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Influences of the Lanthanoid Contraction on the Thermal Dehydration Reactions of Lanthanoid(III) Malonate Hydrates

Kazuo Muraishi, Kenzo Nagase,[†] Masae Kikuchi,[††] Kozo Sone,*[,†††] and Nobuyuki Tanaka[††††]

Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa-machi, Yamagata 990
[†]*College of General Education, Tohoku University, Kawauchi, Sendai 980*
[††]*Institute for Iron, Steel and Other Metals, Tohoku University, Katahiracho, Sendai 980*
[†††]*Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112*
[††††]*Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980*

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The thermal dehydration reactions of lanthanoid(III) malonate hydrates $Ln_2mal_3 \cdot nH_2O$ (Ln=Ce—Lu; mal=$CH_2(COO)_2$; $n=6$ for Ce—Eu and 8 for Gd—Lu) were investigated mainly by the thermogravimetries under conventional conditions and in atmosphere of water vapor at a constant reduced pressure and a superslow heating rate. The latter conditions were useful especially to detect the formation of new intermediate hydrates, and to determine the dehydration temperatures with accuracy. The main features of the results could be reasonably understood in view of the effects of the lanthanoid contraction.

The lanthanoid elements (Ln) are characterized by an overall decrease in size of atoms or ions with increasing atomic number. In the case of Ln^{3+} ions, the effects of this "lanthanoid contraction" appear most dramatically, and its influences on the coordination number (C.N.) and geometry are the unifying concept in the chemistry of Ln(III) compounds.[1,2] Lanthanoid(III) ions have unoccupied inner orbitals, but the ligand field stabilization caused by their presence is said to be much smaller than in the case of 3d-transition metal ions.[3] The C.N. of Ln^{3+} is normally 6 to 9, and the metal-ligand bonds are mainly ionic.

In aqueous solutions, most of Ln^{3+} compounds are labile, but it is said that their coordination spheres seek to achieve a compromise between the most spherical shielding for Ln^{3+} and the minimum interligand repulsion.[2]

In the solid state, polymorphs are often formed because of the small energy differences among possible structures of high C.N., and it is known that, in certain cases, one or two of the ligands are in "partial coordination," to reduce the overcrowdedness of the coordination sphere.[4] Thus the influences of the lanthanoid contraction observed in the solid state may look quite different from those[5] observed in solution.

In the present paper, such influences upon the thermal dehydration reaction of Ln^{3+} malonate hydrates in the solid state will be discussed mainly on the basis of thermogravimetric data.

Experimental

Preparation of $Ln_2mal_3 \cdot nH_2O$. Aqueous solutions of $LnCl_3$ (0.24 mol dm^{-3}) and Na_2mal (0.36 mol dm^{-3}) were mixed quickly at room temperature. Each precipitate obtained was allowed to stand overnight in contact with the mother liquor, washed several times with water by decantation, and filtered. It was further washed with ethanol and ether, and dried at room temperature. Contents of Ln, C, and H in the samples are given in Table 1.

Themogravimetry (TG) and Differential Thermal Analysis (DTA). The TG and DTA curves were obtained with a Shinku Riko TGD-3000 differential thermal microbalance at a heating rate of 3 °C/min in a dry nitrogen stream of 30 cm^3/min, and also at a superslow heating rate of 2 °C/h in water vapor at 10 Torr (1 Torr≈133 Pa).[6] About 20 mg of the powdered sample was used for each run.

