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THERMAL DECOMPOSITION OF Co(II), Ni(II), Cu(II), Zn(II), Cd(II) AND Pb(II) *p*-TOLUENESULPHONATES

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ABSTRACT

Thermal decompositions of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) hexahydrated *p*-toluenesulphonates and Pb(II) anhydrous *p*-toluenesulphonate have been studied in an atmosphere of air and under nitrogen flow. Dehydration enthalpies were measured from the DSC curves and the degradation products of the anhydrous salts were identified by X-ray diffraction.

INTRODUCTION

Literature concerning the thermal behaviour of metallic sulphonates is very rare. Charbonnier has studied the thermal decomposition of alkaline [1], and calcium [2] alkanesulphonates. Meisel et al. reported on the thermal analysis of the alkali and alkaline earth metal benzenesulphonates [3,4], and on the thermal decomposition of some heavy and transition metal benzenesulphonates [5]. Recently, the characterization and thermal decomposition of metallic indigosulphonates have been studied [6].

In previous papers, the thermal behaviour of cobalt, copper and zinc methanesulphonates [7] and the thermal degradation of β-naphthalenesulphonic and 1,5-naphthalenedisulphonic acids, and their corresponding copper salts [8] have been reported.

Within the scope of current research on metallic sulphonates, the results of the thermal decomposition of Co, Ni, Cu, Zn, Cd and Pb *p*-toluenesulphonates are presented in this work.

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EXPERIMENTAL

Synthesis

The *p*-toluenesulphonates of Co, Ni, Cu, Zn, Cd and Pb were prepared in aqueous solution by the reaction between *p*-toluenesulphonic acid and the metallic carbonates (all of analytical grade). The general reaction can be written

$$2CH_3\text{-}C_6H_4\text{-}SO_3H + MCO_3 \rightarrow M(CH_3\text{-}C_6H_4\text{-}SO_3)_2 + CO_2 + H_2O$$

M = Co, Ni, Cu, Zn, Cd, Pb.

Throughout this paper, $CH_3\text{-}C_6H_4\text{-}SO_3^-$ is written as $p\text{TS}^-$.

The solutions obtained were concentrated, filtered and allowed to crystallize in air at room temperature. The products were purified by successive recrystallizations.

The metal contents were determined by EDTA complexometry, employing NET (for Zn, Cd and Pb) and murexide (for Co, Ni and Cu) as indicators [9]. The anion determination was carried out with acid cationic exchange resins, and titration of the eluted acid with NaOH.

The results of the analyses were:

$Co(p\text{TS})_2 \cdot 6H_2O$. Found: Co^{2+}, 11.60%; $p\text{TS}^-$, 66.85%. Calc.: Co^{2+}, 11.58%; $p\text{TS}^-$, 67.22%;

$Ni(p\text{TS})_2 \cdot 6H_2O$. Found: Ni^{2+}, 11.51%; $p\text{TS}^-$, 67.16%. Calc.: Ni^{2+}, 11.53%; $p\text{TS}^-$, 67.25%;

$Cu(p\text{TS})_2 \cdot 6H_2O$. Found: Cu^{2+}, 12.32%; $p\text{TS}^-$, 66.72%. Calc.: Cu^{2+}, 12.36%; $p\text{TS}^-$, 66.61%;

$Zn(p\text{TS})_2 \cdot 6H_2O$. Found: Zn^{2+}, 12.67%; $p\text{TS}^-$, 66.38%. Calc.: Zn^{2+}, 12.68%; $p\text{TS}^-$, 66.38%;

$Cd(p\text{TS})_2 \cdot 6H_2O$. Found: Cd^{2+}, 20.07%; $p\text{TS}^-$, 59.10%. Calc.: Cd^{2+}, 19.97%; $p\text{TS}^-$, 60.80%;

$Pb(p\text{TS})_2$. Found: Pb^{2+}, 38.37%; $p\text{TS}^-$, 61.30%. Calc.: Pb^{2+}, 37.70%; $p\text{TS}^-$, 62.30%.

Instrumentation

TG and DTA experiments were recorded on a Stanton 781 system, with a heating rate of 1–5 °C min^{-1} under still air and under N_2 flow (50 ml min^{-1}). Platinum–rhodium crucibles and Al_2O_3 as reference were used. The samples, about 10 mg, were pyrolysed up to 1000 °C.

