

## KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA. XXIII. THERMAL DECOMPOSITION OF SOME $[\text{Co}(\text{pyridine})_4(\text{NCX})_2]$ TYPE COMPLEXES

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(Received 23 July 1984)

### ABSTRACT

A derivatographic study of the thermal decomposition of  $[\text{Co}(\text{py})_4(\text{NCX})_2]$  type complexes ( $X = \text{O}, \text{S}, \text{Se}$ ) shows the first two decomposition stages to be the release of the four pyridine molecules.  $\text{Co}(\text{NCS})_2$  is a relatively stable intermediate, but the others immediately undergo the further decomposition reactions:  $\text{Co}(\text{NCO})_2 \rightarrow \text{Co}(\text{CN})_2 \rightarrow \text{Co}_3\text{O}_4$  and  $\text{Co}(\text{NCSe})_2 \rightarrow \text{Co}_2(\text{SeO}_3)_3 \rightarrow \text{Co}_3\text{O}_4$ , respectively. Even the  $\text{Co}(\text{NCS})_2$  is oxidized at higher temperatures, presumably giving a mixture of sulphate and oxide. From the TG curves kinetic parameters are derived for the deamination reactions. These parameters depend on the working conditions. A kinetic compensation effect is observed and discussed.

### INTRODUCTION

Pyridine,  $\beta$ - and  $\gamma$ -picoline form coordination compounds with some  $3d^{5-10}$  transition-metals which are slightly soluble in water, containing pseudohalides such as  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{NCSe}^-$ . These complexes have a well-defined composition:  $[\text{M}(\text{NCX})_2(\text{amine})_n]$  ( $n = 2, 4$  and in some cases 6), they are stable in air at room temperature and consequently, some of these derivatives, especially the thiocyanates, have been used for the gravimetric determination of Co, Mn, Cd, Ni and Cu [1].

The thermal decomposition of these precipitates, used in gravimetric analysis, was investigated by Liptay and co-workers [2–4] by means of derivatography. The nature of the intermediate products was studied, as well as the temperature intervals within which weighing forms, suitable for gravimetric determinations, are present.

The factors influencing the stability of the metal–amine(N) bond have been studied and discussed on the basis of IR spectral data and magnetochemical measurements [5].

The derivatographic investigations show the thermal stability of these complexes to increase with increasing stability constants. This behaviour

suggests the idea that at higher temperatures the bond between the central atom and the donor nitrogen atom of the pyridine is broken [6,7].

$[\text{Co}(\text{pyridine})_6(\text{NCO})_2]$  was described by Ripan [8] and Logan and co-workers [9,10]. The manometric study of this compound in hot  $\text{CHCl}_3$  shows the thermal decomposition to imply the following stages:  $[\text{Co}(\text{pyridine})_6(\text{NCO})_2] \rightarrow [\text{Co}(\text{pyridine})_4(\text{NCO})_2] \rightarrow [\text{Co}(\text{pyridine})_2(\text{NCO})_2] \rightarrow \text{Co}(\text{NCO})_2 \rightarrow \text{Co}(\text{CN})_2$  [11].

$[\text{Co}(\text{pyridine})_4(\text{NCS})_2]$  was obtained by Reitzenstein [12] and Pfeiffer and Tilgner [13] from organic polar solvents. The analogous selenocyanate was described by Spacu and Macarovici [14] and by Cotton et al. [15].

In the present paper the thermal decomposition of  $[\text{Co}(\text{py})_4(\text{NCX})_2]$  type complexes was studied under dynamic temperature conditions ( $X = \text{O}, \text{S}, \text{Se}$ ).

## EXPERIMENTAL

### *$[\text{Co}(\text{pyridine})_4(\text{NCO})_2]$ , $[\text{Co}(\text{pyridine})_4(\text{NCS})_2]$ and $[\text{Co}(\text{pyridine})_4(\text{NCSe})_2]$*

0.05 moles of  $\text{Co}(\text{NO}_3)_2$  were dissolved in 300 ml of water, 0.10 mol of  $\text{KCNO}$  ( $\text{KCNS}$  or  $\text{KCNSe}$ , respectively) in 50–60 ml water were added. After 5–10 min the mixtures obtained were treated dropwise with 0.20–0.25 mol of pyridine. Pink crystalline products were separated, washed with 0.5% pyridine solution and water. The products were dried in air.

