Thermochimica Acta, 17 (1976) 335–342

THERMAL ANALYTICAL STUDY ON COORDINATION IN TETRAMETHYLENE SULFOXIDE AND DIMETHYL SULFOXIDE COMPLEXES OF TERVALENT LANTHANOID PERCHLORATES

K. NAGASE AND H. YOKOBAYASHI

College of General Education, Tohoku University, Kawauchi, Sendai 980 (Japan)

A. IWASE

Department of Chemistry, Faculty of Science, Yamagata University, Koshirokawa, Yamagata 990 (Japan)

K. SONE

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112 (Japan)

(Received 8 April 1976)

ABSTRACT

TG–DTA analyses of [Ln(tmso)$_8$] (ClO$_4$)$_3$ (Ln = tervalent ions of the lanthanoid series; tmso = tetramethylene sulfoxide) were carried out in a nitrogen atmosphere and under vacuum. The observed values of the characteristic temperatures show systematic changes along the series, owing to the effects of the "lanthanoid contraction". The corresponding dimethyl sulfoxide complexes were also investigated by the same method.

INTRODUCTION

It is well known that the size of a tervalent ion of the lanthanoid series continuously decreases as the 4f sub-shell is filled up with electrons, and this shrinkage (the so-called "lanthanoid contraction") plays an important role in the coordination chemistry of the lanthanoid elements[1]. Since the bondings between such an ion and common ligands are predominantly electrostatic, they will be in general strengthened by this shrinkage. On the other hand, the repulsion between the ligands will also become more pronounced at the same time and when the ion becomes too small, the repulsion may become large enough to make the structure unstable. In such a case, a decrease in the coordination number of the lanthanoid ion may result.

In this paper, the occurrence of these kinds of phenomena will be exemplified in some detail with regard to the IR and TG–DTA for tetramethylene sulfoxide (TMSO) complexes of lanthanoid perchlorates. There seems to be no former reports on these complexes, although the complexes of DMSO and its analogues have been investigated by many workers[2]. Some data on the DMSO complexes of the lanthanoid perchlorates will also be reported.

EXPERIMENTAL

The preparation and compositions of the DMSO complexes used in this study were already reported by Iwase and Tada[3]. The TMSO complexes were prepared in the same way, using TMSO instead of DMSO. The results of the elemental analyses for C and H are given in Table 1.

TABLE 1

ELEMENTAL ANALYSES OF $[\mathrm{Ln(tmso)_8}](\mathrm{ClO_4})_3$

Ln	*Color*	*Carbon*		*Hydrogen*	
		Found (%)	*Calc. (%)*	*Found (%)*	*Calc. (%)*
La	White	30.53	30.52	5.10	5.08
Ce	White	30.50	30.22	5.23	5.07
Pr	Green	31.38	30.22	5.18	5.07
Nd	Violet	30.40	30.12	5.23	5.06
Sm	White	30.17	29.98	5.30	5.03
Eu	White	30.29	29.94	5.14	5.03
Gd	White	30.10	29.82	5.09	5.00
Tb	White	30.04	29.78	5.08	5.00
Dy	White	30.54	29.70	5.19	4.98
Ho	Pink	30.92	29.64	5.19	4.98
Er	Pink	29.81	29.59	5.10	4.97
Tm	White	29.58	29.55	5.13	4.96
Yb	White	29.73	29.46	5.05	4.94
Lu	White	28.82	29.41	4.97	4.94

The infrared absorption spectra of the TMSO complexes in the frequency region of 4000–250 cm^{-1} were taken in KBr pellets with a Hitachi 215 spectrophotometer. Very similar spectra were also obtained with Nujol mulls.

The thermogravimetric and differential thermal analytical (TG–DTA) curves of the DMSO and TMSO complexes were obtained at the heating rate of 5°C min^{-1} in nitrogen and under vacuum (in the latter case, the system was continuously evacuated by a rotary pump) with a Shinku Riko TGD-3000 differential thermal microbalance. About 5 mg of powdered sample in a platinum crucible were used in each measurement.

