Thermochimica Acta, 159 (1990) 357–368
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND SPECTRAL STUDIES OF 1-BENZYL-2-PHENYLBENZIMIDAZOLE COMPLEXES OF COBALT(II)

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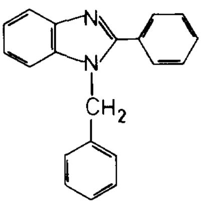
(Received 22 August 1989)

ABSTRACT

Cobalt(II) complexes of 1-benzyl-2-phenylbenzimidazole (BPBI), of general formula $[Co(BPBI)_2X_2]$ ($X \equiv Cl^-$, Br^-, I^- or NCS^-), have been synthesized and characterized. A tetrahedral structure has been suggested for these complexes. The complexes were subjected to a systematic TG/DTG/DTA analysis. All the complexes decompose just after melting, and the decomposition process consists essentially of two stages. The final residue in all cases was found to be CoO. The mass loss data indicate the formation of intermediate complexes with approximate compositions $[Co(BPBI)Cl_2]$, $[Co(BPBI)Br_2]$, [Co(BPBI)I] and $[Co(BPBI)_{0.5}(NCS)_2]$ at the end of the first stage of decomposition. The kinetic parameters were calculated using the Coats–Redfern equation. In all the complexes except the bromo complex, the E_a values for the second stage of decomposition were found to be much higher than those for the first stage. The anomalously smaller E_a and ΔS values exhibited by the bromo complex for the second stage of decomposition indicate catalytic activity for the intermediate bromo complex.

INTRODUCTION

Benzimidazoles play a significant role in the structure and function of a number of biologically important molecules [1]. 5,6-Dimethylbenzimidazole supplies one of the five nitrogen atoms coordinated to cobalt in vitamin B_{12} and, in fact, this has created an interest in the study of coordination compounds of benzimidazole and its derivatives [2]. The derivative 1-benzyl-2-phenylbenzimidazole (BPBI) is interesting from the structural point of view because of its bulky nature and steric effects. The ligand has the structure given below.



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As a part of our programme on the thermal decomposition studies of transition metal complexes, we have synthesized cobalt(II) complexes of BPBI. A literature search revealed that no syntheses of these Co^{II} complexes have been reported, even though details about the BPBI complexes of copper(II), nickel(II) and iron(II) are available [3–5]. Furthermore, no reports of thermal decomposition kinetic studies of any of these BPBI complexes have yet appeared in the literature. In this paper we describe the synthesis, characterization and thermal decomposition kinetics of cobalt(II)–BPBI complexes.

EXPERIMENTAL

Synthesis of the ligand

The ligand BPBI was prepared according to the procedure given in the literature [6].

Synthesis of the complexes

All the halogeno complexes were prepared by the same general procedure. A solution containing 0.005 mol of $CoX_2 \cdot 6H_2O$ (where $X \equiv Cl^-$, Br^- or I^-) in 25 ml of ethanol was added to a solution containing 0.01 mol of BPBI in 25 ml of ethanol. The complex slowly separated out on scratching the sides of the beaker with a glass rod. It was filtered off, washed with ethanol and dried over anhydrous calcium chloride. For the synthesis of the thiocyanato complex, the following procedure was used. First, $Co(NO_3)_2 \cdot 6H_2O$ (0.005 mol) and KSCN (0.01 mol) were separately dissolved in the minimum quantity of ethanol and mixed. The precipitated KNO_3 was filtered off and washed with ethanol. The filtrate was concentrated to a small volume and then added to a solution of 0.01 mol of BPBI in 25 ml of ethanol. The complex that separated out was filtered off, washed with ethanol and dried over anhydrous calcium chloride.

Analytical methods

Cobalt, halogen, and thiocyanate analyses were carried out using standard procedures [7]. Microanalyses for carbon, hydrogen and nitrogen were done on a Perkin–Elmer 2400 CHN elemental analyser. Molar conductances of the complexes in nitrobenzene were determined using a conductivity bridge (Toshniwal) with a dip type cell and a platinized platinum electrode. Magnetic susceptibilities were determined by the Gouy method. Infrared spectra of the ligand and the complexes were taken on KBr discs in the region 400–4000 cm^{-1} with a Carl Zeiss UR-10 recording spectrophotometer. The far-IR spectra of the complexes in the region 200–650 cm^{-1} were taken in a polyethylene matrix on a Polytech FIR-30 Fourier far-IR spectrometer. Solid state electronic spectra of the complexes in the region 400–2000 nm were recorded with a Hitachi U-3410 spectrophotometer using the mull technique [8]. Thermal studies were carried out with a Ulvac Sinku-Riko TA-1500 thermal analyser at a heating rate of 10 °C min^{-1} in an air atmosphere using a platinum crucible. The mass of the samples used was in the range 5–10 mg. The evaluation of kinetic parameters, i.e. order n, energy of activation E_a, entropy of activation ΔS, and pre-exponential factor A, using the Coats–Redfern equation [9] was based on a computer program which was developed for use on a Busybee PC, PC/XT computer (HCL Ltd.).

