

# On the thermal stability and non-isothermal decomposition kinetics of some coordination compounds of cobalt, nickel and copper with a $\beta$ -dicarbonylic compound and 4-benzoylpyridine or 4,4'-dipyridyl as ligands

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## Abstract

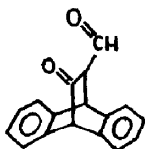
The results of an investigation concerning the thermal behaviour of some coordination compounds of cobalt, nickel and copper are reported.

## INTRODUCTION

In a previous paper [1], we presented the results concerning the thermal stability and non-isothermal decomposition kinetics of some coordination compounds of general formula  $[M(\text{acac})_2(4\text{-bzpy})_2]$  where M is Co or Ni, acac is acetylacetonate and 4-bzpy is 4-benzoylpyridine. In this paper we report new results of our continuing investigation into coordination compounds in which, instead of acetylacetonate, the ligand was the  $\beta$ -dicarbonylic compound 9,10-dihydro-9,10-ethano-12-hydroxymethylene anthracene-11-one, see Form 1. This compound was synthesised by a method described elsewhere [2].

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Form 1. 9,10-Dihydro-9,10-ethano-12-hydroxymethylene anthracene-11-one.

## EXPERIMENTAL

Powders of the following compounds (synthesised and analysed according to methods described in refs. 3 and 4) were used:  $[ML_2](H_2O)_x$ , where M is Co, Ni ( $x = 2$ ), and Cu ( $x = 0$ );  $[ML_2(4\text{-bzpy})_2]$  where M is Co, Ni, Cu;  $[ML_2(4,4'\text{-dipy})]$  where M is Co, Ni, Cu and 4,4'-dipy represents 4,4'-dipyridyl.

The heating curves were recorded using a Q-1500 D derivatograph (MOM Budapest, Paulik–Paulik–Erdey-type) in static air atmosphere, at heating rates between 2.5 and 10  $K\ min^{-1}$  in the range 20–1000°C.

A Dron 3 X-ray diffractometer was used to characterise the crystalline state of these compounds. The diffractograms were recorded using cobalt  $K\alpha$  radiation.

The identification of some reaction intermediates was made using a double-beam Specord UV–VIS spectrometer and a 70-SE.VG. Analytica mass spectrometer. Other intermediates were determined from the derivatographic data.

The experimental data were analysed according to the following integral methods: the Coats–Redfern [5], the Flynn–Wall for constant heating rate ( $\beta = \text{const.}$ ) [6], the Doyle–Gorbachev [7] and the Urbanovici–Segal [8] which is a modified form of the Coats–Redfern method.

A BASIC program was used for automatic data processing [9]. In addition to the evaluation of the non-isothermal kinetic parameters, this program allows the TG curves to be regenerated in  $(\alpha, \theta/^\circ C)$  coordinates; the experimental points can then be positioned on these curves. If these points lie on the regenerated curve, we can confirm the accuracy of the measurements and verify the correctness of the approximations on which the applied integral methods are based.

## RESULTS AND DISCUSSION

### *The thermal decomposition of the ligand*

As shown in Fig. 1, the first significant change in the ligand is its melting which is recorded as an endothermic peak on the DTA curve located at 180°C for  $\beta = 10\ K\ min^{-1}$ . This is followed by two overlapping decomposition steps, the DTG peak of the second one being located at 320°C. Because

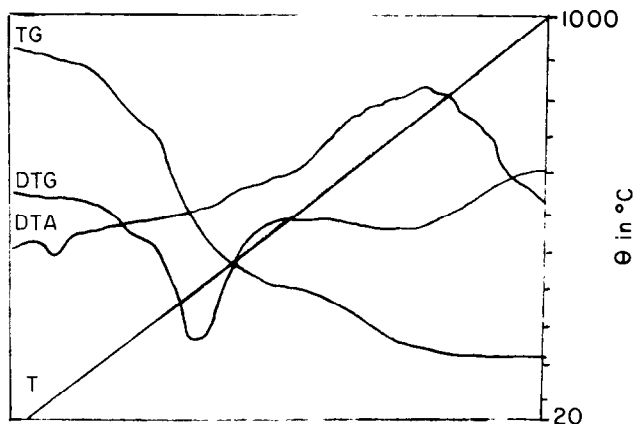


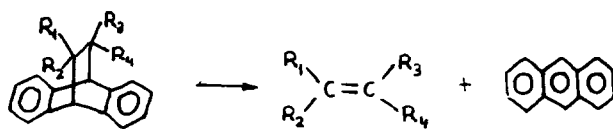
Fig. 1. Derivatogram of the dicarbonylic ligand.

