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THERMAL AND ELECTRICAL STUDIES OF SOME EUROPIUM COMPOUNDS WITH ORGANIC LIGANDS

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ABSTRACT

The preparation, thermal and some electrical properties for tris(1-phenyl-1,3-butanediono)europium(III) 2-hydrate, piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) hydrate, piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III) 3-hydrate and tetrapropylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III) are described. The thermal behaviour of the compounds has been studied by thermogravimetry (TG) and differential thermal analysis (DTA). The compounds piperidinium tetrakis-(1-phenyl-1,3-butanediono)europium(III) hydrate and piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III) 3-hydrate lose water to give the anhydrous compound which in turn decomposes to give europium(III) oxide. The compound tris(1-phenyl-1,3-butanediono) europium(III) 2-hydrate undergoes hydrolysis during the decomposition process and tris(1-phenyl-1,3-butanediono)europium(III) is not produced. The compound tetrapropylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III) decomposes to give europium(III) oxide. Electrical studies show that all of the compounds exhibit ohmic behaviour. For two of the compounds, tris(1-phenyl-1,3-butanediono)europium(III) 2-hydrate and piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) hydrate, only approximate activation energies of conduction are reported due to hydrolysis and decomposition respectively.

INTRODUCTION

Previously reported work from these laboratories concerning the thermal and electrical studies of compounds containing some first row transition elements [1–6] has produced some interesting observations and has led to a similar investigation of some compounds of an element in another transition metal series. We have selected europium for this purpose and report here a

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description and discussion of results for the following compounds: tris(1-phenyl-1,3-butanediono)europium(III) 2-hydrate, $[Eu(C_{10}H_9O_2)_3]2H_2O$; piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) hydrate, $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$; piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III) 3-hydrate, $[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O$; and tetrapropylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III), $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$.

EXPERIMENTAL

Preparation of the compounds

Tris(1-phenyl-1,3-butanediono)europium(III) 2-hydrate, $[Eu(C_{10}H_9O_2)_3]$-$2H_2O$

A solution of 2.5×10^{-2} mol of 1-phenyl-1,3-butanedione in 50 cm^3 of 95% ethanol was added with stirring to a solution containing 5×10^{-3} mol of europium(III) chloride in 200 cm^3 of water. 15 cm^3 of ammonia solution of concentration 1 mol dm^{-3} was added to the resulting suspension over a period of 2 h with stirring. The product was filtered, washed with water and dried in a vacuum desiccator. It was then dissolved in 10 cm^3 of acetone and filtered. The yellow solid obtained was washed with water and dried in air at room temperature overnight. Excess chelating agent (1-phenyl-1,3-butanedione) was removed by stirring with 25 cm^3 of petroleum ether in a closed flask for 30 minutes. The pale yellow solid obtained was filtered, washed with petroleum ether and dried in a vacuum desiccator at room temperature [7]. Analytical results were: C, 52.70%; and H, 4.44%. The calculated values are: C, 53.65%; and H, 4.66%.

Piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) hydrate, $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$

A pale yellow solid was obtained by repeating the preparation above using 0.015 mol piperidine to replace the ammonia solution [7–9]. Analytical results were: C, 60.02%; H, 5.06%; and N, 1.50%. The calculated values are: C, 59.98%; H, 5.61%; and N, 1.55%.

Piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III) 3-hydrate, $[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4] \cdot 3H_2O$

8 mmol piperidine was added to a solution of 8 mmol 1,3-diphenyl-1,3-propanedione and 2 mmol europium chloride in 70 cm^3 hot ethanol. After cooling in an ice bath, yellow needles formed which were filtered off under vacuum, washed with water and air dried. The product was recrystallized from AnalaR methanol [10,11]. Analytical results were: C, 64.12%; H, 4.68%; and N, 1.10%. The calculated values are: C, 65.86%; H, 5.28%; and N, 1.18%.

Tetrapropylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III), $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$

8 mmol of 10% aqueous tetrapropylammonium hydroxide was added to a solution of 8 mmol 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and 2 mmol europium chloride in 75 cm^3 of hot ethanol. Coarse orange fluorescent crystals were obtained on cooling the solution. Dilution of the filtrate with 75 cm^3 of water yielded additional product. Recrystallization was from ethanol [10]. Analytical results were: C, 42.66%; H, 3.21%; and N, 1.64%. The calculated values are: C, 43.07%; H, 3.95%; and N, 1.14%.

