

# Synthesis and Thermal Decomposition of Rare Earth Complexes with Methanesulfonate and 3-Picoline-*N*-oxide Ligands

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de Matos, J. E. X., Niinistö, L., Matos, J. R., Vicentini, G. and Zinner, L. B., 1988. Synthesis and Thermal Decomposition of Rare Earth Complexes with Methanesulfonate and 3-Picoline-*N*-oxide Ligands. – Acta Chem. Scand., Ser. A 42: 111–116.

Hydrated rare earth methanesulfonates react with 3-picoline-*N*-oxide (3-picNO) to form isomorphous compounds of composition  $\text{Ln}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$ , where Ln is La–Lu, Y (excl. Pm). IR spectra indicate that the methanesulfonate anions and the 3-picNO ligands are involved in coordination to the rare earth ion. Thermal decomposition studies in air and nitrogen under different experimental conditions show that anhydrous rare earth methanesulfonates are formed when the 3-picNO ligands are expelled. Further heating in air in the temperature range 400–900 °C produces the dioxosulfate,  $\text{Ln}_2\text{O}_2\text{SO}_4$ , but in nitrogen the decomposition leads to the formation of dioxodisulfide,  $\text{Ln}_2\text{O}_2\text{S}_2$ , which then decomposes to dioxosulfide,  $\text{Ln}_2\text{O}_2\text{S}$ . The cerium complex decomposes in air directly to  $\text{CeO}_2$  without formation of the oxosulfate intermediate.

Charbonnier and coworkers have recently investigated the interesting thermal behaviour of several methanesulfonate compounds formed by main group and transition metals.<sup>1–7</sup> Similar detailed data are not available for the rare earth methanesulfonates, which can have, besides the  $\text{Ln}(\text{CH}_3\text{SO}_3)_3$ -type,<sup>8,9</sup> a more complex composition if additional ligands are available for coordination. Some complexes in the series  $\text{Ln}(\text{CH}_3\text{SO}_3)_3 \cdot 3\text{TMSO}$  (TMSO = tetramethylene sulfoxide) have been characterized by thermogravimetric measurements.<sup>10</sup>

In this paper we report the results of a mainly thermoanalytical study of a new series of methanesulfonate complexes with 3-picoline-*N*-oxide (3-picNO). A thermogravimetric study on rare earth methanesulfonate hydrates is also in progress.<sup>11</sup>

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## Experimental

**Materials.** The compounds were prepared by mixing 3-picNO with the hydrated rare earth methanesulfonate in a molar ratio of 3:1.<sup>8,12</sup> After gently heating the mixture for a few minutes, an oily mass was obtained which was treated with an equal volume of acetone under agitation with a glass rod. In some cases crystallization took place immediately, while in other cases a few days elapsed. The mixture was left to stand for approximately one week to complete the crystal formation. The crystals were then collected, washed with acetone and dried *in vacuo* over anhydrous calcium chloride. Similar results were obtained when triethylorthoformate or 2,2-dimethoxypropane were used instead of acetone.

The rare earth content of the complexes was determined by complexometric titration with EDTA, and the C, H and N analyses were performed by standard microanalytical techniques. Melting ranges were also determined and they varied from 244–248 °C (La) to 115–119 °C (Yb).

Table 1. IR data (1300–600  $\text{cm}^{-1}$ ) on selected  $\text{Ln}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$  complexes and the 3-picNO ligand. Assignments of 3-picNO vibrations are based on Refs. 15 and 16.

Ln	CH in-plane bending	Ring breathing	CH out-of-plane bending			NO bending		Ring bending
3-picNO	1165vs	1024s	950s	856w	751s		796s	680s
La	1149vs	1040s	948m	881w	754s		811s	678s
Gd	1158vs	1050vs	950m	888w	759s	815s	820sh	685s
Yb	1151vs	1048s	947m	884w	753m	810s	815m	682m

Ln	NO stretching + SO asymmetric stretching						SO symmetric stretching	CS stretching					
3-picNO	1286vs	1276vs					—	—					
La	1274s	1263sh	1249vs	1238vs	1195vs	1178sh	1171sh	1165vs	1065sh	1060vs	788sh	782s	772s
Gd	1279s	1267s	1250vs	1235vs	1212vs	1181sh	1179vs	1169vs	1075sh	1070vs	791sh	788s	779s
Yb	1279s	1265sh	1250vs	1239vs	1212vs	1197sh	1175vs	1165vs	1070s	1063sh	786sh	781m	775m

**Methods.** X-ray powder diffraction patterns were obtained using a Norelco instrument with  $\text{CuK}\alpha$  radiation. IR spectra of the compounds were recorded on a Perkin-Elmer 283 spectrophotometer using nujol mulls between KBr plates.

