Thermochimica Acta, 13 (1975) 419–439

STUDIES ON COORDINATION COMPOUNDS

VI. THERMOGRAVIMETRIC, DIFFERENTIAL THERMOGRAVIMETRIC, DIFFERENTIAL THERMAL ANALYSIS AND MASS SPECTROMETRIC STUDIES OF SOME COBALT(II), NICKEL(II) AND COPPER(II) SALICYLALDOXIMATES, 2-INDOLECARBOXYLATES AND 2-THIOPHENECARBOXYLATES

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(Received 17 June 1975)

ABSTRACT

Some cobalt(II), nickel(II) and copper(II) complexes of salicylaldoxime, 2-indolecarboxylic and 2-thiophenecarboxylic acids were prepared and their thermal behaviour studied by TG, DTG, DTA and mass spectrometric methods. Kinetic parameters were calculated for the decomposition reactions if possible. The decomposition processes are discussed.

INTRODUCTION

Salicylaldoxime has for a long time been known as a reagent for the gravimetric determination of copper[1] and later for several other metals. The solubility properties of salicylaldoximates were studied by Treadwell and Ammann[2] and recently by the present authors[3], and the stabilities by us[4] and Burger and Egyed[5]. Earlier Ephraim[1], Feigl and Bondi[6] and Brady[7] had also presented on chemical bases a *trans*-planar structure for copper(II), cobalt(II) and nickel(II) salicylaldoximates, which was shown afterwards by the X-ray method to be correct at least in the case of nickel(II) and copper(II) salicylaldoximates. Cox et al.[8a], found the nickel(II) and palladium(II) salicylaldoximates to be isomorphous and monomeric, and the nickel(II) compound diamagnetic, which was verified by Mellor and Craig[9] and by us[10]. The X-ray studies[8a] also showed the structure to be *trans*-planar. In more detailed X-ray studies this structure was recently verified for nickel(II) salicylaldoximate by Lessor[11] and Merritt et al.[12], and refined by Lingafelter et al.[13]. Therefore, there can be no doubt about the diamagnetism and structure of nickel(II) salicylaldoximate. For copper(II) salicylaldoximate the *trans*-planar structure was verified by the X-ray method by Cox et al.[8a], Jarski and Lingafelter[14], and recently also for salicylaldoxime by Pfluger and Harlow[15].

The structure of cobalt(II) salicylaldoximate, however, seems to be contested. On the basis of the magnetic moment the present authors[10] suggested the structure to be a *trans*-planar square in analogy with the copper(II) and nickel(II) salicylaldoximates. Burger et al.[16,17] on the contrary concluded on the bases of their IR- and UV-spectral[16] and ESCA studies[17] that the cobalt(II) salicylaldoximate has a *cis*-configuration. The true structure seems not to have been determined by the X-ray diffraction method.

The thermal stability of salicylaldoximates has been studied previously by Duval[18] and us[19], and recently by Liptay et al.[20]. The latter concluded that in contrast to the investigated metal pyridine thiocyanate complexes the thermal decomposition of the metal chelates of salicylaldoxime and related ligands does not begin with a scission of the coordinative bond, but with the cleavage of another bond in the chelate ring, which is weakened when the strength of the coordinative bond is increased in the metal chelate series of the same form of structure and ligand.

The ionization and chelate formation tendency of 2-indolecarboxylic[21a] and 2-thiophenecarboxylic acids[21b] in solutions were studied a short time ago by us and Erlenmeyer et al.[22]. Nardelli et al.[23] showed by the X-ray method the 2-thiophenecarboxylic acid molecules to be linked by hydrogen-bonds forming centrosymmetrical dimers with *trans*-planar configuration. The crystal structure of 2-indolecarboxylic acid and of metal chelates of both acids and their thermal properties do not appear to have been investigated earlier.

The present paper concerns the thermal behaviour of cobalt(II), nickel(II) and copper (II) complexes of the three chelating ligands mentioned and tries to bring further insight in these respects and in a close connection to the previous conclusions reviewed above.

EXPERIMENTAL

Reagents, syntheses and analyses of the compounds

Salicylaldoxime (Merck, *p.a.*) was recrystallized three times from benzene and the other product (Schuchardt, *p.a.*) from a chloroform–petrolether (b.p. 40–60 °C) mixture (1:1). The melting point was then 57–58 °C (literature value is 58 °C). 2-Indolecarboxylic acid (Schuchardt, m.p. 202–203 °C, literature value 203 °C) and 2-thiophenecarboxylic acid (Schuchardt, m.p. 126–128 °C, literature value 129–130 °C) were used as such.

$CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were of p.a. quality (Merck). Al_2O_3 (Fisher, for chromatographic analysis) was heated at 1000 °C overnight and stored in a desiccator. All other chemicals used were of best commercial quality available.

The cobalt(II), nickel(II) and copper(II) salicylaldoximates were prepared by adding to 549 mg of salicylaldoxime 38 ml of 0.1 M NaOH solution, then 142 ml of H_2O and finally 20 ml of 0.1 M metal chloride solution. The copper(II) and nickel(II) salicylaldoximates precipitated immediately by adding the metal chloride, the cobalt-

(II) salicylaldoximate during several hours. After several days the formed precipitates were filtered, washed with H_2O and dried in a desiccator.

The cobalt(II), nickel(II) and copper(II) 2-indolecarboxylates were synthesized by adding to 20 ml of 0.5 M ethanol solution of 2-indolecarboxylic acid 5 ml of 1.0 M metal chloride solution, 40 ml of ethanol, 89–92 ml of H_2O and 3–6 ml of 1.0 M NaOH solution. The further procedure was as above, but the precipitates were washed with a water–ethanol mixture (1:1).

The copper(II) 2-thiophenecarboxylate was made by adding to 2.563 g of 2-thiophenecarboxylic acid 20 ml of 1.0 M NaOH solution, 4 ml of 1.0 M HCl solution, 10 ml of 1.0 M $CuCl_2$ solution and 116 ml of H_2O. A bright-blue chelate precipitated, which was separated as above.

The cobalt(II) and nickel(II) 2-thiophenecarboxylates were prepared by adding to 40 ml of 1.0 M ethanol solution of 2-thiophenecarboxylic acid 20 ml of 1.0 M metal chloride solution and 1.0 M NaOH solution so much that the pH of the solution was 6 for the nickel(II) chelate and 3 to 4 for the cobalt(II) chelate. Then about 20 ml of ether was added and the solutions were allowed to stay four days by shaking now and then. The separated precipitates were handled as above, but the washing solution contained also ether to some extent.

The synthetized compounds were analyzed for metals with known methods (Ni as dimethylglyoximate[24] and Cu electroanalytically[24]) and for carbon, hydrogen, nitrogen and sulfur by micro-combustion analyses. The results are presented in Table 1.

Apparatus and measurements

The TG apparatus was a Fisher TGA System Series 100 A equipped with a Cahn electric balance, Model RG, a Cahn time derivative computer, Mark II, which was calibrated with alcohol, and with a Hewlett-Packard 1 mV two-pen recorder, Model Moseley 7100 BM. The TG and DTG curves were run on 8–20 mg of the compounds in Pt-cups and in static air. The heating rate was 5 °C min^{-1}.

