

TGA studies of metoclopramide complexes of cobalt(II) in the solid state

P.R. Chetana^{a,*}, X. Siddaramaiah^b, P.G. Ramappa^c

^a Department of Post Graduate Studies in Chemistry, University of Bangalore, Central College Campus, Bangalore 560001, India

^b Department of Polymer Science and Technology, Sri Jayachamarajendra College of Engineering, Mysore 570 006, India

^c Department of Post Graduate Studies in Chemistry, University of Mysore, Manasagangothri, Mysore 570 006, India

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Abstract

A new series of cobalt(II) complexes with metoclopramide (MCP) ligand have been prepared. The prepared Co(II)–MCP complexes were characterized for various analytical techniques. Conductivity and elemental analysis of complexes have been measured. The thermal stability and degradation kinetics have been measured using thermogravimetric analyser. Kinetic parameter was obtained for each stage of thermal degradation for Co(II)–MCP complexes using Horowitz–Metzger, Coats–Redfern and Broido's methods. The activation energy (E_a) of the complexes for the thermal degradation process lie in the range 31–168, 23–161 and 33–170 kJ mol⁻¹ for Horowitz–Metzger, Coats–Redfern and Broido's methods, respectively.

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1. Introduction

Benzamide-4-amino-5-chloro-*N*-[2-(diethyl amine)ethyl]-2-methoxy monochloride, metoclopramide (MCP), was prepared by Murakami et al. [1]. MCP is a dopamine antagonist clinically used as antiemetics. This drug has therapeutic potential and its mechanism of action at receptor and molecular level was described [2]. MCP is used as a reagent for the extraction-spectrophotometric determination of ion association complex rhenium(IV)-thiocyanate [3,4]. The presence of amide nitrogen and tertiary nitrogen in the structure of MCP ligand enables it to form complexes with transition metals. Metal complexes are extensively used as catalysts, optical modifier, conducting filler, antiradator filler, etc. To select the suitable material for given applications material technologists requires knowledge about their properties. The knowledge of their physico-chemical and thermal properties is useful to exploit these complexes for newer applications. Survey of the literature reveals that the synthesis and characterization of Co(II)–MCP complexes have not been studied.

The present research article deals with the synthesis, physical properties and thermal degradation kinetics of new series of Co(II) complexes with MCP ligand. The thermal degradation kinetic parameters such as energy of activation (E_a) and frequency factor ($\ln A$); and thermodynamic parameters like change in entropy (ΔS), change in enthalpy (ΔH) and change in free energy (ΔG) for each step have been evaluated. The kinetic parameters have been calculated using three relations like Horowitz–Metzger [5], Coats–Redfern [6] and Broido's [7] methods and compared.

2. Experimental

2.1. Materials

Cobalt salts and solvents used were of AR grade. The ligand MCP was obtained as a gift sample from Astra IDL Ltd., Bangalore, India. It is used as it is without further purification.

2.2. Preparation of complexes

An ethanolic solution of 50 ml of 5 mM MCP was slowly added to 50 ml of 5 mM ethanolic Co(II) salt with continu-

* Corresponding author. Fax: +91-80-2386988.

E-mail address: prchetana@hotmail.com (P.R. Chetana).

ous stirring. The mixture was then refluxed in water bath at 65–80 °C for 2 h. The blue coloured precipitate was obtained in each case. The solid complexes formed were cooled, filtered, and washed successively with ethanol and then with ether. The Co(II) complexes were finally dried in a vacuum desiccator over anhydrous silica gel.

2.3. Physical measurements

Magnetic moments were measured by employing Gouy balance. The conductivity measurements were carried out using Equiptronics digital conductivity meter model EQ-DCM-P type at room temperature for 1×10^{-3} M solutions. The hydrogen and carbon content of the complexes have been measured by microelemental procedures. The metal content was determined by complexometric method [8].

2.4. Treatment of TGA data

The thermal degradation parameters of Co(II)–MCP complexes were evaluated using DuPont 9900 TA with 951 TGA module. About 6–8 mg of pure sample was subjected to dynamic TGA scans at a heating rate of 10 °C min⁻¹ in the temperature range of ambient to 900 °C in N₂ atmosphere.

The TG curves were analysed as percentage weight loss as a function of temperature. The three decomposition steps were identified using a derivative of the TG curves. The kinetic and thermodynamic parameters of thermal degradation process have been calculated using three models.

The Horowitz–Metzger [5] relation used to evaluate the degradation kinetics is

$$\ln \left[\frac{\ln(W_0 - W_t^f)}{W - W_t^f} \right] = \frac{E_a \theta}{RT_s^2} \quad (1)$$

where W_0 is the initial weight of the sample, W_t^f the final weight of the sample, W the weight remaining at a given temperature, T , E_a the activation energy, $\theta = T - T_s$, T_s the DTG peak temperature, T the temperature corresponding to weight loss, W .

