

## **THERMOGRAVIMETRIC ANALYSIS OF COBALT(II)- DOTHIEPIN COMPLEXES**

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(Received February 28, 1997; in revised form March 18, 1998)

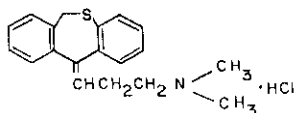
### **Abstract**

The complexes of cobalt(II) with dothiepin (DOT) hydrochloride have been studied for kinetics of thermal degradation by thermogravimetric analysis (TG) and derivative thermogravimetric studies (DTG) in a static nitrogen atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . A general mechanism of thermal decomposition is advanced involving dehydration and decomposition process for both organic and inorganic ligands. The thermal degradation reactions were found to proceed in three steps having an activation energy in the range  $6.75\text{--}170\text{ kJ mol}^{-1}$ . Thermal decomposition kinetics parameters were computed on the basis of thermal decomposition data.

**Keywords:** cobalt(II)-dothiepin, kinetics, TG

### **Introduction**

Cobalt(II) complexes with different organic ligands are widely studied by several authors [1–4] and exploited their uses in different fields [3–6]. The literature survey reveals [7–12] that the thermogravimetric studies, decomposition kinetics and thermodynamic parameters of transition metal complexes have been studied systematically and intensively.



**Fig. 1** Chemical structure of dothiepin (DOT) hydrochloride

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The ligand dothiepin hydrochloride (DOT) is widely used as antidepressant [13] and it has a wide application as a pharmaceutical agent [14, 15]. The structure of DOT is given in Fig. 1. The solid complexes of transition metals with DOT have not been previously investigated. This communication presents the spectral and thermal properties of cobalt(II)-dothiepin complexes. Decomposition kinetic parameters have been calculated for all these complexes.

## Experimental

### Materials

The chemicals and solvents used were of AR grade. DOT·HCl was received as a gift sample from M/s. BOOTS Pharmaceutical Limited, Bombay and used without further purification.

The complexes  $[\text{Co}(\text{DOT})_2(\text{SCN})_2]$  and  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{X}_2]$  where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\frac{1}{2}\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^-$  were prepared by the literature method [1].

### Physico-chemical analyses

IR-spectra were recorded in the range  $4000\text{--}200\text{ cm}^{-1}$  in KBr/nujol mull pellets employing Perkin-Elmer 597 spectrophotometer.

Visible-UV spectra (800–200 nm) were recorded with JASCO model UVIDEC-610 spectrophotometer using DMF as solvent. The percentages of carbon and hydrogen were determined by microanalytical procedures. The metal content was determined volumetrically and halide contents gravimetrically [16]. Proton spectra were recorded on JEOL 60 MHz NMR spectrometer. Molar conductance were measured with Equiptronics digital conductivity meter. Magnetic moments were measured using Gouy balance.

### Thermogravimetric analysis

The TG curves of the complexes were obtained on DuPont 9900 computer/thermal analyser with 951 TGA module, by taking 8–10 mg of complexes in nitrogen media. The sample was subjected for dynamic heating over a temperature range of  $30\text{--}900^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$ .

The TG curves were analysed to give percentage mass loss as a function of temperature. The kinetic parameters, such as activation energy,  $E_a$  and frequency factor,  $\ln A$  of the degradation process were obtained by Broido's method [17]. Integral Procedure Decomposition Temperature (IPDT) values were obtained using Doyle's method [18].

## Results and discussion

The quantitative analysis data are in good agreement with the chemical formulae of the compounds. The molar conductance value ( $11.2\text{--}26.2\text{ mhos cm}^2\text{ mol}^{-1}$ )

confirmed the covalent nature of the complexes. The effective magnetic moment value (4.32 BM) suggest the tetrahedral geometry for cobalt(II) thiocyanato complex [1] and the values (3.89–5.12 BM) suggest octahedral geometry for remaining complexes.

### *Electronic spectra*

These compounds exhibit three sharp bands at 696, 671 and 615 nm region which are attributed to an octahedral environment [19] and one more band at 269 nm can be attributed as metal  $\rightarrow$  ligand charge transfer band. The ligand field parameter (10 Dq) value ( $177 \text{ kJ mol}^{-1}$ ) calculated for cobalt(II) complexes are in agreement with the values obtained for known octahedral complexes [19].

