Journal of Alloys and Compounds 323–324 (2001) 39–44

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Structure and properties of hydrated La(III), Nd(III) and Er(III) methanesulfonates

E.M. Aricó[a,]*, L.B. Zinner[a], B. Kanellakopulos[b], E. Dornberger[b], J. Rebizante[c], C. Apostolidis[c]

[a]Instituto de Química, Universidade de São Paulo, Caixa Postal 26.077, CEP 05513-970, São Paulo, SP, Brazil
[b]Institut für Technische Chemie, Bereich chemisch-physicalische Verfahren, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany
[c]European Commission, Joint Research Center, Institute of Transuranic Elements, Postfach 2340, D-76125 Karlsruhe, Germany

Abstract

Detailed investigations of the methanesulfonates of neodymium and erbium presented in this work show that they have the same kind of structure as the dihydrated cerium, samarium and terbium methanesulfonates, while the lanthanum compound exhibits a very unusual structure with water molecules bridging two metallic centers. The study of the far infrared spectra of the La(III) to Lu(III) compounds in the 700–50 cm^{-1} range has been shown to be a useful tool for the indirect investigation of the structure of these kind of compounds. Thermal analyses indicate loss of water at temperatures of 100–200°C, giving origin to the respective anhydrous salts, stable up to ~400°C. The final residues are oxosulfates.

Keywords: Lanthanide methanesulfonates; Lanthanum; Neodymium; Erbium

1. Introduction

Initial studies on trivalent lanthanide methanesulfonates have shown that this class of compounds can be used as a starting material for further synthesis [1,2]. Attempts to grow single crystals failed. Later on, a systematic investigation of the series [3] yielded new information on the broad spectrum of the metal ion coordination and the crystal structures of the compounds [4]. The methanesulfonates of trivalent cerium, samarium and terbium contain two water molecules coordinated to the central cation [4], while the ytterbium compound obtained under the same conditions, had no water molecules in its structure. Extended single crystal investigations of the Ln(III)-compounds have shown that for trivalent La–Dy, the compounds crystallize with two molecules of water, and the heavier metal ions also give complexes with three- (Tb, Yb), five- (Ho), seven- (Lu), and with eight water molecules (Er, Yb, Lu) depending on the crystallization conditions [5].

We report the preparation, far-infrared spectra (700–50 cm^{-1}), thermal analyses, and X-ray single crystal examinations of the La, Nd, and Er compounds.

2. Experimental

The lanthanide methanesulfonates have been prepared by the reaction of methanesulfonic acid (Aldrich 99.8%) with the lanthanide sesquioxides Ln_2O_3 (Aldrich 99.999%) in water. They were isolated from the reaction solution through crystallization over a water bath. Far-IR spectra (700–50 cm^{-1}) on polycrystalline samples in a polyethylene matrix were collected using a Perkin-Elmer-2000 Fourier transform spectrometer. Thermal analyses were recorded on a Netzsch STA 409 apparatus, using a stream of 50 ml min^{-1} synthetic air, and 5°C min^{-1} heating rate.

Single crystals, suitable for X-ray examinations, were obtained by slow evaporation of water–ethanol (50:50, v/v) solutions. Intensities were measured on a computer controlled Siemens Sloe AED II diffractometer, using graphite-monochromated MoKα radiation (λ=71.073 pm).

Crystal structures of the compounds were resolved by the heavy atom method. The position of the metal and

---

*Corresponding author. Tel.: +55-11-3818-3847; fax: +55-11-3815-5579.

0925-8388/01/$ – see front matter
PII: S0925-8388(01)00975-6

Table 1
Crystal data for $Ln(SO_3CH_3)_3.2H_2O$ (Ln=La, Nd and Er)

Empirical formula	$LaC_3H_{13}S_3O_{11}$	$NdC_3H_{13}S_3O_{11}$	$ErC_3H_{13}S_3O_{11}$
Molecular weight (g mol^{-1})	460.23	465.56	488.58
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P-1*	*P21/c*	*P21/c*
Independent reflections	2582	2842	2151
Range for cell parameters (Refl)	$10.55° < \theta > 17.02°$ (22)	$7.44° < \theta > 14.99°$ (25)	$3.61° < \theta > 15.20°$ (22)
a (Å)	5.247(4)	9.415(2)	9.224(7)
b (Å)	10.114(7)	14.224(2)	13.948(9)
c (Å)	12.73(5)	9.718(1)	9.560(7)
α (°)	98.73(5)		
β (°)	90.92(9)	91.18(1)	91.00(6)
γ (°)	104.55(8)		
Z	2	4	4

