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Synthesis and thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) *m*-benzenedisulphonates

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Abstract

The thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) *m*-benzenedisulphonates have been studied by TG, DTA and DSC techniques in a atmosphere of air and under nitrogen flow. Co(II), Ni(II), Cu(II) and Zn(II) benzenedisulphonates contain six molecules of crystallization water, the Cd(II) salt contains four, and the Pb(II) salt has two. Dehydration enthalpies were measured from the DSC curves and the degradation products of the anhydrous salts were identified by X-ray diffraction.

INTRODUCTION

Heavy and transition metallic salts of sulphonic acids are not well characterized, especially with respect to their thermal behaviour. Charbonnier [1] has studied the thermal decomposition of cobalt alkanesulphonates. Meisel et al. [2] reported on the thermal analysis of the thermal decomposition of some transition metal benzenesulphonates. Recently, we have initiated a study of the thermal decomposition of different metallic sulphonates: the thermal degradation of β-naphthalenesulphonic and 1,5-naphthalenedisulphonic acids, and their corresponding copper salts [3]; the thermal behaviour of cobalt, copper and zinc methanesulphonates [4]; and the thermal decomposition of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) *p*-toluenesulphonates [5].

Here we report the synthesis, characterization and thermal decomposi-

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tion of benzenedisulphonates (BdS) of the transition metal cations Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II), as a part of a larger programme investigating the general properties and syntheses of several metallic sulphonates, that has been carried out over the last five years [6–9].

EXPERIMENTAL

Synthesis

It was first necessary to prepare the benzenedisulphonic acid from Na_2BdS. The salt was converted to the acid by ion exchange and the acid was purified by neutralization of the acid with $Ba(OH)_2$, thus removing almost all the SO_4^{2-} ions. The BaBdS was then recrystallized and converted to acid by ion exchange when it was required for the preparation of another salt. The pure salts and acid obtained contained no SO_4^{2-} impurity [10, 11].

The metallic *m*-BdS salts were prepared in aqueous solution by reaction between *m*-BdS acid and the metallic carbonates (all of analytical grade). The general reaction can be written

$$C_6H_4(SO_3H)_2 + MCO_3 \rightarrow MC_6H_4(SO_3H)_2 \cdot nH_2O + CO_2 + H_2O$$

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

$BdS = C_6H_4(SO_3^-)_2$

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. The anion determination was carried out with acid cationic exchange resins and titration of the eluted acid with NaOH. Carbon and

TABLE 1

Elemental analyses (%) of the metal *m*-benzenedisulphonate complexes

	Metal		BdS^{2-}		Carbon		Hydrogen	
Complex	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$CoBdS \cdot 6H_2O$	14.75	14.62	59.8	58.6	17.35	17.99	3.68	4.46
$NiBdS \cdot 6H_2O$	14.59	14.57	60.0	58.6	17.99	17.87	3.68	4.47
$CuBdS \cdot 6H_2O$	15.82	15.55	59.0	57.8	17.86	17.62	3.81	3.91
$ZNBdS \cdot 6H_2O$	15.85	15.96	60.2	57.6	17.93	17.58	3.62	3.91
$CdBdS \cdot 4H_2O$	26.73	26.72	57.4	56.1	17.31	17.12	2.52	2.85
$PbBdS \cdot 2H_2O$	43.80	43.24	51.2	49.2	15.31	15.02	1.39	1.67

hydrogen elemental analyses were made on a Perkin-Elmer model 2400 CHN analyser.

The results of the analyses are shown in Table 1.

Instrumentation

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

DSC studies were carried out in a Perkin-Elmer DSC-2C with a Perkin-Elmer 3600 data station, at a heating rate of 10°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 Kα radiation.

RESULTS AND DISCUSSION

All the samples studied show very similar behaviour.

The decompositions in air take place in three processes (Fig. 1). The first stage is the dehydration of the compounds, the second is the anion decomposition resulting, in general, in the metallic sulphates which finally decompose to the oxides.

When the decompositions were carried out in N_2 flow (Fig. 2), two main steps can be seen in the TG curves. The first, as in air, is due to the dehydration of the salt; then the decomposition of the anion leads to a mixture of metallic sulphides and carbon. The copper salt is an exception, with copper metal being formed during its thermal degradation.

