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Synthesis and Structural Studies of Transition Metals Complexes with Poly dentate Azo dye ligand Derived from Coumarine

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Abstract

The present work involves the synthesis and characterization of some transition elements complexes derived from (*E*)-3-((3-aminopyridin-2-yl) diazenyl)-4-hydroxy-2*H*-chromen-2-one as novel azo-Lewis base, LH. The new ligand was synthesized by coupling the diazonium salt of 2,6-diaminopyrimidine with alkaline solution of 4-hydroxy-coumarin. The new azo ligand was identified on the basis of C.H.N elemental analysis, EI-MS, NMR and FT-IR spectra. The direct reactions of hydrated chlorides of chromium (III), manganese (II), cobalt (II), nickel (II), copper (II) and zinc (II) with the [L] solution in ethanol solvent with variety of *PH* range of (7.5-8.0) and the mole ratio of ligand to metal ion 1:1 in all synthesized complexes. All the metal complexes were identified by flame atomic absorption spectroscopy, FT-IR and UV-Visible spectra. Furthermore, the molar conductivity and magnetic susceptibility measurements were carried out to confirm their molecular formulas, and their geometry. The data observed from elemental analyses, electronic spectra and magnetic moments revealed the octahedral environment around Cr (III), Mn (II), cobalt (II) and copper (II) ions in the formulas $[Cr(L)Cl_2(H_2O)]Cl$, $[M(L)Cl_2(H_2O)_2]$, M=Mn(II),Co(II) and Cu(II) while the nickel(II) and zinc(II) complex were tetrahedral geometry $[M(L)Cl_2].nH_2O$; M=Ni and Zn(II) and n=0 and 1 respectively. All the complexes were low soluble in DMF and sparingly in ethanol and common organic solvents which revealed the monomeric in nature structures of complexes and possessing metal-chloro bonding in the inner-sphere of complexes.

Keywords: Azo ligands of 4-hydroxycoumarin, metal complexes of coumarin ligands, Spectroscopic studies of azo-dyes complexes

1. Introduction

Transition metal complexes of coumarine and pyridine derivatives have been interesting in many fields of bio-inorganic chemistry due to the presence of azine and mercapto active sites [1-3]. The coupling of diazonium salts of pyridine and pyrimidine derivatives with the derivatives of 7-hydroxy-4-methylcoumarin have exhibited wide ranges of novel spectral studies and applications in the environment chemistry [4,5]. The enzymatic studies with the assistance of metal complexes based-coumarin azo dyes have been effective in investigation the pharmaceutical compounds and their mechanisms through *in vivo* and *in vitro* studies [6-8]. Furthermore, the presence of thiol, hydroxyl and azo functional groups in the structure of the poly dentate ligands have enhanced the physical and photo-chemical characterizations of complexes in solutions which encouraged the authors and scientists to prepare more derivatives due to their stability in certain *PH* and great applications in determination the trace amounts of heavy metals in solutions [9,10]. However, the spectroscopic and biological investigation of coumarin azo dyes have studied deeply by greet authors to put future applications in the microanalyses of trace toxic metals and drug industry [11-13]. The great interesting of bio-inorganic chemistry and pigments industry of azo-based coumarine ligands emerged us to carry out the synthesis of binuclear metal complexes with N_2O donor systems besides.

2. Experimental

2.1. Apparatus and Materials

The melting points of the prepared compounds were determined on Gallen Kamp melting point apparatus. The FT-IR spectra were carried out using Shimadzu FT-IR 8400S, College of Sciences, University of Baghdad. The mass spectra were measured for the derivative of 1,3,4-thiadiazole and the azo ligand [L] on Shimadzu model GC MS QP 1000EX were recorded at college of science, Mustansiriyah University. The electronic spectra of the prepared complexes and the free azo dye were carried out on

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(Varin Cary 100 Conc. UV–Vis) spectrophotometer at chemistry department, college of Science, Mustansiriyah University. The H and ^{13}C-NMR spectra for the free azo dye were done in *d6*-DMSO solvent using on Bruker-500 MHz NMR spectrometer at Jordan University, Amman, Jordan. All reagents and chemicals were commercially were used as received from suppliers. The chemicals like 2,6-diaminopyridine, 4-hydroxycoumarin and the hydrated metal chlorides of $CrCl_3.6H_2O$,$MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ were supplied from Sigma-Aldrich company.

