Synthesis and Characterization of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)Complexes with N,O-Donor Schiff base Ligand

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Abstract:
A series of complexes of the type $[ML_2Cl_2]$, where L = Schiff base formed by condensation of furfuraldehyde and 2-amino-4-methyl pyridine, M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), have been synthesized and characterized on the basis of metal content, molar conductivity, magnetic susceptibility measurements, electronic and infrared spectral studies. Infrared spectra of the complexes agree with the coordination to the central metal atom through the nitrogen of the azomethine group and the oxygen atom of the furan ring. Magnetic susceptibility data and electronic spectra suggest an octahedral structure for the Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes and tetrahedral geometry of the Zn(II) and Cd(II).

Key words: Transition metal ions,Bidentate Schiff base

Introduction:

Schiff base complexes have undergone a phenomenal growth during the recent years because of the versatility offered by these complexes in industry [1,2], catalysis [3] and
biological system[4]. Schiff bases containing nitrogen and oxygen donor atoms and their transition metal complexes play important role in inorganic and biological research. These complexes have studied extensively due to their unique coordination and biological properties[5,6].They have also been employed as anticancer, antihy-pertensive and anti inflammatory agents[7]. Hetrocyclic Schiff base complexes have promoted the interest in the development of bioinorganic chemistry[8] .
Biological active Schiff bases complexes with the formula $[M(LX)_2Y_2]$ where M = Co(II), Ni(II), Cu(II), Mn(II), LX=bidentate ligand derived from pyridine-2-aldehyde, furfuraldehyde, or thiophene-2-carboxy aldehyde with vinyl aniline, Y = Cl, have been prepared and characterized by physical spectra and analytical data and shows an octahedral geometry [9].The Schiff bases prepared by reacting 3-amino-5-methyl isoxazole with 5-methylfuran-2-carboxyaldehyde,5-methylthiophene-2-
carboxaldehyde and pyridine-2-carboxaldehyde with some transition metal chloride have been characterized and biological studied. On bases of IR, UV-VIS, ^1H, ^{13}C, mass spectra, magnetic and thermo gravimetric studies, six coordinated geometry is assigned for these complexes [10]. Synthesis and antimicrobial studies of transition metal complexes containing Schiff base derived from furfural, 4-amino antipyrine and o-phenylene diamine have been reported [11]. The complexes were characterized by IR, ESR, UV, NMR spectroscopy, data suggest square planar geometry araund metals. In this paper synthesis and characterization of transition metal
complexes containing bidentate Schiff base derived from furfural and 2-amino-4-methylpyridine is acheived

Experimental:

Materials and methods

All chemicals used in synthesis were of reagent grade (BDH, Fluka). All organic solvents were obtained as pure grade materials from BDH.

Instruments:

Magnetic susceptibility measurements were determined at 25° C using Bruker-BM6 apparatus. IR spectra of the ligand and complexes were recorded on an FTIR spectrophotometer type Burker Tensor 27 in the 400-4000 cm^{-1} range as KBr pellets. Electronic spectra were obtained using Shimadzu UV-160 spectrophotometer at 25° C in 10^{-3} M DMF.
Conductivity was measured by electronic conductivity device model PCM3-Jenwey for 10^{-3} M solution of the complexes in DMF. Metal content in the complexes were measured using Shimadzu AA67 atomic absorption spectrophotometer.

Preparation of the Schiff base (L)

A solution of 2-amino4-methyl pyridine (0.01 mole) in ethanol (20 ml) was added to a solution of furfuraldehyde (0.01 mole) in ethanol(20 ml) . The resulting solution was refluxed for 5 hours then allowed to cool to room temperature. The yellow precipitate formed was filtered , washed with ethanol, dried .

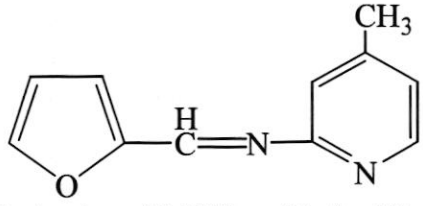

Fig .1: structure of Schiff base (Furfuralidene) 2-amino-4 methyl pyridine

Preparation of the complexes:

A solution of the Schiff base ligand (0.372 gm, 0.002 mol) in ethanol 50 ml was added to a solution of the metal salts (0.001 mol) in ethanol (50 ml) at pH 7-7.5. The reaction mixture was refluxed for 6 hours then left to cool, and the solid thus formed way filtered, washed several times with ethanol and dried.

