

THERMAL DECOMPOSITION OF TRANSITION METAL DITHIOCARBAMATES

*S. Singhal*¹, *A. N. Garg*^{1*} and *K. Chandra*²

¹Department of Chemistry, Indian Institute of Technology, Roorkee 247 667, India

²Institute Instrumentation Centre, Indian Institute of Technology, Roorkee 247 667, India

(Received August 18, 2003; in revised form March 18, 2004)

Abstract

Transition metal dithiocarbamate complexes, $[M(S_2CN(C_2H_5)(CH_2CH_2OH))]$ ($M=Co, Ni, Cu, Zn$ and Cd) have been prepared and characterized by elemental analysis and infrared spectra. Thermal decomposition of all the complexes occurs in two or three stages. The first stage in all the complexes is always fast with 65–70% mass loss. In all cases the end product is metal oxide except in the case of cobalt complex which gives Co metal as an end product. During decomposition of copper complex, first CuS is formed at $\sim 300^\circ C$ which is converted into $CuSO_4$ and finally CuO is formed. However, decomposition in helium atmosphere yields CuS . SEM studies of transition metal dithiocarbamates reveal needle shape crystalline phase at room temperature and formation of metal sulphide/oxide at higher temperatures. The activation energy varies in a large range of 33.8–188.3 kJ mol^{-1} , being minimum for the Cu complex and maximum for the Zn complex possibly due to d^{10} configuration. In the case of Ni, Zn and Cd complexes the order of reaction is two suggesting bimolecular process involving intermolecular rearrangement. However, in other cases it is a unimolecular process. Large negative values of ΔS^\ddagger for all the complexes suggest that the decomposition process involves rearrangement.

Keywords: IR spectra, metal dithiocarbamates, metal oxide, thermal decomposition, thermodynamic parameters

Introduction

Thermal decomposition behaviour of metal dialkyldithiocarbamates is important because of their wide spread industrial applications such as foam rubber, scorch resistant vulcanization accelerators, fungicides, effective heat stabilizers, antioxidant action, reprocessing of polymers etc. [1–3]. Bernard and Borel [4] reported thermogravimetric studies of $Pb(II)$, $Zn(II)$ and $Cd(II)$ dithiocarbamates suggesting evolution of H_2S or CS_2 . It was suggested that metal thiocyanate was formed as an intermediate product, which decomposed into metal sulphide. On the basis of thermal behaviour D'Ascenzo and Wendlandt [5] suggested volatile nature of tris(N, N' -di-

* Author for correspondence: agargfcy@iitr.ernet.in

ethyldithiocarbamate) iron(III) complex. Lyalikov and Kitovskaya [6] investigated a series of dithiocarbamate based fungicides such as Ziram, Ferbam, Tiram and Zineb and determined their biologically active constituents. Sceney *et al.* [7] observed the effect of atmosphere on the thermal behaviour of Cu(II) dialkyldithiocarbamates. Larionov *et al.* [8] studied the thermal behaviour of similar complexes by EPR and confirmed the formation of $\text{Cu}_{1.96}\text{S}$ in an inert atmosphere. Kaushik *et al.* [9] reported thermal behaviour of ammonium-N-(*p*-ethoxyphenyl)dithiocarbamate $\text{NH}_4(\text{PED})$ complexes of iron and other metals wherein three major changes corresponding to the formation of sulphide, oxidation of sulphide to sulphate and the decomposition of sulphate to oxide were suggested.

Kosareva and Larionov [10] studied the sublimation of metal diethyldithiocarbamates in the temperature range 210–275°C and showed the stability sequence, $\text{Zn(II)} > \text{Cu(II)} > \text{Ni(II)} \cong \text{Cd(II)} \cong \text{Pb(II)} > \text{Co(III)} > \text{Cr(III)} > \text{Fe(III)}$. Thus volatility increased with the decreasing oxidation state of the metal. Further, with respect to variation of ligand, volatility increased with branching in the alkyl group of the dithiocarbamate moiety. Lanjewar and Garg [11] studied two series of mixed ligand complexes, $\text{Fe}(\text{dtc})_2\text{L}$ and $\text{Fe}(\text{dtc})\text{L}_2$ with $\text{L} = \text{acetylacetone}$, 8-hydroxyquinoline, glycine, 1,10-phenanthroline, thiomalic acid and phenylalanine. Mössbauer spectra of intermediate and final products showed a six-line pattern corresponding to the formation of Fe_2O_3 at 650°C.

