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Note

THERMOGRAVIMETRIC AND DIFFERENTIAL SCANNING CALORIMETRY STUDIES OF HYDRATED LANTHANIDE PERRHENATE COMPLEXES WITH *TRANS*-1,4-DITHIANE-1,4-DIOXIDE

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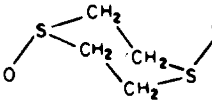
The thermal study of complexes of the general formula $[Ln(H_2O)_x(\eta^1\text{-}TDTD)_2(\eta'\text{-}ReO_4)(\mu\text{-}\eta^2\text{-}TDTD)]_n(ReO_4)_{2n} \cdot n\text{TDTD}$ ($x = 4$, $Ln \equiv$ Pr, Nd, Eu; $x = 3$, $Ln \equiv$ Ho; TDTD is *trans*-1,4-dithiane-1,4-dioxide [1]) is described.



TDTD

The synthesis, characterization and structure of these complexes have been recently described [2].

EXPERIMENTAL

The TG and DSC studies were performed under a nitrogen atmosphere in a Du Pont 1090 system, with weight varying from 3 to 6 mg at a program heating rate of 10 K min^{-1}. Metallic indium was used as a standard for the DSC determinations.

RESULTS AND DISCUSSION

The structure of the neodymium complex, isomorphous with those of praseodymium and europium, was completely determined to an *R*-factor of 0.061 [2]. The coordination polyhedron around the central atom is a dis-

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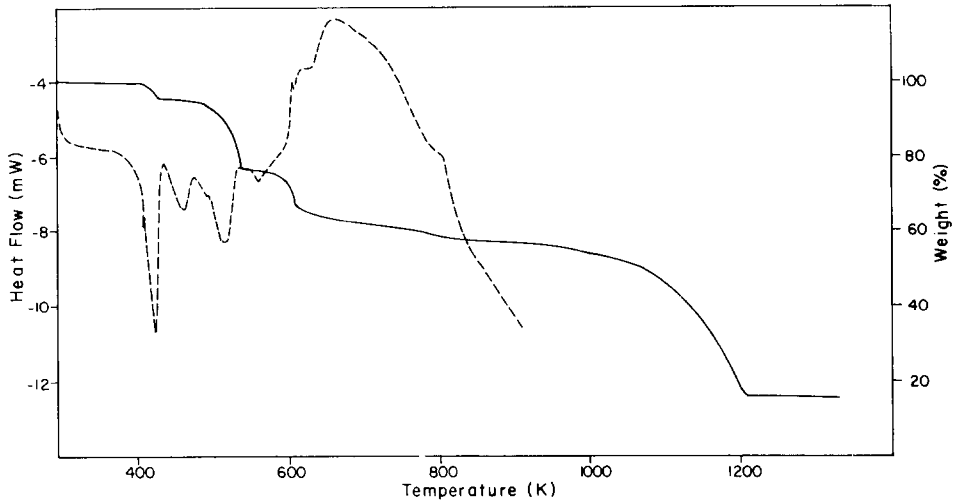

Fig. 1. TG (———) and DSC (- - - - -) curves of the praseodymium compound.

torted capped square antiprism with approximate point symmetry C_{4v}. Four water molecules form the uncapped square base. The opposite base is capped by an oxygen of the perrhenate and is also formed by two crystallographically independent monodentate TDTD groups; the other TDTD group is located at the center of symmetry and its atoms are bridges between neighbouring neodymium cations forming infinite chains of polyhedra along the *c* direction of the crystal. The other uncoordinated TDTD group is located at another center of symmetry.

The structure of the holmium complex is similar to that of neodymium, except that the compound only contains three water molecules, forming a triangular base. The attributed symmetry is D_{2d} [3].

Figure 1 contains typical TG and DSC curves, represented by the praseodymium compound.

