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Thermochemical Studies on the Lanthanoid Complexes of *N,N,N',N'*-Tetramethylurea

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The techniques of thermogravimetry (TG) and differential thermal analysis (DTA) were applied to the study of the thermal decomposition of the lanthanoid (Ln) complexes of *N,N,N',N'*-tetramethylurea (TMU), $Ln(TMU)_6X_3$ ($X=ClO_4$, PF_6, or BPh_4). In general, the ease of decomposition increases in the order of $BPh_4 < ClO_4 < PF_6$; in the latter two cases, the release (and, in the case of ClO_4, partial oxidation) of the coordinated TMU molecules takes place together with the decomposition of the anions, leading finally to the formation of $LnCl_3$ or LnF_3, respectively. The data were also discussed on the basis of the effects of the lanthanoid contraction.

N,N,N',N'-Tetramethylurea (TMU) is an interesting new solvent and coordinating agent. Its donor ability is expected to be quite high, but the four *N*-methyl groups protruding around its coordinating atom (*i.e.*, the C=O oxygen) bring about considerable steric hindrance for its complexation. It is expected, therefore, that stable complexes with it can be formed with large and hard cations, which have strong affinity toward oxygen-containing ligands.[1]

In fact, it has been found that the lanthanoid(III) ions, which just fulfill these conditions, can readily form numerous complexes with TMU; when the coexisting anion is a non-coordinating one (ClO_4^-, PF_6^-, or BPh_4^-), the complexes obtained are usually of the type $Ln(TMU)_6X_3$.[2-4]

We recently tried to apply the techniques of thermogravimetry (TG) and differential thermal analysis (DTA) to these complexes, to study the modes of their thermal decomposition. The obtained results will be briefly summarized and discussed.

Experimental

Preparation of Materials. The complexes studied are listed in Tables 1 and 2. They were prepared according to previously reported methods.[2-4] The complexes of La and Ce were not studied because of the strong hygroscopicity of their perchlorates.

TG-DTA Measurements. The TG and DTA measurements were made with a Shinku Riko TGD-3000 differential thermal microbalance under two conditions, *i.e.*, in static N_2 and in a vacuum (*ca.* 10^{-1} Torr≈13.3 Pa), with the heating rate of 3 °C/min. The sample amount taken in each run was *ca.* 10 mg.

Results and Discussion

Perchlorates. The general appearance of the TG-DTA curves obtained in N_2 is shown in Fig. 1, taking the case of the Nd complex as an example. Essentially similar data are obtained with other perchlorates.

The complex begins to lose a part of its TMU molecules when heated to a certain temperature t_i, and a step AB, which is usually rather dull as shown in Fig. 1, appears on the TG curve. At the end of this step, *n* molecules of TMU are lost from the complex.

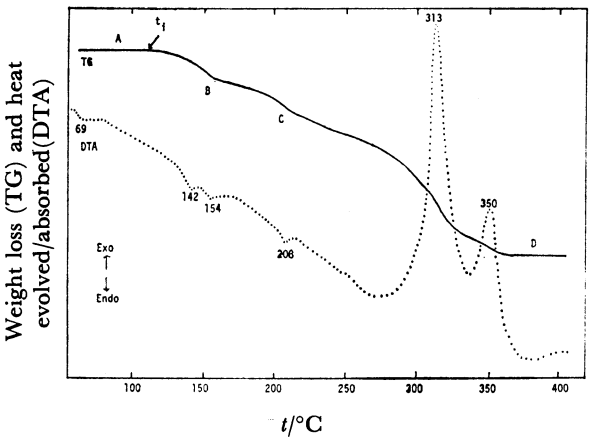

Fig. 1. TG and DTA curves of $Nd(TMU)_6(ClO_4)_3$ in N_2.

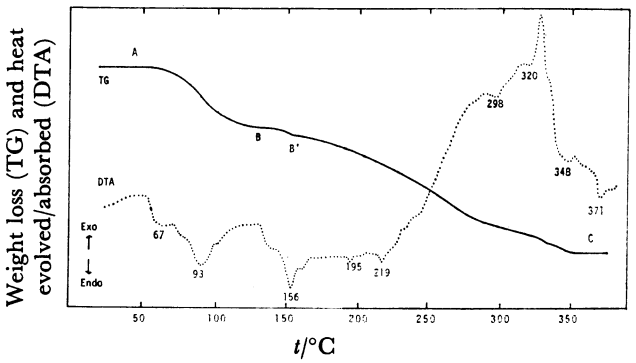

Fig. 2. TG and DTA curves of $Nd(TMU)_6(ClO_4)_3$ in a vacuum.

