Synthesis , Characterization and Theoretical Study of Some Transition Metal Complexes with Some Terpyridines

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Abstract

The present investigation involves the synthesis of new Co(II), Ni(II) and Cu(II) complexes from reaction Co(II), Ni(II) and Cu(II) chlorides with two terpyridines. One of the ligands act as tridentate and the other act as bidentate. All the prepared complexes were characterized by their metal analyses, IR and UV-vis spectroscopy, conductivity, magnetic measurements and theoretical study. Conductivity data in DMSO showed that some complexes are 1:2 (M:L) electrolytes which assigning the formula $[M(L_1)_2(H_2O)_2]Cl_2$ while the other complexes are non-electrolyte which assigning the formula $[M_2(L_2)_2Cl_4]$. Electronic spectral data and magnetic measurements showed that some of the complexes have octahedral geometry while the other complexes have tetrahedral geometry.

الخلاصة

يتضمن البحث تحضير معقدات Co(II) و Ni(II) و Cu(II) وذلك بتفاعل كلوريدات الكوبلت والنيكل والنحاس مع ليكانديين من التيربريدين وقد اتضح بان احد الليكاندات يعمل بشكل ثلاثي السن والاخر بشكل ثنائي السن. تم تشخيص جميع المعقدات المحضرة بطرق تحليل المعقدات وطيف الاشعة تحت الحمراء وفوق البنفسجية وكذلك قياسات الموصلية والمغناطيسية والحسابات النظرية. بينت دراسات الموصلية الكهربائية في مذيب ثنائي مثيل سلفوكساید ان بعض المعقدات ذات توصيلية الكتروليتية بنسبة 1:2 (M:L) واتخذت الصيغة $[M(L_1)_2(H_2O)_2]Cl_2$ واخرى غير موصلة واتخذت الصيغة $[M_2(L_2)_2Cl_4]$ وقد بينت القياسات المغناطيسية واطياف الاشعة فوق البنفسجية بان بعض المعقدات تمتلك بنية ثماني السطوح بينما المعقدات الاخرى تمتلك بنية رباعي السطوح.

Introduction

The coordination chemistry of nitrogen donor ligands in an activate area of research. Organic compounds containing a pyridine ring play an important role in many biological reactions [1].

Many transition and heavy metal cations play an active role in a great number of various biological processes,

being a component of several vitamins and drugs. Pyridinedicarboxylic acids and their derivatives belong to an interesting series of compounds with biological applications [2].

The ligand is an N,N,O donor in case of the Co(II) and Ni(II) complexes but N,N in the case of the Cu(II) complex. The ligand interacts also with Zn(II), Cd(II), Hg(II), As(III), Sb(III) and Bi(III) through N,N donor sites [3]. On other hand, ternary complexes of pyridine and quinoline were characterized spectroscopically [4].

Nayak *et al* [5] reported the preparation of mixed-ligand complexes of the type trans-$[Co(DH)_2LCl]$ where DH=dimethyl glyoximato anion, L=heterocyclic nitrogen donor ligand (pyridine, piperidine, quinoline, isoquinoline, indole) and their physico-chemical characterization.

The aim of this work is the synthesis and physico-chemical study of new cobalt(II), nickel(II) and copper(II) complexes with 4'-phenyl 3,2': 2',3"-terpyridine (L1) or 4'-phenyl 4,2': 2',4"-terpyridine (L2).

Experimental

Materials and Measurements

Benzaldehyde, 3-acetylpyridine, 4-acetylpyridne, ammonium acetate, glacial acetic acid, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ the remaining reagents were products from (BDH or Fluka) and used as supplied. The metal content was estimated spectrophotometer. Melting point were determined by using Buchi 510 melting point apparatus. Infrared spectra were recorded using Perkin-Elmer 580B spectrophotometer in the rang 4000-400cm^{-1} or 4000-200 cm^{-1} as KBr or CsI cells. The electronic spectra were recorded on Shimadzu UV.Visible spectrophotometer UV-160 for 10^{-3}M solution of the complexes in DMSO at 25C^o using 1 cm quartz. Conductivity measurements were carried out on 10^{-3}M solution of the complexes in DMSO using (PMC_3 (Jenway) conductivity model) at room temperature. Magnetic measurements were carried out on the solids by the Faradys method using Bruker BM6 instrument and AA670 for the determination of metal content. Theoretical computation were applied on the suggested structures of the prepared complexes using MM2 CS Chemoffice version 5.0. by Pentium (IV) computer.