The thermal decomposition process of the compounds can be represented by the following steps:

$$3\left\{\left[\mathrm{Ln(H_2O)}_x(\eta^1\text{-}\mathrm{TDTD})_2(\eta'\text{-}\mathrm{ReO_4})(\mu\text{-}\eta^2\text{-}\mathrm{TDTD})\right]_n(ReO_4)_{2n}\cdot \mathrm{n}TDTD\right\}$$

$$\rightarrow 3xn\mathrm{H_2O} + 3\left\{\left[\mathrm{Ln}(\eta^1\text{-}\mathrm{TDTD})_2(\eta'\text{-}\mathrm{ReO_4})(\mu\text{-}\eta^2\text{-}\mathrm{TDTD})\right]_n\text{-}\right.$$

$$\left.(\mathrm{ReO_4})_{2n}\cdot n\mathrm{TDTD}\right\}$$

$$\rightarrow 6n\mathrm{TDTD} + 3\left\{\left[\mathrm{Ln}(\eta'\text{-}\mathrm{ReO_4})(\mu\text{-}\eta^2\text{-}\mathrm{TDTD})\right]_n(\mathrm{ReO_4})_{2n}\cdot n\mathrm{TDTD}\right\}$$

$$\rightarrow 3n\mathrm{TDTD} + 3\left\{\left[\mathrm{Ln}(\eta'\text{-}\mathrm{ReO_4})(\mu\text{-}\eta^2\text{-}\mathrm{TDTD})\right]_n(\mathrm{ReO_4})_{2n}\right\}$$

$$\rightarrow 3n\mathrm{TDTD} + 4n\mathrm{Re_2O_7} + n\mathrm{Ln_3ReO_8}$$

TABLE 1
TG and DSC data

Element	Temperature (K)	Weight loss % and residue (%)		Attribution (x, n)	Peak temperature (DSC) (K)	Enthalpy (kJ mol^{-1})
		Exp.	Theor.			
Pr	420– 430	4	4.58	$-12\ H_2O$	423	+16.2
	445– 545	18	19.36	−6 TDTD	461	+4.3
	570– 615	10	9.68	−3 TDTD	513	+16.1
	615–1200	49	50.75	-3 TDTD $-4\ Re_2O_7$	658	−134.6
	Residue 1320	19	15.83	Pr_3ReO_8		
Nd	405– 435	5	4.57	$-12\ H_2O$	420	+13.6
	445– 545	19	19.32	−6 TDTD	464	+7.9
	545– 615	10	9.66	−3 TDTD	513	+9.3
	615–1200	51	50.65	-3 TDTD $-4\ Re_2O_7$	608	−102.6
	Residue 1295	15	15.80	Nd_3ReO_8		
Eu	400– 450	4	4.55	$-12\ H_2O$	418	+9.5
	455– 540	19	19.23	−6 TDTD	463	+3.5
	560– 620	14	9.61	−3 TDTD	518	+12.4
	620–1210	48	50.40	-3 TDTD $-4\ Re_2O_7$	666	−90.1
	Residue 1295	17	16.21	Eu_3ReO_8		
Ho	420– 460	3	33.42	$-9\ H_2O$	438	+11.2
	470– 545	20	19.29	−6 TDTD	498	+18.6
	545– 650	13	9.61	−3 TDTD	673	−110.2
	650–1185	49	50.56	-3 TDTD $-4\ Re_2O_7$		
	Residue 1295	15	16.99	Ho_3ReO_8		

The TG and DSC data are presented in Table 1, taking into consideration the above equations. The decomposition process is in part related to the structure. First water molecules are lost at temperatures between 400 and 450 K. The first TDTD groups to be removed are those which are non-coordinated and monodentate, and finally the TDTD group that bridges the two lanthanides is removed. Only one rhenium atom remains attached to one lanthanide giving the final residue Ln_3ReO_8. It is interesting to mention that several compounds such as hydrated perrhenates [4] and complexes with the formula $Ln(ReO_4)_3 \cdot 7.5$TMSO (TMSO is tetramethylene sulfoxide) [5] or $Ln(ReO_4)_3 \cdot 4$DMA (DMA is dimethylacetamide) [6] give the respective anhydrous salts on heating. According to Baud and Capestan [7] the decomposition of the anhydrous salts occurs by the sublimation of Re_2O_7 and the residue is Ln_3ReO_8, but Plyuschev and coworkers [4,8,9] found that lanthanide oxide residues were formed. In the case of the complexes with DMA and TMSO, higher values, compared with the oxides, were observed. In the first case the formation of ReO_2 was considered responsible for the higher values, and in the second case it was observed that the residue still contained rhenium at temperatures of about 1070 K.

The DSC curves are complex, with three endothermic peaks. The first peak corresponds to the elimination of water; the second and third both correspond to the loss of one TDTD group. The exothermal curve seems to indicate that several simultaneous processes occur.

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