DSC studies were carried out in a Perkin–Elmer data station at a heating rate of 5 °C min^{-1}.

X-ray diffraction was performed by the powder method in a Siemens K-810 diffractometer with a D-500 goniometer using Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

All the samples studied show a very similar behaviour.

Decompositions in air atmosphere take place in three processes (Figs. 1 and 2). The first stage is the dehydration of the compounds (excluding Pb(*p*TS)$_2$ which is anhydrous), the second is the combustion of the organic compounds resulting in the metallic sulphates which finally decompose to the oxides.

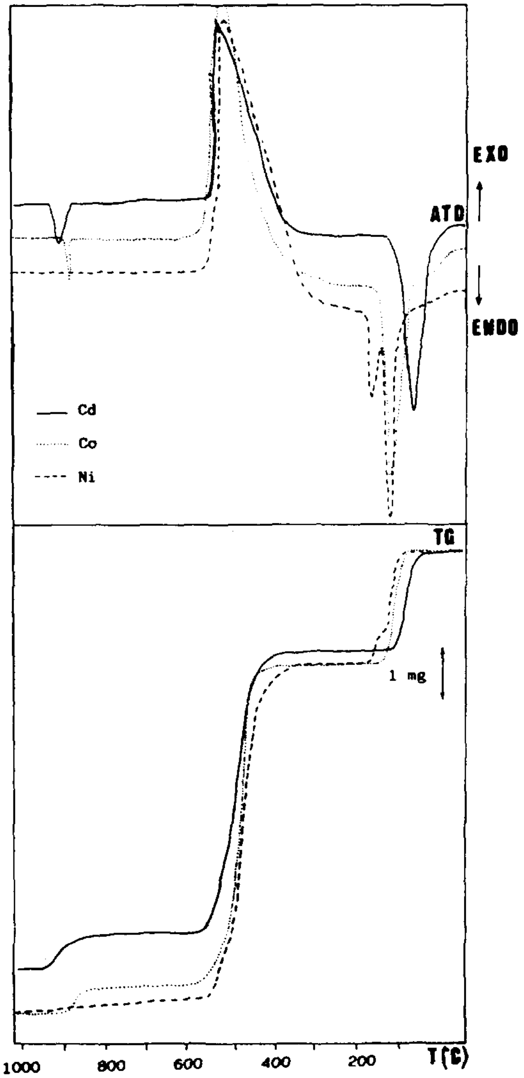

Fig. 1. TG and DTA curves for Co(*p*TS)$_2$·6H$_2$O, Ni(*p*TS)$_2$·6H$_2$ and Cd(*p*TS)$_2$·6H$_2$O in still air.

