Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 977–984

THERMAL STABILITY AND NON-ISOTHERMAL DECOMPOSITION KINETICS

Heteropolynuclear compounds of Cu(II)

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(Received November 7, 1998; in revised form March 20, 1999)

Abstract

Data concerning the thermal behaviour of four heteropolynuclear compounds with the general formula [CuML($CH_3COO)_3$] where *M*=Ni(II), Zn(II), Mn(II) and Co(II); *LH*=2-amino-5-mercapto-1,2,3-thiadiazole were obtained. For the kinetically workable decomposition steps the values of the kinetic parameters were estimated.

Keywords: coordination compounds, non-isothermal kinetics, thermal stability

Introduction

The 1,3,4-thiadiazole derivatives show coordinative as well as biological properties. The inhibitory activity towards carbonic anhydrase has stimulated the interest in their coordinative properties.

Some coordination compounds of transition metals with 2-amino-5-mercapto-1,3,4-thiadiazole ($C_2H_2N_3S_2$) (*LH*) have been investigated [1–3]; the ligand behaves as bidentate through the exocyclic sulphur atom and depending on the nature of the metal, it can engage the exocyclic or heterocyclic nitrogen atom.

Recently, the inhibitory action of some coordination compounds with 2-amino-5-mercapto-1,3,4-thiadiazole toward carbonic anhydrase has been reported [4, 5].

On the other hand, taking into account the metal-sulphur bonds, the thiadiazole coordination compounds are potential materials for the preparation of metal sulphides, via controlled thermal decomposition. This possibility is true for the polynuclear Cu(II) coordination compounds with the thiadiazole derivative (*LH*) [6]. This is the reason why we try to extend our synthesis and thermal decomposition investigations to heteropolynuclear coordination compounds as precursors of mixed sulphides.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Powders of

1. $[CuNiL(CH_3COO)_3]$ or $[CuNiC_8H_{11}N_3O_6S_2]$
2. $[CuZnL(CH_3COO)_3]$ or $[CuZnC_8H_{11}N_3O_6S_2]$
3. $[CuMnL(CH_3COO)_3]$ or $[CuMnC_8H_{11}N_3O_6S_2]$
4. $[CuCoL(CH_3COO)_3]$ or $[CuCoC_8H_{11}N_3O_6S_2]$

were prepared and characterized by chemical analysis, IR, EPR and UV/visible spectroscopy as well as magnetic susceptibility measurements. It has been proved that these compounds act as good in vitro inhibitors toward carbonic anhydrase [7].

The heating curves (TG, T, DTG and DTA) were recorded by means of a Q-1500D derivatograph in static air atmosphere at various heating rates in the range 2.5–10 K min^{-1}.

X-ray diffractograms of the compounds 1–4 as well as of their thermal decomposition intermediates and products were recorded by a DRON3 diffractometer using the K_α radiation of cobalt.

In order to estimate the mean sizes of crystallites, Scherrer's formula [8] was applied.

In order to evaluate the kinetic parameters of the decomposition, three integral methods were used the: Coats-Redfern [9], Flynn-Wall (for constant heating rate) [10] and the Urbanovici-Segal [11] method. These methods permitted the values of the reaction order n, activation energy E and preexponential factor A to be obtained from the equation $d\alpha/dt=k(1-\alpha)^n$.

The experimental data were automatically processed by the program of Dragoe and Segal [12]. From this program, the thermogravimetric curves in coordinates (α, t°C), using the Coats-Redfern values of the kinetic parameters were obtained. The correctness of the values of the estimated kinetic parameters can be checked through the comparison of the so obtained (α, t°C) curve with the experimental points. For correct values of these parameters the experimental points should lie on the curve.

Results and discussion

Table 1 shows some results obtained from a first analysis of the X-ray powder diffraction data of the investigated compounds.

The results indicate that the four investigated compounds are characterized practically by almost identical interplanar distances and relative intensity values i.e. by an elementary cell of the same type and with the same volume. Thus, the difference in the ionic radii from Ni(II) (0.72 Å) to Zn(II) (0.83 Å) is to a certain extent compensated for by the presence of the common Cu(II) (0.80 Å) ion and the common ligand [13].