2.2. Synthesis of (*E*)-3-((3-aminopyridin-2-yl)diazenyl)-4-hydroxy-2*H*-chromen-2-one (HL)

A cold solution of 2,6-diaminopyridine (2.85 g, 2 mmoles) in HCl (5mL) at temperature (0-5) C° was added to cold sodium nitrite (10 mL) with stirring for 20 minute. The mixture was stirred for 40 minutes with maintaining temperature at (0-5) C°. The excess of nitrous acid liberated spontaneously was removed by adding (0.25 g) of urea. Add the solution of diazonium to solution of (1mmol, 1.76gm) 4-hydroxycoumarin in (15) ml NaOH (10%) with stirring well for 30 minutes. , the *p*H of mixture was neutralized by adding HCl (10 wt %) filter the precipitate and washing with cold ethanol re crystallization from hot ethanol, Elemental Analysis; Calc.(Obs.): C, 59.55 (58.91); H, 3.57(3.01); N, 19.85(18.77);,Scheme (1).

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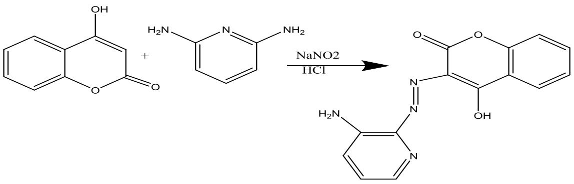


Scheme (1). Synthesis of azo dye

2.3. Synthesis of metal complexes derived from azo dye (HL)

Warm solution of $CuCl_2.2H_2O$ (0.282 g, 2 mmol) in (5ml ethanol +5ml distilled water) was stirred well and added (0.388 g,1 mmol) of HL dissolved in hot ethanol (5 ml), the mixture was heated with stirring under reflux at (75-80) ^{0}C for 1hour. the resulting precipitate filtrated then washed several times with warm water and ethanol then stand overnight for drying in a desicator, Scheme (3).

$2CuCl2.2H2O + HL \rightarrow [Cu(L)Cl(H2O)2]$+ Cl$^-$

Scheme (3). Synthesis of CuL complex

2.4. Synthesis of Mn(II), Co(II), Ni (II), Cu(II), Zn(II) and Cr(III) complexes:

The metal complexes of Mn (II) ,Co(II), Ni(II), Zn(II) and chromium(III) were isolated as colored precipitates through mixing 1:1 mole ratio (M:L) of their hydrated chlorides in ethanol with ethanolic solution of HL followed refluxing the mixtures on water bath for a certain periods of reaction depending on the type of metal ion ,then filtered off the crude and washing it several times with hot ethanol and water, dried over pellets of calcium chloride in desiccator, table (1)

3. Result and discussion

3.1. Physical Properties and elemental analyses:

Table (1) represents the physical properties and the elemental analyses of the synthesized ligand [HL] and its metal complexes. The observed data of CHN elemental analyses were in good agreement with the calculated values then confirm the suggested chemical formula of the prepared azo dye. The observed data from flame atomic absorption spectroscopy revealed that all complexes formed in 1:1 mole ratio of ligand to metal ion except that nickel (II) and zinc (II) complexes were formed by mixing equal ratios of the azo LH and the metal ions. All the complexes are sparingly soluble in common organic solvents and are soluble in DMSO and low soluble in DMF solvent [20,21]. The completion of reactions was followed and monitored by thin-layer chromatography by using silica-gel plates and mixtures of polar and non-polar solvents like (v/v 2:1) of ethyl acetate: hexane in azo-dye and intermediates preparation. However, the toluene and chloroform-methanol mixtures in (3:1 v/v) ratios were used to visualize the spots of formed complexes dissolved in DMF or DMSO solvents.