the weight loss corresponds to one molecule of anthracene, the overall reaction can be described by the equation



where R is an oxygenated reaction product.

The UV–VIS spectra of the evolved gas confirmed that anthracene was a reaction product. The generation of anthracene is most probably due to a retro-diene reaction which is frequently met in such cases [10–14], see Form 2.



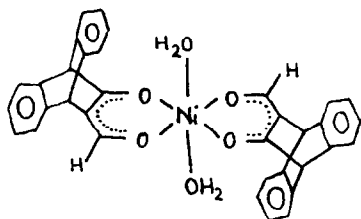
Form 2. The generation of anthracene by a retro-diene reaction.

At higher temperatures, a new exothermic decomposition step (oxidative degradation) occurs, with the DTG peak being located at 743°C. The final reaction product is a polymeric mass, insoluble in water and organic solvents.

#### *The thermal decomposition of $NiL_2(H_2O)_2$*

The X-ray diffraction data indicate that the powdered samples produce amorphous materials following thermal decomposition.

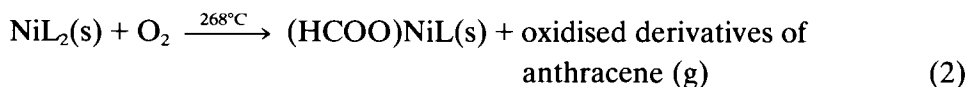
The compound is a trans complex, with both the kelatic ligands and the



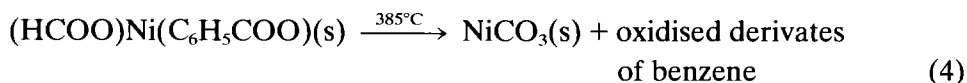
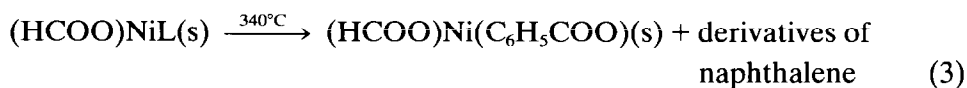
Form 3. The structure of  $\text{NiL}_2(\text{H}_2\text{O})_2$ .

metallic ion in the equatorial plane, and with the water molecules as axial ligands, see Form 3. The derivatograms of this compound show that the loss of water molecules extends over quite a large temperature range (20–200°C). At higher temperatures, there are many oxidative decomposition steps for the ligands, at all the applied heating rates. The final decomposition product is NiO. There are differences in the heating curves (TG, DTG, DTA) recorded at  $\beta = 10 \text{ K min}^{-1}$  and  $\beta = 2.5 \text{ K min}^{-1}$ .

At  $\beta = 10 \text{ K min}^{-1}$ , the following decomposition steps were detected:



corresponding to a weight loss of 48%. (The temperatures written above the arrows correspond to the maximum reaction rate at the peak of the DTG curve and can be conventionally considered as the reaction temperatures.) As mentioned above, the release of anthracene, or of an oxidised product of anthracene, could occur via a retro-diene reaction



which occurs with 15% weight loss. Then



which occurs with 11.4% weight loss.

At  $\beta = 2.5 \text{ K min}^{-1}$ , the derivatograms record two decomposition steps corresponding to 70.2% and 29.7% weight loss.

We recognise that none of these decomposition steps can be analysed kinetically.