Then comes another step BC, which is more dull than the step AB and often is observed as a slight inflection of the TG curve, in the course of which some more TMU molecules are lost. Then comes the decomposition of the remaining complex, first gradually but more and more quickly with the rise of temperature, up to a point D, where the weight of the residue becomes nearly constant. The weight loss at D, expressed in percent of the initial weight, will be denoted with Δ.

Table 1 summarizes the values of t_i, *n*, and Δ of all the perchlorates studied, together with the values observed in a vacuum (see later). One can readily

Table 1. Values of t_i, n, and Δ for the complexes $Ln(TMU)_6(ClO_4)_3$

Ln	In N_2			In a vacuum		
	t_i	n[a]	Δ[b]	t_i	n[c]	Δ
Pr	108	1.2	79.1(78 2)	34	2.9	82.5
Nd	110	1.3	77.6(78.0)	48	2.6, 2.9	88.5
Sm	109	1.3	79.2(77.6)	63	2.3, 3.1	88.5
Eu	115	1.2	80.2(77.5)	65	2.8, 3.1	87.2
Gd	124	1.4	76.8(77 2)	57	1.6, 2.3	89.5
Tb	123	1.4	76.6(77.0)	59	1.6	90.2
Dy	124	1.3	75.8(76.8)	67	1.7	90.4
Ho	122	1.3	75.7(76.6)	66	2.1	89.6
Er	134	1.2	77.1(76.5)	73	1.4	89.2
Tm	134	1.3	76.7(76.4)	72	2.7	88.6
Yb	141	1.2	72.3(76.1)	65	2.6, 2.8	91.2
Lu	140	1.3	76.2(76.0)	70	2.7, 2.9	90.9
Y	143	1.2	82.3(82.0)	73	3.1	92.3

a) The values are only approximate owing to the dullness of the step in most cases. b) The values calculated for the complete transformation into $LnCl_3$ are shown in parentheses. c) Two inflection points are often observed at the foot of the step, as the points B and B′ in Fig. 2. The n values corresponding to each of them are given in such cases.

understand that, as to the thermal changes in N_2, there are the following relationships among these values:

1) The value of t_i rises gradually from Pr to Lu, corresponding to the strengthening of the Ln–TMU bonds caused by the effect of the lanthanoid contraction.

2) The values of n lie in the range of 1—1.5, and do not depend remarkably on the position of Ln in the series. Nearly the same amount of TMU seems to be lost in the next step BC. Taking the dullness of these steps and their possible overlap into account, one can estimate that, in general, about 1.5 molecules of TMU are lost in the step AB, and about 3 in the two consecutive steps AB+BC.

3) The values of Δ correspond, reasonably well, to those expected when the complexes are converted completely into $LnCl_3$ at the end of their decomposition.

4) The steps AB and BC are accompanied by a few weakly endothermic peaks on the DTA curve, but the subsequent decomposition CD is accompanied by a very strong exothermic peak, with a much weaker one which appears at the high temperature end of CD.

All these relationships can now be reasonably well understood by the following picture. On heating the complex, a part of the coordinated TMU molecules are liberated endothermically in two steps which, approximately, can be formulated as follows:

$$Ln(TMU)_6(ClO_4)_3 \longrightarrow Ln(TMU)_{4.5}(ClO_4)_3 + 1.5TMU,$$

$$Ln(TMU)_{4.5}(ClO_4)_3 \longrightarrow Ln(TMU)_3(ClO_4)_3 + 1.5TMU.$$

In the course of these changes,** on the other hand, the ClO_4^- ions will come into closer contact with the Ln^{3+} ions which lost some of their bulky ligands. So they will be polarized and eventually begin to decompose by further heating:[6]

$$ClO_4^- \longrightarrow Cl^- + 4O.$$

The O atoms liberated will oxidize the TMU molecules which are still in the complex. Since the number of O atoms liberated is insufficient to oxidize them completely, there will be partial oxidation or incomplete combustion of the ligands by the anions. This will certainly be a strongly exothermic process. When this combustion is over, $LnCl_3$ is left as the final residue.

The data obtained in a vacuum*** are, in general, similar to those in N_2, but some apparent differences can be discerned.

1) The t_i values are much lower than those in N_2, showing that the initial release of TMU is notably facilitated by evacuation. Here again there is a general rise of t_i along the series, but there are some deviations which suggest that they are composed of three parts, Pr–Eu, Gd–Er, and Tm–Lu, corresponding to the variation of n (see below; *cf.* Fig. 3A).