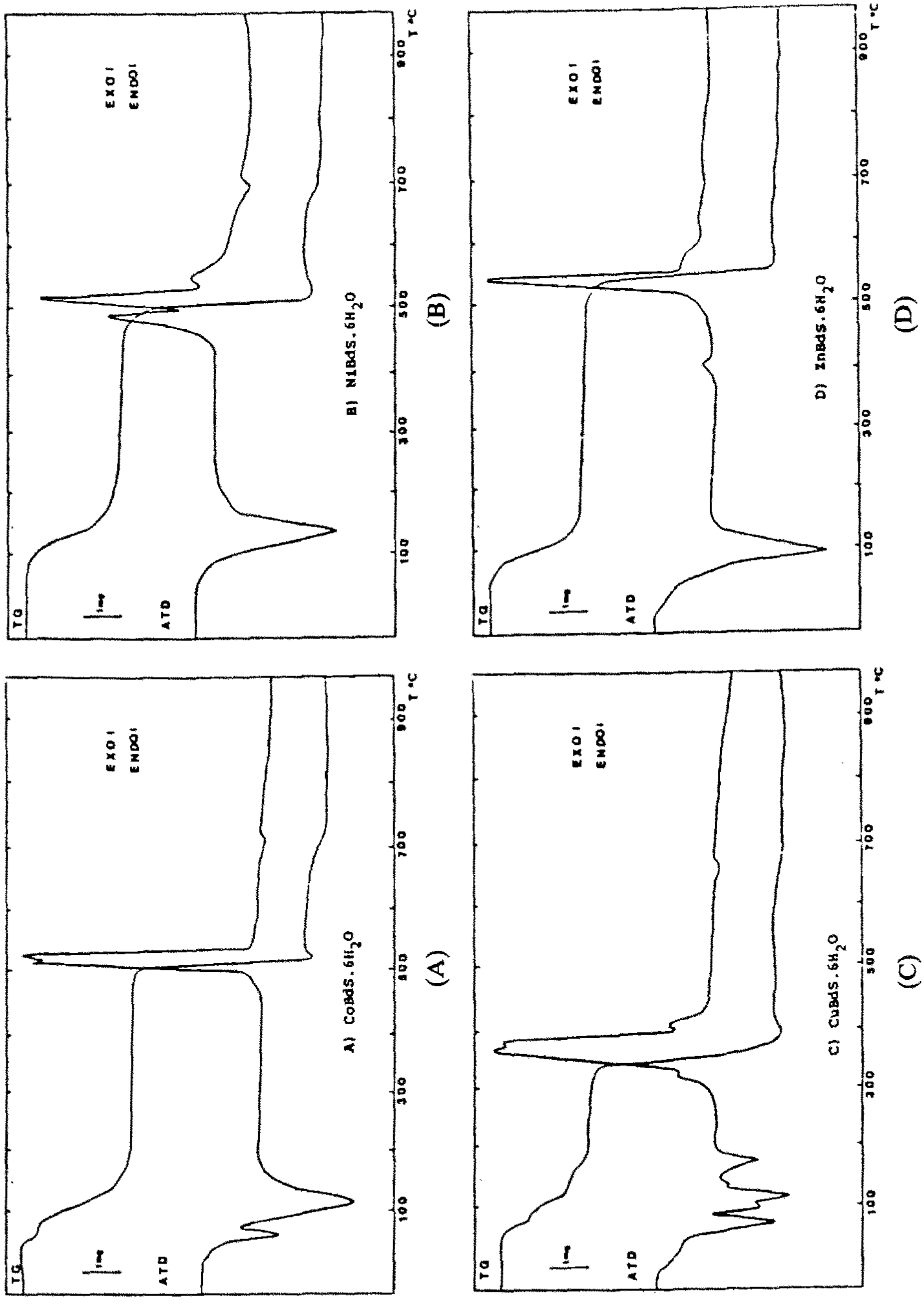
The water content determined from the TG curves agrees with the values calculated by analysis.