IR and X-Ray Diffraction. The infrared spectra in the frequency region of 400—4000 cm^{-1} were obtained by the

Table 1. Analytical data of the malonate hydrates prepared in the present work

Compound	Color	Metal[a)] (%)		Carbon[a)] (%)		Hydrogen (%)	
		Found	Calcd	Found	Calcd	Found	Calcd
$Ce_2mal_3 \cdot 6H_2O$	white	40.18	40.35	15.99	15.57	2.88	2.61
$Pr_2mal_3 \cdot 6H_2O$	green	40.39	40.48	15.33	15.53	3.00	2.60
$Nd_2mal_3 \cdot 6H_2O$	violet	40.65	41.05	15.66	15.38	2.71	2.58
$Sm_2mal_3 \cdot 6H_2O$	white	41.96	42.07	15.51	15.12	2.57	2.54
$Eu_2mal_3 \cdot 6H_2O$	white	41.96	42.31	15.14	15.05	2.78	2.53
$Gd_2mal_3 \cdot 8H_2O$	white	41.30	41.13	13.98	14.14	3.08	2.90
$Tb_2mal_3 \cdot 8H_2O$	white	41.34	41.38	14.06	14.07	2.67	2.89
$Dy_2mal_3 \cdot 8H_2O$	white	41.86	41.90	13.96	13.94	2.87	2.86
$Ho_2mal_3 \cdot 8H_2O$	pink	42.19	42.26	13.56	13.86	3.06	2.84
$Er_2mal_3 \cdot 8H_2O$	pink	42.84	42.61	13.90	13.77	3.15	2.82
$Tm_2mal_3 \cdot 8H_2O$	white	43.21	42.82	13.74	13.72	2.86	2.81
$Yb_2mal_3 \cdot 8H_2O$	white	44.07	43.46	13.97	13.57	2.98	2.78
$Lu_2mal_3 \cdot 8H_2O$	white	43.57	43.73	13.67	13.51	2.73	2.77

a) The metal contents were determined by titration with EDTA and Xylenol Orange in the pH range of 5.1—5.6.

KBr disk method with a Hitachi 215 infrared spectrometer and the powder X-ray diffraction analysis was made with a Rigaku Denki DS X-Ray diffractometer.

Results and Discussion

The samples prepared can be formulated as $Ln_2mal_3 \cdot nH_2O$, where $n=6$ for Ce—Eu and 8 for Gd—Lu (*cf.* Table 1). Hansson has studied the crystal structures of $Nd_2mal_3 \cdot 6H_2O$,[7] $Nd_2mal_3 \cdot 8H_2O$,[8] and $Eu_2mal_3 \cdot 8H_2O$;[9] the hexahydrates and octahydrates prepared in the present study showed essentially the same X-ray diffraction patterns as those of Hansson's $Nd_2mal_3 \cdot 6H_2O$ and $Eu_2mal_3 \cdot 8H_2O$, respectively. The infrared spectra were also divided into two different groups of Ce—Eu and Gd–Lu.

It must be mentioned here that most of these hydrates were already prepared by Azikov *et al.*, who also obtained their TG curves, and stated that their infrared spectra can be divided into two proups of Ce—Gd and Tb—Lu.[10,11] The accuracy of their data, however, is seemingly not very high, and their classification of Gd is not very convincing. Therefore, the TG and DTA behaviors of these hydrates were studied in more detail to get better structural correlations.

TG and DTA in N_2 at the Heating Rate of 3 °C/min. Among the TG and DTA curves of all the samples obtained, those of Eu, Gd, Ho, and Lu are shown in Fig. 1 as typical examples. As seen in the curve of Eu, all the hexahydrates lose their waters in a single step, whereas the octahydrates lose them in two steps, which can be distinguished more clearly with the heavier lanthanoids.

