Synthesis, characterization and thermal studies of nickel (II), copper (II), zinc (II) and cadmium (II) complexes with some mixed ligands

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Dichloro - (DCA) and trichloroacetate (TCA) -cyclic ligand morpholine (Morph)/thiomorpholine (Tmorph)/methylmorpholine (Mmorph)/ dimethyl-piperazine (DMP) complexes of nickel (II), copper (II), zinc (II) and cadmium (II) with the compositions [Ni(tmorph)$_2$ (DCA)$_2$], [Ni (tmorph)$_2$ (TCA)$_2$]. 2H$_2$O, [Cu (DMP)$_2$ (TCA)$_2$], [ML$_2$X$_2$]. nH$_2$O where M = Zn^{II} or Cd^{II}, L = Morph, DMP or tmorph and X = DCA or TCA and n = O except in case of [Cd (Morph)$_2$ (TCA)$_2$] where n = 1 have been synthesised. Some intermediate complexes have been isolated by temperature arrest technique (pyrolysis) and characterised. Configurational and conformational changes have been studied by elemental analyses. IR and electronic spectra, magnetic moment data (in the case of Ni(II) and Cu(II) complexes) and thermal analysis. E_a^*, ΔH and ΔS for the decomposition reaction of these complexes are evaluated and the stability of the complexes with respect to activation energy has also been compared. A linear correlation has been found between E_a^* and ΔS for the decomposition of the complexes.

Nowadays, thermal methods of analysis have attracted the interest of researchers because the technique is used to measure the change in physical and or chemical properties like weight, density, conductivity, structure, magnetic properties of various materials as a function of temperature or time. Although acyclic diamines having the N(CH$_2$)nN grouping acting as chelating agents for transition metal ions are well studied [1,2], but little attention has been paid on cyclic diamine complexes[3]. Cyclic diamine can exist in boat or chair conformation and act as unidentate, bidentate bridging or bidentate chelate, so the thermal study of cyclic ligand complexes are really in-

teresting, regarding the change of mode of co-ordination with the change of conformation of cyclic ligand[1,4-6]. Chloroacetates used as ligand and an anion also act as unidentate, bridging bidentate and (or) bidentate chelate in coordination thus showing flexibility. Considering the flexibility of the cyclic ligand and chloroacetates, the aim of the present work is to synthesise some cyclic ligand complexes and study the thermally induced stereochemical changes in cyclic ligand metal chloroacetate complexes in the solid state.

Experimental

AR grade metal carbonates and dichloro- and trichloroacetic acids were used as received. Metal dichloro- and trichloroacetates were freshly prepared by neutralising dichloro- and trichloroacetic acids with an excess of corresponding metal carbonate and subsequent slow evaporation of the filtrate[1,5]. Morpholine, thiomorpholine, methylmorpholine and N, N' - dimethylpiperazine (Aldrich Co, USA) and N-methylmorpholine (Fluka, Switzerland) were used as received. Diethyl ether and ethanol were dried by standard procedure. Acetone (AR, BDH, India) was used as received.

Synthesis of [Ni (tmorph)$_2$ (DCA)$_2$]

A clear solution of the freshly prepared crystalline nickel dichloroacetate [1] (ca. 1.00g, 3 mmol) in dry ethanol (100 cm^3) was refluxed for 30 min. To this, thiomorpholine (ca. 0.500g, 3 mmol) in 50 cm^3 of dry ethanol was added with constant stirring and refluxed for about 30 min. A light green complex which precipitated on cooling was filtered under suction, washed with ethanol (4 times) followed by diethyl ether (3 times) and kept over fused calcium chloride in a desiccator. Yield: ca. 60%. [Ni (tmorph)$_2$ (TCA)$_2$].2H$_2$O and Cu(DMP)$_2$ (TCA)$_2$] were synthesised similarly. Yield : ca, 50%.

