

Synthesis and Characterization of New Mn(II), Co(II), Ni(II) and Cu(II) Complexes with [α -methyl-N-(3-methylidene indol)-2-amino anthraquinone] Ligand

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Abstract:

The present investigation involves the synthesis of new Mn(II), Co(II), Ni(II) and Cu(II) complexes with L=[α -methyl-N-(3-methylidene indol)-2-amino anthraquinone] in (1:1) and (1:2) metal to ligand molar ratio to give complexes with the general formulae $[MLCl_2]$ and $[M(L)_2Cl_2]$. The complexes were characterized by conductivity measurement, IR and UV-Vis spectroscopy, magnetic measurements and metal content analysis. Conductivity measurement indicated that all complexes were nonelectrolyte, while the magnetic moment and electronic spectra indicated that some complexes have a tetrahedral geometry and the others have an octahedral geometry. This study shows that the ligand behaves as a bidentate chelating ligand.

تحضير معقدات جديدة للـ Mn(II) و Co(II) و Ni(II) و Cu(II) مع [الفا- ميثيل-N-(3- ميثيليدين اندول)-2-امينوانثراكوينون] ليكاند وتشخيصها

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ملخص البحث :

يتضمن البحث تحضير معقدات جديدة للـ Mn(II)، Co(II)، Ni(II) و Cu(II) مع ليكاند من نوع L = [الفا- ميثيل-N-(3- ميثيليدين اندول)-2-امينوانثراكوينون] بنسب مولية

(1:1) و (2:1) فلز: ليكنند لتكوين معقدات ذوات الصيغ العامة $[MLCl_2]$ و $[M(L)_2Cl_2]$. تم تشخيص المعقدات المحضرة بوساطة قياسات التوصيلية الكهربائية المولارية وأطياف الأشعة تحت الحمراء وفوق البنفسجية المرئية والقياسات المغناطيسية وتعيين المحتوى الفلزي. بينت قياسات التوصيلية الكهربائية المولارية أنّ المعقدات غير موصلة. وبينت الأطياف الإلكترونية والعزوم المغناطيسية بأنّ قسماً من المعقدات يمتلك بنية رباعية السطوح والأخرى تمتلك بنية ثمانية السطوح. وقد اظهرت هذه الدراسة ان الليكاند يسلك سلوكاً ثنائي السن .

Introduction:

The role of Schiff bases in coordination chemistry has been extensively studied and was quite satisfactory elucidated⁽¹⁾. A large variety of a cyclic and macrocyclic Schiff bases have been designed and synthesized and the ability of these systems to be encapsulated into their coordination moiety metal ions, giving rise to mononuclear or polynuclear compounds, has been investigated in details^(2,3). Metal complexes of Schiff bases have attracted considerable attention due to their remarkable importance in medicinal and pharmaceutical field. They show biological activities including antibacterial, antifungal anticancer and herbicidal activities⁽⁴⁾.

A new coordinated compounds⁽⁵⁾ of manganese (II), iron (II), cobalt (II), nickel (II), copper (II), tin (II), mercury (II), iron (III) and dioxouranium (VI) with Schiff bases derived from (7-formyl-8-hydroxyquinoline and 2- amino phenol) (H_2L^1) or (2-amino pyridine) (HL^2) were described. Their IR and NMR studies showed that the Schiff bases behaved as mono-dibasic and tridentate ligands.

Canpolat *et.al*⁽⁶⁾ prepared complexes of (5- hydroxyl salicyliden-p-amino acetophenoneoxime) (LH) with Co(II), Ni(II), Cu(II) and Zn(II) salts in (1:2) metal to ligand molar ratio. Their structures were elucidated on the basis of elemental analysis, IR,¹H and ¹³C-NMR, electronic

spectra, magnetic susceptibility measurement, molar conductivity and thermogravimetric analysis .

A novel Schiff bases,⁽⁷⁾ 1-[(2-hydroxy-5-bromo-benzylidene)-amino]- anthraquinone, 1-[(2-hydroxy-5-methyl-benzylidene)amino]-anthraquinone and 1-[(2- hydroxyl-5-nitro- benzylidene)-amino]-anthraquinone have been synthesized and have been used as flourid ion sensors.

Binuclear complexes ⁽⁸⁾ of Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff bases bis-[4-hydroxycuomarin-3-yl]-¹N,⁵N-thio carbohydrazone (H₂L), were characterized by elemental analysis, ¹H-NMR, mass spectrometry, infrared and electronic spectra, as well as room temperature magnetic susceptibilities.

