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# Synthesis and Characterization of Some Complexes of Fe(II) , Co(II) , Ni (II) , Cu(II) , Zn(II) and Cd(II) With New Schiff Base

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## ABSTRACT

Metal complexes of general formula $[ML_2]Cl_2$ and $[FeL_2Cl_2]$ where M is Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) and L is a Schiff base formed by condensation of 2-furaldehyde and 2-aminobenzothiazole (FABTZ), have been prepared and characterized by analytical, spectral, magnetic and conductance measurements . I.R. spectra show that the nitrogen of the azomethine group and oxygen of the furan ring take part in coordination. Magnetic measurements and electronic spectral studies suggest an octahedral structure for the Fe(II) complex, a square planar geometry for $[Ni(FABTZ)_2]Cl_2$ and $[Cu (FABTZ)_2] Cl_2$ complexes and tetrahedral geometry for Co(II), Zn(II) and Cd(II) complexes. Conductance measurements show a 1:2 electrolytic nature of the complexes, with the exception of the $[Fe (FABTZ)_2]Cl_2$ compound.

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# تحضير وتشخيص بعض معقدات الحديد والكوبلت والنيكل والنحاس والخارصين والكادميوم الثنائية الموجبة مع قاعدة شيف جديدة

## الملخص

يتضمن البحث تحضير مجموعة من المعقدات ذات الصيغ العامة $[ML_2]Cl_2$ و $[FeL_2Cl_2]$ حيث ان : M تمثل ايونات الكوبلت ، النيكل ، النحاس ، الخارصين والكادميوم الثنائية الموجبة وان L تمثل قاعدة شيف المشتقة من تفاعل 2- امينو بنزوثايازول مع 2-فورالديهايد . تم تشخيص هذه المعقدات بالطرق الكيميائية والفيزيائية والطرق الطيفية المعروفة. اظهرت قياسات الاشعة تحت الحمراء ارتباط الليكاند من خلال ذرة النتروجين لمجموعة الازو ميثاين وذرة الاوكسجين لحلقة الفيوران لجميع المعقدات . اظهرت قياسات المغناطيسية والاطياف الالكترونية بنية ثماني السطوح لمعقد الحديد وبنية المربع المستوي لمعقدات النيكل والنحاس وكذلك بنية رباعي السطوح لمعقدات الكوبلت والخارصين والكاديوم . دلت قياسات التوصيلية الكهربائية لهذه المعقدات بانها موصلة بنسبة1 : 2 باستثناء معقد الحديد وهو غير الكتروليتي .

## INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, e.g., their catalytic activity in hydrogenation of olefins (Olie and Olive, 1984), transfer of an amino group (Dugas and Penney, 1981), photochromic properties (Margerum and Mller, 1971) and used as antitumors (Sigel, 1976). The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes. Schiff bases which contain different donor atoms, are an important class of ligands in the coordination chemistry, widely reported (Nag et al., 2001 ; Taqa, 2005 ; Li et al., 2004 ; Ruck and Jacobsen, 2002 ; Konstantinovic et al., 2003 ; Ciobanu et al., 2003). Metal complexes of sulphur-nitrogen chelating ligands have attracted considerable attention because of their interesting physicochemical properties, pronounced biological activities (Ali et al., 1992) and as models of the metalloenzyme active sites. It is well known that sulphur and nitrogen atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules (Karlin and Zubieta, 1983 ; Ali et al., 1998 ; Gupta et al., 2003).

Investigation on metal complexes of thiazole derivatives (containing sulphur and nitrogen donor atoms), particularly the 2-substituted ones have received considerable attention, owing to their importance in biological and industrial processes (Campbell, 1979 ; Hassan, 2002).

There are many routes to prepare Schiff bases complexes , but one of them using Schiff bases components including 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 (Chandra and Gupta 2001 , Wu et al .,2001) .

The present paper describes the synthesis of the Schiff base (FABTZ), which has been synthesized using 2-furaldehyde and 2-aminobenzothiazole. This ligand has been reacted with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions using the template reaction. Tentative structures have been proposed on the basis of analytical, spectral, magnetic and conductance measurements.

## EXPERIMENTAL

### Materials and Methods :

All chemicals used in this work were either analar or reagent grade used without purification such as $FeCl_2.4H_2O$ (99%) , $CoCl_2.6H_2O$ (98%) , $NiCl_2.6H_2O$ (99%) , $CuCl_2.2H_2O$ (99%) , $ZnCl_2$ (98%) , $CdCl_2$ (99%) , 2-aminobenzothiazole (97%) except for 2-furaldehyde which was purified according to a given procedure (Perrin et al., 1980).