Table (1). Some physical properties and elemental analyses of HL and its complexes

Compound Molecular Formula	M.wt (g/mole)	M.P ^{0}C	Color	Yield %	%M*
HL $C_{14}H_{10}N_4O_3$	282.23	188-190	Dark orange	88	-
[CrLCl $(H_2O)_2$]Cl $C_{14}H_{14}Cl_2CrN_4O_5$	702.5	>300 Dec	Dark green	70	10.11 (9.66)
[MnLCl $(H_2O)_2$] $C_{14}H_{14}ClMnN_4O_5$	637.5	>290 Dec	Dark Green	85	9.18 (8.11)
[CoLCl $(H_2O)_2$] $C_{18}H_{15}Cl_3Co_2N_8O_5$	645	>311 Dec	Brown	88	8.20 (7.98)
[NiCl(L)]$2H_2O$ $C_{14}H_{14}ClN_4NiO_5$	645.5	>312 Dec.	Deep Green	90	11.88 (10.97)
[CuLCl$(H_2O)_2$] $C_{14}H_{14}ClCuN_4O_5$	656	292-294	Deep Green	90	12.02 (11.55)
[Zn (L)Cl] $C_{14}H_{13}ClN_4O_3Zn$	623.5	>222 Dec	Brown	85	13.961 (12.95)

*= M% was estimated by flame atomic absorption spectroscopy, Dec=decomposed

3.2. Mass Spectra:

The mass spectrum of azo-dye ligand showed peak at molecular ion *m/e*=283 which indicates the molecular weight of the expected $C_{14}H_{14}N_4O_3$ formula, then confirms formation of the azo dye [10]. The other fragments of azo dye, HL in the gaseous phase could be assigned to the departure of $–NH_2$ and –OH groups at around *m/*e=245 , *m/*e=199 and then breaking the –C-O of coumarin rings respectively [10,14]. As well as the agreement of the mass spectrum data with the elemental micro-analysis confirms the coupling of diazonium salt of 2,6-

diaminpyridine with the active –C3- atom of 4-hydroxycoumarine derivative [9,13], Figure (1).

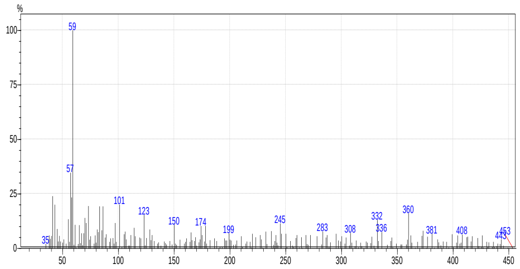


Figure 1. MS spectrum of azo ligand, LH

3.3. FT-IR Spectra:

The starting material 4-hydroxy-coumarin showed strong absorptions around (1750) and (1520-1620) cm^{-1} assigning to the carbonyl and –C=C- functional groups. The IR spectrum of the free azo ligand characteristic absorption abroad band 3271 cm^{-1} due to the stretching vibration of the hydroxyl group overlapped with hydrogen bonded $–NH_2$ at C_6 position of pyridine ring. Furthermore the strong band at 1687 cm^{-1} may be attributed to the stretching vibration of the carbonyl group –C=O of chromene-2-one ring and the other medium band at 1626 cm^{-1} is already belonged to -C=C-H of aromatic moiety [22]. As well as the strong sharp band at (1352-1396cm^{-1}) showed the wave number of (C-N) of pyridine ring in the compares of IR spectra of 2-amino pyrmidine with IR spectra of azo ligand shown absence of vibrations of amine group and appear the vibration azo group (N=N).The IR spectra of all azo complexes were showed the non-ligand bands observed at (600-515) cm^{-1} and (499-420) cm^{-1} due to region of (M-O) and (M-N) stretching vibrations .Furthermore the copper the IR spectrum are displayed medium bands of (N=N) at (1577) cm^{-1} besides the weak bands at 558-488) cm^{-1} ,Figures(2 & 3) which gives strong evidence for M-O and M-N bonding in all the prepared complexes. Furthermore, the appearance of broad bands in the regions (3358-3600) cm^{-1} reveals the presence of coordination water molecules [26].