Bendeira and Motos [12] reported thermal study of uranyl(VI) dithiocarbamates in air and nitrogen atmosphere under different conditions and showed the formation of anhydrous uranyl dithiocarbamate which produced U_3O_8 as final product on further heating in air at 437–959 K. Cesur *et al.* [13] studied the thermal decomposition of some divalent transition metal complexes of benzylpiperazine (KBPDTC) dithiocarbamate and showed the formation of metal thiocyanates as stable solid intermediates during decomposition under nitrogen atmosphere. Ali *et al.* [14] have reported thermal analysis of dialkyldithiocarbamates of Ni(II) and Cu(II) suggesting mechanism and the nature of intermediate products. In recent years several workers [15–18] have emphasized the importance of thermokinetic parameters in transition metal dithiocarbamate complexes.

In our earlier studies [19, 20] on thermal decomposition behaviour of iron(III) dialkyldithiocarbamate complexes, it was observed that ferric thiocyanate was formed as an intermediate product but finally Fe_2O_3 was formed as the end product. Further, in order to see the effect of metal ion variation on the complexes of unsymmetrically substituted dithiocarbamate ligand N-ethyl-N'-hydroxyethyldithiocarbamate, we have prepared its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The complexes were characterized by elemental analysis and IR spectra. Thermal decomposition studies have shown the formation of metal oxide as final product except in the case of cobalt complex where cobalt metal is formed. Kinetic and thermodynamic parameters were evaluated by Freeman and Carroll method [21].

Experimental

Preparation of the complexes

The complexes were prepared by mixing metal salt solution with that of sodium salt of the ligand in 1:2 molar ratio as described earlier [19, 20]. Ethanolic solution of 0.1 M cobalt(II) nitrate, nickel(II) nitrate, copper(II) nitrate, zinc(II) sulphate (AR grade, E. Merck) and cadmium(II) nitrate (Ottokemi) were mixed with 0.2 M solution of sodium N-ethyl-N'-hydroxyethyl dithiocarbamate. Calculated amounts of metal salts and of sodium N-ethyl-N'-hydroxyethyl dithiocarbamate ligand were dissolved separately in a minimum amount of absolute ethanol and mixed with thorough stirring for 2 h at room temperature when solid complexes separated out.

These were washed with water and then with ethanol followed by dried diethyl ether. Finally these were dried over fused calcium chloride in vacuum desiccator for overnight. The purity and stoichiometry of the complexes was checked by the elemental analysis of C, H, N and S carried out at the Central Paper and Pulp Research Institute, Saharanpur. Iron was determined by atomic absorption spectrophotometer (GBC, Avanta) after calibration. The colour of the complexes and their analytical data are given in Table 1.

Physical measurements

All the infrared spectra in the range 4000–400 cm^{-1} were recorded in KBr medium on a Perkin Elmer 1600, FT-IR spectrophotometer. Further spectra were also recorded down to 250 cm^{-1} at the Regional Sophisticated Instrumentation Centre, IIT-Madras. TG curves were recorded on a thermogravimetric analyser system, STA-780 series (Stanton Redcroft, UK) in static air and He atmosphere using Al_2O_3 as reference material. SEM photographs of some samples were recorded on a LEO, U.K., SEM model 435 VP. The samples were also heated in air atmosphere for half an hour at various temperatures (as ascertained from TG plots) and then cooled to room temperature for recording SEM photographs.

