decomp.}(-0.30\text{dbc})]{290°C} 0.36La(\text{dbc})Cl_3, 0.64LaCl_3 \rightarrow \text{decomp.}$$

$NdCl_3 \cdot 6H_2O$

$$NdCl_3 \cdot 6H_2O \xrightarrow[-3H_2O]{106°C} NdCl_3 \cdot 3H_2O \xrightarrow[-H_2O]{118°C} NdCl_3 \cdot 2H_2O \xrightarrow[-H_2O]{138°C} NdCl_3 \cdot H_2O$$

$$\xrightarrow[-H_2O]{200°C} NdCl_3 \xrightarrow{>312°C\ ^{b}} \text{decomp.}$$

$NdCl_3 \cdot 6H_2O$–dbc mixture

$$(NdCl_3 \cdot 6H_2O, \text{dbc}) \xrightarrow[-3H_2O]{70°C} (NdCl_3 \cdot 3H_2O, \text{dbc}) \xrightarrow[-H_2O]{90°C} (NdCl_3 \cdot 2H_2O, \text{dbc})$$

$$\xrightarrow[-H_2O]{106°C} (NdCl_3 \cdot H_2O, \text{dbc})$$

$$\xrightarrow[\text{melt} \rightarrow \text{complexing}]{159°C} 0.74Nd(\text{dbc})Cl_3 \cdot H_2O, 0.26NdCl_3 \cdot H_2O, 0.26\text{dbc}$$

$$\xrightarrow[-H_2O]{169°C(\text{exo})} 0.74Nd(\text{dbc})Cl_3, 0.26NdCl_3, 0.26\text{dbc}$$

$$\xrightarrow[-0.26\text{dbc}]{234°C} 0.74Nd(\text{dbc})Cl_3, 0.26NdCl_3$$

$$\xrightarrow[\text{melt} \rightarrow \text{decomp.}(-0.38\text{dbc})]{295°C} 0.36Nd(\text{dbc})Cl_3, 0.64NdCl_3 \rightarrow \text{decomp.}$$

$SmCl_3 \cdot 6H_2O$

$$SmCl_3 \cdot 6H_2O \xrightarrow[-3H_2O]{80°C} SmCl_3 \cdot 3H_2O \xrightarrow[-H_2O]{96°C} SmCl_3 \cdot 2H_2O \xrightarrow[-H_2O]{114°C} SmCl_3 \cdot H_2O$$

TABLE 1 (continued)

$$\xrightarrow[-H_2O]{206°C} SmCl_3 \xrightarrow{>328°C\ ^{b}} \text{decomp.}$$

$SmCl_3 \cdot 6H_2O$ – dbc mixture

$$(SmCl_3 \cdot 6H_2O, \text{dbc}) \xrightarrow[-3H_2O]{78°C} (SmCl_3 \cdot 3H_2O, \text{dbc}) \xrightarrow[-1.5H_2O]{92°C} (SmCl_3 \cdot 1.5H_2O, \text{dbc})$$

$$\xrightarrow[-H_2O]{113°C} (SmCl_3 \cdot 0.5H_2O, \text{dbc})$$

$$\xrightarrow[\text{melt} \rightarrow \text{complexing}]{159°C} 0.71Sm(\text{dbc})Cl_3 \cdot 0.5H_2O,\ 0.29SmCl_3 \cdot 0.5H_2O,\ 0.29\text{dbc}$$

$$\xrightarrow[-0.5H_2O]{170°C(\text{exo})} 0.71Sm(\text{dbc})Cl_3,\ 0.29SmCl_3,\ 0.29\text{dbc}$$

$$\xrightarrow[-0.29\text{dbc}]{234°C} 0.71Sm(\text{dbc})Cl_3,\ 0.29SmCl_3$$

$$\xrightarrow[\text{melt} \rightarrow \text{decomp.}(-0.41\text{dbc})]{282°C} 0.30Sm(\text{dbc})Cl_3,\ 0.70SmCl_3 \rightarrow \text{decomp.}$$