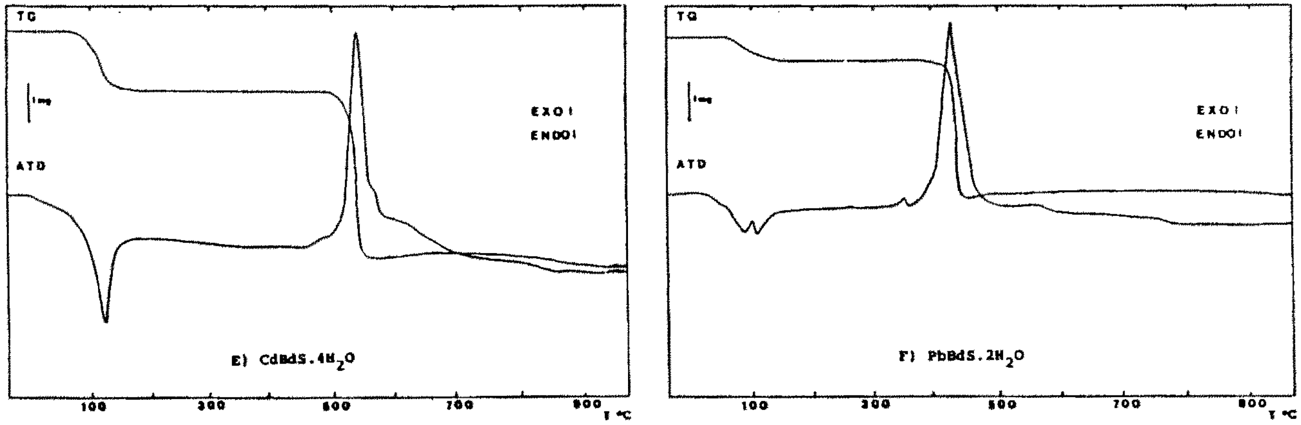
The temperature ranges of the decomposition reactions, in addition to the temperature of the DTA peaks, are listed in Table 2.

Dehydration

The dehydration process occurs in the same way in both static air and flowing nitrogen atmospheres. The weight losses found during dehydration, as well as the calculated values and number of water molecules lost in each case, are shown in Table 3.

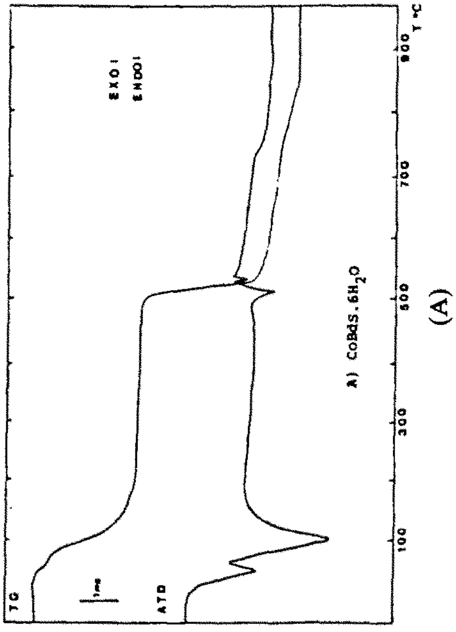
The curves for the nickel, zinc and cadmium salts show a single step corresponding, respectively, to the loss of six, six and four water molecules. However, the cobalt and lead compounds show two successive steps. For CoBdS, the first corresponds to the elimination of one water molecule, the second corresponding to the loss of the five remaining water molecules. In PbBdS, each of the two steps corresponds to loss of a single


TG
ATD
EXO↑
ENDO↓
T °C
100
300
500
700
900
A) CoBdS.6H$_2$O
(A)
B) NiBdS.6H$_2$O
(B)
C) CuBdS.6H$_2$O
(C)
D) ZnBdS.6H$_2$O
(D)

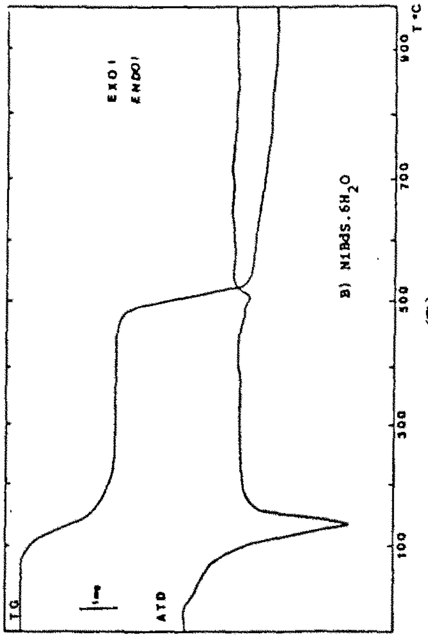


(E) (F)