In order to evaluate thermokinetic parameters Freeman and Carroll method [21] was used. It has the advantage of requiring fewer experimental data than in the isothermal method, and the kinetics can be studied over an entire range in a continuous manner without any missing regions. The order of reaction, n and activation energy of the reaction were calculated using the relationship

$$\frac{-(E_a/2.3R)\Delta(1/T)}{\Delta \log W_r} = -n + \frac{\Delta \log(dw/dt)}{\Delta \log W_r} \quad (1)$$

where $W_r = W_c - W$, in which W_c is the maximum mass loss, and W is the total mass loss up to the time t . The graph between $\Delta \log(dw/dt)/\Delta \log W_r$ vs. $\Delta(1/T)/\Delta \log W_r$ is always a straight line with an intercept of $-n$ and slope equal to $-E_a/2.3R$ for any physical or chemical reaction. The rate constant (K) was calculated using the equation

$$\log K = \log A - E_a/2.303RT \quad (2)$$

Table 1 Analytical data and infrared stretching frequencies of bis(N-ethyl-N'-hydroxyethylthiocarbamato) metal complexes

[M(S ₂ CNR'R'') ₂] M (colour)	Found (calc.)/%						Infrared frequency/cm ⁻¹			
	C	H	N	S	M		v(N=C)	v(N-C ₂)	v(C=S)	v(M-S)
Co (green)	30.6 (31.0)	5.23 (5.17)	7.12 (7.24)	32.7 (33.1)	15.0 (15.2)		1476	1183	989 1356	359
Ni (green)	30.8 (31.0)	5.26 (5.17)	7.22 (7.24)	32.9 (33.1)	15.4 (15.2)		1480	1185	988 1384	392
Cu (brown)	29.9 (30.6)	5.16 (5.10)	7.03 (7.15)	32.1 (32.7)	15.7 (16.2)		1497	1174	962 1382	—
Zn (white)	30.1 (30.5)	5.16 (5.08)	7.02 (7.11)	31.8 (32.5)	15.7 (16.6)		1495	1176	980 1375	375
Cd (white)	26.8 (27.2)	4.46 (4.54)	6.27 (6.35)	28.6 (29.1)	24.6 (25.5)		1490	1180	975 1370	372

where value of $\log A$ was obtained from the intercept of straight line plot between $\ln(d\alpha/dt/(1-\alpha)^n)$ vs. E_a/RT where α is the fraction of compound decomposed. With the help of these two kinetic parameters, the thermodynamic parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) were calculated.

Results and discussion

Besides elemental analysis, all the complexes were characterized by infrared spectra. Characteristic frequencies are listed in Table 1. Thermogravimetric plots for Co, Ni, Zn and Cd dithiocarbamates are shown in Fig. 1. Similar plots for the copper complex in air and helium atmosphere are shown in Fig. 2. Thermogravimetric data for the transition metal complexes are given in Table 2. Thermokinetic parameters for the complexes are listed in Table 3.

IR studies

Several workers [22–27] have reported IR spectra of transition metal dithiocarbamates and identified stretching vibrations corresponding to double bond character of $N=C$, chelating character of $C=S$ and $Fe-S$ bond [26–27]. IR spectra have been used to distinguish between monodentate and bidentate nature of the dithiocarbamate ligand [22, 23].

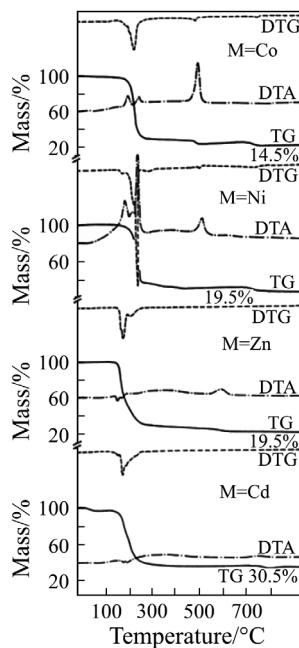


Fig. 1 TG curves of some typical bis(N-ethyl-N'-hydroxyethylthiocarbamato)M ($M=Co, Ni, Zn$ and Cd) complexes

