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Thermochimica Acta 311 (1998) 155–162

thermochimica
acta

Thermal analysis of oxamates, thiooxamates and their complexes
Part 2. The Cu (II) complexes

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Received 3 July 1997; received in revised form 19 November 1997; accepted 24 November 1997

Abstract

The article describes the thermal behaviour of Cu(II) complexes formed with ligands $R_1R_2NCXCOOK$ (R_1R_2=H or CH_3, X=O or S). The oxamates form 2/1 complexes $Cu(R_1R_2NCOCOO)_2{\cdot}xH_2O$ and deprotonated ionic complexes $K_2Cu[R_2NCOCOO]_2{\cdot}yH_2O$. These compounds form polymers by thermal decomposition and deprotonation of the primary or secondary amide function. The ligands break at the C–C bond by forming mainly CO_2 and oxamides ($R_1R_2NCOCONR_1R_2$), by recombination of the amide functional groups. The thiooxamates also form 2/1 complexes and decompose without forming any other stable compound. © 1998 Elsevier Science B.V.

Keywords: Cu complexes; DTA; Oxamates; TGA; TGA–MS; Thiooxamates

1. Introduction

It is becoming increasingly apparent that the coordination chemistry of oxamato and thiooxamato ligands is a central theme in transition-metal chemistry. The interest ranges from purely chemical [1–3] and spectroscopic problems [4,5] to a renaissance in the field of heterometallic chemistry [6–8], molecular magnetism [8] and advanced materials [9].

The preparation and characterisation of some transition metal complexes with oxamates [5,10] and thiooxamates [11,12] and their ligands [13,14] was recently published.

The thermal analysis of the oxamate and thiooxamate ligands has recently been published [15]. In this article, we fully describe the thermal analysis of the different Cu(II) complexes. The formation of stable intermediates and some polymeric structures are confirmed by vibrational spectroscopy.

2. Experimental

All Cu(II) complexes, under investigation, were synthesized according to the procedure available in literature [5,10–12].

The IR spectra were recorded in KBr pellets on a Bruker IFS 113 V F.T. spectrometer. The thermal analysis was performed on T.A. Instruments S.D.T. 2960, T.G.A. 2950, and D.S.C. 2920. All experiments were performed under dry nitrogen atmosphere (50 ml/min), generally heating at 5°C/min. Simultaneously, TGA–MS was used for the identification of gases such as CO, CO_2 and NH_3 evolved during the decomposition, using 2 thermolab quadrupole

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PII S0040-6031(97)00450-4

Table 1
Elemental analysis of the complexes. Exp. (theor.)

Compound	Cu	C	H	N	S	K
$Cu(H_2NCSCOO)_2$	23.2 (23.7)	17.3 (17.6)	1.5 (1.6)	10.1 (10.3)	20.8 (23.6)	
$Cu(CH_3HNCSCOO)_2$	21.6 (21.2)	23.7 (24)	2.7 (2.7)	9.0 (9.3)	20.7 (21.4)	
$Cu[(CH_3)_2NCSCOO]_2$	19.6 (19.7)	27.0 (29.2)	3.5 (3.6)	7.8 (8.5)	18.8 (19.5)	
$Cu(H_2NCOCOO)_2{\cdot}H_2O$	24.4 (23.2)	17.9 (18.7)	2.7 (2.4)	10.4 (10.9)		
$K_2Cu[HNCOCOO]_2$	17.6 (20.4)	15.6 (15.3)	0.8 (0.6)	8.8 (8.9)		24.7 (25.0)
$(CuHNCOCOO)_n$	38.0 (42.0)	15.6 (16.0)	1.2 (0.7)	7.9 (9.3)		
$Cu(CH_3HNCOCOO)_2$	24.3 (24.3)	26.3 (27.0)	3.0 (3.0)	10.4 (10.5)		
$K_2Cu[CH_3NCOCOO]_2{\cdot}2H_2O$	17.8 (18.5)	16.0 (21.0)	0.7 (1.8)	9.2 (8.2)		22.7 (23.1)
$(CuCH_3NCOCOO)_n$	34.5 (39.3)	21.1 (21.9)	2.0 (1.8)	7.1 (8.5)		
$Na_2[CuCH_2(CH_2NCOCOO)_2]{\cdot}1.5H_2O$	17.3 (19.3)	24.0 (24.6)	2.1 (2.4)	7.6 (8.2)		
$Cu[(CH_3)_2NCOCOO]_2$	Impure material					