Khaledi *et.al* ^(9,10) studied the structure of copper (II) [Cu(C₁₇H₁₄N₃S₂)₂].2C₃H₇NO and palladium (II) [Pd(C₁₇H₁₄N₃S₂)₂].2C₃H₇NO complexes by x-ray diffraction and they showed that the Cu and Pd atoms are chelated by N, S of the deprotonated, Schiff bases forming distorted square- planer geometries around the Cu and Pd atoms.

Ni(II) and Co(II) complexes of the type [HLCu₂Cl₃], [HLCu₂O(CO)(CH₃)₃], [HLM₂Cl₄(H₂O)₃] and [HLM₂(OC(O)CH₃).4H₂O)₃] had been prepared. ⁽¹¹⁾ Electronic and magnetic moments of these complexes indicate that the geometries of the metal centers are either distorted octahedral, or square planer.

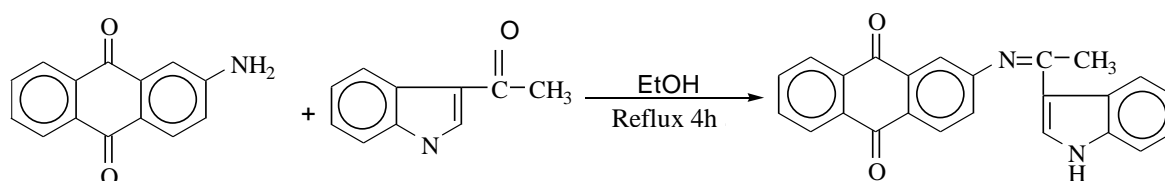
In the present work, the synthesis and characterization of the new Schiff base [α -methyl-N-(3-methylidene indol -2- amino an thraquinone] and its complexes Mn(II), Co(II), Ni(II) and Cu(II) in (1:1) or (1:2) metal to ligand molar ratio had been described in details.

Experimental:

IR spectra were recorded on spectrophotometer Tensor 27 Co. Bruker (FT-IR) in the (4000-200 cm^{-1}) range using Nujol mulls or CsI disc. The metal content was estimated spectrophotometrically using Shimadzu AA670 spectrophotometer. Conductivity measurements were made on 10^{-3}M solution of the complexes in dimethyl formamide (DMF) solvent at ambient temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV-Vis spectrophotometer UV-160 for 10^{-3}M solution of the complexes in DMF using 1cm quartz cell. The magnetic measurements were carried out at 25°C on the solid by Faraday's method using Bruker BM6 instrument.

Preparation of ligand:

Schiff base ligand was prepared by mixing ethanolic solution (20 cm^3) of (3-acetyl indol) (0.16 g, 1mmol) with (0.22g, 1mmol) of (2-aminoanthraquinone) in ethanol (20 cm^3). The mixture was refluxed for 4h. The precipitate was obtained after evaporation of solution to about 1/3 of its volume, which was filtered off, washed with ethanol then ether and recrystallized from ethanol. This ligand synthesis is shown in the following equation :



Preparation of complexes:

1- Preparation of $[\text{MLCl}_2]$ complexes ($\text{M}=\text{Mn(II)}$, Co(II) , Ni(II) , Cu(II)) :

Ethanolic solution (20 cm^3) of [α -methyl-N-(3-methylidene indol) - 2-amino anthraquinone (0.37g, 1mmol) was added to an ethanolic

solution of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.16g, 1mmol). Then the mixture was refluxed for 2h., with continuous stirring. The mixture was cooled to room temperature and the solid formed was filtered off, washed with ethanol and diethyl ether then dried under vacuum for several hours. Similar procedure were used for the preparation of Co(II), Ni(II), Cu(II) complexes. The weight of the metal salt in relation to the weight of ligand is shown in table (1).

Table (1) : The weight of metal salt and ligand used.

salt	w(g) of metal salt	w(g) of ligand
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.24	0.37
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	0.24	0.37
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	0.17	0.37

2- Preparation of $[\text{M}(\text{L})_2 \text{Cl}_2]$ complexes (M=Mn(II), Co(II), Ni(II), Cu(II)) :

A solution of $[\alpha\text{-methyl-N-(3-methylidene indol)-2-amino anthraquinone}$ (0.74g, 2mmol) in ethanol (20 cm^3) was added to a solution of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) in (20 cm^3) ethanol. The mixture was refluxed for 2h., with continuous stirring, the precipitates were obtained after evaporation of solution to about 1/3 of its volume, which was filtered out, washed with ethanol and diethyl ether, then dried under vacuum for several hours.