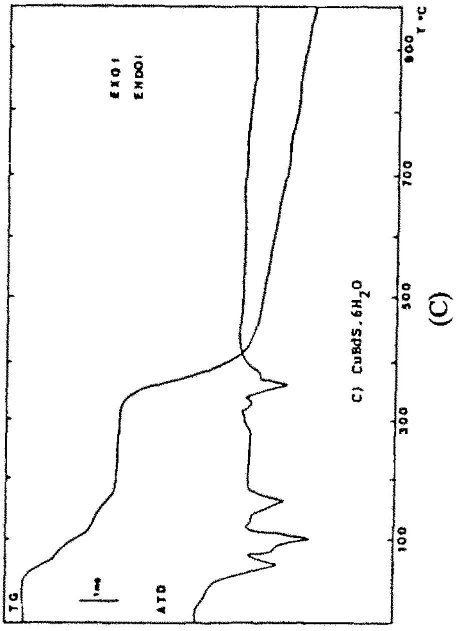
Fig. 1. TG and DTA curves for (A) CoBdS · $6H_2O$, (B) NiBdS · $6H_2O$, (C) CuNdS · $6H_2O$, (D) ZnBdS · $6H_2O$, (E) CdBdS · $4H_2O$, and (F) PbBdS · $2H_2O$ in static air.


TG
1mg
ATD
EXO↑
ENDO↓
A) CoBdS.6H₂O
100
300
500
700
900
T °C

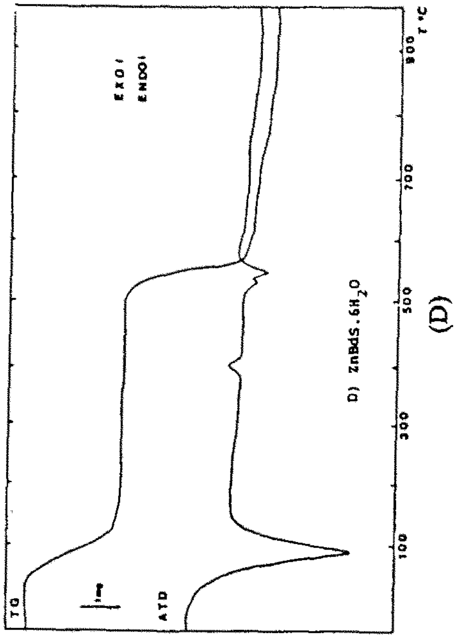
(A)


TG
1mg
ATD
EXO↑
ENDO↓
B) NiBdS.6H₂O
100
300
500
700
900
T °C

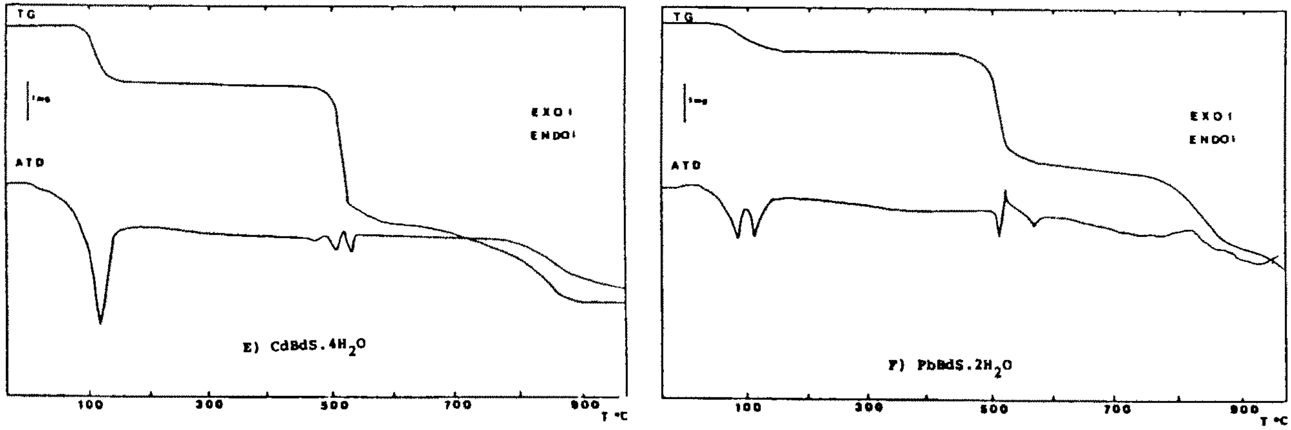
(B)


TG
1mg
ATD
EXO↑
ENDO↓
C) CuBdS.6H₂O
100
300
500
700
900
T °C

(C)


TG
1mg
ATD
EXO↑
ENDO↓
D) ZnBdS.6H₂O
100
300
500
700
900
T °C

(D)



(E)

(F)

Fig. 2. TG and DTA curves for (A) $CoBdS \cdot 6H_2O$, (B) $NiBdS \cdot 6H_2O$, (C) $CuBdS \cdot 6H_2O$, (D) $ZnBdS \cdot 6H_2O$, (E) $CdBdS \cdot 4H_2O$, and (F) $PbBdS \cdot 2H_2O$ under flowing nitrogen.