RESULTS AND DISCUSSION

The elemental analyses in Table 1 show that all the TMSO complexes have the formulas $[\mathrm{Ln(tmso)_8}](\mathrm{ClO_4})_3$, differing from the corresponding DMSO[3] and dimethylacetamide[4] complexes which show a lower coordination number for the heavier metals (see later).

The infrared spectra of all the TMSO complexes were nearly the same, and showed three peaks at ca. 540, 380 and 350 cm^{-1}. The ligands in these complexes are now expected to be coordinated at their oxygens, since infrared spectral studies on transition metal[5] and lanthanoid[6] complexes of DMSO have all shown oxygen coordination (except for Pd and Pt complexes[7] in which sulfur coordination occurs). Later data of Berney and Weber[8] on these complexes and some TMSO complexes, showed further that the $\tilde{\nu}_{MO}$ (metal–oxygen stretching) peak lies generally in the vicinity of 400 cm^{-1}, but sometimes around 500 cm^{-1} (at 499 cm^{-1}, for example, in the case of [Al(tmso)$_6$] (ClO$_4$)$_3$. Since a lanthanoid ion is much larger and heavier than Al^{3+}, the $\tilde{\nu}_{MO}$ peak in the spectra of [Ln(tmso)$_8$] (ClO$_4$)$_3$ is expected to lie at a shorter wave number than that of the Al^{3+} complex, so that the peak at 380 cm^{-1} can most probably be identified with it. This assignment is supported by the fact that there exists a definite relation between the wave number of this peak and $1/r$ (r = ionic radius of a lanthanoid ion[9]) as shown in Fig. 1. On the other hand, the wave numbers of the other two peaks at 540 and 350 cm^{-1} remain nearly unchanged throughout the series.

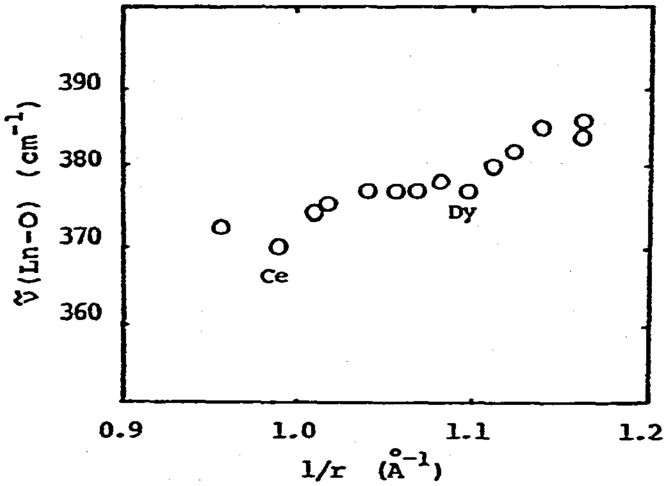

Fig. 1. Relation between v_{MO} and $1/r$.

As can be seen from Fig. 1, the wave number of the $\tilde{\nu}_{MO}$ vibration (and, therefore, the strength of the M–O bond) continuously increases from La^{3+} to Lu^{3+}, roughly in parallel with the increase of $1/r$. Drops of the curve observed at Ce^{3+} and Dy^{3+} are peculiar, but they are relatively small in comparison with possible experimental error ($\pm$1 cm^{-1}).

Examples of the TG–DTA curves of the TMSO complexes measured under vacuum and in nitrogen are shown in Fig. 2. In vacuum (Fig. 2A), the TG curve shows that most of the complexes studied begin to decompose by slight heating, evolving, in total, about two molecules of TMSO, while some of them with heavier lanthanoids (Er, Tm and Yb) tend to evolve about three molecules of TMSO in two or three steps.

