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Synthesis and Thermal Behaviour of Co(II), Ni(II) and Cu(II) Complexes of *N*,*N*-di-*n*-propyl-*N*′-(2-chlorobenzoyl)thiourea

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The Co(II), Ni(II) and Cu(II) complexes of *N*,*N*-di-*n*-propyl-*N*′-(2-chlorobenzoyl)thiourea were synthesized and the thermal behaviour of all complexes was studied by differential thermal analysis and thermal gravimetry methods. A GC-MS combined system was used to identify the decomposition products. The pyrolytic end products were identified by X-ray powder diffraction method. Both nickel and copper complexes decomposed in three stages, but cobalt complex decomposed in two stages. End products of the decomposition reactions were identified as Ni_3S_2, Co_4S_3 and $Cu_{1.96}S$. The decomposition of the complexes begins with breakage the longer metal-oxygen bond in chelate ring, since these complexes decompose at higher temperatures proportional to 1/metal-ligand bond length.

Key Words: Benzoylthiourea, Metal complexes, Thermal behaviour, Pyrolysis, DTA/TG.

INTRODUCTION

Thiourea derivatives are selective analytical reagent for the determination of transition metals in complex interfering matrices[1] and yield highly sensitive reactions with the transition metals in solutions. The synthesis, characterization and some properties of thiourea derivatives and some of their transition metal complexes have been reported[2-25]. The complexation capacity of thiourea derivatives has been reported in several studies[1,26,27]. In addition, thioureas have been shown to possess antibacterial, antifungal, antitubercular, antithyroid and insecticidal properties. The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions[18,21,24,28-31].

Binzet *et al.*[8,16,21] have previously reported the preparation, antimicrobial activities and crystal structure of N,N-di-*n*-propyl-N′-(2-chlorobenzoyl)-thiourea (DPBT) and their metal complexes. The thermal properties of metal complexes of DPBT have not been studied previously. In this study, we report the thermal decomposition characteristics of Cu(II), Ni(II) and Co(II) complexes of DPBT. We have also investigated relationship between the metal-ligand bond length and decomposition initial temperature.

EXPERIMENTAL

Synthesis of the ligand: A solution of 2-chlorobenzoyl chloride (0.01 mol) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (0.01 mol) in acetone (30 cm^3). The reaction mixture was heated under reflux for 0.5 h and then cooled to room temperature. A solution of di-*n*-propylamine (0.01 mol) in acetone (10 cm^3) was added and the resulting mixture was stirred for 2 h. Hydrochloric acid (0.1 N, 300 cm^3) was added and the solution filtered. The solid product was washed with water and recrystallizated from ethanol:dichloromethane mixture (1:1)[21]. *N*,*N*-di-*n*-propyl-*N*'-(2-chloro-benzoyl)thiourea, (HL): Anal. Calcd. for $C_{14}H_{19}N_2OSCl$: C 56.3, H 6.4, N 9.4. Found: C 56.3, H 6.5, N 9.5%.

Synthesis of metal complexes: A solution of the corresponding metal acetate (0.01 mol) in ethanol (30 cm^3) was added dropwise to a solution of the ligand in a 1:2 ratio with a small excess of ligand in ethanol (50 cm^3) at room temperature and the resulting mixture was stirred for 0.5 h. The solid complexes were filtered and recrystallized from ethanol:dichloromethane mixture (1:1)[21]. *Bis*(*N*,*N*-di-*n*-propyl-*N*'-(2-chloro-benzoyl)thioureato)-nickel(II), [NiL_2]: Anal. Calcd. for $C_{28}H_{36}N_4O_2S_2Cl_2Ni$: C 51.4, H 5.6, N 8.6. Found: C 51.3, H 5.6, N 8.5%. *Bis*(*N*,*N*-di-*n*-propyl-*N*'-(2-chloro-benzoyl)thioureato)copper(II), [CuL_2]: Anal. Calcd. for $C_{28}H_{36}N_4O_2S_2Cl_2Cu$: C 51.0, H 5.5, N 8.5. Found: C 50.6, H 5.6, N 8.5 %. *Bis*(*N*,*N*-di-*n*-propyl-*N*'-(2-chloro-benzoyl)thioureato)cobalt(II), [CoL_2]: Anal. Calcd. for $C_{28}H_{36}N_4O_2S_2Cl_2Co$: C 53.0, H 5.7, N 8.8. Found: C 53.1, H 5.7, N 8.8 %.