Synthesis of [Zn(DMP)$_2$(DCA)$_2$]

A dry ethanolic solution (50 cm^3) of the freshly prepared zinc dichloroacetate[1] (ca. 1.050g, 3 mmol)

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Table -1 : Analytical data of the complexes.

| Sl. no | Complex* (colour) | Found (Calcd.) % | | | | μ_{eff} |
		C	N	H	M	(BM)
1a	[NiL₂(DCA)₂] Light green	27.76 (27.72)	(5.30) (5.39)	3.41 (3.47)	11.25 (11.32)	3.26
1b	.[NiL (DCA)₂] Light green	23.03 (23.00)	3.15 (3.30)	2.00 (2.39)	14.00 (14.08)	3.20
2a	[ZnL₂″ (DCA)₂] White	35.04 (35.01)	10.20 (10.21)	5.40 (5.47)	11.95 (11.93)	-
2b	[ZnL″ (DCA)₂] White	27.52 (27.62)	6.30 (6.45)	3.60 (3.68)	15.00 (15.05)	-
3a	[CdL₂″ (DCA)₂] White	32.00 (32.19)	9.30 (9.38)	5.03 (5.03)	18.80 (18.84)	-
3b	[CdL″ (DCA)₂] White	24.80 (24.87)	5.78 (5.80)	3.30 (3.31)	23.20 (23.30)	-
4a	[NiL₂(TCA)₂].2H₂O Bluish green	24.40 (24.50)	4.70 (4.76)	3.00 (3.06)	9.90 (9.98)	3.20
5a	[CdL₂ (TCA)₂] White	22.40 (22.45)	4.30 (4.36)	2.89 (2.80)	17.50 (17.52)	-
5b	[CDL(TCA)₂] White	17.19 (17.19)	2.50 (2.59)	1.50 (1.48)	20.80 (20.83)	-
6a	[ZnL'₂' (TCA)₂] White	28.40 (28.84)	4.70 (4.80)	3.70 (3.77)	11.22 (11.20)	-
6b	[ZnL' (TCA)₂] White	22.43 (22.43)	2.90 (2.90)	2.10 (2.28)	13.50 (13.58)	
7a	[CdL' (TCA)₂].H₂O White	19.30 (19.31)	2.50 (2.51)	2.33 (2.33)	20.15 (20.20)	
8a	[CuL₂ ″ (TCA)₂] Green	31.10 (31.14)	4.50 (4.54)	9.06 (9.08)	10.20 (10.20)	2.07
8b	[CuL″ (TCA)₂] Light chocholate	23.80 (23.88)	2.70 (2.78)	5.57 (5.57)	12.60 (12.63)	2.23
9a	[ZnL₂ ″ (TCA)₂] White	31.00 (31.05)	9.00 (9.04)	4.50 (4.52)	10.40 (10.57)	-
9b	[ZnL ″ (TCA)₂] White	23.70 (23.79)	5.56 (5.55)	2.40 (2.78)	12.85 (12.97)	-
10a	[CdL₂ ″ (TCA)₂] White	28.70 (28.85)	4.20 (4.20)	8.43 (8.41)	16.80 (16.89)	-
10b	[CdL ″ (TCA)₂]	21.79 (21.76)	2.55 (2.54)	5.05 (5.07)	20.30 (20.38)	-

* Where L = thiomorpholine; L' = N-methylmorpholine and   L" = dimethylpiperazine

was treated with the ligand (ca. 0.650, 6 mmol) in dry ethanol (100 cm³) with constant stirring to yield the precipitate of the complex. The precipitate was collected by filtration under suction, washed with a little dry ethanol followed by diethyl ether (3 times) and dried over fused calcium chloride in a desiccator. Yield : ca. 70%.. Following the same procedure [Cd (DMP)₂ (DCA)₂]. [Cd(Mmorph) (TCA)₂].H₂O, [Zn (DMP)₂ (TCA)₂], [Cd (DMP)₂ (TCA)₂] and [Cd (tmorph)₂ (TCA)₂] were synthesized. Yield :ca. 70%.

Nickel, copper, zinc and cadmium were estimated gravimetrically[7]. C, H and N were determined using Carlo Erba and Heraeus CHN-O-rapid elemental ana-

lyzer and the values are given in Table 1. Thermal investigations (TGA and DTA) were carried out with Shimadzu DT-30 thermal analyser under dynamic nitrogen atmosphere with a heating rate of 10°C min⁻¹ and α-alumina as a standard reference substance. Activation energy (E_a*) has been evaluated using the equation of Horowitz and Metzger[8] Coats and Redfern[9] and Freeman and Carroll[10]. E_a* has also been evaluated from DTA curve using the equation of Borchardt and Daniels[11]. The enthalply change (ΔH) was evaluated using the relation $\Delta H = KA$, where, K is the heat transfer coefficient[11] (the calibration constant or cell constant). The cell used was a platinum crucible and it's constant K was evalu-

ated from the data obtained using indium metal as a calibrant, A is the total area under the particular DTA peak measured using a compensating planimeter with optical tracer Fuji Corona 027. The entropy change, ΔS was calculated using the relation [11], $\Delta S = \Delta H / T_m$, where T_m is the DTA peak temperature in kelvin. IR spectra were recorded lusing Perkin-Elmer 363, 783 model in Kbr discs. UV- vis spectra were recorded in the solid state using Hitachi U-3400 (UV-VIS-NIR) model electronic spectrophotometer. The effective magnetic moments were evaluated from the results of magnetic suscepltibility measurmennts using EG and G PAR vibrating sample magnetometer. Solid residues obtained after pyrolysis were identified by qualitative analyses.