3.4. H^1 NMR spectra and C^{13} NMR

The H NMR spectrum of azo ligand showed multiple peaks around (7.03-7.05) ppm assigning to the spin-spin coupling of pyriidine rings. The singlet absorption at 6.360 ppm is associated with the nuclear resonance of $H\text{-}C^2\text{=}C\text{-}$ of coumarin ring thereby confirms the coupling of hydroxy coumarin derivative with the diazonium salt of 2-aminopyrimidine. As well as the disappearance of resonance of –OH supports the exchange of acidic proton with the deuterium of d_6-DMSO solvent. The medium peak at 5.35 ppm was associated with the protons of $-NH_2$ directly related with pyridine ring. The multiple peaks at (8.02-8.75) ppm may be assigned to Py-H protons [13,15]. Furthermore the C^{13} NMR spectrum of [HL] in d_6-DMSO solvent. As well as the absorptions at 159.994 , 128.025, (152.7-153.7), 73.318 and 124-73.318 ppm which are assigned to the C=O, -C=N-, -C=C- and –C-O of 4-hydroxycoumarin and pyridine rings, whereas the peak observed at 13.029 ppm is preliminarily associated with the methyl $–CH_3$- at C4 of coumarin ring. The agreement of carbon atoms numbers with their positions confirms the suggested structure of the synthesized ligand [HL]. As well as the H NMR spectrum of ZnL complex in *d*6-DMSO solvent showed remarkable changes in the nuclear resonance of aromatic Ar-H protons at (6.5-7.80) ppm and absence of peak related to OH which supports the deprotonation the ligand up on coordination with the Zn(II) ion [16,17].

3.5. Electronic Spectra and Magnetic Susceptibility Measurements:

The electronic spectra of HL and its complexes were noted in ethanol and DMSO solution. The azo dye was detailed band at range 225 nm due to the interaction of ligand (π→π*) transition. The peaks at 347 was assigned to (n→π*) of (C=N-) group. The red solution of CrL complex in DMSO solvent displayed spin-allowed transitions around 430 and 342 nm and a high intensity peak at 226 nm, which are associated with the expected transitions of octahedral chromium(III) complexes $^4A_2g\rightarrow {}^4T_2g$, $^4A_2g\rightarrow {}^4T_1g(F)$ and LMCT respectively. The dark brown solution of manganese (II), MnL complex exhibited three absorptions around 430, 346 and 227 nm which were assigning to $^6A_1g \rightarrow {}^4Eg$, LMCT and π→π* transitions respectively. The cobalt (II) complex CoL solution displayed distinct spin-allowed peaks around 650, 450 and 342 nm and which are resulted from $^4T_1g\rightarrow {}^4T_2g$ (F), $^4T_1g\rightarrow {}^4A_2g(F)$ and LMCT respectively, then supports the octahedral environment around cobalt(II) ion[19,23]. As well as the nickel (II) complex NiL showed three peaks at 780,500 and 280 nm supporting the$^3T_1\rightarrow {}^3T_2$ (F) ,$^3T_1\rightarrow {}^3T_1$ and LMCT respectively, and the lowering in energies of d-d spectra is consistent with the tetrahedral geometry of nickel(II) complexes. Furthermore the absorptions around 375 and 950 nm of copper(II) complex may be assigned to MLCT and $^2Eg \rightarrow {}^2T_2g$ of distorted octahedral .The observed magnetic moments for chromium(III) complex was 3.88 BM confirmed the presence of three odd electrons in the outer shell of Cr(III) ion of the expected octahedral complexes. As well as the enhancement in the magnetic susceptibility values for cobalt (II) and nickel(II) complexes in the range 5.02 and 2.47 BM confirmed the orbital contribution of high-spin octahedral cobalt(II) complex and the tetrahedral nickel(II) of ^4e $^4t_2$ configurations respectively[10,22]. In addition of the red solution of Zinc (II) complex in DMF exhibited four intense peaks around 410, 346 and 229nm these are assigned to MLCT ,n-π* and π-π* transitions respectively these confirm its geometry [20,21].