TABLE 1

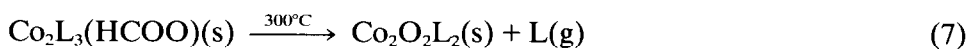
Intensities  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  of  $\text{CoL}_2(\text{H}_2\text{O})_2$ 

Line	$I$	$d/\text{Å}$	$l/\text{Å}$
1	9	13.28	
2	49	11.46	
3	40	10.02	
4	53	8.87	
5	9	7.92	
6	22	7.30	
7	10	6.99	
8	9	6.64	
9	100	6.20	110
10	76	5.54	
11	32	4.01	
12	11	4.69	
13	10	4.56	
14	27	4.42	
15	12	4.24	
16	11	4.08	
17	11	4.01	
18	12	3.78	
19	10	3.61	
20	19	3.49	
21	14	3.17	
22	11	3.10	
23	18	2.88	

*The thermal decomposition of  $\text{CoL}_2(\text{H}_2\text{O})_2$* 

Table 1 lists the X-ray diffraction data for this compound, comprising the intensities of the diffraction lines  $I$ , the interplanar distances  $d$  and the mean crystallite size  $l$ , relative to the most intense line, calculated by Scherrer's formula [15].

As described for the nickel compound, the water molecules are released up to 200°C. At  $\beta = 7.85 \text{ K min}^{-1}$ , the following overlapping steps corresponding to weight losses of 23.5% and 25.3%, respectively probably occur, with the release of one molecule of ligand from polymeric forms.



At higher temperatures, a decomposition step with 40.4% weight loss

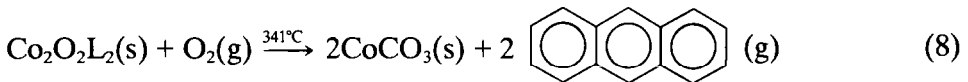
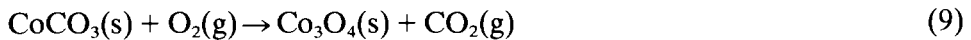
TABLE 2

Values of the non-isothermal kinetic parameters of reaction (6) at  $\beta = 7.85 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	2.6	2.6	2.6	2.5
$A \text{ (s}^{-1}\text{)}$	$2.1 \times 10^{24}$	$0.9 \times 10^{24}$	$2.1 \times 10^{24}$	$0.3 \times 10^{24}$
$E \text{ (kcal mol}^{-1}\text{)}$	62.5	61.4	62.5	60.5
$r^a$	-0.9926	-0.9986	-0.9985	-0.9985

<sup>a</sup> The correlation coefficient of the linear regression.

takes place according to the equation

which probably occurs through a retro-diene reaction. This is followed by the oxidative decomposition of  $\text{CoCO}_3$ 

Only step (6) proved to be kinetically workable. The values of the non-isothermal kinetic parameters, reaction order  $n$ , pre-exponential factor  $A$  and activation energy  $E$ , are listed in Table 2, which gives the values of the non-isothermal kinetic parameters obtained by the four methods applied. Figure 2 shows the TG curve regenerated on  $(\alpha, \theta/^\circ\text{C})$  coordinates, obtained using the Coats–Redfern method: the experimental points lie practically on the curve.

At  $\beta = 2.5 \text{ K min}^{-1}$ , two steps corresponding to 33.47% and 66.52% weight losses were detected. These steps cannot be kinetically analysed.

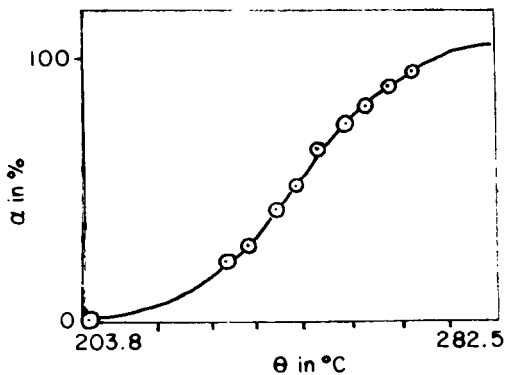
Fig. 2. Regenerated  $(\alpha, \theta/^\circ\text{C})$  curve (—) and experimental points ( $\odot$ ) for reaction (6).