Table 1 Relative intensities, interplanar distances and mean crystallite sizes of the investigated compounds

Compound	*d*/Å	Relative intensity	*l*/Å
$CuNiL(CH_3COO)_3$	3.24	65	285
	2.76	70	
	2.59	100	
	2.34	35	
	1.71	45	
$CuZnL(CH_3COO)_3$	3.25	60	250
	2.75	80	
	2.62	100	
	2.33	20	
	1.73	50	
$CuMnL(CH_3COO)_3$	3.25	65	270
	2.74	70	
	2.61	100	
	2.34	30	
	1.72	45	
$CuCoL(CH_3COO)_3$	3.24	60	290
	2.74	80	
	2.62	100	
	2.35	35	
	1.74	40	

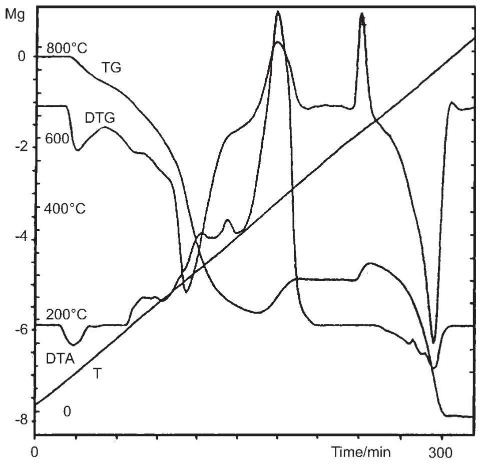

Fig. 1 The TG, DTG and DTA curves of $[CuNiL(CH_3COO)_3]_{(s)}$

Decomposition of [$CuNiC_8H_{11}N_3O_6S_2$]

The TG, DTG and DTA curves corresponding to the heating of the compound [$CuNiL(CH_3COO)_3$] in the temperature range 25–810°C are shown in Fig. 1. For the other compounds investigated in this work, the TG, DTG and DTA curves were similar.

The heating curves TG, DTG and DTA permitted us to evidence the following decomposition stages:

$$[CuNiC_8H_{11}N_3O_6S_2]_{(s)} \xrightarrow{90^\circ C} CuNiC_6H_7N_3O_4S_2{}_{(s)} + CH_3COOH_{(g)} \tag{1}$$

$$[CuNiC_6H_7N_3O_4S_2]_{(s)} + 10.5O_2{}_{(g)} \xrightarrow{130-415^\circ C} CuNiS_2{}_{(s)} + 6CO_{2(g)} + 3NO_{2(g)} + 7H_2O \tag{2}$$

$$2CuNiS_2{}_{(s)} + 3.5O_2{}_{(g)} \xrightarrow{450^\circ C} CuSO_4{}_{(s)} + CuO_{(s)} + 2NiS_{(s)} + SO_2{}_{(g)} \tag{3}$$

$$CuSO_4{}_{(s)} + CuO_{(s)} + 2NiS_{(s)} + 3.5O_2{}_{(g)} \xrightarrow{600^\circ C} CuSO_4{}_{(s)} + CuO_{(s)} + NiSO_4{}_{(s)} + NiO_{(s)} + SO_{2(g)} \tag{4}$$

$$CuSO_4{}_{(s)} + CuO_{(s)} + NiSO_4{}_{(s)} + NiO_{(s)} \xrightarrow{725^\circ C} 2CuO_{(s)} + 2NiO_{(s)} + 2SO_{3(g)} \tag{5}$$

The temperatures above the arrows correspond to the maximum reaction rate at $\beta=2.5$ K min^{-1}.

The presence of the mixed sulphide $CuNiS_2$ as a product of reaction (2) was confirmed by chemical analysis and by powder X-ray diffractometry. The same method allows to identify a mixture of CuO and NiO as components of the final decomposition product obtained at 810°C.

The TG and DTG curves indicated that the only kinetically workable decomposition steps were (1) and (5). Tables 2 and 3 list the values of the non-isothermal kinetic parameters for these steps.

