ELSEVIER

Thermochimica Acta 336 (1999) 97–103

thermochimica acta

www.elsevier.com/locate/tca

Thermal behaviours of Co(II), Ni(II), Cu(II)), and Pb(II) complexes of N,N-dipropyl-N′-benzoylthiourea

N. Ozpozan[a,*], T. Ozpozan[a], H. Arslan[b], F. Karipçin[c], N. Külcü[b]

[a]*Chemistry Department, Erciyes University, Kayseri, Turkey*
[b]*Chemistry Department, Mersin University, Mersin, Turkey*
[c]*Chemistry Department, Süleyman Demirel University, Isparta, Turkey*

Received 23 April 1999; accepted 1 July 1999

Abstract

The Co(II), Ni(II), Cu(II)), and Pb(II) complexes of N,N-dipropyl-N′-benzoylthiourea (DPBT) are synthesised. The order, the activation energies, the entropies, and the pre-exponential factors of the thermal decomposition reactions are calculated with the thermogravimetric curves. The kinetic analysis of the thermogravimetric data was performed by using the Coats–Redfern and Horowitz–Metzger methods.

Keywords: N,N-dipropyl-N′-benzoylthiourea; Co(II), Ni(II), Cu(II), and Pb(II) complexes; Thermal behaviours; DTA/TG/DTG; Decomposition kinetics

1. Introduction

The natural resources of Co, Ni, Cu, and Pb are used in bulk quantities in nature. Industrial production and the use of these elements can cause environmental pollution. On the other hand some of these metals are essential elements for biological systems present in trace quantities. In each case, trace analysis of these elements require pre-concentration prior to their analysis. To accomplish this pre-concentration process, a water insoluble complex of the trace metal has to be obtained and the solvent to enrich the complex has to be removed. In our previous studies [1,2] some N-substituted alkylbenzoylthiourea derivatives having such properties and their metal complexes are synthesised and their thermal behaviours are examined. N,N-dipropyl-N′-benzoylthiourea is another such example some metal complexes of which are examined from the thermal behavioural point of view in the present study.

2. Experimental

2.1. Preparation of samples

Metal solutions of Co(II), Cu(II), Ni(II) and Pb(II) ions are prepared from analytical purity reagents of $CoCl_2.6H_2O$, $NiCl_2$, $CuCl_2.2H_2O$ and $Pb(NO_3)_2$ salts. Metal complexes, $M(DPBT)_2$, (where M = Co, Ni, Cu, and Pb) are obtained from the reactions of the metal solutions with the alcoholic ligand solutions and solid complexes are filtered out from the liquid phase [3].

2.2. Instrumental

The TG/DTG curves and DTA profiles were obtained on a DT-40 Model DTA/TG simultaneous

*Corresponding author. Tel.: +352-4374901; fax: +352-4374933

0040-6031/99/$ – see front matter
PII: S0040-6031(99)00208-7

Table 1
Thermoanalytical results on metal complexes of N,N-dipropyl-N′-benzoylthiourea

Complexes	Stage	Temperature range (K)	DTG_{max}	Mass loss (%)		Evolved moiety
				TG	Theoretical	
$Co(DPBT)_2$	1a	476–513	496	36.0	35.1	DPB
	Ib	513–568	547	35.4	35.1	DPB
	II	568–833	803	14.2	14.4	SCN + CN
	Residue	>833	-	14.5	15.4	CoS
$Ni(DPBT)_2$	I	423–559	534	70.2	70.1	2DPB
	II	559–700	666	9.9	9.7	SCN
	III	700–958	775	4.4	4.4	CN
	Residue	>958	-	15.5	15.6	NiS
$Cu(DPBT)_2$	Ia	471–495	484	34.8	34.8	DPB
	Ib	495–561	578	34.8	34.8	DPB
	II	561–759	640	19.7	19.6	2SCN
	Residue	>759	-	10.8	10.8	Cu
$Pb(DPBT)_2$	I	470–538	505	55.8	55.9	2DPB
	II	538–724	603	15.8	15.8	2SCN
	Residue	>724	-	29.0	28.3	Pb