The differential thermal analysis (DTA) and thermal gravimetry (TG) curves were obtained by a Shimadzu DTG-60H system equipped with DTA and TG units. The thermal analysis system was used over the temperature range of 273-1200 K. The samples were placed in Pt crucibles and α-Al_2O_3 was used as the reference material. Measurement was performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 50 mL min^{-1}. The heating rate was 10 K min^{-1} and the sample sizes ranged in mass from 7 to 8 mg. A GC-MS system, VG-ZabSpect model DFMS was used to identify pyrolysis products evolving during heating. Microanalyses were obtained using a Carlo Erba MOD 1106 instrument. X-ray powder diffraction analyses of the final residues were made with a Siemens F model diffractometer equipped with an X-ray generator, Phillips, PW-1010 model ranging from 20 to 40 kV and 6 to 50 mA while using a fine focus CuK_α radiation (λ = 1.5406 Å).

RESULTS AND DISCUSSION

Co(II), Ni(II) and Cu(II) complexes were studied by thermogravimetric analysis from ambient temperature to 1200 K in nitrogen atmosphere. The range of temperature and the experimental and calculated mass losses of the decomposition reactions are given in Table-1.

TABLE-1
THERMOANALYTICAL RESULTS OF METAL COMPLEXES OF
N,N-DI-*n*-PROPYL-*N'*-(2-CHLORO-BENZOYL) THIOUREA

Sample	Stage	DTA_{max} (K)	TG Temp. Range (K)	Mass loss (%)		Evolved moiety*
				Exper.	Calcd.	
NiL_2	I	513	489-543	36.58	36.64	$-C_{13}H_{18}NOCl$
	II	566	543-704	37.03	36.64	$-C_{13}H_{18}NOCl$
	III	-	704-1145	14.81	14.49	**
	Residue		-	11.56	12.23	Ni_3S_2
CuL_2	I	429	416-549	35.88	36.37	$-C_{13}H_{18}NOCl$
	II	595	549-709	45.03	45.18	$-C_{13}H_{18}NOCl$ -SCN
	III	-	709-1420	7.14	6.33	**
	Residue		-	11.93	12.12	$Cu_{1.96}S$
CoL_2	I	528	465-631	81.28	82.13	$-C_{13}H_{18}NOCl$ $-C_{13}H_{18}NOCl$ -SCN
	II	-	631-1256	5.69	5.19	**
	Residue		-	12.81	12.68	Co_4S_3

*$C_{13}H_{18}NOCl$: 2-chloro-*N,N*-di-*n*-propylbenzamide. **Unknown product.

Cu(II) complex ($C_{28}H_{36}N_4O_2S_2Cl_2Cu$): The Cu(II) complex of DPBT is stable up to 416 K and decomposition begins beyond this temperature as indicated by the first mass loss stage in the TG curve. At this stage, copper complex decomposes and losses 35.9 % of its mass. The decomposition reaction occurs in three stages. $Cu_{1.96}S$, the end product of the decomposition reaction, corresponds to an experimental mass of 11.9 %, which is equal to the expected theoretical mass (Fig. 1).

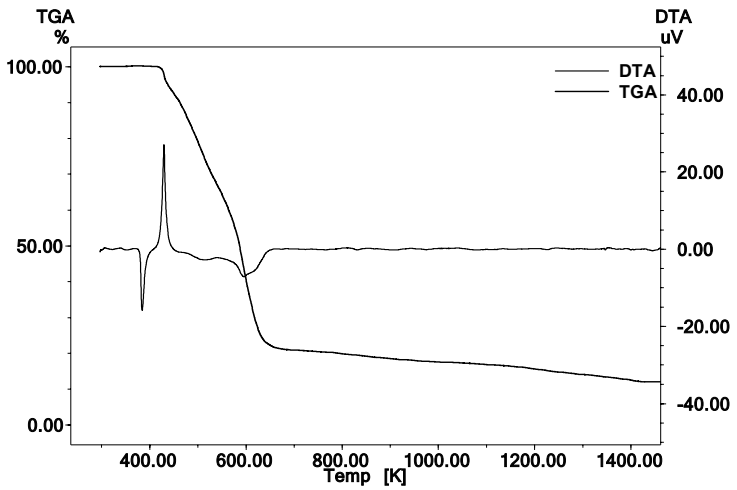
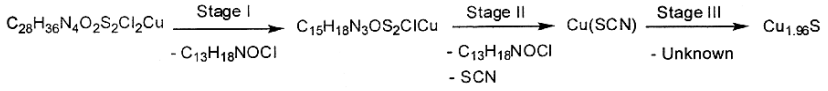


Fig. 1. DTA/TG diagram of *bis*(*N,N*-di-*n*-propyl-*N'*-(2-chloro-benzoyl)-thioureato) copper(II) complex

The first decomposition occurs between 416 and 549 K with a 35.9 % mass loss, the second decomposition occurs between 549 and 709 K with a 45.0 % mass loss and the third decomposition occurs between 709 and 1420 K with a 7.14 % mass loss. The expected theoretical decomposition mechanism is given in **Scheme-I** and the black end product, $Cu_{1.96}S$ (JCPD File no: 29-0578) of decomposition was identified by X-ray powder diffraction pattern data (Fig. 2).