Results and Discussion :

The direct reaction of [α -methyl-N-(3-methylidene indol)-2-amino anthraquinone] with Mn(II), Co(II), Ni(II) and Cu(II) ions in ethanol using (1:1) or (1:2) metal to ligand molar ratio afford complexes of the type $[MLCl_2]$ and $[M(L)_2Cl_2]$.

The prepared complexes are colored solids, stable in air at room temperature. The chemical analytical data of the synthesized complexes are listed in table (2). Molar conductance of the complexes in DMF are within the range of (8-28) ($\text{ohm}^{-1}.\text{cm}^2.\text{mol}^{-1}$) and it indicated that all complexes are nonelectrolyte. ⁽¹²⁾

IR Spectra :

The IR spectra analysis gave information about the mode of coordination of the ligand to the metal ions. The characteristics bands are presented in table (3). The ligand spectrum showed an absorption bands at 1621 and 1673 cm^{-1} that assigned to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{O})$ respectively. ^(13,14) The position of the band corresponding to $\nu(\text{C}=\text{N})$ vibration group is shifted to lower values in the spectra of the complexes indicating that the C=N nitrogen atom shared in coordination with metal ion in these complexes, ^(15,16) whereas the $\nu(\text{C}=\text{O})$ absorption shift to lower frequency indicated that the ligand coordinated to the metal ions through the oxygen of the carbonyl group. ^(14,17)

New bands which are not present in the spectrum of the prepared ligand, were appeared at the region (420-470) and (473-514) cm^{-1} , which were attributed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations respectively, indicating that the ligand coordinated through the azomethine nitrogen and the carbonyl oxygen. ^(15,18,19)

Furthermore the IR spectra of all complexes showed a new band in the region (315-340) cm^{-1} which may be due to $\nu(\text{M}-\text{Cl})$ vibration. ^(20,21)

Electronic spectra:

The electronic spectra of the ligand contained an absorption bands in (22727 - 36496 cm^{-1}), (table 3), which can be assigned to $n \rightarrow \pi^*$ transition of the C=O and C=N chromophore groups, and $\pi \rightarrow \pi^*$ transition of the benzene ring of the ligand. ⁽¹⁵⁾

The electronic spectra of the Mn(II) complexes (1) tetrahedral and (5) octahedral geometries showed different bands, (table 3), which were attributed to the charge transfer transitions, ^(17,22,23) since the ground state for both are 6A_1 .

The Co(II) complex (2) showed a band in the visible region (14925 cm^{-1}), which correspond to a transition ${}^4A_2(F) \rightarrow {}^4T_1(P)$ in the tetrahedral geometry ^(19,24) and other bands at (22321, 27624) cm^{-1} region which could be attributed to charge transfer transition.

Cobalt (II) complex (6) gave three bands at (10845, 14970, 20421) cm^{-1} which were attributed to transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ respectively. These values indicated that the geometry for this complex is octahedral. ^(23,25)

The electronic spectra of the Ni(II) complex (3) showed a band at (13645) cm^{-1} region due to the transition ${}^3T_1(F) \rightarrow {}^3T_1(P)$ ν_3 in tetrahedral geometry ^(26,27) and the other bands at (24509, 37037) cm^{-1} which could be assigned as charge transfer transition, whereas the Ni(II) complex (7) showed the presence of three transition bands at (10416, 15321, 28409) cm^{-1} regions assignable to transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively. ^(26, 28) These bands are consistent with the octahedral geometry of the complex.

Cu(II) complex (4) showed a broad band at (10922) cm^{-1} due to the transition ${}^2T_2 \rightarrow {}^2E$ which indicated that the complex has tetrahedral

structure and other transitions at (22522, 32051) cm^{-1} can be attributed to charge transfer transitions ^(6,29).

Cu(II) complex (8) also showed the presence of one broad band at (13291) cm^{-1} which results from union of three transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ in the electronic spectra, point out the octahedral geometry, while other transition at (33585) cm^{-1} could be due to charge transfer transition. ⁽³⁰⁾

Magnetic measurements:

The results of the magnetic measurements are presented in (Table 2). The magnetic moment of Mn(II) complex (1) was (5.64) B.M which is characteristic for a tetrahedral environment while the complex (5) had magnetic moment of (5.89) B.M which was attributed to high spin octahedral geometry. ^(16, 17)

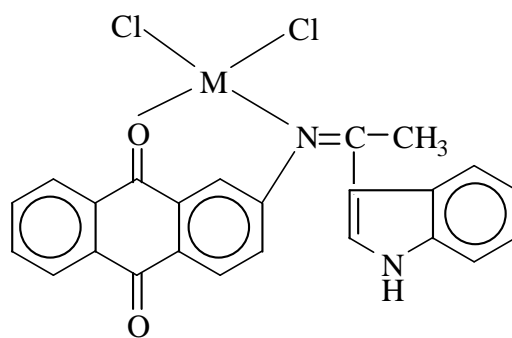
The Co(II) complex (2) possess a magnetic moment value of (4.27) B.M which is corresponding to tetrahedral geometry, this high value is due to the 2nd-order orbital contribution, while Co(II) complex (6) showed magnetic moments value of (4.75) B.M and this high value is due to the orbital contribution in high spin octahedral geometry. ^(18, 19, 23)

The magnetic moment of Ni(II) complex (3) was (3.35) B.M and this value is typical of tetrahedral environment around the nickel.