Thermogravimetric studies were performed with Perkin-Elmer TGS-2 or TGA-7 instruments equipped with a controller unit and coupled to a computer for the evaluation of the data. Three

series of TG runs were performed for all samples (La–Lu, Y) in a dynamic atmosphere as follows: (i)  $1^\circ\text{C min}^{-1}$  in air, (ii)  $1^\circ\text{C min}^{-1}$  in  $\text{N}_2$ , and (iii)  $10^\circ\text{C min}^{-1}$  in  $\text{N}_2$ . Standard platinum crucibles were used and the sample weight was approximately 5 mg. In addition, several other experimental conditions, including isothermal heating in air and in nitrogen, were tried in individual cases.

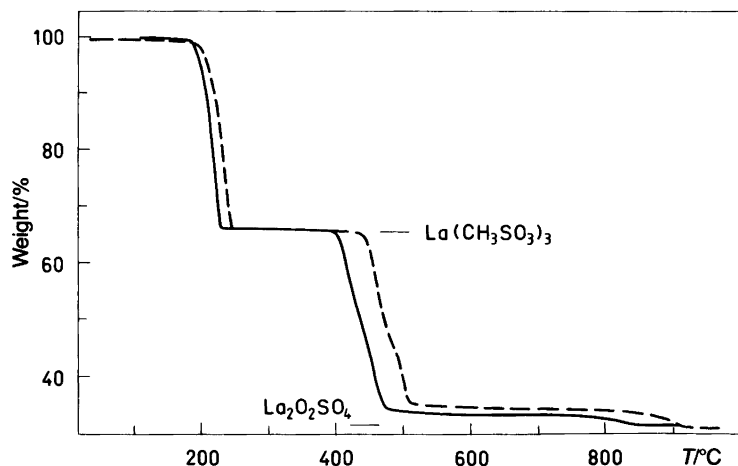


Fig. 1. Thermogravimetric curve for  $\text{La}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$  in dynamic air atmosphere. Heating rates: (—)  $1^\circ\text{C min}^{-1}$ , (---)  $10^\circ\text{C min}^{-1}$ . The levels correspond to calculated (theoretical) compositions.

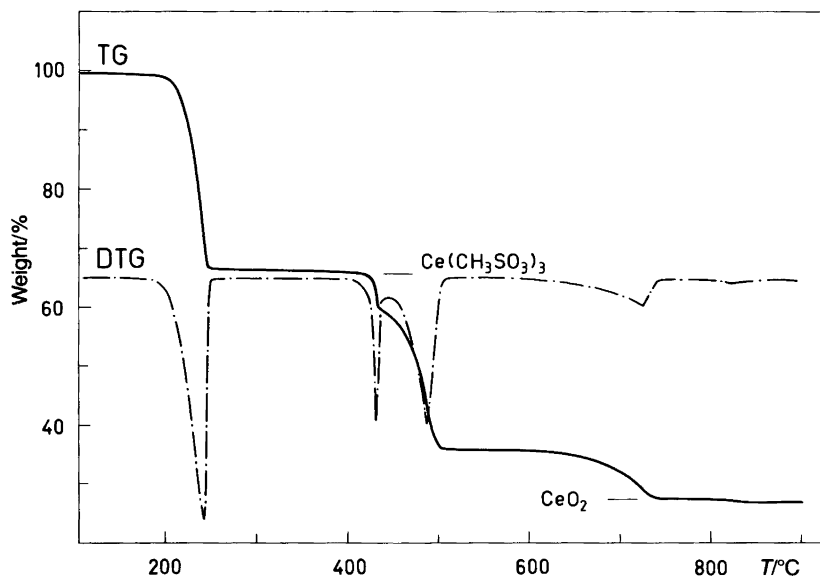


Fig. 2. Thermogravimetric (TG) curve and its derivative (DTG) for  $\text{Ce}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$  in dynamic air atmosphere. Heating rate:  $10^\circ\text{C min}^{-1}$ .

