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Thermal degradation kinetics of cobalt(II)–doxepin complexes

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Abstract

A series of new complexes formed by the interaction of cobalt(II) with doxepin hydrochloride (DOX) have been isolated and characterized by elemental analysis, and electronic, IR, magnetic moment and conductivity measurements. Based on the spectral data, an octahedral structure is suggested for the metal complexes. Thermogravimetric (TG) studies of the complexes have been performed in order to establish the mode of their thermal degradation. The thermal degradation was found to proceed in three steps. The kinetics and thermodynamic parameters were computed from the thermal decomposition data. The activation energy of the thermal degradation process is in the range 11.8–172 kJ mol^{-1}.

Keywords:

1. Introduction

Doxepin hydrochloride (DOX), chemically *N*,*N*-dimethyl-3-dibenz[*b*, *e*] oxepin-11-(6*H*)-ylidene-1-propanamine, is a useful trycyclic antidepressant [1,2]. Although its spectrophotometric assay has been reported [3], its complexation ability has seldom been explored.

Thermogravimetric studies of metal complexes have been carried out by several researchers [4–6]. Thermal decomposition parameters, namely, E, $\ln A$, ΔH, ΔS and ΔG, were also computed for transition metal complexes [7–10]. The present paper

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reports the syntheses, spectral studies and thermal degradation of new cobalt(II) complexes using thermogravimetric analysis. Kinetic and thermodynamic parameters have been calculated using Broido's relation [11].

2. Experimental

2.1. Materials

All the chemicals and solvents used were of AR grade. The ligand doxepin hydrochloride (DOX) was obtained as a gift sample from INTAS Pharmaceutical, Ahmedabad, India.

The Co(II) complexes with DOX were prepared by warming a hot ethanolic solution of DOX with an ethanolic solution of metal ions in a water bath (75–85°C). The solid complexes were filtered, washed successively with cold ethanol and then ether, and dried in a vacuum desiccator over anhydrous silica gel.

2.2. Physical measurements

IR spectra of the ligand and its complexes were recorded in KBr pellets using a Perkin-Elmer 597 spectrophotometer. A JASCO Model UVIDEC-610 spectrophotometer was used for recording the electronic spectra. Proton NMR spectra were recorded on a JEOL 60 MHz spectrometer. Magnetic moments were measured using a Gouy balance. An Equiptronics conductivity meter was used for measuring molar conductance. The elemental analyses were recorded at the Department of Chemical Technology, University of Bombay. The metal content was determined by a complexometric method [12].

2.3. Thermogravimetric analysis

The coordination compounds were evaluated for thermal degradation kinetics on a DuPont 9900 TA, 951 TGA module system. About 6–8 mg of pure sample was subjected to dynamic TGA scans at a heating rate of 10°C min^{-1} in a nitrogen atmosphere, 50 $\text{cm}^3\ \text{min}^{-1}$ flow rate, in the temperature range from ambient to 900°C.

The TG curves were analysed as percentage weight loss as a function of temperature. The number of decomposition step was identified using a derivative of the TGA curves. The activation energy E_a and frequency factor of the degradation process were obtained by Broido's method [11].

3. Results and discussion

The results of the elemental analysis indicates a metal to ligand stoichiometry of 1:2. The molar conductance values fall in the range 17.15–27.10 mhos $\text{cm}^2\ \text{mol}^{-1}$ indicating that they are non-electrolytes.

Electronic spectra of the complexes were recorded in the wavelength range 200–900 nm. These complexes exhibit five bands at 14368, 15008 and 15982 cm^{-1} which are assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively. The fourth and fifth bands at approx. 37750 and 34203 cm^{-1} were due to L → M charge transfer bands. The electronic spectra suggest an octahedral geometry [13] for the complexes, and the CFSE (*Dq*) value obtained (177 kJ mol^{-1}) is in agreement with the values obtained for known octahedral complexes [14]. The magnetic moments of these new complexes were found in the range 4.21–5.12 BM, which supports an octahedral geometry for the complexes [15].