The DTA apparatus was a Fisher DTA System Series 200 A equipped with the mentioned recorder. The DTA curves were taken on pure compounds (100–135 mg) and Al_2O_3 mixtures in quartz tubes. A corresponding amount (± 2 mg) of Al_2O_3, mesh No. 100–200, served as a reference. The heating rate was 10 °C min^{-1}, if not separately mentioned. The temperature calibration was done against an ice–water mixture. Caoline, benzoic acid, silver nitrate and calcium oxalate were used as check compounds above 100 °C.

The mass spectra were determined on solid samples through a direct inlet system on a Perkin-Elmer mass spectrometer, Model 270 B. The excitation energy was 70 eV[25].

TABLE 1

ANALYTICAL DATA FOR THE SALICYLALDOXIMATES, 2-INDOLECARBOXYLATES AND 2-THIOPHENECARBOXYLATES

Complex	*Analysis %*									
	M.w.	*Color*	*C*		*H*		*N or S*		*Metal*	
			Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
$(C_7H_6O_2N)_2Co$	331.193	brown	50.77	48.24	3.65	3.61	8.46	8.26	—	—
$(C_7H_6O_2N)_2Ni$	330.970	green	50.81	49.76	3.65	3.59	8.46	8.49	17.74	17.67
$(C_7H_6O_2N)_2Cu$	335.806	grey-green	50.07	49.29	3.60	3.47	8.34	8.32	18.92	18.95
$(C_9H_6O_2N)_2Co\cdot 2H_2O$	415.267	red-brown	52.06	50.97	3.88	3.78	6.75	6.65	—	—
$(C_9H_6O_2N)_2Ni\cdot 2H_2O$	415.044	yellow	52.09	52.00	3.89	3.78	6.75	6.80	14.15	14.10
$(C_9H_6O_2N)_2Cu\cdot 2H_2O$	419.880	green	51.49	51.23	3.84	3.77	6.67	6.58	15.13	14.91
$(C_5H_3O_2S)(C_2H_6O)CoCl\cdot H_2O$	285.608	red-brown	29.44	29.88	3.88	2.28	11.23	9.2	—	—
$(C_5H_3O_2S)(C_2H_6O)NiCl\cdot H_2O$	285.385	pale green	29.46	30.66	3.88	2.80	11.23	10.9	20.57	21.76
$(C_5H_3O_2S)_2Cu\cdot H_2O$	335.836	pale blue	35.76	35.08	2.40	2.30	—	—	18.92	18.94

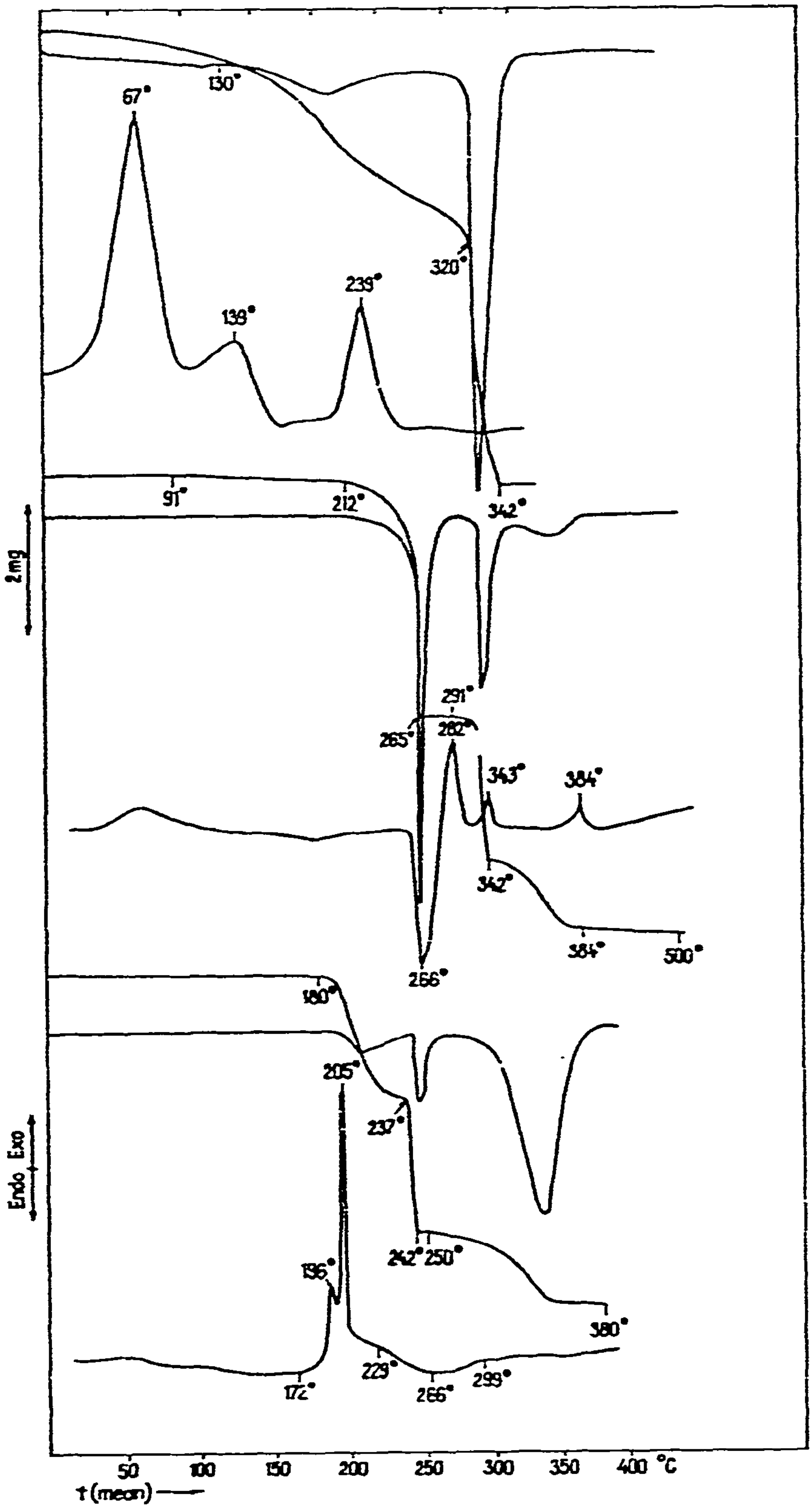


Fig. 1. TG, DTG and DTA curves of cobalt(II), nickel(II) and copper(II) salicylaldoximates. All in this order from the top downwards. *t*(mean) is for TG and TDG. For Co(II) chelate the DTG scale was 2 mg min^{-1}, for Ni(II) chelate 4 mg min^{-1}; for Cu(II) chelate 10 mg min^{-1} to 260 °C and 0.4 mg min^{-1} from this upwards. For DTA curve of Cu(II) chelate the heating rate was 5 °C min^{-1}.

RESULTS AND DISCUSSION

A. The TG, DTG and DTA data

1. Salicylaldoximates

The thermal curves of cobalt(II), nickel(II) and copper(II) salicylaldoximates are represented in Fig. 1 and the thermal data elucidated from them in Table 2. The forms of the present TG curves are different from those reported earlier[19], which were run in porcelain crucibles on a Chevenard thermobalance in macroscopic scale (the sample amount varied from 180 to 290 mg). The curves point, however, to the same initial main reaction[19]:

$$(C_7H_6O_2N)_2Me \rightarrow C_7H_7O_2N + C_7H_5O_2NMe \qquad (1)$$

and the following more or less complicated decomposition to metal oxide. The initial decomposition and oxide level temperatures are generally considerably lower or the same as the previous ones[19]. Liptay et al.[20] obtained for the initial decomposition temperatures of nickel(II) and copper (II) salicylaldoximates the values 240 and 170 °C, while we obtained in a previous paper[19] 259 and 229 °C, but in this paper 91 and 180 °C, respectively. A rapid decomposition of nickel(II) salicylaldoximate began,

TABLE 2

TG AND DTA DATA FOR SALICYLALDOXIMATES

endo = endothermic; exo = exothermic.