Coats–Redfern [6] relation is as follows:

$$\log \left\{ -\log \left[\frac{1 - \alpha}{T^2} \right] \right\} = \log \left\{ \left(\frac{AR}{aE_a} \right) - \left(\frac{E_a}{2.3RT} \right) \right\} \quad (2)$$

where α is the fraction of sample decomposed at time T , T the derivative peak temperature, A the frequency factor, a the heating rate, E_a the activation energy, R the gas constant.

A plot of $\log\{-\log(1 - \alpha)/T^2\}$ versus $1/T$ gives the slope for evaluation of the activation energy most appropriately.

Mathematical expression of Broido's [7] method is as follows:

$$\ln \left\{ \ln \left(\frac{1}{y} \right) \right\} = \left\{ \left(-\frac{E_a}{R} \right) \left(\frac{1}{T} \right) \right\} \quad (3)$$

where y is the fraction of number of initial molecules not yet decomposed, T the peak temperature of derivative curve

of TG, R the gas constant, E_a the activation energy can be calculated from the plot of $\ln\{\ln(1/y)\}$ versus $1/T$.

3. Results and discussion

3.1. Physical analysis

All the synthesized divalent cobalt complexes with MCP were blue in colour, and nonhygroscopic towards air and moisture. The elemental analysis results obtained by microanalytical measurement and metal content determination data indicate 1:1 metal to ligand stoichiometry. The molar conductance values of these complexes (1.0×10^{-3} M in DMF) lie in the range 27.76–44.58 mho cm⁻¹ mol⁻¹, which reveals that these complexes are nonelectrolytes.

3.2. Thermogravimetric analysis

TGA and its derivative thermograms for MCP and cobalt complexes are shown in Figs. 1–2, respectively. From the thermograms it can be observed that two-step thermal degradation processes for MCP, whereas its cobalt complexes shows three-step thermal degradation behaviour. In order to determine the thermal stability trend the temperature characteristics such as T_0 (temperature at the onset of decomposition), T_{10} (temperature at 10% weight loss), T_{20} (temperature at 20% weight loss), T_{50} (temperature at 50% weight loss), T_{\max} (temperature at maximum rate of decomposition) and integral procedure for decomposition temperature (IPDT) values of the degradation process were calculated (Table 1).

T_0 , T_{10} , T_{20} and T_{\max} are the main criteria of the thermal stability of complexes. The higher the value of T_0 , T_{10} , T_{20} and T_{\max} , higher will be the heat stability of complexes [9]. 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.

Chemical structure and nature of inorganic ligands will affect the thermal stability and degradation pattern of Co(II)–MCP complexes. From Table 1 it was noticed that the thermal stability of all Co(II)–MCP complexes are lesser than 128 °C except [Co(MCP)(SCN)₂] complex. This is due to the presence of water ligand in all other complexes. From Table 1, it was noticed that high IPDT value of 586 °C for [Co(MCP)(SCN)₂] compared to other inorganic ligands. The greater thermal stability of [Co(MCP)(SCN)₂] may be ascribed to greater heat resistance character of –SCN linkage compared with those of other inner sphere inorganic ligands [10,11]. The lowest thermal stability of [Co(MCP)Br₂] complex may be due to low electronegative nature of bromide ion. The trend of thermal degradation stability for the complexes are given in Tables 1 and 2.

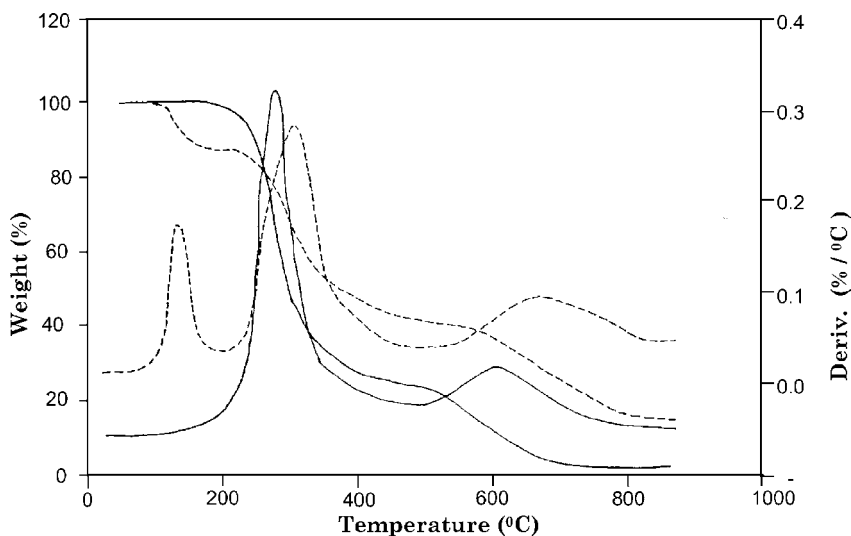


Fig. 1. TGA and derivative thermograms of MCP (—) and $[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{SO}_4]$ (---).