#### *Analysis*

Calc. for  $[\text{Co}(\text{pyridine})_4(\text{NCO})_2]$  (mol. wt. 459.4): Co, 12.84; N, 23.03. Found: Co, 12.91; N, 22.66.

Calc. for  $[\text{Co}(\text{pyridine})_4(\text{NCS})_2]$  (mol. wt. 491.5): Co, 12.00; S, 13.04; N, 17.10. Found: Co, 12.17, S, 13.23 (as  $\text{BaSO}_4$ ); N, 16.77.

Calc. for  $[\text{Co}(\text{pyridine})_4(\text{NCSe})_2]$  (mol. wt. 585.3): Co, 10.07; N, 14.36. Found: Co., 10.13; N, 14.19.

The IR spectra of the above compounds were recorded in KBr pellets. The  $\nu\text{C}=\text{N}$  stretching, vibrations appear at:  $\nu\text{CNO}$ , 2080;  $\nu\text{CNS}$ , 2100;  $\nu\text{CNSe}$ , 2100;  $\nu\text{C}-\text{S}$ , 760;  $\nu\text{C}-\text{Se}$ , 710  $\text{cm}^{-1}$ . These frequencies prove that the  $\text{Co}-\text{NCX}$  bond is made through the nitrogen atom. From the characteristic pyridine frequencies the  $\delta\text{C}-\text{C}$  in-plane deformation vibrations (near 630  $\text{cm}^{-1}$ ) and the  $\delta\text{C}-\text{C}$  out-of-plane deformation vibrations near 420–440  $\text{cm}^{-1}$  were identified, very slightly influenced by coordination effects [24].

The thermal decomposition of the complexes has been studied under dynamic temperature conditions using a MOM derivatograph and a thermobalance constructed on the basis of literature data [25]. Calculations were performed by means of a Felix 256 computer.

## DERIVATOGRAPHIC INVESTIGATIONS

The DTA and TG curves of the complexes studied are given in Figs. 1–3. The sample weights corresponding to the loss of several pyridine molecules are marked on the TG curves. The DTA peak temperatures are given in Table 1.

As seen, the thermal decomposition of the three complexes has some common features, but there are also important differences. It begins with the loss of the pyridine molecules in two successive endothermic reactions

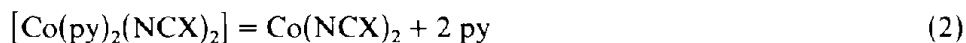
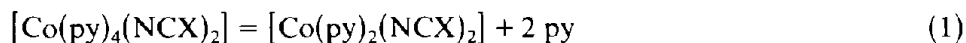


TABLE 1

DTA peak temperatures ( $^{\circ}\text{C}$ ) at the thermal decomposition of  $[\text{Co}(\text{pyridine})_4(\text{NCX})_2]$  type complexes

	Endothermal peaks			Exothermal peaks	
	A	B	C	D	E
NCO	100, 250	–	930	390, 585	865, 910
NCS	170, 204	–	915	395, 450, 490	830, 895
NCSe	200	640	935	305, 490, 590	850, 910

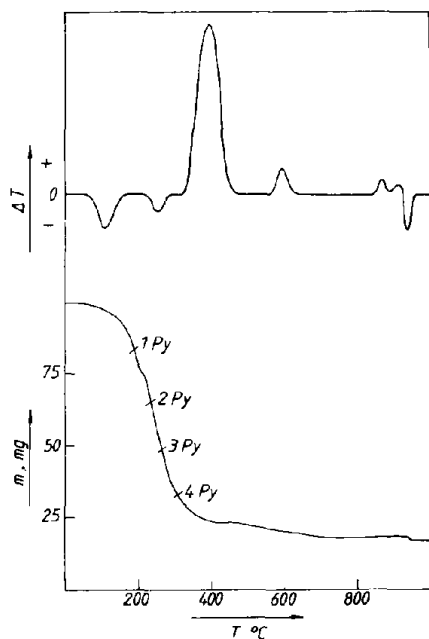


Fig. 1. TG and DTA curves of  $[\text{Co}(\text{py})_4(\text{NCO})_2]$ ,  $q = 20^{\circ}\text{C min}^{-1}$ .