Table 2 Non-isothermal kinetic parameters of reaction (1) at $\beta=2.5$ K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\lvert r\rvert$*
Coats-Redfern	1.7	103	$1.3\cdot10^{12}$	0.9970
Flynn-Wall	1.7	104	$1.7\cdot10^{12}$	0.9973
Modified Coats-Redfern	1.6	102	$7.4\cdot10^{11}$	0.9968

*r is the correlation coefficient of the linear regression

Table 3 Non-isothermal kinetic parameters of reaction (5) at $\beta=2.5$ K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\lvert r\rvert$
Coats-Redfern	1.1	369	$2.97\cdot10^{16}$	0.9945
Flynn-Wall	1.1	366	$2.08\cdot10^{16}$	0.9950
Modified Coats-Redfern	1.0	365	$1.89\cdot10^{16}$	0.9943

A fairly good agreement of the values obtained by means of the three methods used can be noticed.

Decomposition of [$CuZnC_8H_{11}N_3O_6S_2$]

The decomposition curves, mainly the TG curves reveal that during the heating of this compound in the temperature range 20–800°C, the following decomposition steps can be detected:

$$[CuZnC_8H_{11}N_3O_6S_2]_{(s)} \xrightarrow{70^\circ C} [CuZnC_6H_7N_3O_4S_2]_{(s)}+CH_3COOH_{(g)} \tag{6}$$

$$[CuZnC_6H_7N_3O_4S_2]_{(s)}+10.5O_{2\,(g)} \xrightarrow{110-490^\circ C} CuZnS_{2\,(s)}+6CO_{2\,(g)}+3NO_{2\,(g)}+7H_2O_{(g)} \tag{7}$$

$$2CuZnS_{2\,(s)}+3.5O_{2\,(g)} \xrightarrow{530^\circ C} CuSO_{4\,(s)}+CuO_{(s)}+ZnSO_{4\,(s)}+ZnO_{(s)}+2SO_{2\,(g)} \tag{8}$$

$$CuSO_{4\,(s)}+CuO_{(s)}+ZnSO_{4\,(s)}+ZnO_{(s)} \xrightarrow{780^\circ C} 2CuO_{(s)}+2ZnO_{(s)}+2SO_{3\,(g)} \tag{9}$$

The solid product of reaction (7) is a mixed sulphide of formula $CuZnS_2$, crystallized in the blende lattice. The residue obtained at 815°C consists of a stoichiometric mixture of CuO and ZnO. The values of the kinetic parameters of reaction (6) are listed in Table 4. A satisfactory agreement of the values obtained using the three mentioned integral methods can be noticed in this case, too.

Table 4 Non-isothermal kinetic parameters of reaction (6) at β=2.5 K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\lvert r\rvert$
Coats-Redfern	1.8	100	$4.27\cdot10^{16}$	0.9977
Flynn-Wall	1.8	100	$5.34\cdot10^{16}$	0.9991
Modified Coats-Redfern	1.8	102	$1.00\cdot10^{16}$	0.9971

Decomposition of [$CuMnC_8H_{11}N_3O_6S_2$]

The TG and DTG curves indicate that the thermal decomposition occurs through the following steps:

$$[CuMnC_8H_{11}N_3O_6S_2]_{(s)} \xrightarrow{70^\circ C} [CuMnC_6H_7N_3O_4S_2]_{(g)}+CH_3COOH_{(g)} \tag{10}$$

$$[CuMnC_6H_7N_3O_4S_2]_{(s)}+10.5O_{2\,(g)} \xrightarrow{120-475^\circ C} CuMnS_{2\,(s)}+6CO_{2\,(g)}+3NO_{2\,(g)}+7H_2O_{(g)} \tag{11}$$

$$4CuMnS_{2\,(s)}+14.5O_{2\,(g)} \xrightarrow{530^\circ C} 2CuSO_{4\,(s)}+2CuO_{(s)}+2MnSO_{4\,(s)}+Mn_2O_{3\,(s)}+4SO_{2\,(g)} \tag{12}$$

$$2CuSO_{4\,(s)}+2CuO_{(s)}+2MnSO_{4\,(s)}+Mn_2O_{3\,(s)}+0.5O_{2(g)} \xrightarrow{830^\circ C} 2CuMn_2O_{4\,(s)}+CuO_{(s)}+4SO_{3\,(g)} \tag{13}$$

Actually, reaction (11) results from the superposition of several steps difficult to separate in the temperature range 120–475°C.