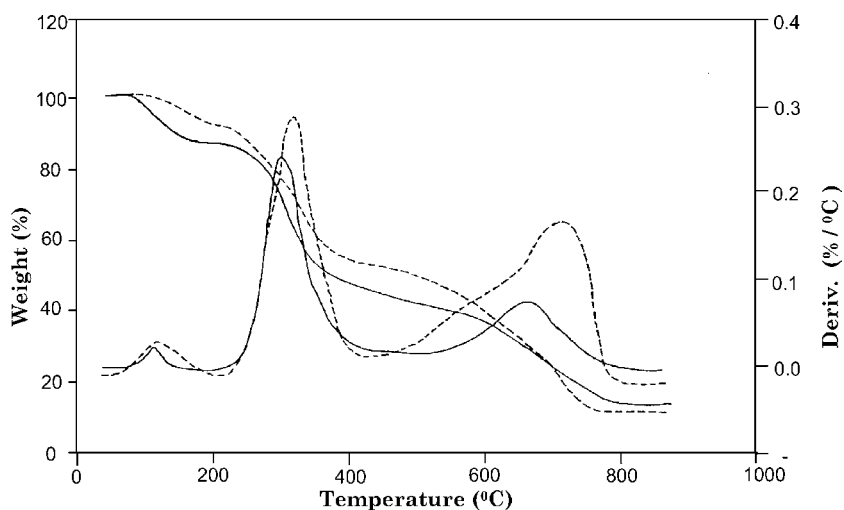


Fig. 2. TGA and derivative thermograms of $[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{Cl}_2]$ (—) and $[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{Br}_2]$ (---).

3.2.1. First stage of thermal decomposition

The first step of thermal decomposition of Co(II) complexes starts at 105 °C and is marked with a regular loss in mass up to 275 °C. The initial mass loss for the complexes

varies from 6.2 to 7.8%, obtained in pyrolysis and agrees well with the theoretically expected loss of 6.5–7.3%. This is mainly due to the elimination of two-molecule of coordinated water [11,12].

Table 1

Characteristic transition temperature and IPDT values of Co–MCP complexes obtained by TGA scans

Complexes	Temperature at different weight loss +2 °C					
	T_0	T_{10}	T_{20}	T_{50}	T_{max}	IPDT
MCP	235	248	262	295	656	497
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$	225	267	271	283	564	414
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{Br}_2]$	110	193	290	509	761	554
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{Cl}_2]$	108	148	270	389	795	500
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2\text{SO}_4]$	121	145	267	374	890	523
$[\text{Co}(\text{MCP})(\text{NCS})_2]$	208	280	292	446	656	486
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2(\text{NO}_3)_2]$	106	238	296	451	675	490
$[\text{Co}(\text{MCP})(\text{H}_2\text{O})_2(\text{CH}_3\text{COO})_2]$	128	193	277	406	634	538

Table 2
Stepwise thermal degradation data obtained from TGA curves for Co(II)–MCP complexes

Complexes	Process	Temperature range (°C)	T_{\max} (°C)	Products	Weight loss (%)		No. of moles	Residue (%)		Nature
					Calculated	Experimental		Calculated	Experimental	
MCP	I	235–440	276	L	–	75.4	0.8	–	0.2	
	II	459–705	594	L	–	24.4	0.2			
[Co(MCP)(H ₂ O) ₂ (ClO ₄) ₂]	I	225–305	278	H ₂ O + ClO ₄ + L	78.8	69.7	2.0 + 2.0 + 0.8	12.1	3.8	CoO
	II	331–590	499	L	12.6	26.8	0.2			
[Co(MCP)(H ₂ O) ₂ Br ₂]	I	110–199	129	H ₂ O	6.5	6.1	2.0	13.5	11.7	CoO
	II	215–410	322	L	40.5	40.2	0.8			
	III	414–770	716	L + Br	41.8	42.0	0.2 + 2.0			
[Co(MCP)(H ₂ O) ₂ Cl ₂]	I	108–176	116	H ₂ O	7.7	7.8	2.0	16.1	16.0	CoO
	II	215–510	303	L	48.3	46.6	0.8			
	III	416–820	720	L + Cl	30.7	29.6	0.2 + 2.0			
[Co(MCP)(H ₂ O) ₂ SO ₄]	I	121–201	135	H ₂ O	7.3	7.4	2.0	15.4	15.1	CoO
	II	201–489	302	L	45.8	45.6	0.8			
	III	489–844	661	L + SO ₄	35.0	32.6	0.2 + 1.0			
[Co(MCP)(NCS) ₂]	I	208–375	236	L	47.7	46.8	0.8	15.8	15.8	CoO
	II	375–410	345	L + CN	26.1	25.0	0.2 + 2.0			
	III	525–805	738	S	13.5	12.3	2.0			
[Co(MCP)(H ₂ O) ₂ (NO ₃) ₂]	I	106–206	114	H ₂ O	6.9	6.7	2.0	14.3	14.4	CoO
	II	213–435	335	L	42.6	41.5	0.8			
	III	490–630	728	L + NO ₃	38.5	37.8	0.2 + 2.0			
[Co(MCP)(H ₂ O) ₂ (CH ₃ COO) ₂]	I	128–216	162	H ₂ O	7.0	7.1	2.0	14.6	14.2	CoO
	II	218–430	327	L	43.8	43.6	0.8			
	III	505–742	634	L + CH ₃ COO	37.1	35.1	0.2 + 2.0			