$EuCl_3 \cdot 6H_2O$

$$EuCl_3 \cdot 6H_2O \xrightarrow[-4H_2O]{93,104°C} EuCl_3 \cdot 2H_2O \xrightarrow[-H_2O]{121°C} EuCl_3 \cdot H_2O$$

$$\xrightarrow[-H_2O]{213°C} EuCl_3 \xrightarrow{>312°C\ ^{b}} \text{decomp.}$$

$EuCl_3 \cdot 6H_2O$ – dbc mixture

$$(EuCl_3 \cdot 6H_2O, \text{dbc}) \xrightarrow[-3H_2O]{82°C} (EuCl_3 \cdot 3H_2O, \text{dbc}) \xrightarrow[-1.5H_2O]{92°C} (EuCl_3 \cdot 1.5H_2O, \text{dbc})$$

$$\xrightarrow[-H_2O]{111°C} (EuCl_3 \cdot 0.5H_2O, \text{dbc})$$

$$\xrightarrow[\text{melt} \rightarrow \text{complexing}]{160°C} 0.79Eu(\text{dbc})Cl_3 \cdot 0.5H_2O,\ 0.21EuCl_3 \cdot 0.5H_2O,\ 0.21\text{dbc}$$

$$\xrightarrow[-0.5H_2O]{168°C(\text{exo})} 0.79Eu(\text{dbc})Cl_3,\ 0.21EuCl_3,\ 0.21\text{dbc}$$

$$\xrightarrow[-0.21\text{dbc}]{230°C} 0.79Eu(\text{dbc})Cl_3,\ 0.21EuCl_3$$

$$\xrightarrow[\text{melt} \rightarrow \text{decomp.}(-0.35\text{dbc})]{253°C} 0.44Eu(\text{dbc})Cl_3,\ 0.56EuCl_3 \rightarrow \text{decomp.}$$

$DyCl_3 \cdot 6H_2O$

$$DyCl_3 \cdot 6H_2O \xrightarrow[-5H_2O]{96,110°C} DyCl_3 \cdot H_2O \xrightarrow[-H_2O]{206°C} DyCl_3 \xrightarrow{>295°C\ ^{b}} \text{decomp.}$$

$DyCl_3 \cdot 6H_2O$ – dbc mixture

$$(DyCl_3 \cdot 6H_2O, \text{dbc}) \xrightarrow[-5.5H_2O]{93,104,110°C} (DyCl_3 \cdot 0.5H_2O, \text{dbc})$$

TABLE 1 (continued)

$$\xrightarrow[\text{melt} \to \text{complexing}]{161^\circ\text{C}} 0.86\text{Dy(dbc)Cl}_3\cdot 0.5\text{H}_2\text{O}, 0.14\text{DyCl}_3\cdot 0.5\text{H}_2\text{O}, 0.14\text{dbc}$$

$$\xrightarrow[-0.5\text{H}_2\text{O}, -0.14\text{dbc}]{212\text{–}222^\circ\text{C(exo)}} 0.86\text{Dy(dbc)Cl}_3, 0.14\text{DyCl}_3$$

$$\xrightarrow[\text{melt} \to \text{decomp.}(-0.32\text{dbc})]{235\text{–}285^\circ\text{C(broad)}} 0.54\text{Dy(dbc)Cl}_3, 0.46\text{DyCl}_3 \to \text{decomp.}$$

$ErCl_3\cdot 6H_2O$

$$\text{ErCl}_3\cdot 6\text{H}_2\text{O} \xrightarrow[-4\text{H}_2\text{O}]{102^\circ\text{C}} \text{ErCl}_3\cdot 2\text{H}_2\text{O} \xrightarrow[-\text{H}_2\text{O}]{130^\circ\text{C}} \text{ErCl}_3\cdot \text{H}_2\text{O} \xrightarrow[-\text{H}_2\text{O}]{195^\circ\text{C}} \text{ErCl}_3 \xrightarrow{>285^\circ\text{C}^{\,b}} \text{decomp.}$$