1. Preparation of the ligands (L_1 and L_2)[6].

A mixture of (0.01 mol; 1.03gm) benzaldehyde, (0.02 mol; 2.42gm) 3-acetyl pyridine or 4-acetyl pyridine and (10gm) ammonium acetate in (50ml) of hot glacial acetic acid was refluxed for (1) hor. After adding of (100ml) of 25% aquious ethanol. The reaction mixture was cooled in ice bath and the white product which was first formed, was filtered and washed with mixture of (ethanol/benzene) (1:1) and dried in air and finally in discator.

2. Preparation of the complexes $[M(L_1)_2(H_2O)_2]Cl_2$, $[M_2(L_2)_2Cl_4]$

$MCl_2.nH_2O$ where M=Co(II), Ni(II) and Cu(II), (1 mol) and the ligand (2 mol) were added to about (25ml) of ethanol. The mixture was stirred at room temperature for (30) min and then warmed on water bath for (1) hor. The precipitated product was obtained which was filtered, washed with ethanol. The product was then washed with ether and dried in discator. Similar procedure for the preparation of the complexes $[M_2(L_2)_2Cl_4]$ but used (2:2) ligand to metal molar ratio.

3. Theoretical calculations

The optimizated geometry and steric energy of the prepared complexes were done using MM2 CS Chemoffice

5.0 molecular modeling program package. These calculations were performed using computer Pentium (IV) with processor operating at 2400 MHz.

Results and Discussion

The reaction of the ligands (fig. 1) with metal chloride in (2:1) ligand to metal molar ratio afford the complexes of the general formula $[M(L_1)_2(H_2O)_2]Cl_2$ while (2:2) ligand to metal molar ratio afford the complexes of the general formula $[M_2(L_2)_2Cl_4]$ (fig.2). The physical properties of the complexes are tabulated in table (1). They are quite stable in air and melt or decompose above 236C^o. They are insoluble in most organic solvent but soluble in DMF and DMSO.

Infrared spectra

The IR spectra of the complexes (table 2) show a medium band around (425-468)cm^{-1} which assigned to ν(M-N) indicating that the metal ion coordinated through nitrogen atom [7]. Furthermore the ν(M-Cl) band is observed at 294-348cm^{-1} indicating the coordination occur from chloro atom [8]. The IR spectra of the some complexes showed another band were observed at about (423-514) cm^{-1} which may be due to ν(M-OH_2) strehching vabration [9].

Electronic spectra and magnetic moments

The values of magnetic moment of Co(II) complex (no.1) is (4.76) B.M. The electronic spectrum (table 2) of Co(II) complex (no.1) show the presence of three bands in the region 10472-10651, 13108-15071 and 26182-27986 cm^{-1} are assigned to $^4T_1g(F)\rightarrow{}^4T_2g(F)(\nu_1)$, $^4T_1g(F)\rightarrow{}^4A_2g(F)$ (ν_2) and $^4T_1g(F)\rightarrow{}^4T_1g(P)$ (ν_3) transitions respectively. This show that the Co(II) complex have an octahedral geometry [8]. The Ni(II) complex (no. 2) show a magnetic moment of (3.04) B.M. The electronic spectra of the Ni(II) complex show the presence of three bands in the region 27028-28600, 12113-13151 and 10557-12502cm^{-1} which are assigned to $^3A_2g\rightarrow{}^3T_1g(P)$ (ν_3), $^3A_2g\rightarrow{}^3T_1g(F)$ (ν_2) and $^3A_2g\rightarrow{}^3T_2g(F)$ (ν_1) transitions respectively. This show that the Ni(II) complex have an octahedral geometry [9].