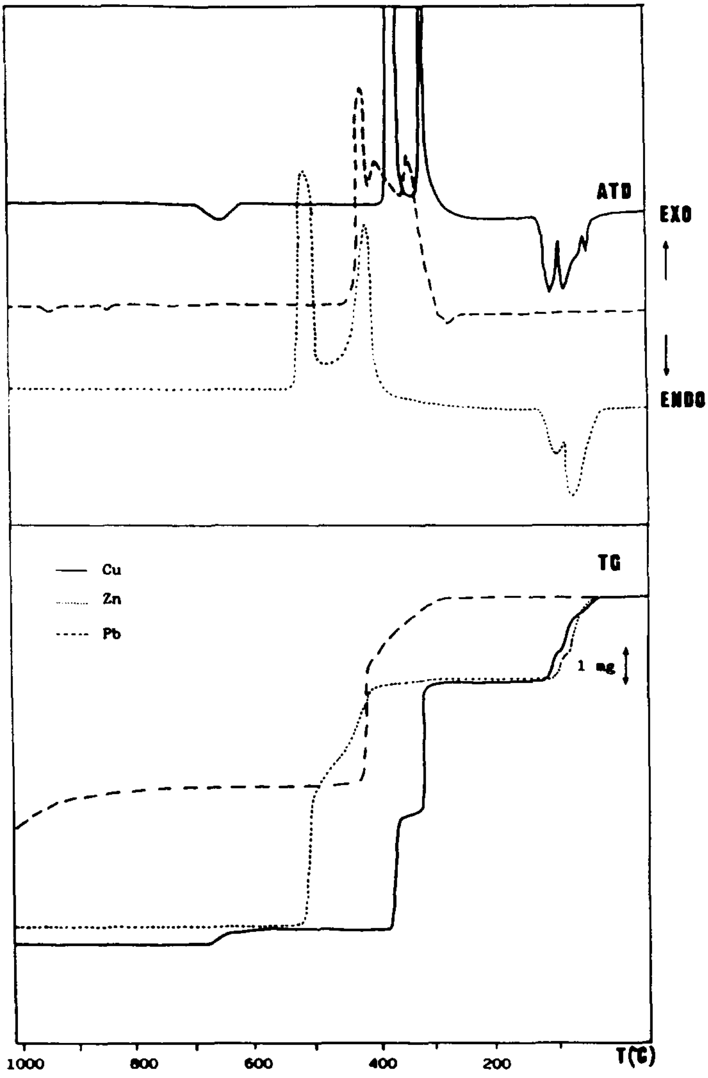

Fig. 2. TG and DTA curves for Cu(pTS)$_2$·6H$_2$O, Zn(pTS)$_2$·6H$_2$O and Pb(pTS)$_2$ in still air.

When the treatments are carried out in N_2 flow (Figs. 3 and 4), two main steps can be seen in the TG curves. Decomposition of the organic group leads to a mixture of metallic sulphides and carbon, the copper salt being an exception, with formation of copper metal during its thermal degradation.

Only the lead p-toluenesulphonate, under the conditions applied, exhibits a reversible polymorphic transition between room and decomposition temperatures; the others decompose directly in the solid state.

The water contents, determined from the TG curves, are in agreement with the values calculated by analysis. The temperature ranges of the

TABLE 1

Thermal decomposition data

Compound	Still air						Nitrogen flow				
	DTA peaks			TG steps			DTA peaks			TG steps	
	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2	T_3	T_1	T_2
$Co(pTS)_2 \cdot 6H_2O$	116	530	710	80–150	475–584	705–770	100	500/530	971	80–126	475–557
$Ni(pTS)_2 \cdot 6H_2O$	120/145	484	–	107–181	380–584	–	120/157	494/530	–	83–157	475–553
$Cu(pTS)_2 \cdot 6H_2O$	54/89/116	312/350	644	49–126	287–380	566–667	60/83/105	320/333	–	47–110	296–509
$Zn(pTS)_2 \cdot 6H_2O$	78/100	415/500	–	54–110	349–534	–	78/100	434/472	–	50–116	434–623
$Cd(pTS)_2 \cdot 6H_2O$	80	494	915	51– 93	399–557	876–976	70	557	900	35– 83	472–584
$Pb(pTS)_2$	279	341/396/419	890	–	292–442	941	279	446	881	–	410–520

