*Thermochimica Acta*, 204 (1992) 251–260
Elsevier Science Publishers B.V., Amsterdam

# Studies on the thermal behaviour and decomposition mechanism of complexes of rare earth(III) nitrates with 18-crown-6

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(Received 27 September 1991)

## Abstract

The thermal dissociation reactions and mechanisms of fifteen complexes of lanthanide(III) nitrates (except Pm) with the ligand 18-crown-6 were investigated by means of TG–DTG, DSC and DTA, with IR and elementary analysis as complementary methods. The thermal analysis tests were carried out in a dynamic atmosphere of dry nitrogen or in static air. The results have shown that the dissociation processes of the complexes consist of several steps, one of which is a fast decomposition reaction. The enthalpies of dehydration, and the enthalpies and the apparent activation energies of the fast decomposition reaction were obtained. The results have also shown that the thermal stability of these complexes (except Ce and Tm) decrease, while the temperatures of dehydration increase, with increasing atomic number of the lanthanides.

## INTRODUCTION

There has been considerable interest in the rare earth(III) complexes of crown ethers during the past several years. However while the thermal behaviour of only one of or a few complexes has been reported in many papers, the decomposition mechanism has not been investigated. In a previous paper, we reported investigations on the solid-state thermal behaviour of fifteen complexes of rare earth(III) nitrates with benzo-15-crown-5 [1]. In this study, we performed detailed investigations on the solid-state thermal behaviour of fifteen complexes of rare earth(III) nitrates (except Pm) with 18-crown-6 (18C6) by TG–DTG, DSC and DTA, and present here their dissociation steps and possible mechanisms, using IR and elementary analyses as complementary methods.

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## EXPERIMENTAL

### *Preparation of the complexes*

The rare earth nitrate complexes with ligand 18C6 were prepared as previously reported [2]. The stoichiometries of the complexes are RE$(NO_3)_3 \cdot$18C6 (RE = La–Nd), 4RE$(NO_3)_3 \cdot$3(18C6) (Re = Sm, Eu), Gd$(NO_3)_3 \cdot$18C6$\cdot 2H_2O$ and RE$(NO_3)_3 \cdot$18C6$\cdot 3H_2O$ (RE = Tb–Lu and Y).

### *Apparatus and conditions of experiments*

TG and DTG data were obtained simultaneously using a Perkin–Elmer model TGS-2, and DSC data were obtained using a DSC-2C. DTA data were obtained using a model LCT-1 differential thermal balance instrument made in the Beijing Optical Instrument Plant. All TG–DTG and DSC tests were carried out in a dynamic atmosphere of dry nitrogen (40 ml min$^{-1}$) at a heating rate of 10°C min$^{-1}$. Sample masses were about 1 mg and an aluminium crucible was used for DSC and TG–DTG tests. DTA tests were carried out in static air with about 4 mg of sample in an alumina crucible.

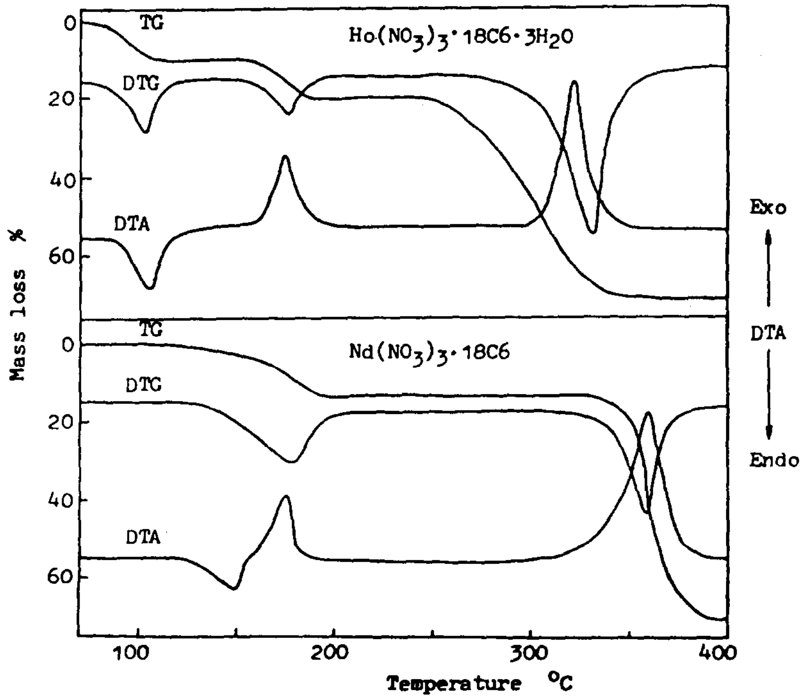


Fig. 1. TG–DTG and DTA curves of the Ho and Nd complexes.