As reflected in the plots of Fig. 3A, the initial weight-loss temperature (t_i) of the complexes of La^{3+}–Sm^{3+} remains nearly unchanged, but that of the complexes

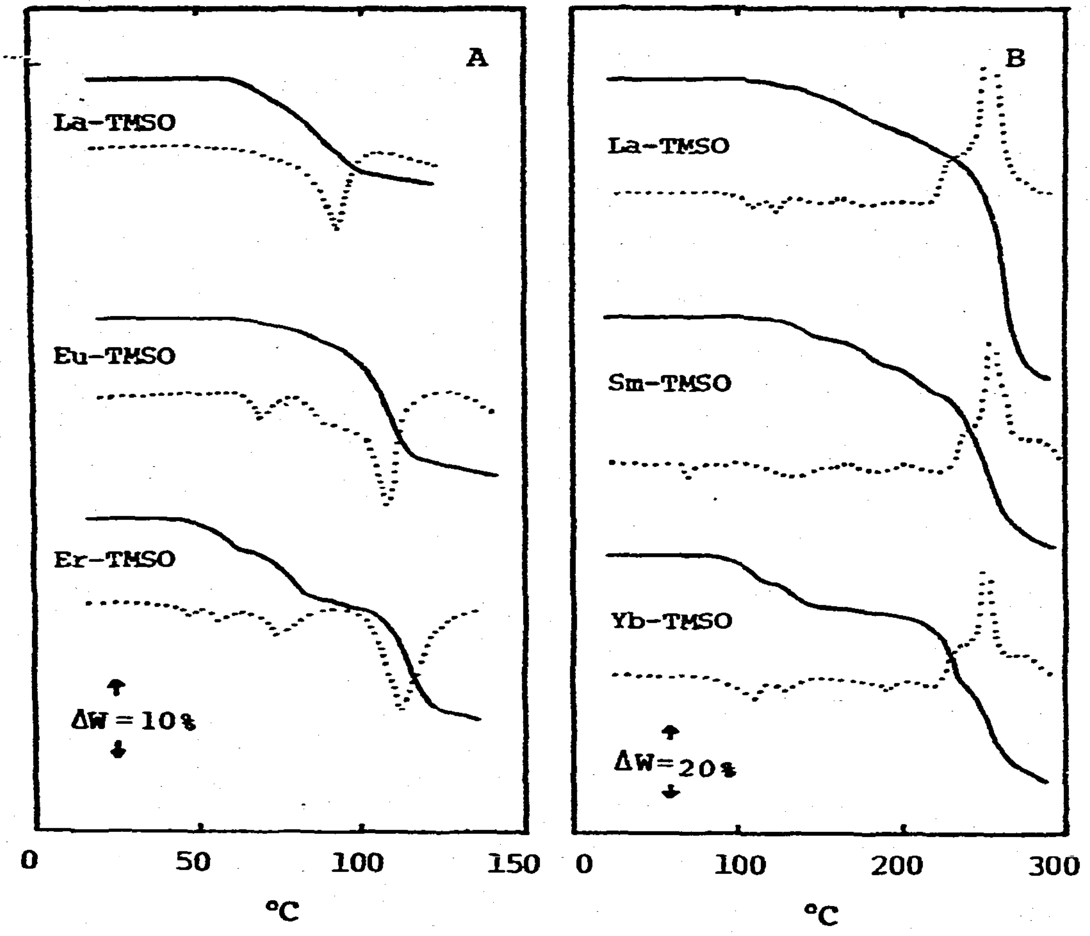

Fig. 2. TG-DTA curves of some TMSO complexes in vacuum (A) and in nitrogen (B).

