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Research Article

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Syntheses, characterization and Thermal Studies of Cadmium (II) Complexes of Some Heterocyclic Ligands

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ABSTRACT

Cadmium (II) acetate complexes of some heterocyclic ligands like 2,2' – bipyridine (bipy) and 1,10 – phenanthroline (phen)were synthesized. These complexes were characterized with the help of elemental analyses, i.r. spectral studies, molar conductance measurement and thermal analyses studies. They were found to have the formulae:

$\left[Cd\,L_2^1\left(OAc\right)_2\right].2H_2O$ *and* $\left[Cd\,L_2^2\left(OA_C\right)_2\right].H_2O$ *where* $L^1 = 2,2'-$ *bipyridine(bipy),* $L^2 = 1,10-$ *phenanthrolile and OAc = acetate ion. From the thermal analyses, thermodynamic parameters such as* Ea^* *(activation energy),* ΔH *(enthalpy change) and* ΔS *(entropy change) for the dehydration and decomposition reactions of the complexes, were evaluated using some standard methods. The order of stability of the anhydrous complexes, was found to be of the following increasing order:*

$$\left[Cd\left(phen\right)_2\left(OAc\right)_2\right] < \left[Cd\left(bipy\right)_2\left(OAc\right)_2\right]$$

Key words : Cadmium (II) acetate,heterocyclic ligands, elemental analyses, infrared spectra and thermal analyses.

INTRODUCTION

On extensive literature survey, it was found that works on 2,2'- bipyridine and 1,10 – phenanthroline complexes of cadmium (II) acetate, was very rare. To the best of my knowledge, no one had reported thermal investigations of thecadmium(II)acetate complexes of 2,2'–bipyridine and 1,10 – phenanthroline in detail. Besides this these two complexes were not reported except some similar types [1-11].

The present aim of the work is to synthesize cadinium (II) acetate complexes of 2,2'-bipydine and 1,10-phenanthroline and to carry out thermal investigations (both TGA and DTA) by pyrolyticheating of these complexes under non- isothermal conditions and to evaluate thermodynamic parameters such as Ea* (activation energy), ΔH (enthalpy change) and ΔS (entropy change) of dehydration and decomposition reaction of complexes using standard methods [12 -14].

Thermalstability order of the complexes are to be compared.

EXPERIMENTAL SECTION

Cadmium(II)acetate (AR grade), 2,2'–bipyridine (AR grade) and 1,10 – phenanthroline (AR grade), were used as received. Ethanol and diethylether were dried using the standard procedure [15].

Syntheses of Metal complexes:

$\left[\mathbf{Cd}\left(\mathbf{bipy}\right)_2\left(\mathbf{OAc}\right)_2\right]\mathbf{.2H_2O(1):}$

15 ml of ethanolic solution of 2,2’ – bipyridine (4 mmol) was added drop by drop to 25 ml of cadmium (II) acetate solution (8mmol) in ethanol with constant stirring. To the resulting mixture dry ether was added drop by drop with vigorous stirring and thereby white shiny complex separated out immediately. It was, then, filtered, washed with dry ether and dried over fused calcium chloride in a dessiccator. Yield: *ca.*80%.

$\left[\mathbf{Cd}\left(\mathbf{phen}\right)_2\left(\mathbf{OAc}\right)_2\right]\mathbf{.H_2O(2):}$

This complex was also prepared in the same way as that of complex (1) mentioned above. Here, the colour of the complex is also white.Yield :*ca.* 85%

Cadmium was estimated gravimetrically using the standard procedure [16]. C,H and N analyses were done by Perkin – Elmer 240C and Carlo Erba 1106 elemental analysers. Thermal investigations (both TGA and DTA) were carried out on a Shimadzu Thermal Analyzer DT-30 under a dynamic nitrogen atmosphere with a heating rate of 10^0C min^{-1} and α -alumina as the standard reference substance.

