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# Thermoanalytical and Spectral Characterization of Cadmium(II) Complexes of Propantheline Bromide

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Synthesis, structure and properties of Cd(II) complexes of propantheline bromide (PPB) have been studied. The isolated complexes are characterised by various physico-chemical methods. Based on the data, tetrahedral structure has been suggested for the new metal complexes. Thermogravimetric studies of the complexes have been performed in order to establish the mode of their thermal stability. The thermal degradation process was found to proceed in two steps. Kinetic and thermodynamic parameters are evaluated on the basis of thermal degradation data. The values of activation energies are found to be in the range 8.5–33.5 kJ $mol^{-1}$.

## INTRODUCTION

Propantheline bromide *i.e.*, (2–hydroxyethyl)-diisopropyl methyl ammonium bromide xanthene-9-carboxylate is found to exhibit anticholinergic parasympatholytic and spasmolytic action[1] and hence used in medicinal chemistry. In our earlier publication[2] cobalt-(II)-propantheline bromide (PPB) complexes have been reported. The present investigation aims at the synthesis and thermal characterization of Cd(II) complexes with propantheline bromide to give a better understanding of the various decomposition mechanisms of metal derivatives.

## EXPERIMENTAL

Propantheline bromide is obtained from Searle (India) Ltd., Ankaleswar. Other chemicals of AR grade were used without further purification.

The solid state electronic spectra and $^1$H NMR spectra were recorded on a Pye Unicam DP 8100 UV/VIS and AMX-400FT NMR spectrometer respectively. The molar conductances were measured using Philips PR500 conductivity bridge. The analyses of metal content, sulphur, chloride, nitrate and iodide were measured according to reported methods[3]. Nitrogen content was estimated by Kjeldahl's methods[4]. The elemental analyses of carbon and hydrogen were determined by micro analytical methods. The complexes were evaluated for thermal degradation kinetics on Du Pont 9900 TA with 951 TGA module. About 6–8 mg of pure sample was subjected to dynamic TGA scan at a heating rate of 10°C/min in the

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oxygen atmosphere (50 mL/min flow rate) from ambient to 900°C. TG curves were analysed to give the percentage weight loss as a function of temperature. The number of transitions were identified by using derivative of TGA curves.

### Isolation of the complexes

All the complexes were isolated according to the following general method. 50 mL of 5 mmol hot ethanolic solution of the ligand was slowly added to 2.5 mmol hot ethanolic solution of Cd(II) metal salt with continuous stirring. The mixture was then refluxed on a water bath at 60–70°C for 2 h. The white precipitates obtained in each case, after cooling to room temperature were filtered and washed several times with absolute alcohol, finally with ether and dried over anhydrous silica gel.

## RESULTS AND DISCUSSION

The results of the elemental analyses indicate 1 : 2 metal to ligand stoichiometry. The molar conductance of 1 mmole solution in DMSO falls in the range 10.4–17.3 $ohm^{-1} cm^{2} mol^{-1}$ (Table-1) indicating the covalent nature of the complexes.

TABLE-1
ANALYTICAL, PHYSICAL, AND MOLAR CONDUCTNACE DATA

| Complex (yield %) | Dec. temp. (°C) | % analysis, found (calcd.) | | | | $\Omega_m$ $ohm^{-1}cm^{2}$ $mol^{-1}$ |
|---|---|---|---|---|---|---|
| | | C | H | N | Cd | |
| $[Cd(C_{22}H_{27}NO_3)_2(NO_3)_2]$ | 210 | 56.40 | 5.71 | 5.85 | 11.77 | 12.6 |
| 80 | | (55.78) | (5.75) | (5.91) | (11.86) | |
| $[Cd(C_{22}H_{27}NO_3)_2SO_4]$ | 201 | 57.76 | 5.89 | 3.09 | 12.36 | 146.5 |
| 62 | | (57.48) | (5.92) | (3.05) | (12.23) | |
| $[Cd(C_{22}H_{27}NO_3)_2Cl_2]$ | 206 | 59.37 | 6.06 | 3.15 | 12.67 | 17.3 |
| 82 | | (59.09) | (6.09) | (3.13) | (12.56) | |
| $[Cd(C_{22}H_{27}NO_3)_2Br_2]$ | 210 | 53.98 | 5.50 | 2.81 | 11.31 | 16.9 |
| 72 | | (53.75) | (5.54) | (2.85) | (11.43) | |
| $[Cd(C_{22}H_{27}NO_3)_2I_2]$ | 199 | 48.90 | 5.01 | 2.56 | 10.33 | 16.2 |
| 65 | | (49.06) | (5.05) | (2.60) | (10.43) | |
| $[Cd(C_{22}H_{27}NO_3)_2(CH_3COO)_2]$ | 138 | 61.54 | 6.38 | 2.92 | 12.06 | 10.4 |
| 60 | | (61.24) | (6.42) | (2.98) | (11.94) | |

