Thermochimica Acta, 107 (1986) 387–391
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMAL ANALYSIS OF HYDRATED RARE-EARTH TRIFLUOROMETHANESULFONATE COMPLEXES WITH *TRANS*-1,4-DITHIANE-1,4-DIOXIDE (TDTD)

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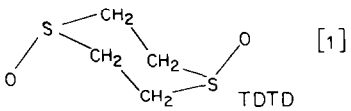
(Received 7 April 1986)

This note describes the thermal analysis of complexes with general formula: $[Ln(CF_3SO_3)(TDTD)_2(H_2O)_3](CF_3SO_3)_2 \cdot 2TDTD$ (Ln = La–Lu, Y):



[1]

EXPERIMENTAL

The complexes were obtained by slowly evaporating mixtures of aqueous solutions containing lanthanide trifluoromethanesulfonates and TDTD (molar ratio 1 : 4). Analytical results for Ln, C and H indicate a general formula $Ln(TDTD)_4(CF_3SO_3)_3 \cdot 3H_2O$. X-ray powder patterns obtained in a Norelco Instrument indicate that all compounds are isostructural. TG studies were performed under nitrogen atmosphere in a Perkin-Elmer TGS-1 system, using samples varying in weight from 0.722 to 0.898 mg and a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

The compounds behave as 1 : 2 electrolytes in methanol. IR spectra show bands attributed to $\nu_{as}(SO_3)$ at ~1285s, 1240s and 1220m, $\nu_s(SO_3)$ at ~1030s, 1020s, 1010m and 1000w, $\delta_{as}(SO_3)$ at ~630s $\delta_s(SO_3)$ at ~515m due to ionic and monodentate CF_3SO_3 anions and ν(SO) at 980s and 970sh

0040-6031/86/$03.50

TABLE 1

Thermoanalytical data of the compounds of formula $[Ln(CF_3SO_3)(TDTD)_2(H_2O)_3](CF_3SO_3)_2 \cdot 2TDTD$

Ln	Weight loss attribution and residue	Weight loss and residue (%)		Temperature range (°C)
		Calc.	Obs.	
La	$-3H_2O$	4.32	5.1	80–140
	−1TDTD	12.19	12.7	210–250
	−1TDTD	12.19	11.4	250–280
	−1TDTD	12.19	10.8	280–330
	−1TDTD	12.19	12.5	330–360
	$-3COF_2 - 3SO_2$	31.23	32.7	360–440
	LaF_3	15.68	15.0	
Ce	$-3H_2O$	4.32	5.6	75–150
	−1TDTD	12.18	9.9	215–265
	−1TDTD	12.18	10.6	265–290
	−1TDTD	12.18	11.3	290–340
	−1TDTD	12.18	12.0	340–370
	$-3COF_2 - 3SO_2$	31.22	36.3	370–530
	CeF_3	15.77	14.2	
Pr	$-3H_2O$	4.32	4.4	130–160
	−1TDTD	12.17	10.4	160–255
	−1TDTD	12.17	10.4	255–305
	−1TDTD	12.17	10.1	305–330
	−1TDTD	12.17	13.7	330–375
	$-3COF_2 - 3SO_2$	31.20	34.9	375–440
	PrF_3	15.82	16.2	
Nd	$-3H_2O - 1.5TDTD$	22.53	24.5	160–290
	−1TDTD	12.14	13.5	290–335
	−1TDTD	12.14	12.2	335–375
	$-0.5TDTD - 3COF_2 - 3SO_2$	37.17	35.1	375–445
	NdF_3	16.04	14.8	
Sm	$-3H_2O - 1TDTD$	16.37	16.8	130–275
	−1TDTD	12.08	13.1	275–315
	−0.5TDTD	6.04	8.3	315–340
	−1TDTD	12.08	11.5	340–360
	$-0.5TDTD - 3COF_2 - 3SO_2$	37.00	35.7	360–520
	SmF_3	16.45	15.7	

TABLE 1 (continued)

Ln	Weight loss attribution and residue	Weight loss and residue (%)		Temperature range (°C)
		Calc.	Obs.	
Eu	$-3H_2O-2TDTD$	28.41	29.8	190–210
	$-0.5TDTD$	6.03	7.5	210–340
	$-1TDTD$	12.06	11.6	340–370
	$-0.5TDTD-3COF_2-3SO_2$	36.94	33.4	370–435
	EuF_3	16.56	16.6	
Gd	$-3H_2O-1TDTD$	16.27	15.3	200–250
	$-1TDTD$	12.01	13.5	250–300
	$-0.5TDTD$	6.01	8.1	300–350
	$-1TDTD$	12.01	12.3	350–380
	$-0.5TDTD-3COF_2-3SO_2$	36.80	30.8	380–435
	GdF_3	16.90	17.1	
Tb	$-3H_2O-0.5TDTD$	10.26	9.3	160–210
	$-1TDTD$	12.00	9.8	210–280
	$-1TDTD$	12.00	13.2	280–315
	$-0.5TDTD$	6.00	8.4	315–350
	$-1TDTD-1SO_2$	17.04	15.6	350–395
	$-3COF_2-2SO_2$	25.70	27.8	395–510
	TbF_3	17.01	16.0	
Dy	$-3H_2O-1TDTD$	16.22	17.0	160–280
	$-1TDTD$	11.96	13.2	280–315
	$-1TDTD$	11.96	9.8	315–350
	$-1TDTD$	11.96	14.8	350–395
	$-3COF_2-3SO_2$	30.65	24.5	395–430
	DyF_3	17.25	17.8	
Ho	$-3H_2O-0.5TDTD$	10.20	10.8	180–235
	$-1TDTD$	11.94	9.1	235–280
	$-1TDTD$	11.94	13.3	280–315
	$-1TDTD$	11.94	9.8	315–355
	$-0.5TDTD-1SO_2$	10.99	12.3	355–385
	$-3COF_2-2SO_2$	25.57	27.5	385–435
	HoF_3	17.40	17.3	
Er	$-3H_2O-0.5TDTD$	10.19	8.0	130–240
	$-2TDTD$	23.84	24.7	240–295
	$-1TDTD$	11.92	11.3	295–340
	$-0.5TDTD-1SO_2$	10.97	11.7	340–370
	$3COF_2-2SO_2$	25.53	28.5	370–525
	ErF_3	17.53	15.8	