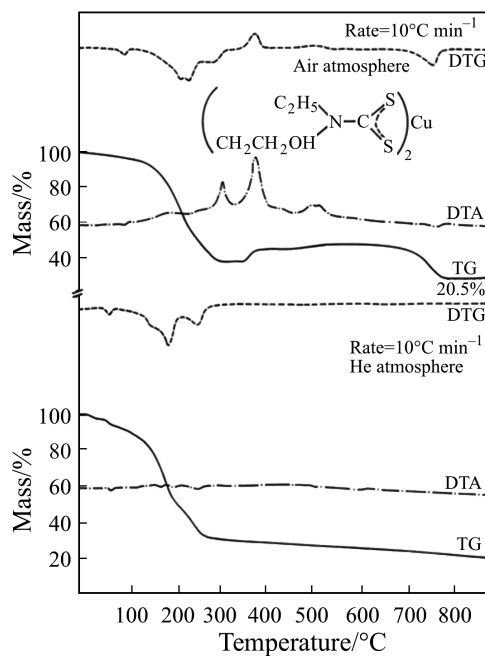
Table 2 Thermogravimetric data for bis(N-ethyl-L-N'-hydroxyethyl)dithiocarbamate)metal complexes

$[M(S_2CNRR'')_2]$ <i>M</i>	Initial decomp. temperature/°C	DTA peak/°C	Decomp. process	Constant mass temperature/°C	Final mass/ %	Expected MO/ %
Co	175	160, 210, 485	Fast and slow, three-stage	890	14.5	19.4 (15.2 for Co)
Ni	150	140, 205, 470	Fast and slow, two-stage	860	19.5	19.3
Cu	140	270, 340	Fast and slow, three-stage	800	20.5	20.3
Zn	150	140	Fast and slow, two-stage	810	19.5	20.6
Cd	145	140	Fast and slow, two-stage	805	30.5	29.1

Table 3 Kinetic and thermodynamic parameters of bis(N-ethyl-N'-hydroxyethyl)dithiocarbamate) metal complexes at 550 K

$[M(S_2CNR'R'')_2]$ M	$E_a/$ kJ mol^{-1}	n	$\Delta H^\ddagger/$ kJ mol^{-1}	$\Delta G^\ddagger/$ kJ mol^{-1}	$\Delta S^\ddagger/$ $\text{J mol}^{-1} \text{K}^{-1}$
Co	137.3	0.77	133.8	158.8	-45.4
Ni	88.3	2.18	78.3	156.8	-142.8
Cu	33.8	0.38	32.1	144.6	-204.5
Zn	187.3	2.28	176.8	150.2	+48.7
Cd	105.9	2.06	96.6	153.4	-103.3

Bradley and Gitlitz [22] reported $\nu(\text{C}=\text{S})$ for different metal dithiocarbamates in the region $994\text{--}1004 \text{ cm}^{-1}$ suggesting chelating character of the C-S group. In the present study we have observed a strong band in the region $962\text{--}989 \text{ cm}^{-1}$ (Table 1). Another $\text{C}=\text{S}$ stretching mode at $\sim 1360 \text{ cm}^{-1}$ is in accordance with the literature [25]. Bradley and Gitlitz [22] also reported the thioureide ($\text{N}=\text{C}$) band at $\sim 1500 \text{ cm}^{-1}$ as a characteristic of the ligand indicating considerable double bond character in the $\text{S}_2\text{C}=\text{NR}_2$ bond. We have observed $\nu(\text{C}=\text{N})$ in the range $1476\text{--}1497 \text{ cm}^{-1}$. Another strong band in the region $1174\text{--}1185 \text{ cm}^{-1}$ is attributed to the N-C₂ bond [23, 24]. The metal-sulphide stretching vibration is observed in the region $392\text{--}359 \text{ cm}^{-1}$ corresponding to different

**Fig. 2** TG curves of bis(N-ethyl-N'-hydroxyethyl)dithiocarbamate)Cu in different atmospheres

metals as given in Table 1. Unlike iron(III)dialkyldithiocarbamates, no band was observed near 250 cm^{-1} corresponding to low spin \leftrightarrow high spin behaviour [20]. No correlation was observed between $\nu_{\text{M-S}}$ and d^n of the transition metal atom.