### *Infrared spectra*

The broad IR band observed at  $3500\text{--}3400 \text{ cm}^{-1}$  in complexes is due to the presence of coordinated water molecules. The broad band at  $2550\text{--}2400 \text{ cm}^{-1}$  in ligand due to tertiary nitrogen atom attached to alkyl group combined with halogen, which is absent in the spectra of all the complexes suggest the nitrogen atom involvement in bonding [20]. The band in the region  $760 \text{ cm}^{-1}$  in ligand is attributed to C–S–C symmetric stretching vibration which is present in all complexes [20]. The new bands in the complexes at  $445\text{--}430 \text{ cm}^{-1}$  and  $380\text{--}360 \text{ cm}^{-1}$  are assigned to  $\nu_{\text{Co-N}}$  and  $\nu_{\text{Co-X}}$  stretching, respectively [3].

### *Proton NMR spectra*

The spectra of the complex  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$  in DMSO- $d_6$  solution exhibit chemical shifts at lower fields for N–CH<sub>3</sub> protons which appear at  $\delta=2.6\text{--}2.75$  ppm compared with the position in free ligand ( $\delta=2.45\text{--}2.6$  ppm). This indicates that the bonding of metal ion to the nitrogen of the side chain.

### *Thermogravimetric studies*

The TG curves obtained under dynamic scans were analysed and a sample TG curve and its derivative is given in Fig. 2 for  $[\text{Co}(\text{DOT})_2\text{Br}_2(\text{H}_2\text{O})_2]$  in order to determine thermal stability trend, the temperature characteristics such as  $T_0$  (temperature of onset of decomposition),  $T_{10}$  (temperature for 10% mass loss),  $T_{20}$  (temperature for 20% mass loss),  $T_{\text{max}}$  (temperature of maximum mass loss) and IPDT of the degradation process were calculated and presented in Table 1.

$T_0$ ,  $T_{10}$ ,  $T_{20}$  and  $T_{\text{max}}$  are the main criteria of the thermal stability of complexes and signal features of the TG curves. The higher the value of  $T_0$ ,  $T_{10}$ ,  $T_{20}$  and  $T_{\text{max}}$  higher will be the heat stability of complexes. To obtain the quantitative picture of the relative stability, IPDT values can be regarded of significant importance, since they represent the overall nature of the thermogravimetric curves.

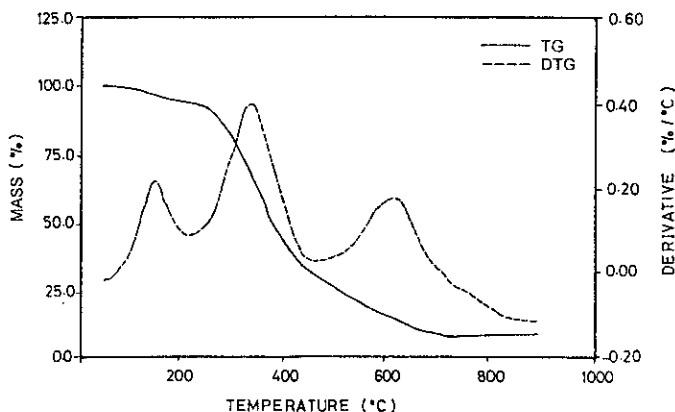


Fig. 2 TG and its derivative curves for  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Br}_2]$

The thermal stability and nature of degradation of the complexes are affected by the structure and basic character (involving the metal-ligand bond strength, electronic effects, etc.) of organic and inorganic ligands.

Table 1 Data obtained from TG analysis (Temperature characteristics and Integral Procedure Decomposition Temperature)(IPDT)

Compound	$T_0/$	$T_{10}/$	$T_{20}/$	$T_{\text{max}}/$	IPDT/
	°C				
$[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$	96	145	175	628	402
$[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Br}_2]$	120	148	180	705	390
$[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$	110	130	210	685	348
$[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{COO})_2]$	140	175	220	710	392
$[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{SO}_4]$	125	155	190	725	413
$[\text{Co}(\text{DOT})_2(\text{SCN})_2]$	214	282	301	846	435

The cobalt(II) thiocyanato complex gave relatively more thermal stability compared to other inorganic ligand complex and least thermal stability observed for cobalt(II) chloride complex. The greater stability of cobalt(II) thiocyanato complex may be ascribed to a greater heat resistance character of the nitrogen linkage to central cobalt(II) metal compared with those of other inner sphere inorganic ligand complex [10]. The lowest stability of cobalt(II) chloride complex may be due to a purely high electronegative nature of chloride ion. The trend of thermal degradation stability for the complex is shown in Table 1 and is in the order