## Results and discussion

**Characterization.** Analytical data are consistent with the general formula  $\text{Ln}(\text{CH}_3\text{SO}_3)_3 \cdot$

$2(3\text{-picNO})$  for all compounds ( $\text{Ln} = \text{La-Lu, Y}$ ). X-ray powder diffraction data indicate that they are isomorphous.

Judging from the non-electrolytic behaviour in

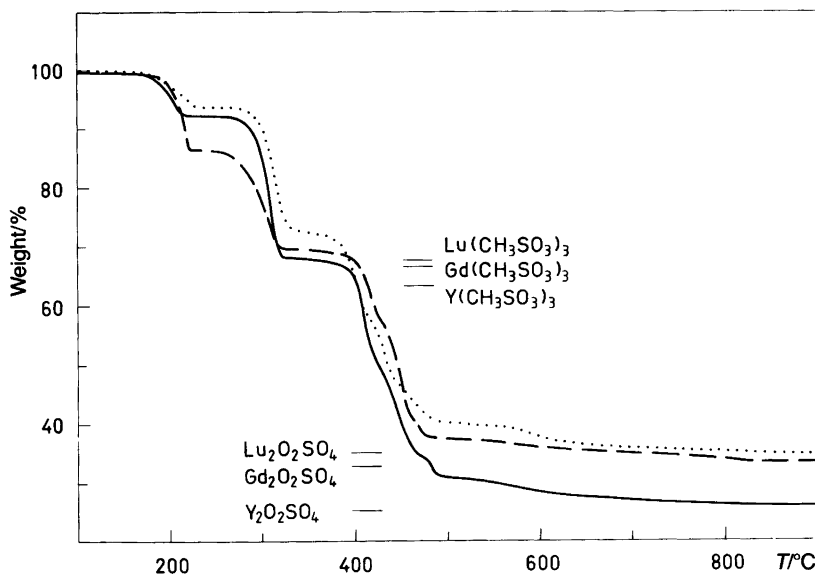


Fig. 3. TG curves for  $\text{Ln}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$ , where  $\text{Ln} = \text{Y}$  (—),  $\text{Gd}$  (---) and  $\text{Lu}$  (.....). A heating rate of  $10^\circ\text{C min}^{-1}$  and a dynamic air atmosphere were employed.

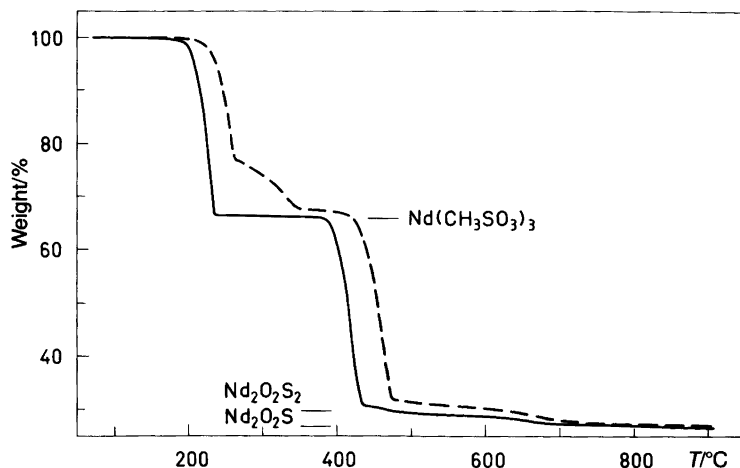


Fig. 4. Thermal decomposition of  $\text{Nd}(\text{CH}_3\text{SO}_3)_3 \cdot 2(3\text{-picNO})$  in dynamic nitrogen atmosphere. Heating rates: (—)  $1^\circ\text{C min}^{-1}$ , (---)  $10^\circ\text{C min}^{-1}$ .