Analytical, thermal and electrical measurements

The carbon, hydrogen and nitrogen analyses were determined using a Carlo Erba elemental analyser.

The thermal analysis studies were carried out on a Stanton Redcroft Model STA 781 thermobalance. Thermogravimetry curves were obtained at a heating rate of 10 °C min^{-1} in static air. In all cases the 20–800 °C temperature range was studied.

Electrical data, involving measurement of the current–voltage characteristics at room temperature and the temperature dependence of conductivity were obtained using discs formed from the compressed compounds. The details of the method have been previously described [1–6] and the conditions were as follows: disc diameter, 13 mm; disc thicknesses in the range 1.00–1.35 mm; conductive silver paint electrode diameter, 4.99 mm; and applied potential for the temperature dependence of conductivity, 10 V. All currents were measured using a Keithley 610C electrometer in a d.c. circuit.

RESULTS AND DISCUSSION

The analytical results for the compounds agree with the given stoichiometry. With the exception of tetrapropylammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III) which is anhydrous, all of the compounds contain water molecules.

The TG and DTA curves for the compounds are given in Figs. 1–4. The TG curve for tris(1-phenyl-1,3-butanediono)europium(III) 2-hydrate, Fig. 1, indicates that the anhydrous compound is not produced. The hydrated compound begins losing water at about 50 °C. It has been suggested in the literature [7] that hydrolysis complicates this dehydration process and that the compound undergoes the following reaction

$$[Eu(C_{10}H_9O_2)_3]2H_2O \rightarrow [Eu(C_{10}H_9O_2)_2OH] + HC_{10}H_9O_2 + H_2O$$

In the DTA curve (Fig. 1) this process is apparent as an endothermic peak which is followed, at higher temperature, by an exothermic peak attributed

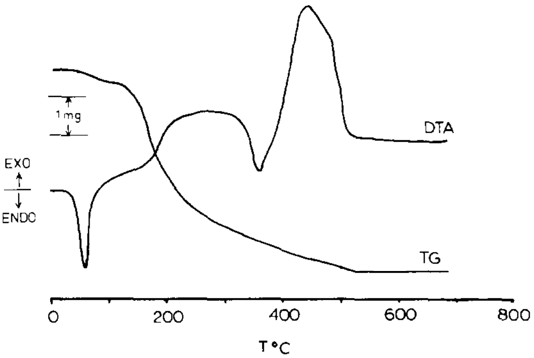

Fig. 1. TG/DTA curves for $[Eu(C_{10}H_9O_2)_3]2H_2O$. Sample weight = 9.15 mg.

to decomposition to Eu_2O_3. The TG and DTA curves for piperidinium tetrakis(1-phenyl-1,3-butanediono)europium(III) hydrate (Fig. 2) and piperidinium tetrakis(1,3-diphenyl-1,3-propanediono)europium(III) 3-hydrate (Fig. 3) are similar. The dehydration of the compounds takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 1). The expected endothermic peak for the dehydration processes of these compounds is observed in the DTA curves and the calculated dehydration enthalpies are given in Table 1. Decomposition of the anhydrous compounds follows immediately after the dehydration processes and the residual weights are in good agreement with the values required for europium(III) oxide. The DTA curves show these decomposition processes to be exothermic and the corresponding temperature ranges are shown in Table 2. The TG curve (Fig. 4) for tetrapropyl ammonium tetrakis(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanediono)europium(III) shows