The solid state electronic spectra of complexes show one absorption band in the region 19600 $cm^{-1}$which is due to metal ligand charge transfer process and is ascribed to a charge transfer from d-orbitals of the metal to the $\pi^*$ system of the ligand[5,6] . The more intense band appearing at 21310 $cm^{-1}$ corresponds to an intra-ligand transition $n \rightarrow \pi^*$. These complexes exhibit tetrahedral configuration[7] and are diamagnetic as expected for $d^{10}$ configuration.

In the infrared spectra of the ligand the strong and broad band in the region 3000–2900 $cm^{-1}$ can be attributed to the tertiary nitrogen atom attached to alkyl group combined with bromide ion[8]. The sharp peaks occurring at 1150 and 1725 $cm^{-1}$ are due to ν(C—O—C) of the heterocyclic ring and ν(COO) vibrations of the side chain respetively.

In the spectra of the corresponding Cd(II) complexes, the broad band around 3000–2900 $cm^{-1}$ has completely disappeared thereby indicating that tertiary nitrogen of the ligand is the site of coordination. The other bands ν(C—O—C) of the heterocyclic ring and ν(COO) of the side chain remain at the same positions in the IR spectra of the respective Cd(II) complexes suggesting that heterocyclic oxygen atom and oxygen atom of the COO group were not involved in bonding with Cd(II) ions. The IR data suggest that the ligand PPB acts as unidentate ligand.

The PMR-spectra of the ligand PPB exhibits a triplet at δ 1.16 ppm which is assigned to $C—(CH_3)_4$. The sharp signal (singlet) at δ 3.30 ppm is due to the tertiary nitrogen attached to the alkyl group *i.e.*, $—N—CH_3$. The multiplet centered at δ 3.7 ppm is attributed to $—N—CH_2$. The other multiplets δ 7.1 to 7.4 ppm is due to aromatic protons.

In the spectra of Cd(II) complexes all these resonance signals are retained except a sharp signal at δ 3.30 ppm, *i.e.*, $N—CH_3$ has completely disappeared indicanting the bonding of Cd(II) ion to the tertiary nitrogen atom of the ligand.

**Thermogravimetric analysis**

$T_0$, $T_{10}$, $T_{20}$, $T_{50}$ and $T_{max}$ are the main criteria of the thermal stability of the complexes. Higher the value of $T_0$, $T_{10}$, $T_{20}$, $T_{50}$ and $T_{max}$, higher will be the heat stability of the complexes. To obtain a quantitative picture of the relative stability IPDT (Integral Percentage for Decompostion Temperature) values, these can be regarded of significant importance since they represent the overall nature of the thermogravimetric curves. The Doyle's method[9] was used for obtaining IPDT values. It is noticed from Table-2 that $Cd(II)NO_3$-PPB complex has high IPDT value (546) compared to other inorganic ligands and lowest thermal stability for Cd(II) acetate-PPB complex (423). The greater thermal stability of Cd(II) nitrate complex may be ascribed to a higher coordination bond energy between nitrogen and the central Cd(II) compared with those of other inner sphere inorganic ligand complexes.[10] This indicates that the thermal stability of Cd(II) complexes depends also on the nature of the inorganic ligands. The decrease in the thermal stability of the complexes is in the following order

$$NO_3^- > SO_4^{2-} > Cl^- \geq Br^- \geq I^- > CH_3COO^-$$

This order indicates that basicity/inductive effect of the inorganic ligands may have a strong effect on the thermal stability of the complexes.