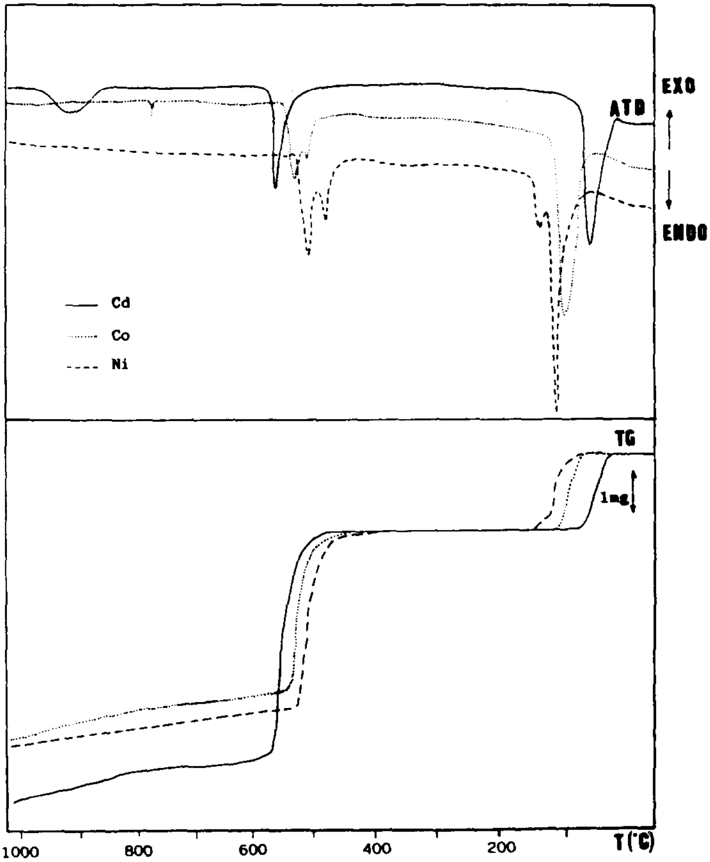

Fig. 3. TG and DTA curves for Co(pT)$_2$·6H$_2$O, Ni(pTS)$_2$·6H$_2$O and Cd(pTS)$_2$·6H$_2$O under N$_2$ flow.

decomposition reaction, in addition to the temperature of the DTA peaks, are listed in Table 1.

Dehydration

The dehydration process occurs in the same way in both air atmosphere or nitrogen flow. The weight losses during dehydration as well as the calculated values and the number of water molecules lost in each case are shown in Table 2.

All the water molecules are lost in a single step for cobalt p-toluenesulphonate hexahydrate, whose DTA curve has an endothermic effect centred on 100 °C.

In the curves for nickel and zinc p-toluenesulphonates, two successive steps can be seen. The first corresponding to the elimination of four water molecules (at 78 °C for Zn and at 120 °C for Ni), and the second (at 100 °C

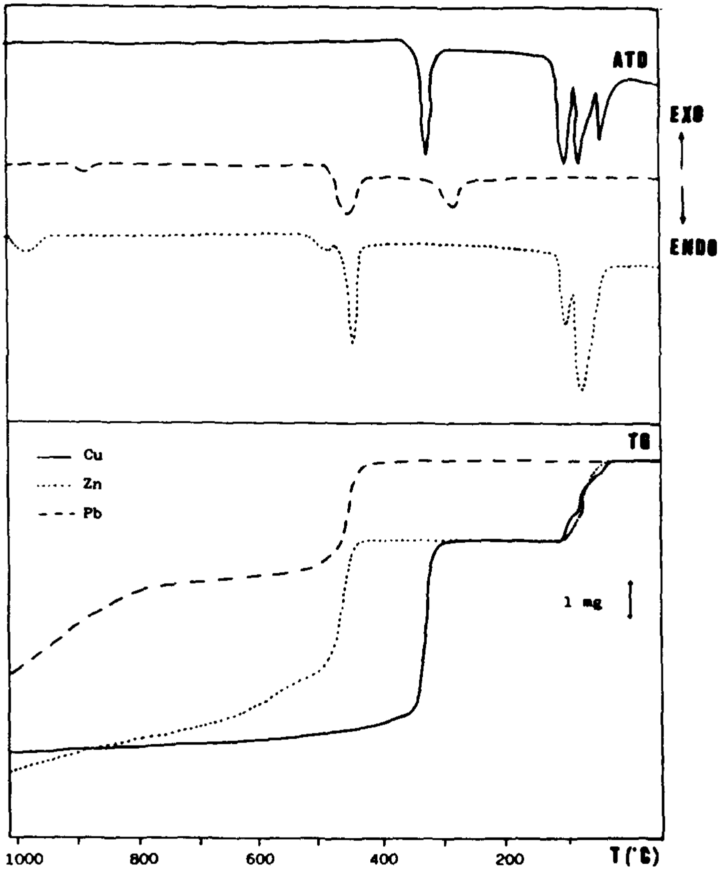

Fig. 4. TG and DTA curves for Cu(pTS)$_2$·6H$_2$O, Zn(pTS)$_2$·6H$_2$O and Pb(pTS)$_2$ under N$_2$ flow.

TABLE 2

Dehydration process

Compound	T (°C)	m_{found} (%) [a]	$m_{\text{calc.}}$ (%)	n H$_2$O	H (kJ mol^{-1})
Co(pTS)$_2$·6H$_2$O	20–100	20.86	21.20	6	41.458
Ni(pTS)$_2$·6H$_2$O	20–120	14.25	14.14	4	
	20–220	20.83	21.11	6	58.702
Cu(pTS)$_2$·6H$_2$O	20– 60	3.54	3.50	1	
	20– 80	13.76	14.01	4	
	20–105	20.86	21.01	6	58.700
Zn(pTS)$_2$·6H$_2$O	20– 80	13.74	13.96	4	
	20–100	20.91	20.94	6	51.450
Cd(pTS)$_2$·6H$_2$O	20–100	19.38	19.19	6	50.610

[a] Weight losses have been calculated as a percentage of the original sample.

for Zn and 145 °C for Ni) corresponding to loss of the two remaining water molecules. Both process are overlapping in the DTA curves.