Activation energy (Ea*) was evaluated from TGA curve using the equation of Horowitz and Metzger [12] and from DTA curve using that of Borchardt and Daniels [13]. ΔH was evaluated from DTA curve using the relation [13], $\Delta H = KA,$ where K is the heat transfer co-efficient (cell constant or calibration constant, here the cell is platinum crucible and its constant, K was evaluated using indium metal as calibrant) and A is the total area under the particular DTA curve measured with a compensating planimeter with optical tracer of Fuji corona 027. ΔS was calculated from the relation [14], $\Delta S = \dfrac{\Delta H}{Tm}$, Tm being the DTA peak temperature in kelvin.

Infrared and far i.r. – spectra were recorded with Beckmann IR20A and Perkin Elmer 783 Spectrometers in KBr and polythene powder discs. Conductivity measurements of the complexes in DMF at the concentrator of 10^{-3} M were recorded at room temperature with PC 510 P^H and conductivity bench meter (Eutech).

RESULTS AND DISCUSION

The complexes (1) and (2) were not reported earlier. Both are white in colour. The complexes were characterized by elemental analyses, infrared spectral data, thermal analyses data and molar conductance measurements. They were found to have the formulae: $\left[Cd\ (bipy)_2\,(OAc)_2\right].2H_20$ (1) and $\left[Cd\ (phen)_2\,(OAc)_2\right].H_20$ (2) respectively.

Elemental analyses data and Molar conductance values:

Elemental analyses data of complexes (1) and (2) (Table1) prove that both the heterocyclicligands – 2,2’– bipyridine(bipy) and 1,10–phenanthroline(phen) are coordinated with cadmium metal in their corresponding complexes.

TABLE – 1 : Elemental Analyses data and molar conductance values of 2,2’-bipyridine (bipy) and 1,10-phenanthroline (phen) Complexes of Cd(II).

Complex compounds	Colour	Yield (%)	Elemental Analyses:Found (Calcd.) %				Λ_M (Ohm^{-1}cm^{2}mol^{-1})
			Cd	C	H	N	
(1) $\left[CdL^1_2(OAc)_2\right].2H_2O$	White	80%	19.48 (19.42)	49.80 (49.75)	4.42 (4.49)	9.70 (9.67)	10
(2) $\left[CdL^2_2(OAc)_2\right].H_2O$	White	85%	18.50 (18.46)	55.23 (55.18)	3.74 (3.94)	9.44 (9.19)	8

Here, L^1=2,2’ – bipyridine (bipy) and L^2=1,10 – phenanthroline (phen).

Their molar conductance values are too low (as shown intable-1) showing that these complexes (1) and (2) are non-electrolytic in character [17-18]. Such non-electrolyticbehaviour of complexes (1) and (2), further supports their octahedral geometry.

Infrared Spectral Studies:
The key IR spectral data of complexes (1) and (2) are shown in table–2. In case of complexes (1) and (2), the $\nu(OH)$ bands appear at 3460cm^{-1} and 3420 cm^{-1} respectively (table-2), showing the presence of lattice water molecules [19].Presence of such lattice water molecules, is further supported by the appearance of $\delta(HOH)$ bands at 1600 cm^{-1} and 1660 cm^{-1} for complexes (1) and (2) respectively. $\nu_a\left(COO^-\right)$ for both the complexes (1) and (2) appear at 1715 cm^{-1}and that of $\nu s\left(COO^-\right)$ appear at 1460 cm^{-1}.

TABLE – 2: Key IR Spectral bands (cm^{-1}) of Metal Complexes

Metal Complexes	$\nu(OH)$	$\delta(HOH)$	$\nu_a\left(COO^-\right)$	$\nu_s\left(COO^-\right)$	$\Delta\nu$	$\nu(Cd-N)$	$\nu(Cd-O)$
(1) $\left[CdL_2^1(OAc)_2\right].2H_2O$	3460(br)	1600(vs)	1715(s)	1460(s)	255	540 (w) 450(br)	340 (w) 320 (w)
(2) $\left[CdL_2^2(OAc)_2\right].H_2O$	3420(br)	1660(w)	1715(ms)	1460(s)	255	530 (w) 450(w)	350 (w) 265 (w)

Here, v=very, s=strong, m=medium, w=weak, and br=broad.