Broido method[11] was used to evaluate the kinetic parameters like activation energy ($E_a$) and frequency factor (ln A ) for both degradation steps of all the complexes. The sample plots of ln [ln 1/y] *vs.* 1/T [where y is the fraction of the number of initial molecules not yet decomposed] for first and second degradation steps of Cd(II) complexes are shown in Fig.1 and Fig. 2. The activation energy and frequency factor have been calculated from slopes and intercepts respectively of these plots and presented in Table-3.

TABLE-2
TEMPERATURE CHARACTERISTICS OBTAINED FROM
TG ANALYSIS OF THE COMPLEXES

| Complex | $T_0$ (°C) | $T_{10}$ (°C) | $T_{20}$ (°C) | $T_{50}$ (°C) | $T_{max}$ (°C) | IPDT |
|---|---|---|---|---|---|---|
| $[Cd(C_{22}H_{27}NO_3)_2(NO_3)_2]$ | 203 | 241 | 263 | 333 | 562 | 546 |
| $[Cd(C_{22}H_{27}NO_3)_2SO_4]$ | 199 | 241 | 259 | 314 | 592 | 513 |
| $[Cd(C_{22}H_{27}NO_3)_2Cl_2]$ | 214 | 267 | 280 | 323 | 647 | 508 |
| $[Cd(C_{22}H_{27}NO_3)_2Br_2]$ | 212 | 239 | 254 | 306 | 592 | 498 |
| $[Cd(C_{22}H_{27}NO_3)_2I_2]$ | 197 | 254 | 276 | 327 | 536 | 473 |
| $[Cd(C_{22}H_{27}NO_3)_2(CH_3COOO)_2]$ | 136 | 207 | 224 | 284 | 560 | 423 |

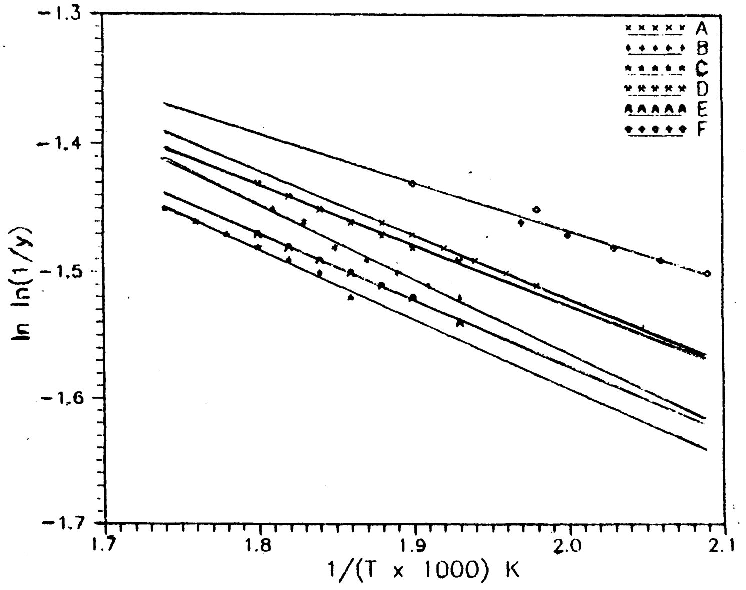

Fig. 1 Plots of ln [ln (1/y)] *vs.* 1/T for the first degradation process of: A. $[Cd(PPB)_2(NO_3)_2]$; B. $[Cd(PPB)_2SO_4]$; C. $[Cd(PPB)_2Cl_2]$; D. $[Cd(PPB)_2Br_2]$; E. $[Cd(PPB)_2I_2]$; F. $[Cd(PPB)_2(CH_3COO)_2]$.