The IR spectra and elementary analyses of the complexes and intermediates formed as the complexes were heated, were obtained using a Perkin–Elmer model 580B infrared spectrophotometer and a Carlo Erba Strumentazione model 1106 elemental analyser, respectively.

## RESULTS AND DISCUSSION

### *Thermal decomposition mechanism of the complexes*

Four examples of thermoanalytical curves obtained for rare earth(III) complexes of 18-crown-6 are given in Figs. 1 and 2, in which the Nd complex is regarded as an example of the type $RE(NO_3)_3 \cdot 18C6$ (RE = La–Nd) and Ho, Yb and Y as of the type $RE(NO_3)_3 \cdot 18C6 \cdot 3H_2O$ (RE = Tb–Lu and Y).

The TGA data of the rare earth nitrate complexes with 18C6 are reported in Table 1.

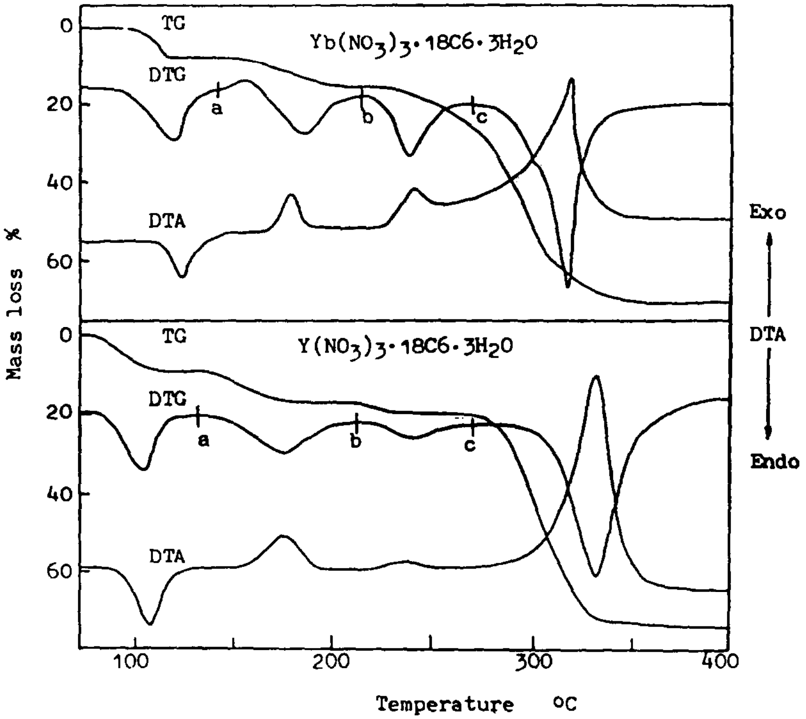


Fig. 2. TG–DTG and DTA curves of Yb and Y complexes. The a, b and c positions are the points at which the sample was cooled and IR and elemental analyses were carried out.