TABLE 2

Thermal decomposition data (°C)

Compound		Still air		Flowing nitrogen	
		DTA peaks	TG steps	DTA peaks	TG steps
$CoBdS \cdot 6H_2O$	T_1	58, 108	44–178	61, 108	45–177
	T_2	521	468–531	523, 541	475–575
	T_3	718	628–730	–	–
$NiBdS \cdot 6H_2O$	T_1	122	89–300	136	66–235
	T_2	530	472–570	514	459–564
$CuBdS \cdot 6H_2O$	T_1	78, 117, 174	50–207	66, 107, 164	20–211
	T_2	357	312–424	360	306–479
	T_3	668	606–681	–	–
$ZnBdS \cdot 6H_2O$	T_1	101	51–177	101	51–178
	T_2	548	491–593	548	494–593
$CdBdS \cdot 4H_2O$	T_1	120	66–184	120	51–169
	T_2	552	503–577	512, 538	490–578
	T_3	850	755–880	–	–
$PbBdS \cdot 2H_2O$	T_1	97, 120	58–153	94, 108	46–151
	T_2	456	358–484	532	423–602

TABLE 3

Dehydration processes

Compound	T (°C)	m (%) [a]		$n H_2O$	H (kJ mol^{-1})
$CoBdS \cdot 6H_2O$	20–66	Found	4.23	1	
		Calc.	4.46		
	20–178	Found	27.42	6	70.500
		Calc.	26.79		
$NiBdS \cdot 6H_2O$	20–300	Found	26.45	6	75.019
		Calc.	26.80		
$CuBdS \cdot 6H_2O$	20–90	Found	8.30	2	
		Calc.	8.81		
	20–132	Found	18.01	4	
		Calc.	17.62		
	20–207	Found	25.35	6	74.266
		Calc.	26.43		
$ZnBdS \cdot 6H_2O$	20–177	Found	25.52	6	76.316
		Calc.	26.38		
$CdBdS \cdot 4H_2O$	20–184	Found	16.84	4	68.073
		Calc.	17.12		
$PbBdS \cdot 2H_2O$	20–110	Found	3.80	1	
		Calc.	3.75		
	20–153	Found	6.85	2	73.760
		Calc.	7.51		

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

water molecule. Finally, the copper salt shows three successive steps corresponding to the elimination of two water molecules in each step.

Figure 3 show the DSC curves obtained for the six compounds in the temperature range corresponding to water elimination. Enthalpies calculated by integration are shown in Table 3. (The value corresponds to the complete dehydration because of the overlap of the peaks.)

Decomposition in air

The anhydrous salts are stable up to about 300–400°C. At these temperatures, the DTA curves show a large exothermic effect corresponding to combustion of the organic group. The residues found were identified by X-ray diffraction. The reactions are

$$\mathrm{CoBdS} \xrightarrow{468\text{–}531^\circ\mathrm{C}} \tfrac{1}{2}\mathrm{CoSO_4} + \tfrac{1}{6}\mathrm{Co_3O_4} \xrightarrow{628\text{–}730^\circ\mathrm{C}} \tfrac{1}{3}\mathrm{Co_3O_4}$$

$$\mathrm{NiBdS} \xrightarrow{472\text{–}570^\circ\mathrm{C}} \mathrm{NiO}$$

$$\mathrm{CuBdS} \xrightarrow{312\text{–}424^\circ\mathrm{C}} \tfrac{1}{5}\mathrm{CuSO_4} + \tfrac{4}{5}\mathrm{CuO} \xrightarrow{606\text{–}681^\circ\mathrm{C}} \mathrm{CuO}$$

$$\mathrm{ZnBdS} \xrightarrow{491\text{–}593^\circ\mathrm{C}} \mathrm{ZnO}$$

$$\mathrm{CdBdS} \xrightarrow{503\text{–}577^\circ\mathrm{C}} \tfrac{1}{9}\mathrm{Cd_3O_2(SO_4)} + \tfrac{2}{3}\mathrm{CdO} \xrightarrow{755\text{–}880^\circ\mathrm{C}} \mathrm{CdO}$$

$$\mathrm{PbBDS} \xrightarrow{358\text{–}484^\circ\mathrm{C}} \tfrac{1}{2}\mathrm{Pb_2O(SO_4)}$$

The experimental and calculated weight losses, and the temperatures at which the residues were identified, are presented in Table 4.