TABLE 3

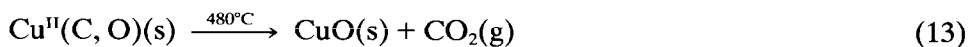
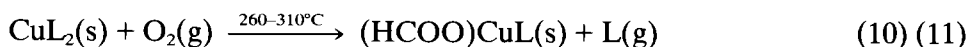
Intensities  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  of  $\text{CuL}_2$ 

Line	$I$	$d/\text{Å}$	$l/\text{Å}$
1	100	9.22	110
2	70	8.95	
3	25	7.42	
4	34	6.69	
5	7	5.56	
6	37	5.00	
7	20	4.82	
8	38	4.50	
9	17	4.47	
10	9	4.31	
11	20	4.10	
12	22	3.72	
13	11	3.63	
14	13	3.20	
15	9	3.04	
16	20	2.84	
17	35	2.04	
18	50	1.85	

*The thermal decomposition of  $\text{CuL}_2$* 

Table 3 lists the crystalline data of this compound.

According to the derivatographic data recorded at  $\beta = 9.89 \text{ K min}^{-1}$ , there are four decomposition steps. However, at  $\beta = 2.38 \text{ K min}^{-1}$ , only two, almost equal, main decomposition steps were recorded. At  $\beta = 2.38 \text{ K min}^{-1}$ , the first step corresponds to a weight loss of 51.55% (almost one molecule of ligand). The sum of the first two steps at  $\beta = 9.89 \text{ K min}^{-1}$  is equal to the first step recorded at  $\beta = 2.38 \text{ K min}^{-1}$ . Thus at  $9.89 \text{ K min}^{-1}$ , the decomposition of  $\text{CuL}_2$  proceeds in the steps:



Steps (12) and (13) correspond respectively to 36% and 12.4% weight losses. The only kinetically workable step is step (12), whose non-isothermal kinetic parameters are listed in Table 4.

At  $\beta = 2.38 \text{ K min}^{-1}$ , the second decomposition step equals the sum of steps (12) and (13) at  $\beta = 9.89 \text{ K min}^{-1}$ . The values of the non-isothermal kinetic parameters are listed in Table 5. It should be noted that the value of

TABLE 4

Values of the non-isothermal kinetic parameters of reaction (12) at  $\beta = 9.89 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0	0	0	0
$A \text{ (s}^{-1}\text{)}$	$3.31 \times 10$	$1.15 \times 10$	$3.41 \times 10$	$1.1 \times 10$
$E \text{ (kcal mol}^{-1}\text{)}$	8.4	9.7	8.4	9.7
$r$	-0.9948	-0.9969	-0.9948	-0.9975

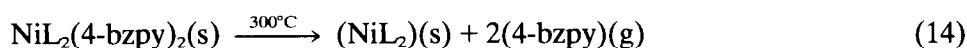
the pre-exponential factor is close to that predicted by the transition state theory [16].

9,10-Anthracendione was identified in the mass spectrum of the gas evolved by heating the compound  $\text{CuL}_2$  at  $\beta = 5 \text{ K s}^{-1}$  and  $p = 10^{-6} \text{ mbar}$ , up to  $500^\circ\text{C}$ .

The  $\text{ML}_2(4\text{-bzpy})_2$  compounds, described next, are coordination compounds, with the chromophore  $[\text{MO}_4\text{N}_2]$  in the transconfiguration, see Form 4.

#### *The thermal decomposition of $\text{NiL}_2(4\text{-bzpy})_2$*

Table 6 list the data concerning the crystalline state of  $\text{NiL}_2(4\text{-bzpy})_2$ . According to the derivatograph data the release of benzoylpyridine occurs in a single step



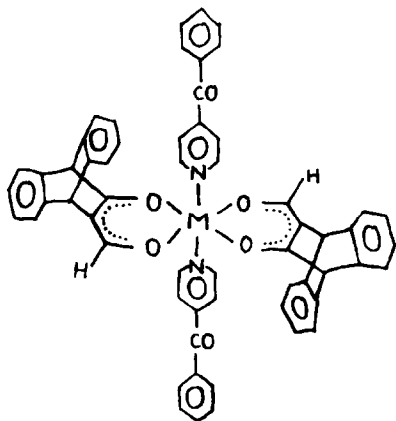
This behaviour is similar to that exhibited by  $\text{M}(\text{acac})_2(4\text{-bzpy})_2$  which first

