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Thermal Behavior of Schiff base Ligand (3,4-MeO-ba)$_2$en and its Cd(II) and Co(II) Complexes

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ABSTRACT

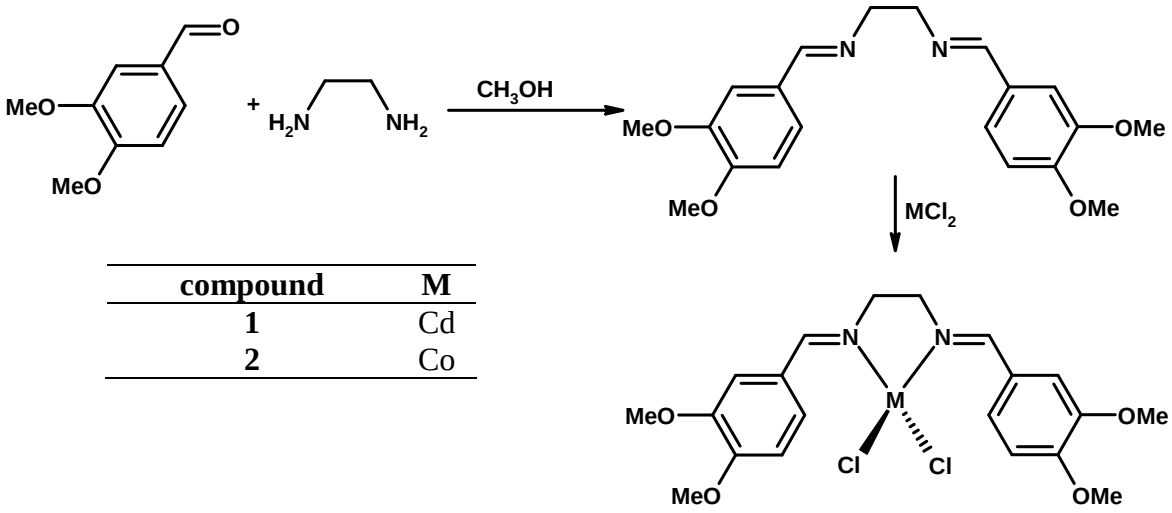
*Cd(II) and Co(II) complexes of bidentate Schiff base ligand (3,4-MeO-ba)$_2$en ((3,4-MeO-ba)$_2$en =N,N′-bis(3,4-dimethoxybenzylidene)-1,2-diaminoethane) have been prepared and characterized by elemental analyses and FT-IR spectroscopy. Thermal decomposition of the ligand and synthesized complexes were studied by thermogravimetric analyses (TG) in order to evaluate their thermal stability and thermal decomposition pathway. Three similar decomposition steps occurred for the two Cd(II) (**1**) and Co(II) (**2**) complexes, yielding Cd and Co as final residue, respectively, while decomposition of the Schiff base ligand (3,4-MeO-ba)$_2$en occurred in two steps. The general formula established from experimental data were found to be MCl$_2$(3,4-MeO-ba)$_2$en (M = Cd(II) (**1**) and Co(II) (**2**)).*

Key Words Cd(II) and Co(II) complexes, Schiff base, Spectroscopy, Thermogravimetry.

INTRODUCTION

Bidentate Schiff bases derived from diamine and aldehydes, as *N*,*N*′-bis[(E)-3-(2-nitrophenyl)allylidene)]benzene-1,2-diamine (nca$_2$ph), are one of the most important synthetic ligands in development of coordination chemistry of transition metal [1-2], bioactive complexes [3], electrochemical studies [4] and catalytic investigations [5,6]. $M^{II}LX_2$ complexes of these ligands have tetrahedral coordination sphere and the molecular structures of these complexes determined using X-ray diffraction method are given in literature [7-9]. The study of Cd(II), Pb(II) and Co(II) complexes with Schiff base ligands is an important objective because of their interesting synthetic, structural and spectroscopic features [2-4,9,10-13]. However, reported on the thermal decomposition of the transition metal complexes with tetradentate N_2O_2 Schiff-base ligands have been extensively studied in recent years [14-23], reported on the thermal behavior of Cd(II) and Co(II) complexes with bidentate N_2 Schiff-base have been very rare.