The calculated thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS) and free energy (ΔG) values are given in Table-3. TGA thermogram and derivative curve shows two decomposition steps of all the complexes.

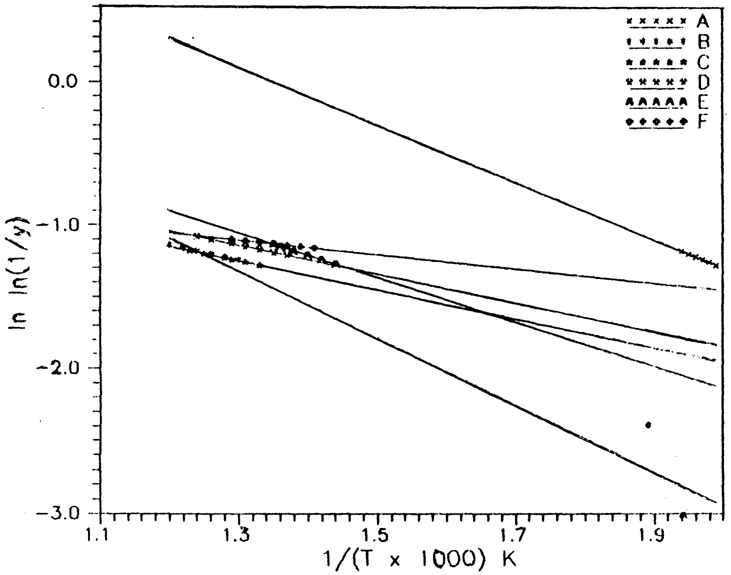

Fig. 2. Plots of ln[ln (1/y)] *vs.* 1/T for the second degradation process of: A. $[Cd(PPB)_2(NO_3)_2]$; B. $[Cd(PPB)_2SO_4]$; C. $[Cd(PPB)_2Cl_2$; D. $[Cd(PPB)_2Br_2]$; E. $[Cd(PPB)_2I_2]$; F. $[Cd(PPB)_2(CH_3COO)_2]$

### TABLE-3
### KINETIC AND THERMODYNAMIC PARAMETERS FOR THE DEGRADATION PROCESS OF COMPLEXES

| Complex | Tr | $E_a \pm 2$ kJ $mol^{-1}$ | ln A ± 2 $min^{-1}$ | ΔH ± 2 kJ $mol^{-1}$ | ΔS ± 2 $JK^{-1}mol^{-1}$ | ΔG ± 2 kJ $mol^{-1}$ |
|---|---|---|---|---|---|---|
| $[Cd(C_{22}H_{27}NO_3)_2(NO_3)_2]$ | I | 10.2 | 7.9 | 5.8 | −27.3 | 20.3 |
| | II | 33.5 | 12.2 | 28.6 | −15.5 | 30.8 |
| $[Cd(C_{22}H_{27}NO_3)_2SO_4]$ | I | 11.1 | 8.1 | 6.5 | −28.2 | 22.1 |
| | II | 20.0 | 9.4 | 12.5 | −24.9 | 32.0 |
| $[Cd(C_{22}H_{27}NO_3)_2Cl_2]$ | I | 9.5 | 7.6 | 4.9 | −30.6 | 11.9 |
| | II | 19.4 | 9.3 | 12.3 | −24.9 | 33.1 |
| $[Cd(C_{22}H_{27}NO_3)_2Br_2]$ | I | 8.5 | 7.4 | 9.6 | −31.8 | 21.1 |
| | II | 19.1 | 9.1 | 12.8 | −23.5 | 28.4 |
| $[Cd(C_{22}H_{27}NO_3)_2I_2]$ | I | 9.9 | 7.8 | 5.5 | −27.8 | 20.4 |
| | II | 18.7 | 9.6 | 12.6 | −21.5 | 28.3 |
| $[Cd(C_{22}H_{27}NO_3)_2(CH_3COO)_2]$ | I | 8.4 | 7.4 | 3.9 | −30.4 | 20.4 |
| | II | 15.8 | 8.9 | 9.6 | −25.7 | 29.3 |

## Mechanism of thermal degradation of Cd(II) complexes

*First stage of thermal degradation*: The major weight loss occurs in first thermal decomposition step at the temperature range 156–415°C. The weight loss in this step corresponds to the expulsion of coordinated propantheline ligand. The per cent weight loss in these transitions are in the range 68.73–78.90. The activation energy of this step for the complexes are lies in the range of 8 .4–11.1 kJ/mole.