Process	*TG*			*DTA*			
	Temp. range (°C)	*Residue (%)*		*Peak temp. (°C)*	*Temp. range (°C)*	*Peak nature*	*Chelate (%)*
		Found	*Calc.*				
$(C_7H_6O_2N)_2Co$							100
	30–320			67	25– 71	exo	
				139	71–167	exo	
$(C_7H_5O_2N)Co$		65.7	58.6				
	320–342			239	221–264	exo	
$1/3Co_3O_4$	342→	25.8	24.2				
$(C_7H_6O_2N)_2Ni$							100
	91–265			266		endo	
$(C_7H_5O_2N)Ni$	265–291	57.5	58.6				
	291–500			282, 343, 384		exo	
NiO	500→	19.4	22.6				
$(C_7H_6O_2N)_2Cu$							100
	180–237			196[a]–207[b]		exo	
$(C_7H_5O_2N)Cu$		72.0	59.2				
	237–380			205[a]–210[b]		exo	
CuO	380→	25.3	23.7				

[a] 5 °C min^{-1}. [b] 10 °C min^{-1}.

however, at about 212°C (Fig. 1). It should be observed also that the previous initial decomposition temperatures[19,20] were obtained for macroscopic amounts of the samples ($\geq$ 200 mg).

The DTG curves are in agreement with the TG curves, but the DTA curves show for cobalt(II) and nickel(II) salicylaldoximates more and for copper(II) salicylaldoximate fewer peaks as to be expected. The DTA peaks are all exothermic, except the first one for nickel(II) salicylaldoximate.

For nickel(II) salicylaldoximate DTA curves were run also for 70, 50, 30, 20 and 10% mixtures of the chelate in Al_2O_3. The last two curves were similar showing one exothermic peak at the corresponding temperature range of the TG curve. The other mixtures showed two exothermic peaks, whereas the pure complex exhibited one endothermic and three exothermic peaks (Fig. 1, Table 2). The experiments indicated that the form of the DTA curve depends on the chelate–Al_2O_3 ratio. Contrary to this the form of the DTA curve of copper(II) salicylaldoximate did not vary with dilution in Al_2O_3. The curve revealed an exothermic double peak which is clearest at the heating rate 5°C min^{-1} (Fig. 1, Table 2).

As a special feature it may be noticed that the product at 342°C (a bend in the TG curve) in the decomposition of nickel(II) salicylaldoximate (Fig. 1) may be expected to have the composition NiNCO. The theoretical yield is 30.4%, the observed 32.0%. (The composition NiN_2C is also possible.) Similarly we obtain for copper(II) salicylaldoximate (Fig. 1) at 242–250°C theoretically 43.9% and experimentally from the curve 42.0% for the composition $Cu(NCO)_2$. The intermediates are obviously not, however, definite compounds (cyanates (OCN)), because no peaks (*m/e* 100, 147) corresponding to these mass numbers were observed in the mass spectra of nickel(II) and copper(II) salicylaldoximates, respectively.

2. *2-Indolecarboxylates*

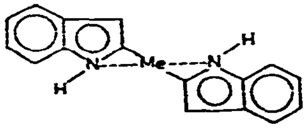
The thermal properties of 2-indolecarboxylates do not appear to have been studied previously. The main features of the thermal processes seem to be the escape of crystal water:

$$(C_9H_6O_2N)_2Me \cdot 2H_2O \rightarrow (C_9H_6O_2N)_2Me + 2H_2O \qquad (2)$$

followed by the cleavage of carbon dioxide (due to the carboxylic groups):

$$(C_9H_6O_2N)_2Me \rightarrow (C_8H_6N)_2Me + 2CO_2 \qquad (3)$$

and finally the decomposition of the indole complex (an organometallic compound) to metal oxide (Fig. 2, Table 3). A *trans*-planar structure



(Me = Co^{2+}, Ni^{2+}, Cu^{2+})

is suggested for the metal indole compounds.

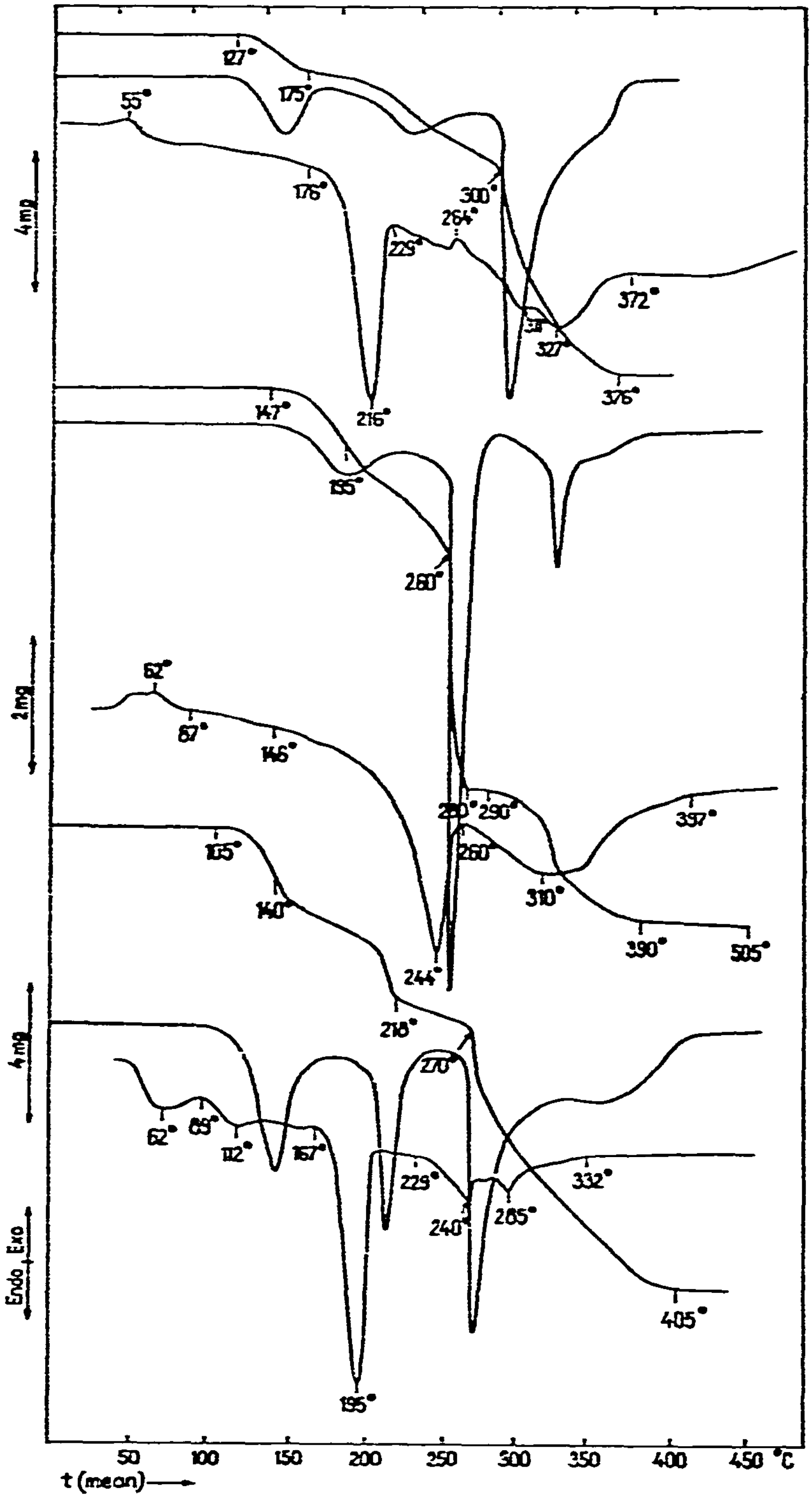


Fig. 2. TG, DTG and DTA curves of cobalt(II), nickel(II) and copper(II) 2-indolecarboxylates. All in this order from the top downwards. t (mean) for TG and DTG. The DTG scale was 2 mg min^{-1}.