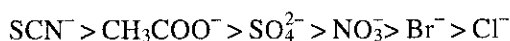
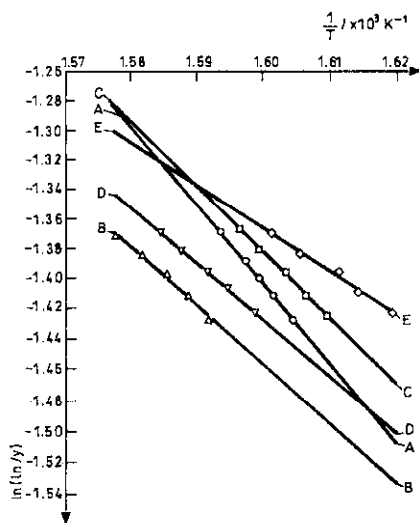
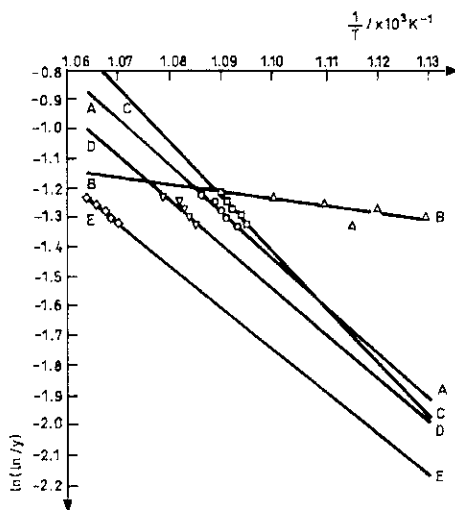


Table 2 Thermogravimetric characteristics of the complexes under study

Complex	Process	$T_{\text{range}}/^\circ\text{C}$	Product	Mass/%		No. moles	Residue		Nature
				calc.	expt.		calc.	expt.	
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Cl <sub>2</sub> ]	dehydration	96-241	H <sub>2</sub> O	4.1	5.0	2	9.2	8.9	CoO
	decomposition of coordination sphere (L, Cl)	241-410	L	77.6	76.4	1			
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Br <sub>2</sub> ]	dehydration	413-684	Cl	9.0	9.6	2	8.8	9.4	CoO
	decomposition of coordination sphere (L, Br)	125-230	H <sub>2</sub> O	4.0	3.7	2			
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	dehydration	235-420	L	69.0	68.8	1			
	decomposition of coordination sphere (L, NO <sub>3</sub> )	420-690	Br	18.1	18.0	2			
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	dehydration	130-220	H <sub>2</sub> O	4.1	4.8	2	9.1	10.5	CoO
	decomposition of coordination sphere (L, NO <sub>3</sub> )	220-470	L	72.0	71.6	1			
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	dehydration	475-705	NO <sub>3</sub>	14.7	12.9	2			
	decomposition of coordination sphere (L, CH <sub>3</sub> COO)	145-250	H <sub>2</sub> O	4.1	4.1	2	9.0	8.5	CoO
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ]	dehydration	250-435	L	72.7	72.4	1			
	decomposition of coordination sphere (L, SO <sub>4</sub> )	440-695	CH <sub>3</sub> COO	14.0	14.9	2			
[Co(DOT) <sub>2</sub> (SCN) <sub>2</sub> ]	dehydration	140-240	H <sub>2</sub> O	4.2	3.9	2	9.2	9.1	CoO
	decomposition of coordination sphere (L, SCN)	240-400	L	74.4	75.0	1			
[Co(DOT) <sub>2</sub> (SCN) <sub>2</sub> ]	decomposition of coordination sphere (L)	405-740	SO <sub>4</sub>	12.1	11.8	2			
	decomposition of coordination sphere (L, SCN)	233-429	L	76.4	76.0	1	9.3	10.0	CoO
[Co(DOT) <sub>2</sub> (SCN) <sub>2</sub> ]	decomposition of coordination sphere (L, SCN)	474-682	CN	6.1	5.8	2			
	decomposition of coordination sphere (L, SCN)	688-842	S	8.0	8.1	2			



**Fig. 3** Plots of  $\ln(\ln 1/y)$  vs.  $1/T$  for second degradation process of; A –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ ; B –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Br}_2]$ ; C –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ ; D –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{COO})_2]$  and E –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{SO}_4]$



**Fig. 4** Plots of  $\ln(\ln 1/y)$  vs.  $1/T$  for third degradation process of; A –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ ; B –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Br}_2]$ ; C –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ ; D –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{COO})_2]$  and E –  $[\text{Co}(\text{DOT})_2(\text{H}_2\text{O})_2\text{SO}_4]$

TG curves of cobalt(II) complexes show three significant temperature transitions of mass loss, termed as three stages of thermal degradation. The thermal decomposition of the complexes under study take place according to mechanisms involving dehydration and decomposition process of organic ligand followed by

inorganic ligand. The estimation of mass losses, the degradation temperatures and nature of the decomposition products are given in Table 2.