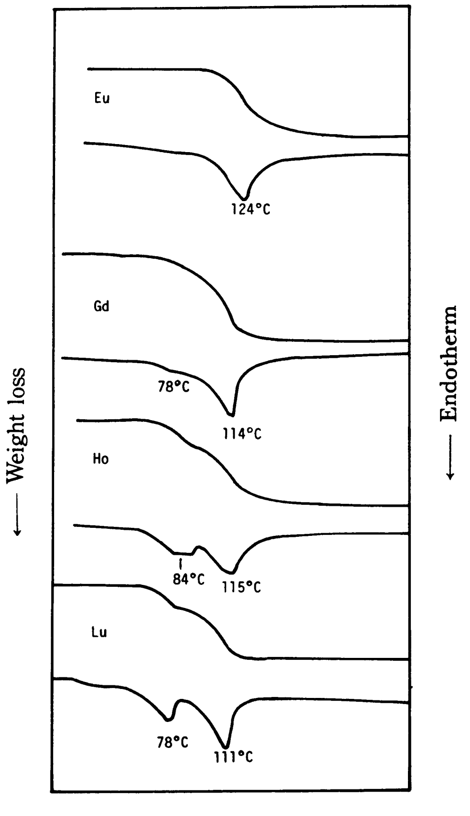

Fig. 1. TG and DTA curves of $Ln_2mal_3 \cdot nH_2O$ in N_2. The temperatures in the figure correspond to DTA peaks.

This difference in the mode of dehydration can be related with the structural data of these hydrates. It is known that the two Ln^{3+} in $Ln_2mal_3 \cdot 6H_2O$ are equivalent, and all the waters in them are coordinated to the Ln^{3+}, so that the hexahydrates can be represented as $[Ln_2mal_3(H_2O)_6]$ in which the C.N. of each Ln^{3+} is 9.[7] On the other hand, two waters in $Ln_2mal_3 \cdot 8H_2O$ are coordinated to one Ln^{3+} with C.N. 8, and three to another with C.N. 9, and the remaining three are held as lattice waters in two different ways.[9] Thus the octahydrates can be represented as $[Ln_2mal_3(H_2O)_5] \cdot 2H_2O \cdot \underline{H_2O}$.

Therefore, we can roughly say that, upon dehydration, the hexahydrates lose all of the coordination waters in a single step, but the octahydrates lose the lattice waters in the first step, and then the coordination waters in the second. Closer observations, however, reveal some more facts of interest.

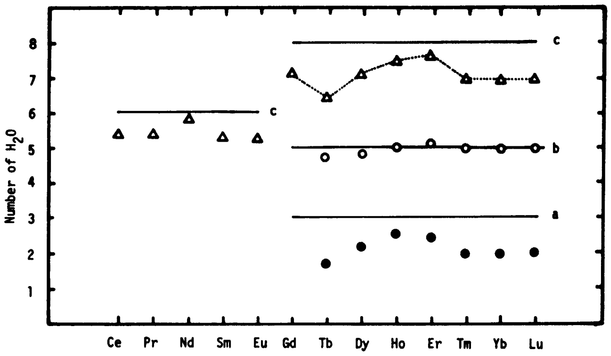

Fig. 2. Numbers of H_2O lost in the complete dehydration (△), and those lost in the first (●) and second (○) step, respectively, which were determined by TG in N_2. The solid lines indicate the theoretical values for lattice waters (a), coordination waters (b) and total waters (c).

When the numbers of H_2O lost by the complete dehydration are plotted against the symbols of Ln arranged in the order of increasing atomic number (Fig. 2), it is seen that they are somewhat smaller than expected; in the case of the octahydrates they are not exactly 8, and in most cases, nearly 7. This fact indicates that, among the waters in it, one of the lattice waters (the underlined one in the above formula) is held especially weakly, and easily lost from the sample in advance of the TG measurement.** So we represent the whole change as follows:

$$[Ln_2mal_3(H_2O)_5] \cdot 2H_2O \cdot H_2O \xrightarrow[\text{I}]{-H_2O}$$

$$[Ln_2mal_3(H_2O)_5] \cdot 2H_2O \xrightarrow[\text{II}]{-2H_2O}$$

$$[Ln_2mal_3(H_2O)_5] \xrightarrow[\text{III}]{-5H_2O} Ln_2mal_3.$$

** TG measurement on fresh samples in static air indicates, in all cases, an approximately quantitative loss of water.

Step I seems to occur very easily, so that it is either not observed on the TG curves (Lu, Yb, and Tm), or seemingly appears in combination with Step II (Ho and Er). The temperature difference between Steps II and III becomes smaller with the decrease of atomic number (or increase of ion size) of Ln as shown in Fig. 1, showing that the difference between the two kinds of waters in these hydrates decreases in the same way. We can imagine that, as the coordination sphere of Ln^{3+} expands in this direction, the lattice waters will gradually get involved in it, or get more "coordinated" in nature. This will be the reason why there is no distinct break between Steps II and III with Gd; when Ln^{3+} becomes still larger, all the waters get coordinated, forming the hexahydrates.