The difference between$\nu_a\left(COO^-\right)$ and $\nu_s\left(COO^-\right)$,i.e.,$\Delta\nu$ for each of the complexes is found to be 255 cm^{-1} which is very high and establishes the fact that the acetato group$\left(CH_3COO^-\right)$ acts as unidentate ligand by linking one donor O-atom with cadmiumin both the complexes (1) and (2) respectively [19 -20].

Further, appearance of $\nu(Cd-N)$ bands for both the complexes (1) and (2) in the range 540 – 450 cm^{-1} supports the coordination of both 2,2'-bipyridine and 1,10-phenathroline with cadmium through their N-donor atoms in their corresponding complexes [21-22].

Again, appearance of $\nu(Cd-O)$ bands for both the complexes (1) and (2) in the range 350-265cm^{-1}, proves the coordination of acetato$\left(CH_3\,COO^-\right)$group with cadmium through their O-donor atoms in their corresponding complexes [21].

Thermal Analyses Studies:
When complex (1) is heated under non-isothermal condition, mass loss in its TGA curve in thetemperature range 93-132^{0}C (as shown in Fig.1) corresponds to the loss of two lattice water molecules forming the complex $\left[Cd\,(bipy)_2\,(OAc)_2\right]$ (step 1(a)).

For this step 1(a), DTA curve shows an endothermic peak at 102^{0}C andvalues of ΔH and ΔS are 44 KJmol^{-1} and 117JK^{-1}mol^{-1}respectively (as shown in table 3).

On further heating $\left[Cd\,(bipy)_2\,(OAc)_2\right]$is converted intoCd(OAc)$_2$via the intermediate$\left[Cd\,(bipy)(OAc)_2\right]$ as shown as in steps 1(b) and 1(c) for which the corresponding temperature ranges are 132-250^{0}C and 250-303^{0}C respectively. The endothermic DTA peak temperatures of steps 1 (b) and 1 (c) are 228^{0}C and 300^{0}C respectively. And the values of Ea* (from TGA) for these two steps are 80 KJmol^{-1}and 206KJmol^{-1} respectively (Table – 3).

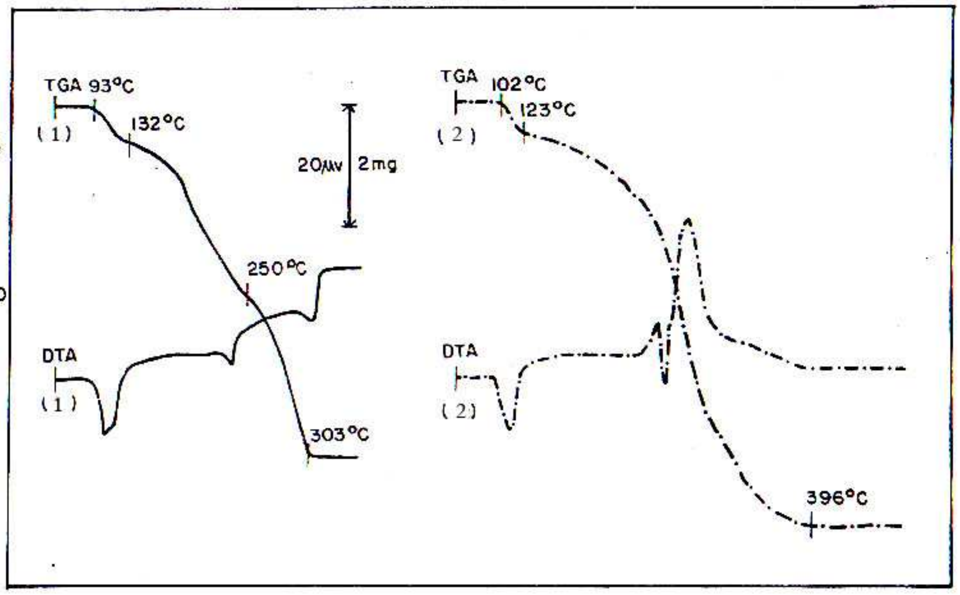

Fig.1. Thermal curves of $[Cd(bipy)_2(OAc)_2]\cdot 2H_2O$ (1) (——) sample mass 9.6 mg sample mass 9.6 mg and $[Cd(phen)_2(OAc)_2].H_2O$ (2) (—·—·—) sample mass 15.0 mg.