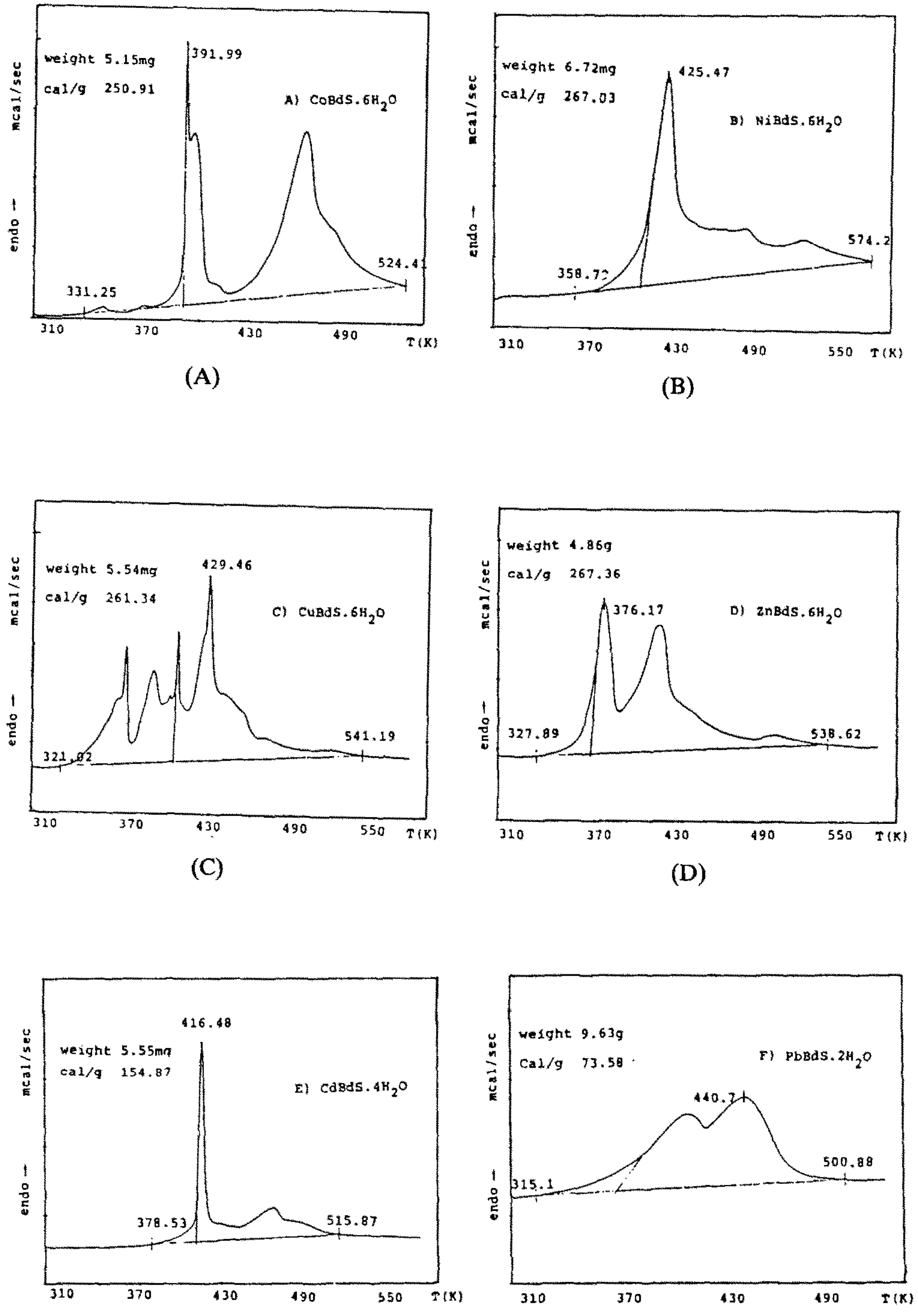
In Ni(II) and Zn(II) benzenedisulphonates, the oxide is formed (NiO, ASTM 4-0835; ZnO, ASTM 5-664).