The Cu(II) complex (no. 3) show a magnetic moment (1.81) B.M. The electronic spectrum of the Cu(II) complex show the presence of a bands 12091-15340 and 27027-28601cm^{-1} which may assigned to $^2B_1g\rightarrow{}^2B_2g$, and $^2B_1g\rightarrow{}^2Eg$ transitions this show that the Cu(II) complex have an octahedral geometry [10].

The values of magnetic moment of Co(II) complex (no.4) is (4.01) B.M. The electronic spectrum of Co(II) complex shows abroad band at 11612 and 13324cm^{-1} due to $^4A_2\rightarrow{}^4T_1p$ (ν_3) transition due to spin orbit coupling similar to those reported for $[CoCl_4]^{-2}$ and $[CoI_4]^{-2}$ suggesting a tetrahedral geometry of Co(II) complex [11].

The Ni(II) complex (no.5) show a magnetic moment of (3.26) B.M. The electronic spectra of the complex show a band at 12016-12242cm^{-1} which correspond to the transition $^3T_1(F)\rightarrow{}^3T_1(P)$ (ν_3) in tetrahedral environment [12].

The Cu(II) complex (no.6) show a magnetic moment (2.15) B.M. The electronic spectra showed a band at 12988cm^{-1} which correspond to the transition $^2B_1g\rightarrow{}^2A_2g$ or $^2B_1g\rightarrow{}^3Eg$ and another band at 31200cm^{-1} correspond to charge transfer. This show that the Cu(II) complex has tetrahedral geometry [13].

Conductivity measurements

The molar conductivities of 10^{-3} solution of the complexes (table 1) indicate that the complexes (no 1-3) are

1:2 electrolytes in DMSO while the complexes (4-6) are non electrolyte [14].

Theoretical calculations

Theoretical calculations [15,16] have paid a considerable attention to the characterization and inferences of geometrical optomization of the prepared complexes, therefore we could obtained the optimized geometry for each complex by computing the minimum steric energy and the theoretical physical parameters, such as, bond length and bond angles using MM2 CS Chemoffice version 5.0 molecular modeling program. The steric energies of the some prepared complexes are listed in (table 3). The configuration of complexes (4, 5) and (6) (fig. 3, 4 and 5, respectively) were drawn here as an example with some selected calculated parameters (table 4, 5 and 6 respectively).

Table 1: Physical properties of the free ligands and complexes

Seq.	Compounds	Colour	m.p. ^oC	Cond. Λ_m $ohm^{-1}.cm^{-1}.mol^{-1}$	$\mu_{eff.}$ B.M.	M العملية / M (النظرية)
	L_1	White	209	-	-	-
	L_2	White	277	-	-	-
1	$[Co(L_1)_2(H_2O)_2]Cl_2$	Dark pink	226	78.1	4.76	(7.51) 7.46
2	$[Ni(L_1)_2(H_2O)_2]Cl_2$	Yellow green	236*	73.4	3.04	(7.49) 7.42
3	$[Cu(L_1)_2(H_2O)_2]Cl_2$	Brown	248*	69.7	1.81	(8.05) 7.98
4	$[Co_2(L_2)_2Cl_4]$	Yellow brown	286*	16.3	4.01**	(13.41) 13.31
5	$[Ni_2(L_2)_2Cl_4]$	Green	302*	9.8	3.26**	(13.38) 13.23
6	$[Cu_2(L_2)_2Cl_4]$	Dark blue	298*	13.6	2.15**	(14.31) 14.18

* Decomposition ** per metal ion

Table 2: IR spectra (cm^{-1}) and electronic spectra of the complexes

Seq.	ν(M-N)	ν(M-Cl)	ν(M-OH_2)	$M_{max.}$ (UV)
1	446 (w)	338 (s)	514 (m)	10472, 10582, 10651, 13108, 13232, 15071, 26182, 27986
2	425 (m)	309 (w)	423 (w)	10557, 11039, 12113, 12502, 13151, 27028, 28600
3	436 (m)	348 (s)	457 (m)	12091, 12124, 15340, 27027, 27981, 28601
4	468 (m)	328 (m)	-	11612, 13324
5	453 (m)	316 (m)	-	12016, 12242
6	462 (m)	294 (m)	-	12988, 31200