Results and discussion

Thermal decomposition results showed that the complex $[Ni(tmorph)_2 (DCA)_2]$ (1a) : which has not been reported earlier, on pyrolysis, decomposed into $Ni(DCA)_2$ in two steps in the ranges of 25-190 and 191-267 °C rerspectively. Mass loss in the TGA curve via the intermediate $[Ni(tmorph) (DCA)_2$ (1b)] corresponds to one molecule of cyclic ligand for each step. The DTA peaks appeared at 110 (endothermic) and 180 °C (exothermic) for the first step and an endothermic peak at 245 °C for the second step. Values of E_a^*, ΔH and ΔS for the conversions of (1a) → (1b) are 37 kJmol^{-1}, 81 kJ mol^{-1}, 211 JK^{-1} mol^{-1} and for (1b) → $Ni(DCA)_2$ are 112 kJmol^{-1}, 42 kJmol^{-1} and 81 JK^{-1} mol^{-1} respectively.

All the other complexes on pyrolysis underwent decomposition to the corresponding metal salt after the liberation of the organic ligand molecule. Activation energy E_a^*, enthalpy change ΔH and entropy change, ΔS were evaluated for each step of decomposition with the standard equations[8-11] and the values were in the range of 30-120 kJmol^{-1}, 30-80 kJmol^{-1} and 50-210 JK^{-1} mol^{-1} respectively.

The colour and magnetic moment of the complexes are given in Table 1. The colour, IR and electronic spectra, and effective magnetic moment for 1a, 1b, 4a, 8a and 8b (Table 1) of the complexes suggested their octahedral configuration [1,4-6]. In the complex (1a), the cyclic ligand (tmorph) would act as a bidentate chelate (boat form) coordinating through nitrogen and sulphur as indicated by the increased number of IR active bands than that of free cyclic ligand which exists in the chair form [1,6,12-18] and

dichloroacetate ion (DCA) could act as unidentate ligand which is confirmed by the value of $\Delta \upsilon$ (223 cm^{-1})[1,13,14,17,18]. The complex (1b) was isolated. The cyclic ligand and dichloroacetate ions act as bidenate chelate which is supported by IR spectral data.

The nature of the coordination of the cyclic ligand and the chloroacetate ion in all other complexes have been confirmed with the IR spectra [1,13-18]. The intermediate complexes were isolated and also characterised.

The values of activation energy reported by some workers [19-21] using Horowitz and Metzger equation[8] for the decomposition reactions of the simple salts are higher with respect to the values evaluated by Coats and Redfern[9], and Freeman and Carroll [10] equation. In this investigation the same trend was also noticed in most cases.

No systematic conclusion can be drawn on the stability order with respect to the activation energy in case of dichloroacetate complexes.

The stability order for N, N'-dimethylpiperazine trichloroacetate complexes follows the trend Zn(II) < Cd(II) < Cu(II) for the first step of decomposition whereas in the second step of decomposition the order is Zn(II) =Cd(II)<Cu(II).But in methylmorpholine and thiomorpholine complexes, no conclusion can be drawn on the stability order.

In case of the complexes of Zn(II) and Cd(II) having the same cyclic ligand (dimethylpiperazine) of DCA and TCA complexes 2a , 9a and 3a, 10a (Table 1), it has been observed that in case of Zn(II), DCA complex is more stable than TCA complex (with respect to DTA peak temperature) for both steps of thermochemical reaction whereas in Cd(II) complex, the same trend is noticed in the first step of decomposition but the order is reversed in the second step. The less stability of trichloroacetato complexes may be due to its steric effect besides the nature of the coordination of both the ligands before and after heating.

Further, a linear correlation was obtained by plotting the values of E_a^* vs ΔS for the decomposition of the complexes, which showed that a system having a higher entropy change (ΔS) requires less energy E_a^* for its thermal decomposition.

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