As to the hexahydrates, the numbers of waters lost by their complete dehydration are again somewhat smaller than expected, mostly being 5—5.5 instead of 6.** As mentioned above, all these hydrates contain their waters in a highly crowded coordination sphere (C.N. 9), and the energy difference between possible structures of C.N. 9 and C.N. 8 will be small. So it is conceivable that a small part of it is easily "squeezed out" of the coordination sphere and lost in advance of the TG study, as the case of the lattice water of the octahydrate. After this initial loss, however, the remaining waters are lost in a single step, as expected from their original formula $[Ln_2mal_3(H_2O)_6]$.

TG Analysis in Water Vapor of Constant Reduced Pressure at a Superslow Heating Rate. In order to see the nature of the steps in more detail, the TG curves were obtained in an atmosphere of water vapor at a constant reduced pressure (10 Torr) at a superslow heating rate of 2 °C/h. This technique, developed by us and reported in the preceding paper,[6] was found to be especially useful to study the dehydration of hydrated salts (such as $CuSO_4 \cdot nH_2O$), since (1) each of the dehydration steps becomes notably steeper, and more easily distinguishable, and (2) the whole pattern of the TG curve becomes remarkably similar to the true equilibrium weight-temperature relation under the specified water vapor pressure.

The comparison of the two curves in Fig. 3, which are given for examples, shows that this technique can be applied effectively to the present case. As expected, the steps of Curve A are very much steeper, in comparison with Curve B. The first step on A seems to correspond to the tail of Step I mentioned in the preceding section. Closer comparison of these curves shows that, although the total of the waters lost on Curve B is about 7(=2+5), those estimated from Curve A is about 6.7(=0.4+2.3+4). Under the present conditions, therefore, the eight waters are not lost in the order of (1)-2-5, but approximately (2)-2-4 by way of a tetrahydrate. Since the original hydrate contained only 3 lattice waters, a structural change is expected to occur when it is heated extremely slowly at a constant water vapor pressure (under quasi equilibrium conditions). In the course of the heating, a coordination water is squeezed out of the coordination sphere, and the dehydration proceeds as if the original complex should be formulated as $[Ln_2mal_3(H_2O)_4] \cdot 2H_2O \cdot 2H_2O$, losing $2H_2O$ at first,*** and then 2 and $4H_2O$ at the two main steps, respectively.

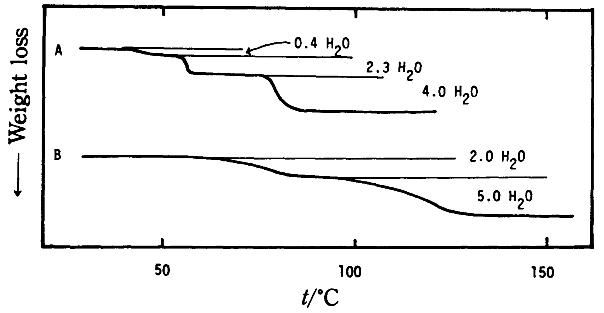

Fig. 3. TG curves of $Lu_2mal_3 \cdot 8H_2O$ obtained under two different conditions: (A) at a heating rate of 2 °C/h in water vapor at 10 Torr and (B) at a heating rate of 3 °C/min in N_2 stream of 30 cm^3/min. In both cases, some water molecules were lost before the TG measurements.**