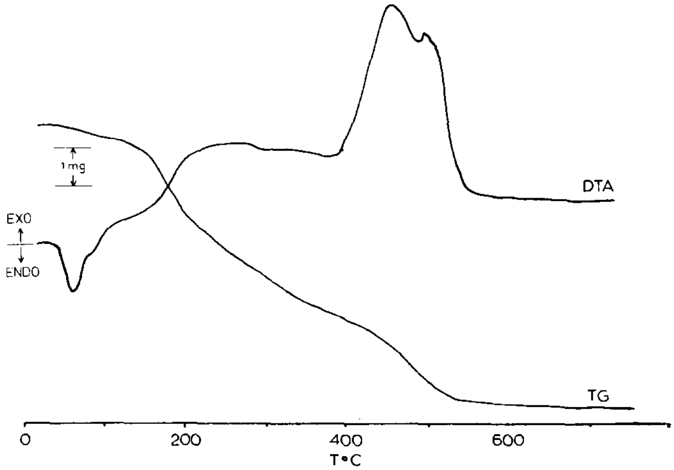

Fig. 2. TG/DTA curves for $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$. Sample weight = 8.51 mg.

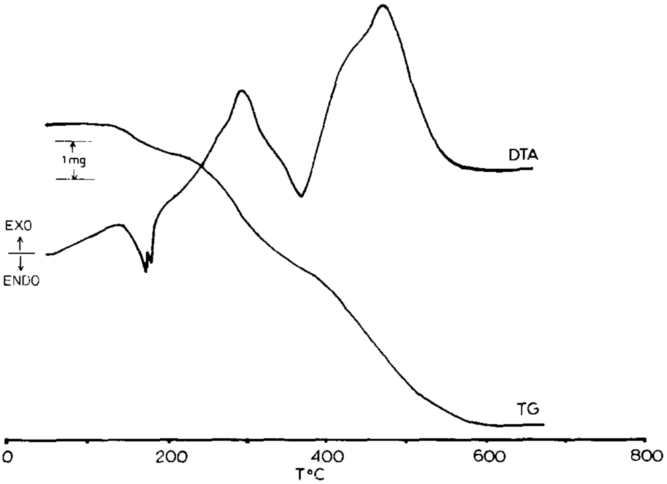

Fig. 3. TG/DTA curves for $[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O$. Sample weight = 8.78 mg.

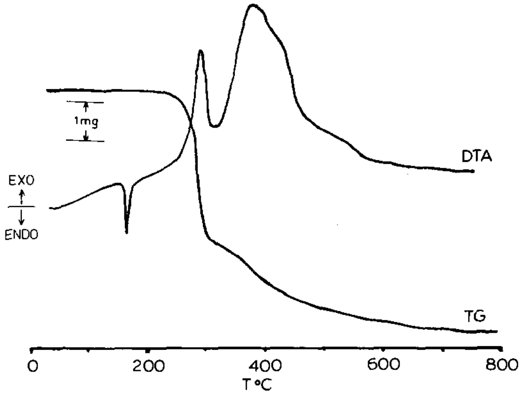

Fig. 4. TG/DTA curves for $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$. Sample weight = 9.18 mg.

TABLE 1

Dehydration processes of the europium compounds

Process	Temperature at DTA peak (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O \rightarrow [C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]$	58	Endo	2.00	2.30	80
$[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O \rightarrow [C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]$	176	Endo	4.52	4.26	99

TABLE 2

Decomposition processes of the anhydrous europium compounds

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]$ [a] → Eu_2O_3	102–694	Exo	19.54	19.88
$[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]$ [a] → Eu_2O_3	192–592	Exo	14.71	14.94
$[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$ → Eu_2O_3	170–740	Exo	14.34	13.72

[a] These compounds were produced by dehydration of the corresponding prepared hydrous compounds.

TABLE 3

Electrical properties of the initial compounds

Compound	Conductivity at room temperature (Ω^{-1} m^{-1})	ΔE [a] (eV)
$[Eu(C_{10}H_9O_2)_3]2H_2O$	1.2×10^{-7}	0.7 [b]
$[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$	7.4×10^{-8}	1.0 [b]
$[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O$	1.9×10^{-7}	1.5 [c]
$[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$	6.3×10^{-8}	1.5 [c]

[a] ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$.

[b] ΔE is obtained from the gradient of the tangent to the $\ln\sigma$ vs T^{-1} plot at room temperature for heating.

[c] ΔE is obtained from the gradient of the least-squares-fitted line to the points in an Arrhenius plot using combined heating and cooling data.