TABLE 3

TG AND DTA DATA FOR 2-INDOLECARBOXYLATES

Process	*TG*			*DTA*			
	Temp. range (°C)	*Residue (%)*		*Peak temp. (°C)*	*Temp. range (°C)*	*Peak nature*	*Chelate (%)*
		Found	*Calc.*				
$(C_9H_6O_2N)_2Co \cdot 2H_2O$				55		exo	70
	127–175			216	176–230	endo	
$(C_9H_6O_2N)_2Co$	175–180	90.8	91.3				
	180–300			264		exo	
				311		endo	
$(C_8H_6N)_2Co$		67.8	70.1				
	300–376			327	264–372	endo	
$1/3Co_3O_4$	376→	19.1	19.3				
$(C_9H_6O_2N)_2Ni \cdot 2H_2O$				62	24– 87	exo	70
	147–195						
$(C_9H_6O_2N)_2Ni$		91.6	91.3				
	195–260			244	146–260	endo	
$(C_8H_6N)_2Ni$		75.2	70.1				
	260–505			310	260–397	endo	
NiO	505→	18.8	18.0				
$(C_9H_6O_2N)_2Cu \cdot 2H_2O$				62	24– 89	endo	100
	105–140			112	89–167	endo	
$(C_9H_6O_2N)_2Cu$		91.4	91.4				
	140–218			195	167–208	endo	
$(C_8H_6N)_2Cu$		70.4	70.5				
	218–405			240, 285	229–332	endo	
CuO	405→	19.1	18.9				

After reaction (3) the formed nickel(II) and copper(II) indole compounds seem to decompose in a different way. Obviously $(C_8H_6N)_2Ni$ leaves one $C_8H_6N^-$ ion, because the residue is 39.3% at 280°C while the theoretical value is 42.1%. On the other hand $(C_8H_6N)_2Cu$ leaves one molecule of HCN; the residue $(C_{15}H_{11}NCu)$ is 64.5% at 269°C and the calculated value 64.0%.

In this case the DTA curves resemble more closely the course of the TG and DTG curves showing mostly endothermic processes. An exception is the weak exothermic peak at the beginning of each DTA curve (except for the Cu(II) chelate) corresponding obviously to a crystal structure change in the metal carboxylates.

By comparing the beginning temperatures (Table 3) of the reactions (3) with the first stability constants ($\log \beta_{1,0}$) of the complexes in aqueous solutions[21a] the thermal stabilities are found to be the reverse of the stabilities in solutions.

On the basis of the similarity of the compositions of the 2-indolecarboxylates (Table 1) with those of 2-pyridinecarboxylates, 2-quinolinecarboxylates and 8-quinolinecarboxylates[10] and the general resemblance of bivalent cobalt, nickel and copper ions and thermal behaviour (Table 3) a *trans*-planar octahedral structure is suggested for the 2-indolecarboxylates studied here. The structure of a compound is completed to an octahedral, which may be slightly distorted, by two water molecules in opposite positions to the metal atom–organic ligands plane, in which the organic ligands are situated in *trans*-planar configurations around the metal ion[10a].

3. 2-Thiophenecarboxylates

Because of the destroying effect of sulfur on a Pt thermocouple DTA curves were not run for 2-thiophenecarboxylates. As described above two types of 2-thio-

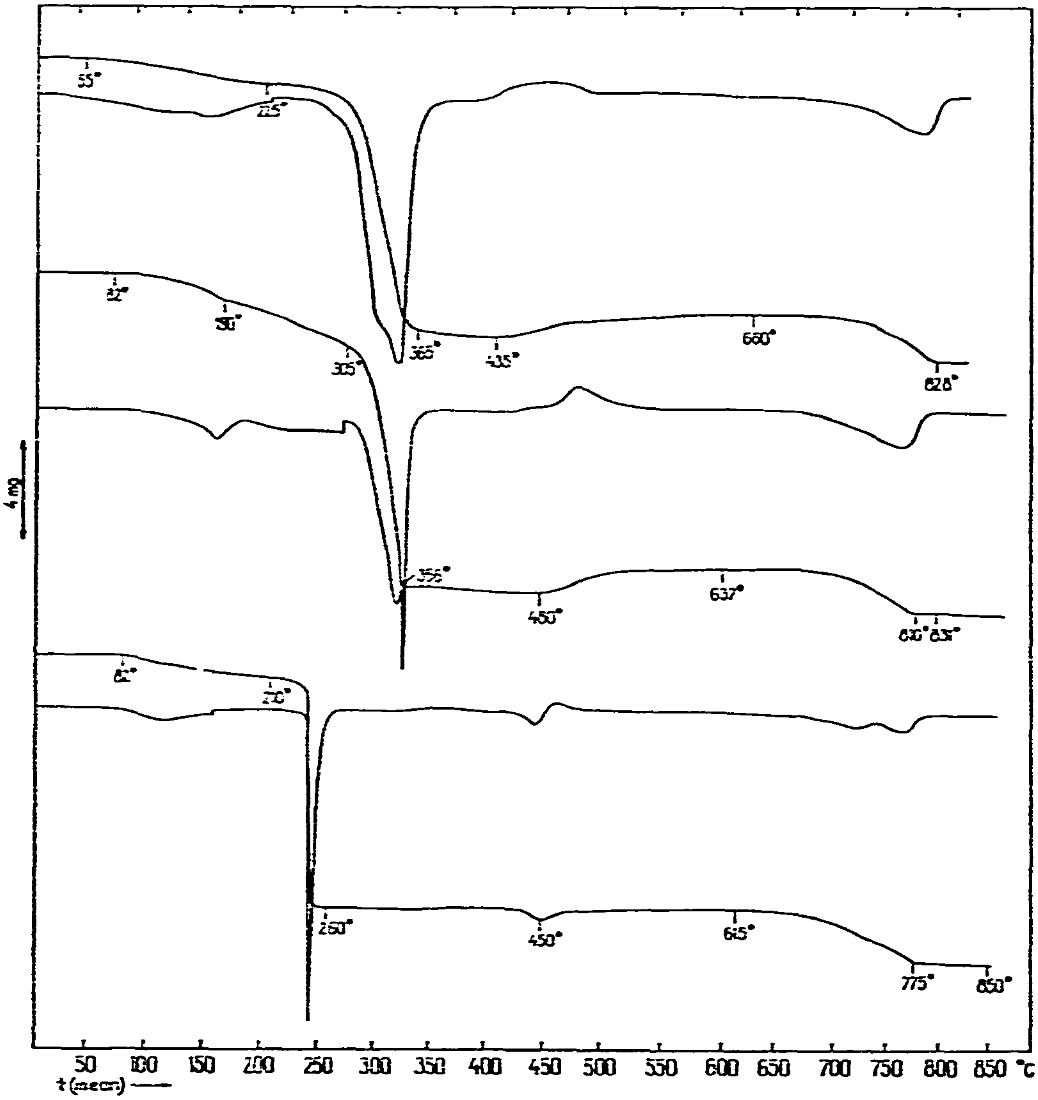


Fig. 3. TG and DTG curves of cobalt(II), nickel(II) and copper(II) 2-thiophenecarboxylates. All in this order from the top downwards. The DTG scale was for Co(II) complex 1 mg min^{-1} to 230 °C and 2 mg min^{-1} from this upwards; for Ni(II) complex 4 mg min^{-1} at 305–490 °C, otherwise 2 mg min^{-1}; for Cu(II) complex 2 mg min^{-1} to 165 °C, 10 mg min^{-1} at 165–290 °C and 4 mg min^{-1} above 290 °C.