In the TG curve of the copper salt, it can be seen that the water elimination takes place in three steps, corresponding to the loss of 1, 3 and 2

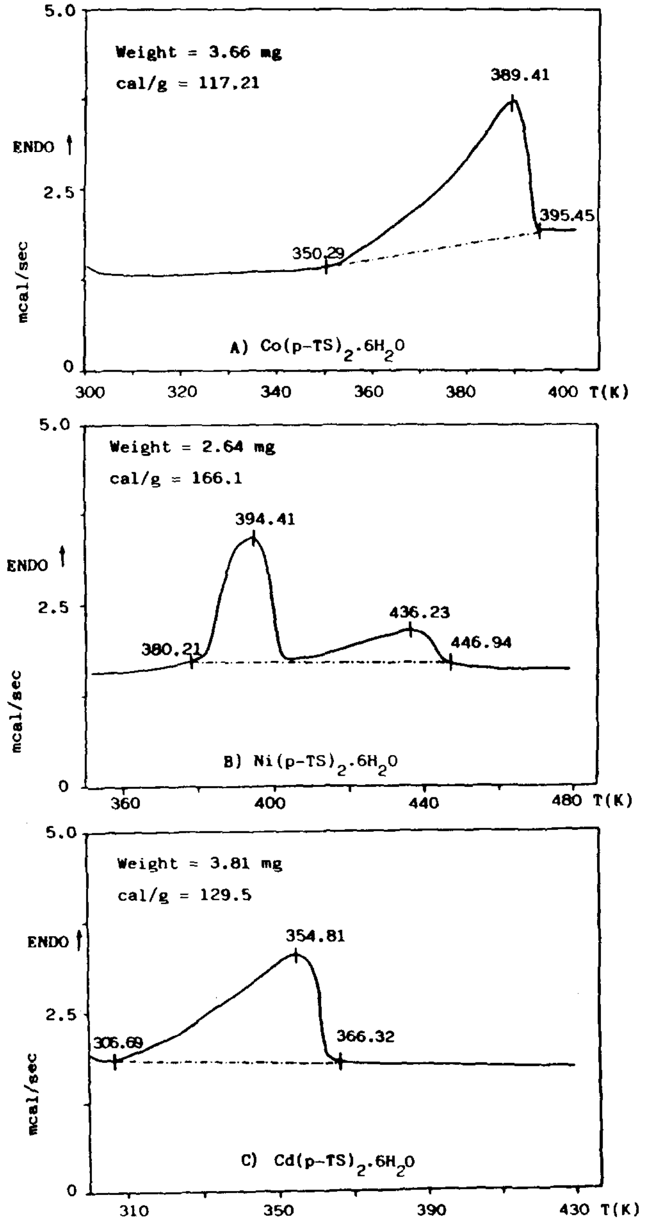

Fig. 5. DSC curves for (A) Co(pTS)$_2$·6H$_2$O, (B) Ni(pTS)$_2$·6H$_2$O, (C) Cd(pTS)$_2$·6H$_2$O, (D) Zn(pTS)$_2$·6H$_2$O and (E) Cu(pTS)$_2$·6H$_2$O.