TABLE 1

TG data of the rare earth nitrate complexes with 18C6

| RE | Decomposition steps | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | | II | | III | | IV | |
| | Weight loss (%) | | Weight loss (%) | | Weight loss (%) | | Weight loss (%) | |
| | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| La | – | – | 11.2 | 11.4 | – | – | 72.4 | 69.0 |
| Ce | – | – | 11.2 | 10.0 | – | – | 72.2 | 70.0 |
| Pr | – | – | 11.2 | 11.8 | – | – | 72.1 | 69.5 |
| Nd | – | – | 11.1 | 13.3 | – | – | 71.7 | 70.5 |
| Sm [a] | – | – | – | – | – | – | 67.4 | 69.0 |
| Eu [a] | – | – | – | – | – | – | 67.2 | 70.4 |
| Gd [b] | 5.6 | 6.1 | 15.9 | 14.8 | – | – | 71.8 | 70.6 |
| Tb | 8.1 | 7.5 | 18.1 | 18.8 | – | – | 72.4 | 72.5 |
| Dy | 8.1 | 8.0 | 18.0 | 17.6 | – | – | 72.0 | 71.5 |
| Ho | 8.1 | 8.7 | 17.9 | 17.0 | – | – | 71.2 | 70.7 |
| Er | 8.0 | 8.3 | 17.9 | 20.4 | 23.8 | 23.8 | 71.5 | 71.8 |
| Tm | 8.0 | 7.3 | – | – | 23.7 | 22.0 | 71.3 | 70.0 |
| Yb | 8.0 | 7.8 | 17.7 | 18.6 | 23.5 | 25.1 | 70.9 | 69.3 |
| Lu | 8.0 | 9.1 | 17.7 | 18.0 | 23.5 | 23.9 | 70.9 | 70.0 |
| Y | 9.1 | 9.3 | 18.0 | 17.5 | 20.2 | 20.1 | 81.0 | 80.2 |

[a] The stoichiometry of Sm and Eu complexes is $4RE(NO_3)_3 \cdot 3(18C6)$.
[b] The stoichiometry of Gd complex is $Gd(NO_3)_3 \cdot 18C6 \cdot 2H_2O$.

The thermal decomposition mechanisms of these complexes determined on the basis of the TG results are as follows:

$$RE(NO_3)_3 \cdot 18C6 \xrightarrow{II} 4RE(NO_3)_3 \cdot 18C6 \xrightarrow[*]{IV} RE_2O_3 \qquad (RE = La\text{–}Nd)$$

$$4RE(NO_3)_3 \cdot 3(18C6) \xrightarrow[*]{IV} RE_2O_3 \qquad (RE = Sm \text{ and } Eu)$$

$$RE(NO_3)_3 \cdot 18C6 \cdot nH_2O \xrightarrow{I} RE(NO_3)_3 \cdot 18C6 \xrightarrow{II}$$
$$4RE(NO_3)_3 \cdot 3(18C6) \xrightarrow[*]{IV} RE_2O_3$$
$$(RE = Gd,\ n = 2;\ RE = Tb\text{–}Ho,\ n = 3)$$

$$RE(NO_3)_3 \cdot 18C6 \cdot 3H_2O \xrightarrow{I} RE(NO_3)_3 \cdot 18C6 \xrightarrow{II}$$
$$4RE(NO_3)_3 \cdot 3(18C6) \xrightarrow{III} 5RE(NO_3)_3 \cdot 3(18C6) \xrightarrow[*]{IV} RE_2O_3$$
$$(RE = Er\text{–}Lu \text{ and } Y, \text{ no step II for Tm})$$

As can be seen, the first step of the dissociation process corresponding to the endothermic peak in DTA is dehydration for the hydrated complexes. The decomposition processes of dehydrated or non-hydrated complexes can be divided into two kinds: La–Nd, Gd–Ho and Tm complexes decompose by a two-step process; Er, Yb, Lu and Y complexes decompose

TABLE 2

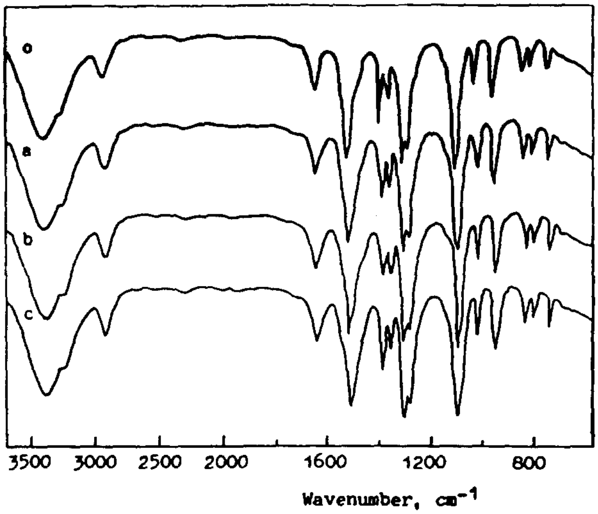
Elementary analysis data (%) of the intermediates formed during dissociation of Yb and Y complexes