mass spectrometers (V.G. Fisons instruments). H_2S was identified by passing the gas through a dilute $AgNO_3$ solution, forming an Ag_2S precipitate and CO gas in a dilute $PdCl_2$ solution as a precipitate of metallic Pd.

3. Results and discussion

The elemental analysis of the Cu(II) complexes is given in Table 1. All compounds were of good purity, except the compound formed with the tertiary oxamidate, which showed very poor analytical results due to the impurities in ligand and KCl.

4. The neutral oxamate complexes with $H_2NCOCOOK$

$H_2NCOCOOK$ forms, with Cu(II), a neutral 2/1 complex with coordination on the oxygen of the amide and one oxygen of the carboxylate group, as given in Fig. 1(B). The TG, DTA and DTG signals for $Cu(H_2NCOCOO)_2{\cdot}H_2O$ are given in Fig. 2.

The first step is the release of hydrated water at $(\mathrm{d}m/\mathrm{d}t)_{\mathrm{max}}=152^\circ\mathrm{C}$, the loss of weight of 7% exactly corresponding to 1 mol of water. This is confirmed by comparing the IR spectra of the stable compounds A and B which only differ in the water bands. The second step is the decomposition of compound B in an endothermal process forming a stable polymer, as shown in Fig. 1(C), with copper in an O_3N coordination.

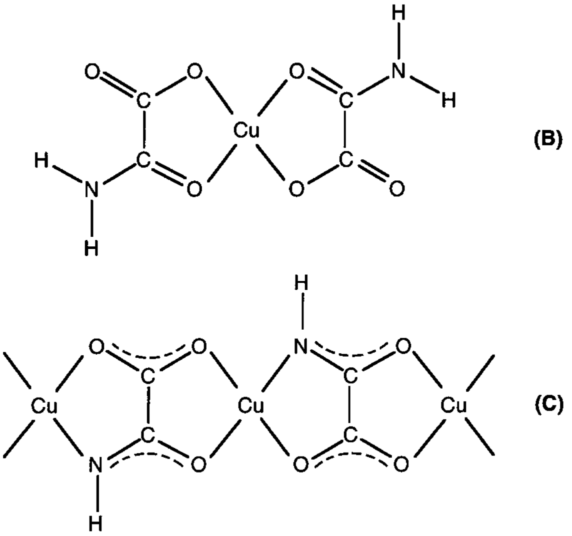

Fig. 1. The molecular geometry of the CuL_2H_2 and $(CuL)_n$ polymer for the oxamidates $R_1R_2NCOCOO$.

Table 2 gives some important fundamental vibrations, characteristic of the ligand and compounds A and C. The ligand and compound A exhibit the same functional groups (i.e. the carboxylate and the primary amide group). For the primary amide group we observe an increased ν_{CN} and a decreased ν_{CO} mode, typical for an amide coordination through the oxygen atom [5]. The increased $\nu_{\mathrm{as\,CO_2}}$ and decreased $\nu_{\mathrm{s\,CO_2}}$ values and especially the increased frequency difference between these fundamentals, are a clear indication of the monodentate carboxylate coordination [15].

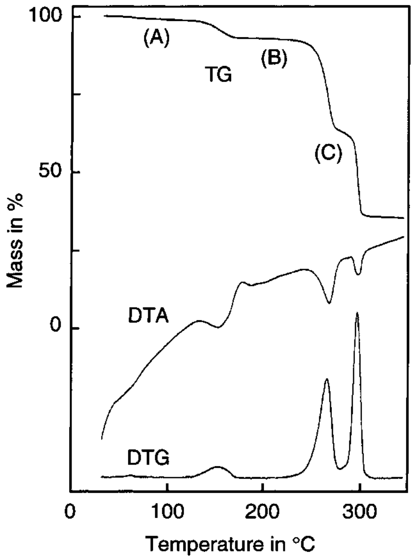

Fig. 2. TG, DTA and DTG curves for $Cu(H_2NCOCOO)_2{\cdot}H_2O$.

