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Preparation and Physico-Chemical Investigation Studies for the of Mn(II),Co(II),Ni(II) and Cu(II) Metal Complexes with Ligand 2- Hydroxybenzaldine Urea

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Abstract :

Some of metal compounds have been synthesized of record ligand from aldehid interaction of a substance which is salicyladehyde with another material which is urea. During the analysis of the metal component, The prepared complexes were characterized by elemental analysis, IR ,UV-visible , conductivity and magnetic susceptibility measurements. this confirms the ratio[1:1] between the metal and ligand. It is found that theortical values agree with practical values All the studied complexes are suggested as an octahedral stereochemistry.

Key Words: Schiff base complexes, Transition metals and Octahedral stereochemistery

Introduction:

Schiff base ligands are potentially capable of forming stable complexes with different metal ions [1]. Because of the facile synthesis of Schiff bases, many ligands of diverse structure types have been synthesized. Schiff base can accommodate different metal centers involving variouscoordination modes thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry [2]. Now adays, Schiff bases are attracting biochemist as they are known to be medicinally important and are used to design medicinal compounds [3]. It has been reported that the biological active compounds show greater activity when administered as metal complexes than as free organic compound [4]. The azomethine (C=N) linkage in Schiff bases imports in elucidating the mechanism of transamination and resamination reactions in biological system [5]. The coordination compounds display a large diversity offered by the great variety of metal centers and ligand shapes [6] . In modern coordination compounds almost all organic and inorganic compound can be used as ligands, then the design and synthesis of coordination compound have attracted much attention from chemists [7] . The cyclic systems containing carbon atoms and at least one

other element are called heterocyclic such as furan, pyrrol, oxazol, thazole, thiazole, pyrazole, and pyrrolidine [8]. We have prepared and the diagnosis of several compounds of some metallic ions consisting of interaction ligand record of the amino acid interaction Al tyrosine with a salicyladehyde and through several diagnostic techniques found that these compounds possess octahedral shape [9] .

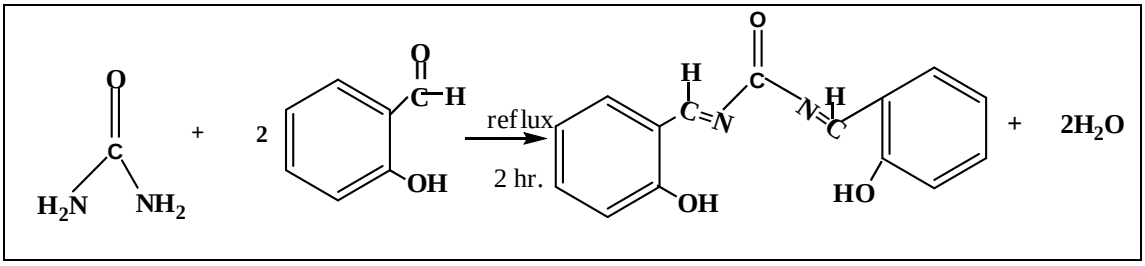
Materials and Methods:-

Materials and Instrumentation

All materials, used in this investigation were purchased from Sigma / Aldrich and used as received, salicylaldehyde, urea, metal salts ($MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$), (C_2H_5OH),(DMF), (NaOH), and distilled water was used during the experimental procedures. The FT-IR for ligand and their metal complexes were recorded in the range 4000-400 cm^{-1} as a (KBr) disc on IR-Prestige-21,Single Beam Path Laser Shimadzu Infrard Spectrophotometer (FT-IR) -8300. Using instrument with specifications UV-1650 PC Shimadzu in the range 1100-200 nm, it was measured UV spectrum of the compounds prepared . At room temperature, the magnetic sensitivity of the complexes prepared values are measured by Apparatus Balance Magnetic Suceptibility Model MSB- MKT. When dissolved, 0.001 M of prepared complexes in ethanol absolute solvent, It was measured molar conductivity using Pw –Digital Meter of Conductivity, using the Stuart Melting Point Apparatus measured the melting point of ligands and prepared complexes.

Preparation of Schiff Base (L) [10]

Dissolved (0.02 mole, 2.47g) of salicyladehyde in the 25 cm^3 of absolute ethanol, and in the same volume of solvent dissolved (0.01mole,0.66g) of urea, mixing the solution and added three drops of solution sodium hydroxide, heating the mixture with refluxing for 2 hours, then obtaind to precipitate of ligand, Table (1) show the physical properties for prepared ligand. And the rout of preparation of ligand (L) illustrated in Scheme (1).



Scheme (1): Shows the rout of preparation 2-hydreoxybenzaldine urea (L)

Preparation of Complexes

By using the absolute ethanol as a solvent in the complexes prepared method, dissolved 0.01 mole of metal ions Mn(II),Co(II),Ni(II) and Cu(II) [2.45, 3.15, 2.78 and 1.67] g. respectively in 15 ml of solvent, mixing this solution with solution of ligand, heating the mixture with refluxing for 1 hr. ,then the obtaind the precipitate of complexes, the physical properties of complexes are shown in Table(1).

Results and Discussion

Microanalysis

Table(1) comprises is the found data which in a good agreement with those theoretical ones, and the obtained analytical data indicate the formation of 1:1 [M: L] complexes.