3.1. *Infrared spectra*

The IR spectra of the ligand and its complexes were recorded in the range 4000–250 cm^{-1}. The occurrence of a broad band in the region 2270–2500 cm^{-1} is due to the tertiary nitrogen atom attached to an alkyl group combined with halogen [16]. This band has totally disappeared in the metal complexes, suggesting that the bonding takes place through the heterocyclic nitrogen atom to the Co(II) ion. The band at 1100 cm^{-1} in the ligand can be attributed to the ν(C–O–C) band [15] which appeared at almost the same region in the corresponding metal complexes, suggesting that the oxygen atom is not involved in bonding.

In the IR spectra of the thiocyanato complex, the CN stretching frequency appears as a strong band at 2050 cm^{-1} and the ν(NC) mode is at 830 cm^{-1}, suggesting M–NCS bonding in the complex. The ν(NCS) mode appears at 470 cm^{-1} for the ambidentate thiocyanato group, confirming the coordination through the nitrogen end of the thiocyanato group [17]. The presence of water molecules is evidenced by the appearance of new bands at 3420–3380 cm^{-1} which are assigned to OH stretching frequencies of the coordinated water [17]. The participation of nitrogen was also evidenced by the appearance of absorption in the far-IR region at 440–420 cm^{-1} and 340–370 cm^{-1} which are assigned to ν(M–N) and ν(M–X) stretching, respectively [18].

3.2. *^1H NMR*

The ^1H NMR spectra of the ligand and its complex $[Co(DOX)_2(H_2O)_2Cl_2]$ have been recorded using DMSO $- d_6$ solvent. The ^1H NMR spectrum of the ligand shows signals at $\delta = 2.3$, 2.7–2.8, 3.8 and 7.0–7.5 ppm due to $-CH_2-CH_2$, $N-(CH_3)_2$, C–H and aromatic protons, respectively. The spectra of the complexes exhibit signals at 2.8 ppm and 3.01 ppm and the remaining signals, i.e., $\delta = 2.3$, 7.0–7.5 ppm are at the same position as in the free ligand. This shows the shift of alkyl protons attached to the tertiary nitrogen, thereby suggesting the involvement of tertiary nitrogen atoms in coordination with Co(II) ions. Thus ^1H NMR data support the conclusion drawn on the basis of the IR data regarding the involvement of tertiary nitrogen atoms in bonding with Co(II) ions.

3.3. *Thermal analysis*

The temperature of decomposition, the pyrolysed products, the percentage weight loss of the ligands, and the percent ash are given in Table 1. TG curves of the Co(II)

Table 1
Thermogravimetric characteristics of the complexes under study

Complex	Process	Temperature range/°C	Product	Weight/%		No. of moles	Residue		Nature
				Calc.	Expt.		Calc.	Expt.	
$[Co(DOX)_2(H_2O)_2Cl_2]$	Dehydration	107–240	H_2O	4.9	5.1	2	10.3	10.1	CoO
	Decomposition of coordination sphere (L, Cl)	240–394	L	75.1	71.4	1			
		449–725	Cl	9.7	13.4	2			
$[Co(DOX)_2(H_2O)_2Br_2]$	Dehydration	128–215	H_2O	4.4	3.8	2	9.1	10.8	CoO
	Decomposition of coordination sphere (L, Br)	220–395	L	67.5	59.0	1			
		450–715	Br	19.7	26.4	2			
$[Co(DOX)_2(H_2O)_2(NO_3)_2]$	Dehydration	152–220	H_2O	4.2	6.5	2	9.5	9.3	CoO
	Decomposition of coordination sphere (L, NO_3)	230–450	L	70.3	74.83	1			
		450–760	NO_3	15.9	9.37	2			
$[Co(DOX)_2(H_2O)_2(CH_3COO)_2]$	Dehydration	115–240	H_2O	5.0	6.2	2	10.1	9.3	CoO
	Decomposition of coordination sphere (L, CH_3COO)	212–412	L	77.1	71.7	1			
		412–740	CH_3COO	7.8	9.8	2			
$[Co(DOX)_2(H_2O)_2SO_4]$	Dehydration	140–210	H_2O	4.4	3.8	2	9.9	11.0	CoO
	Decomposition of coordination sphere (L, SO_4)	210–436	L	73.4	70.3	1			
		436–795	SO_4	12.3	14.1	2			
$[Co(DOX)_2(NCS)_2]$	Decomposition of coordination sphere (L, NCS)	230–420	L	75.1	69.8	1	9.6	10.2	CoO
		450–650	(CN_2)	7.1	10.3	2			
		650–815	S_2	8.2	9.6	2			