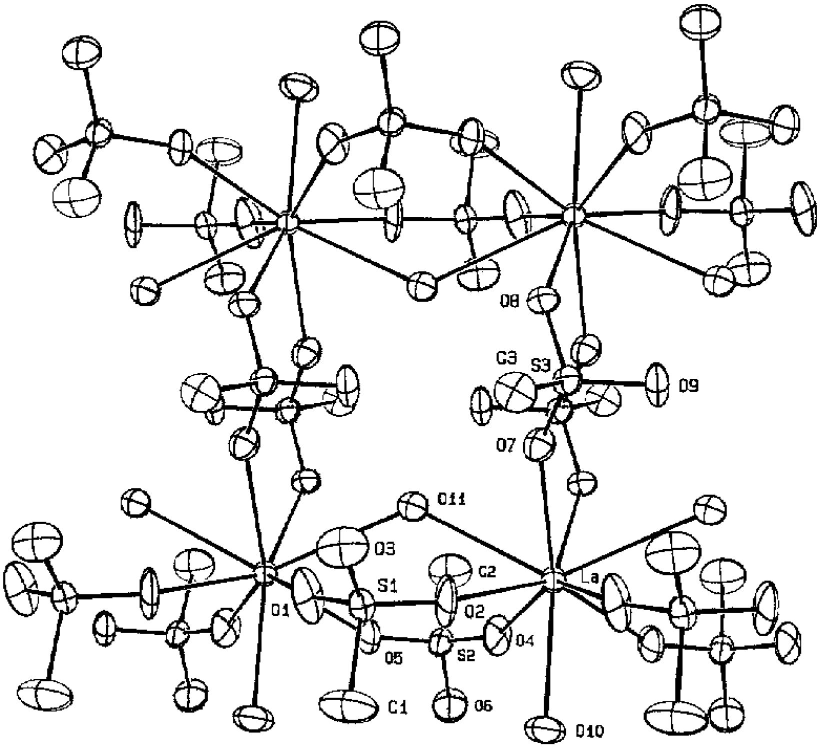

Fig. 1. Perspective drawing of the trivalent lanthanum methanesulfonate structure.

Table 2
Selected bond angles (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom2	Distance	Atom1	Atom2	Distance
La	O1′	2.435(6)	Nd	O1	2.416(3)	Er	O1	2.327(6)
La	O2	2.454(6)	Nd	O2	2.438(3)	Er	O2	2.339(6)
La	O4	2.474(5)	Nd	O4	2.404(3)	Er	O4	2.272(7)
La	O5′	2.464(5)	Nd	O5	2.400(3)	Er	O5	2.320(6)
La	O7	2.471(5)	Nd	O7	2.436(3)	Er	O7	2.345(7)
La	O8″	2.533(5)	Nd	O8	2.389(3)	Er	O8	2.257(7)
La	O10	2.580(6)	Nd	O10	2.487(4)	Er	O10	2.351(7)
La	O11	2.856(5)	Nd	O11	2.485(4)	Er	O11	2.384(7)
La	O11′	2.935(5)						

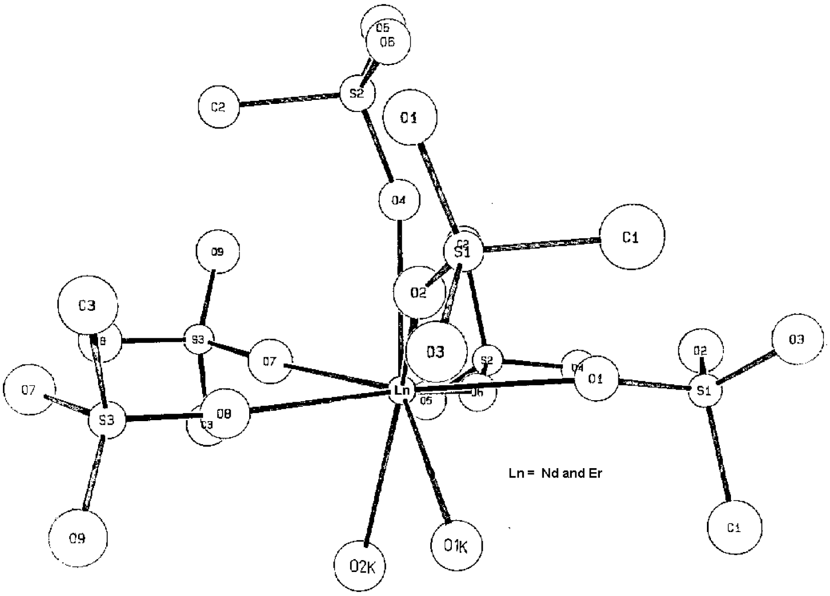

Fig. 2. Perspective drawing of the trivalent neodymium and erbium methanesulfonate structures.