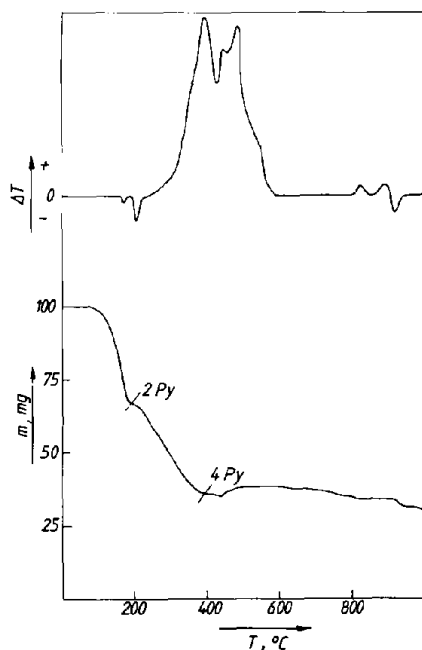


Fig. 2. TG and DTA curves of  $[\text{Co}(\text{py})_4(\text{NCS})_2]$ ,  $q = 20^\circ\text{C min}^{-1}$ .

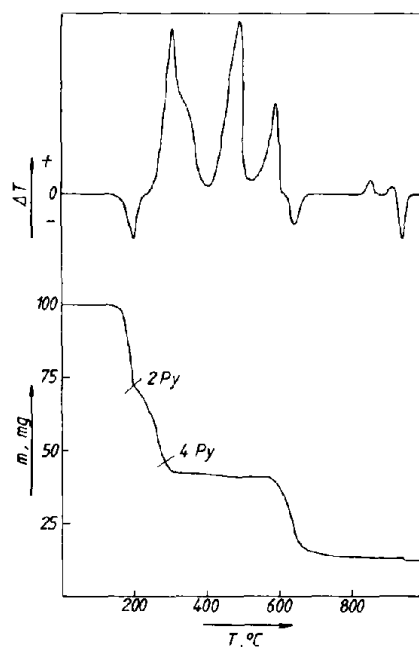


Fig. 3. TG and DTA curves of  $[\text{Co}(\text{py})_4(\text{NCSe})_2]$ ,  $q = 20^\circ\text{C min}^{-1}$ .

These reactions lead to the formation of relatively stable intermediates only with NCS, and in the first stage also with NCSe. In the case of the NCO derivative the two endothermic peaks (A) suggest that reactions (1) and (2) do occur, but in the first TG stage reaction (1) is not complete, whereas in the second stage another decomposition reaction is already superimposed on reaction (2), even before the appearance of the first exothermic peak (D). This could imply the reaction



The NCSe derivative shows a single endothermic peak (A), since a very strong exothermic peak (the first D peak) appears at a much lower temperature, than with the other complexes and presumably overlaps the second endothermic peak (A). Thus, after a weight loss stop corresponding to the completion of reaction (1), a decomposition stage follows in which the weight loss is larger than expected for reaction (2).

The exothermic reactions corresponding to peaks D are rather different for the three complexes studied. In the case of the NCO derivatives they lead to the formation of  $\text{Co}_3\text{O}_4$  at about  $700^\circ\text{C}$ . The oxidation of  $\text{Co}(\text{NCS})_2$  is more complicated, even leading to a temporary increase in weight, presumably due to the formation of cobalt sulfate, but not in stoichiometric amounts,

TABLE 2

Weight losses up to the end of the first decomposition stages expressed as number of moles of pyridine evolved

$q$ (°C min <sup>-1</sup> )	$m$ (mg)	NCO				NCS		NCS <sub>e</sub>
		I <sub>a</sub>	I <sub>b</sub>	I	II	I	II	I
5	25	1.56	2.71	–	4.52	2.12	3.67	2.17
	50	1.67	2.56	–	4.65	2.09	3.87	1.96
	75	1.80	2.48	–	4.63	1.97	3.79	1.96
	100	1.74	2.32	–	4.59	1.96	4.03	2.02
10	25	1.53	2.58	–	4.53	1.87	3.83	1.87
	50	1.62	2.43	–	4.64	2.16	3.66	2.18
	75	–	–	2.05	4.65	1.97	4.02	2.07
	100	–	–	2.17	4.45	2.00	4.00	1.88
15	25	–	–	2.48	4.56	2.22	3.84	1.86
	50	–	–	2.35	4.80	2.08	3.96	2.14
	75	–	–	2.21	4.60	2.17	4.05	1.75
	100	–	–	2.32	4.64	1.98	3.87	1.82
mean value		1.65	2.51	2.26	4.60	2.05	3.88	1.97

Co<sub>3</sub>O<sub>4</sub> is also formed simultaneously. In the case of the NCS<sub>e</sub> derivative the general picture is completely different, since the exothermal reactions are followed by an endothermal one, accompanied by an important weight loss. According to the TG curve one may presume the exothermal reactions to lead to the formation of Co<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub> which is decomposed at about 600°C and eventually Co<sub>3</sub>O<sub>4</sub> is obtained at about 700°C, as with the NCO derivative.