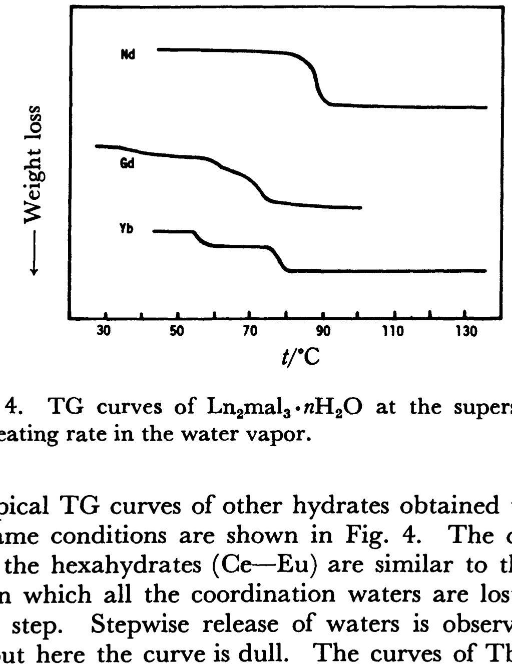

Fig. 4. TG curves of $Ln_2mal_3 \cdot nH_2O$ at the superslow heating rate in the water vapor.

Typical TG curves of other hydrates obtained under the same conditions are shown in Fig. 4. The curves of all the hexahydrates (Ce—Eu) are similar to that of Nd, in which all the coordination waters are lost in a single step. Stepwise release of waters is observed at Gd, but here the curve is dull. The curves of Tb—Yb are more or less similar, and show two clear steps as can be seen on the curve of Yb. Then comes Lu, with one more additional step as mentioned above.

The numbers of H_2O lost with each sample are now plotted in Fig. 5, just as in Fig. 2. The numbers corresponding to the complete dehydration of the octahydrates are 5 to 6, showing that they lose much of its lattice waters in advance of the TG measurement.*** About 2 H_2O among them are then lost in the first TG step, and 3 to 4 in the second. On the other hand, the hexahydrates lose about one of its coordination waters in advance, just as in the case of the TG in N_2, and then all the rest of it in a single step.

Although at present it is difficult to explain the

*** In the present case, these molecules seemingly escape from the sample during the preliminary evacuation which takes a few hours before the start of the TG measurement.

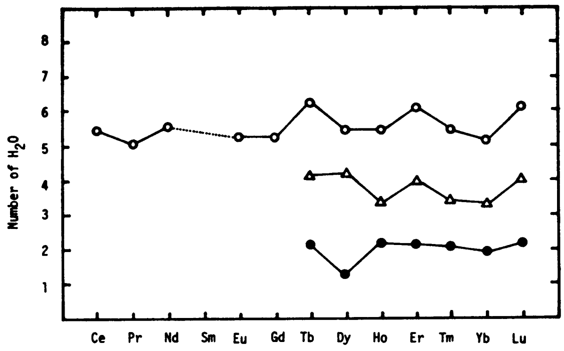

Fig. 5. Numbers of H_2O lost in the complete dehydration (○), and those lost in the first (●) and second (△) step, respectively, which were determined by TG with the superslow heating rate in the water vapor. The dehydration did not proceed completely with Sm, probably owing to the recombination of water vapor under these conditions.

complicated "ups and downs" among these numbers (see later), it is fairly certain that the mode of dehydration of the octahydrate is dependent on the atmosphere and heating rate, and the patient "squeezing" (*i.e.*, very slow heating in a diffuse water vapor) can release more water than the hasty one (*i.e.*, quick heating under 1 atm of N_2) which can only sweep out the lattice water.