Thermal decomposition of transition metal dithiocarbamates

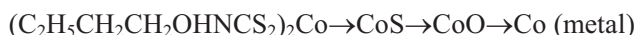
Thermogravimetric plots in Figs 1 and 2 suggest that all the complexes undergo decomposition in two stages except Co and Cu complexes for which three-stage decomposition takes place (Table 2). The first stage starts at $\sim 150^\circ\text{C}$ and is completed upto $\sim 300^\circ\text{C}$ except in case of Cd complex where it is completed at 250°C . The mass loss during the first stage is 60–70% depending on the nature of metal ion (Fig. 1). After this decomposition occurs very slowly and extends upto $\sim 900^\circ\text{C}$ when metal oxide is formed. The final mass percentage of the residue in all cases lies in the range 14.5–30.5% corresponding to the formation of metal oxide (MO) except in the case of cobalt complex (Fig. 1). It is observed that Co and Cu complexes decompose in three stages presumably due to different decomposition mechanism. In the case of cobalt its oxide CoO is not a stable product and it is reduced to cobalt metal in confirmation with the observations of D'Ascenzo and Wendlandt [5].

In the case of copper complex, first stage of decomposition is completed at $\sim 300^\circ\text{C}$ where the mass% of 25.6 (calculated 24.5) corresponds to the formation of CuS. On further heating upto 400°C the mass increases (Fig. 2) due to the formation of CuSO_4 in air atmosphere. When the decomposition was studied in helium atmosphere this mass increase was not observed. Therefore, it is concluded that CuS gains mass in air atmosphere and is converted into CuSO_4 . Sceney *et al.* [7] have reported that in air atmosphere $\text{Cu}(\text{Et}_2\text{NCS}_2)_2$ is found to yield Cu_2S as the end product in the first stage of decomposition, and it is further oxidised to CuSO_4 and CuO and finally into CuO.

In all other cases of Ni, Zn and Cd complexes decomposition occurs in two stages with the formation of metal oxide as end product. This is confirmed by the percentage of metal oxide as given in Table 2. A careful look of the TG curves of Cd and Cu complexes shows some mass loss ($\sim 5\%$ in air and upto $\sim 10\%$ in He atmosphere for Cu complex) before the first stage of decomposition. In case of Cd complex it could possibly be due to a water molecule associated with the complex but it could not be verified from the analytical data. However, for the decomposition of Cu complex in air and helium atmosphere, a continuous decrease in mass is observed. Possibly it could be due to the moisture content in the complex.

In cases of Co and Ni complexes each two small exotherms are observed at temperatures just before the end of the first stage of decomposition. For Zn and Cd complexes, however, very small endotherms are observed. For Cu complex, it is a broad exotherm. These may correspond to the melting of the complexes followed by the decomposition. Also a much sharper exothermic peak is observed in the range $350\text{--}500^\circ\text{C}$ for Co, Ni and Cd complexes and this may correspond to structural changes during decomposition [28]. Interestingly no change in DTA curve is observed for the Cu complex in helium atmosphere suggesting air oxidation leading to the formation of CuSO_4 , which is not possible in inert atmosphere.

On the basis of initial thermal decomposition temperatures in transition metal complexes, it is observed that Co complex starts decomposing at the highest temperature of 175°C whereas for Cu complex it is lowest (140°C). It suggests that cobalt complex is most stable. Thus, stability of the complexes follows the order, Cu < Cd < Zn = Ni < Co. On the basis of above discussion, transition metal complexes undergo decomposition according to the mechanism [3]:



It is observed that areas under exotherms corresponding to Co and Cu complexes are large suggesting the role of oxidation processes involving large change in ΔH . Since a small hump is observed in DTA of Ni complex, possibly NiS may also be formed as an intermediate. However, DTA of Zn and Cd complexes do not involve any change and hence direct oxidation may occur. Thus, it is amply clear that decomposition of transition metal dithiocarbamate complexes depends not only on the nature of alkyl group but also on the metal ion.