### a. Synthesis of the ligand :

An ethanolic solution of 2-furaldehyde (1.922 gm , 0.02 mol) was added to an ethanolic solution of 2-aminobenzothiazole (3.01 gm , 0.02 mol) and refluxed for ~8 hrs. The resulting solution was concentrated and the precipitate was separated by filtration, washed with ethanol and then air-dried.

**b. Synthesis of the $ML_2Cl_2$ complexes :**

All the complexes were prepared by the same general method using the template synthesis (Wu et al., 2001) as following :

A mixture of 2-furaldehyde (3.844 gm , 0.04 mol), 2-aminobenzothiazole (6.02 gm , 0.04 mol) in ethanol was added to an ethanolic solution of metal chlorides (0.02 mol). The mixture of reactants was refluxed for 12 hrs. The excess of the solvent was then distilled. The resulting 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, 1981). Melting points were determined by using Richerk Jung Heizbank melting point apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using $10^{-3}$ M dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker (tensor 27) spectrophotometer in the 4000-400 $cm^{-1}$ range using KBr disc. Electronic spectra were recorded on a Shimadzu 160 spectrophotometer in DMF at 25°C for $10^{-3}$ M solution of the compounds using a 1 cm quartz cell. Magnetic susceptibility measurements of the complexes in the solid state were determined by the Fraday method at room temperature using a Bruker BM6 apparatus.

## RESULTS AND DISCUSSION

The complexes of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with the ligand (FABTZ) appear as powders. They are not soluble in most organic solvents, such as ethanol and chloroform but soluble in DMF. The molar conductance of the complexes in DMF are in the range 137-154 $ohm^{-1}$ $cm^{-2}$ $mol^{-1}$ (Table 1) indicating a 1:2 electrolytic nature, while $[Fe(FABTZ)_2 Cl_2]$ compound ($\Lambda_M$ = 18 $ohm^{-1}$ $cm^2$ $mol^{-1}$ indicating a non-electrolytic nature (Geary, 1971).

Table 1: Analytical and some physical properties of the complexes

| Compound | m.p. $^0C$ | Colour | Yield % | % Metal | $\Lambda_m$ $cm^2$ $ohm^{-1}$ $mol^{-1}$ | $\mu_{eff}$ B.M. |
|---|---|---|---|---|---|---|
| | | | | Found (Calcd.) | | |
| FABTZ | 144 | Dark yellow | 73 | ---- | ---- | ---- |
| $[Fe(FABTZ)_2Cl_2]$ | 177 | Dark red | 81 | 10.22 (9.58) | 18 | 5.22 |
| $[Co(FABTZ)_2]Cl_2$ | 194 | Dark blue | 76 | 10.41 (10.05) | 143 | 4.54 |
| $[Ni(FABTZ)_2]Cl_2$ | 165 | Brown | 79 | 9.89 (10.02) | 140.2 | Diam |
| $[Cu(FABTZ)_2] Cl_2$ | 156 | Brown | 82 | 10.53 (10.75) | 154 | 1.77 |
| $[Zn(FABTZ)_2] Cl_2$ | 231 | Yellow | 76 | 11.34 (11.03) | 137.4 | Diam |
| $[Cd(FABTZ)_2] Cl_2$ | 171 | Yellow | 68 | 17.9 (17.57) | 152.1 | Diam |

Some important IR bands of (FABTZ) and its complexes together with their assignments are presented in Table 2. The IR spectrum of the ligand shows a band at 1660 cm$^{-1}$ which is assigned to the ν(C=N) of the azomethine group and a band at 1613 cm$^{-1}$ corresponding to the ν(C=N) stretching of the thiazole ring. The comparison of the positions of these bands with those observed in the IR spectra of the complexes indicates that the band at 1660 cm$^{-1}$ shifts towards lower frequencies, while that at 1613 cm$^{-1}$ does not show a marked shift. This behaviour suggests that FABTZ is coordinated to the centeral metal ion through the azomethine nitrogen. The proof of the coordination to the N atom is provided by the occurrence of the bands in the 500-509 cm$^{-1}$ region in the IR spectra of the complexes (Li et al., 2004 ; konstantinovic et al., 2003).