The lower $\nu_{as\,NH_2}$ and $\nu_{s\,NH_2}$ values observed in compound A are due to the hydrogen bonding between the water molecule and the hydrogen atoms of the amide function.

The IR spectrum of compound C shows no primary amide bands but only the fundamentals typical for the carboxylate and the '*cis*' secondary amide functional groups. The lowering of ca. 60 cm^{-1} of $\nu_{as\,CO_2^-}$ value, compared with the monodentate carboxylate in product A, indicates a bridged carboxylate function.

The amide function cannot be compared as we have a primary amide and a typical '*cis*' secondary amide. This reaction clearly gives the deprotonation of a primary amide function, only by heating the compound.

So we can conclude that compound C can be described as a polymer, with a geometry as given in Fig. 1(C). During the second step, $H_2NCOCONH_2$ (oxamide) has been formed at the end of the oven tube (oxamide sublimes at 218°C [17]). This compound can only be formed by recombination of two primary amide radicals. These radicals are probably formed by breaking the C–C bond in $H_2NCOCOOH$, so the other compound formed could be oxamic acid. Oxamic acid, however, is not stable at this temperature and directly decomposes [18].

The overall reaction for the formation of the polymer (C) is as follows:

$$
\begin{aligned}
&n\mathrm{Cu(H_2NCOCOO)_2(B)}\\
&\quad\rightarrow [\mathrm{Cu(HNCOCOO)}]_n\mathrm{(C)}\\
&\quad + n/2\mathrm{(COOH)_2} + n/2\mathrm{(CONH_2)_2}
\end{aligned}
$$

The loss of weight in this process (30%) agrees with one ligand per complex unit as can be observed from Fig. 2.

The third step in this decomposition is an endothermal process giving the decomposition of the polymer to mainly CuO. The energy required for this decomposition is ca. 1/3 of the energy to form the polymer. TG–MS measurements give CO, CO_2 and NH_3 as the main gases during the decomposition of the polymer.

The activation energy E_a [19], was calculated for the release of the water molecule and the formation of the polymer, the results for different heating rates are given in Table 3. The comparable E_a values obtained for different rates indicate that the water molecule is probably not involved in the crystalline structure. The decreasing values obtained for the decomposition of the polymer indicate that this decomposition is not similar over the whole range.

Table 2
Significant IR fundamentals (cm^{-1}) for $KOOCCONH_2$ and the Cu(II) complexes

	$KOOCCONH_2$	(A) $Cu(OOCCONH_2)_2{\cdot}H_2O$	(C) $[Cu(OOCCONH)]_n$
$\nu_{as\,CO_2^-}$	1637	1655	1596
$\nu_{s\,CO_2^-}$	1363	1335	1330
$\gamma_{CO_{am.}}$	1692	1655	1634
$\nu_{CN_{am.}}$	1438	1461	1463
$\nu_{as\,NH_2}$	3386	3336	3319 (ν_{NH})
$\nu_{s\,NH_2}$	3233	3189	1300 (δ_{NH}) 764 (π_{NH})

Table 3
E_a values for the dehydration of $Cu(H_2NCOCOO)_2{\cdot}H_2O$ and the formation of polymer $[Cu(HNCOCOO)]_n$

α	$-H_2O$ (kJ/mol)	Polymers (kJ/mol)
0.1	182	283
0.2	188	271
0.3	189	244
0.4	186	224
0.5	183	209
0.6	182	201
0.7	177	187
0.8	173	183
0.9	170	179