Results and discussion

The resulting complexes are air stable, coloured solids. They are not soluble in ethanol, soluble in acetone and DMF, The low values of molar

conductivity (Λ) of the divalent Mn, Fe, Co, Ni and Cu complexes in DMF indicate non electrolyte behavior of these complexes with the exception of Zn(II) and Cd(II) complexes which are 2:1 electrolyses. The physical and analytical data of the Schiff base ligand (L) and the metal complexes are given in Table (1).

Table (1): Analytical and physical data of the ligand and their complexes.

No.	Compound	Colour	m.p (°C)	Yield %	Λ $ohm^{-1}.cm^2.mol^{-1}$	M % Calculated (found)
1	L	Yellow	186-188	85	-----	-----
2	MnL_2Cl_2	Red	213-215	70	26.52	11.02 (10.56)
3	FeL_2Cl_2	Brown	218-220	75	28.67	11.19 (10.73)
4	CoL_2Cl_2	Redis brown	190-192	78	32.88	11.73 (11.24)
5	NiL_2Cl_2	Green	248-250	85	19.95	11.69 (11.28)
6	CuL_2Cl_2	Dark green	214-216	82	25.34	12.54 (11.98)
7	$[Zn(L)_2]Cl_2$	White	232-234	74	138.24	12.85 (12.37)
8	$[Cd(L)_2]Cl_2$	White	244-246	88	145.66	20.23 (19.84)

I.R Spectra

The important infrared frequencies exhibited by the free ligand and the complexes are given in the (Table 2).

The comparison of the IR spectra of the Schiff base and their metal complexes indicated that the ligand was coordinated to the metal ions in two ways,thus acting as bidentate ligand.The strong band appearing at 1618 cm^{-1} due to υ (C=N) stretching vibration of azomethine group in the ligand is shifted to lower frequencies in the complexes indicating the participation of the azomethine nitrogen in coordination with the metals ions[12] .Another band at about 1280 cm^{-1} assigned to υ (C-O-C) stretching vibration of the furan ring is also shifted to lower values for all complexes suggesting the involvement of the furan ring oxygen in the coordination.Abroad band appearing at 1520 cm^{-1} corresponding to the υ (C=N) stretching vibration of the pyridine ring did not show a marked shift in the spectra of complexes suggesting non-involvemant of pyridine ring in bonding, further conclusive evidence of the coordination of the Schiff base with the metal ions was shown by the appearance of weak new bands at (504-5012 cm^{-1}) and (445-458 cm^{-1}) these were assigned to the metal –oxygen (M-O) and metal-nitrogen (M-N) vibration respectively and were observed in the spectra of the metal complexes and not in the spectra of the Schiff base ligand. Thus confirming participation of the O and N atoms in the coordination[13].

Table (2): Select I.R bands (cm^{-1}) of the ligand and complexes..

No.	Compound	υ (C=N)	Y ($C=N_{py}$)	υ (C-O-C) Furan ring	υ (M-O)	υ (M-N)
1	Schiff base(L)	1618	1520	1280	-----	-----
2	MnL_2Cl_2	1610	1522	1254	512	453
3	FeL_2Cl_2	1607	1520	1260	506	449
4	CoL_2Cl_2	1609	1521	1255	504	457
5	NiL_2Cl_2	1611	1520	1250	508	445
6	CuL_2Cl_2	1604	1522	1248	505	458
7	$[Zn(L)_2]Cl_2$	1602	1520	1262	506	446
8	$[Cd(L)_2]Cl_2$	1608	1520	1255	510	455

Magnetic moment and electronic spectra

The magnetic moment at room temperature of the Mn (II) complex was found to be (5.73) B.M indicative of five unpaired electrons in an octahedral environment [14]. The electronic spectra of Mn(II) complex don't show any d-d transition spectra as expected [15] . the magnetic moment value of Fe(II) complex was lie (5.04) B.M , correspond to octahedral geometry [16]. The electronic spectrum of the Fe(II) complex showed two bands. The band at 10930 cm^{-1} may be assigned to the $^5T_2g \longrightarrow {}^5Eg$ transition [17] and the other at 20510 cm^{-1} to change transfer [18]. Simitar types of transitions were reported for octahedral Fe(II) complexes.