The last portions of both TG and DTA curves, above 800°C, are very similar to each other for all the complexes studied. The two small exothermal peaks (E) do not correspond to any weight loss, and might be due to some phase transition of Co<sub>3</sub>O<sub>4</sub>. The last endothermal peak (C) and the corresponding small weight loss have also been observed with the thermal decomposition of other cobalt complexes and have been assigned to the transformation Co<sub>3</sub>O<sub>4</sub> → CoO [2].

#### DERIVATION OF KINETIC PARAMETERS

In order to derive kinetic parameters for the deamination reactions, TG curves were recorded up to 400°C using different heating rates and sample weights.

In the case of the NCO derivative, three decomposition stages are observed (I<sub>a</sub>, I<sub>b</sub> and II) if the heating rate is  $q = 5^\circ\text{C min}^{-1}$  irrespective of the

sample weight, and for  $q = 10^\circ\text{C min}^{-1}$  when the sample weight is small, i.e.,  $m = 25$  or  $50$  mg.

In the other cases only two decomposition stages appear (I and II). With the NCS derivative, in all the working conditions there are two stages. In the case of the NCSe derivative only the first stage gives clear TG curves, suitable for deriving kinetic parameters.

In order to obtain a clear image upon the stoichiometry of the decomposition reactions the weight losses up to the end of the different decomposition stages are given in Table 2. The weight losses are expressed as the number of moles of pyridine evolved. As it can be seen, in stage I the relatively stable intermediate  $[\text{Co}(\text{py})_2(\text{NCX})_2]$  is formed in the case of the NCS and NCSe derivatives. In stage II, the formation of  $\text{Co}(\text{NCX})_2$  only occurs with the NCS derivative.

In the case of the NCO derivative no exact stoichiometry is observed. In stage Ia reaction (1) is not complete, but at the end of stage Ib or I, the weight loss is generally much higher than expected on the basis of reaction (1). In stage II the weight losses indicate that a further decomposition occurs after reaction (2). This might be reaction (3), but reactions (1), (2) and (3) imply a weight loss corresponding only to 4.4 "pyridine" molecules. If the product were  $\text{Co}_3\text{O}_4$ , the weight loss would correspond to 4.79 pyridine molecule units. Thus, one may presume that at  $400^\circ\text{C}$  a mixture of  $\text{Co}(\text{CN})_2$  and  $\text{Co}_3\text{O}_4$  is present which is gradually transformed into  $\text{Co}_3\text{O}_4$  up to about  $700^\circ\text{C}$ .

From the TG curves apparent kinetic parameters were derived by using a computerized integral method, proposed in an earlier paper [16] as "method 3". The apparent reaction order,  $n$ , activation energy,  $E$ , and the log  $Z$  values are given in Table 3. (The pre-exponential factor values were calculated by expressing time in seconds.)

## DISCUSSION

As seen from Table 3, all the parameters derived strongly depend on the working conditions. Since the same 12 working conditions were used with all substances studied, one can compare the mean values calculated for different heating rates, irrespective of the sample weight and for different sample weights, irrespective of the heating rate. These mean values are presented in Table 4. The apparent reaction order increases with increasing heating rate and generally also with increasing sample weight. This effect can be easily explained, since the higher the heating rate and the larger the sample, the more the diffusion of the gaseous products is hindered. Consequently, the slope of the TG curve is reduced, especially in the last portion of the decomposition stage. In terms of kinetic parameters such a modification of the shape indicates a higher reaction order and a lower activation energy [17].

TABLE 3

Apparent kinetic parameters of the first decomposition stages derived from TG curves