phenecarboxylates were obtained depending whether alcoholic or pure water solutions were used in syntheses (Table 1).

All prepared complexes are monohydrates which leave the water molecule as a first thermal process (Fig. 3 and Table 4). After this the anhydrous cobalt(II) carboxylate is decomposed:

$$(C_5H_3O_2S)(C_2H_6O)CoCl \rightarrow 0.5Co_2SCl_2 \qquad (4)$$

TABLE 4

TG DATA FOR 2-THIOPHENECARBOXYLATES

Process	*TG*		
	Temp. range (°C)	*Residue (%)*	
		Found	*Calc.*
$(C_5H_3O_2S)(C_2H_6O)CoCl \cdot H_2O\rceil$	– 55		
	55–225		
$(C_5H_3O_2S)(C_2H_6O)CoCl$		94.5	93.7
	225–365		
$1/2Co_2SCl_2$	435	39.2	38.7
	365–620		
$1/2CoSO_4 \cdot CoCl_2$	660	44.5	49.9
	690–828		
$1/3Co_3O_4$	828→	34.3	28.1
$(C_5H_3O_2S)(C_2H_6O)NiCl \cdot H_2O\rceil$	– 82		
	82–190		
$(C_5H_3O_2S)(C_2H_6O)NiCl$		94.2	93.7
	190–356		
NiS	356–480	31.4	31.8
	480–637		
$NiSO_4$		36.3	54.2
	637–810		
NiO	810→	27.0	26.2
$(C_5H_3O_2S)_2Cu \cdot H_2O\rceil$	– 82		
	82–210		
$(C_5H_3O_2S)_2Cu$		94.5	94.6
	210–260		
$1/2CuS \cdot CuSO_4$	260–615	38.7	38.0
	615–790		
CuO	790→	25.8	23.7

The formed product is oxidized partly:

$$0.5Co_2SCl_2 \rightarrow 0.5CoSO_4 \cdot CoCl_2 \qquad (5)$$

which is further oxidized to Co_3O_4 still containing $CoSO_4$ (828 °C).

The anhydrous nickel(II) carboxylate is decomposed to sulfide:

$$(C_5H_3O_2S)(C_2H_6O)NiCl \rightarrow NiS \qquad (6)$$

which is partly oxidized to sulfate and finally to NiO.

The anhydrous copper(II) 2-thiophenecarboxylate decomposes to a sulfide–sulfate mixture:

$$(C_5H_3O_2S)_2Cu \rightarrow 0.5CuS \cdot CuSO_4 \qquad (7)$$

and further to CuO.

By considering the preparation of cobalt(II) and nickel(II) 2-thiophenecarboxylate complexes it is interesting to note that adding the base solution just after the metal chloride solution to the alcoholic solution of the carboxylic acid causes one ligand ion to be replaced by one chloride ion and attachment of one alcohol molecule.

A further discussion of the structure of the prepared 2-thiophenecarboxylate mixed complexes is not possible on the basis of the present data, but the structure may be assumed to have some polymeric nature. The copper(II) 2-thiophenecarboxylate may be suggested, however, to have as a base crystal structure unit a copper(II) ion surrounded by two 2-thiophenecarboxylic ions in a *trans*-planar arrangement and in analogy with the crystal structure of 2-thiophenecarboxylic acid[23]. The water molecules may complete the structure to a distorted octahedral.

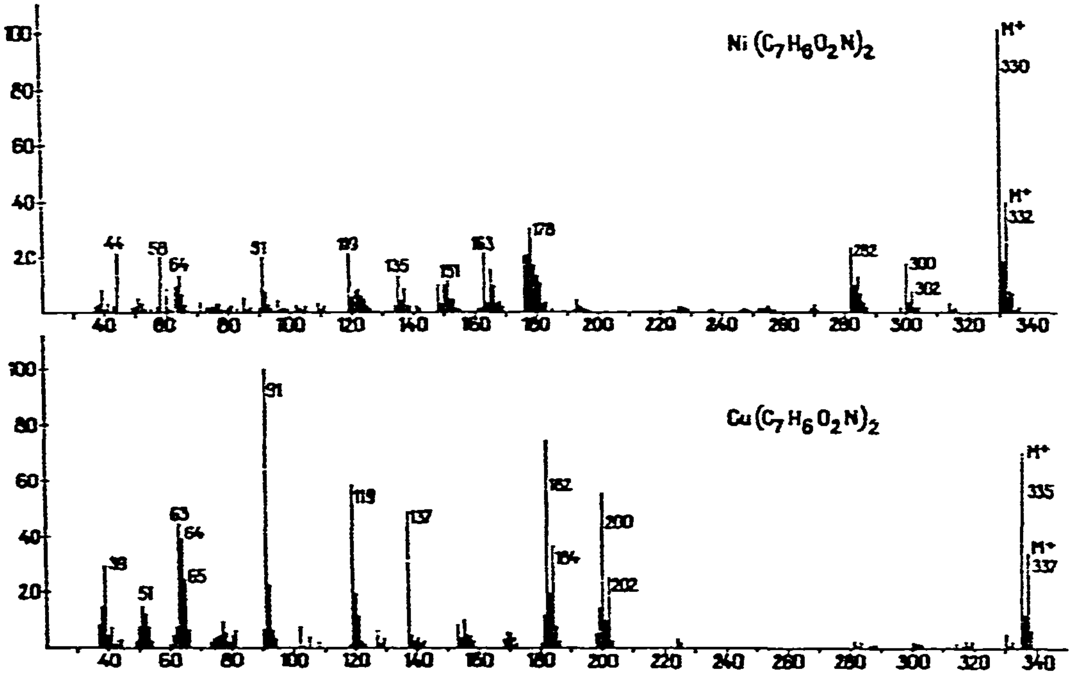
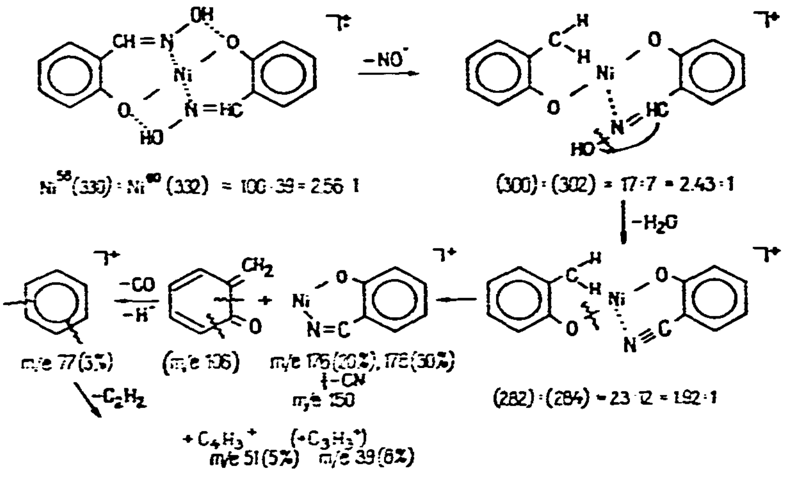