The band observed in the free ligand spectrum at 719 cm$^{-1}$ can be ascribed to ν(C-S-C) stretching vibration (Nag et al., 2001). The IR spectra of the complexes, a band appears at the same region, which remains almost unchanged on complexation. This observation suggests that the sulphur atom does not take part in coordination. A band appears at 1290 cm$^{-1}$ in the ligand spectrum are due to ν(C-O-C) stretching vibration of furan. This band shifted to 1223-1246 cm$^{-1}$ in the spectra of the complexes. These shifts refer to the coordination through a furan oxygen atom (Dawod et al., 1989 ; Sharma and Bahel, 1982). New bands are found in the spectra of the complexes in the regions 531-547 cm$^{-1}$ (furan O), which are assigned to ν(M-O) stretching vibrations for the metal complexes.

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

| **Compound** | **ν (C=N) Azomethine** | **ν (C=N) Thiazole** | **ν (C-O-C) Furan** | **νC-S-C** | **ν (M-O)** | **ν (M-N)** |
|---|---|---|---|---|---|---|
| **FABTZ** | 1660 | 1613 | 1290 | 719 | ---- | ---- |
| **[Fe(FABTZ)$_2$Cl$_2$]** | 1644 | 1609 | 1223 | 717 | 531 | 509 |
| **[Co(FABTZ)$_2$]Cl$_2$** | 1647 | 1610 | 1241 | 711 | 547 | 501 |
| **[Ni(FABTZ)$_2$]Cl$_2$** | 1646 | 1611 | 1246 | 711 | 545 | 500 |
| **[Cu(FABTZ)$_2$] Cl$_2$** | 1646 | 1612 | 1244 | 712 | 545 | 500 |
| **[Zn(FABTZ)$_2$] Cl$_2$** | 1641 | 1611 | 1246 | 711 | 544 | 501 |
| **[Cd(FABTZ)$_2$] Cl$_2$** | 1641 | 1610 | 1244 | 711 | 543 | 501 |

The electronic spectrum of the Schiff base (FABTZ) and its complexes were recorded in DMF. Two bands at 25773 and 31250 $cm^{-1}$ were observed in the spectrum of the ligand, which is attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the C=N chromophore and the aromatic ring, respectively (Williams and Fleming, 1989). The electronic spectrum of the iron(II) complex shows absorption band at 11764 $cm^{-1}$ assignable to the $^5T_2g \rightarrow {}^5Eg$ transition consistent with an octahedral geometry for iron(II) complex (Lobana et al., 1985). The room temperature magnetic moment (5.22 B.M) corresponds to an octahedral geometry of iron (II) (Lobana et al., 1985 ; Chaudhary et al., 2001). The electronic spectra of the Co(II) complex around 14556 $cm^{-1}$ ($\nu_3$) arising from $^4A_2(F) \rightarrow {}^4T_1(P)$ as well as the magnetic moment value of 4.54 B.M., reveal the tetrahedral coordination of ligand around Co(II) ion (Nicholls, 1973 ; Duta and Syamal, 1992). The diamagnetism of the Ni(II) complex indicates an essentially square planar environment about Ni(II), which is in agreement with the electronic spectrum of the $[Ni(FABTZ)_2]Cl_2$ compound. The bands at 22727 and 15822 $cm^{-1}$ can be assigned to the transitions $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1A_2g$ , respectively (Lever, 1984 ; Duta and Syamal, 1992). The electronic spectrum of Cu(II) complex shows absorption bands at 19230 and 15698 $cm^{-1}$ assignable to $^2B_1g \rightarrow {}^2Eg$ and $^2B_1g \rightarrow {}^2A_1g$ transitions, supporting square planar configuration (Lever, 1984). These transitions, as well as the measured value of the magnetic moment ($\mu_{eff}$ = 1.77 B.M.)suggest a square planar stereochemistry of the compound (Duta and Syamal, 1992). Since the zinc and cadmium ions have $d^{10}$ configuration, the absorption at 25252 $cm^{-1}$ for the zinc complex and at 24570 $cm^{-1}$ for the cadmium complex could be assigned to a charge transfer transition (Radovanovic and Andjelkovic, 1997). However, taking into account the spectra and other physiochemical evidences, four-coordinated tetrahedral geometry is suggested for Zn(II) and Cd(II) complexes (Lever, 1984).