$ErCl_3\cdot 6H_2O$–dbc mixture

$$(\text{ErCl}_3\cdot 6\text{H}_2\text{O}, \text{dbc}) \xrightarrow[-4.5\text{H}_2\text{O}]{93^\circ\text{C}} (\text{ErCl}_3\cdot 1.5\text{H}_2\text{O}, \text{dbc}) \xrightarrow[-\text{H}_2\text{O}]{124^\circ\text{C}} (\text{ErCl}_3\cdot 0.5\text{H}_2\text{O}, \text{dbc})$$

$$\xrightarrow[\text{melt} \to \text{complexing}]{157^\circ\text{C}} 0.87\text{Er(dbc)Cl}_3\cdot 0.5\text{H}_2\text{O}, 0.13\text{ErCl}_3\cdot 0.5\text{H}_2\text{O}, 0.13\text{dbc}$$

$$\xrightarrow[-0.5\text{H}_2\text{O}]{\text{ca.}175^\circ\text{C}} 0.87\text{Er(dbc)Cl}_3, 0.13\text{ErCl}_3, 0.13\text{dbc}$$

$$\xrightarrow[-0.13\text{dbc}]{193^\circ\text{C(broad)}} 0.87\text{Er(dbc)Cl}_3, 0.13\text{ErCl}_3$$

$$\xrightarrow[\text{melt} \to \text{decomp.}(-0.35\text{dbc})]{213\text{–}261^\circ\text{C(broad)}} 0.52\text{Er(dbc)Cl}_3, 0.48\text{ErCl}_3 \to \text{decomp.}$$

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[a] Temperatures are endothermic maxima on DTA curves.

[b] Mass loss temperatures on TG curves.

Authentic lanthanum–dbc complex

Dehydration of the complex took place in vacuo (5.5 mol), at 38°C (1 mol) and at 86°C (0.5 mol). Elimination of the uncomplexed dbc (0.07 mol) was observed in the range 150–250°C. The endothermic decomposition at 295°C was attributed to melting and the release of dbc (ca. 0.5 mol; 50%) from the complex because no endothermic peaks were observed on the DTA curve for $LaCl_3 \cdot 7H_2O$ or for dbc alone.

$LaCl_3 \cdot 7H_2O$–dbc mixture

Dehydration was completely achieved by four steps up to ca. 160°C with endothermic peaks. The quantity of water liberated in each step showed little distinction between lanthanum chloride and its mixture with dbc. After the melting of dbc, simultaneous complexation progressed to 163°C, and then evaporation of unreacted dbc followed above 240°C. The complex formation achieved was 66%. About 50% of the complex La(dbc)Cl_3 decomposed to $LaCl_3$ endothermally, releasing dbc under a fused state at 295°C. Further decompositions of the complex and $LaCl_3$ proceed gradually above 320°C.

$NdCl_3 \cdot 6H_2O$–dbc mixture

Despite the same quantities of water liberated in every step, the dehydration temperatures are 30–40°C lower in the mixture than in $NdCl_3 \cdot 6H_2O$. At 159°C melting and complexation (74%) occurred, retaining 1 mol of coordinated water. This water molecule is liberated from the complex at 169°C by a characteristic exothermic reaction, though the last-step dehydration of $NdCl_3 \cdot H_2O$ was endothermic. After the evaporation of unreacted dbc at 234°C, 49% of the complex Nd(dbc)Cl_3 decomposed into $NdCl_3$ at 295°C. The remaining Nd(dbc)Cl_3 and $NdCl_3$ gradually decompose above 300°C. In the following systems similar reactions have been observed above 280–300°C.

$SmCl_3 \cdot 6H_2O$–dbc mixture

The temperatures of dehydration up to the third step were close to that of samarium chloride, while the fourth step was lower by ca. 40°C after complexation in this mixture. The quantity of water liberation is distinct on the second and fourth dehydration steps. After the third-step dehydration, melting and complexation (71%) occurred at 159°C possessing 0.5 mol of coordination water. This water molecule evolved from the complex exothermally at 170°C, and then evaporation of unreacted dbc took place at 234°C. The complex Sm(dbc)Cl_3 decomposed 41% to $SmCl_3$ at 282°C by eliminating the complexed dbc.

