

Synthesis and Characterization of Some Zinc(II) and Cadmium(II) Complexes with Schiff Bases

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ABSTRACT

A number of zinc(II) and cadmium(II) complexes with two Schiff base ligands have been prepared. The ligands derived from the condensation of furfuraldehyde with butylamine (FBA) and hexylamine (FHA). The complexes which have the molar ratio of 1:2 (metal to ligand) had general formula $[M(L)_2]X_2$ (where $M = Zn(II)$ or $Cd(II)$; while $X = Cl, NO_3$ or $\frac{1}{2} SO_4$). The complexes were characterised by molar conductance measurements and the study of their infrared and ultraviolet absorption spectra, while zinc and cadmium contents were determined by standard procedures. These studies revealed the action of both ligands as neutral bidentate chelating ligands, formed complexes with tetrahedral structure.

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INTRODUCTION

A large number of Schiff bases and their complexes have been prepared and characterised since the discovery of such type of compounds by Schiff in 1864. Schiff bases have received renewed attention because of their proven antitumour and carcinostatic activity (Hassan *et al.*, 2002; Li *et al.*, 2004). The presence of azomethine group in these molecules made them acting as suitable ligands towards metal ions and forming different coordination compounds (Alemi and Shaabani, 2000; Bhattacharyya *et al.*, 1998; Ciobanu *et al.*, 2003; Mashaly *et al.*, 1999; Sousa *et al.*, 2003; Wu *et al.*, 2001).

The biological activity of Schiff bases was attributed to the formation of stable chelates with the metal ions present in the cell (Chohan *et al.*, 2000; Konstantinovic *et al.*, 2003; Liu *et al.*, 1996). In addition, Schiff bases and their metal complexes used in many fields such as oxidation catalysis (Djebbar *et al.*, 1998), electrochemistry (Hamada, 1997).

There are many routes to prepare Schiff bases complexes, but one of them using Schiff bases components which include the amine and the aldehyde or the ketone which are mixed together with the metal salt and the reaction is carried out. This kind of reaction is called a template reaction and almost gives a high percentage in yield (Spinu and Kriza, 2000; Wu *et al.*, 2001).

In the present work, we report the synthesis and spectral properties of some Zn(II) and Cd(II) complexes with Schiff bases using the template reaction (Spinu and Kriza, 2000).

EXPERIMENTAL

Materials and methods:

Analard grade chemical reagents supplied by B.D.H., and Fluka were used without further purification.

a. Preparation of the ligands:

An ethanolic solution of furfuraldehyde (0.193 g, 0.002 mol, 25 ml) was added to an ethanolic solution of butylamine (BA) (0.147 g, 0.002 mol, 25 ml) or hexylamine (HA) (0.21 g, 0.002 mol, 25 ml) and refluxed for 16 hr. followed by concentration of the solution, the precipitate was separated by filtration, washed with ethanol and then air-dried.

b. Preparation of the complexes:

A mixture of furfuraldehyde (0.385 g, 0.004 mol, 50 ml), and BA (0.293 g, 0.004 mol, 50 ml) or HA (0.405 g, 0.004 mol, 50 ml) in ethanol was added to an ethanolic solution of metal salts (0.002 mol, 50 ml). The mixture was refluxed for 20 hr. The excess of the solvent was then distilled. The separated compounds were filtered off, washed with ethanol and then air-dried.

Analysis and physical measurements:

The metal contents were determined according to the standard procedure (Vogel, 1961). Conductivity measurements for the complexes were carried out for 10^{-3} M solution in dimethylformamide (DMF) using LF-42 digital conductivity meter at 25 °C. Infrared absorption spectra of the ligands and their complexes were recorded on Pye Unicam SP 1100 Spectrophotometer in the range 400-4000 cm^{-1} using KBr pellets. The UV-spectra of the ligands and their complexes were recorded on Shimadzu UV-160 spectrophotometer for 10^{-3} M solution in dimethylformamide (DMF) at 25°C using a 1 cm quartz cell.

RESULTS AND DISCUSSION

The complexes were air stable at room temperature. All the complexes were insoluble in water but they were soluble in DMF. The values of molar conductivities (Table 1) for the complexes in DMF approached those expected for 1:2 electrolytes except those for sulphate complexes, which demonstrated 1:1 electrolytes (Geary, 1971). Based on the metal contents (Table 1), and the measurements of the experimental molecular weights for all the complexes (Sharma and Sharma, 1986; James and Prichard,

1985) have been supported the formula $[M(L)_2]X_2$ and that all the complexes acted as mononuclear complexes (monomer).

Table 1: Analytical and some physical properties of the complexes.

Compound	m.p °C	Colour	Yield %	Theoretical / Experimental M.Wt	Molar Conductance $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$	Analysis % Found (Calcd.) M*
$[\text{Zn}(\text{FBA})_2]\text{Cl}_2$	233	White	76.3	438.7 / 433	136	14.8 (14.9)
$[\text{Zn}(\text{FBA})_2]\text{SO}_4$	242	Yellowish white	70.1	463.8 / 459	78	14.72 (14.09)
$[\text{Zn}(\text{FHA})_2]\text{Cl}_2$	258	Pale yellow	67.4	494.8 / 487	145	13.76 (13.21)
$[\text{Zn}(\text{FHA})_2]\text{SO}_4$	266	Pale yellow	78.2	519.9 / 511	83	12.25 (12.57)
$[\text{Cd}(\text{FBA})_2]\text{Cl}_2$	221	Dark yellow	61.1	485.7 / 482	119	23.68 (23.14)
$[\text{Cd}(\text{FBA})_2](\text{NO}_3)_2$	219	Brown	64.2	538.8 / 532	124	20.81 (20.86)
$[\text{Cd}(\text{FHA})_2]\text{Cl}_2$	233	Brown	77.7	541 / 536	128	21.21 (20.74)
$[\text{Cd}(\text{FHA})_2](\text{NO}_3)_2$	222	Brown	80.2	594.9 / 585	131	19.14 (18.89)