The present study deals with synthesis and characterization of *N,N′*-bis(3,4-dimethoxybenzylidene)-1,2-diaminoethane as bidentate ligand and its Cd(II) and Co(II) complexes with general formula of MCl_2(3,4-MeO-ba)$_2$en (Fig. 1). The complexes have pseudotetrahedral geometry in C_{2v} point group. We have also investigated thermal behaviors of synthetic Schiff base ligand and its Cd(II) (**1**) and Co(II) (**2**) complexes to understand the mechanisms of decomposition pattern of the species.



compound	M
1	Cd
2	Co

Fig-1 Chemical formula of Schiff-base ligand (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2) complexes.

MATERIALS AND METHODS

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Infrared spectra were recorded using KBr disks on a FT-IR Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. Thermogravimetric analyses were done on a Perkin Elmer TG/DTA lab system l (Technology by SII) in nitrogen atmosphere with a heating rate of 20ºC/min from 35-700 ºC.

Preparation of (3,4-MeO-ba)$_2$en

The Schiff base ligand (3,4-MeO-ba)$_2$en was prepared by condensation of 3,4-dimethoxybenzaldehyde with ethylenediamine following literature methods [24].

Preperation of MCl_2(3,4-MeO-ba)$_2$en (M = Cd(II) (1) and Co(II) (2))

A solution of Schiff base ligand (34-MeO-ba)$_2$en (0.2 mmol, in 5 mL chloroform) was added to a hot solution of MCl_2 (0.2 mmol) in 15 mL ethanol and the mixture was stirred for 2.5 h in air. After completion of the reaction, the white precipitation obtained were filtered, washed with ethanol twice and dried at room temperature for several days. The precipitates were recrystallized from EtOH/DMF mixture (5:1 *v/v*).

RESULTS AND DISCUSSION

The results of the elemental analyses as well the thermogravimetric and FT-IR spectroscopic data confirmed the proposed formula for the compounds **1** and **2**. The yield and analytical results of the ligand and its Cd(II) (**1**) and Co(II) (**2**) complexes are listed in Table 1.

Table-1 Physical data and analytical results of the (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2)complexes

Compound	Chemical Formula	Yield (%)	Found / calc. (%)		
			C	H	N
(34-MeO-ba)$_2$en	$C_{20}H_{24}N_2O_4$	88	67.47 / 67.40	6.83 / 6.79	7.91 / 7.86
1	$C_{20}H_{24}Cl_2N_2O_4Cd$	75	44.59 / 44.51	4.64 / 4.48	5.25 / 5.19
2	$C_{20}H_{24}Cl_2N_2O_4Co$	79	49.44 / 49.40	4.95 / 4.98	5.79 / 5.76

FT-IR spectroscopic studies

The most characteristic absorption of the bidentate Schiff base ligand (34-MeO-ba)$_2$en and its complexes along with their assignment are presented in Table 2. The corresponding Cd(II) and Co(II) complexes exhibit ligand absorption at different frequencies indicating the coordination of the ligand. Frequencies assigned to the starting materials including 3,4-dimethoxybenzaldehyde and 1,2-ethylenediamine at about 1700 and 3100-3300 cm^{-1} were not observed in the FT-IR spectrum of the Schiff base ligand [24-26]. The FT-IR spectrum of (34-MeO-ba)$_2$en showed frequencies at 2835-3001 cm^{-1} assigned to C-H aromatic and aliphatic groups, and slightly affected by coordination of the ligand to the metal centers, 2832-3000 cm^{-1} in **1** and 2840-3018 cm^{-1} in **2** [1,7,27,28]. The vibrational frequency at 1636 cm^{-1} in (34-MeO-ba)$_2$en can be assigned to azomethine group (-C=N-) [24-26] and slightly shifted in the spectra of the complexes, indicating coordination through the azomethine nitrogen (Figure 1) [1,7,27,28].

Table-2 FT-IR spectral data of the Schiff base ligand (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2)complexes

Compound	υ C-H arom.	υ C-H alip.	υ C-H imine	υ C=N	υ C-N	υ C=C
Ligand	3001	2883-2962	2835	1636	1373	1603, 1579, 1506
1	3000	2875-2967	2829	1633	1345	1598, 1582, 1514
2	3018	2873-2996	2840	1635	1338	1597, 1582, 1514

Thermogravimetric analysis

Thermogravimetric analyses of ligand and complexes under N_2 were examined. The TG graphs, at a 20 K min^{-1} heating rate, of the ligand and complexes are represented in Figure 2. The decomposition steps, temperature range, as well as found and calculated mass loss percentage of the all compound are given in Table 3. A probable decomposition pathway of the Schiff base ligand (34-MeO-ba)$_2$en and its Cd(II) (**1**) and Co(II) (**2**) complexes is proposed in Fig. 3.