5. The neutral oxamate complexes with $HCH_3NCOCOOK$

The TG, DTA and DTG curves for the decomposition of $Cu(CH_3HNCOCOO)_2$ are given in Fig. 3. The decomposition is very similar to the previous compound and the two processes (the formation of the polymer and its decomposition) nearly overlap. The polymer formed was obtained by an isothermal process at 215°C with a loss of weight of one ligand (38%) per complex unit (Fig. 4). The formation of the polymer can be written as follows:

$$n\mathrm{Cu(CH_3HNCOCOO)_2} \rightarrow [\mathrm{Cu(CH_3NCOCOO)}]_n + n/2\mathrm{(COOH)_2} + n/2\mathrm{(CH_3HNCO)_2}$$

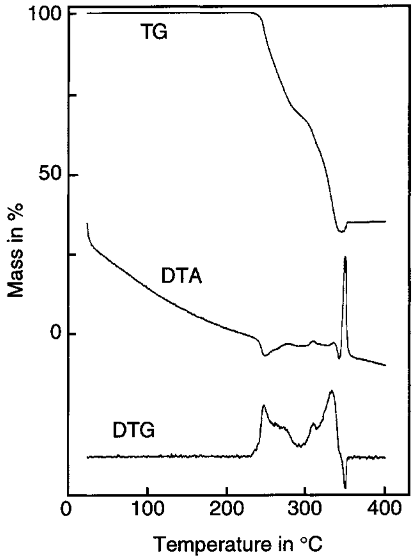

Fig. 3. TG, DTA and DTG curves for $Cu(CH_3HNCOCOO)_2$.

oxalic acid decomposes at this temperature mainly by forming CO and CO_2, *N,N'*dimethyloxamide was already sublimed at 140°C [16] and is formed as a white powder at the end of the oven tube.

The IR spectrum of the polymer only exhibits bridged tertiary amide and carboxylate functions, the structure can consequently be proposed as given in Fig. 1 by substituting the amide hydrogen by a methyl group.

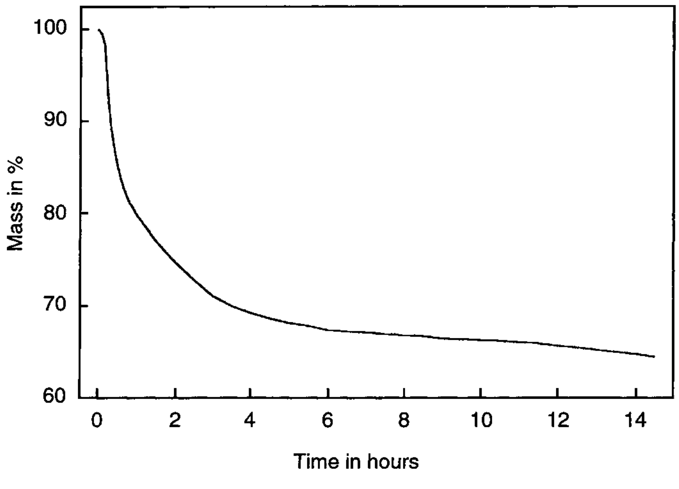

Fig. 4. The formation of the $[Cu(CH_3NCOCOO)]_n$ polymer at 215°C.

Table 4
$(\Delta m/\Delta t)_{max}$ for the formation and decomposition of Cu(RNHCOCOO)$_2$

	Endothermal formation		Exothermal decomposition	
	1	2	1	2
R=CH_3	248	262	308	334
R=C_2H_5	232	246	279	329
R=C_3H_7	232	250	285	332
R=c.C_3H_7	251	261	276	326
R=C_4H_9	207	207	270	307

TG–MS measurements indicate the formation of CO, CO_2 and CH_3NH_2 in exothermic reactions during the decomposition of the polymer.

The splitting of the DTG signal by the formation of the polymer is a direct indication for the complex character of the reaction; the complicated character has been already indicated by the different E_a values calculated for the formation of the polymer [Cu(HNCOCOO)]$_n$.

The DTA shows a very intense exothermal signal in the 340°C region, indicating the oxidation of the copper, which is very sensitive to traces of oxygen [20].