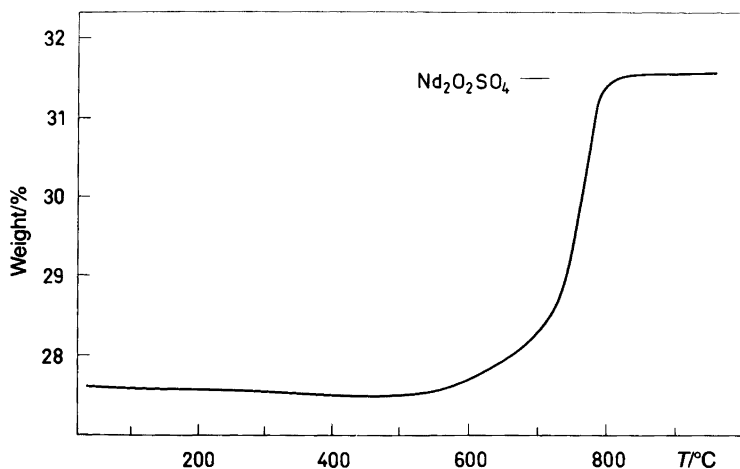


Fig. 5. TG curve obtained for the end product of Fig. 4 by cooling in nitrogen and then changing the atmosphere to oxygen and heating at  $20^\circ\text{C min}^{-1}$ .

methanol, and from the IR spectra, it is clear that both the methanesulfonate and the 3-picNO ligands are involved in coordination to the lanthanoid ion. This is in contrast with the behaviour of lanthanoid 4-picNO complexes with trifluoromethanesulfonate, where the weakly coordinating trifluoromethanesulfonate ligand remains outside the inner coordination sphere.<sup>13,14</sup> The N–O stretching vibration could not be unequivocally distinguished from the asymmetric S–O stretching band since they both occur in the same

region (Table 1). It is certain, however, that the N–O band is shifted towards lower frequencies. The splitting of the asymmetric S–O stretching band indicates lowering of the symmetry through coordination of the  $\text{CH}_3\text{SO}_3^-$  anion, probably in a bidentate or bridging mode. The emission spectrum of the europium compound indicates that the most probable point group symmetry is  $C_3$ .<sup>12</sup>

**Thermal decomposition.** The first step in the thermal degradation process, both in air and nitro-

gen, is the loss of the 3-picNO ligands. This starts at 150–200 °C and is complete some 100–150 °C higher, the exact temperatures depending on experimental conditions and on the nature of the rare earth ions (Figs. 1–3). When a low heating rate (1 °C min<sup>-1</sup>) is employed, the loss of the 3-picNO ligands takes place in a single step for the lighter rare earths (La–Gd), while for the heavier lanthanoids and yttrium it is a two-step process. With a 10 °C min<sup>-1</sup> heating rate, all rare earths except lanthanum and cerium decompose in a multi-step fashion. The intermediate phase does not, however, correspond to the loss of 1 mol of 3-picNO, the observed values under these experimental conditions ranging from 0.4 to 0.8 mol depending on the nature of the rare earth ion (Fig. 3).

The anhydrous lanthanoid methanesulfonates are stable in air up to 350–400 °C where rapid decomposition begins followed, above 500 °C, by a much slower process. In the case of lanthanum and cerium, the decomposition rate above 500 °C is first minimal but increases again above 700–800 °C (Figs. 1 and 2). The end product below 1000 °C for all rare earths except cerium is the dioxosulfate, Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> (Figs. 1, 3), as is the case with the rare earth sulfates.<sup>17</sup> The oxosulfate is stable over a wide temperature range, especially for the lighter lanthanoids, and its decomposition produces the sesquioxide, usually at temperatures well above 1000 °C.<sup>18</sup> In the case of cerium, the oxosulfate intermediate is not present, and formation of CeO<sub>2</sub> is complete at 750 °C (Fig. 2).

The interpretation of the TG curves for N<sub>2</sub> atmosphere is not straightforward. The fast reaction step around 400 °C converts the anhydrous methanesulfonate to an intermediate phase which then slowly decomposes to the final product, which is not Ln<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> but Ln<sub>2</sub>O<sub>2</sub>S. Fig. 4 depicts the thermal degradation of the Nd complex as a typical example. The formation of lanthanoid dioxosulfide instead of dioxosulfate was ascertained by an X-ray diffraction analysis and by measuring the weight change occurring when the residue was heated in air and converted to dioxosulfate.<sup>19</sup> The calculated and observed weight changes for decomposition of Nd(CH<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> · 2(3-picNO) to Nd<sub>2</sub>O<sub>2</sub>SO<sub>4</sub> are 68.5 and 68.4 %, respectively (Fig. 5).