$q$ ( $^{\circ}\text{C min}^{-1}$ )	$m$ (mg)	$n$	$E$ (kJ)												$\log(Z)$				
			NCO		NCS		NCSe		NCS		NCSe		NCO		NCS		NCSe		
			Ia	II	Ia	II	I	II	I	II	I	II	Ia	Ib	II	I	II	I	II
5	25	0.25	1.37	0.91	0.70	2.02	1.09	52.7	106	102	107	125	178	5.0	11.1	8.1	11.7	11.9	21.7
	50	0.56	1.25	1.03	0.61	1.20	0.87	44.0	144	81.7	67.3	94.2	117	3.8	16.5	5.8	6.5	8.0	13.1
	75	0.02	1.47	1.23	-0.19	2.56	1.30	44.4	110	110	38.5	121	112	3.7	11.4	8.5	1.9	10.8	12.6
	100	0.31	0.97	1.73	1.02	2.33	0.78	45.6	105	145	95.2	87.1	113	4.0	10.7	12.4	10.6	6.7	12.3
10	25	0.95	2.64	0.84	0.84	1.62	0.75	107	191	93.8	107	85.7	124	13.1	22.9	7.3	13.1	7.3	14.5
	50	0.17	0.58	1.33	1.05	1.58	0.80	54.3	65.7	143	76.9	86.5	85.0	5.4	6.0	12.4	8.0	7.1	9.0
	75	1.56	1.84	0.97	2.98	1.42	73.3	91.2	117	84.2	106	110	7.6	9.4	8.5	9.1	12.2	10.8	
	100	3.02	1.30	0.52	2.34	1.33	91.2	95.8	66.1	86.1	98.7	11.0	7.0	6.0	6.7	10.8	10.8		
15	25	1.86	0.97	1.00	1.51	0.33	49.0	85.3	73.3	133	55.2	4.6	6.5	7.6	12.1	4.9	14.9	14.9	
	50	2.67	1.81	1.20	2.25	1.63	99.5	148	76.9	103	130	11.9	12.9	7.9	9.0	14.9	14.9		
	75	1.94	1.67	2.23	1.66	1.07	67.3	113	81.7	91.3	85.7	7.1	9.1	8.3	7.6	9.1	9.1		
	100	3.47	2.28	1.76	2.48	1.44	111	127	61.9	77.5	66.5	13.0	10.5	5.5	5.8	6.4	6.4		

TABLE 4  
 Mean values of the apparent reaction order and the activation energy of the first decomposition stages

	$n$		$E$ (kJ)									
	NCO		NCS		NCSe		NCO		NCS		NCSe	
	I	II	I	II	I	II	I	II	I	II	I	II
$q = 5^\circ\text{C min}^{-1}$	0.77	1.22	0.56	2.03	0.96	2.03	81.4	109.2	77.0	106.8	130.0	
$q = 10^\circ\text{C min}^{-1}$	1.69	1.33	0.84	2.13	1.07	2.13	93.4	112.4	83.5	91.1	104.0	
$q = 15^\circ\text{C min}^{-1}$	2.49	1.68	1.55	1.98	1.12	1.98	81.7	118.5	73.6	101.2	84.4	
$m = 25$ mg	1.49	0.91	0.85	1.72	0.72	1.72	92.4	93.7	95.8	114.6	119.1	
$m = 50$ mg	1.32	1.39	0.95	1.68	1.03	1.68	84.5	124.2	73.7	94.6	110.7	
$m = 75$ mg	1.42	1.58	1.00	2.43	1.26	2.43	72.6	113.3	68.1	106.1	102.6	
$m = 100$ mg	2.38	1.77	1.10	2.38	1.18	2.38	92.5	122.6	74.4	83.4	92.8	
General mean	1.65	1.41	0.98	2.05	1.05	2.05	85.5	113.4	78.0	99.7	106.3	



TABLE 5

Compensation parameters for the first decomposition stages

NCX	Stage	$a$				$b$		$\rho$	$a'$	
		(mol J <sup>-1</sup> )				(mol J <sup>-1</sup> )				
NCO	I <sub>a</sub>	0.149	-2.78	1.000	0.157					
	I <sub>b</sub>	0.137	-3.37	0.999	0.133					
	I	0.142	-2.42	0.995	0.146					
	II	0.105	-2.71	0.997	0.108					
NCS	I	0.152	-3.88	0.993	0.138					
	II	0.116	-3.02	0.992	0.114					
NCS <sub>e</sub>	I	0.136	-2.67	0.999	0.137					

The mean values of the activation energy given in Table 4 do not show such a systematic variation with  $q$  and  $m$  as does the reaction order, nevertheless, a tendency to decrease can be observed both with increasing heating rate and increasing sample weight, as expected on the basis of the

TABLE 6

 $T_{0.1}$  values for the first decomposition stages (°C)