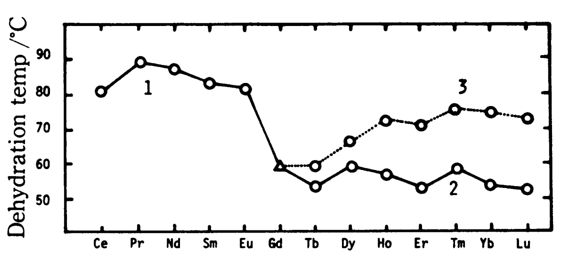

Fig. 6. Dehydration temperatures (t_i) obtained from TG with the superslow heating rate in the water vapor. As to the meaing of (1)—(3), see text. The value of Gd is given by (△), because here the two steps overlap.

The initial weight-loss temperature (t_i), or the temperature from which the TG curve begins to drop, may be taken as a measure of the relative strengths of Ln^{3+}–OH_2 bonds. In the TG studies in N_2, it was quite hard to determine exact t_i values, because all the steps observed were too dull (*cf.* Fig. 1). In the present case, the steps are much steeper (*cf.* Fig. 3), so we can quite accurately determine the t_i values for most of the steps observed, and plot them as shown in Fig. 6. The t_i values thus obtained can roughly be divided in three groups, *i.e.*: (1) Ce to Eu (hexahydrates); (2) Gd to Lu (octahydrates), 1st step; (3) Gd to Lu, 2nd step. The t_i's in the groups (1) and (3) are the temperatures at which the coordination waters hegin to escape. In both cases, in general, the t_i first rises, and then drops through a flat maximum, in the order of increasing atomic number. This can be understood as a balance between the two counteracting tendencies, *i.e.*, the strengthening of Ln^{3+}–OH_2 bond resulting from the decrease in size of Ln^{3+}, and the increase in interligand repulsion caused by the same effect. In previous studies[12,13] on lanthanoid dimethyl sulphoxide, tetrahydrothiophene 1-oxide and *N,N,N′,N′*-tetramethylurea complexes, their general TG–DTA behaviours could also be explained by these two tendencies.

However, the sudden drop of the t_i at Gd (or the double periodicity between the former half and the latter half of the Ln sequence) can not be explained in such a simple way, because the lanthanoid contraction continues with little break from Ce to Lu.[14] Such "gadolinium break" has been often found among the thermodynamic data of lanthanoid complex formation in solution.[15] As one of the reasons for such a break, a change in C.N. has been suggested in the case of the formation constants of Ln^{3+} complexes with various amino polycarboxylates.[5] However, in the present case, this view is inconsistent with the trends of the t_i, since the ions of Gd—Lu with the smaller C.N. (see above) is expected to bind H_2O more strongly, and to bring about an elevation of t_i's.

By the way, among these hydrates, it is natural to suppose that the Ln^{3+}–OH_2 coordinate bonds will become weaker, when the Ln^{3+}–mal^{2-} bonds become stronger. By the X-Ray analysis,[7,9] it is known that there are two kinds of malonate ions in the hexahydrate, a chelated one and an open and bridging one, while all malonate ions in the octahydrate are chelated. These facts lead to the view that the ions of Gd—Lu are probably more suitable in size for the formation of chelate rings than those of Ce—Eu. The drop of the t_i for the malonate hydrates of the former ions thus may be due to the much more rigid Ln^{3+}–mal^{2-} bondings in them, which is reflected on the more pronounced chelation, in comparison with those in the hydrates of the latter ions.

The t_i's in the group(2) are the temperatures at which the waters squeezed out of the coordination sphere begin to escape, and generally drop from Gd to Lu, although some irregularities are observed. This kind of waters become more and more loosely held when the coordination waters lost at the last step become more and more firmly bound. The irregularities observed seem to be related to the number of H_2O contained in the hydrates, *i.e.*, the t_i's of the hydrates with more H_2O are relatively lower (*cf.* Fig. 5). These "ups and downs" may be related to the differences in the $4f^n$ electronic configurations, whose influences upon thermodynamic properties of Ln^{3+} were reviewed.[16]

In conclusion, we can say that, although the obtained results look highly complicated, their main features can be reasonably understood in view of the effects of the lanthanoid contraction.

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