Chemical analysis of the solid product of reaction (11) reveals the composition $CuMnS_2$. The X-ray diffractogram of the same product shows the peaks corresponding to MnS with no peaks of copper sulphide. Thus, a mixed sulphide $CuMnS_2$ (and not a stoichiometric mixture of CuS and MnS) is formed in reaction (11). This conclusion is supported by the close values of the ionic radii of Cu(II) and Mn(II). The solid residue obtained at temperatures higher than 810°C consists of CuO and the mixed oxide with spinellic structure $CuMn_2O_4$.

Tables 5 and 6 list the values of the kinetic parameters of reactions (10) and (13). As in the former curve, a satisfactory agreement of the values obtained by the applied methods should be noticed.

Table 5 Non-isothermal kinetic parameters of reaction (10) at β=2.55 K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\|r\|$
Coats-Redfern	1.9	128	$2.82\cdot 10^{16}$	0.9990
Flynn-Wall	1.9	127	$2.23\cdot 10^{16}$	0.9991
Modified Coats-Redfern	1.9	133	$2.17\cdot 10^{16}$	0.9989

Table 6 Non-isothermal kinetic parameters of reaction (13) at β=2.55 K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\|r\|$
Coats-Redfern	1.3	518	$1.13\cdot 10^{22}$	0.9963
Flynn-Wall	1.3	510	$5.06\cdot 10^{21}$	0.9965
Modified Coats-Redfern	1.2	523	$2.59\cdot 10^{22}$	0.9953

Decomposition of [$CuCoC_8H_{11}N_3O_6S_2$]

The TG, DTG and DTA curves of this compound allowed to detect the following decomposition steps which occur on its heating in the temperature range 20–810°C.

$$[CuCoC_8H_{11}N_3O_6S_2]_{(s)} \xrightarrow{75^\circ C} [CuCoC_6H_7N_3O_4S_2]_{(g)}+CH_3COOH_{(g)} \tag{14}$$

$$[CuCoC_6H_7N_3O_4S_2]_{(s)}+10.5O_{2\,(g)} \xrightarrow{130-410^\circ C} CuCoS_{2\,(s)}+6CO_{2\,(g)}+3NO_{2\,(g)}+7H_2O_{(g)} \tag{15}$$

$$2CuCoS_{2\,(s)}+7.5O_{2\,(g)} \xrightarrow{440^\circ C} CuSO_{4\,(s)}+CuO_{(s)}+2CoSO_{4\,(s)}+SO_{2\,(g)} \tag{16}$$

$$CuSO_{4\,(s)}+CuO_{(s)}+2CoSO_{4\,(s)}+0.5O_{2\,(g)} \xrightarrow{760^\circ C} 2CuCo_2O_{4\,(s)}+CuO_{(s)}+3SO_{3\,(g)} \tag{17}$$

The formation of $CoCuS_2$ as the solid product of reaction (15) is confirmed by chemical analysis and X-ray diffraction data. The solid residue obtained at 810°C, according to the X-ray diffraction data, consisted of a mixture of $CuCo_2O_4$ and CuO.

In Table 7 the values of the kinetic parameters of reaction (14) are listed.

Table 7 Non-isothermal kinetic parameters of reaction (14) at β=2.5 K min^{-1}

Method	n	E/kJ mol^{-1}	A/s^{-1}	$\|r\|$
Coats-Redfern	1.9	97	$1.73\cdot 10^{11}$	0.9972
Flynn-Wall	1.9	93	$2.52\cdot 10^{11}$	0.9975
Modified Coats-Redfern	1.9	96	$7.77\cdot 10^{11}$	0.9972

Inspection of the table shows that the three applied integral methods lead to values which are in a satisfactory agreement.