analyser. The measurements were performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 ml min^{-1} up to 1273 K. The heating rate was 10 min^{-1} and the sample sizes ranged in mass from 5 to 10 mg. Platinum crucible is used as sample container, and a Al_2O_3 is used as reference substance. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Shimadzu 435 spectrophotometer, using KBr pellets. X-ray powder diffraction analyses of the final residues were made with a Siemens F model diffractometer. X-ray generator is Phillips, PW-1010 model and ranging from 20 to 40 kV and 6 to 50 mA while using fine focus CuK_α radiation (λ = 1.5406 Å). The analyses of the characteristic absorption bands of the sample were made with Hitachi 150–20 model double beam UV-VIS absorption spectrophotometer. The control of melting points was made with the Electro Thermal 9200 model digital melting point apparatus.

3. Results and discussions

3.1. Thermal analysis

All the complexes were studied by thermogravimetric analysis from ambient temperature to 1273 K in nitrogen atmosphere. The temperature ranges and percentage mass losses of the decomposition reaction are given in Table 1, together with the temperature of greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass losses. The thermal curves obtained for most of the compounds examined were similar in character. All the complexes show two-stage mass loss except Ni(II) complex in their TG/DTG curves. The first mass loss corresponds to the formation of their respective thiocyanates. While the second mass loss is due to the decomposition of the thiocyanates. The end products were confirmed with the XRD data. As an example the X-ray pattern of the end product of Ni(II) complex can be shown in Fig. 1.

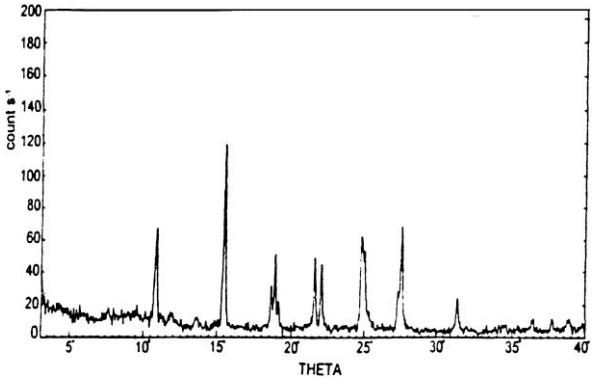

Fig. 1. X-ray powder diffraction pattern of NiS.