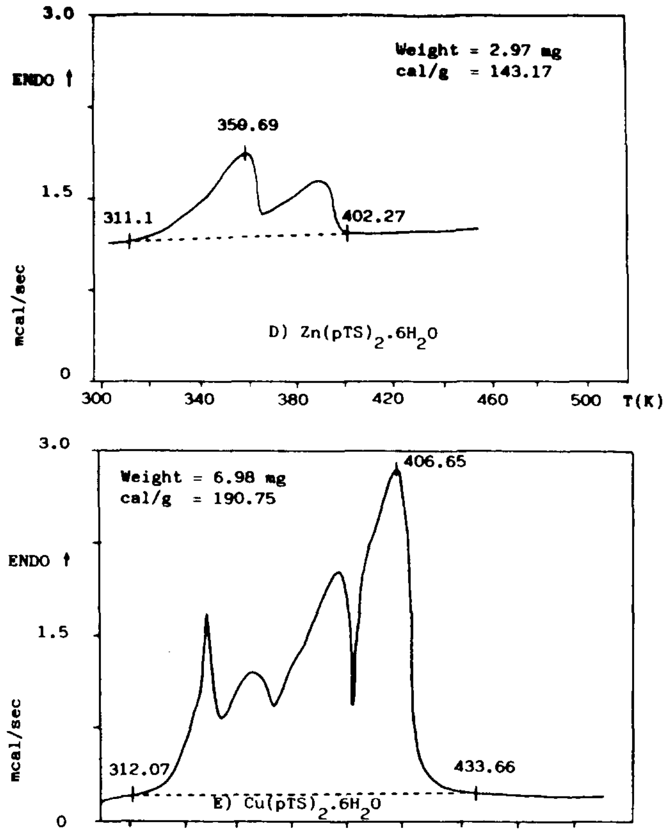

Fig. 5 (continued).

water molecules. The DTA curve shows three endothermic peaks at 60, 85 and 105 ° C respectively, which are also overlapping.

The crystal structures of cobalt [10], nickel [11], copper [12] and zinc [13] salts show that all the water molecules are in equivalent positions. However, the six water molecules of cadmium *p*-toluenesulphonate hexahydrate are lost in a single endothermic process, which takes place at 80 ° C, although structural studies [11] have shown no equivalence between them.

Figure 5 shows DSC curves obtained for the five compounds in the temperature range corresponding to dehydration. Enthalpies calculated by integration are shown in Table 2. (The value corresponds to the complete dehydration because of the overlap of peaks.)

Decomposition in air

The anhydrous salts are stable up to about 300–400 ° C. At those temperatures, the DTA curves show a big exothermic effect corresponding to

TABLE 3

Decomposition in still air

Compound	m [a] (%)		T final (°C)	Residue
	Found	Calculated		
Co(pTS)$_2$·6H$_2$O	83.57	84.24	1000	CoO
Ni(pTS)$_2$·6H$_2$O	84.73	85.32	1000	NiO
Cu(pTS)$_2$·6H$_2$O	79.94	79.54	1000	CuO
Zn(pTS)$_2$·6H$_2$O	82.48	84.22	1000	ZnO
Cd(pTS)$_2$·6H$_2$O	77.31	77.18	1000	CdO
Pb(pTS)$_2$	61.80	59.40	800	PbO

[a] Weight losses have been calculated as a percentage of the original sample.

combustion of the organic group. The residues found at 600 °C were identified by X-ray diffraction. The reactions are as follows

$$\mathrm{Co}(p\mathrm{TS})_2 \rightarrow x\mathrm{CoSO_4} + y\mathrm{Co_3O_4}$$

$$\mathrm{Ni}(p\mathrm{TS})_2 \rightarrow \mathrm{NiO}$$

$$\mathrm{Cu}(p\mathrm{TS})_2 \rightarrow \tfrac{1}{2}x\mathrm{Cu_2(SO_4)O} + y\mathrm{CuO}$$

$$\mathrm{Zn}(p\mathrm{TS})_2 \rightarrow \mathrm{ZnO}$$

$$\mathrm{Cd}(p\mathrm{TS})_2 \rightarrow 1/3\mathrm{CdSO_4}\cdot 2\mathrm{CdO}$$

$$\mathrm{Pb}(p\mathrm{TS})_2 \rightarrow x\mathrm{PbSO_4}\cdot\mathrm{PbO} + y\mathrm{PbO}$$

The decomposition behaviour is probably similar to that of trivalent metallic methanesulphonates in which oxosalts are also formed [14].

For Zn and Ni p-toluenesulphonates, the oxide is formed, probably due to the loss of p-toluenesulphonic anhydride. However, gases formed during the decomposition process could not be analysed.

Where oxosalts are formed, there is another endothermic process resulting in the corresponding oxide.

Weight losses, experimental and calculated, and the decomposition temperatures are presented in Table 3.

Cobalt sulphate (ASTM 11-125) decomposition takes place at 730 °C and a partial weight loss of 2.89% is found.