A realistic explanation for the anion effect can be provided by defect diffusion model [13]. When a reaction takes place in a solid, the formation of transition state results in a point defect in the lattice. These defects are analogous to the substituted ion Schottky and Frenkel defects [14]. When a volatile ligand like water is lost from a complex, a situation analogous to the Frenkel defect is formed. This introduces distortion in the structure of the crystal leading to transition state. The fraction of free space in crystal increases as the difference between the size of the cation and anion increases [15,16]. The activation energies in Table 3 of the reported Co(II)–MCP complexes for deaquation reaction decreases in the order perchlorate > sulphate > acetate > bromide > chloride > nitrate. The fraction of free space is much lower when cation and anions are of equal size. Therefore in perchlorate compounds deaquation reactions take place with difficulty [17].

3.2.2. Second stage of thermal decomposition

The major weight loss of about 40–48% occurred in second step degradation process in the temperature range 200–510 °C. The weight loss in this step is due to partial decomposition of organic ligand. The degradation pattern is on par with that of the MCP ligand. The activation energy values for this step are in the range 38.2–76.4 kJ mol⁻¹ in Horowitz–Metzger method that are comparable with Coats–Redfern and Broido's methods.

3.2.3. Third stage of thermal decomposition

The mass loss in the temperature range 414–844 °C corresponds to third step degradation process of complexes. The weight loss in this step is about 29.5–42.0%. The weight loss in this step is due to the elimination of inorganic ligand and 25% of MCP ligand. The residue of pyrolysis of complexes corresponds to cobalt oxide [18], which was chemically confirmed. In all the three degradations of all complexes there is correlation between the calculated and the experimental weight losses.

Though the Co(II) thiocyanate complex show three stage degradation, the pattern is different from that of other complexes [19,20]. The major portion of MCP ligand is eliminated in the first stage degradation, the elimination of remaining portion of MCP ligand and (CN)₂ occurred in second stage degradation. Sulphur is eliminated in the third stage of the degradation process.

Co(II)-perchlorate complex shows only two-step decompositions. It is stable up to 277 °C and rapidly decomposes at this step; weight loss is about 69.7%. The first stage corresponds to elimination of a part of the MCP ligand, water molecules and perchlorate ions. In the second stage the remaining portion of the MCP ligand decomposes. The sudden decomposition of this complex may be due to the explosive nature of perchlorate ion present in it. This complex shows a different type of decomposition from those of other complexes. This suggests that the ligand water molecule be

Table 3
Activation energy and correlation co-efficient values for the thermal degradation of Co–MCP complexes