$EuCl_3 \cdot 6H_2O$–dbc mixture

Up to the third-step dehydration, their temperatures lowered by 10°C and the quantity of water liberated exhibited little distinction. Melting and complexation progressed to 160°C retaining 0.5 mol of coordinated water. The complex formation achieved was 79%. After complexation, the fourth dehydration was completed exothermally at 168°C. The temperature is 45°C lower than that observed in $EuCl_3 \cdot 6H_2O$ with an endotherm. Unreacted dbc volatilized at 230°C. The complex Eu(dbc)Cl_3 fused and 55% decomposed to $EuCl_3$ at 253°C by releasing dbc.

$DyCl_3 \cdot 6H_2O$–dbc mixture

Prior to the melting of dbc, 5.5 mol water dehydrated continuously, whose DTA curve showed the first peak, the second and the third shoulder peaks. These temperatures are close to that of $DyCl_3 \cdot 6H_2O$, whereas the quantity of water liberated revealed a slight difference. After the melting of dbc, 86% complexation occurred at 161°C, there was 0.5 mol of coordination water. It is found that the coordinated water is retained to a higher temperature: the last-step dehydration started at 212°C; the temperature was higher by ca. 6°C, than that for $DyCl_3 \cdot 6H_2O$. Subsequent evolution of unreacted dbc was observed up to 222°C. At 235–285°C the complex fused and 63% decomposed to $DyCl_3$.

$ErCl_3 \cdot 6H_2O$–dbc mixture

Dehydration was completed in three steps. The first and second steps in this mixture were ca. 10°C lower than those for $ErCl_3 \cdot 6H_2O$, however, the third step was very similar. The quantity of water liberated exhibited small differences in the first- and third-step dehydrations. After the second dehydration (124°C), the melting of dbc and complexation with a reaction rate of 87% proceeded at 157°C. The third dehydration ($0.5H_2O$) occurred at 175°C, then unreacted dbc evaporated at 193°C. The complex $Er(dbc)Cl_3$ decomposed 60% to $ErCl_3$ at 213–261°C.

The formation ratio of the $Ln(dbc)Cl_3 \cdot nH_2O$, under the conditions taken in this thermal reaction, was in the range 66–87%. The characteristic profile for the thermal behavior of the above mixtures is as follows. (1) In the lanthanum–dbc mixture, all of the water molecules dehydrated prior to complexation. A large thermal stability was exhibited in the complex $La(dbc)Cl_3$ with no coordinated water. (2) In the mixtures of neodymium–dbc, samarium–dbc, and europium–dbc, 1 or 0.5 mol of water seems to be necessary for complexation with dbc. The coordinated water, however, was immediately released by an exothermal reaction due to the formation of additional ion–dipole interactions between dbc–oxygen and the lanthanoid(III) ion, where the $Ln(III)–OH_2$ bond had existed. The thermal stability of the $Ln(dbc)Cl_3$ (Ln = Nd, Sm, and Eu) complexes decreases with the lanthanoid contraction. (3) In the mixtures of dysprosium–dbc and erbium–dbc, 0.5 mol of water is considered to be necessary for complex formation with dbc. The coordinated water is involved in the complex up to higher temperatures than in the rare earth salt $LnCl_3 \cdot 6H_2O$ (Ln = Dy and Er). Since it was liberated endothermally, no additional ion–dipole interaction was considered, which was seen in the Nd–, Sm–, and Eu–dbc systems. After the evolution of coordination water, the complex becomes thermally unstable. (4) As mentioned above, dehydration from the mixture $LnCl_3 \cdot nH_2O$–dbc showed a distinct thermal behavior compared to that of the rare earth salt $LnCl_3 \cdot nH_2O$ under the present reduced-pressure and under unreduced conditions [6]. The hydrated water molecules play an important part in complexation, and they are more stable in the complex with smaller lanthanoid(III) ion radius.