Kinetic parameters

From the steep part of the first stage of TG curves (Figs 1 and 2) of the complexes linear plots were obtained between $\Delta \log(dw/dt)/\Delta \log W_r$ vs. $\Delta(1/T)/\Delta \log W_r$ as shown in Fig. 3. Various kinetic and thermodynamic parameters were calculated as listed in Table 3. Apparently all the parameters vary with the nature of metal ion. The activation energy (E_a) varies in a large range of 33.8–188.3 kJ mol⁻¹, being minimum for the Cu complex and maximum for the Zn complex. It may possibly be due to d^{10} configuration of Zn but so is the case for Cd where E_a is found to be 105.9 kJ mol⁻¹. In an earlier study, Silva *et al.* [18] have observed difference in decomposition behavior of Zn (II) dialkyldithiocarbamate complexes with different alkyl groups. Thus, the nature of alkyl group also affects the thermal decomposition process and kinetic parameters [15–18]. Order of reaction is found in a wide range of 0.38–2.28. In the case of Ni, Zn and Cd the order of reaction is two suggesting bimolecular process involving intermolecular rearrangement. In other cases, however, it is a unimolecular process representing an intramolecular rearrangement leading to the formation of metal sulphide [20]. A perusal of activation thermodynamic parameters, enthalpy (ΔH^\ddagger), entropy (ΔS^\ddagger) and free energy change (ΔG^\ddagger) given in Table 3 shows that ΔG^\ddagger values were in a narrow range of 156.8–191.8 kJ mol⁻¹. However, ΔH^\ddagger and ΔS^\ddagger vary in a wide range of 32.1–176.8 kJ mol⁻¹ and –204.5 to +48.7 J mol⁻¹ K⁻¹, respectively. Largest negative value of ΔS^\ddagger for the copper complex suggests that the decomposition process involves orientational change in intramolecular rearrangement during the formation of CuSO₄ [29]. In other cases, however, it may involve lesser change in orientation due to bimolecular process.

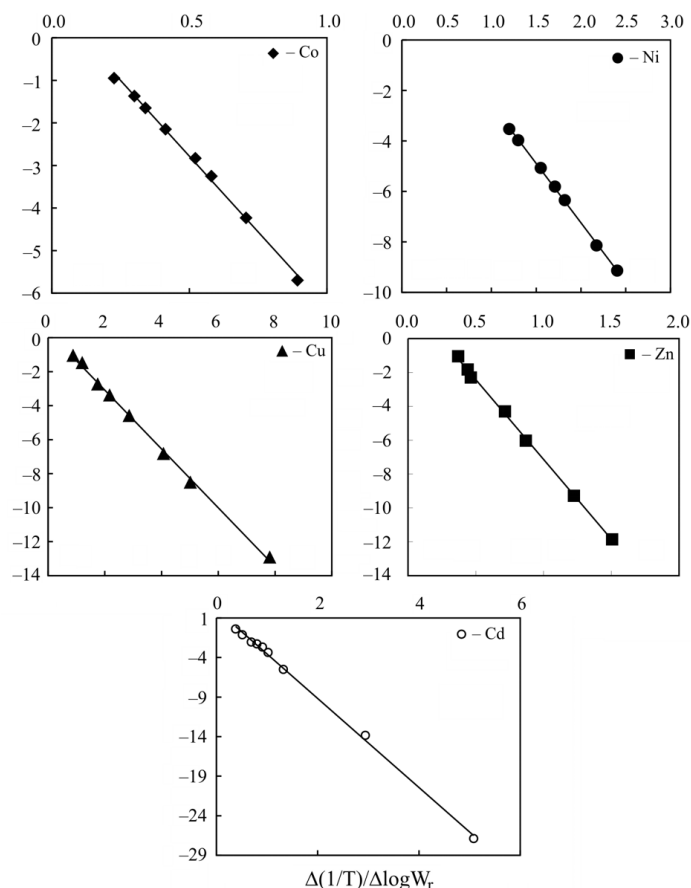


Fig. 3 Plots of $\Delta \log(dw/dt)/\Delta \log W_r$ vs. $\Delta(1/T)/\Delta \log W_r$ for the first stage of decomposition of bis(N-ethyl-N'-hydroxyethylthiocarbamato) M(II) ($M = \text{Co, Ni, Cu, Zn}$ and Cd) complexes