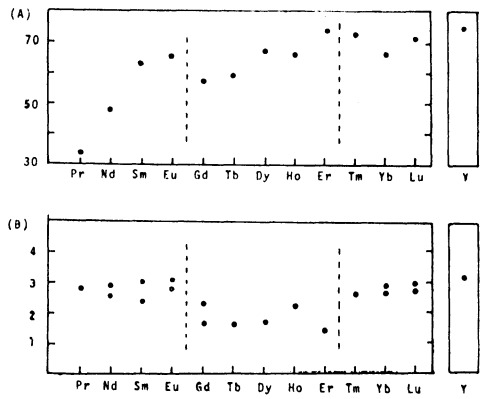

Fig. 3. t_i and n values of $Ln(TMU)_6(ClO_4)_3$ in a vacuum plotted against the atomic number of Ln.

2) The n values are again *ca.* 1.5 for the middle-weight members of the series, Gd–Er, but are definitely larger and *ca.* 3 for the lighter and heavier members and Y. In these latter cases, the two steps AB and BC observed in N_2 are seemingly united into a single more well-defined step; one can also say that, in a vacuum, all the three TMU molecules which are lost in two steps in N_2 are driven off at once, at temperatures which are much lower than in N_2. In the case of the middle-weight members, however, the complex $Ln(TMU)_{4.5}(ClO_4)_3$ retain certain thermal stability even in a vacuum, and the release of further TMU ligands and the final decomposition occur without any clear step (*cf.* Fig. 3B).

These results can now be explained as follows: The complexes of the lighter members, with larger ionic radii of Ln^{3+}, will contain weaker Ln–TMU bonds, and

** It is highly probable that the complexes thus formed, with 4.5 and 3 molecules of TMU, respectively, are dimeric or polymeric in nature; for example, the one with 4.5 TMU can be formulated as $Ln_2(TMU)_9(ClO_4)_6$, *i.e.*, a dimer with each Ln^{3+} surrounded by three terminal and three bridging TMU ligands.[5]

*** Only TG data will be discussed here, because the DTA curves obtained in a vacuum are complicated in their appearance, and their accuracy cannot be as high as those in N_2 in principle.

it is also possible that their coordination spheres are not perfectly packed with six TMU ligands, so that the $Ln^{3+}\cdots ClO_4^-$ interaction will be stronger than in the complexes with smaller Ln^{3+} ions. These situations will favor the driving out of as many TMU molecules as possible by slight heating. In the case of the heavier members, on the other hand, the coordination spheres will be heavily crowded with TMU ligands, and their mutual repulsion will destabilize the structure, so that the driving out of many TMU molecules by heating is again favored. There is probably a "safety zone" between these two extremes, where the complexes $Ln(TMU)_{4.5}X_3$ can enjoy their thermal stability.

3) The Δ values are all much higher than those in N_2, and the differences between the two sets of values increase from Pr to Lu (*cf.* Table 1). In most cases, rather strangely, the weights of the final residues were even lower than those of the lanthanoid elements themselves in the original samples. Taking the experimental conditions (relatively low temperature, slow heating rate, *etc.*) and the nature of the samples into account, the most probable reason for this anomaly seems to be found in the formation of some volatile Ln-containing product in the course of the decomposition. Such a product will escape from the sample as soon as it is formed in a vacuum, causing the decrease of Δ as observed.**** However, we could not identify this volatile complex, mainly owing to its small quantity (at most 1 mg).

Table 2. Values of t_i and Δ for the complexes $Ln(TMU)_6X_3$, where X is PF_6 or BPh_4

Ln	X	In N_2		In a vacuum	
		t_i	Δ	t_i	Δ[a]
Sm	PF_6	73	80.5	40	82.8(83.8)
Gd	PF_6	64	80.8	43	81.1(83.4)
Dy	PF_6	79	81.2	43	81.7(83.1)
Er	PF_6	85	77.8	53	82.6(82.7)
Nd	BPh_4	176	82.0	119	86.6
Eu	BPh_4	136	82.2	131	—
Y	BPh_4	194	86.5	154	93.5

a) The values for the complete transformation into LnF_3 are shown in parentheses.

Hexafluorophosphates. The complexes $Ln(TMU)_6(PF_6)_3$ shown in Table 2 all show a single step in their TG curves, either in N_2 or in a vacuum (see Fig. 4 for an example), and the Δ values observed roughly correspond to those of LnF_3 formed by the reaction:

$$Ln(TMU)_6(PF_6)_3 \longrightarrow LnF_3 + 3PF_5 + 6TMU.$$

It can be seen that the t_i values for this single step are much lower than in the case of the perchlorates, corresponding to the high heats of formation of LnF_3 and PF_5.[7] Since PF_5 is a fairly stable molecule, only a strong endothermic peak is observed on the DTA curves, corresponding to the total disintegration of the complex.