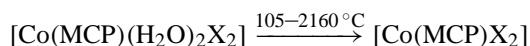
Compounds	Process	$E_a \pm 2\%$ (kJ mol ⁻¹)			Correlation co-efficient, $ r^2 $		
		H-M	C-R	Broido's	H-M	C-R	Broido's
MCP	I	88.4	79.3	88.5	0.975	0.976	0.981
	II	31.2	19.1	33.5	0.988	0.957	0.986
[Co(MCP)(H ₂ O) ₂ (ClO ₄) ₂]	I	168.7	161.4	170.6	0.732	0.710	0.733
	II	38.2	25.4	38.3	0.988	0.976	0.989
[Co(MCP)(H ₂ O) ₂ Br ₂]	I	45.5	44.2	45.4	0.963	0.955	0.956
	II	44.2	34.2	44.1	0.998	0.997	0.998
	III	62.6	46.0	62.4	0.995	0.989	0.994
[Co(MCP)(H ₂ O) ₂ Cl ₂]	I	37.4	43.6	40.2	0.882	0.862	0.901
	II	54.9	45.2	54.8	0.954	0.988	0.993
	III	33.6	23.8	29.3	0.987	0.944	0.987
[Co(MCP)(H ₂ O) ₂ SO ₄]	I	51.9	55.2	51.9	0.961	0.960	0.970
	II	44.2	34.8	44.4	0.977	0.973	0.984
	III	23.2	17.8	23.3	0.987	0.903	0.989
[Co(MCP)(NCS) ₂]	I	72.6	68.7	74.3	0.987	0.903	0.989
	II	76.2	73.6	65.5	0.995	0.906	0.923
	III	54.0	48.0	52.8	0.981	0.968	0.915
[Co(MCP)(H ₂ O) ₂ (NO ₃) ₂]	I	35.6	41.0	36.5	0.984	0.896	0.982
	II	48.7	37.5	59.4	0.915	0.906	0.894
	III	51.5	49.4	51.9	0.962	0.987	0.922
[Co(MCP)(H ₂ O) ₂ (CH ₃ COO) ₂]	I	51.5	52.3	50.35	0.957	0.891	0.980
	II	76.4	74.0	76.9	0.908	0.901	0.996
	III	69.3	64.5	68.5	0.889	0.893	0.959

retained even at a high temperature, since the bulky perchlorate ion cannot easily migrate towards the inner sphere [21]. This fact seems to account for the mechanism by which the deaquation reaction is initiated by the migration of the anion as explained by defect diffusion model.

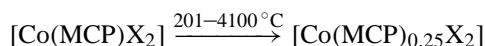
3.2.4. Degradation mechanism

The broad outline for thermal decomposition mechanism of Co(II)–MCP complexes is as follows:

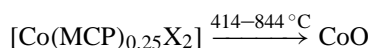
- First step degradation



- Second step degradation



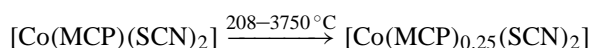
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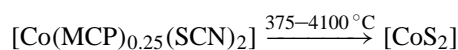
where X = Cl⁻, Br⁻, (1/2)SO₄²⁻ · NO₃⁻ or CH₃COO⁻.

The decomposition pattern in the Co(SCN)–MCP complex is as follows:

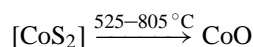
- First step degradation



- Second step degradation

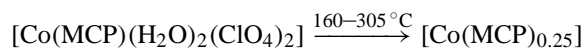


- Third step degradation

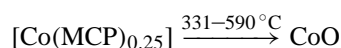


The decomposition of Co(II)–perchlorate complex may be formulated as:

- First step degradation



- Second step degradation



3.3. Kinetics and thermodynamics applied to pyrolysis

The three decomposition steps of the complexes were subjected to nonisothermal kinetic and thermodynamic studies and the parameters such as apparent activation energy (E_a), pre-exponential factor (A), rate constant (K_r), entropy of activation (ΔS), enthalpy of activation (ΔH) and free energy of activation (ΔG) are calculated and the values are given in Tables 3–5. Arrhenius plots in Figs. 3 and 4 were drawn by least square method and corresponding cor-

Table 4

Pre-exponential factors and rate constant values for thermal degradation of Co(II)–MCP complexes

Compounds	Process	ln A ± 2 (min ⁻¹)			K _r (min ⁻¹)		
		H-M	C-R	Broido's	H-M	C-R	Broido's
MCP	I	19.0	16.0	19.0	0.702	0.246	0.702
	II	2.0	0.7	2.3	0.100	0.135	0.107
[Co(MCP)(H ₂ O) ₂ (ClO ₄) ₂]	I	37.2	35.0	37.6	1.340	0.617	1.355
	II	4.1	2.5	4.1	0.154	0.223	0.154
[Co(MCP)(H ₂ O) ₂ Br ₂]	I	13.2	7.2	13.2	0.677	0.002	0.676
	II	7.8	4.4	7.7	0.300	0.082	0.299
	III	5.8	3.9	5.7	0.154	0.182	0.154
[Co(MCP)(H ₂ O) ₂ Cl ₂]	I	11.0	6.7	12.0	0.594	0.025	0.639
	II	10.6	7.2	10.5	0.398	0.104	0.397
	III	1.6	1.2	0.9	0.082	0.199	0.072
[Co(MCP)(H ₂ O) ₂ SO ₄]	I	15.0	10.0	15.0	0.748	0.038	0.749
	II	8.1	5.0	8.1	0.320	0.101	0.321
	III	0.2	0.2	0.3	0.064	0.124	0.064
[Co(MCP)(NCS) ₂]	I	16.7	10.8	17.2	0.672	0.004	0.688
	II	14.1	7.9	11.9	0.481	0.002	0.413
	III	4.4	3.7	4.2	0.127	0.130	0.124
[Co(MCP)(H ₂ O) ₂ (NO ₃) ₂]	I	13.9	10.6	14.2	0.733	0.119	0.748
	II	8.5	6.2	10.8	0.317	0.291	0.386
	III	4.1	3.5	4.2	0.124	0.084	0.125
[Co(MCP)(H ₂ O) ₂ (CH ₃ COO) ₂]	I	13.8	10.1	13.4	0.653	0.013	0.638
	II	14.7	9.7	14.8	0.511	0.006	0.515
	III	7.6	5.5	7.5	0.203	0.047	0.200