TABLE – 3: Thermal parameters of 2,2'-bipyridine (L^1) and 1,10 – phenanthroline (L^2) complexes of Cd(II) (values are to the nearest whole number)

Dehydration and Decomposition reactions of Metal complexes.	Temperature range (^{0}C)	DTA peak temperature (^{0}C)		Ea* (KJmol^{-1})^a		Enthalpy^a change ΔH $(KJmol^{-1})$	Entropy^a change ΔS $(JK^{-1}mol^{-1})$
		Endo	Exo	TGA	DTA		
1(a) $\left[CdL_2^1(OAc)_2\right].2H_2O\rightarrow\left[CdL_2^1(OAc)_2\right]$	93-132	102	-	-	-	44	117
(b) $\left[CdL_2^1(OAc)_2\right]\rightarrow\left[CdL^1(OAc)_2\right]$	132-250	228	-	80	-	-	-
(c) $\left[CdL^1(OAc)_2\right]\rightarrow Cd(OAc)_2$	250-303	300	-	206	-	-	-
2(a) $\left[CdL_2^2(OAc)_2\right].H_2O\rightarrow\left[CdL_2^2(OAc)_2\right]$	102-123	113	-	-	-	24	62
(b) $\left[CdL_2^2(OAc)_2\right]\rightarrow Cd(OAc)_2$	123-396	-	253	99	69	136	259

[a] In some cases thermodynamic parameters are not possible to evaluate due to some irregular nature of the TGA and DTA curves.

Again, when the complex (2) is heated under non-isothermal condition, mass loss in step 2 (a) of TGA in the temperature range 102-123^{0}C (fig.1) confirms the presence ofone molecule of lattice water in complex (2).
And corresponding DTA endothermic peak temperature is 113^{0}C (table- 3).The values of ΔH and ΔS are found to be 24KJmol^{-1} and 62JK^{-1}mol^{-1}respectively (as shown in table-3).

The complex $\left[Cd(phen)_2(OAc)_2\right]$ which is formed in step 2(a), undergoes decomposition leading to the formation of $Cd(OAc)_2$ in a single step (step 2(b)) along with the complete expulsion of 1,10-phenanthroline, in the temperature range 123-396^{0}C. For this step 2(b), DTA shows an exothermic peak at 253^{0}C (fig.1). The values of

Ea* for this step 2 (b) are 99 and 69 $KJmol^{-1}$ from TGA and DTA respectively. The corresponding values of ΔH and ΔS for this step 2 (b) are 136 $KJmol^{-1}$ and $259JK^{-1}mol^{-1}$ respectively (table -3).

From the above discussion, the less stability of the complex $\left[Cd\left(phen\right)_2\left(OAc\right)_2\right]$ than $\left[Cd\left(bipy\right)_2\left(OAc\right)_2\right]$, may be attributed to more pronounced steric effect (repulsive force) between acetato (CH_3COO^-) groups and more bulkier phenanthroline groups around the large size cadmium ion.

CONCLUSION

Cadmium (II) acetate forms octahedral complexes with 2,2'-bipyridine and 1,10-phenanthroline respectively. And the thermal stability order of the anhydrous forms of cadmium (II) acetate complexes of 2,2'-bipyridine and 1,10 –phenanthroline, follows the trend: $\left[Cd\left(phen\right)_2\left(OAc\right)_2\right] < \left[Cd\left(bipy\right)_2\left(OAc\right)_2\right]$.

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