| RE | Element | Intermediates of several steps | | | | | |
|---|---|---|---|---|---|---|---|
| | | I | | II | | III | |
| | | Calc. | Found | Calc. | Found | Calc. | Found |
| Yb | C | 23.10 | 23.05 | 19.37 | 18.63 | 16.69 | 16.83 |
| | H | 3.85 | 3.89 | 3.23 | 3.08 | 2.78 | 2.77 |
| | N | 6.74 | 6.65 | 7.54 | 6.90 | 8.11 | 6.76 |
| Y | C | 26.70 | 25.38 | 23.59 | 22.88 | 22.82 | 21.80 |
| | H | 4.45 | 4.30 | 3.94 | 4.00 | 3.80 | 3.74 |
| | N | 7.39 | 7.49 | 8.61 | 8.47 | 8.88 | 7.96 |

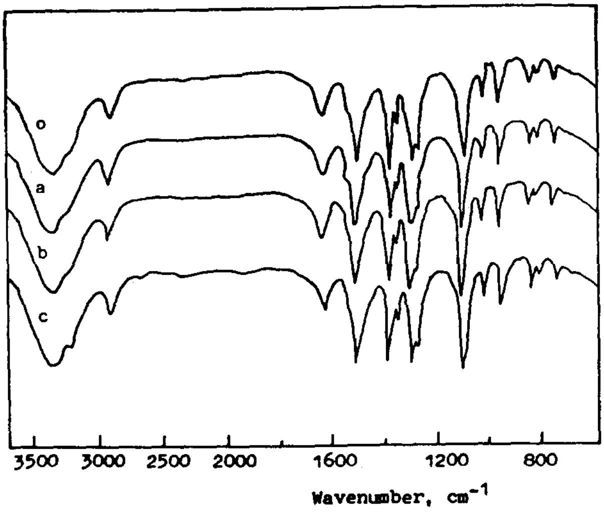
by a three-step process. The steps marked * are fast decomposition reactions. Because $4RE(NO_3)_3 \cdot 3(18C6)$ complexes were synthesised only, steps II and III are absent for Sm and Eu. Step II is also absent for Tm.

In order to examine the decomposition mechanism mentioned above, we have identified the intermediates (corresponding to compounds formed at points a, b and c of the DTG curves in Fig. 2) formed during the thermal decomposition of Yb and Y complexes, using IR spectra and elementary analyses. The results in Table 2 show that the percentages found for C, H and N in the intermediates of each of several dissociation steps are in agreement with those calculated. The IR spectra (Fig. 3) show no change in the absorption bands at 955 and 1100 $cm^{-1}$ attributed to the ligand 18C6, which indicates that the changes in mole ratio of $Yb(NO_3)_3$ or $Y(NO_3)_3$ with ligand 18C6 occur before the fast decomposition of their complexes.

Moreover, as can be seen in the DTA or DSC curves (Fig. 4) the endothermic and exothermic peaks appear successively in the first step (corresponding to step II in the decomposition mechanism mentioned above) of the decomposition process of the lighter lanthanide (La–Nd) complexes, although the exothermic peak of the La complex appears only in the sealed sample cell. This phenomenon can be explained by the following facts. The endothermic process is attributed to the liberation of a part of undecomposed ligand during the decomposition of the complex. A white sublimate which was collected during the decomposition, was identified from its melting point and IR spectrum as 18C6. The decomposition temperature range of the ligand 18C6 is 170–240 ° C. It is shown in Table 3 that the endothermic peaks (DSC) of Ce, Pr and Nd complexes, i.e. the liberation of a part of the ligand, occur in the temperature range 152.9–177.1°C, followed by the thermal decomposition (the exothermic peak) of the ligand, while the endothermic temperature of the La complex is higher (222.7°C). In this case the exothermic decomposition peak of the ligand



Yb complex



Y complex

Fig. 3. IR spectra of Yb and Y complexes and their residues after the thermal decomposition process: o, untreated sample; a, b, and c, samples from the corresponding positions in Fig. 2.

would not appear because its sublimation obviously increases with temperature; only in a sealed sample cell does the exothermic decomposition peak appear.