## CONCLUSIONS

In this paper we report the preparation, isolation and characterization of a bidentate Schiff base ligand derived from 2-furaldehyde and 2-minobenzothiazole (FABTZ), and its complexes with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The products were characterized by analytical analysis, magnetic and spectroscopic measurements data, one can estimate the stereochemistry of the prepared complexes : octahedral for the $[Fe(FABTZ)_2Cl_2]$ , square planar for the $[M(FABTZ)_2]Cl_2$ (M = Ni(II) or Cu(II)) and tetrahedral for the $[M(FABTZ)_2]Cl_2$ (M = Co(II), Zn(II) or Cd(II) compounds. The proposed structural formulas of these compounds are presented in figures 1,2, and 3.

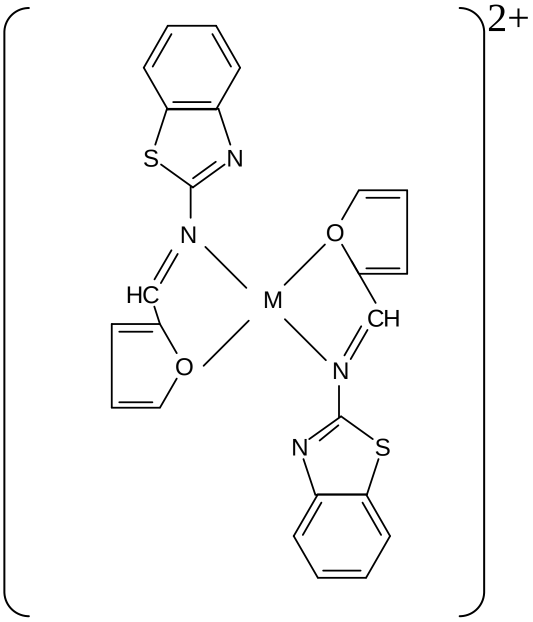

Fig. 1 : The proposed structure of the complexes $[M(L)_2]Cl_2$ (M = Ni (II) or Cu (II))

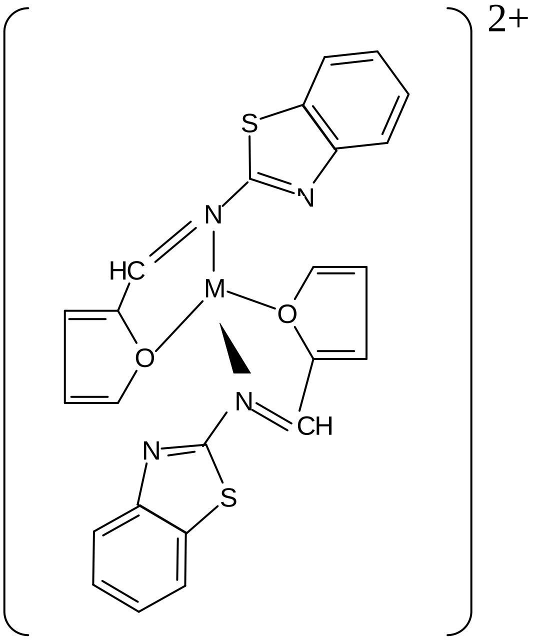

Fig. 2 : The proposed structure of the complexes $[M(L)_2]Cl_2$ (M = Co (II) , Zn (II) or Cd (II)).

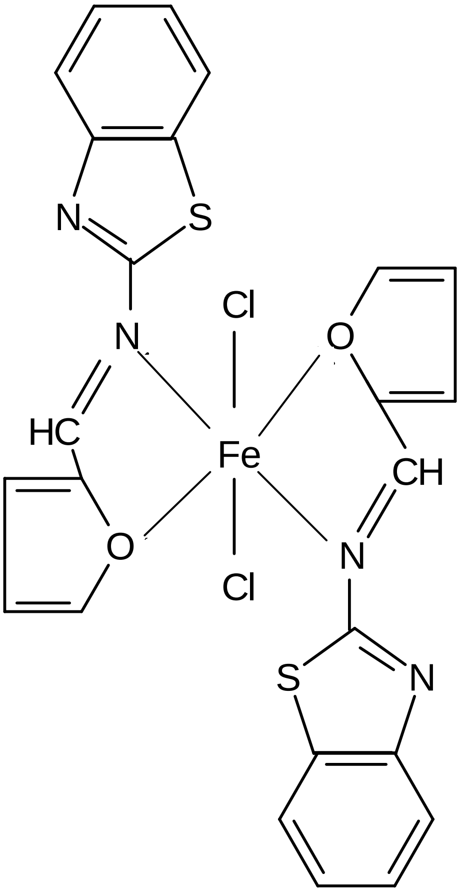

Fig. 3 : The proposed structure of the complex [Fe(L)$_2$Cl$_2$]

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