Table 3
Summary of thermoanalytical results for $Ln(SO_3CH_3).2H_2O$ (Ln=La, Nd and Er)

Ln	Mass loss % H_2O		Temp. (°C)	Temp. (°C) $Ln(SO_3CH_3)_3$	Residue $(LnO)_2SO_4$	
	Calc.	Exp.			Calc.	Exp.
La	7.8	7.3	110–142	142–410	44.1	44.4
Nd	7.7	7.7	152–200	200–421	44.7	42.2
Er	7.4	7.4	116–169	169–340	47.4	45.6

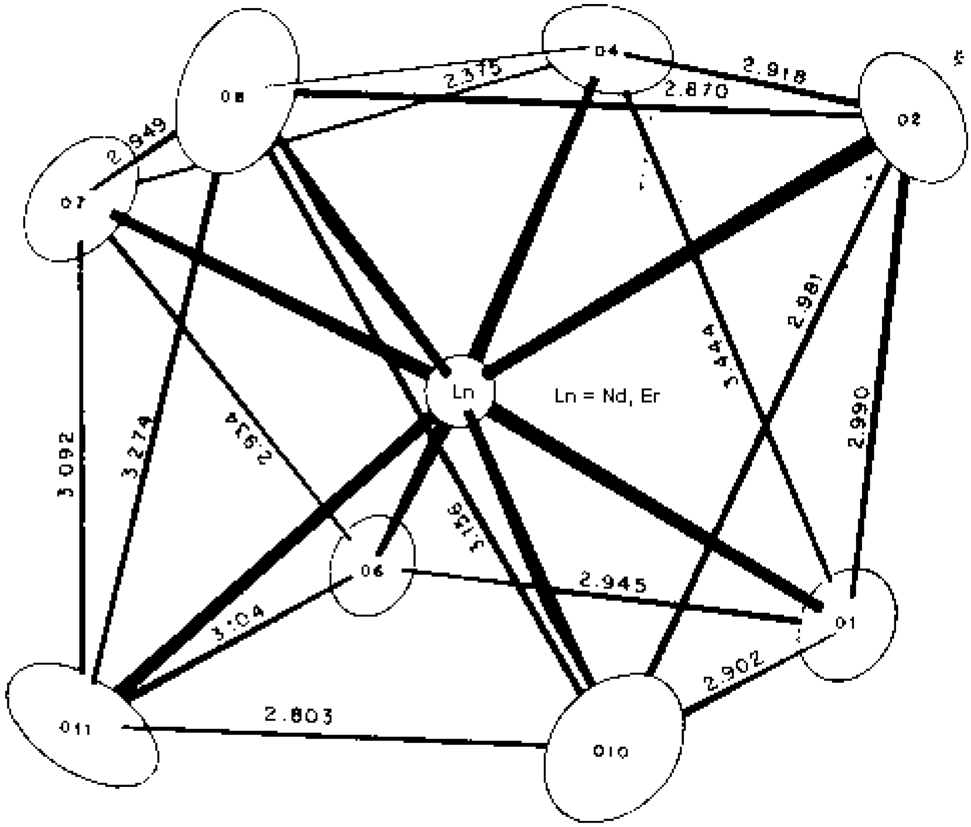

Fig. 3. Coordination polyhedra of the trivalent neodymium and erbium methanesulfonates.