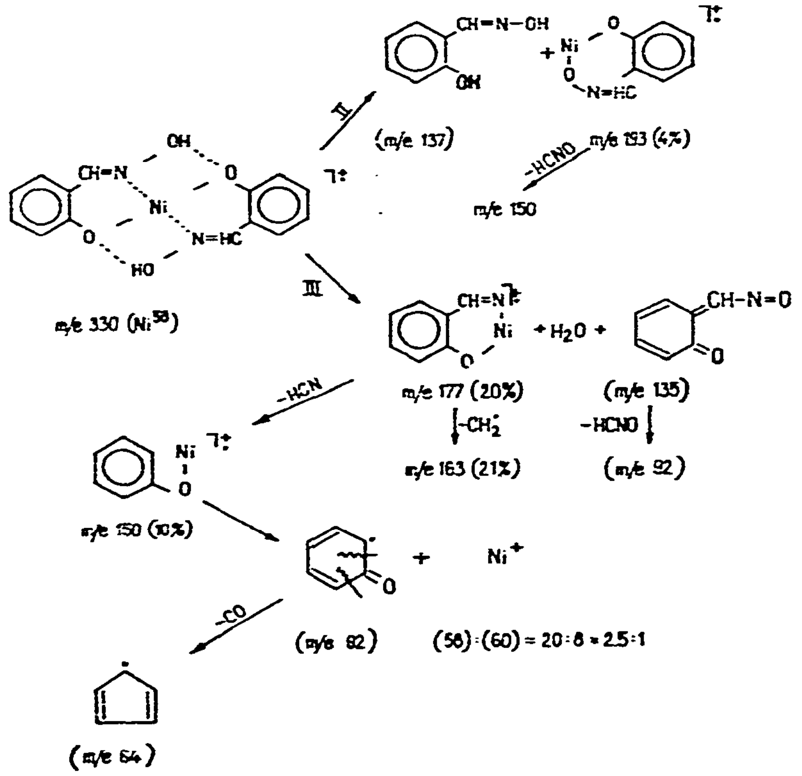
Fig. 4. Mass spectra of nickel(II) and copper(II) salicylaldoximates. The relative abundance (%) is plotted against *m/e*.

B. Mass-spectrometric data

Mass spectra were obtained only for nickel(II) and copper(II) salicylaldoximates of the studied compounds (Fig. 4). The mass spectrum of nickel(II) salicylaldoximate gave molecular peaks at *m/e* 330 and 332 in intensity ratio 2.56:1 and in agreement



Scheme I



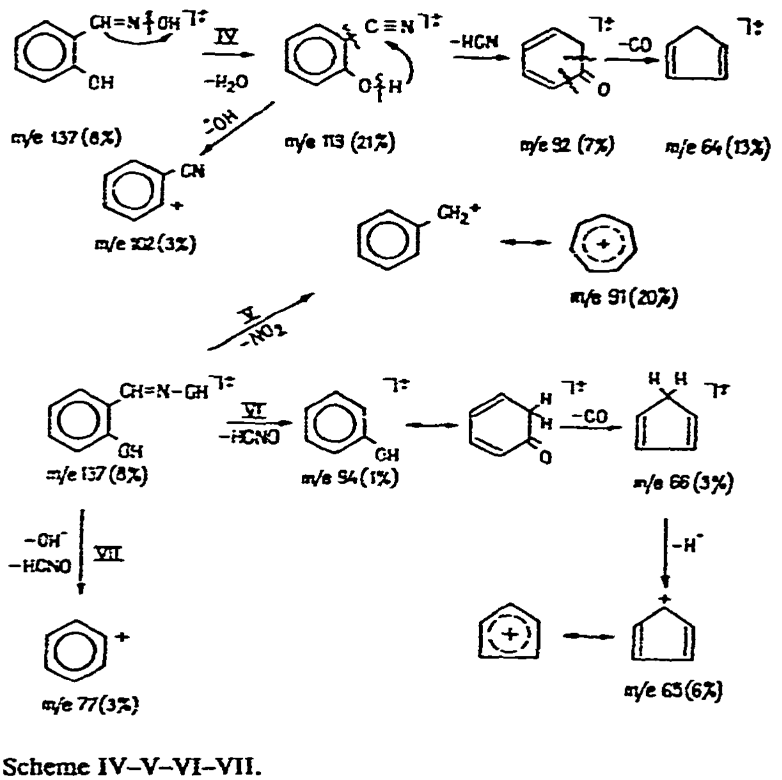
Scheme II–III.

with the abundance ratio of ^{58}Ni to ^{60}Ni which is 67.88:26.23 = 2.59:1 (ref. 26). The satellite mass peaks are partly due to the other Ni isotopes[25] (*m/e* 333, 334, 336). The mass spectrum may be explained through three main decomposition routes of nickel(II) salicylaldoximate and the fragmentation processes of the formed salicylaldoxime.

The first route may be presented as in Scheme I. The compound with *m/e* 106 is obviously further decomposed immediately (mass peak not observed) and the fragments *m/e* 176–182 as shown in Scheme III.

The two other decomposition routes of nickel(II) salicylaldoximate may be presented as in Schemes II and III.

In accordance with the mass spectrum (Fig. 4) the fragmentation processes of the released salicylaldoxime may be given as done in Schemes IV–VII.



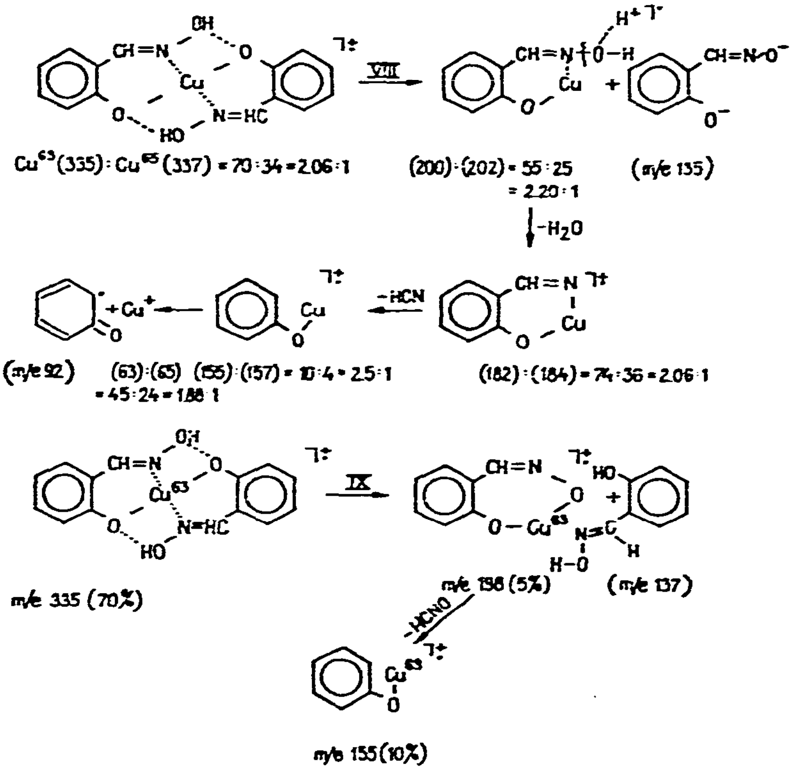
Scheme IV–V–VI–VII.