Table 5
Entropy ΔS , free energy ΔG and enthalpy ΔH values for Co–MCP complexes

Compounds	Process	ΔS (kJ mol ⁻¹)			ΔG (kJ mol ⁻¹)			ΔH (kJ mol ⁻¹)		
		H-M	C-R	Broido's	H-M	C-R	Broido's	H-M	C-R	Broido's
MCP	I	-92.3	-117.6	-92.2	134.6	139.5	134.6	83.8	74.7	83.9
	II	-236.9	-248.4	-233.6	229.4	227.1	228.8	24.0	11.9	26.3
[Co(MCP)(H ₂ O) ₂ (ClO ₄) ₂]	I	59.0	39.3	62.4	131.7	135.2	131.7	164.2	156.9	166.0
	II	-218.7	-232.4	-218.9	201.0	198.6	201.0	31.8	19.0	31.8
[Co(MCP)(H ₂ O) ₂ Br ₂]	I	-137.4	-187.8	-137.6	97.4	116.4	97.4	42.2	40.9	42.1
	II	-186.4	-214.0	-186.7	150.3	156.7	150.3	39.4	29.2	39.1
	III	-207.1	-222.5	-207.3	259.3	257.9	259.3	54.41	37.8	54.2
[Co(MCP)(H ₂ O) ₂ Cl ₂]	I	-155.4	-191.5	-147.5	94.6	104.9	94.4	34.2	30.3	37.0
	II	-162.7	-190.8	-163.0	143.9	150.3	143.9	50.1	40.4	49.9
	III	-241.8	-244.7	-247.4	265.6	258.6	266.7	25.4	15.5	21.0
[Co(MCP)(H ₂ O) ₂ SO ₄]	I	-122.9	-164.0	-122.8	98.7	108.87	98.7	48.5	41.8	48.5
	II	-183.2	-209.0	-182.8	144.9	150.4	144.9	39.4	30.0	39.6
	III	-252.4	-252.7	-252.3	251.3	246.1	251.2	15.5	9.9	15.5
[Co(MCP)(NCS) ₂]	I	-110.2	-159.7	-106.7	124.5	145.8	124.4	68.3	64.4	70.1
	II	-133.6	-185.7	-152.3	153.6	183.1	154.4	71.11	68.5	60.3
	III	-218.8	-224.6	-220.2	266.8	266.63	267.0	45.6	39.6	44.4
[Co(MCP)(H ₂ O) ₂ (NO ₃) ₂]	I	-161.8	-198.9	-159.2	99.4	99.3	93.3	33.7	27.8	33.3
	II	-180.3	-199.5	-161.2	153.3	153.8	152.3	43.7	42.4	54.3
	III	-220.9	-226.3	-220.5	264.3	267.6	264.3	43.2	41.1	43.5
[Co(MCP)(H ₂ O) ₂ (CH ₃ COO) ₂]	I	-133.4	-164.2	-136.4	105.9	120.21	106.0	47.8	48.7	46.6
	II	-128.8	-169.8	-127.9	148.7	170.8	148.7	71.5	68.9	71.9
	III	-190.9	-208.5	-192.0	234.9	246.1	235.1	61.8	56.9	60.9

relation co-efficient were also calculated and tabulated in Table 3.

The activation energy values for Co(II)–MCP complexes are above 35.6 kJ mol⁻¹ for the dehydration reactions in all the three methods. These values are more than the activation energy values for the removal of lattice

water [22]. The activation energy values for the second stage decomposition are in the range 38–76 kJ mol⁻¹ for Horowitz–Metzger method. The E_a values for other two methods are also in the same range. E_a of the third step degradation also follow the same trend in all the methods (Table 3).