Scheme-I

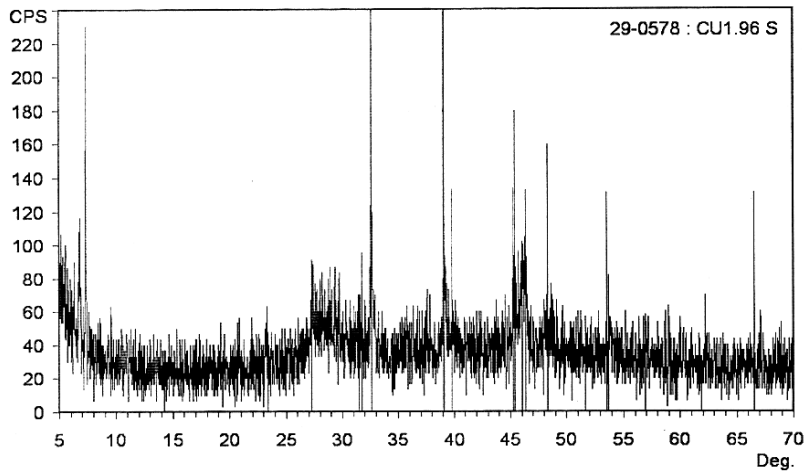


Fig. 2. X-ray powder diffraction pattern of $Cu_{1.96}S$ (File No: 29-0578)

Ni(II) complex ($C_{28}H_{36}N_4O_2S_2Cl_2Ni$): The TG studies of the Ni(II) complex of DPBT shows that the initial decomposition begins at 489 K and ends at 1145 K with a total of 88.4 % mass loss. A yellowish-bronze solid residue is corresponds to a mass of 11.6 % (Fig. 3).

Examination of the TG curve showed that the sample decomposes in three stages. The sample losses 36.6 % of its mass between 489 and 543 K, 37.0 % between 543 and 704 K and 14.8 % between 704 and 1145 K. The expected theoretical decomposition mechanism is given in **Scheme-II** and the yellowish-bronze end product, Ni_3S_2 (JCPD File no: 76-1870), is identified by X-ray powder diffraction pattern data.

Scheme-II

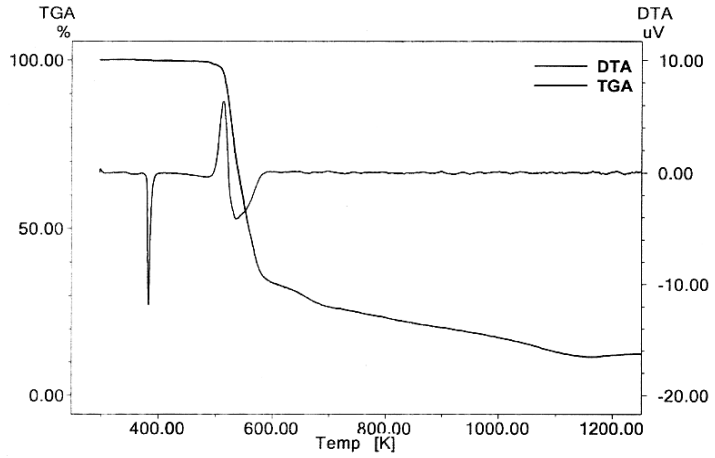


Fig. 3. DTA/TG diagram of *bis*(*N*,*N*-di-*n*-propyl-*N'*-(2-chloro-benzoyl)-thioureato)nickel(II) complex

Co(II) complex ($C_{28}H_{36}N_4O_2S_2Cl_2Co$): The Co(II) complex of DPBT begins to decompose at 465 K and ends at 1256 K in two stages with a total mass loss about 87.0 %. The black solid rest product of the decomposition reaction was identified by X-ray powder diffraction as Co_4S_3 (JCPD File no: 02-1338) which corresponds to a calculated mass loss about 12.7 % of the complex Fig. 4).