For all the DTA and DTG signals of similar alkyl-substituted Cu complexes, we could approximately see an analogue decomposition, i.e. two endothermic processes for the formation of the polymer and two distinct exothermic reactions for the decomposition of the polymer (see Table 4).

The E_a values (the average from the data obtained for nine heating rates) for the formation of the polymer are comparable for the CH_3 and C_2H_5 derivatives (±185 kJ/mol) and are calculated at ca. 250 kJ/mol for the C_3H_7, cC_3H_5 and C_4H_9 derivatives.

6. The neutral oxamate complex with $(CH_3)_2NCOCOOK$

The Cu[$(CH_3)_2NCOCOO]_2$ complex decomposes at ca. 165°C without forming a stable polymer intermediate. In the previous processes, we always observed a deprotonation of the amide function by the formation of the polymer, as the tertiary amide group cannot be deprotonated, consequently no polymer formation was observed.

TG–MS measurements indicated that CO, CO_2 and $(CH_3)_2NH$ were the main gases, the white crystals observed at the end of the oven tube were identified by IR as tetramethyloxamide $(CH_3)_2NCOCON(CH_3)_2$ (sublimes at 128°C [16]). This is an indication that the ligand decomposes by breaking the C–C bond.

The complexes, as given in Fig. 1(B), are stabilized by strictly planar structures. The very low temperature for the decomposition of the dimethyl complex is due to the sterical hindrance between the amide methyl group and the oxygen of the carboxylate group in this planar configuration.

7. The ionic complexes with oxamates

Cu(II) also forms ionic complexes in strong alkaline media [5] with deprotonation at the amide function. The general structure of these complexes is given in Fig. 5.

The TG, DTA and DTG for the decomposition of $K_2[Cu(HNCOCOO)_2]$ (R=H in Fig. 5) are given in Fig. 6. This planar water-free compound decomposes at ca. 200°C; the decomposition occurs in three distinct exothermal processes. The resultant product consisted of a mixture of Cu and K_2CO_3. The loss of weight of ca. 14%, in the first step, corresponds to 1 mol of ligand, the IR spectrum of the product at this point is very similar to the polymer form and some traces of KOCN and K_2CO_3. The second step is the decomposition of the polymer and the third step is the decomposition of the inorganic material KOCN, K_2CO_3 and CuO.

The $K_2[Cu(CH_3NCOCOO)_2]\cdot 2H_2O$ decomposes as shown in Fig. 7, the molecular structure of this octahedral complex consists of an equatorial plane, as

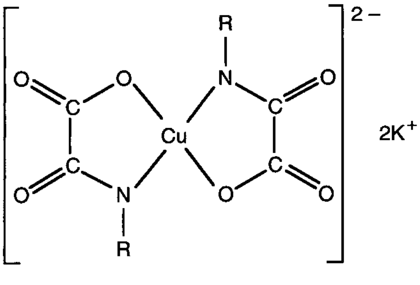

Fig. 5. Molecular geometry of $K_2[Cu(RNCOCOO)_2]$.

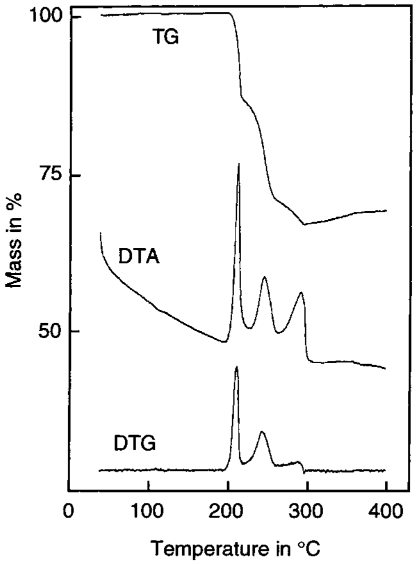

Fig. 6. TG, DTA and DTG curves for $K_2[Cu(HNCOCOO)_2]$.