Thus the chelate decomposition reaction (1) beginning at 91 °C (Fig. 1 and Table 2), when one salicylaldoxime molecule has escaped, is also confirmed by the mass spectrum (Fig. 4), which shows the mass peak of salicylaldoxime, *m/e* 137 (8%). The decomposition of the reaction residue $C_7H_5O_2NNi$ passes several ways as shown by the mass peaks of the fragmentation products of $C_7H_5O_2NNi$ in the mass spectrum.

The mass spectrum of copper(II) salicylaldoximate gave molecular peaks at *m/e* 335 and 337 in the intensity ratio 2.06:1. These correspond to the abundances of the isotopes ^{63}Cu and ^{65}Cu for which the abundance ratio is 69.09:30.91 = 2.24:1

(ref. 26). The mass spectrum may be explained in limits of two cleavage processes of copper(II) salicylaldoximate and of the fragmentation routes of the formed salicylaldoxime (Schemes IV–VII).

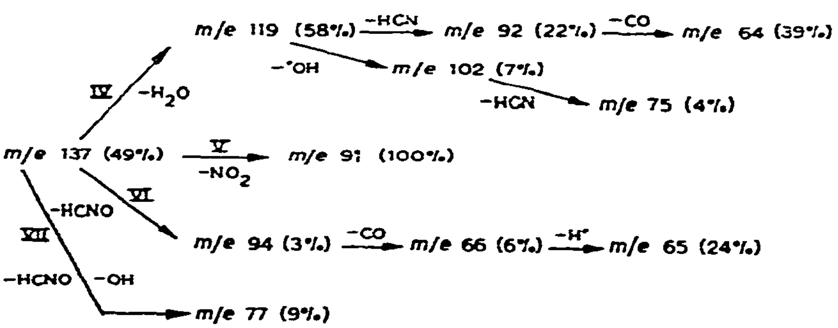
The first cleavage process of copper(II) salicylaldoximate (Scheme VIII) is similar to Scheme III of nickel(II) salicylaldoximate. No peak of *m/e* 135 is, however, observed in the mass spectrum pointing to a totally unstable character of this fragment.



Scheme VIII — IX.

The second cleavage process (Scheme IX) of copper(II) salicylaldoximate is similar to Scheme II of nickel(II) salicylaldoximate.

The fragmentation processes of the escaped salicylaldoxime seem to resemble those in the case of nickel(II) salicylaldoximate:



The fragments *m/e* 39 (29%) and 51 (15%) with their satellite peaks are cleavage products of the formed benzene (cf. Scheme I).

It is interesting to notice that according to the mass spectra the direct dissociation of one molecule of salicylaldoxime from the complex is more prevailing in the decomposition of copper(II) salicylaldoximate (*m/e* 137 (49%)) than of nickel(II) salicylaldoximate (*m/e* 137 (8%)).

The presented fragmentation processes of salicylaldoxime are in agreement with the mass spectrum of salicylaldoxime alone. For this we obtained the main mass peaks as follows: *m/e* 137 (18% [M^+]), 122 (3), 121 (6), 120 (20), 119 (100), 102 (4), 94 (2), 93 (7), 92 (15), 91 (84), 90 (5), 77 (3), 76 (5), 75 (4), 66 (9), 65 (14), 64 (36), 63 (26), 62 (7), 61 (5), 53 (5), 52 (10), 51 (7), 50 (10), 41 (7), 40 (3), 39 (19), 38 (14), 37 (8). The relative abundances in % are given in brackets. Differences observed in the relative abundances of the mass peaks when compared with those in the mass spectra of the metal salicylaldoximates are natural and due to different initial conditions of salicylaldoxime in the ion source.

Mass spectrometric studies of aldoxime compounds are generally few, but those done on substituted aromatic aldoximes[27] gave fragmentation routes of parallel nature to those suggested in this paper.

When considering the suggestion of Liptay et al.[20] that the thermal decomposition of nickel(II) and copper(II) salicylaldoximates would begin instead of a scission of the coordinative bond by the cleavage of another bond in the chelate ring, that is weakened by an increase in strength of the coordinative bond, then because the complex stability of the copper(II) chelate in solutions is higher than that of the nickel(II) chelate[20], the former should show a higher cleavage tendency mentioned above. In contrast, however, it is nickel(II) salicylaldoximate which shows, according to the mass spectrum, such a cleavage tendency in greater extent (*cf.* Scheme I).

C. The kinetic data

The methods used to obtain the kinetic data, activation energies and reaction orders, are often applied to the decomposition reaction:

$$A(s) \rightarrow B(g) + C(s) \qquad (8)$$

by assuming the decomposition rate of A to follow the equation:

$$dX/dt = -kX^n \qquad (9)$$

where n is the reaction order and X the undecomposed part of A. The reaction rate constant k is further assumed to follow the Arrhenius equation:

$$k = A \cdot e^{-E/RT} \qquad (10)$$

where A is the frequency factor, E the activation energy, R the general gas constant and T the absolute temperature. By assuming a linear heating rate $u = dT/dt$ [K min^{-1}] and combining the equations it follows:

$$-dX/X^n = (A/u)e^{-E/RT}\,dT \qquad (11)$$

Depending now on how further derivation is done and what assumptions are made different representations are obtained for the relation between E and n. In this paper three of these were applied.

According to the method of Freeman and Carroll[28] both the activation energy and the reaction order of a decomposition reaction may be calculated directly on the basis of the TG curve from the equation:

$$\frac{\Delta \log (\mathrm{d}w/\mathrm{d}t)}{\Delta \log W_r} = \frac{-E}{2.303\,R} \cdot \frac{\Delta(1/T)}{\Delta \log W_r} + n \tag{12}$$

where W_r is the undecomposed sample amount ($= X$) and $\mathrm{d}w/\mathrm{d}t$ the decomposition rate at the same moment. Eqn (12) is of the form $y = ax+b$ and a program (FREECA) was prepared in FORTRAN to calculate E and n by the method of least squares in eqn (12)[29].

In the method of Coats and Redfern[30] the activation energy E and the reaction order n of a reaction are calculated on the basis of the TG curve from the equation:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = -E/2.303\,RT + \log \frac{AR}{aE}\left[1-\frac{2RT}{E}\right]$$

$$\cong -E/2.303\,RT + \text{const.} \tag{13}$$

where $n \neq 1$, α is the decomposition degree, a [K min^{-1}] the heating rate and the other symbols have the meaning mentioned above. The method is a line fitting method for which a program in FORTRAN was prepared[29]. The program (CORE 3) searches the reaction order and activation energy with the method of least squares increasing n in increments of 0.01 unit until the best fitting with the experimental data is reached.

As a third method we used the method of Broido[31] for the case $n \neq 1$ in the form:

$$\log(1-y^{1-n}) = -E/2.303\,RT + \text{const.} \tag{14}$$

where y is the ratio of the unreacted sample to the total sample $(1-\alpha)$. A program (BROIDO 2) in FORTRAN[29] searches again with the method of least squares the values of n and E which give the best fitting line through the experimental points.