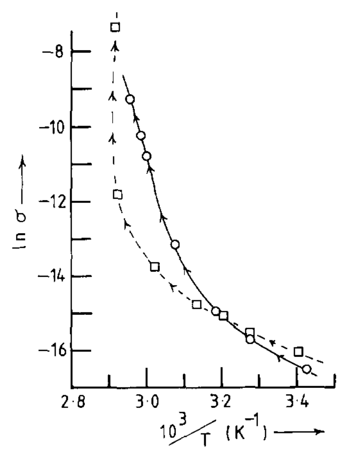

Fig. 5. Plots of $\ln\sigma$ versus $10^3/T$ (with σ and T in units of Ω^{-1} m^{-1} and K respectively) for: □- - - - -□, $[Eu(C_{10}H_9O_2)_3]2H_2O$; and o———o, $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$.

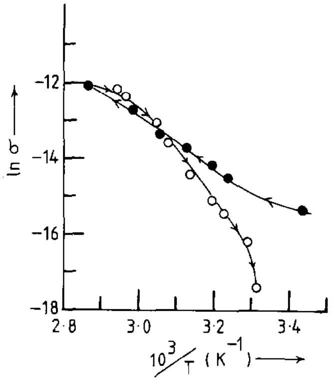

Fig. 6. Plot of lnσ versus $10^3/T$ (with σ and T in units of Ω^{-1} m^{-1} and K respectively) for $[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O$ for heating (●) and cooling (○).

that the compound is thermally stable in the range 20–170 °C. Its decomposition begins at 170 °C and finishes at 740 °C with formation of europium(III) oxide. The DTA curve (Fig. 4) shows an endothermic peak at 169 °C due to melting and the liquid then decomposes immediately producing exothermic peaks.

The discs of all four of the initially prepared compounds, i.e. $[Eu(C_{10}H_9O_2)_3]2H_2O$, $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$, $[C_5H_{10}NH_2]$ $[Eu(C_{15}H_{11}O_2)_4]3H_2O$ and $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$ exhibit ohmic characteristics at room temperature. The room temperature conductivities as deduced from the gradients of the current versus voltage characteristics, assuming current flow perpendicular to the electrodes, are listed in Table 3. These conductivities only span a factor of 3.0.

The results of the conductivity (σ) measurements as a function of absolute temperature (T) are shown as Arrhenius plots in Figs. 5–7. For $[Eu(C_{10}H_9O_2)_3]2H_2O$ and $[C_5H_{10}NH_2][Eu(C_{10}H_9O_2)_4]H_2O$ (Fig. 5), the plots are non-linear: this is due to their dehydration which is associated with a large increase in conductivity. Only rough values of the activation energy, ΔE, appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ could be determined and are based on the gradients of the tangents to the corresponding Arrhenius plots at the lower end of the temperature range covered. The resulting values are given in Table 3. For the other two initial compounds, i.e. $[C_5H_{10}NH_2][Eu(C_{15}H_{11}O_2)_4]3H_2O$ (Fig. 6) and $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$ (Fig. 7), because of their much higher temperatures before dehydration (176 °C) and decomposition (170 °C) respectively, it was possible to reach the maximum temperature (78 °C) for the temperature dependence of conductivity measurements without chemical change occurring. For these compounds, measurements were obtained during cooling in addition to heating although, as seen from Figs. 6 and 7, the reproducibility was poor. The activation energy, ΔE, for each compound, as deduced from the line of

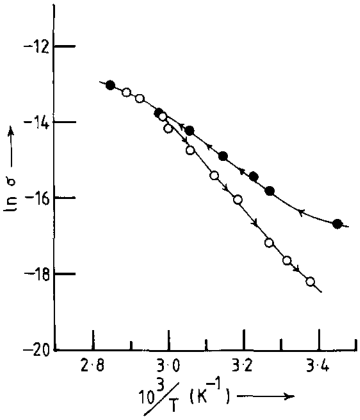

Fig. 7. Plot of lnσ versus $10^3/T$ (with σ and T in units of Ω^{-1} m^{-1} and K respectively) for $[(C_3H_7)_4N][Eu(C_8H_5F_3O_2S)_4]$ for heating (●) and cooling (○).

best fit (in a least-squares sense) through all the points obtained during heating and cooling are given in Table 3.

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