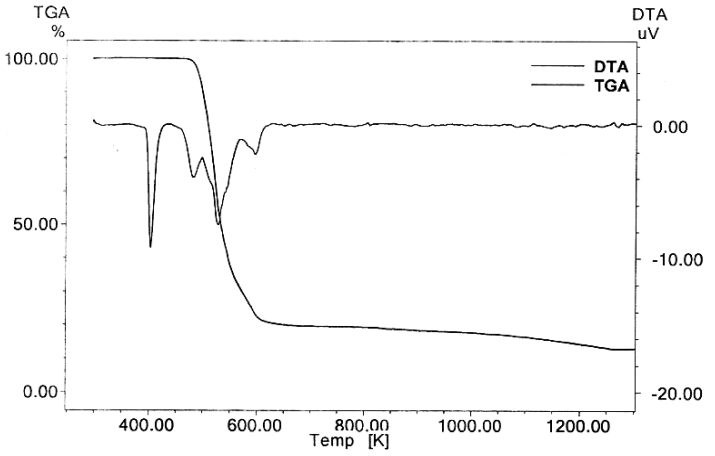
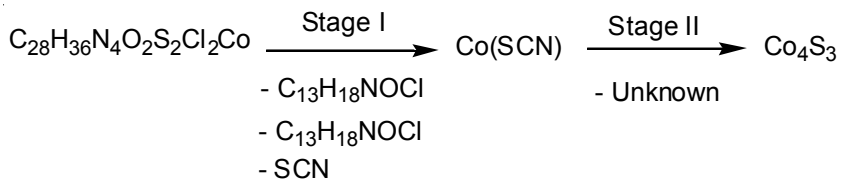


Fig. 4. DTA/TG diagram of *bis*(*N*,*N*-di-*n*-propyl-*N'*-(2-chloro-benzoyl)-thioureato)cobalt(II) complex

The TG curve shows that the sample decomposes in two stages, losing 81.3 and 5.7 % of its mass, respectively. The temperature range of each stage was found between 465 and 631, 631 and 1256 K, respectively. The Co(II) complex of DPBT loses two moles $C_{13}H_{18}NOCl$ and one mole SCN in the first stage (**Scheme-III**).



Scheme-III

Thermal behaviour: The thermal behaviour of these chelates was studied in detail. The melting point of Co(II), Ni(II) and Cu(II) complexes are 481, 381 and 383 K, respectively. The Co(II), Ni(II) and Cu(II) complexes of DPBT are thermally stable up to 465, 489 and 416 K, respectively. Both nickel and copper complexes decompose in three stages, but cobalt complex decompose in two steps. According to TG curves, the overall mass loss of the complexes was found 87.9 % for CuL_2, 87.8 % for NiL_2 and 87.3 % for CoL_2. End products of the decomposition reactions were identified as Ni_3S_2 (JCPD File no: 76-1870), Co_4S_3 (JCPD File no: 02-1338) and $Cu_{1.96}S$ (JCPD File no: 29-0578) by X-ray powder diffraction method. All of these data confirmed by both GC-MS data and TG data.

In the first stage, the evolved decomposition moiety of Ni(II) and Cu(II) complexes was 2-chloro-N,N-di-*n*-propylbenzamide ($C_{13}H_{18}NOCl$), whereas the Co(II) complex yields 2 mol of $C_{13}H_{18}NOCl$ and 1 mol SCN. The intermediate products ($C_{13}H_{18}NOCl$ (239 m/z) and SCN (58 m/z)) of decomposition reaction was confirmed by GC-MS studies. The theoretical and experimental mass losses obtained from these decomposition stages are also in agreement with each other.

Common to all complexes in the first stage is the 2-chloro-*N*,*N*-di-*n*-propylbenzamide moiety. It seems that the decomposition reaction begins with breakage the metal-oxygen bond. The decomposition temperature of 2-chloro-*N*,*N*-di-*n*-propylbenzamide moiety for Cu(II)-, Co(II)- and Ni(II)-complexes are 416 K, 465 K and 489 K, respectively. The shorter the metal-ligand bond length, the greater the metal-ligand bond energies. Therefore, decomposition of the complexes should begin with breakage the longer metal-ligand bond, since these complexes decompose at higher temperatures proportional to 1/d (d = metal-ligand bond length). The measured decomposition temperatures agree well with bond length of Cu-O (1.931 Å)[21], Co-O (1.920 Å)[18] and Ni-O (1.859 Å)[8] bonds which were determined by XRD method in the complex form:

$$T_{Ni} = 489 \text{ K} > T_{Co} = 465 \text{ K} > T_{Cu} = 416 \text{ K}$$
$$1/d_{Ni\text{-}O} = 0.538 \text{ Å}^{-1} > 1/d_{Co\text{-}O} = 0.521 \text{ Å}^{-1} > 1/d_{Cu\text{-}O} = 0.518 \text{ Å}^{-1}$$