However, no endothermic processes except dehydration appear in the DTA or DSC curves of the other lanthanide (and Y) complexes.

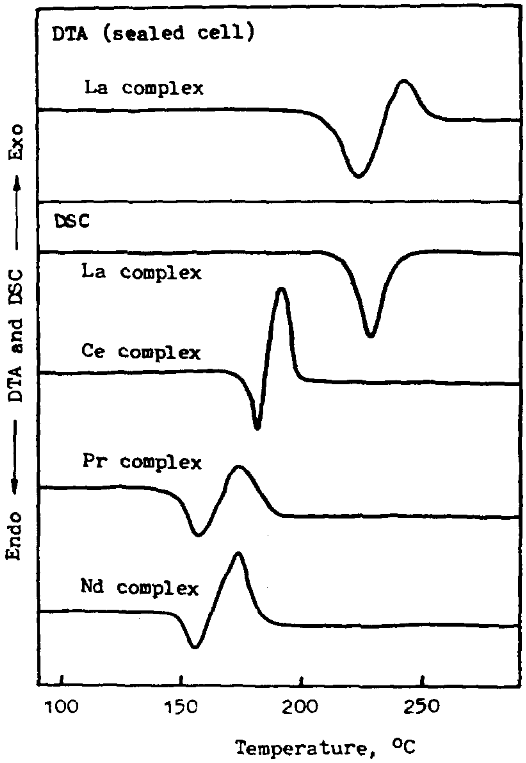


Fig. 4. DSC or DTA curves of the lighter lanthanide (La–Nd) complexes at the first decomposition step.

### *Enthalpies and activation energies of the dehydration and decomposition reaction*

It can be seen in Table 4 that the fast decomposition peak temperatures $T_d$ of all the complexes (except Ce) are above 297°C and their values, except for Ce and Tm, decrease regularly with increasing atomic number, as with the complexes with ligand B15C5 (see ref. 1). As can be seen in Fig. 5, the $T_d$ values of La–Gd complexes decrease more slowly with increasing atomic number of the lanthanide, while those of Gd–Lu complexes decrease rapidly, contrary to the complexes with ligand B15C5. Two straight lines of different slopes are obtained for light and heavy rare earth ions,

TABLE 3

The endothermic peak temperatures obtained from DSC at the first decomposition step of La–Nd complexes

| RE | La | Ce | Pr | Nd |
|---|---|---|---|---|
| Peak temp. (°C) | 222.7 | 177.1 | 153.7 | 152.9 |

TABLE 4

Data obtained from DSC for the complexes

| | Dehydration | | | Fast decomposition | | |
|---|---|---|---|---|---|---|
| | $T_h$ (°C) | $\Delta H_h$ (kJ $mol^{-1}$) | $E_h$ (kJ $mol^{-1}$) | $T_d$ (°C) | $\Delta H_d$ (kJ $mol^{-1}$) | $E_d$ (kJ $mol^{-1}$) |
| La | – | – | – | 363.4 | 332.8 | 185.6 |
| Ce | – | – | – | 297.4 | 343.1 | 166.4 |
| Pr | – | – | – | 357.3 | 365.1 | 157.6 |
| Nd | – | – | – | 355.7 | 383.0 | 143.0 |
| Sm | – | – | – | 350.4 | 426.8 | 163.9 |
| Eu | – | – | – | 352.8 | 345.2 | 229.5 |
| Gd | 97.0 | 175.1 | 72.7 | 350.5 | 387.2 | 253.7 |
| Tb | 104.5 | 123.7 | 57.3 | 343.3 | 388.5 | 213.6 |
| Dy | 107.4 | 180.7 | 73.6 | 335.6 | 407.0 | 334.7 |
| Ho | 107.4 | 191.1 | 86.9 | 333.6 | 354.5 | 239.5 |
| Er | 126.6 | 150.5 | 64.8 | 323.4 | 427.9 | 278.0 |
| Tm | 121.0 | 122.1 | 140.1 | 353.8 | 381.1 | 216.7 |
| Yb | 121.3 | 185.8 | 68.1 | 314.3 | 386.8 | 431.8 |
| Lu | 145.1 | 172.1 | 82.3 | 303.4 | 230.3 | 372.8 |
| Y | 104.9 | 163.9 | 73.2 | 334.1 | 388.7 | 423.9 |