M* = zinc(II) or cadmium(II)

The IR spectra of the ligands exhibited a band at $1624\text{-}1637 \text{ cm}^{-1}$ assignable to $\nu_{(\text{C}=\text{N})}$ (Table 2). This band was shifted to a lower frequency by about $23\text{-}30 \text{ cm}^{-1}$, suggesting the coordination through N atom of the azomethine group (Li *et al.*, 2004; Konstantinovic *et al.*, 2003). The band at $1280\text{-}1287 \text{ cm}^{-1}$ observed in free ligand assigned to furan ring (C-O-C) stretching vibration was shifted to lower values with $26\text{-}31 \text{ cm}^{-1}$, suggesting the involvement of oxygen atom of the furan moiety in the coordination (Dawod *et al.*, 1989; Sharma and Bahel, 1982). Further support for this coordination was indicated by the appearance of new bands at $499\text{-}505$ and $460\text{-}481 \text{ cm}^{-1}$ in the infrared spectra of the complexes which were assigned to M-O and M-N stretching vibrations, respectively (Li *et al.*, 2004; Konstantinovic *et al.*, 2003). The other new bands located at 1391 cm^{-1} , $570\text{-}574 \text{ cm}^{-1}$ and $1131, 620 \text{ cm}^{-1}$ for nitrate, chloride and sulphate complexes, respectively. The shape and positions of these bands suggested the ionic nature and the non-involvement of these groups in coordination (Nakamoto, 1978), and therefore remained outside the coordination sphere. These observations were in a good agreement with the conductance values which have been supported the given formulation of the complexes.

Table 2: Important I.R. spectral bands (cm^{-1}).

Compound	$\nu (\text{C}=\text{N})$	$\nu (\text{C}-\text{O}-\text{C})$	$\nu (\text{M}-\text{O})$	$\nu (\text{M}-\text{N})$
FBA	1624	1280	---	---
FHA	1637	1287	---	---
$[\text{Zn}(\text{FBA})_2]\text{Cl}_2$	1601	1249	499	462
$[\text{Zn}(\text{FBA})_2]\text{SO}_4$	1604	1254	500	460
$[\text{Zn}(\text{FHA})_2]\text{Cl}_2$	1607	1261	503	475
$[\text{Zn}(\text{FHA})_2]\text{SO}_4$	1611	1263	503	473
$[\text{Cd}(\text{FBA})_2]\text{Cl}_2$	1602	1255	500	480
$[\text{Cd}(\text{FBA})_2](\text{NO}_3)_2$	1613	1260	500	480
$[\text{Cd}(\text{FHA})_2]\text{Cl}_2$	1613	1266	505	479
$[\text{Cd}(\text{FHA})_2](\text{NO}_3)_2$	1618	1266	504	481

The UV spectra of the ligands showed two absorption bands assigned to the transition $n \rightarrow \pi^*$ of azomethine group at 28169 cm^{-1} and $\pi \rightarrow \pi^*$ transition of furan ring at 30303 cm^{-1} . Both bands showed a red shift on coordination with the metal ions. These observations represented a further indication about the coordination of the ligands with the metal ions.

From this study, it can be concluded that the ligands acted as bidentate chelating ligand coordinated to the metal ions through both furan oxygen and azomethine nitrogen atoms. As a result tetrahedral structure was suggested for all the complexes as shown in Figure 1.

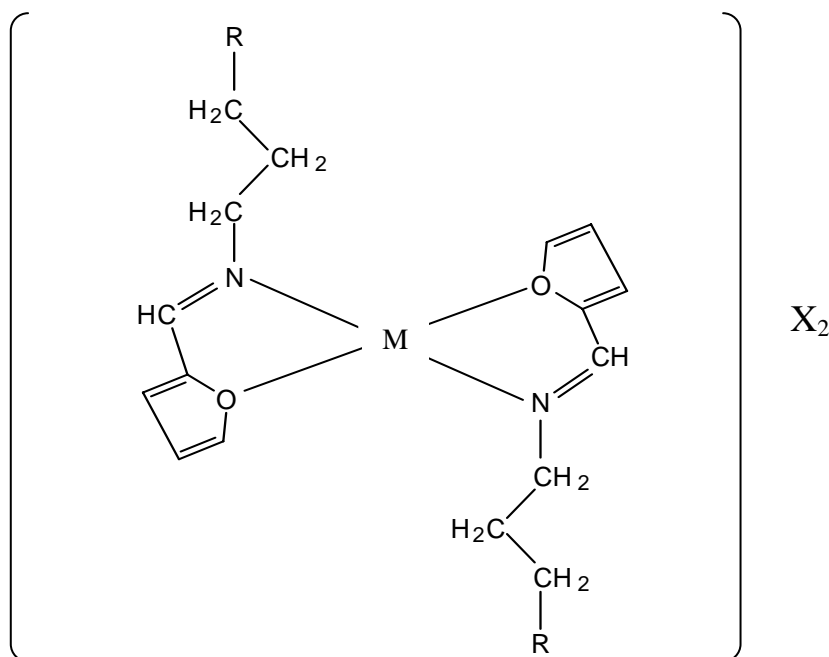


Fig. 1: Suggested Structures of $[M(L)_2]X_2$ complexes; (M=Zn(II) or Cd(II); L=FBA or FHA ; X=Cl⁻, NO₃⁻, 1/2 SO₄²⁻); R= -CH₃ or -CH₂CH₂CH₃

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