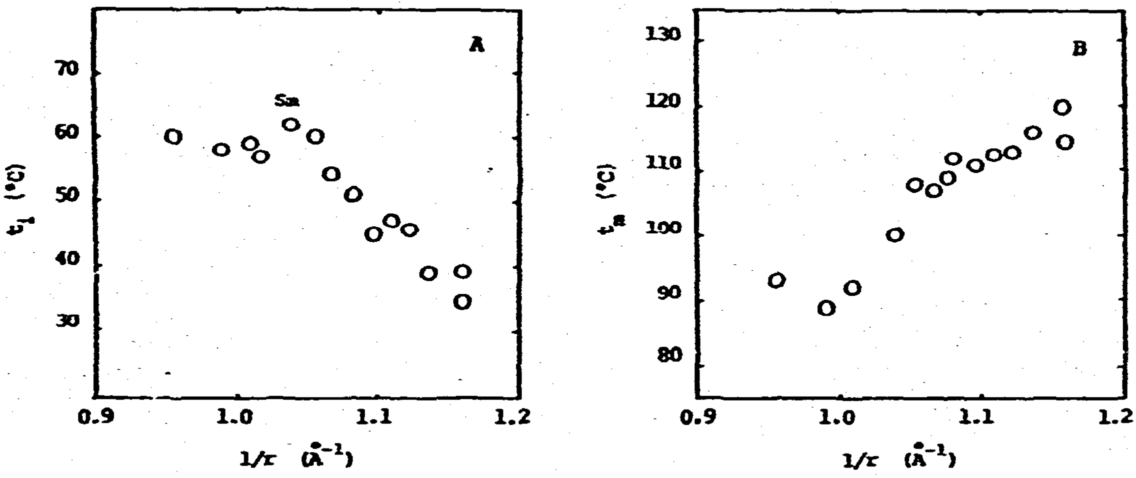

Fig. 3. Relation between t_i or t_m and $1/r$ when the TMSO complexes were heated in vacuum.

of Sm^{3+} –Lu^{3+}decreases steadily with the increase of $1/r$. This can be understood as follows: the ease of losing one ligand molecule from the eight-coordinated coordination sphere in these complexes is governed by two factors, i.e., (1) the metal–ligand bond strength which increases with the increase of $1/r$, and (2) mutual repulsion between ligands which also increases in the same direction. In the first half of the lanthanoid series, these two factors may be almost cancelled, but after Sm^{3+} the second factor begins to predominate, until the case of the smallest Lu^{3+} where the coordination sphere is strongly overcrowded with ligands and quite unstable (despite of the stronger metal–ligand bonds in them), so that one of the ligands is very easily lost on heating.

On the other hand, the main peak temperature (t_m) on the DTA curve, which corresponds to the point at which the main decomposition process, i.e., the dissociation of the second and/or third TMSO molecules occurs, rises with the increase of $1/r$ in a way which is very similar to the curve in Fig. 1 (cf., Fig. 3B). Thus one is led to the view that, while the loss of the first TMSO molecule is governed chiefly by the "overcrowdedness" of the ligands in the complex and occurs most easily in the case of the smallest lanthanoid ions, the ease of the loss of further molecules is governed chiefly by the strength of metal–ligand bonds themselves and, therefore, occurs most easily in the case of the largest lanthanoid ions.

The TG–DTA data in nitrogen (Fig. 2B) are considerably different from those in vacuum. Here, the thermal decomposition occurs much more difficultly, and the points corresponding to t_i are shifted remarkably (ca. 50°C) toward higher temperatures. The steps of the evolution of TMSO observed on the TG curve are much more indistinct here, so that it is difficult to define the number of TMSO molecules evolved

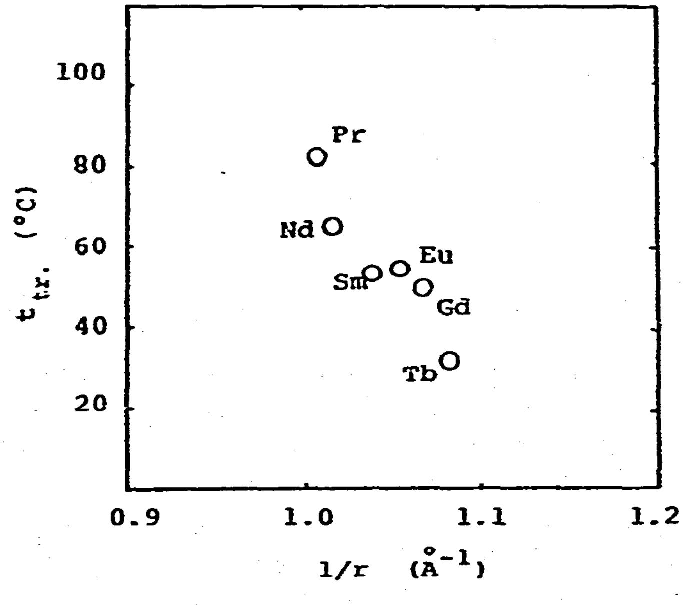

Fig. 4. Relation between t_{tr} and $1/r$ when the TMSO complexes were heated in nitrogen.