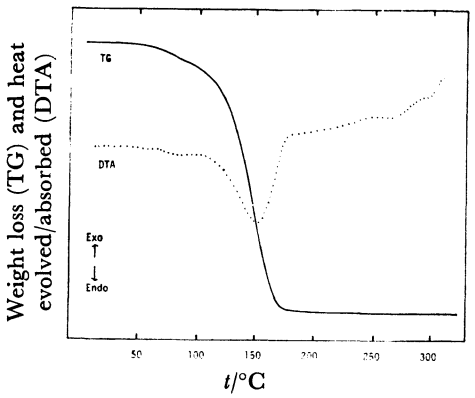

Fig. 4. TG and DTA curves of $Gd(TMU)_6(PF_6)_3$ in a vacuum. Essentially similar curves are obtained, either in N_2 or in a vacuum, with the complexes shown in Table 2. In some case it is seen that a small part of TMU is lost in advance of the main decomposition (*cf.* the small DTA peak (and weak TG shoulder) at *ca.* 85 °C and the large peak at 152 °C in this figure), but its amount is difficult to estimate.

Tetraphenylborates. On the other hand, the complexes $Ln(TMU)_6(BPh_4)_3$, also shown in Table 2, decompose only with much difficulty. Their TG curves are more or less like those of the hexafluorophosphates, composed of a single TG step and DTA peak, but their t_i values are quite high, and their Δ values are incompatible with any simple picture for their decomposition.

Although the nature of the thermal changes involved here is thus not clear as yet, the higher t_i values (or difficulty of decomposition) of these complexes can certainly be related to the inability of BPh_4^- for coordination. We can imagine that the thermal decompositions observed here are, in general, initiated by the S_N2-type attack of the anion (or a part of the anion, such as F^-), by which some TMU ligands are driven out of the coordination sphere. If this idea is essentially true, it is easy to see why the ease of decomposition increases in the following order of anions:

$$BPh_4^- < ClO_4^- < PF_6^-,$$

since BPh_4^- is a practically non-coordinating anion, and PF_6^- is easily split into F^- and PF_5, they will come before and after ClO_4^- in this series, respectively.

Thus we see that TG and DTA techniques can bring about a number of new insights into these complexes, as in the case of the Ln complexes of dimethyl sulfoxide and tetrahydrothiophene 1-oxide studied before.[8] The earlier TG-DTA data of Seminara *et al.*[9-10] on the Ln complexes of various urea derivatives, including $Gd(TMU)_3Cl_3$, may also be of interest in connection with the present study.

**** At first, it was suspected that the complexes $Ln(TMU)_3Cl_3$ may be the volatile complexes, but preliminary studies on them (Ln=Nd and Er) showed that they are not remarkably volatile in a vacuum, and lose their TMU molecules by heating (t_i: 85—90 °C) in a complicated way.

References

1) As to the general properties and solvent behaviors of TMU, *cf.* B. J. Barker and J. A. Caruso, "The Chemistry of

Nonaqueous Solvents," ed by J. J. Lagowski, Academic Press, New York (1976), Vol. 4, p. 110.

2) E. Giesbrecht and M. Kawashita, *J. Inorg. Nucl. Chem.*, **32**, 2461 (1970).

3) M. K. Kuya, S. M. Melo, and O. A. Serra, *An. Acad. Brasil. Cienc.*, **51**, 239 (1979).

4) M. K. Kuya and O. A. Serra, *J. Coord. Chem.*, **10**, 13 (1980).

5) *Cf.* also M. Perrier, R. Najjar, and G. Vicentini, *An. Acad. Brasil. Cienc.*, **42**, 439 (1970), where the data on the complex $LaCl_3 \cdot 3.5$ TMU are given and the possibility of its dimeric nature is suggested.

6) As to the thermal decomposition of perchlorates, *cf.* A. J. Downs and C. J. Adams, "Comprehensive Inorganic Chemistry," ed by J. C. Bailar, Jr., *et al.*, Pergamon Press, Oxford, (1973), Vol. 2, p. 1448.

7) *Cf.* N. V. Sidgwick, "Chemical Elements and Their Compounds," Clarendon Press, Oxford (1950), Vol. 1, p. 757, where a similar decomposition of the diazonium salts of PF_6^- is described.

8) K. Nagase, H. Yokobayashi, A. Iwase, and K. Sone, *Thermochim. Acta*, **17**, 335 (1976).

9) A. Seminara, A. Musumeci, and G. Condorelli, *Ann. Chim. (Rome)*, **59**, 978 (1969).

10) A. Seminara and G. Condorelli, *Ann. Chim. (Rome)*, **59**, 990 (1969).