S=strong, m=medium, w=weak

Table (3): Computational steric energies of the ligands and some complexes

No.	Steric energy (Kcal/mol)
L_1	7.8371
L_2	7.6044
4	143.775
5	189.562
6	141.982

Table (4): Some selected calculated parameters of the complex (4), $[Co_2(L_2)Cl_4]$

	Selected calculated parameters	value
Bond Length (A^o)	Co_1-N_1	1.907
	Co_1-N_2	1.906
	Co_2-N_3	1.907
	Co_2-N_4	1.905
Bond Angle (^{o})	N_1-Co_1-N_1	38.7
	N_3-Co_2-N_4	38.6
	Cl_1-Co_1-Cl_2	109.1
	Cl_3-Co_2-Cl_4	108.1

Table (5): Some selected calculated parameters of the complex (5), $[Ni_2(L_2)_2Cl_4]$

	Selected calculated parameters	value
Bond Length (A^o)	Ni_1-N_1	1.889
	Ni_1-N_2	1.890
	Ni_2-N_3	1.889
	Ni_2-N_4	1.890
Bond Angle (^{o})	N_1- Ni_1-N_2	38.3
	N_3-Ni_2-N_4	38.3
	Cl_1-Ni_1-Cl_2	109.9
	Cl_3-Ni_2-Cl_4	109.9

Table (6): Some selected calculated parameters of the complex (6), $[Cu_2(L_2)_2Cl_4]$

	Selected calculated parameters	value
Bond Length (A^o)	Cu_1-N_1	1.892
	Cui_1-N_2	1.892
	Cu_2-N_3	1.891
	Cu_2-N_4	1.892
Bond Angle (^{o})	N_1-Cu_1-N_2	37.9
	N_3-Cu_2-N_4	37.9
	Cl_1-Cu_1-Cl_2	105.6
	Cl_3-Cu_2-Cl_4	105.7

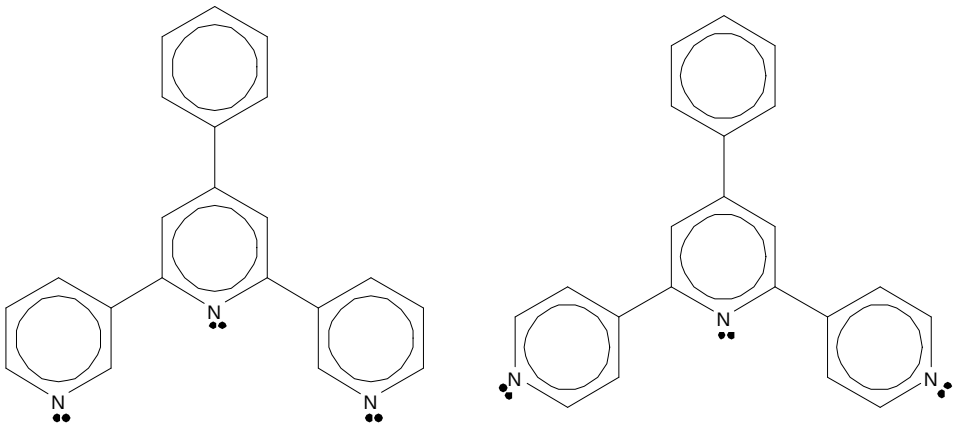
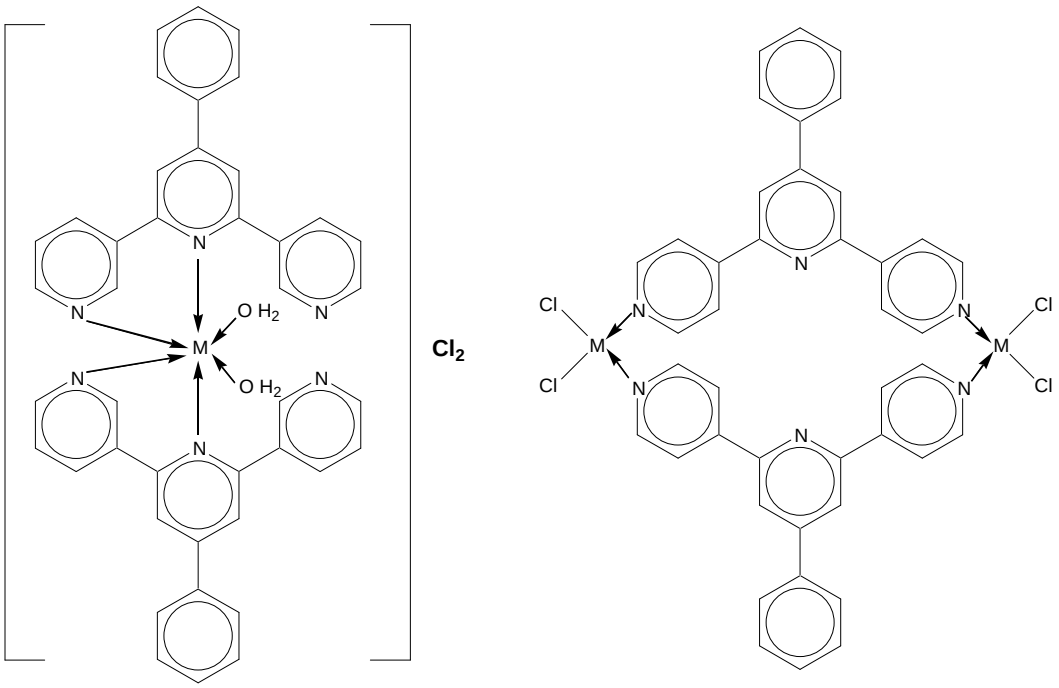


