THERMAL STABILITY AND NON-ISOTHERMAL KINETIC STUDY OF TWO COORDINATION COMPOUNDS OF COBALT(II) WITH LIGANDS DERIVED FROM THIOAMIDES AND ETHYLENDIAMINE

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ABSTRACT

Results are presented concerning the thermal behaviour of two coordination compounds of Co(II) synthesized in template condensation reactions of thioacetamide and thiobenzamide with ethylendiamine. A non-isothermal kinetic analysis of the single decomposition steps has also been carried out.

INTRODUCTION

This paper deals with the thermal stability of the following two coordination compounds. For the decomposition steps which behave as single steps, the non-isothermal kinetic parameters have also been evaluated.
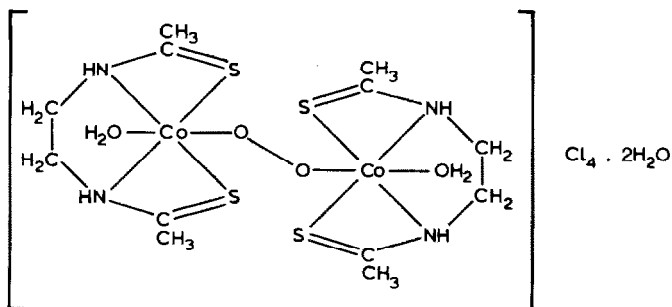
or $[Co_2(O_2)(H_2O)_2C_{12}H_{24}N_4S_4]Cl_4 \cdot 2H_2O$ (1)
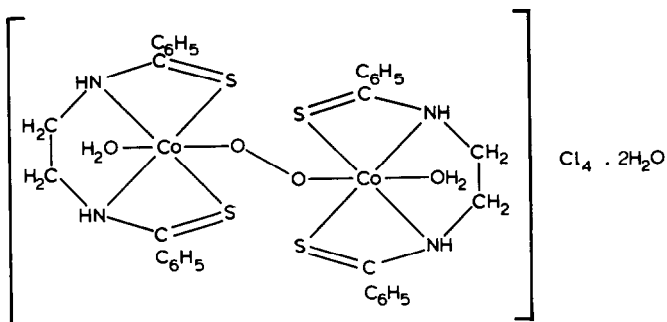
or $[Co_2(O_2)(H_2O)_2C_{32}H_{32}N_4S_4]Cl_4 \cdot 2H_2O$ (2)

EXPERIMENTAL

Substances

Powders of compounds 1 and 2 were used, synthesized and analysed according to methods described elsewere [1].

Equipment

The heating curves (TG, T, DTA and DTG) were recorded using an MOM Budapest Paulik–Paulik–Erdey type derivatograph, in a static air atmosphere at various heating rates of between 2 and 10 K min^{-1}. A Phillips X-ray diffractometer P.W. 1140 was used to obtain information on the crystalline state of compounds 1 and 2, their intermediates, and the final products of heating up to 1000°C. The diffractograms were recorded in the $K\alpha$ radiation of chromium.

Treatment of experimental data

The Coats–Redfern method [2], the Flynn–Wall method for constant heating rate [3], and the Coats–Redfern method as modified by Urbanovici and Segal [4] were used to evaluate the non-isothermal kinetic parameters.

The experimental data were worked up automatically using an original program [5], two programs developed by Coseac and Segal [6,7], and a program which regenerates the thermogravimetric curves using coordinates α, T (°C) [8].

Mean crystallite sizes were obtained by Scherrer's method [9].

RESULTS AND DISCUSSION

The interplanar distances d (Å), relative intensities and mean crystallite sizes l (Å) for compounds 1 and 2 are listed in Table 1.

Inspection of the data given in Table 1 shows that the two compounds under investigation exhibit similar crystal structures (isomorphism).