*Second stage of thermal degradation:* The second thermal decomposition step occurs in the temperature range 395–650°C corresponding to the loss of coordinated inorganic ligands. In these stages per cent weight losses are in the range 7.94–23.56. The activation energies are in the range 15.8–33.5 kJ/mole.

The final residue of the decomposition at above 650°C in the complexes corresponds to Cd(II) oxide which is in conformity with the observed and calculated weights of pyrolysis products (Table-4).

TABLE-4
DATA OBTAINED FROM TGA CURVES AND THEIR COMPOSITION

| Complex | Tr | Temp range (°C) | Leaving product | Weight (%) | | Residue (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Cal. | Exptl. | Nature | Calc. | Exptl. |
| $[Cd(C_{22}H_{27}NO_3)_2(NO_3)_2]$ | I | 179–370 | 2L | 75.05 | 77.28 | CdO | 13.51 | 12.75 |
| | II | 427–620 | $2NO_3$ | 13.03 | 12.57 | | | |
| $[Cd(C_{22}H_{27}NO_3)_2SO_4]$ | I | 246–395 | 2L | 77.33 | 75.93 | CdO | 19.92 | 20.16 |
| | II | 432–650 | $SO_4$ | 10.44 | 9.38 | | | |
| $[Cd(C_{22}H_{27}NO_3)_2Cl_2]$ | I | 212–391 | 2L | 79.49 | 78.90 | CdO | 14.31 | 13.75 |
| | II | 415–585 | 2Cl | 7.94 | 7.75 | | | |
| $[Cd(C_{22}H_{27}NO_3)_2Br_2]$ | I | 188–415 | 2L | 72.31 | 74.45 | CdO | 13.01 | 12..68 |
| | II | 436–628 | 2Br | 16.25 | 15.98 | | | |
| $[Cd(C_{22}H_{27}NO_3)_2I_2]$ | I | 182–388 | 2L | 66.01 | 68.73 | CdO | 11.88 | 10.22 |
| | II | 395–560 | 2I | 23.56 | 22.84 | | | |
| $[Cd(C_{22}H_{27}NO_3)_2 (CH_3COO)_2]$ | I | 156–385 | 2L | 75.53 | 74.29 | CdO | 13.60 | 12.33 |
| | II | 404–620 | $2CH_3COO$ | 12.53 | 12.03 | | | |

Tr = Transition; L = $C_{22}H_{27}NO_3$

The activation energy and IPDT values of the Cd(II)-PPB complexes also follow the same order of thermal degradation stability.

## Thermodynamic parameters

The thermodynamic parameters such as enthalpy ($\Delta H$), entropy($\Delta S$) and free energy ($\Delta G$) were evaluated for different thermal degradation steps of Cd(II)-PPB complexes, and calculated values are presented in Table-3. The comparison of the value of enthalpy with those of $T_0$ (from TG curve) for the complexes shows that, with decreasing $\Delta H$ value the onset of decomposition temperature ($T_0$) also decreases. The $\Delta H$ approximately characterizing the bond strength provides valuable information[12] on stepwise nature of the process. The free energy ($\Delta G$)

values are positive and vary from 11.9 to 33.1 kJ mol$^{-1}$. The ΔH values are compensated by the values of enthalpy of activation leading to the same value for the free energy of activation[13]. This shows that the basic steps involved in the first and second thermal degradation steps were identical. The free energy of activation was also following the same trends as activation energy. ΔH, ΔS and ΔG are lower for the first step and higher for the second degradation. These values reveal that inorganic ligands have stronger effect and on the themal stability of cadmium(II) complexes.

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