RESULTS AND DISCUSSION

All the complexes are crystalline and non-hygroscopic, and are quite stable to atmospheric oxidation. The complexes are slightly soluble in methanol, acetone and nitrobenzene. The analytical data of the complexes are presented in Table 1. The data show that the complexes have the general formula $[Co(BPBI)_2X_2]$ (where $X \equiv Cl^-$, Br^-, I^- or NCS^-). The molar conductance values suggest that the complexes are non-electrolytes in nitrobenzene.

Magnetic measurement studies

The distinction of octahedral and tetrahedral complexes of Co^{II} from the magnetic moment values is possible to a certain extent. Usually, the moments of octahedral high spin complexes of Co^{II} are observed around 5 μ_B and those of tetrahedral complexes are in the range 4.4–4.8 μ_B [10]. Magnetic moment values of BPBI complexes (Table 2) are around 4.6 μ_B, which suggest a tetrahedral structure for these complexes.

Infrared spectra

The band of medium intensity at 1500 cm^{-1} in the spectrum of the free BPBI ligand may be attributed to the C–N stretching vibration. In the case of the present complexes this band shifts to 1485 cm^{-1}. The shifting of this band to a lower frequency was observed by earlier workers [3–5], and has been suggested as being due to the coordination of the N-3 atom of BPBI to the metal atom. The thiocyanato complex shows a strong band at 2100 cm^{-1}, which can be assigned to the ν(C–N) of the thiocyanate group [11], and a medium band at 490 cm^{-1}. A band around 490 cm^{-1} is usually seen for thiocyanato complexes in which the NCS group is bonded through

TABLE 1

Analytical data

Substance	Colour	Carbon (%) (Calc.)	Hydrogen (%) (Calc.)	Nitrogen (%) (Calc.)	Cobalt (%) (Calc.)	Anion (%) (Calc.)
$[Co(BPBI)_2Cl_2]$	Blue	67.98	4.32	8.01	8.31	10.08
		(68.78)	(4.59)	(8.02)	(8.34)	(10.15)
$[Co(BPBI)_2Br_2]$	Greenish blue	60.51	4.01	7.08	7.37	20.24
		(61.01)	(4.07)	(7.08)	(7.48)	(20.30)
$[Co(BPBI)_2I_2]$	Bluish green	53.87	3.41	6.42	6.59	28.72
		(54.50)	(3.63)	(6.42)	(6.68)	(28.79)
$[Co(BPBI)_2(NCS)_2]$	Deep blue	67.01	4.08	7.51	7.81	15.69
		(67.84)	(4.31)	(7.51)	(7.92)	(15.63)

TABLE 2

Magnetic moment and electronic spectral data

Substance	Magnetic moment (B.M.)	Absorption maxima (cm^{-1})	Tentative assignment
$[Co(BPBI)_2Cl_2]$	4.6	17260 16290 15480	$^4A_2 \rightarrow {}^4T_1(P)$
		6770	$^4A_2 \rightarrow {}^4T_1(F)$
		5190	$^4A_2 \rightarrow {}^4T_2$
$[Co(BPBI)_2Br_2]$	4.6	16830 15880 15070	$^4A_2 \rightarrow {}^4T_1(P)$
		6750	$^4A_2 \rightarrow {}^4T_1(F)$
		5200	$^4A_2 \rightarrow {}^4T_2$
$[Co(BPBI)_2I_2]$	4.7	16220 15200 14310	$^4A_2 \rightarrow {}^4T_1(P)$
		6930	$^4A_2 \rightarrow {}^4T_1(F)$
		5230	$^4A_2 \rightarrow {}^4T_2$
$[Co(BPBI)_2(NCS)_2]$	4.5	20200 17850 16250	$^4A_2 \rightarrow {}^4T_1(P)$
		8180	$^4A_2 \rightarrow {}^4T_1(F)$
		5160	$^4A_2 \rightarrow {}^4T_2$

nitrogen, and this band has been assigned to the NCS deformation [12]. The band at 490 cm^{-1} for the present thiocyanato complex suggests that bonding of the thiocyanate group has taken place through the nitrogen atom.