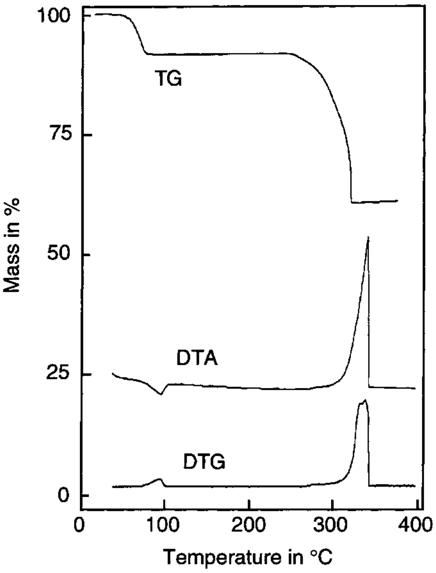

Fig. 7. TG, DTA and DTG curves for $K_2[Cu(CH_3NCOCOO)_2]\cdot 2H_2O$.

given in Fig. 5, and two water molecules in the axial position.

The coordinated water molecules (ca. 9%), released by an endothermal process at very low temperature, indicate the Jahn-Teller effect, resulting in weak bonding at the axial positions for Cu(II) octahedral complexes. The inductive effect of the methyl-group increases the thermal stability by ca. 100°C and the water-free complex starts decomposing at ca. 300°C. The three different steps observed in the decomposition of $K_2Cu(HNCOCOO)_2$ now coincide, resulting in one endothermic signal.

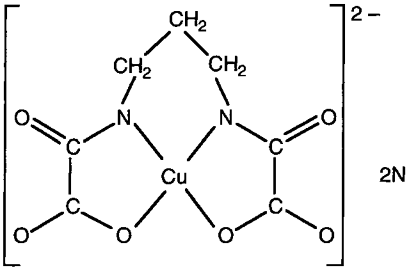

Fig. 8. Molecular structure of the Cu(II)–*bis*-oxamic acid complex.

The higher stability of the CH_3 derivative is due to the higher stability of this ligand enhanced by the chelate complexation and not by a stronger metal-ligand bond formation. The $\nu_{Cu\text{–}N}$ for both complexes is situated at ca. 400 cm^{-1} and the $\nu_{Cu\text{–}O}$ occurs in the 330 cm^{-1} region, these assignments have been controlled by $^{63}Cu/^{65}Cu$ isotopic substitution [6].

The geometry of the Cu(II) complex with propylene–*bis*-oxamide in alkaline medium [21] is given in Fig. 8. The structure can very well be compared with the compounds given in Fig. 6, for the surrounding of the Cu(II)-ions. The main difference is the supplementary six ring in a (5,6,5) sequence and the two N atoms in a '*cis*' position. For this supplementary ring we can expect a greater stability. The chemical stability is reflected by the fact that the propylene derivative is stable in water, while the methyl compound directly hydrolyses. The stronger metal-ligand bond is indicated by the $\nu_{Cu\text{–}N}$ (455 cm^{-1} compared with 400 cm^{-1} for the CH_3 derivative) and $\nu_{Cu\text{–}O}$ (341 cm^{-1} compared with 327 cm^{-1} for the CH_3 derivative). The stronger bonding on the carboxylate oxygen is also reflected in the greater difference between the $\nu_{as\,CO_2^-}$ and $\nu_{s\,CO_2^-}$ ($\Delta\nu$=322 cm^{-1} for the propylene and 307 cm^{-1} for the CH_3 derivative) [15]. The scan for this propylene derivative is given in Fig. 9. The compound decomposes by two endothermic processes at 95 and 347°C. The first step is the release of 1.5 mol of water. The second process is the