From the three methods mentioned above and used in this paper the method of Freeman and Carroll[28] is the oldest and most criticized[32,33], but still generally used. Some of the latest criticizers are Sharp and Wentworth[34,35], according to whom the method gives unsignificant values for the reaction order and experimental points may frequently be scattered. This depends on the selection of the beginning values within a narrow interval when the differences between the points are small. Instead of this Mickelson and Einhorn[36] hold as the only weakness of the method the difficulty to determine the decomposition rate, $\mathrm{d}w/\mathrm{d}t$, which is to be known exactly at each moment. In the present work the values of $\mathrm{d}w/\mathrm{d}t$ were read directly from the DTG

TABLE 5

KINETIC PARAMETERS, ACTIVATION ENERGIES (E) (kJ mol^{-1}) AND REACTION ORDERS (n) OF SOME DECOMPOSITION REACTIONS OF COBALT(II), NICKEL(II) AND COPPER(II) SALICYLALDOXIMATES, 2-INDOLECARBOXYLATES AND 2-THIOPHENECARBOXYLATES CALCULATED BY THREE DIFFERENT METHODS

Reaction	*FREECA*		*CORE 3*		*BROIDO 2*		*Decomposition temp. (K)*
	E	n	E	n	E	n	
Salicylaldoximates							
$(C_7H_6O_2N)_2Co \rightarrow (C_7H_5O_2N)Co + C_7H_7O_2N$	50.0	0.61	24.4	0.60	31.9	0.62	303
$(C_7H_6O_2N)_2Ni \rightarrow (C_7H_5O_2N)Ni + C_7H_7O_2N$	167	1.08	89.7	0.02	98.2	0.02	364
$(C_7H_6O_2N)_2Cu \rightarrow (C_7H_5O_2N)Cu + C_7H_7O_2N$	501	6.39	328	4.00	352	4.00	453
2-Indolecarboxylates							
$(C_9H_6O_2N)_2Co \cdot 2H_2O \rightarrow (C_9H_6O_2N)_2Co + 2H_2O$	199	1.51	195	2.14	204	2.18	400
$(C_9H_6O_2N)_2Co \rightarrow (C_8H_6N)_2Co + 2CO_2$	85.8	0.98	69.7	0.04	88.7	0.82	453
$(C_9H_6O_2N)_2Ni \cdot 2H_2O \rightarrow (C_9H_6O_2N)_2Ni + 2H_2O$	114	0.17	127	0.28	134	0.28	420
$(C_9H_6O_2N)_2Ni \rightarrow (C_8H_6N)_2Ni + 2CO_2$	—	—	35.7	0.02	43.3	0.02	468
$(C_9H_6O_2N)_2Cu \cdot 2H_2O \rightarrow (C_9H_6O_2N)_2Cu + 2H_2O$	144	0.31	170	0.86	176	0.86	378
$(C_9H_6O_2N)_2Cu \rightarrow (C_8H_6N)_2Cu + 2CO_2$	—	—	28.2	0.02	36.0	0.02	413
2-Thiophenecarboxylates							
$(C_5H_3O_2S)(C_2H_6O)CoCl \cdot H_2O \rightarrow (C_5H_3O_2S)(C_2H_6O)CoCl + H_2O$	33.8	1.91	30.7	1.22	36.8	1.16	328
$(C_5H_3O_2S)(C_2H_6O)NiCl \cdot H_2O \rightarrow (C_5H_3O_2S)(C_2H_6O)NiCl + H_2O$	40.7	0.05	37.0	0.02	44.2	0.02	355
$(C_5H_3O_2S)_2Cu \cdot H_2O \rightarrow (C_5H_3O_2S)_2Cu + H_2O$	55.9	—	39.4	0.02	45.1	0.02	355

curves, for which the possible error in determining the decomposition rate as the tangent of the TG curve is lower.

Calculations of the kinetic parameters, the activation energies and reaction orders, were done on a Honeywell 1642 computer with the programs[29] mentioned above for some decomposition reactions of the studied compounds. The results are represented in Table 5.

The results in Table 5 show the programs CORE 3 and BROIDO 2 to give generally the activation energy and reaction order values of the same order of magnitude. The program FREECA gives activation energy values of the same order of magnitude as the two other programs, whereas the reaction order values are in many cases different. Therefore the results would seem to support the criticism of Sharp and Wentworth[34,35]. However, it is interesting to observe by comparison of the data in Table 5 with the forms of the TG curves in Figs. 1–3 that the results obtained with the method of Freeman and Carroll are closest to those calculated with the two other methods, when the part of the TG curve corresponding to the studied reaction approaches a smooth S-shape[25].

The results (the activation energies and decomposition temperatures) for salicylaldoximates (Table 5) show parallelism between the thermal stability and complex stability in solutions[20] in contrast to the results of Liptay et al.[20]. No parallelism is, however, observed with respect to 2-indolecarboxylates[21a].

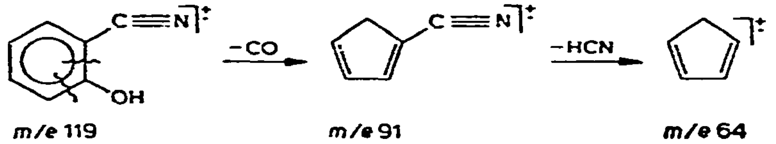
In agreement with the unobtainable molecular mass peak (in this work) the results (Table 5) show that cobalt(II) salicylaldoximate is rather unstable as compared with nickel(II) and copper(II) salicylaldoximates, but do not justify the assumption that cobalt(II) salicylaldoximate has the exceptional *cis*-configuration as assumed by Burger et al.[16,17]. In this respect *cf.* the discussion of Nishikawa and Yamada[37] on the UV spectrum of cobalt(II) salicylaldoximate. (It should also be mentioned that the assignments of the ionization constants of salicylaldoxime with respect to the ionizing groups done by Burger et al.[16] must be wrong, and therefore also their assignments of the UV absorption bands of salicylaldoxime in aqueous solutions. In this respect *cf.* refs. 3, 38 and 39. The pK_1 (actually pK_2) value 10.9 ± 0.1 in 1.0 M aqueous solution of $NaClO_4$ at 20°C reported by Burger et al.[16] is about 1.8 unit too high[3].)

The activation energy values of the water loss reactions of the 2-indolecarboxylates are exceptionally high and point to the coordination of the two water molecules to the central metal ion and to the fact that they are true components of the complex structure as suggested before. The low activation energy values of the carbon dioxide splitting show the cleavage to happen easily and parallel with the decomposition temperatures of the anhydrous 2-indolecarboxylates.

In the case of 2-thiophenecarboxylates the results (Table 5) point the water molecules to have rather a cluster character, but do not exclude the structure completing role in the copper(II) carboxylate proposed above.

Note added in proof

Instead of the suggested fragmentation route of salicylaldoxime in Scheme V on page 432, a more probable route may be the following:



(Cf., J. M. Fernández-G., E. Cortés and J. Goméz Lara., *J. Inorg. Nucl. Chem.*, 37 (1975) 1385.)

ACKNOWLEDGEMENTS

Thanks are due to Miss Kaisa Nieminen for some preliminary measurements. Financial support from the National Research Council for Sciences (Finland) is also gratefully acknowledged.

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