The present Co(II) complex has magnetic moment (4.59) B.M suggest an octahedral geometry [19]. The absorption spectrum of the Co(II) complex show bands at 10980, 15985 and 20126 cm^{-1} attibuted to $^4T_1g \longrightarrow {}^4T_2g$,$^4T_1g \longrightarrow {}^4A_2g$ and $^4T_1g \longrightarrow {}^4T_1g$ transition respectively in an octahedral field[20].

The Ni(II) complex show magnetic moment value (2.96) B.M which agree with the known value for Ni(II) complex in octahedral geometry [21]. The Ni(II)

complex exhibited transitions at 11322, 17670 and 24955 cm^{-1} assignable respectively to the transitions $^3A_2g \longrightarrow {}^3T_2g$, $^3A_2g \longrightarrow {}^3T_1g$ and $^3A_2g \longrightarrow {}^3T_1g$ of octahedral geometry [22].

The magnetic moment value of Cu(II) complex was (1.98) B.M falls within the normal rang absorved for octahedral complex [23]. The Cu(II) complex show only one broad absorption band at 14548 cm^{-1} corresponding to the transition $^2Eg \longrightarrow {}^2T_2g$. That indicating an octahedral configuration [24,25]. The Zn(II) and Cd(II) complexes are diamagnetic and no d-d transition are expected [26-28].

Table (3): Magnetic moment and electronic spectral data of the complexes.

Compound	Magnetic moment B.M	Electronic spectra cm^{-1}
MnL_2Cl_2	5.73	------
FeL_2Cl_2	5.04	10930, 20510
CoL_2Cl_2	4.59	10980, 15985, 20126
NiL_2Cl_2	2.96	11322, 17670, 24955
CuL_2Cl_2	1.98	14548

On the basis of the above observations, it is suggested that the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes show an octahedral geometry but the Zn(II) and Cd(II) complexes show a tetrahedral geometry in which the Schiff base act as bidentate ligand and possibly accommodato itselve around the metal atom in such a way that stable chelate ring of the complex is formed hence, giving the following stable structure of the complexes.

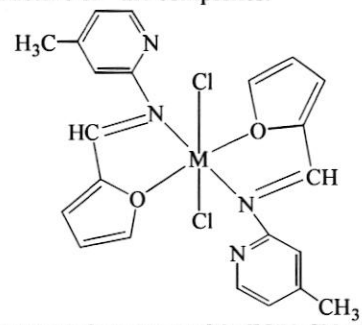

Fig. 1: The proposed structures of the $[M(L)_2Cl_2]$ complexes M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)

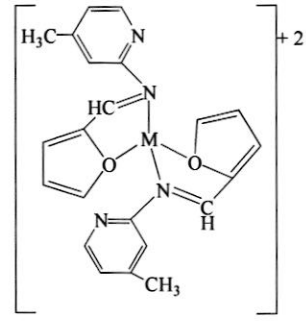

Fig. 2: The proposed structures of the $[M(L)_2]Cl_2$ complexes M = Zn(II) and Cd(II)

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.تحضير وتشخيص معقدات المنغنيز (II) والحديد (II) والكوبلت (II) والنيكل (II) والنحاس (II) والزنك (II) والكادميوم (II) مع قاعدة شيف مانحة اوكسجين ونتروجين

عامرة فارس محمد

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الملخص

يتضمن البحث تحضير وتشخيص عدد من المعقدات من النوع $[ML_2Cl_2]$ اذ ان L= قاعدة شيف محضرة من تفاعل الفورفورالديهايد مع 2-امينو-4-مثيل بريدين، M= Mn(II)، Fe(II)، Co(II)، Ni(II)، Cu(II)، Zn(II)، Cd(II) ، تم تشخيص المعقدات المحضرة بالتحليل العنصري والتوصيلية الكهربائية والقياسات المغناطيسية فضلا عن قياسات الاطياف الاليكترونية والاشعة تحت الحمراء. حيث اشارت قياسات الاشعة تحت الحمراء الى ارتباط الفلزات مع ذرة النتروجين لمجموعة الازوميثان وذرة الاوكسجين لحلقة الفيوران، اما قياسات المغناطيسية والاطياف الالكترونية فقد اشارت الى بنية ثماني السطوح لمعقدات Mn(II)، Fe(II)، Co(II)، Ni(II)، Cu(II)، وبنية رباعي السطوح لمعقدات Zn(II)، Cd(II).