SEM studies

In order to further confirm the nature of intermediate and final products of decomposition, SEM photographs were recorded after heating the complexes for half an hour at various temperatures. It is observed that bis(N-ethyl-N'-hydroxyethylthiocarbamato) complexes of Ni(II), Zn(II) and Cd(II) form needle shaped crystals as can be typically seen in SEM photographs for Zn complex at RT and after heating at 500 and 900°C (Fig. 4). Interestingly, these are the complexes for which intermediate formed at 500°C is metal sulfide which is then converted into oxide. Further, ZnO also forms very fine rectangular shaped crystals whereas for NiO and CdO highly irregular shaped crystals are formed. This fact is characteristic of the soft process of decomposition from the metal-organic precursors [30]. For cobalt complex, CoS and CoO formed at 300 and 500°C, irregular crystals seem to have been formed. When cobalt complex

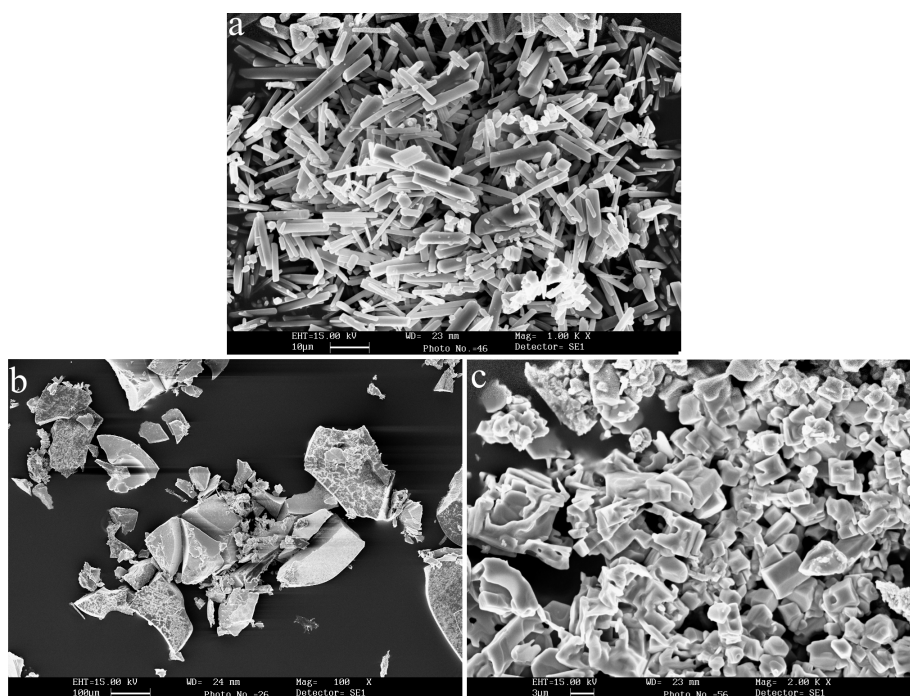


Fig. 4 SEM photographs of bis(N-ethyl, N'-hydroxyethyl)dithiocarbamato)Zn(II) at a and b – after heating at 500°C and c – 900°C

is further heated up to 900°C, a lump of mass with different sizes is obtained and as per literature studies, it may correspond to the formation of cobalt metal. Thus, it is amply clear that thermokinetic process in transition metal (II) dialkyldithiocarbamates is largely affected by the nature of metal ion as well as the alkyl group in the dialkyldithiocarbamato ligand.

* * *

Grateful thanks are due to the Council of Scientific Industrial Research, New Delhi for the award of Senior Research Fellowship to SS.