All the complexes show a strong band at 295 cm^{-1} in the far-IR region, which may be attributed to the Co–N (benzimidazole) stretching vibration. The bands observed at 320 cm^{-1} for the chloro complex and at 260 cm^{-1} for the bromo complex may be due to Co–Cl and Co–Br stretching modes respectively, as these bands are unique to these complexes and are not seen in the other BPBI complexes. In the thiocyanato complex, the band observed at 380 cm^{-1} may be due to the Co–N (thiocyanate) stretching vibration [13].

Electronic spectra

All the complexes exhibit an absorption band with fine structure around the region 15000–20000 cm^{-1} (Table 2). This absorption band can be assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ electronic transition. The fine structure observed for the complexes in this region is characteristic of the tetrahedral complex, and arises due to spin–orbit coupling of the T state [14]. The broad

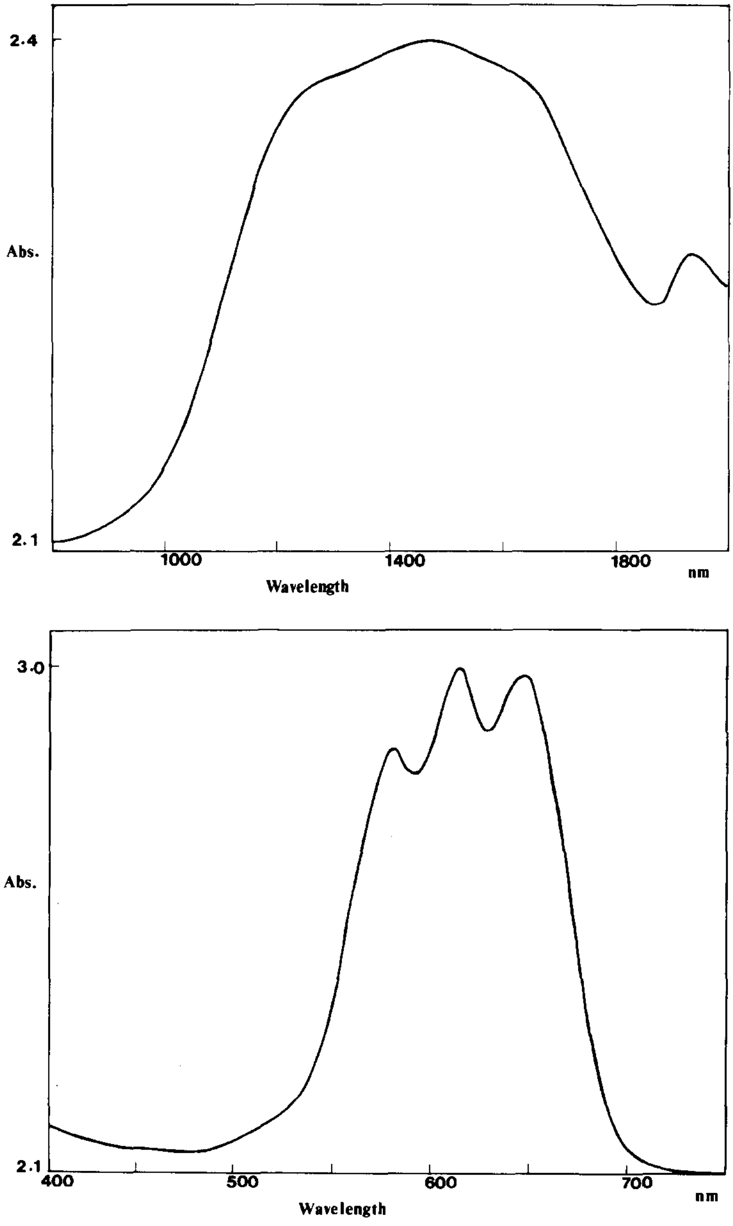

Fig. 1. Electronic spectra of Co(BPBI)$_2$Cl$_2$.

absorption band in the region 6000–9000 cm^{-1} is assigned to $^4A_2 \rightarrow {}^4T_1(F)$. The low energy band expected for tetrahedral complexes is seen around 5000 cm^{-1} in the case of the present complexes, and is due to the $^4A_2 \rightarrow {}^4T_2$ transition (Fig. 1).