Copper oxosulphate (ASTM 13-189) decomposition is registered on the DTA curve as an endothermic process, corresponding to CuO formation and centred at 644 °C. The final residue was identified as CuO (ASTM 5-0661) by X-ray diffraction.

In the cadmium salt, this process (oxosalt → oxide) occurs at 915 °C. Oxosulphate (ASTM 26-238) is transformed into oxide (ASTM 5-0640) with a partial mass loss of 5.88%.

A polymorphic transformation at 846 °C is seen in the DTA curve for $\mathrm{PbSO_4}\cdot\mathrm{PbO}$ (ASTM 6-0276), whose melting and decomposition to the oxide are observed at 890 °C.

Thus, the final residues of the thermal treatments up to 1000 °C in air atmosphere were identified as the corresponding metallic oxides.

Decomposition in nitrogen flow

When the experiments were carried out in an inert atmosphere, the decomposition temperatures were found to be very close to those in air atmosphere (see Table 4).

The decomposition of anhydrous cobalt *p*-toluenesulphonate occurs between 475 and 560 °C. In this temperature range, two overlapping endothermic processes are recorded, leading to a mixture of α-$CoSO_4$ (ASTM 11-125), Co_9S_8 (ASTM 19-364), CoO (ASTM 9-402) and C (ASTM 26-1078). At 740 °C, another endothermic effect is produced. This is due to α-$CoSO_4$ decomposition. At 1000 °C, the residue is a mixture of undetermined ratio of Co_9S_8 (ASTM 19-364), CoO (ASTM 9-402) and C (ASTM 26-1078).

Anhydrous nickel *p*-toluenesulphonate is stable up to 475 °C. As with the cobalt salt, two endothermic effects are shown on the DTA curve. The residue at 700 °C was identified as NiO (ASTM 4-0835) and Ni_6S_7 (ASTM 14-275).

Decomposition of the anhydrous copper salt takes place at 290 °C. This is the starting point for the organic group decomposition. Two steps can be clearly seen on the TG curve, corresponding to two endothermic effects on the DTA curve centred at 320 and 333 °C respectively. The final degradation product was Cu (ASTM 4-0836) with traces of carbon black.

Zinc *p*-toluenesulphonate is stable up to 430 °C. Under the conditions applied, two weight losses occur but no intermediate phase could be isolated. Both steps can be seen on the DTA curve as two endothermic peaks at 434 and 472 °C respectively. Because of the reducing environment created by degradation of the organic group in N_2 flow, and due to its high stability, ZnS (wurtzite, ASTM 10-434) is obtained as the final residue. At 972 °C, the DTA curve shows an endothermic process probably due to transformation

TABLE 4

Decomposition in nitrogen flow

Compound	*T* decomposition (°C)	% found [a]	Residue at 1000 °C
$Co(pTS)_2 \cdot 6H_2O$	475	66.51	$CoO + Co_9S_8 + C$
$Ni(pTS)_2 \cdot 6H_2O$	475	71.26	$NiO + Ni_7S_6 + C$
$Cu(pTS)_2 \cdot 6H_2O$	296	76.33	Cu + C
$Zn(pTS)_2 \cdot 6H_2O$	434	80.34	ZnS
$Cd(pTS)_2 \cdot 6H_2O$	472	77.93	C
$Pb(pTS)_2$	415	59.53	Amorphous (XRD)

[a] Weight losses have been calculated as a percentage of the original sample.

of ZnS (blende) to ZnS (wurtzite) which for the pure blende takes place at 1020 °C, though impurities can lead to lower transition temperatures [15].

In the cadmium salt, an endothermic transformation occurs between 540 and 560 °C. This, corresponding to the degradation of the organic compound results in cadmium sulphide (ASTM 6-0314) and carbon (ASTM 26-1078). Over 600 °C, a continuous weight loss is registered on the TG curve, and a slight endothermic peak can be seen on the DTA curve at 900 °C. This is due to sublimation of CdS which is produced at 980 °C in N_2 [16].

Before the decomposition of the lead *p*-toluenesulphonate, a reversible endothermic transformation occurs, at 279 °C. This process has been seen before for other salts with similar characteristics [5]. Salt decomposition takes place between 410 and 520 °C, and the final residue was identified by X-ray diffraction as PbS (ASTM 5-0579) with traces of carbon black.

ACKNOWLEDGEMENTS

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