complexes show three significant steps in the decomposition. In the first step, the loss of ligand water molecule occurred in the range 107–210°C with a mass loss of 4.2–5.1%. The losses observed for cobalt chloride and acetate complexes are higher than those calculated, due to the loss of loosely bound water molecules (impurity water) in addition to coordinated water molecules. The decomposition temperature of second stage lies in the range of 220–412°C, which represents the loss of organic ligand moiety with a mass loss in the range 59–72.73%. These experimental values are in agreement with the expected value. The onset of the third step of decomposition is above 412°C, corresponding to the loss of inorganic ligands.

In the case of the cobalt thiocyanato complex, the first step refers to the decomposition of the organic moiety (temperature 230–420°C). The second and third steps refer to the decomposition of cyanate (approx. 450°C) and sulphur (approx. 650°C) ions [19,20].

The ash from the cobalt complexes obtained in each case has been chemically identified as pure cobalt(III) oxide [18]. The experimental values of the ash content are in the expected range (9.3–11%).

The thermograms obtained during TGA scans were analysed to give the percentage weight loss as a function of temperature. T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss) and T_{max} (temperature of maximum weight loss) are the main criteria to indicate the heat stability of the complexes. The higher the values of T_0, T_{10} and T_{max}, the higher the heat stability.

Broido's method was used to evaluate the kinetic parameters from the TG curve. Using Broido's method, plots of ln(ln 1/y) vs. 1/T (where Y is the fraction not yet decomposed) for different stages of the thermal degradation process of the complexes were made and are shown in Figs. 1 and 2. Fig.1 is for second step of the degradation

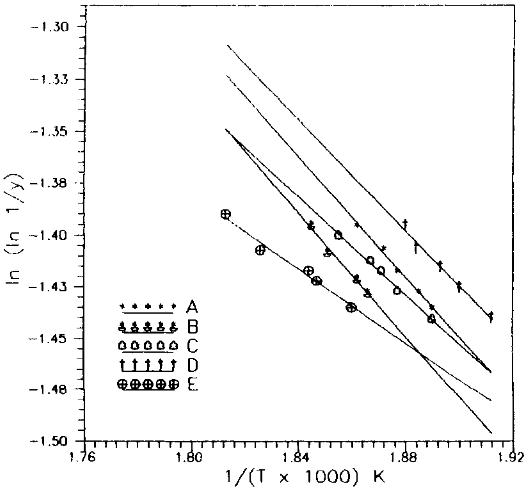

Fig. 1. Plots of ln(ln 1/y) vs. 1/T for the second degradation process of: A, $[Co(DOX)_2(H_2O)_2Cl_2]$; B, $[Co(DOX)_2(H_2O)_2Br_2]$; C, $[Co(DOX)_2(H_2O)_2(NO_3)_2]$; D, $[Co(DOX)_2(H_2O)_2(CH_3COO)_2]$; and E, $[Co(DOX)_2(H_2O)_2SO_4]$.

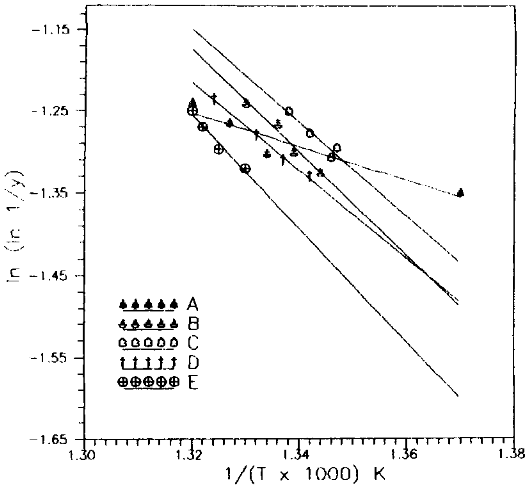

Fig. 2. Plots of ln(ln $1/y$) vs. $1/T$ for the third degradation process of: A, $[Co(DOX)_2(H_2O)_2Cl_2]$; B, $[Co(DOX)_2(H_2O)_2Br_2]$; C, $[Co(DOX)_2(H_2O)_2(NO_3)_2]$; D, $[Co(DOX)_2(H_2O)_2(CH_3COO)_2]$; and E, $[Co(DOX)_2(H_2O)_2SO_4]$.