### *First stage of thermal degradation*

The mass loss occurring in the range 96–250°C in TG curves of complexes is termed as the first stage of thermal degradation. In these steps, percent mass loss is in the range 4.02–4.21%. The mass loss in these steps are due to dehydration of coordinated water molecule [21].

### *Second stage of thermal degradation*

The mass loss in the range 220–470°C in TG curves of complexes is termed as the second stage of thermal degradation. In these cases, the percent mass loss is in the range 69.01–77.66%, which may be attributed to the oxidation of organic moiety.

### *Third stage of thermal degradation*

This stage occurs in the range 405–740°C. In this stage, percent mass loss is in the range 9.02–18.13%, which may be attributed to loss of inorganic ligand bonding to the metal ion. The obtained experimental values of mass loss are in agreement with the expected values.

### *Degradation behaviour of thiocyanato complex*

The TG curve for all complexes indicate common behaviour associated with the mechanism of thermal decomposition of inorganic ligands except thiocyanato complex. Eventhough thiocyanato complex also undergo three steps degradation, the mass loss in first step due to organic ligand (DOT) and mass loss in second and third steps are due to inorganic ligand (SCN<sup>-</sup>).

The common thermal processes are associated with SCN<sup>-</sup> decomposition and elimination of the products by thermooxidative processes. In this complex the sulphur is eliminated constantly between 688 and 810°C, while (CN)<sub>2</sub> is eliminated before sulphur by thermooxidative processes influenced by the organic ligand [10].

The black residue of cobalt(II) complexes obtained in each case has been identified as pure cobalt(II) oxide [1]. The experimental values of residue are in the expected range (8.51–10.53%).

Broido's method [17] is used to evaluate the kinetic parameters. From the TG curve using Broido's equation, plots of  $[\ln(\ln 1/y)]$  vs.  $1/T$  (where  $y$  is the fraction of the number of initial molecule not yet decomposed) for various stages of thermal degradation of cobalt(II) complexes (except thiocyanato complex) were plotted and are shown in Figs 3 and 4. The activation energies ( $E_a$ ) and frequency

**Table 3** Kinetic parameters for the degradation process of complexes

Complexes	Process	$E_a \pm 2/$ $\text{kJ mol}^{-1}$	$\ln A \pm 2/$ $\text{min}^{-1}$
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (Cl <sub>2</sub> )]	I	10.68	9.30
	II	40.20	15.20
	III	150.80	30.21
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> Br <sub>2</sub> ]	I	6.75	6.50
	II	59.53	18.25
	III	83.00	13.30
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	I	14.90	10.63
	II	47.41	16.21
	III	160.05	30.50
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ]	I	9.83	8.80
	II	35.61	12.67
	III	147.00	27.48
[Co(DOT) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> SO <sub>4</sub> ]	I	13.50	20.20
	II	55.01	17.52
	III	168.91	28.68
[Co(DOT) <sub>2</sub> (SNC) <sub>2</sub> ]	I	15.58	10.67
	II	64.20	17.12
	III	170.00	27.50

factors ( $\ln A$ ) have been calculated from slopes and intercepts, respectively, of these plots and the values are given in Table 3. The activation energies are low in first stage transition and higher in third stage transitions (6.75–170  $\text{kJ mol}^{-1}$ ). The lowest value for first steps due to low energy utilized to remove the loosely bound water (ligand) molecules.

## Conclusions

The synthesized Co(II)–DOT complexes were characterized by the spectral and thermal studies. Thermal stability lies in the order  $\text{SCN}^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Br}^- > \text{Cl}^-$ . All the complexes undergo three steps of thermal degradation. The activation energy lies in the range of 6.75 to 170  $\text{kJ mol}^{-1}$  and follow the simple  $n$ th order Arrhenius relation.

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The authors wish to thank Prof. K. Natarajan for IR spectra, Prof. Kulkarni for elemental analyses and M/s. BOOTS Pharamaceutical Limited, Bombay for gift sample of DOT. One of us (H. S. B) is grateful to University of Mysore for the award of Research Fellowship.

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