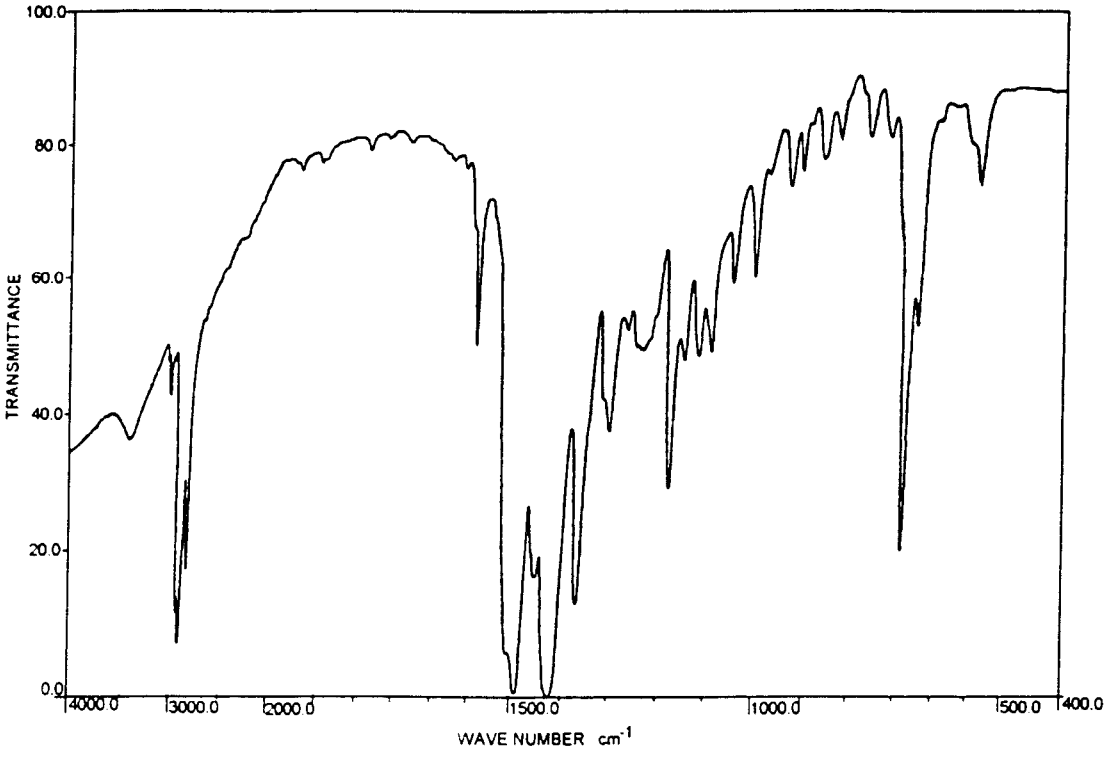

Fig. 2. IR spectra of Ni(II)-N-N-dipropyl-N′-benzoylthiourea complex.

It may also be noted that the absence of dehydration peaks in the DTG curves and the absence of hydroxyl bands in the IR spectra indicate that all the compounds under investigation are anhydrous. The IR spectrum of $Ni(DPBT)_2$ is presented in Fig. 2. The TG and DTG curves of the complexes are presented in Fig. 3. The DTA profiles of Co(II), Ni(II), Cu(II), and Pb(II) complexes are shown in Fig. 4.

In general, decomposition begins between 420 and 490 K, followed by a rapid mass loss over 60%. It was presumed that metal-thiocyanate is formed at the end of this step for which the calculated mass losses show close agreement with the experimental values. The mass losses at this stage are attributed to the evolved moieties dipropylbenzamide (DPB = $PhCON(C_3H_7)_2$). In the case of $Co(DPBT)_2$ and $Cu(DPBT)_2$, however, the decomposition of metal complexes to $M(SCN)_2$ occurs in two sub-stages. The first sub-stage (Ia) mass losses in $Co(DPBT)_2$, $Cu(DPBT)_2$, correspond to the formation of M(SCN)(DPBT) while the second sub-stage (Ib) is responsible for the mass losses due to the decomposition of the other 1 mole of DPBT. At the end of the second stage, the second mass loss is due to the decomposition of the SCN radicals to the metal sulphur or the elemental metal.

3.2. *Co(DPBT)$_2$*

The complex is thermally stable up to 476 K. The mass loss at sub-stage Ia in the temperature ranging from 476 to 513 K corresponds to the decomposition of the complex to Co(DPBT)(SCN). This is followed by another mass loss at stage Ib in the temperature range 513–568 K due to the decomposition of Co(DPBT)(SCN) to $Co(SCN)_2$. The last mass loss in the temperature range 568–833 is due to the thermal decomposition of $Co(SCN)_2$ to CoS.

The DTA curve shows two endothermic and one exothermic effect, at 401, 474 and 545 K. The former corresponds to the melting of the complex, the second to its decomposition to $Co(SCN)_2$ and the latter