Where sulphates (or oxosulphates) are formed, CoBdS ($\mathrm{CoSO_4}$, ASTM 14-309), CuBdS ($\mathrm{CuSO_4}$), ASTM 15-775), CdBdS ($\mathrm{Cd_3O_2(SO_4)}$, ASTM 32-140), PbBdS ($\mathrm{Pb_2O(SO_4)}$, ASTM 6-0276), there generally follows another endothermic process resulting in the corresponding oxide ($\mathrm{Co_3O_4}$, ASTM 9-419, CuO, ASTM 5-0661 and CdO, ASTM 5-0640).

Decomposition in nitrogen flow

The decomposition temperatures when the experiments were carried out in an inert atmosphere, were found to be very close to those in air atmosphere (see Table 5).

Anhydrous cobalt benzenedisulphonate is stable up to 475°C. In the 475–575°C temperature range, two overlapping endothermic processes are



(A) (B)

(C) (D)

(E) (F)

Fig. 3. DSC curves for (A) CoBdS · $6H_2O$, (B) NiBdS · $6H_2O$, (C) CuBdS · $6H_2O$, (D) ZnBdS · $6H_2O$, (E) CdBdS · $4H_2O$, and (F) PbBdS · $2H_2O$.

TABLE 4

Decomposition in still air

Compound	m (%)[a]		T (°C)	Residue
	Found	Calc.		
$CoBdS \cdot 6H_2O$	74.80	74.79	550	$CoSO_4 + Co_3O_4$
	80.04	80.09	1000	Co_3O_4
$NiBdS \cdot 6H_2O$	81.16	81.45	1000	NiO
$CuBdS \cdot 6H_2O$	76.27	76.61	450	$CuSO_4 + CuO$
	78.96	80.53	1000	CuO
$ZnBdS \cdot 6H_2O$	79.08	80.12	1000	ZnO
$CdBdS \cdot 4H_2O$	62.32	63.13	600	$Cd_3O_2(SO_4) + CdO$
	66.45	69.47	1000	CdO
$PbBdS \cdot 2H_2O$	49.21	50.08	900	$Pb_2O(SO_4)$

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

registered, but only one step can be seen on the TG curve. The final degradation product at 1000°C is Co_9S_8 (ASTM 19-364).

Nickel(II) benzenedisulphonate is stable up to 459°C. As with the cobalt salt, two endothermic effects are shown on the DTA curve, with only one step on the TG curve. The residue at 1000°C was identified as Ni_3S_2 (ASTM 42-0778).

Anhydrous copper benzenedisulphonate is stable up to 306°C. In the range 306–479°C, one step can be seen on the TG curve, corresponding to one endothermic effect on the DTA curve centred at 360°C. The final residue of the thermal treatment is copper metal (ASTM 4-0836) with traces of black carbon.

Decomposition of zinc benzenedisulphonate takes place at 494°C. This is the starting point for the decomposition of the organic group. Two overlapping endothermic effects on the DTA curve correspond to one step

TABLE 5

Decomposition in flowing nitrogen

Compound	$T_{Decomposition}$ (°C)	m_{found} (%)[a]	Residue at 1000°C
$CoBdS \cdot 6H_2O$	475–575	78.32	Co_9S_8
$NiBdS \cdot 6H_2O$	459–564	80.13	Ni_3S_2
$CuBdS \cdot 6H_2O$	306–479	84.44	Cu + C
$ZnBdS \cdot 6H_2O$	494–593	76.20	ZnS
$CdBdS \cdot 4H_2O$	490–578	65.66	CdS
$PbBdS \cdot 2H_2O$	423–600	50.08	PbS

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

on the TG curve. ZnS (wurtzite, ASTM 10-432) is obtained as the final residue at 1000°C.

In the cadmium salt, an endothermic transformation occurs between 490 and 578°C. In the TG curve, only one step appears in this temperature range. The final residue was CdS (ASTM 6-0314).

The process of thermal decomposition of the lead benzenedisulphonate was similar to that of the other salts. Salt decomposition takes place between 423 and 600°C and the residue found was identified as PbS (ASTM 5-592).

ACKNOWLEDGEMENT

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