The Schiff base ligand (34-MeO-ba)$_2$en is stable up to 308 K, and during further heating undergoes decomposition in two steps. In the first step, ligand shows a mass loss of 61.13% (217.87 g) in the temperature range 308–584 K, is major decomposition and corresponds to the elimination of four methoxy groups and one Ph-C group (calcd. 59.54%, 212.24 g). In the second step, Ligand shows a mass loss of 38.87% (138.54 g) in the temperature range 584–895 K, is another major step of the decomposition, and corresponds to the elimination of Ph-CH=N-CH$_2$-CH$_2$-N group (calcd. 40.45%, 144.17 g).

The title compounds CdCl$_2$(34-MeO-ba)$_2$en (**1**) and CoCl$_2$(34-MeO-ba)$_2$en (**2**) are stable up to 308 K, and during further heating undergoes decomposition in Cd and Co occurs in three stages. In the first stage, complex **1** shows a mass loss of 24.18% (130.49 g) in the temperature range 308–449 K, and complex **2** shows a mass loss of 11.34% (55.14 g) in the temperature range 308–448 K, is partial decomposition and corresponds to the elimination of four methoxy group (calcd. 23.00%, 124.14 g) in complex **1** and two methoxy group (calcd. 12.76%, 62.07 g) in complex **2**.

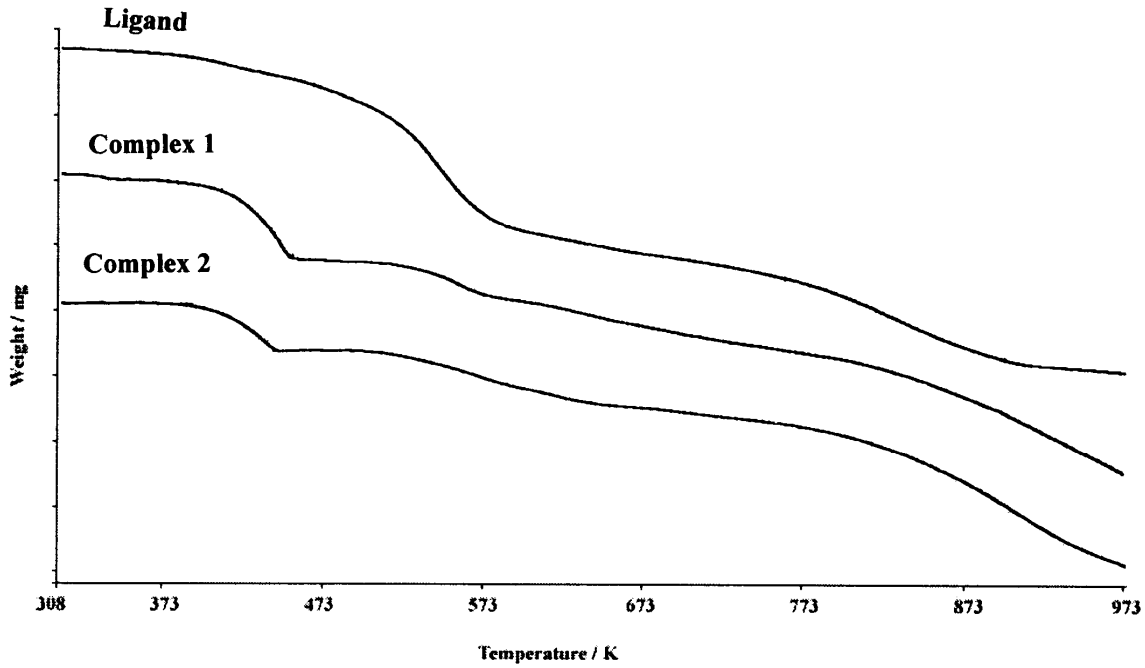


Fig-2 The TG graphs of the Schiff base ligand (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2) complexes

In the second step, complex **1** shows a mass loss of 9.18% (49.54 g) in the temperature range 449–564 K, corresponds to the partial decomposition of **1** and elimination of one Cl and one CH_2 group (calcd. 9.17%, 49.48), while complex **2** shows a mass loss of 11.91% (57.91 g) in the temperature range 448–588 K, corresponds to the partial decomposition of **2** and elimination of two methoxy groups (calcd. 12.76%, 62.07).

The third decomposition step of **1** is mainly decomposition and shows a mass loss of 49.57% (267.55 g) in the temperature range 564–973 K, corresponds to the elimination of one Cl, one CH_2 and two Ph-CH=N groups (calcd. 47.01%, 253.71 g), while complex **2** shows a mass loss of 66.29% (322.33 g) in the temperature range 588–973 K, corresponds to the elimination of one Ph-CH=N-CH_2-CH_2-N=CH-Ph group and two Cl (calcd. 62.35%, 303.18 g).