References

- 1 J. O. Hill and R. J. Magee, *Rev. Inorg. Chem.*, 3 (1981) 141.
- 2 A. K. Sharma, *Thermochim. Acta*, 104 (1986) 339.
- 3 J. O. Hill, J. P. Murray and K. C. Patil, *Rev. Inorg. Chem.*, 14 (1994) 363.
- 4 M. A. Bernard and M. M. Borel, *Bull. Soc. Chim. Fr.*, (1969) 3066.
- 5 G. D'Ascenzo and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, 32 (1970) 2431.
- 6 Yu. S. Lyalikov and M. I. Kitovskaya, *J. Thermal Anal.*, 4 (1972) 271.
- 7 C. G. Sceney, J. F. Smith, J. O. Hill and R. J. Magee, *J. Thermal Anal.*, 9 (1976) 415.

- 8 S. V. Larionov, L. A. Kosareva, A. F. Malikova and A. A. Shklyayev, *Zh. Neorg. Khim.*, 22 (1977) 2401.
- 9 N. K. Kaushik, G. R. Chhatwal and A. K. Sharma, *Thermochim. Acta*, 58 (1982) 231.
- 10 L. A. Kosareva and S. V. Larionov, *Neorg. Khim.*, 24 (1979) 2834.
- 11 R. B. Lanjewar and A. N. Garg, *Ind. J. Chem.*, 31A (1992) 849.
- 12 P. N. Bandiera and J. E. X. De Matos, *An Assoc. Bras. Quim.*, 45 (1996) 25.
- 13 H. Cesur, T. K. Yazicilar, B. Bati and V. T. Yilmaz, *Synth. React. Inorg. Metal Org. Chem.*, 31 (2001) 1271.
- 14 B. F. Ali, W. S. Al-Akramawi, K. H. Al-Obaidi and A. H. Al-Kabroli, *Thermochim. Acta*, 419 (2004) 39.
- 15 J. R. Botelho, A. G. Souza, L. M. Nunes, A. P. Chagas, I. M. Garcia Dos Santos, M. M. Da Conceicao and P. O. Dunstan, *J. Therm. Anal. Cal.*, 67 (2002) 413.
- 16 D. Ondrusova, E. Jona and P. Simon, *J. Therm. Anal. Cal.*, 67 (2002) 147.
- 17 J. R. Botelho, A. D. Gondim, I. M. G. Santos, P. O. Dunstan, A. G. Souza, V. J. Fernandes and A. S. Araujo, *J. Therm. Anal. Cal.*, 75 (2004) 607.
- 18 M. C. D. Silva, M. M. Conceicao, M. F. S. Trindade, A. G. Souza, C. D. Pinheiro, J. C. Machado and P. F. A. Filho, *J. Therm. Anal. Cal.*, 75 (2004) 583.
- 19 S. Singhal, C. L. Sharma, A. N. Garg and K. Chandra, *Trans. Metal Chem.*, 26 (2001) 81.
- 20 S. Singhal, C. L. Sharma, A. N. Garg and K. Chandra, *Polyhedron*, 21 (2002) 2489.
- 21 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 22 D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc., A* (1969) 1152.
- 23 T. M. Brown and J. N. Smith, *J. Chem. Soc., Dalton Trans.*, (1972) 1614.
- 24 A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark and S. H. Strauss, *Inorg. Chem.*, 13 (1974) 886.
- 25 K. Nakanishi and P. H. Solomon, *Infrared Absorption Spectroscopy*, 2nd Edn., Holdenday Inc., San Francisco 1977, p. 50.
- 26 G. R. Hall and D. N. Hendrickson, *Inorg. Chem.*, 15 (1976) 607.
- 27 R. J. Butcher, J. R. Ferraro and E. Sinn, *Inorg. Chem.*, 15 (1976) 2077.
- 28 W. W. Wendlandt, *Thermal Methods of Analysis*, 3rd Ed., Interscience, New York 1986.
- 29 D. Dollimore in: E. L. Charsley, S. B. Warrington (Eds), *Thermal Analysis Techniques and Applications*, The Royal Society of Chemistry, London 1992, p. 31.
- 30 I. Gil de Muro, F. A. Mautner, M. Insausti, L. Lezama, M. I. Arriortua and T. Rojo, *Inorg. Chem.*, 37 (1998) 3243.