Fig. 1: The suggested structures of the ligands



$[M(L_1)_2(H_2O)_2]Cl_2$ $[M_2(L_2)_2Cl_4]$

M=Co(II), Ni(II), Cu(II)

Fig. 2: The suggested structures of the complexes

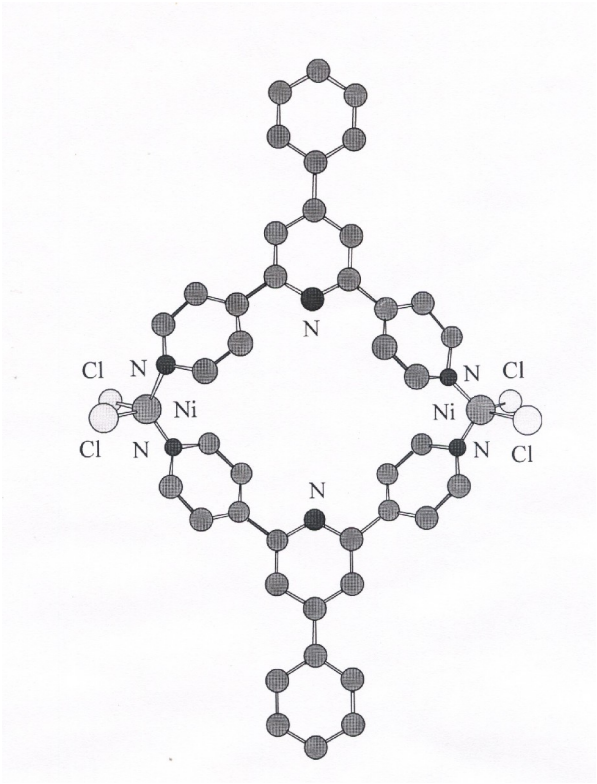


Fig. 3: Configuration of complex (4), $[Co_2(L_2)_2Cl_4]$ optimized by MM_2CS molecular modeling program package