Table-3 Thermal analysis data of the Schiff base ligand (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2) complexes

Compounds	Temperature range / K	Mass loss %		Products	Residue
		Exp.	Calcd.		
Ligand	308-584	61.13	59.54	4 CH_3O and 1 C_7H_4	$C_9H_8N_2$
	584-895	38.37	40.45	1 $C_9H_8N_2$	--------
1	308-449	24.18	23.00	4 CH_3O	$C_{16}H_{12}Cl_2N_2Cd$
	449-564	9.18	9.17	1 Cl and 1 CH_2	$C_{15}H_{10}ClN_2Cd$
	567-973	49.57	47.01	1 Cl, 1 CH_2 and 2 C_7H_4N	Cd
2	308-448	11.34	12.76	2 CH_3O	$C_{18}H_{18}Cl_2N_2O_2Co$
	448-588	11.91	12.76	2 CH_3O	$C_{16}H_{12}Cl_2N_2Co$
	588-973	66.29	62.35	2Cl and 1 $C_{16}H_{12}N_2$	Co

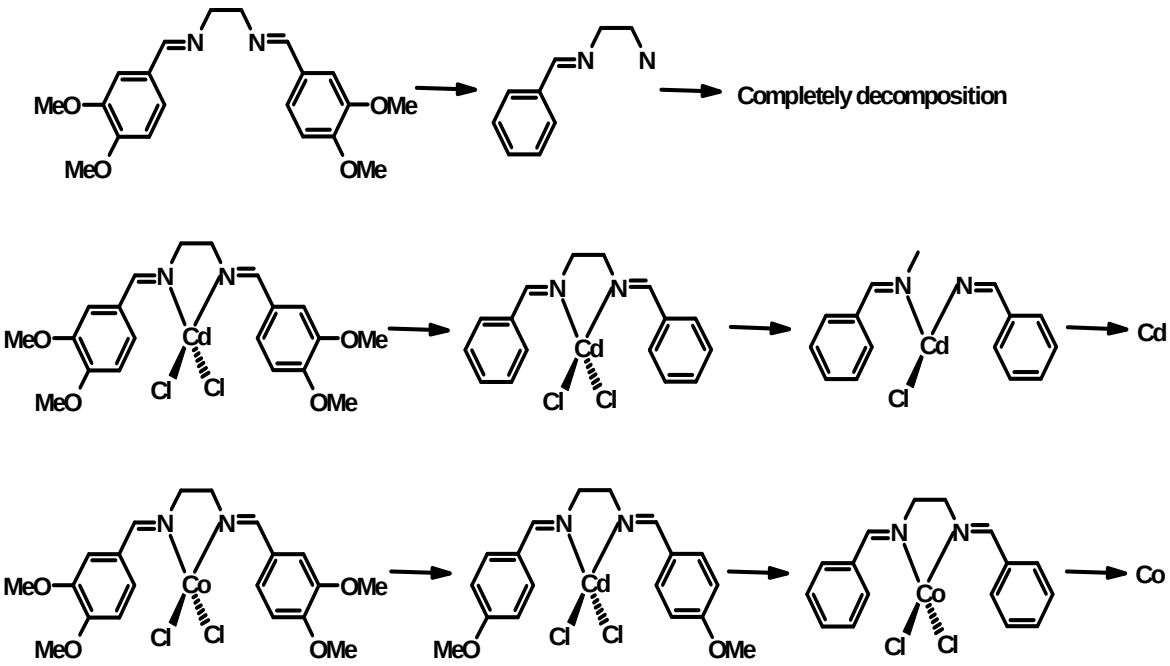


Fig-3 A part of the probable decomposition diagram of the Schiff base ligand (34-MeO-ba)$_2$en and its Cd(II) (1) and Co(II) (2) complexes

CONCLUSION

Bident ateSchiff-base ligand (34-MeO-ba)$_2$en and its Cd(II) (**1**) and Co(II) (**2**) complexes were obtained. The structureal of ligand and complexes were proposed based on elemental analyses, FT-IR spectroscopy and thermal analysis. From the FT-IR spectra, it was concluded that the ligand is natural bidentate N_2 chelating and is coordinated to the metal ions through the two azomethine nitrogen atoms. However, the complexes have similar structure, but they have not similar decomposition steps.

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