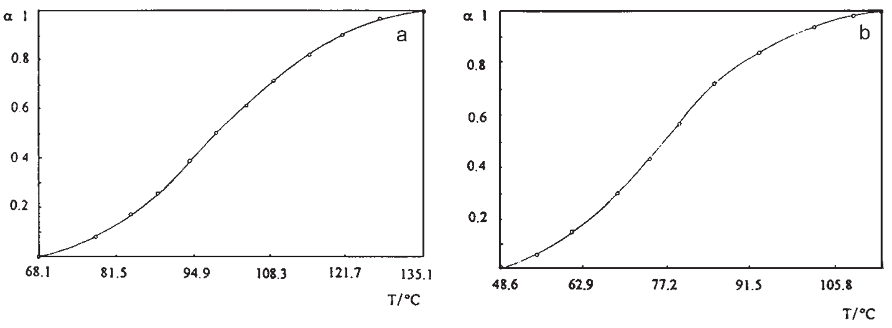

Fig. 2 Regenerated thermogravimetric curve using coordinates α, t(°C) for reaction (1): —, calculated curve, o – experimental points (a); for reaction (6) (b)

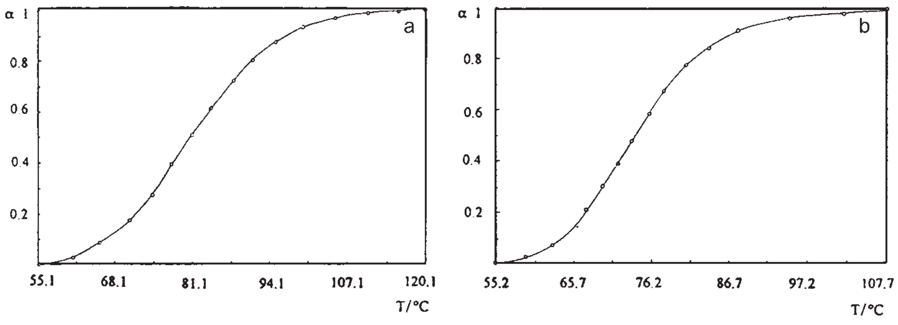

Fig. 3 Regenerated thermogravimetric curve using coordinates α, t(°C) for reaction (10): —, calculated curve, o – experimental points (a); for reaction (14) (b)

Figures 2–3 show the regenerated (simulated) TG curves in coordinates α *vs.* t°C for reactions (1), (6), (10) and (14) using the Coats-Redfern values of the kinetic parameters as well as the experimental points in the same coordinates. As it can be seen, the experimental points lie practically in the curve, thus confirming the reliability of the reported values of the kinetic parameters.

The practically identical crystallographic structures of the four investigated compounds as well as their similar chemical structures should result in similarities in their thermal behaviour. As already shown, their heating curves exhibit practically the same decomposition steps. Moreover, the values of the kinetic parameters of reactions (1), (6), (10) and (14) are relatively close. Slight differences in the values of the activation parameters are compensated. The same conclusion is valid for the kinetic parameters of reactions (5) and (13).

As far as the fractional values close to 2 of the reaction order are concerned, these are due to the decomposition of almost two structural units of the coordination compound in steps (1), (6), (10), (14).

General conclusions

1. The main decomposition steps for four heteropolynuclear coordination compounds [CuML(CH_3COO)$_3$], where *M*=Mn(II), Co(II), Ni(II) and Zn(II) and *LH*=2-amino-5-mercapto-1,3,4-thiadiazole ($C_2H_2N_3S_2$), were established.
2. For the kinetically workable steps, the value of the kinetic parameters were determined.
3. The solid product of the second decomposition step is a mixed metal sulphide of formula $CuMS_2$ which is stable in the range of 30–40°C and consequently can be isolated.
4. The final residue obtained in the case of the compounds [CuMnL(CH_3COO)$_3$] and [CuCoL(CH_3COO)$_3$] contains, besides CuO, the mixed metal oxides with spinel structures $CuMn_2O_4$ and $CuCo_2O_4$.

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