To confirm complete complexation, the dependence of the molar ratio X (where $X = LnCl_3 \cdot nH_2O/(LnCl_3 \cdot nH_2O + dbc)$) has been investigated under the same conditions. The DTA curves for the $SmCl_3 \cdot 6H_2O$–dbc mixture with several molar ratios are illustrated in Fig. 5, where no correction by

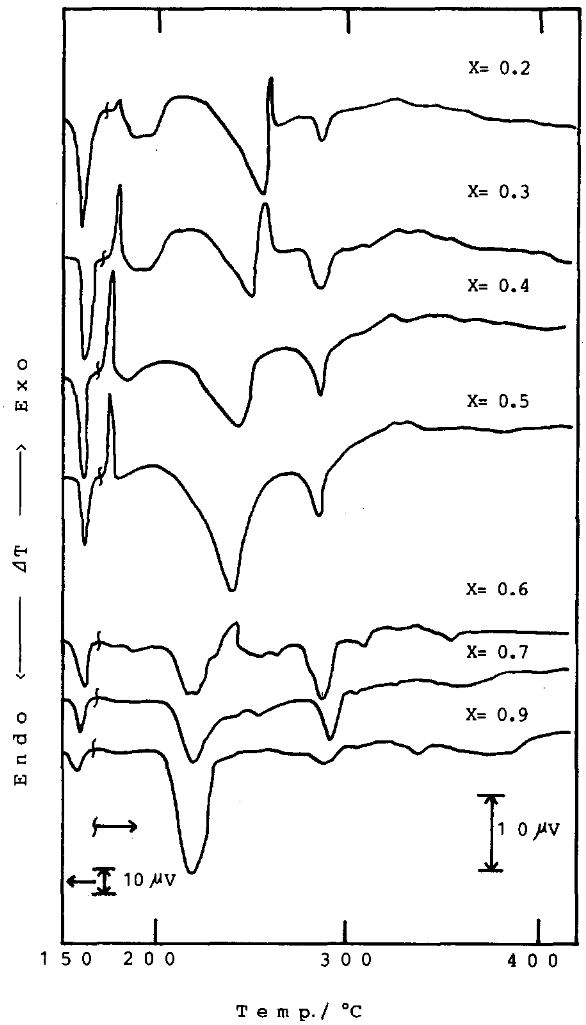

Fig. 5. Dependence of the molar ratio, X, in the Ln–dbc mixture upon the DTA curve.

sample weight has been done. With respect to the molar ratios from 0.2 to 0.5, a broad endothermic peak was found in the range 230–250°C. This was assigned to the liberation of excess plus unreacted dbc from the TG analyses. In the cases $X = 0.6$–0.9, the last-step dehydration from the excess amounts of $SmCl_3 \cdot 6H_2O$ was observed in the endothermic peak at 212°C but DTA change with the evolution of unreacted dbc was very small. Thus, the thermal reaction approaches complete complexation when the excess amounts of rare earth salt against dbc have been used.

Heat of complex formation

The overall enthalphy for the reactions of melting and complexation was estimated from the apparent area of endothermic peaks on DTA measured with a constant amount of Al_2O_3 in each run. The overall enthalpy, ΔH_{all}, was obtained in the mixture with $X=0.9$ in order to achieve complete complex formation. The enthalpy for the complexation, ΔH_{com}, was estimated by subtracting the heat of fusion of dbc, ΔH_{dbc}, from ΔH_{all} according to eqn. (1).

$$\Delta H_{com} = \Delta H_{all} - \Delta H_{dbc} X_w \quad (1)$$

where $\Delta H_{all} = kA(M_n/WX_w)$; k, apparatus constant; A, DTA peak area; M_n, molecular weight of $LnCl_3 \cdot nH_2O$; W, sample weight of the $LnCl_3 \cdot nH_2O$–dbc mixture; X_w, weight percentage of $LnCl_3 \cdot nH_2O$ in the mixture;