TABLE 1 (continued)

Ln	Weight loss attribution and residue	Weight loss and residue (%)		Temperature range (°C)
		Calc.	Obs.	
Tm	$-3H_2O-2.5$TDTD	33.98	33.7	125–305
	−1TDTD	11.90	11.2	305–355
	-0.5TDTD $-1SO_2$	10.96	11.5	355–380
	$-3COF_2-2SO_2$	25.50	28.7	380–440
	TmF_3	17.66	16.1	
Yb	$-3H_2O-2.5$TDTD	33.85	34.0	125–300
	−1TDTD	11.86	11.5	300–350
	-0.5TDTD $-1SO_2$	10.92	11.1	350–375
	$-3COF_2-2SO_2$	25.41	26.5	375–435
	YbF_3	17.93	17.0	
Lu	$-3H_2O$	4.20	4.8	115–155
	−1TDTD	11.85	11.9	155–240
	−2TDTD	23.70	23.4	240–300
	−1TDTD $-1COF_2-1SO_2$	21.97	21.6	300–375
	$-2COF_2-2SO_2$	20.24	24.7	375–435
	LuF_3	18.05	18.7	
Y	$-3H_2O$	4.50	4.6	125–165
	−2TDTD	25.40	29.0	165–300
	−1TDTD	12.70	11.7	300–355
	−1TDTD	12.70	14.0	355–385
	$-3COF_2-3SO_2$	32.54	30.4	385–520
	YF_3	12.17	12.3	

cm^{-1}, indicating two different modes of TDTD coordination. The absorption spectrum of the neodymium and emission spectra of the europium compounds were determined. X-ray study of the Nd complex showed it to be triclinic ($P_{\bar{1}}$). The Nd^{3+} ion is eight-coordinated by four oxygens from TDTD molecules; one oxygen of the $CF_3SO_3^-$ anion and three water oxygens. The fluorescence spectrum suggests a distorted D_{2d} symmetry [2].

Figure 1 shows the TG curves obtained for all the complexes and Table 1 contains the thermoanalytical data. The compounds from lanthanum to praseodymium lose water, followed in several steps by TDTD loss, giving the respective anhydrous salts. The decomposition of the salts occurs with evolution of COF_2 and SO_2 [3]. For the other complexes water and part of TDTD are evolved together and the anhydrous salts are not formed. The evolution of TDTD occurs along with SO_2 and/or SO_2 and COF_2. In all cases the respective lanthanide fluorides are obtained as observed in the

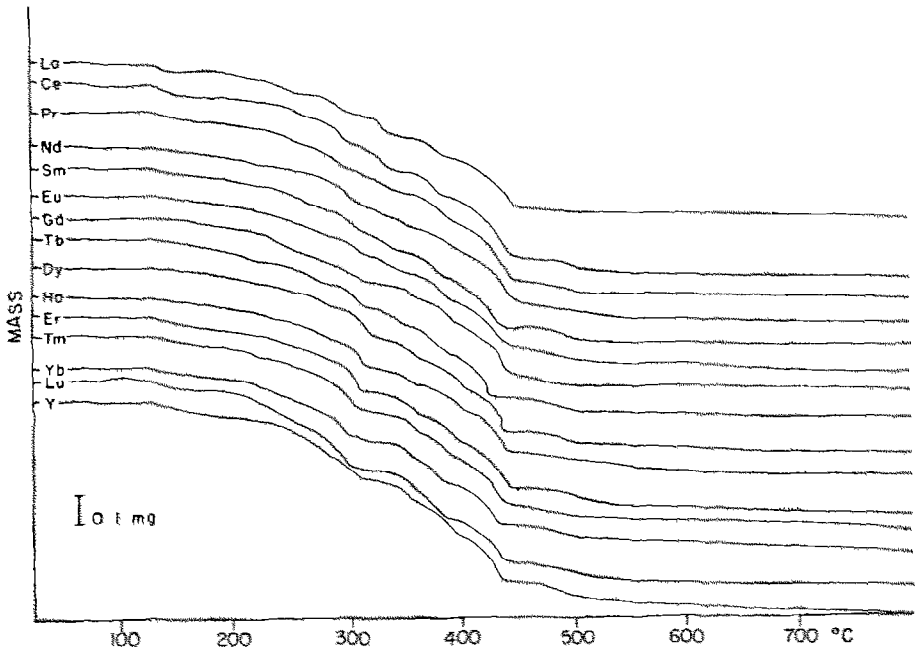


Fig. 1. TG curves of the compounds of formula $[Ln(CF_3SO_3)(TDTD)_2(H_2O)_3](CF_3SO_3)_2 \cdot 2TDTD$ (Ln = La–Lu, Y).

thermal decomposition of $Ln(CF_3SO_3)_3 \cdot 9H_2O$ [3], $Ln(CF_3SO_3)_3 \cdot 7.5TSO$ [4] and $Ln(CF_3SO_3)_3 \cdot 7.5DMSO$ [5].

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