TABLE 3

Thermal decomposition data

Substance	Peak temperature in DTA (° C)	Temperature range in DTA (° C)	Peak temperature in DTG (° C)	Temperature range in DTG (° C)	Stage of decomposition	Loss (%) from TG (Calc.)	Probable composition of expelled group	Composition of residue
$[Co(BPBI)_2Cl_2]$	220 endo (m)(sh)	200–240	355 s	250–450	I	45.00	BPBI	$[Co(BPBI)Cl_2]$
	345 endo (v.w.)	340–350				(40.70)		
	355 exo (v.w.)	350–375	560 v.s.	450–625	II	52.00	BPBI and 2 Cl	CoO
	550 exo (v.s.)	400–620				(50.86)		
$[Co(BPBI)_2Br_2]$	230 endo (m)(sh)	225–240	320 v.s.	290–350	I	33.50	BPBI	$[Co(BPBI)Br_2]$
	310 endo (v.w.)	300–320				(36.10)		
	330 exo (v.w.)	320–350	510 s	490–560	II	59.00	BPBI and 2 Br	CoO
	490 exo (s)	360–530				(56.41)		
$[Co(BPBI)_2I_2]$	240 endo (m)(sh)	225–250	265 s	240–350	I	46.50	BPBI and I	[Co(BPBI)I]
	275 exo (v.w.)	260–290				(46.65)		
	390 exo (v.s.)	330–430	410 v.s.	380–440	II	42.50	BPBI and I	CoO
						(46.65)		
$[Co(BPBI)_2(NCS)_2]$	195 endo (m)(sh)	190–210	320 v.s.	210–350	I	57.00	1.5 BPBI	$[Co(BPBI)_{0.5}(NCS)_2]$
	305 endo (v.w.)	300–310				(57.35)		
	310 exo (v.w.)	310–320	490 s	425–550	II	26.00	0.5 BPBI and NCS	
	470 exo (v.s.)	350–550				(26.93)		
	720 exo (v.w.)	650–800	700 w	650–750	III	7.00	NCS	CoO
						(7.81)		

Abbreviations: v.s. = very strong; s = strong; w = weak; v.w. = very weak; m = medium; sh = sharp; endo = endothermic; exo = exothermic.

Thermal behaviour

The TG/DTG/DTA curves for all the complexes are shown in Fig. 2. Thermoanalytical data for the complexes are presented in Table 3. The percentage mass loss and the probable compositions of the expelled groups and the residues are also given in this table.

All the complexes have a fairly wide stability range. The DTG curves show two peaks for the halogeno complexes and three peaks for the