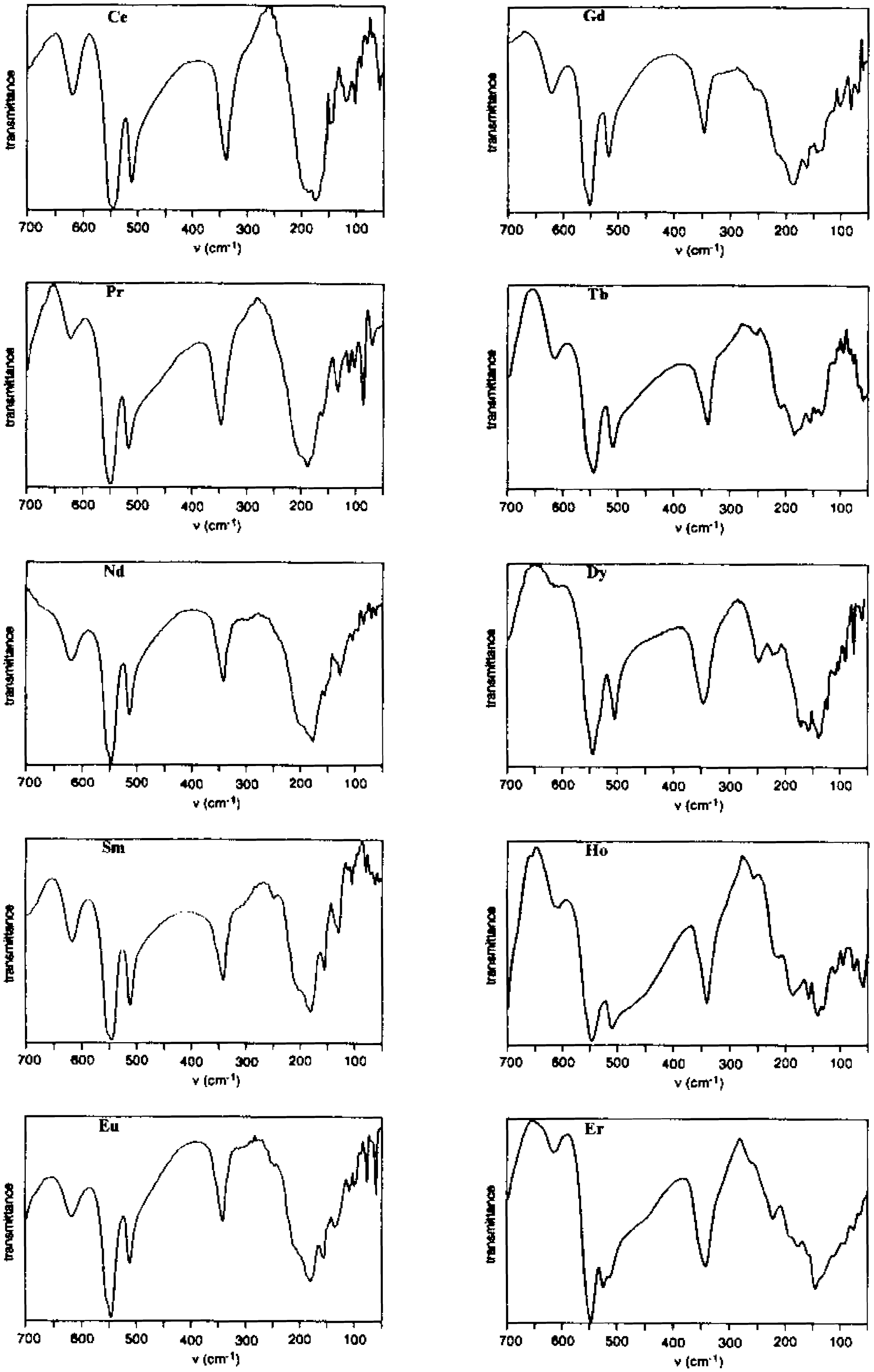

Fig. 4. Far infrared spectra of the $Ln(SO_3CH_3)_3.2H_2O$, Ln=Ce–Er.

sulfur atom were deduced from the Patterson maps. The remaining atoms were located in successive Fourier difference maps. The position and thermal parameter were refined successively by the full-matrix-least-square method using a SHELXTL PLUS program system [6] on a ENRAF-NONIUS CAD 4 Microvax II computer [7]. Atomic factors were taken from the international tables [8].

3. Results and discussion

The isostructural tris(methanesulfonate)dihydrates of trivalent Nd and Er crystallize in the monoclinic system, space group *P21/c* (No. 14). The homologous lanthanum-dihydrate compound crystallizes in a triclinic system, space group *P-1.* The crystal parameters are summarized in Table 1.