The decomposition of $[Co_2(O_2)(H_2O)_2C_{12}H_{24}N_4S_4]Cl_4 \cdot 2H_2O$

The TG and DTG curves indicate that thermal decomposition occurs according to the following steps. The temperatures above the arrows correspond to the maximum reaction rates.

$$[Co_2(O_2)(H_2O)_2C_{12}H_{24}N_4S_4]Cl_4 \cdot 2H_2O(s)$$

$$\xrightarrow{115°C} 2CoC_6H_{12}N_2S_2Cl_2(s) + 4H_2O(g) + O_2(g) \qquad (1)$$
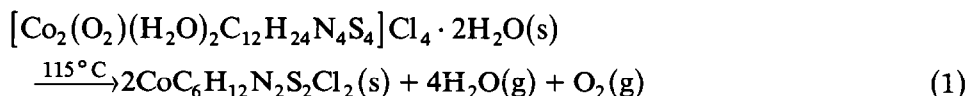
The absence from the IR spectra of the reaction product of the absorption band at 840 cm^{-1} corresponding to $\nu_{O-O}(O_2^{2-})$ as well as the broad band from 2800–3600 cm^{-1} characteristic of $\nu_{O-H}(H_2O)$ confirms the thermogravimetric results, indicating that oxygen and water are evolved in reaction (1).
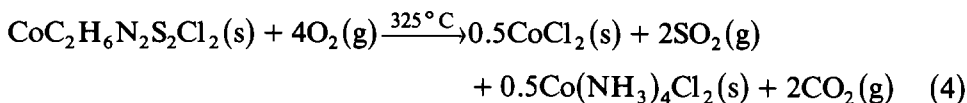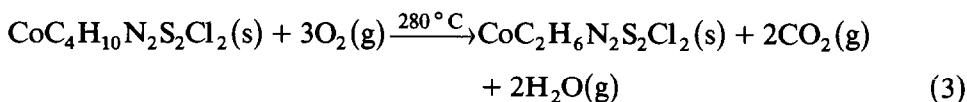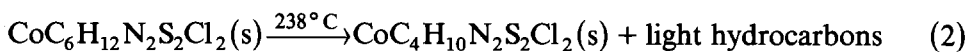
$$CoC_6H_{12}N_2S_2Cl_2(s) \xrightarrow{238°C} CoC_4H_{10}N_2S_2Cl_2(s) + \text{light hydrocarbons} \qquad (2)$$

$$CoC_4H_{10}N_2S_2Cl_2(s) + 3O_2(g) \xrightarrow{280°C} CoC_2H_6N_2S_2Cl_2(s) + 2CO_2(g)$$
$$+ 2H_2O(g) \qquad (3)$$

$$CoC_2H_6N_2S_2Cl_2(s) + 4O_2(g) \xrightarrow{325°C} 0.5CoCl_2(s) + 2SO_2(g)$$
$$+ 0.5Co(NH_3)_4Cl_2(s) + 2CO_2(g) \qquad (4)$$
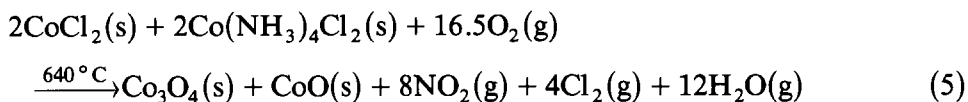
TABLE 1

Crystalline state and mean crystallite sizes

Compound	Relative intensity	d (Å)	l (Å)
$[Co_2(O_2)(H_2O)_2C_{12}H_{24}N_4S_4]Cl_4 \cdot 2H_2O$	86	6.15	
	65	5.78	
	57	3.89	
	74	3.40	
	100	3.06	283.2
$[Co_2(O_2)(H_2O)_2C_{32}H_{32}N_4S_4]Cl_4 \cdot 2H_2O$	85	6.04	
	65	5.73	
	58	3.84	
	77	3.35	
	100	3.02	202.6

TABLE 2

Values of non-isothermal kinetic parameters for reaction (1): $\beta = 2.42$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	1.9	1.77×10^4	5.54×10^8
Flynn–Wall	1.9	1.81×10^4	1.24×10^9
Modified Coats–Redfern	1.8	1.72×10^4	2.46×10^8

The X-ray diffractogram of the solid product of reaction (4) confirms the existence of $CoCl_2$; the existence of $Co(NH_3)_4Cl_2$ is confirmed by the IR spectrum showing absorption bands corresponding to $\nu_{s(N-H)}(NH_3)$ and $\nu_{as(N-H)}(NH_3)$.

$$2CoCl_2(s) + 2Co(NH_3)_4Cl_2(s) + 16.5O_2(g)$$

$$\xrightarrow{640\,^\circ C} Co_3O_4(s) + CoO(s) + 8NO_2(g) + 4Cl_2(g) + 12H_2O(g) \qquad (5)$$

The X-ray diffractogram of the solid product confirms the existence of Co_3O_4 and CoO.