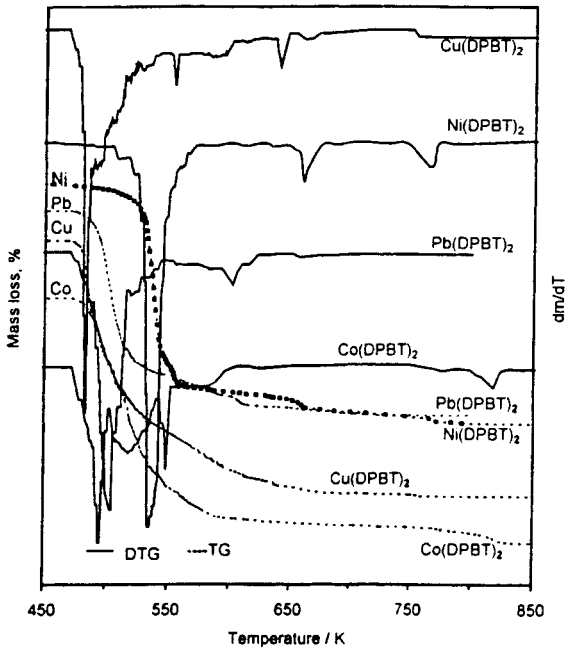

Fig. 3. TG/DTG curves for Co(II)-, Ni(II)-, Cu(II)-, and Pb(II)-N,N-dipropyl-N′-benzoylthiourea complexes.

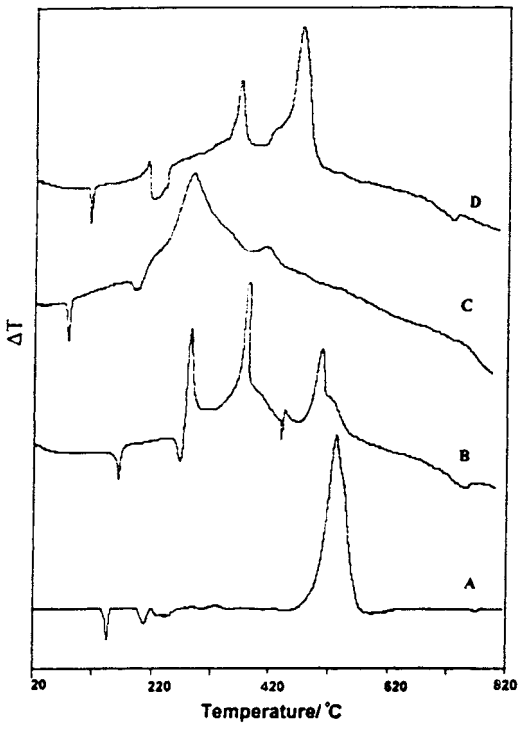

Fig. 4. DTA profiles for (A) Co(II)-, (B) Ni(II)-, (C) Pb(II)-, and (D) Cu(II)- N,N-dipropyl-N′-benzoylthiourea complexes.

exothermic peak corresponds to dimerisation of dipropylbenzamid group.

3.3. $Ni(DPBT)_2$

The TG curve shows an initial mass loss in the temperature range 423–559 K, corresponding to the decomposition of the complex to $Ni(SCN)_2$. This is followed by another mass loss in the temperature range 561–700 K due to the thermal decomposition of $Ni(SCN)_2$ to NiSCN. The last decomposition step occurs in the temperature range 714–958 K and it corresponds to the formation of NiS.

3.4. $Cu(DPBT)_2$

The TG curve indicates that the mass change begins at 471 K and continues up to 496 K. The mass loss corresponds to the formation of Cu(DPBT)(SCN). The next decomposition step occurs in the temperature range 496–561 K and corresponds to the formation of $Cu(SCN)_2$. The last decomposition step occurs in the temperature range 561–759 K and corresponds to the formation of metallic copper.

The DTA profile shows two endothermic and two exothermic effects. The first, at 376 K, corresponds to the melting of the complex, while the second, at 503 K corresponds to the decomposition of the complex to $Cu(SCN)_2$. Exothermic effects correspond to the dimerisation of dipropylbenzamid group.

3.5. $Pb(DPBT)_2$

The TG of this complex reveals a mass loss in the temperature range 470–538 K corresponding to the formation of $Pb(SCN)_2$. The next decomposition step occurs in the temperature range 538–724 K and corresponds to the formation of metallic lead.