$q$ (°C min <sup>-1</sup> )	$m$ (mg)	NCO				NCS		NCS <sub>e</sub>
		I <sub>a</sub>	I <sub>b</sub>	I	II	I	II	I
5	25	58.0	117.5	-	172.4	105.1	164.3	106.1
	50	52.5	116.0	-	202.5	91.8	165.0	107.1
	75	55.1	122.5	-	216.2	95.5	180.1	101.0
	100	50.1	125.0	-	217.4	118.5	182.6	112.1
10	25	82.5	120.0	-	200.0	104.6	165.0	103.2
	50	65.1	112.5	-	220.1	99.6	175.0	102.5
	75	-	-	90.1	222.5	112.5	192.8	109.0
	100	-	-	75.1	228.8	109.6	194.5	115.5
15	25	-	-	74.9	202.5	99.6	190.2	97.6
	50	-	-	85.2	202.3	107.5	192.5	118.1
	75	-	-	85.2	227.5	112.5	197.6	108.1
	100	-	-	101.0	227.5	109.8	211.0	115.1
$q = 5^\circ\text{C min}^{-1}$		53.9	120.2	-	202.1	102.7	173.0	106.6
$q = 10^\circ\text{C min}^{-1}$		73.8	116.2	82.6	217.8	106.6	181.8	107.6
$q = 15^\circ\text{C min}^{-1}$		-	-	86.6	215.0	107.4	197.9	109.7
$m = 25 \text{ mg}$		-	-	-	191.6	103.1	173.2	102.3
$m = 50 \text{ mg}$		-	-	-	208.3	99.6	177.5	109.2
$m = 75 \text{ mg}$		-	-	-	222.1	106.8	190.2	106.2
$m = 100 \text{ mg}$		-	-	-	224.6	112.6	196.0	114.2
General mean		60.5	118.9	85.2	211.6	105.5	184.2	108.0

above considerations. The values of  $\log Z$  vary in parallel with the activation energies, due to the "kinetic compensation effect", frequently leading to the following type of law [18].

$$\log Z = aE + b \quad (4)$$

A plot of the experimental  $\log Z$  values versus  $E$  shows a good linearity, separately for each of the decomposition stages of the complexes studied. The compensation parameters,  $a$  and  $b$ , derived from our experimental data by means of the least-squares method are given in Table 5. The same table also contains Jaffé's correlation coefficient,  $\rho$  [19], indicating a very good linearity.

For the meaning of the compensation parameters, it was presumed [20] that the stronger the leaving group is bonded, the smaller the parameter  $a$ . According to Garn [21], the parameter  $a$  depends only upon the "decomposition temperature",  $T_c$ , i.e.

$$a' = \frac{1}{2.3RT_c} \quad (5)$$

This decomposition temperature is not a well-defined variable and we shall take the clearly defined  $T_{0.1}$  value for  $T_c$ , i.e., the temperature at which the transformation degree in the TG stage considered is  $\alpha = 0.1$ . The  $T_{0.1}$  values are given in Table 6.

It is clear, particularly from the mean values calculated for the same heating rates and sample weights, respectively, that  $T_{0.1}$  increases both with increasing heating and sample weights. This effect of the heating rate is to be expected even for ideal TG curves [22,23], and neither is the effect of the sample weight surprising, since the diffusion of the gaseous product evolved is hindered more in large than in small samples.

By using the mean  $T_{0.1}$  values obtained for different decomposition stages,  $a'$  values were calculated by means of eqn. (5) and by taking  $T_c = T_{0.1}$ . The results are given in Table 5.

By comparing the  $T_{0.1}$  values obtained for the first decomposition stage, i.e., for reaction (1) (see Table 6), with the corresponding DTA peak temperatures (first peak A in Table 1), it is clear that both temperatures increase in the order  $\text{NCO} < \text{NCS} < \text{NCSe}$ , giving the order of the "thermal stability" of the complexes studied.

As can be seen from Table 5, the compensation parameter,  $a$ , does not respect this order and an inversion occurs between NCO and NCS. Although the  $a$  and  $a'$  values are generally very close to each other,  $a$  is smaller than  $a'$  in the case of NCO, but is much larger than  $a'$  with NCS. A similar inversion can be observed with respect to the mean activation energy of the first decomposition stage (Table 4). This means that the compensation parameter,  $a$ , not only reflects the decomposition temperature, but is also sensitive to other effects.

According to a previous interpretation [20], the results given in Table 5 show the Co-pyridine bond to be stronger in the NCO derivative, as compared to the NCS one, but to be the strongest in the NCSe derivative. This conclusion is consistent with the order of the mean activation energies, as well as with some vapour pressure data [11].

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