The decomposition steps which behave as single steps are (1) and (5). The values of the non-isothermal kinetic parameters reaction order n, activation energy E, and pre-exponential factor A for these steps are listed in Tables 2 and 3.

Inspection of these results indicates that the values of the non-isothermal kinetic parameters determined by the three methods are in agreement.

The decomposition of $[Co_2(O_2)(H_2O)_2C_{32}H_{32}N_4S_4]Cl_4 \cdot 2H_2O$

Despite the isomorphism between this compound and the former one indicated by the following result, the decomposition steps are different. According to the heating curves, thermal decomposition occurs according to the following steps.
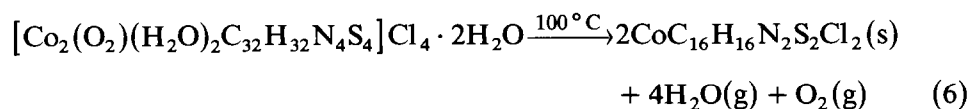
$$[Co_2(O_2)(H_2O)_2C_{32}H_{32}N_4S_4]Cl_4 \cdot 2H_2O \xrightarrow{100\,^\circ C} 2CoC_{16}H_{16}N_2S_2Cl_2(s)$$

$$+ 4H_2O(g) + O_2(g) \qquad (6)$$

TABLE 3

Values of non-isothermal kinetic parameters for reaction (5): $\beta = 2.22$ K min^{-1}

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	0	2.35×10^4	3.95×10^2
Flynn–Wall	0	2.55×10^4	5.26×10^3
Modified Coats–Redfern	0	2.30×10^4	6.08×10^2

The absence from the IR spectrum of the solid reaction product of an absorption band at 900 cm^{-1}, corresponding to ν_{O-O} (O_2^{2-}), confirms this formulation, as does the absence of a band corresponding to $\nu_{O-H}(H_2O)$.

The following two steps overlap to some extent, so we were not able to isolate and characterize the intermediates. The overall stoichiometric reaction which occurs between 160 and 450°C is

$$CoC_{16}H_{16}N_2S_2Cl_2(s) + H_2O(g) + 1.5O_2(g) \rightarrow CoC_2H_6N_2S_2Cl_2(s)$$
$$+ 2C_6H_6(g) + 2CO_2(g) \quad (7)$$
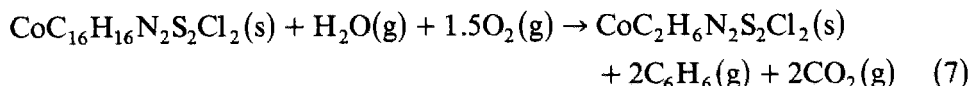
This formulation is confirmed by the vibration spectrum of the solid product, which exhibits a band between 600 and 800 cm^{-1} corresponding to ν_{C-S} and a split band at 3350–3500 cm^{-1} corresponding to $\nu_{s(N-H)}$ and $\nu_{as(N-H)}$. The X-ray diffractogram of the solid product does not indicate that CoS or CoCl$_2$ are present.

$$3CoC_2H_6N_2S_2Cl_2(s) + 24.5O_2(g) \xrightarrow{640°C} Co_3O_4(s) + 6CO_2(g) + 6SO_2(g)$$
$$+ 3Cl_2(g) + 9H_2O(g) \quad (8)$$
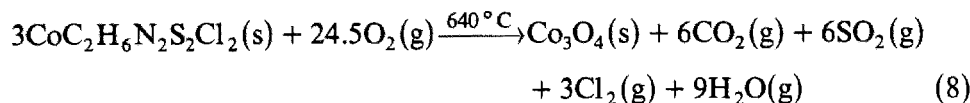
Heating the sample to 1000°C brings about a partial conversion of Co$_3$O$_4$ into CoO. This is shown by the X-ray diffractogram of the solid product, which exhibits lines corresponding to both Co$_3$O$_4$ and CoO.