TABLE 5

Values of the non-isothermal kinetic parameters for the second decomposition of  $\text{CuL}_2$  at  $\beta = 2.38 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	1	0.9	1	0.9
$A \text{ (s}^{-1}\text{)}$	$2.28 \times 10^{13}$	$4.18 \times 10^{12}$	$2.28 \times 10^{13}$	$4.35 \times 10^{12}$
$E \text{ (kcal mol}^{-1}\text{)}$	47.3	45.2	47.3	45.2
$r$	-0.9981	-0.9983	-0.9981	-0.9983





Form 4. The structure of the  $ML_2(4\text{-bzpy})_2$  compounds. M is Co, Ni, Cu.

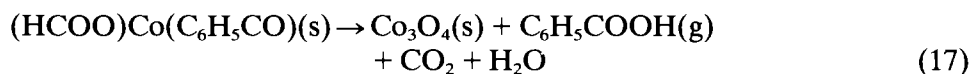
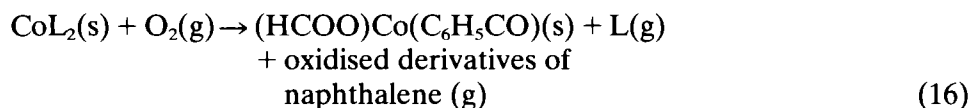
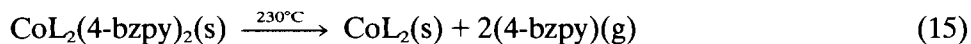
releases the axial monodentate ligand. The relatively high stability of the structure of the  $\beta$ -dicarbonylic ligand is quite surprising.

The release of the ligand yielding NiO occurs at higher temperatures, in a multi-step oxidative degradation.

The values of the non-isothermal kinetic parameters for reaction (14) recorded at two heating rates are given in Tables 7 and 8. The difference between the values of the non-isothermal kinetic parameters at the two heating rates may be the result of heat transfer. It is interesting to note that the rate constant at  $250^\circ\text{C}$  calculated for  $n = 2$  is:  $k = 1.1 \times 10^{-3}$  at  $\beta = 4.60 \text{ K min}^{-1}$ , and  $k = 2.4 \times 10^{-3}$  at  $\beta = 2.37 \text{ K min}^{-1}$ , i.e. a compensation effect to the heating rate has to be considered.

#### *The thermal decomposition of $CoL_2(4\text{-bzpy})_2$*

Table 9 lists the data concerning the crystalline state of this compound. The derivatogram recorded, at a programmed heating rate of  $2.5 \text{ K min}^{-1}$ , detected the following decomposition steps:



The values of the non-isothermal kinetic parameters for reactions (15), (16) and (17) are listed in Tables 10, 11 and 12, respectively. Figure 3 shows

TABLE 6

Intensities  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  of  $\text{NiL}_2(4\text{-bzpy})_2$ 

Line	$I$	$d/\text{Å}$	$l/\text{Å}$
1	35	8.75	
2	25	8.57	
3	20	7.50	
4	29	6.64	
5	14	6.43	
6	29	6.03	
7	33	5.63	
8	100	5.02	168
9	29	4.63	
10	10	4.13	
11	33	3.86	
12	40	3.80	
13	14	3.46	
14	42	3.33	
15	10	3.20	
16	10	2.01	

TABLE 7

Values of the non-isothermal kinetic parameters for reaction (14) at  $\beta = 4.60 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	2	2	2	2
$A \text{ (s}^{-1}\text{)}$	$8.17 \times 10^{30}$	$2.24 \times 10^{30}$	$8.19 \times 10^{30}$	$3.96 \times 10^{30}$
$E \text{ (kcal mol}^{-1}\text{)}$	81.4	79.4	81.4	83
$r$	-0.9998	-0.9998	-0.9998	-0.9998