with certainty. There is, however, a rough relation that t_i tends to decrease with $1/r$. Above 200°C another kind of drastic decomposition, with a strong exothermic peak on the DTA curve, takes place.

It can be seen that the Sm complex gives a small endothermic peak without any weight-loss at 73°C. The sample heated slightly above 73°C looked somewhat wet and was found to be nearly amorphous to X-rays, but when it was cooled to room temperature, well-defined X-ray diffraction lines appeared again. This change seems, therefore, to correspond to a phase transition. A similar phase transition was observed with the complexes of Pr–Tb. It was also found that the temperature of this phase transition (t_{tr}) drops sharply with increasing $1/r$ as seen in Fig. 4.

All these results seem to indicate that, under these experimental conditions, some kind of reversible deformation of the coordination sphere takes place before the commencement of the evolution of TMSO, the more easily the smaller the lanthanoid ion. One can imagine further that, owing to this deformation, one (or a few) of the TMSO molecules is to some extent squeezed out of the coordination sphere, so that it is evolved easily by further heating. It is also possible that, above the

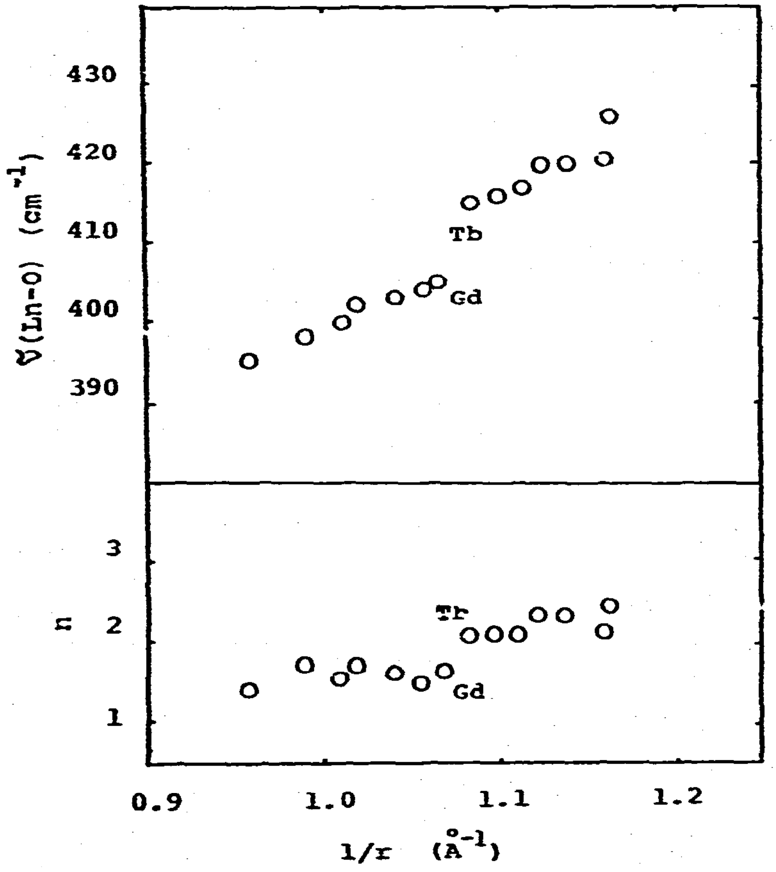

Fig. 5. Relation between v_{LnO} and $1/r^3$, and that between the number of DMSO evolved (n) and $1/r$.

transition point corresponding to this change, the order among the TMSO molecules is considerably disturbed, so that they get in an amorphous state which is even somewhat "liquid" in nature.