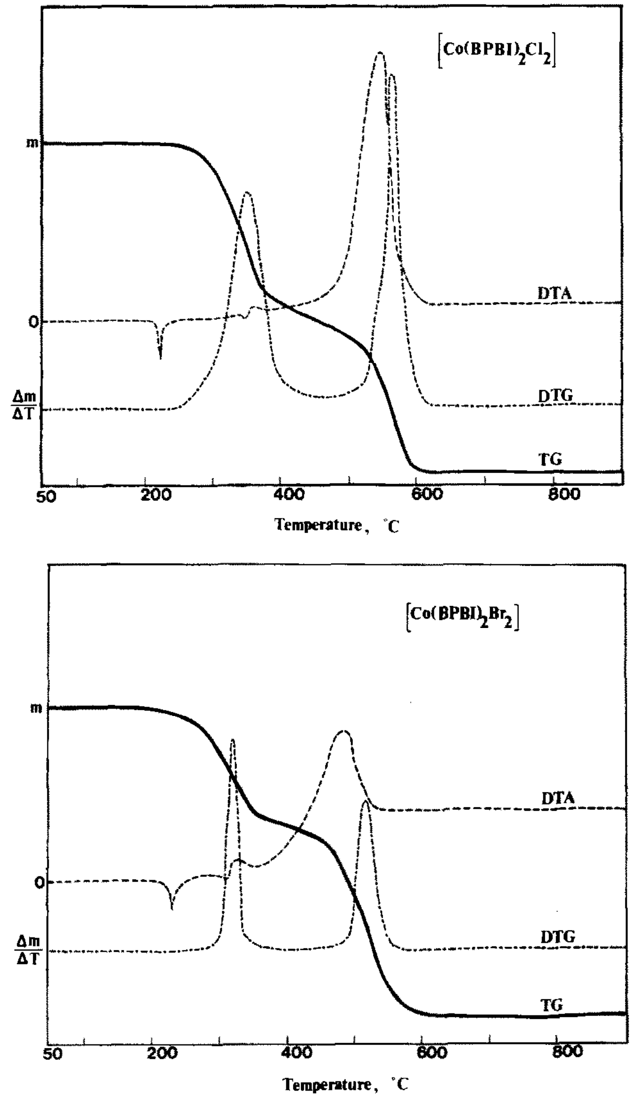

Fig. 2. TG, DTG and DTA curves of complexes.

thiocyanato complex. All these DTG peaks have their parallel DTA peaks. The DTA peak corresponding to the first stage of decomposition is a very weak endothermic peak, followed immediately by a weak exothermic peak. The decomposition reactions should normally be endothermic; the exothermicity in this case could be due to the concomitant decomposition and oxidation processes taking place at this stage. The heat of decomposition released during the oxidation process might thus have swamped the endothermicity of the decomposition reactions.

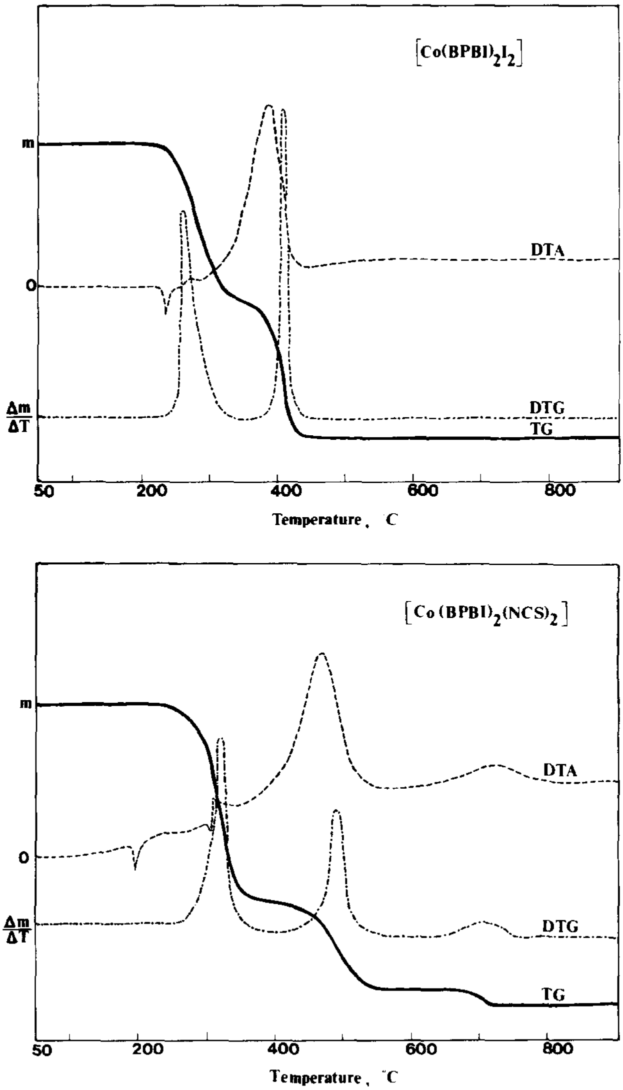

Fig. 2 (continued).

The mass loss at the first stage corresponds to the expulsion of one BPBI molecule in the case of the chloro and the bromo complexes, one BPBI molecule and one iodine atom in the case of the iodo complex and 1.5 BPBI molecule in the case of the thiocyanato complex. The IR spectra of the residues after this stage showed the presence of the BPBI ligand in all cases, indicating only a partial removal of the BPBI ligand at this stage. The elemental analyses (for Co and the anion) of the residue after the first stage indicated the approximate composition of the intermediate complexes to be $[Co(BPBI)Cl_2]$, $[Co(BPBI)Br_2]$, $[Co(BPBI)I]$ and $[Co(BPBI)_{0.5}(NCS)_2]$.