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REFERENCES

1. M. Schuster, *Fresenius J. Anal. Chem.*, **342**, 791 (1992).
2. N. Ozpozan, H. Arslan, T. Ozpozan, N. Ozdes and N. Külcü, *Thermochim. Acta*, **343**, 127 (2000).
3. N. Ozpozan, H. Arslan, T. Ozpozan, M. Merdivan and N. Külcü, *J. Thermal Anal. Cal.*, **61**, 955 (2000).
4. G. Avsar, N. Külcü and H. Arslan, *Turk. J. Chem.*, **26**, 607 (2002).
5. H. Arslan, U. Florke and N. Kulcu, *Acta Cryst.*, **E59**, o641 (2003).
6. H. Arslan, N. Külcü and U. Flörke, *Transition Met. Chem.*, **28**, 816 (2003).
7. H. Arslan, U. Florke and N. Kulcu, *J. Chem. Crystallogr.*, **33**, 919 (2003).
8. G. Binzet, U. Flörke, Külcü and H. Arslan, *Acta Cryst.*, **E59**, m705 (2003).
9. H. Arslan, D. Vanderveer, F. Emen and N. Külcü, *Z. Kristallog. NCS.*, **218**, 479 (2003).
10. F.M. Emen, U. Flörke, N. Külcü and H. Arslan, *Acta Cryst.*, **E59**, m582 (2003).
11. D. Ugur, U. Flörke, N. Külcü and H. Arslan, *Acta Cryst.*, **E59**, o1345 (2003).
12. G. Avsar, H. Arslan, H-J. Haupt and N. Külcü, *Turk. J. Chem.*, **27**, 281 (2003).
13. H. Arslan, U. Florke and N. Kulcu, *Turk. J. Chem.*, **28**, 673 (2004).
14. H. Arslan, U. Flörke and N. Külcü, *Acta Chim. Slov.*, **51**, 787 (2004).
15. H. Arslan, U. Flörke and N. Külcü, *Z. Kristallog. NCS.*, **219**, 409 (2004).
16. G. Binzet, U. Flörke, N. Külcü and H. Arslan, *Z. Kristallog. NCS.*, **219**, 395 (2004).
17. N. Külcü, U. Flörke and H. Arslan, *Turk. J. Chem.*, **29**, 1 (2005).
18. F.M. Emen, H. Arslan, N. Külcü, U. Flörke and N. Duran, *Polish J. Chem.*, **79**, 1615 (2005).
19. H. Arslan, U. Flörke, N. Külcü and F.M. Emen, *J. Coord. Chem.*, **59**, 223 (2006).
20. H. Arslan, N. Külcü and U. Flörke, *Spectrochim. Acta*, **64A**, 1065 (2006).
21. G. Binzet, H. Arslan, U. Flörke, N. Külcü and N. Duran, *J. Coord. Chem.*, **59**, 1395 (2006).
22. D. Ugur, H. Arslan and N. Külcü, *Russian J. Coord. Chem.*, **32**, 671 (2006).
23. H. Arslan, U. Flörke, N. Külcü and E. Kayhan, *Turk. J. Chem.*, **30**, 429 (2006).
24. H. Arslan, N. Duran, N.O. Sahin and N.Külcü, *Asian J. Chem.*, **18**, 1710 (2006).
25. H. Arslan, F.M. Emen and N. Külcü, *Asian J. Chem.*, **19**, 1888 (2007).
26. M. Schuster, B. Kugler and K.H. König, *J. Anal. Chem.*, **338**, 717 (1990).
27. K.H. König, M. Schuster, G. Schneeweis and B. Steinbrech, *Zeit. Anal. Chem.*, **319**, 66 (1984).
28. F.A. Frech and E.J. Blanz, *Cancer Res.*, **25**, 1454 (1965).
29. E.J. Blanz and F.A. French, *Cancer Res.*, **28**, 2419 (1965).
30. F.A. Frech and E.J. Blanz, *J. Med. Chem.*, **9**, 585 (1966).
31. F.A. Frech, E.J. Blanz, J.R.D. Amaral and D.A. French, *J. Med. Chem.*,**13**, 1117 (1970).

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