TABLE 8

Values of the non-isothermal kinetic parameters for reaction (14) at  $\beta = 2.37 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	1.9	1.9	1.9	1.9
$A \text{ (s}^{-1}\text{)}$	$5.8 \times 10^{35}$	$1.1 \times 10^{35}$	$5.8 \times 10^{35}$	$4.04 \times 10^{37}$
$E \text{ (kcal mol}^{-1}\text{)}$	92.4	89.8	92.4	97
$r$	-0.9879	-0.9874	-0.9879	-0.9839

TABLE 9

Intensities  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  of  $\text{CoL}_2(4\text{-bzpy})_2$ 

Line	$I$	$d/\text{\AA}$	$l/\text{\AA}$
1	22	10.24	
2	12	9.70	
3	43	8.70	
4	33	8.54	
5	25	7.50	
6	47	6.59	
7	37	6.45	
8	56	6.00	
9	60	5.60	
10	56	4.99	
11	18	4.77	
12	68	4.63	
13	16	4.35	
14	37	4.13	
15	27	3.89	
16	50	3.86	
17	66	3.79	
18	35	3.74	
19	8	3.65	
20	52	3.45	
21	100	3.33	168
22	10	3.25	
23	46	3.18	
24	15	3.12	
25	12	3.02	
26	15	3.00	
27	16	2.91	
28	18	2.80	
29	12	2.74	
30	16	2.65	

TABLE 10

Values of the non-isothermal kinetic parameters for reaction (15) at  $\beta = 2.32 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0.8	0.8	0.8	0.7
$A \text{ (s}^{-1}\text{)}$	$1.24 \times 10^{24}$	$5.11 \times 10^{23}$	$1.24 \times 10^{24}$	$2.6 \times 10^{23}$
$E \text{ (kcal mol}^{-1}\text{)}$	61.2	60.1	61.1	59.7
$r$	-0.9987	-0.9988	-0.9987	-0.9987

TABLE 11

Values of the non-isothermal kinetic parameters for reaction (16) at  $\beta = 2.64 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0.4	0.4	0.4	0.4
$A \text{ (s}^{-1}\text{)}$	$1.3 \times 10^{19}$	$7.9 \times 10^{18}$	$1.3 \times 10^{19}$	$3.17 \times 10^{19}$
$E \text{ (kcal mol}^{-1}\text{)}$	58.6	58.0	58.6	59.6
$r$	-0.9820	-0.9833	-0.9820	-0.9831

TABLE 12

Values of the non-isothermal kinetic parameters for reaction (17) at  $\beta = 2.06 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0	0	0	0
$A \text{ (s}^{-1}\text{)}$	$3.17 \times 10^{32}$	$7.52 \times 10^{31}$	$3.17 \times 10^{32}$	$7.15 \times 10^{32}$
$E \text{ (kcal mol}^{-1}\text{)}$	98.3	95.8	98.3	99.3
$r$	-1.0000	-1.0000	-1.0000	-1.0000

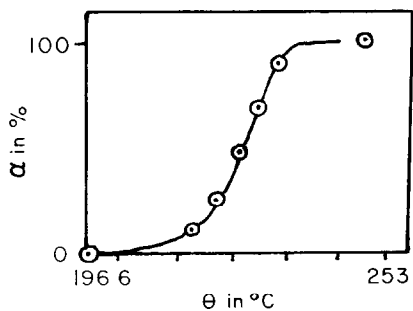
Fig. 3. Regenerated ( $\alpha, \theta/^{\circ}\text{C}$ ) curve (—) and experimental points ( $\odot$ ) for reaction (15).