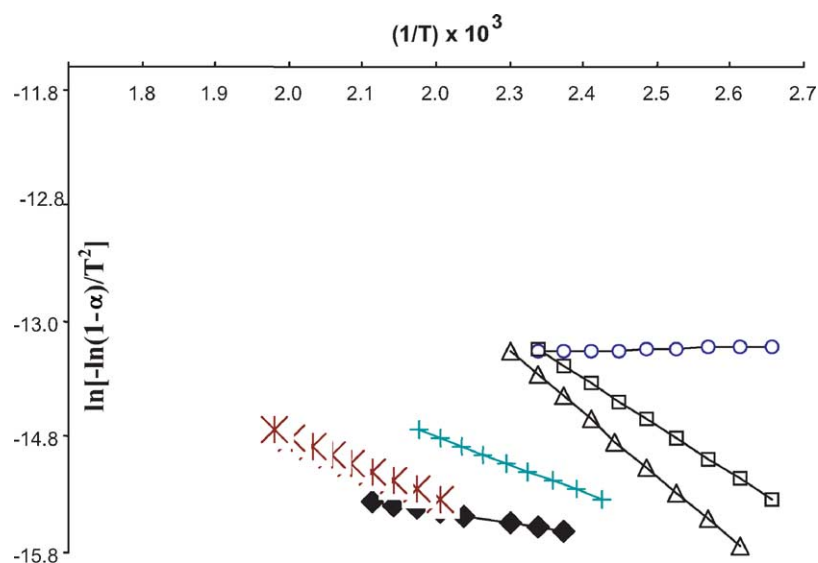


Fig. 3. Typical Coats–Redfern plot for the determination of activation energies for second step degradation of Co(II)–MCP complexes: [Co(MCP)(H₂O)₂Cl₂] (○), [Co(MCP)(H₂O)₂(NCS)₂] (□), [Co(MCP)(H₂O)₂(SO₄)] (Δ), [Co(MCP)(H₂O)₂Br₂] (◆), [Co(MCP)(H₂O)₂(NO₃)₂] (+), [Co(MCP)(H₂O)₂(CH₃COO)₂] (*).

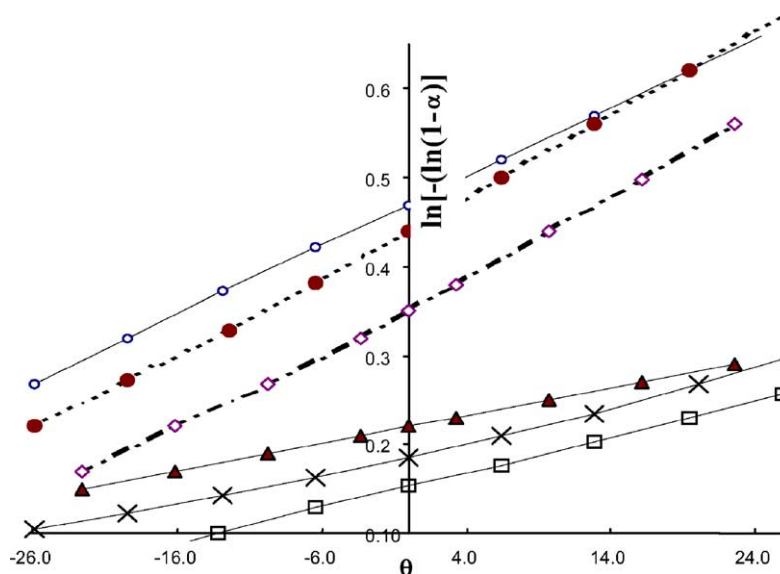


Fig. 4. Typical Horowitz–Metzger plot for the determination of activation energies for third degradation step degradation of Co–MCP complexes: [Co(MCP)(H₂O)₂Br₂] (○), [Co(MCP)(H₂O)₂Cl₂] (□), [Co(MCP)(H₂O)₂SO₄] (▲), [Co(MCP)(H₂O)₂(NCS)₂] (◇), [Co(MCP)(H₂O)₂(CH₃COO)₂] (●), [Co(MCP)(H₂O)₂(NO₃)₂] (×).

From the TGA thermograms it is observed that the curves for the metal chelates are broader while the curve for the ligand is steeper. On the basis of this it is assumed that the rate of the pyrolysis of metal chelate is slower than that of the ligand [23]. This fact is also supported by the rate constant values given in Table 4. The frequency factor for the removal of two coordinated water molecules is larger as they are loosely bound and can be easily removed. The pre-exponential value decreases from second to third stage degradation. The values of pre-exponential factor $\ln A$, also indicate that the decomposition of Co(II)–MCP complexes were slow [24] process.