Table 2
Data obtained from TGA analysis: temperature characteristics, activation energies and frequency factors of decomposition process

Compound	T_0/°C	T_{10}/°C	T_{max}/°C	Process	$E_a \pm 2$/kJ mol^{-1}	ln $A \pm 2$/ min^{-1}
$[Co(DOX)_2(H_2O)_2Cl_2]$	100	130	710	I	16.8	13.25
				II	26.5	15.52
				III	162.0	36.87
$[Co(DOX)_2(H_2O)_2Br_2]$	112	125	705	I	18.1	13.70
				II	28.3	15.89
				III	148.0	34.84
$[Co(DOX)_2(H_2O)_2(NO_3)_2]$	121	133	725	I	15.9	12.95
				II	24.8	15.00
				III	138.0	32.99
$[Co(DOX)_2(H_2O)_2(CH_3COO)_2]$	95	122	750	I	16.2	13.13
				II	29.4	16.36
				III	172.0	30.53
$[Co(DOX)_2(H_2O)_2SO_4]$	126	158	715	I	11.8	11.66
				II	25.3	16.12
				III	120.8	30.21
$[Co(DOX)_2(NCS)_2]$	218	280	840	I	16.8	12.95
				II	45.3	15.86
				III	159.8	31.38

and Fig.2 for the third. The plots are linear over the conversion range of about 0.1–0.9, supporting the assumption of first-order reaction kinetics.

In order to determine the thermal stability trend, the parameters T_0, T_{10}, T_{max}, activation energy (E_a) and frequency factor (ln A), were evaluated and are given in Table 2. The values of Table 2 indicate that the thermal stability of the Co(II) complexes depends on the nature of the inorganic ligand. The decrease in the thermal stability of the complexes is in the order: $NCS^- > SO_4^{2-} > NO_3^- > Br^- > CH_3COO^- > Cl^-$.

This means that the electronegativity/basicity of the inorganic ligands may have a strong effect on the thermal stability of the complexes. The activation energies for all three steps of degradation are in the range 11.8–172 kJ mol^{-1}. The lowest values are observed for the first degradation step because this energy is utilized to remove the loosely bound water (impure and ligand) molecules.

The thermodynamic parameters, enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) of activation, were calculated using standard equations and the values are given in Table 3.

The values of the enthalpy for all degradation steps of all the complexes are positive. The entropies of activation are negative for the first two steps and positive for the third [19,20]. However, the negative values of the entropies of activation are compensated by the values of the enthalpies [19] of activation, leading to almost the same values (276–490 kJ mol^{-1}) for the free energies of activation. The data clearly indicate that the basic steps are similar in the thermal degradation of these complexes.

Table 3
Thermogravimetric parameters for the thermal degradation of the complexes

Compound	Process	ΔH/kJ mol^{-1}	ΔS/J K^{-1}	ΔG/kJ mol^{-1}
$[Co(DOX)_2(H_2O)_2Cl_2]$	I	12.78	−33.37	289.2
	II	22.10	−15.59	303.3
	III	155.70	152.0	410.8
$[Co(DOX)_2(H_2O)_2Br_2]$	I	14.12	−28.3	276.9
	II	23.85	−14.2	314.7
	III	141.70	135.3	408.2
$[Co(DOX)_2(H_2O)_2(NO_3)_2]$	I	11.80	−35.47	291.0
	II	20.36	−20.43	312.7
	III	131.80	122.8	406.9
$[Co(DOX)_2(H_2O)_2(CH_3COO)_2]$	I	12.22	−32.50	278.0
	II	29.39	−2.60	307.5
	III	163.80	165.4	405.5
$[Co(DOX)_2(H_2O)_2SO_4]$	I	7.78	−44.35	292.0
	II	20.80	−20.72	320.1
	III	113.70	96.3	413.6
$[Co(DOX)_2(NCS)_2]$	I	12.47	−34.20	302.9
	II	39.06	−4.99	428.1
	III	151.60	115.3	490.6

4. Conclusions

The new complexes have been tentatively assigned an octahedral structure. The inorganic ligands have a stronger effect on the thermal stability of the complexes. The activation energy of the thermal degradation is in the range 11.8–172 kJ mol^{-1}.

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