In all the complexes, the first DTG peak is followed by a very strong DTG peak. The mass loss at this stage corresponds to the removal of one BPBI molecule and two chlorine atoms in the case of the chloro complex, one BPBI molecule and two bromine atoms in the case of the bromo complex, one BPBI molecule and one iodine atom in the case of the iodo complex, and 0.5 BPBI molecule and one thiocyanate group in the case of the thiocyanato complex. This DTG peak is paralleled by a very strong exothermic DTA peak. The exothermicity of these peaks, here also, may be due to the concomitant oxidation processes. The thiocyanato complex shows one more DTG peak, and the mass loss for this stage seems to agree with the expulsion of one NCS group. In all cases, the residue after the final stage of decomposition was found to be CoO.

In addition to the DTA peaks mentioned above, a sharp endothermic peak appeared just before the decomposition of the complexes. This DTA peak, which has no parallel in DTG, represents melting. Independent determination of the melting points of the complexes confirmed this.

Decomposition kinetics

The kinetic parameters n, E_a, ΔS and A for two clear-cut decomposition stages of each of the BPBI complexes have been calculated using the Coats–Redfern equation, and are presented in Table 4. The order, n, of the reaction in these cases does not provide any meaningful information about the mechanism of decomposition of the complexes. However, the parameters E_a and ΔS may be employed for the comparison of a given decomposition process for similar compounds [15]. In the present investigation, these values have been evaluated using the same equation for nearly the same experimental conditions (same heating rate, furnace atmosphere, sample weight, etc), and hence can be used conveniently for comparison purposes.

The activation energy for the first stage of decomposition of the chloro and bromo complexes was found to have nearly the same value, suggesting a similar type of mechanism for the decomposition reaction $[Co(BPBI)_2X_2] \rightarrow [Co(BPBI)X_2] + BPBI$ (where $X \equiv Cl^-$ or Br^-). The iodo and thiocyanato complexes, however, have different E_a values, indicating a mechanism different from that for the chloro and bromo complexes. Moreover, the

TABLE 4

Kinetic data

Substance	Stage	Order (n)	E_a (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	A (s^{-1})
[Co(BPBI)$_2$Cl$_2$]	I	0.85	92.50	−147.14	2.694×10^5
	II	1.4	373.85	−35.67	0.241×10^{12}
[Co(BPBI)$_2$Br$_2$]	I	0.73	91.16	−141.56	4.977×10^5
	II	0.70	105.82	−169.42	2.318×10^4
[Co(BPBI)$_2$I$_2$]	I	1.54	152.82	−14.69	0.189×10^{13}
	II	1.42	302.5	158.00	0.255×10^{22}
[Co(BPBI)$_2$(NCS)$_2$]	I	0.40	113.65	−105.82	3.658×10^7
	II	1.38	198.60	−33.65	0.278×10^{12}

differences in stoichiometry of the intermediate iodo and thiocyanato complexes formed after the first stage of decomposition (Table 3) also indicate a difference in behaviour.

The E_a values for the first stage are much lower than those for the second stage in the case of all the complexes except the bromo complex, indicating the rate of decomposition for the first stage to be greater than that for the second stage. It is generally observed that stepwise formation constants decrease with an increase in the number of ligands attached to the metal ion [16]. It can therefore be expected that the rate of removal of the remaining ligands will be smaller after the expulsion of one or two ligands. Moreover, in the present case, steric strain caused by the bulky BPBI ligands would further enhance the rate of decomposition in the first stage.

The negative ΔS values for the first stage show that all the complexes are more ordered in the activated state [17]. This may be due to the chemisorption of gases, probably oxygen present in the air, by these complexes. The ΔS values for the second stage are larger than those for the first stage, suggesting more disorder during this stage, which can be expected from the decreased association of molecules at elevated temperatures. For the iodo complex, ΔS values were found to be much higher than those of the other BPBI complexes for both the stages of decomposition, which might be due to the release of iodine during the first stage itself.

The E_a and ΔS values for the second stage of decomposition of the bromo complex were found to be anomalously low. The lower value of E_a indicates increased rate at this stage, and might be due to the catalytic effect of the intermediate [Co(BPBI)Br$_2$] complex in the oxidation of the ligands and other decomposition products. This possibility is also reflected in the negative ΔS value, indicating more chemisorption of oxygen molecules by the complex during this stage. Catalytic activity can be expected in such complexes with vacant coordination sites. Indeed, systems containing cobalt(II) and bromide ions are known catalysts for oxidation reactions involving molecular oxygen or air [18–20].

ACKNOWLEDGEMENT

The authors thank Professor K.L. Sebastian for developing the computer program for the evaluation of kinetic parameters.

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