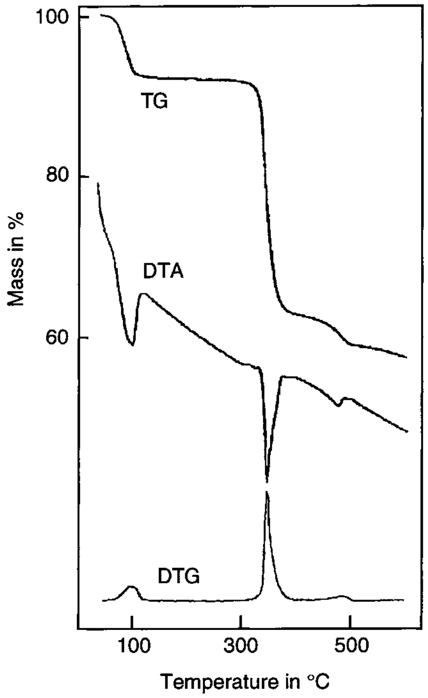

Fig. 9. TG, DTG and DTA for Cu(II)–propylene-*bis*-oxamide complex.

decomposition of the complex, while this process is exothermal for the CH_3 derivative.

8. The thiooxamate complexes

The Cu–oxathioamidates exhibit planar structures with CuS_2O_2 surrounding as given in Fig. 10 [22]. The TG, DTA and DTG curves for the different complexes are given in Fig. 11. For $R_1=R_2=H$ (Fig. 11(A)) and $R_1=R_2=CH_3$ (Fig. 11(C)). We observe the same decomposition for the three compounds, starting with an endothermic process, directly followed by an

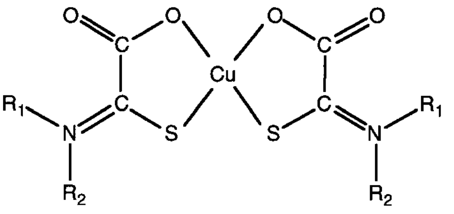

Fig. 10. Molecular structure of the Cu(II)–oxathioamidate complex.

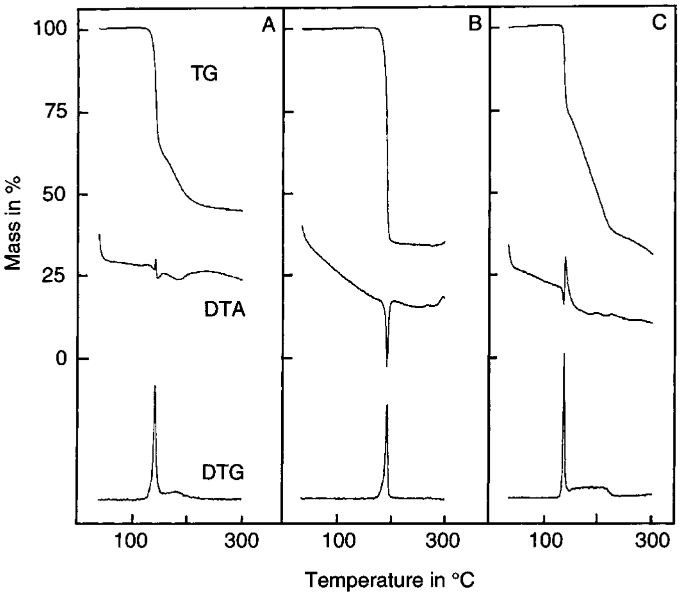

Fig. 11. TG, DTA and DTG curves for $Cu(R_1R_2NCSCOO)_2$ complexes.

Table 5
$(\Delta m/\Delta t)_{\max}$ and metal-ligand modes (cm^{-1}) for the $Cu(R_1R_2NCSCOO)_2$ complexes

R_1	R_2	$(\Delta m/\Delta t)_{\max}$	ν_{MS}	ν_{MO}
H	H	140	343	218
CH_3	H	194	360	270
CH_3	CH_3	140	351	251

exothermic process. The Cu complex, with R_1=CH_3, R_2=H, decomposes at higher temperature and only one strong endothermic process was observed.

The $(\Delta m/\Delta t)_{\max}$ can clearly be related to the metal-ligand modes as given in Table 5. The inductive effect of the methyl group, which makes the metal-ligand bond more electron-rich and therefore stronger, results in a greater thermal stability and higher metal-ligand vibrations for the monomethyl derivative. Steric hindrance between the $R_2(CH_3)$ group and the oxygen of the carboxylate group has strongly reduced this supplementary stability, resulting in a decreased bond strength and thermal stability for the dimethyl complex.