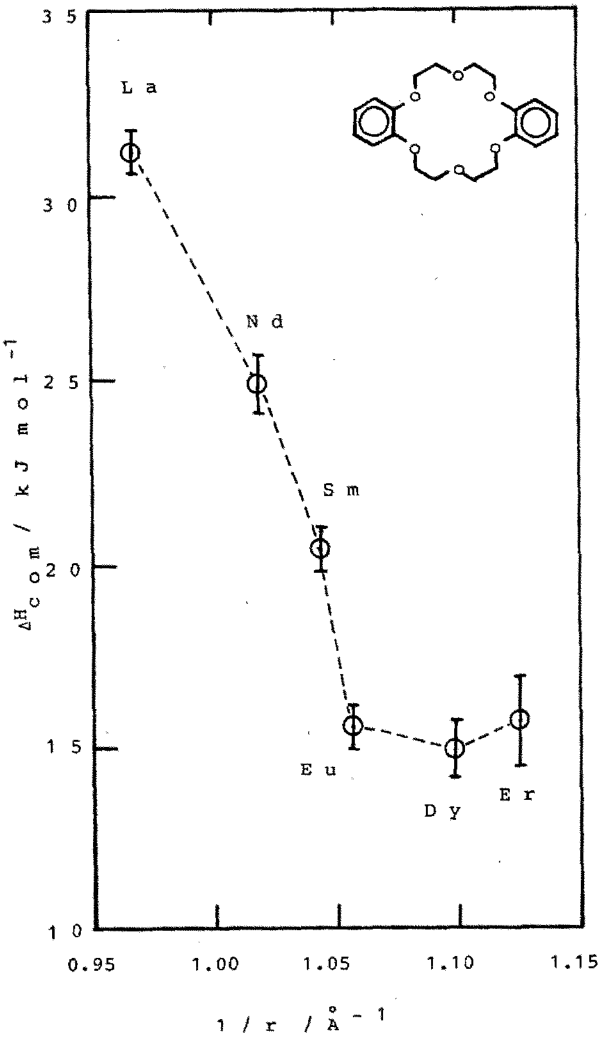

Fig. 6. Plots of the enthalpies for complexation against the reciprocal of the radius of the Ln(III) ion.

and ΔH_{dbc} is the heat of fusion for dbc in the mixture. The heat of fusion for indium metal was used as a standard enthalpy to determine the apparatus constant k. The peak area on the DTA curve was estimated by a planimeter. The influence of the excess rare earth salt on the heat of fusion of dbc was neglected. The obtained ΔH_{com} values are plotted against the reciprocal of lanthanoid(III) ionic radius in Fig. 6. The formation enthalpies of lanthanoid cation complexes were positive and decreased with reduced ion size; the reverse was found at the end of the lanthanoid series taken in this study. The values of ΔH_{com} (kJ mol^{-1}) are as follows: La–dbc (31.0) > Nd–dbc (24.9) > Sm–dbc (20.3) > Eu–dbc (15.5) > Dy–dbc (14.9) < Er–dbc (15.7).

Izatt et al. reported that the stability constants of the complexation between 18-crown-6 and Ln(III) chloride in methanol decrease as cation size diminishes proceeding across the series La^{3+} to Lu^{3+} [7]. A sudden drop in stability beyond Ga^{3+} has been explained since the coordination number decreases at or near Gd^{3+}, and the entropy contribution from loss of solvent molecules becomes smaller because the stability is enthalpic from La^{3+} to Nd^{3+}, while it is entropic from Sm^{3+} to Gd^{3+}. Massaux et al. also reported that the stability of the La^{3+} to Lu^{3+} complexes with 4,4′(5′)-di-*tert*-butylbenzo-18-crown-6, in propylene carbonate, decreases uniformly through the lanthanoid series [8].

The thermal stability of the complex in this study generally decreases with increasing atomic number proceeding across the series La^{3+} to Eu^{3+} and the opposite trend is revealed in the Dy^{3+} and Er^{3+} complexes based on their decomposition temperatures. The above stability and enthalpy lead to the conclusion that the stability for the dbc complexes from La^{3+} to Eu^{3+} is enthalpic and it is entropic for Dy^{3+} and Er^{3+}. On complexation of the latter lanthanoid series, the water molecule might make up for the size of the lanthanoid(III) associated with the chloride ion for filling the cavity of dbc. The present $Ln(dbc)Cl_3$ complexes, except for the samarium and europium ones, exhibited periodical alteration for the thermal stability as was seen for those of the $Ln(dbc)(SCN)_3$ complexes [2].

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