In all the investigated compounds the methanesulfonate anion acts as a bidentate ligand, bridging two metallic centers to yield polymeric structures. The Nd and Er are octacoordinated to six methanesulfonate anions and two water molecules giving origin to a distorted bicapped prism as a coordination polyhedron.

Contrary to the other lanthanide cations, trivalent La is nine-coordinated, with a remarkable structure. Six methanesulfonate anions are coordinated to the central as well as three water molecules. One water molecule is coordinated in a terminal form while the other two are bidentate coordinated bridging two La(III) ions with an angle of 129.9(2)°.

Some selected bond lengths are presented in Table 2. The Ln–O bonds in the coordinated methanosulfonate are somewhat shorter than Ln–water oxygen. This effect is more pronounced in the lanthanum compound in which the two water molecules bridge metallic centers.

The perspective drawings of the structure of the trivalent lanthanum, neodymium and erbium methanesulfonates are presented in Figs. 1 and 2 and the coordination polyhedra of the Nd(III) and Er(III) methanesulfonates are shown in Fig. 3.

The far infrared spectra of the whole trivalent lanthanide methanesulfonates are presented in Figs. 4 and 5. Their comparison, according to the band positions and shapes, allow us to order them in an isomorphous series which is coherent with the isostructural series observed from their X-ray crystal determination.

Thermal analyses show that water molecules are lost in the ~110–200°C range, with formation of the respective anhydrous methanesulfonates, stable up to ~400°C. Above this temperature, a sharp decomposition occurs giving, essentially, the respective oxosulfates, $(LnO)_2SO_4$ (Table 3).

Fig. 6 presents a typical decomposition curve, obtained for the neodymium salt. The formation of the anhydrous salts and of the oxosulfates was verified by IR spectroscopy of the respective residues.

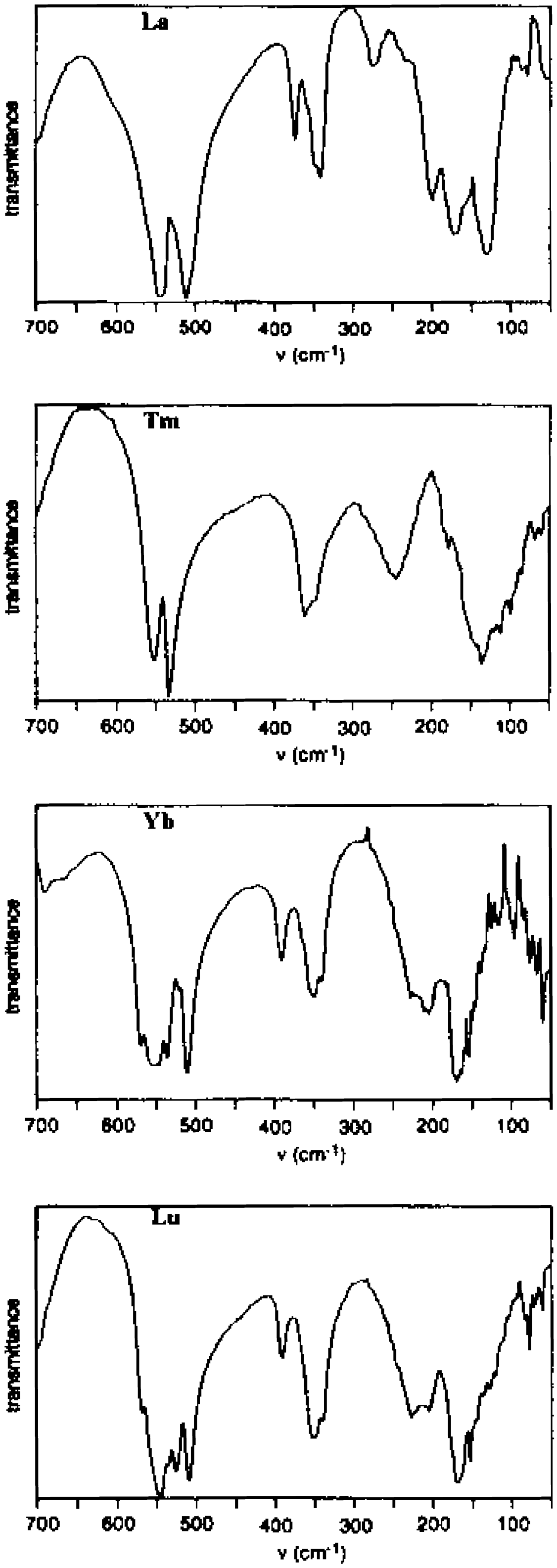

Fig. 5. Far infrared spectra of the $Ln(SO_3CH_3)_3.2H_2O$, Ln=La, Tm, Yb and Lu.