All other metals appear as octahedral complexes with two molecules of water in the axial position [11,12]. The Cu compounds are, as can be seen from the thermogram, entirely water-free and strictly planar due to the Jahn-Teller effect.

The thiocompounds are clearly decomposed by first breaking the metal-ligand bonds, while all the oxamate complexes decompose by breaking the C–C bond in the ligand. The free thio-ligands are decomposed first by forming H_2S and nitriles, as indicated by the IR spectra; therefore, it is impossible to form dithiooxamides from thiooxamates.

Acknowledgements

The authors wish to thank the FWO for the thermal analysis instrumentation, R. Keuleers thanks the FWO for the obtained grant. The authors also thank G. Thijs for technical assistance.

References

[1] P. Arrizabalaga, P. Castan, J.P. Laurent, Trans. Met. Chem. 5 (1980) 204.

[2] P.Th. Veltsistas, S.P. Perlepes, M.I. Karayannis, T.M. Tsangaris, Monath. Chem. 121 (1990) 703.

[3] V. Lazaridou, S.P. Perlepes, T.M. Tsangaris, Th.F. Zafiropoulos, J. Less-Common Met. 158 (1990) 1.

[4] G. Schoeters, D. Deleersnyder, H.O. Desseyn, Spectrochim. Acta 39A (1983) 71.

[5] H.O. Desseyn, G. Schoeters, Bull. Soc. Chim. belg 95 (1986) 13.

[6] Y. Pei, Y. Journaux, O. Kahn, A. Dei, D. Gatteschi, J. Chem. Soc. Commun. (1986) 1300.

[7] Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, J.P. Renard, Inorg. Chem. 26 (1987) 138.

[8] H.O. Stumf, Y. Pei, O. Kahn, J. Sletten, J.P. Renard, J. Am. Chem. Soc. 115 (1993) 6738.

[9] O. Guillou, O. Kahn, R.L. Oushoorn, K. Boubekeur, P. Bartali, Inorg. Chim. Acta 198 (1992) 119.

[10] C. Vansant, H.O. Desseyn, S.P. Perlepes, Transition Met. Chem. 20 (1995) 454.

[11] M. Hereygers, H.O. Desseyn, K.A.F. Verhulst, A.T.H. Lenstra, S.P. Perlepes, Polyhedron 15(20) (1996) 3437.

[12] M. Hereygers, H.O. Desseyn, A.T.H. Lenstra, E. Manessi-Zoupa, S.P. Perlepes, Transition Met. Chem. 21 (1996) 273.

[13] M. Hereygers, H.O. Desseyn, S.P. Perlepes, K.A. Verhulst, A.T.H. Lenstra, Journ. of Chem. Crystallography 24(9) (1994) 615.

[14] M. Hereygers, H.O. Desseyn, S.P. Perlepes, K.A. Verhulst, A.T.H. Lenstra, Journ. of Chem. Crystallography 25(4) (1995) 181.

[15] R. Keuleers, J.F. Janssens, H.O. Desseyn, Thermochim. Acta, to be published.

[16] S.J.H. De Beukeleer, J.F. Janssens, H.O. Desseyn, J. Thermal. Anal. 48 (1997) 225.

[17] G.B. Deacon, R.J. Philips, Coord. Chem. Rev. 33 (1980) 227.

[18] K. Muraishi, Y. Suzuki, Thermochim. Acta 232 (1994) 195.

[19] J.H. Flynn, L.A. Wall, Polymer Letters 4 (1996) 323.

[20] J. Mullens, A. Vos, R. Carleer, J. Yperman, L. Van Poucke, Thermochim. Acta 207 (1992) 337.

[21] K. Nonoyama, H. Ojima, M. Nonoyama, Inorg. Chim. Acta 20 (1976) 127.

[22] R. Krause, R. Mattes, Z. Naturforsch 45b (1990) 100.