The DTA curve shows two endothermic peaks at 389 and 508 K. the former corresponds to the melting of the complex, and the latter to its decomposition to $Pb(SCN)_2$

4. Discussion

The results of TG and DTG evaluations are presented in Table 1. The TG studies reveal that the first step decomposition of Pb(II) and Ni(II) complexes result in the formation of the respective thiocyanates, Pb $(SCN)_2$ and Ni$(SCN)_2$. The former decomposes to metallic lead, while the latter to NiS yielding SCN and CN radicals in two stages. In case of Cu(II) and Co(II), the first step decompositions occurs in two sub-stages yielding metallic Cu and CoS, respectively.

From the TG curves, the order *n,* activation energy E^*, entropies ΔS^*, and pre-exponential factors A, of the thermal decompositions have been elucidated by the methods of Coats–Redfern and Horowitz–Metzger [4,5]. The linearisation curves are shown in Figs. 5 and 6, respectively. The results of kinetic studies of TG-DTG are presented in Table 2.

Among these four complexes having the same square-planar geometry and the similar decomposition steps, the smaller size of Co(II) as compared to Cu(II), (which are these two complexes decomposed in the two sub-stages) permits a closer approach of the ligand to the Co(II) ion [6]. Hence the E^* value for the Co(II) complex is higher than that of Cu(II). The same is also true for the second sub-stages.

In a similar way, because of smaller ionic radius of Ni(II), the E^* value for the first decomposition of Ni(II) complex is higher then that of Pb(II) complex both of which lose two DPB molecules at this stage.

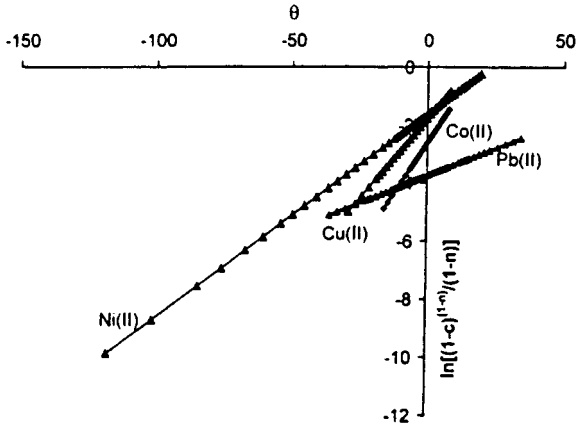

Fig. 6. Linearisation curves of the first decomposition steps of Horowitz–Metzger Method for Co(II)-, Ni(II)-, Cu(II)-, and Pb(II)-N,N-dipropyl-N′-benzoylthiourea complexes.

Finally, the positive values of entropies of activation (except Pb(II) complex) in the first decomposition step indicates that the activated complexes have less ordered structures than the reactants [7]. The negative values of ΔS^* in the first step of the decomposition of Pb(II) and other steps of Co(II), Ni(II), and Cu(II) complexes indicate that the reactions are slower than normal [8,9]. The reaction orders found at all the decomposition stages of the complexes are nearly

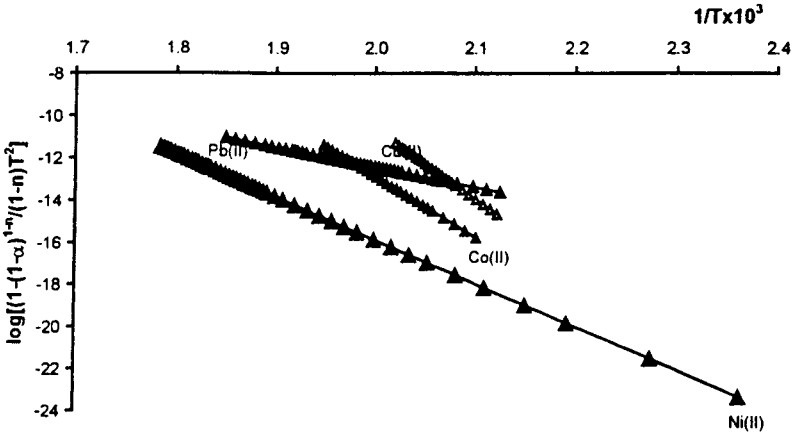

Fig. 5. Linearisation curves of the first decomposition steps of Coats–Redfern Method for Co(II)-, Ni(II)-, Pb(II)-, and Cu(II)-N,N-dipropyl-N′-benzoylthiourea complexes