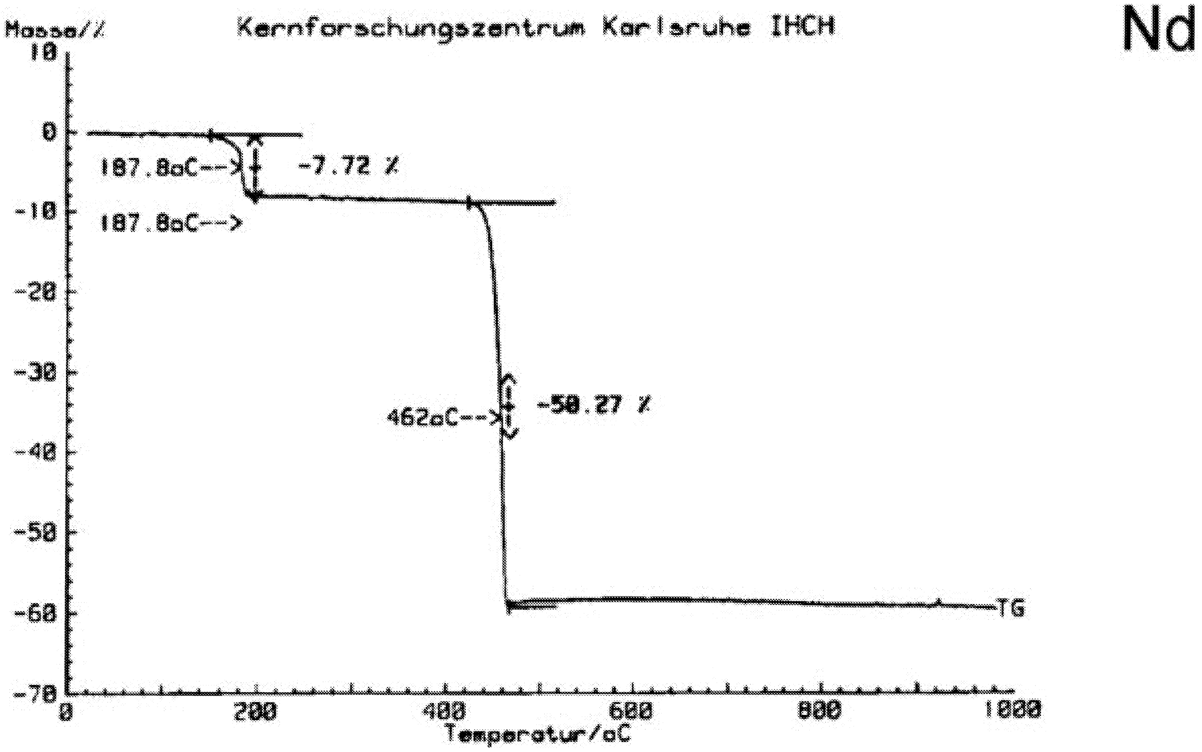

Fig. 6. Decomposition curve of the $Nd(SO_3CH_3)_3.2H_2O$.

Acknowledgements

The financial support of Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and of Deutscher Akademischer Austauschdienst (DAAD) is gratefully acknowledged.

References

[1] L.B. Zinner, An. Acad. Bras. Ciênc. 30 (1979) 27.

[2] L.B. Zinner, An. Acad. Bras. Ciênc. 32 (1980) 715.

[3] E.M. Aricó, Thesis, University of São Paulo, 1994.

[4] E.M. Aricó, L.B. Zinner, C. Apostolidis, E. Dornberger, B. Kanellakopulos, J. Rebizant, J. Alloys Comp. 249 (1997) 111.

[5] C. Apostolidis, E.M. Aricó, E. Dornberger, J. Rebizant, to be published.

[6] W. Sheldrich, SHELXTL-PLUS Program, Siemens, Siemens Analytical X-ray Instruments Corp., Madison, WI, USA, 1989.

[7] Enraf-Nonius SDP-Plus, Structure Determination Package, Enraf-Nonius, Delft, Netherlands, 1987.

[8] International Tables for X-Ray Crystallography, Vol. 4, The Kynoch Press, Birmingham, 1974.