The values of the non-isothermal kinetic parameters of reactions (6) and (8) are listed in Tables 4 and 5.

As can be seen from Tables 4 and 5, the values of the non-isothermal parameters obtained using the three different methods agree satisfactorily.

Figures 1 and 2 show regenerated thermogravimetric curves for reactions (1) and (6) calculated by means of the Coats–Redfern integral equation

TABLE 4

Values of non-isothermal kinetic parameters for reaction (6): $\beta = 2.31$ K min^{-1})

Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	1.1	1.29×10^4	2.57×10^5
Flynn–Wall	1.1	1.35×10^4	1.02×10^6
Modified Coats–Redfern	1.1	1.30×10^4	3.46×10^5

TABLE 5

Values of non-isothermal kinetic parameters for reaction (8): $\beta = 2.50$ K min^{-1}

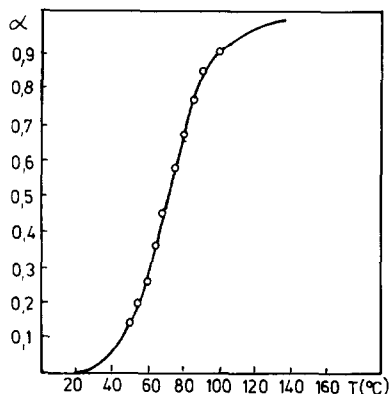| Method	n	E (cal mol^{-1})	A (s^{-1})
Coats–Redfern	0.4	1.82×10^4	1.44×10
Flynn–Wall	0.3	2.00×10^4	2.29×10
Modified Coats–Redfern	0.4	1.78×10^4	2.66×10

Fig. 1. Regenerated thermogravimetric curve using coordinates α, t($^\circ$C) for reaction (1): ———, calculated curve, o experimental points.

using the experimental values of the non-isothermal parameters, plotted in coordinates α, T ($^\circ$C). The experimental points lie practically on the same curve, which indicates the accuracy of the Coats–Redfern approximation, even reduced to its first term.

The fractionary values of the reaction order between zero and unity show a mixed regime of control (kinetic and diffusional) of the occurrence of the reaction [10], with the purely kinetic regime corresponding to $n = 1$. As for values of the reaction order higher than unity, these could be attributable to the decomposition of more than one structural unit in various ratios.
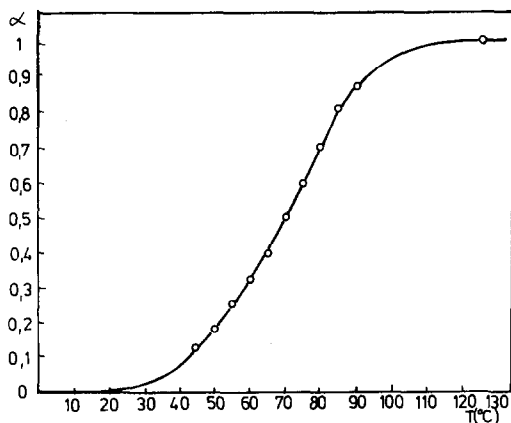

Fig. 2. Regenerated thermogravimetric curve using coordinates α, t($^\circ$C) for reaction (6): ———, calculated curve, o experimental points.

CONCLUSIONS

The main decomposition steps which occur on heating of $[Co_2(O_2)(H_2O)_2Cl_{12}H_{24}N_4S_4]Cl_4 \cdot 2H_2O$ and $[Co_2(O_2)(H_2O)_2C_{32}H_{32}N_4S_4]Cl_4 \cdot 2H_2O$ have been established.

The non-isothermal kinetic parameters of the single decomposition steps have been evaluated.

The values of the non-isothermal kinetic parameters obtained using the three different methods agree satisfactorily.

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