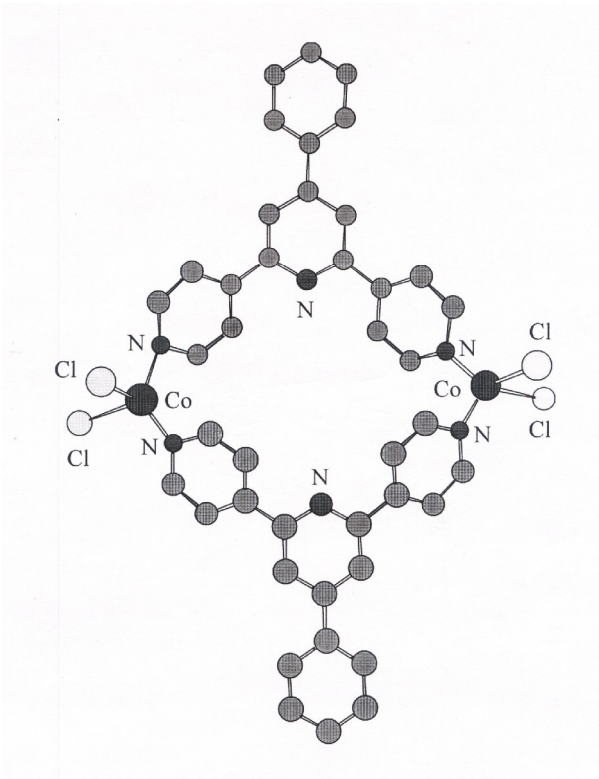


Fig. 4 : Configuration of complex (5), $[Ni_2(L_2)_2Cl_4]$ optimized by MM_2CS molecular modeling program package

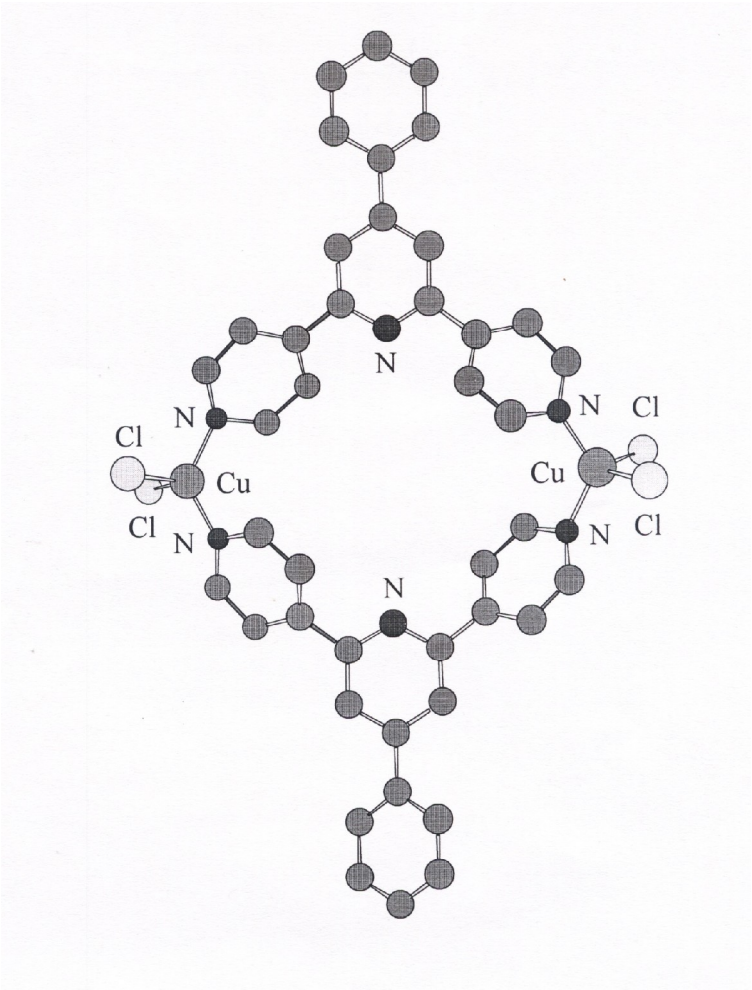


Fig. 5: Configuration of complex (6), $[Cu_2(L_2)_2Cl_4]$ optimized by MM_2CS molecular modeling program package

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