It is now of interest to compare these results with those of the DMSO complexes. The compositions of the DMSO complexes of the lanthanoid perchlorates reported by various authors do not perfectly agree. According to Iwase and Tada[3] the lighter lanthanoids (La–Gd) form octa-coordinated complexes $[Ln(dmso)_8](ClO_4)_3$ while the heavier ones (Tb–Lu) form hepta-coordinated complexes $[Ln(dmso)_7](ClO_4)_3$. Figure 5 is the result of these authors on the relation between $\tilde{\nu}_{MO}$ (now found at 400–420 cm^{-1}) and $1/r$, and the numbers of DMSO molecules (about 1.5 for La–Gd and 2–2.5 for Tb–Lu) evolved by heating in vacuum. Figure 6 shows some TG–DTA curves for these complexes in vacuum. As pointed out by Iwase and Tada[3] already, here $\tilde{\nu}_{MO}$ increases almost linearly with $1/r$, but there is a discontinuity between the octa- and hepta-coordinated groups, the values for the latter being distinctly higher. This means that the DMSO molecules in the latter are combined more strongly than those in the former, even when the difference in r is taken into account. A similar discontinuity is found in the relation between n and $1/r$; the smaller lanthanoid ions tend to lose more DMSO molecules by heating; on the other hand, the larger ions which hold one more DMSO molecule in their complexes, tend to keep more

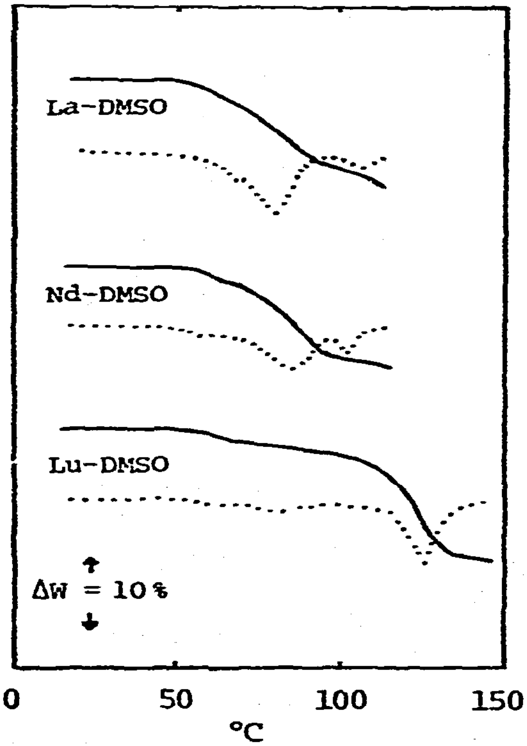

Fig. 6. TG–DTA curves of the DMSO complexes in vacuum.

ligands even when heated. No distinct relation was found between t_i and $1/r$, the former fluctuating between 40 and 50°C, but, as in the case of TMSO complexes, t_m rises approximately linearly against $1/r$ from 78°C of La to 125°C of Lu.

REFERENCES

1 D. G. Karraker, *J. Chem. Educ.*, 47 (1970) 424.
2 For example: D. K. Koppikar and S. Soundararajan, *J. Inorg. Nucl. Chem.*, 38 (1976) 174.
3 A. Iwase and S. Tada, *Nippon Kagaku Kaishi*, (1973) 60.
4 T. Moeller and G. Francis, *J. Inorg. Nucl. Chem.*, 27 (1965) 1477.
5 F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 82 (1960) 2986.
6 V. N. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem.*, 29 (1967) 517.
7 F. A. Cotton, R. Francis and W. D. Horrocks, Jr., *J. Phys. Chem.*, 64 (1960) 1534.
8 C. V. Berney and J. H. Weber, *Inorg. Chem.*, 7 (1968) 283; in J. R. Ferraro (Ed.), *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum, New York, 1971, p. 103.
9 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, B25 (1969) 925; B26 (1970) 1046.