Table 2
Kinetic data on metal complexes of N,N-dipropyl-N′-benzoylthiourea[a]

Complex	Stage	Reaction order(n)	Parameters	From Coats–Redfern eqn.	From Horowitz–Metzger eqn.
$Co(DPBT)_2$	Ia	0.852	E^*	237.1	234.6
			A	7.2×10^{22}	3.5×10^{22}
			ΔS^*	213.9	182.2
			R	0.9974	0.9955
	Ib	0.821	E^*	78.6	83.4
			A	2.1×10^5	7.6×10^5
			ΔS^*	−121.8	−137.1
			r	0.9958	0.9965
	II	0.780	E^*	93.4	91.1
			A	$4.9x10^3$	3.2×10^3
			ΔS^*	−152.9	−185.8
			r	0.9478	0.9649
$Ni(DPBT)_2$	I	0.760	E^*	169.9	170.8
			A	2.5×10^{14}	3.6×10^{14}
			ΔS^*	51.9	28.7
			r	0.9853	0.9898
	II	0.713	E^*	67.0	83.1
			A	612	14200
			ΔS^*	−170.3	−172.0
			r	0.9879	0.9919
	III	0.924	E^*	261.5	270.7
			A	1.74×10^{15}	6.2×10^{15}
			ΔS^*	68.1	49.3
			r	0.9981	0.9975
$Cu(DPBT)_2$	Ia	0.925	E^*	274.3	281.3
			A	6.1×10^{27}	3.5×10^{28}
			ΔS^*	308.3	297.5
			r	0.9955	0.9973
	Ib	0.968	E^*	92.5	103.1
			A	1.2×10^7	1.5×10^8
			ΔS^*	−134.3	−152.6
			r	0.9946	0.9948
	II	0.841	E^*	42.0	48.5
			A	7.6	30.1
			ΔS^*	−206.7	−222.7
			r	0.9913	0.9938
$Pb(DPBT)_2$	I	0.982	E^*	77.8	80.8
			A	8.4×10^5	1.4×10^6
			ΔS^*	−110.2	−131.9
			r	0.9963	0.9976
	II	0.946	E^*	34.8	35.8
			A	1.6	2.4
			ΔS^*	−219.2	−243.3
			r	0.9920	0.9975

[a] Unit of parameters: E^* in kJ mole^{-1}, A in s^{-1}, ΔS^* in J mole^{-1} K^{-1}, r–correlation coefficient of the linear plot, n–order of reaction.

equal to unity. The melting points of the complexes increase in the order; Cu(II) < Pb(II) < Co(II) < Ni(II) corresponding the numerical values in Kelvin; 376, 389, 401, 420 in the same order.

References

[1] N. Ozpozan, H. Arslan, T. Ozpozan, N. Ozdes, N. Külcü, Themochim. Acta, in press.

[2] N. Ozpozan, H. Arslan, T. Ozpozan, M. Merdivan, N. Külcü, J. Ther. Anal. (submitted).
[3] M. Schuster, Ph.D. Thesis, Johan Wolfgang Goethe Universität, Germany, 1986
[4] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[5] H.H. Horowitz, G. Metzger, Anal. Chem. 35 (1963) 1464.
[6] N.K. Tunali, S. Özkar, Inorganic Chemistry, Gazi University Publication, Pub. No. 185, Ankara, 1993.
[7] M.L. Kantouri, G.A. Katsoulos, C.C. Hadjikostas, P. Kokorotsikos, J. Ther. Anal. 35 (1989) 2411–2422.
[8] A.A. Frost, R.G. Pearson, Kinetics and Mechanism, Wiley, New York, 1961
[9] V. Indira, G. Parameswaran, J. Ther. Anal. 39 (1993) 1417–1429.