respectively, and they intersect at Gd. The two linear functions can be described using the two expressions

$$T_d = 462.2 - 1.76n$$

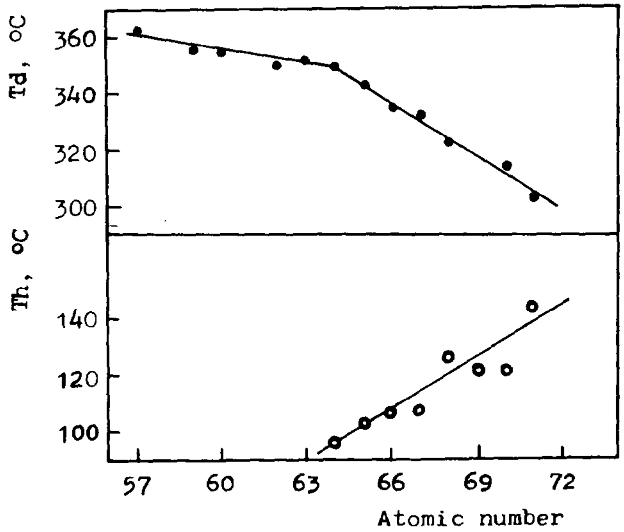


Fig. 5. $T_d$ of the fast decomposition and $T_h$ of the dehydration as a function of atomic numbers for lanthanide.

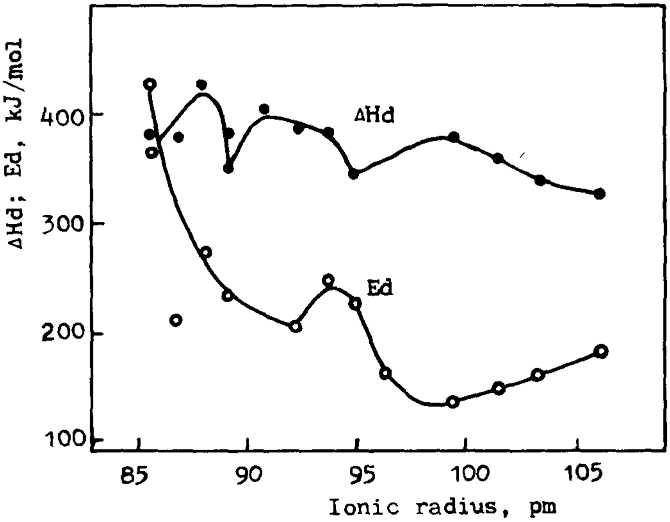


Fig. 6. Plot of $\Delta H_d$ and $E_d$ values vs. ionic radius of rare earth cations (RE = La–Lu and Y).

where $n = 57$–$64$ (except 58 and 61), the correlation coefficient being 0.9394, and

$$T_d = 759.4 - 6.39n$$

where $n = 64$–$71$ (except 69), the correlation coefficient being 0.9932.

The dehydration peak temperatures $T_h$ of all the complexes (Gd–Lu) show an increase with the atomic number of lanthanide, approaching a straight line.

In order to obtain the enthalpies of dehydration $\Delta H_h$ and of the fast decomposition reaction $\Delta H_d$, DSC tests were carefully carried out using a sample size of 1 mg and a heating rate of 10°C $min^{-1}$. From the DSC peak temperatures at various heating rates (2.5, 5, 10, 20 and 40°C $min^{-1}$), the apparent activation energies of dehydration $E_h$ and of the fast decomposition reaction $E_d$ were obtained by means of Kissinger's method [3]. The results are shown in Table 4. It is shown in Table 4 that the enthalpies and the apparent activation energies of dehydration fall in the ranges 122.1–191.1 kJ $mol^{-1}$ and 57.3–140.1 kJ $mol^{-1}$, respectively; these values do not display any obvious regularity.

If the fast decomposition $\Delta H_d$ and $E_d$ are plotted against the ionic radius of the rare earth cations, the curves show the so called "tetrad effect" (see Fig. 6), similar to that observed for the complexes with B15C5 [1].

## ACKNOWLEDGEMENTS

The authors express their gratitude to Gan-Che Wang, Xi-Mei Guo and Xi-Ning Xu for their assistance.

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