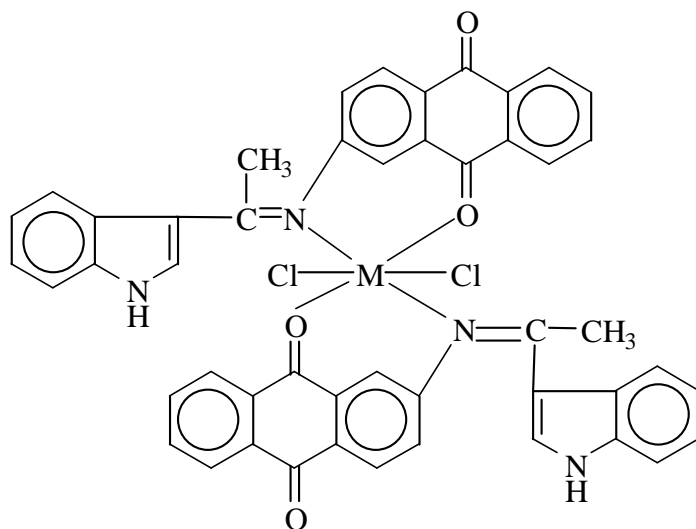
Complex (7) had a magnetic moment (3.10) B.M which correspond to the octahedral geometry. ⁽³¹⁾

The Cu(II) complexes (4,8) which had magnetic moments (2.15 and 1.8) B.M which were in agreement with tetrahedral and octahedral environment respectively. ^(6,32)

From the above discussion, the following structures, shown in figure 1, can be suggested for the prepared complexes in this work.



Complexes No. (1,2,3,4)



Complexes No. (5,6,7,8)

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

Fig 1: Suggested Structures for the complexes

Table (2) : physical properties of the ligand and the complexes.

No.	compound	colour	M.p (C)	Yield %	Analysis found	Λ_M in DMF (ohm ⁻¹ . mol ⁻¹ . cm ²)	Meff (B.M)
					M % / cal. (found)		
L	C ₂₄ H ₁₈ O ₂ N ₂	Dark brown	270	86	----	----	----
1.	[Mn L Cl ₂]	Brown	152-154	80	11.16 (11.10)	17.0	5.64
2.	[Co L Cl ₂]	Dark green	200°d	93	11.88 (11.93)	22	4.27
3.	[Ni LCl ₂]	Orange	308-310	86	11.84 (11.79)	8.0	3.35
4.	[Cu LCl ₂]	Dark brown	206-210	75	12.69 (12.76)	10.2	2.15
5.	[Mn (L) ₂ Cl ₂]	Pale yellow	116-120	85	6.40 (6.48)	15	5.89
6.	[Co (L) ₂ Cl ₂]	Green	214°d	82	6.83 (6.76)	28	4.75
7.	[Ni (L) ₂ Cl ₂]	Pale brown	157-160	90	6.81 (6.78)	13	3.10
8.	[Cu (L) ₂ Cl ₂]	Brown	140-143	88	7.30 (7.25)	21	1.80

d= Decomposition temperature.

Table (3) : Electronic and IR spectra data of the ligand and the complexes

No.	IR band assignments (cm ⁻¹)					UV. Visible band λ max (cm ⁻¹)	
	ν (C=N)	ν (C=O)	ν (M-O)	ν (M-N)	ν (M-Cl)	d→d	C.T
L	1621	1673	----	----	----	22727 (n→π*), (32797- 36496) (π→π*)	
1.	1612	1650	432	514	315	----	20275, 26218, 31250
2.	1605	1637	464	474	322	14925	22321, 27624
3.	1607	1650	461	481	340	13645	24509, 37037
4.	1605	1663	420	474	334	10922	22522, 32051
5.	1611	1660	422	513	339	----	22222, 28409, 33783
6.	1607	1649	462	473	300	10845, 14970, 20421	-----
7.	1608	1637	422	513	324	10416, 15321, 28409	-----
8.	1605	1650	470	512	315	13291	33585

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