The observed weight loss at the intermediate level in nitrogen corresponds not only to formation of Ln<sub>2</sub>S<sub>3</sub>,<sup>10</sup> but also to the formation of Ln<sub>2</sub>O<sub>2</sub>S<sub>2</sub>. The molecular weights and thereby the theoretical weight losses are initially identical; for instance, in the case of La<sub>2</sub>S<sub>3</sub> and La<sub>2</sub>O<sub>2</sub>S<sub>2</sub> the molecular weights are 373.99 and 373.93, respectively. The La<sub>2</sub>O<sub>2</sub>S<sub>2</sub> alternative was considered more plausible for the following reasons: (i) the formation of Ln<sub>2</sub>O<sub>2</sub>S from Ln<sub>2</sub>O<sub>2</sub>S<sub>2</sub> is facile and does not require the presence of oxygen, (ii) the observed stability range of Ln<sub>2</sub>O<sub>2</sub>S<sub>2</sub> corresponds well with the temperatures used for its synthesis,<sup>20</sup> and (iii) the formation of Ln<sub>2</sub>O<sub>2</sub>S<sub>2</sub> from Ln(CH<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> does not require complete breakdown of the Ln–O bond system which is known from X-ray crystal structure determinations to be

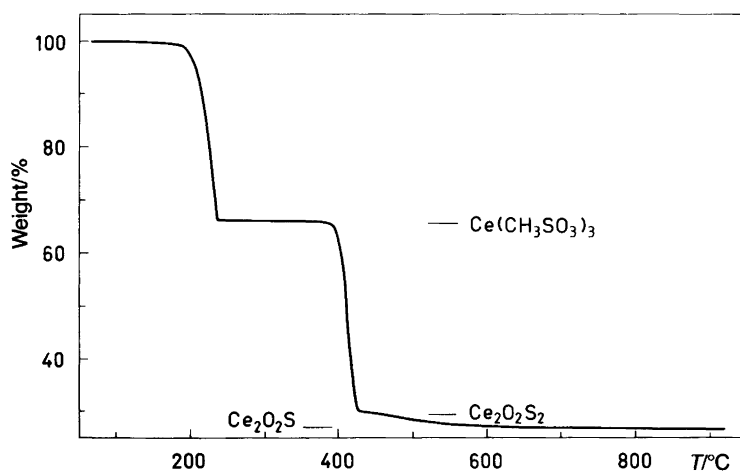


Fig. 6. TG curve for Ce(CH<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> · 2(3-picNO) in dynamic nitrogen atmosphere. Heating rate: 1 °C min<sup>-1</sup>.

present in related sulfonate compounds.<sup>21</sup> Even the cerium compound appears to follow this decomposition mechanism, although the stability of the Ce<sub>2</sub>O<sub>2</sub>S<sub>2</sub> phase is very limited (Fig. 6).

It is interesting to compare the thermal behaviour of the lanthanoid compounds with those of other transition metal (M) methanesulfonates.<sup>6</sup> It appears that in an inert atmosphere — depending on the relative strengths of the M–S and M–O bonds and on the M<sup>n+</sup>/M oxidation potential — elemental metal, binary sulfide, oxide, or a mixture thereof, may form. As the trivalent rare earth ions are hard acids or a-type ions, and thus have a preference for forming strong bonds with oxygen,<sup>22</sup> it is not surprising that the lanthanoid methanesulfonates adopt a reaction route via the dioxodisulfide to the stable dioxosulfide. This interesting sequence of thermal reactions offers new possibilities for the synthesis of rare earth oxosulfides,<sup>12</sup> which are known for their important technical applications as phosphor materials.<sup>23</sup>

**Acknowledgements.** The authors wish to thank Ms. Jaana Myllykangas, M.Sc., for carrying out some of the TG measurements. A scholarship from CNPq (Brazil) towards the stay of J.E. X. de Matos at the Helsinki University of Technology is gratefully acknowledged.

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Received August 13, 1987.