TABLE 13

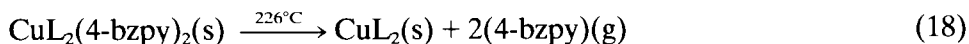
Values of non-isothermal kinetic parameters for reaction (XIX) at  $\beta = 2.27 \text{ K min}^{-1}$ 

Kinetic parameter	Method			
	Coats–Redfern	Flynn–Wall $\beta = \text{const.}$	Doyle–Gorbachev	Modified Coats–Redfern
$n$	1.9	1.9	1.9	1.8
$A \text{ (s}^{-1}\text{)}$	$7.43 \times 10^{11}$	$1.01 \times 10^{12}$	$7.45 \times 10^{11}$	$2.15 \times 10^{11}$
$E \text{ (kcal mol}^{-1}\text{)}$	33.3	33.5	33.3	32.1
$r$	-0.9992	-0.9993	-0.9992	-0.9993

the TG curve regenerated in  $(\alpha, \theta/^\circ\text{C})$  coordinates for reaction (15) at  $\beta = 2.32 \text{ K min}^{-1}$ : the experimental points lie just on the curve, thus indicating the correct description of the decomposition kinetics by the determined values of the non-isothermal kinetic parameters.

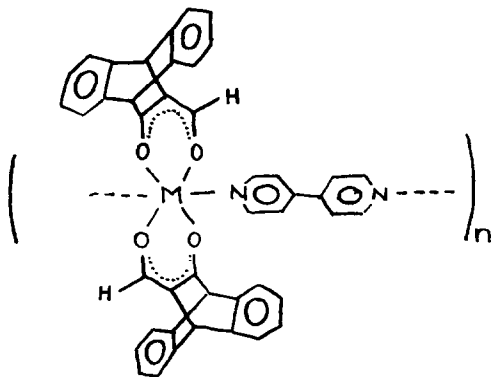
#### The thermal decomposition of $\text{CuL}_2(4\text{-bzpy})_2$

The only kinetically workable decomposition step is



The values of the non-isothermal kinetic parameters of reaction (18) at  $\beta = 2.27 \text{ K min}^{-1}$  are listed in Table 13.

The last group of compounds to be investigated are described by the general formula  $\text{ML}_2(4,4'\text{-dipy})_2$ , see Form 5.



Form 5. The structure of the  $\text{ML}_2(4,4'\text{-dipy})_2$  compounds.

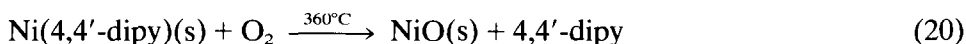
TABLE 14

Intensity  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  for  $\text{NiL}_2(4,4'\text{-dipy})$ 

Line	$I$	$d$ (Å)	$l/\text{Å}$
1	13	13.16	
2	45	11.50	
3	91	7.38	
4	50	6.59	
5	100	5.43	84
6	43	4.87	
7	18	4.08	
8	6	3.70	
9	34	3.45	
10	15	3.37	
11	43	3.23	
12	50	2.95	
13	15	2.57	
14	7	2.45	
15	6	2.37	
16	6	2.00	
17	15	1.97	
18	9	1.88	

*The thermal decomposition of  $\text{NiL}_2(4,4'\text{-dipy})$* 

Table 14 lists the X-ray data concerning the crystalline structure of this compound. The following thermal decomposition steps were detected from the derivatographic data



Step (19) was the only kinetically workable step. The values of the non-isothermal kinetic parameters are listed in Table 15.

TABLE 15

Values of the non-isothermal kinetic parameters for reaction (19) at  $\beta = 2.40 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0.2	0.2	0.2	0.2
$A$ ( $\text{s}^{-1}$ )	$1.09 \times 10^5$	$4.41 \times 10^5$	$1.11 \times 10^5$	$1.09 \times 10^5$
$E$ ( $\text{kcal mol}^{-1}$ )	22.0	23.1	22.0	19.3
$r$	-0.9940	-0.9951	-0.9940	-0.9961

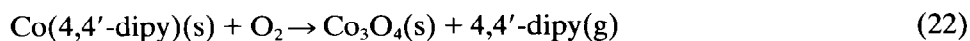
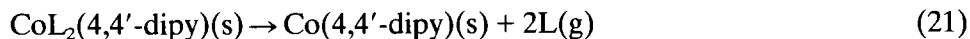
TABLE 16

Intensities  $I$ , interplanar distances  $d$  and mean crystallite size  $l$  of  $\text{CoL}_2(4,4'\text{-dipy})$ 