3.6. UV-Vis Spectral Study of Cu(II)-[HL] Solutions:

Th reaction of copper (II) chloride with the azo dye ligand have been studied spectra photo metrically in solution. As soon as Cu(II) salt solution was added, the orange HL solution was rapidly changed to dark-brown and the changes in the spectra appear immediately after mixing. A great bath chromic shift (~375nm) in the visible region was detected in the complex solution spectra according to that of the free ligand. The comparison of electronic spectra between the azo dye in ethanol solvent with its copper(II) complex at variable pH have taken in considerations to give at least simple study for complexes formation in solution and then supports the well-agreement with their solid structures [22,23]._Figure (2) shows the relationship between the measured absorbance against molar ratio of the two components of CuL complex.The measurements have been held at the optimal pH, concentration and wave length. The result indicates the formation of (1:1) (metal: ligand) ratio for CuL complex formed at pH = 7.5.

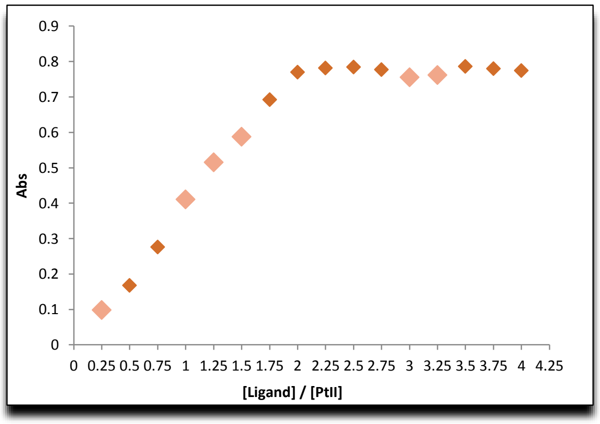
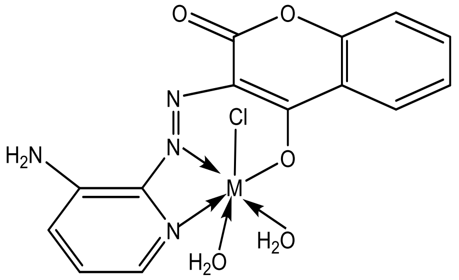


Figure (2). Mole ratio of CuL complex at 375 nm

4. Conclusions:

The observed data from elemental analyses, NMR , FT-IR , UV-visible spectra and magnetic moments, the structures of chromium(III), manganese, cobalt, nickel, copper and zinc(II) complexes with azo-dye coumarin based ligand (*E*)-3-((3-aminopyridin-2-yl)diazenyl)-4-hydroxy-2H-chromen-2-one were octahedral geometry through active sites of the azo ligand NNO system with deprotonation the hydroxyl moiety in C-4 of coumarin ring. As well as the nickel(II) and zinc(II) complexes were tetrahedral as shown in figure (3). As well as the UV-Visible study for copper(II) complex on the basis of mole ratio method confirmed the evidence for the chemical formula for all complexes and the optimum conditions of their preparation in the solutions.



M=Mn(II),Co(II) and Cu(II)

Figure (3). Geometrical structures of the synthesized complexes

Conflict of Interest:

"There are no conflicts to declare about publication this paper".

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