The relative sizes of inorganic ligands and the free volumes may explain the entropy effects, which are shown by the data given in Table 5. The water molecules may be able to slip into an interstitial position causing little or no lattice distortion, when there is a large difference between the size of the cation and anion. Therefore, the entropy of activation is small. When the cation and anion are of approximately the same size, water can occupy an interstitial position only with considerable lattice expansion so that the entropy of activation is more. The entropy of activation for Co(II)–MCP complexes follows the same order of thermal stability as that of the ligands. The lower entropy values were observed in the second stage decomposition, when compared to the values of, that of the first stage decomposition. In the second stage, it is the major portion of the MCP ligand, which is undergoing oxidation. Due to its larger size, compared to that of the water molecules there will be larger distortion in the lattice structure of the remaining portion of the molecule. Hence, second step degradation has lower entropy values than that of the first step degradation. Once again the increase in the entropy values in the third step degradation

may be due to the smaller sizes of inorganic ligands and remaining portions of the MCP ligand.

4. Conclusion

A new series of Co(II) complexes were prepared and characterized by the elemental analysis and spectral studies, based on these studies they have been assigned octahedral geometry. TGA data supports the presence of coordinated water. The thermal stability of the complexes was explained considering the transition temperature and IPDT values. For cobalt(II)–MCP complexes, the stability decreases in the order perchlorate > acetate > sulphate > bromide > chloride > nitrate. The decomposition of all the complexes takes place in three steps, except perchlorate complex. The effect of anions in the deaquation reaction can be explained by defect diffusion model. On the basis of this model the stability towards deaquation reaction decreases in the order $\text{ClO}_4^- > \text{CH}_3\text{COO}^- > \text{SCN}^- > \text{SO}_4^{2-} > \text{Br}^- > \text{Cl}^- > \text{NO}_3^-$.

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References

- [1] M. Murakami, N. Inukai, A. Koda, K. Nakano, *Chem. Pharm. Bull.* 19 (8) (1971) 1696.

- [2] L. Anker, J. Lauterwein, H.V. de Waterbeemed, B. Bernard Testa, *Helv. Chim. Acta* 67 (1984) 706.
- [3] P.G. Ramappa, K.S. Ramachandra, *J. Asian Chem.* 1 (1989) 19.
- [4] P.G. Ramappa, K.S. Ramachandra, *J. Inst. Chem.* 59 (1987) 115.
- [5] H. Horowitz, G. Metzger, *Anal. Chem.* 35 (1964) 68.
- [6] A.W. Coats, J.P. Redfern, *Nature* 201 (1964) 68.
- [7] A. Broido, *J. Poly. Sci. A* 2 (1969) 1761.
- [8] A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, 4th ed., Longmans Green, ELBS, London, p. 462.
- [9] M.M. Kotan, Y.N. Sazonov, *Polym. Sci. USSR* 15 (1973) 1857.
- [10] N. Calu, L. Odochain, G.L. Brinzan, N. Bilba, *J. Therm. Anal.* 30 (1985) 547.
- [11] H.S.B. Naik, Siddaramaiah, P.G. Ramappa, *J. Therm. Anal. Calorimetry* 55 (1998) 841–849.
- [12] M. Nath, R. Yadav, *Synth. React. Met. Org. Chem.* 25 (9) (1995) 1529.
- [13] J.E. House Jr., *Thermochim. Acta* 38 (1981) 59.
- [14] A.R. West, *Solid State Chemistry and its Applications*, Wiley, New York, 1984, pp. 318–333.
- [15] H. Schmalzried, *Solid State Reactions*, 2nd ed., VEB Chemie, Weinheim, 1974, pp. 24–27.
- [16] J. Casabo, T. Flor, F. Teixidor, J. Ribas, *Inorg. Chem.* 25 (1986) 3166.
- [17] M. Mori, R.T. Tsuchiya, *Bull. Chem. Soc. Jpn.* 33 (1960) 841.
- [18] P.G. Ramappa, K.G. Somasekharappa, *Synth. React. Inorg. Met. Org. Chem.* 22 (1992) 1267.
- [19] H.S. Bhojya Naik, Siddaramaiah, P.G. Ramappa, *Thermochim. Acta* 2998 (1996) 1.
- [20] C. Pariya, A. Gosh, N.R. Chaudhuri, *Thermochim. Acta* 273 (1996) 185.
- [21] A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata, J. Oda, *Bull. Chem. Soc. Jpn.* 48 (1) (1975) 262.
- [22] K.K. Mohammed Yusuff, R. Sreekala, *Thermochim. Acta* 179 (1991) 313.
- [23] K.H. Halawani, K.M. Abd El-Salaam, F.A. Fakiha, *Int. J. Chem.* 4 (1992) 201.
- [24] R.K. Bansal, R. Agrawal, K. Keshav, *Angew. Makromol. Chem.* 117 (1983) 211.