Line	$I$	$d/\text{\AA}$	$l/\text{\AA}$
1	9	10.47	
2	21	7.50	
3	42	6.28	
4	99	5.50	84
5	7	5.52	
6	20	4.92	
7	13	4.06	
8	18	3.18	
9	27	3.48	
10	5	3.39	
11	10	3.32	
12	24	2.98	

*The thermal decomposition of  $\text{CoL}_2(4,4'\text{-dipy})$* 

The X-ray diffraction data concerning the crystalline state of this compound are listed in Table 16. The derivatographic data showed the following two decomposition steps:



For reaction (21), which was kinetically workable, the values of the non-isothermal kinetic parameters are listed in Table 17.

TABLE 17

Values of the non-isothermal kinetic parameters for reaction (21) at  $\beta = 2.40 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coats–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0	0	0	0
$A (\text{s}^{-1})$	$1.3 \times 10^{17}$	$1.0 \times 10^{17}$	$1.3 \times 10^{17}$	$1.4 \times 10^{16}$
$E (\text{kcal mol}^{-1})$	35.2	35.6	35.1	34.7
$r$	-0.9965	-0.9965	-0.9965	-0.9965

*The thermal decomposition of  $\text{CuL}_2(4,4'\text{-dipy})$* 

The following decomposition steps were detected on the heating curves:

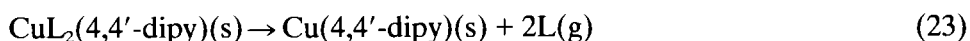
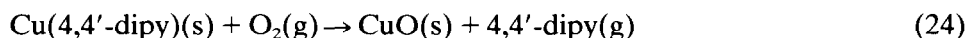


TABLE 18

Values of the non-isothermal kinetic parameters for reaction (23) at  $\beta = 1.99 \text{ K min}^{-1}$ 

Kinetic parameters	Method			
	Coates–Redfern	Flynn–Wall ( $\beta = \text{const.}$ )	Doyle–Gorbachev	Modified Coats–Redfern
$n$	0	0	0	0
$A \text{ (s}^{-1}\text{)}$	$5.5 \times 10^3$	$2.74 \times 10^4$	$5.56 \times 10^3$	$1.50 \times 10^4$
$E \text{ (kcal mol}^{-1}\text{)}$	14.3	5.4	14.4	15.2
$r$	-0.9980	-0.9928	-0.9911	-0.9982



The values of the non-isothermal kinetic parameters for reaction (23) are listed in Table 18. The results obtained suggest that the change in the thermal decomposition steps with the heating rate, as in case of  $[\text{ML}_2](\text{H}_2\text{O})_x$ , can be ascribed to false equilibria which occur mainly at high values of the heating rate.

As can be seen from the results, the non-isothermal kinetic parameters determined using the four integral methods are in satisfactory agreement. Moreover, as seen from Figs. 2 and 3, the TG curves regenerated using the determined values of the non-isothermal kinetic parameters are practically the same as for the experimental values.

For the various reactions, the reaction order varies over quite a broad range of values, from 0 to 2. Values of a reaction order below unity correspond to the reaction taking place in a mixed diffusional and kinetic region [17]. Reaction order values above unity are due to the decomposition of structural units which consist of more than one molecule.

Reactions (19), (21) and (23) are examples of diffusion-limited decomposition. These reactions are characterised by a reaction order of around zero. Moreover, because the activation energies  $E$  change in the same way as the pre-exponential coefficient values, there is a compensation effect in operation for these three reactions and they occur with practically the same rates:  $k = 6 \times 10^{-4}$  (290°C) for reaction (21); and  $k = 3.79 \times 10^{-4}$  (165°C) for reaction (23). For these three reactions, the crystalline lattice exhibits practically the same diffusional resistance.

## CONCLUSIONS

An investigation into the thermal behaviour of some coordinate compounds of cobalt, nickel and copper was carried out, and the values of the non-isothermal kinetic parameters were determined for the kinetically



workable reactions. The values obtained using four integral methods agree satisfactorily.

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