Table 1: Molecular formula, Physical Properties and atomic of spectrum of the Schiff base and its complexes

Compounds	M.W g.mol^{1-}	color	M.P.C^0	Yield %	Elemental analysis Found(Calc.)			Metal % M Found (Calc.)	Cl% Found (Calc.)
					%C	%H	%N		
$C_{15}H_{12}N_2O_3$ (L)	268	Yellow	105	65	67.55 (67.16)	4.51 (4.47)	10.21 (10.44)	-	-
$[MnL(H_2O)_2].H_2O$	375	Light brown	210	62	48.71 (48.00)	4.53 (4.26)	7.93 (7.46)	14.27 (14.66)	Nil
$[CoL(H_2O)_2].H_2O$	379	Green	185	85	47.63 (47.49)	4.12 (4.22)	6.94 (7.38)	15.13 (15.56)	Nil
$[NiL(H_2O)_2].H_2O$	378	Light green	180	70	47.13 (47.61)	4.88 (4.23)	7.62 (7.40)	15.92 (15.34)	Nil
$[CuL(H_2O)_2].H_2O$	383	Light green	140	55	46.17 (46.99)	3.78 (3.13)	7.86 (7.31)	16.63 (16.44)	Nil

Infrared Spectra

IR spectrum for the prepared ligand 2-hydroxybenzaldine urea L exhibit a broad band at 3329 cm^{-1} may be due to intervention of the two OH phenolic groups[11]. The range 3395-3205 cm^{-1} indicates the broad band of free Schiff base ligand in region 3329 cm^{-1} .It split and shifted,this divided in ligand bands suggest the atom oxygen in phynolic group coordination to the metal ions. The band at 1620 cm^{-1} can refer to stretching of (C=N) this band is shifted to lower frequencies contrast to the spactrum bands formation complexes, this change assigned to coordination imine with the metal ions [12] that there are no vibration of carbonyl group, this means that this group has not entered into coordination, through the Oxygen atoms for the C-O group of the ligand which appeared in the range 1262 cm^{-1} It was observed that these beams shifted to higher frequencies, this confirms the consistency with metallic ions[13]. It was observed that appeared bands in the spectrum complexes did not appear in the spectrum of ligand 2-hydroxybenzaldine urea in the region 575-671 cm^{-1} and 444-540 cm^{-1} which represent vibrations to υ (M-N) and υ (M-O) respectively[14], that there are water molecules consistency with metal ions band appear bands in the region (865-875) cm^{-1}, The spectra of complexes revealed a broad band at (3441.0-3446.7) cm^{-1} which represents V (OH) indicates OH groups of the adsorbed water molecules[15].

Table (2): Infrared spectral data of the Schiff base and its complexes (cm^{-1})

Compounds	V(OH)	V(C=N)	V(C=O)	V(C-O)	V(M-N)	V(M-O)
L	3329	1620	1625	1262	-	-
$[MnL(H_2O)_2].H_2O$	3295	1616	1625	1273	671	467
$[CoL(H_2O)_2].H_2O$	3390	1605	1625	1280	575	540
$[NiL(H_2O)_2].H_2O$	3205	1612	1625	1277	594	444
$[CuL(H_2O)_2]H_2O$	3395	1616	1625	1270	581	450

Electronic Spectra, Magnetic Moments and Molar Conductivity

The Ultra-violate spectrum for ligand 2-hydroxybenzaldine urea shows peaks of wave number at (45454 and 38610) cm^{-1} may be assigned to $\pi \rightarrow \pi^*$ transition of the aromatic rings and $n \rightarrow \pi^*$ transition to the imine respectively[16]. Generality of

complexes formed of transition metal are chromatic and their chromatic are various from the transition metal salts and ligands, this indicates of coordination. The molar conductivity measurements of all the complexes by using the dimethylformamide as a solvent, the result of these measurements indicates that all complexes of the nature of the non-electrolytic. The electronic spectral, magnetic moments and molar conductivity data of the Mn, Co, Ni and Cu complexes are summarized in Table3, the manganese(II) complex with color light brown show band at 19048 cm^{-1} which attributed to ^6A_1g (S) → ^4T_1g(G) , and band at 18018 cm^{-1} which assign to ^6A_1g (S) → ^4T_2g(G), the value of magnetic moment for Mn complex is 5.8 BM, from these results, the octahedral structure suggested for manganese complex[17]. Three bands for cobalt complex(II) presents with green color at the region(27472, 15037 and 12285) which refer to ^4T_1g(F) → 4T1g(G) , ^4T_1g→ ^4A_2g and ^4T_1g → ^4T_2g respectively . This transitions and the result of magnetic moment indicate the proposed structure is octahedral for Co complex[18], the magnetic moment for nickel(II) complex is 3.46 BM., This complex is light green color and displays electronic assimilation at (27777, 19920 and 13071) cm^{-1} which assigned (^3A_2g → ^3T_1g(P), ^3A_2g → ^3T_1g(F) and ^3A_2g → ^3T_2g) respectively, All these results for Ni complex confirm proposed format for it is octahedral [19], two bands present in the spectrum copper (II) complex at 39370 cm^{-1} and 27548 cm^{-1} which corresponding which refers to the transition charge transfer and other band at 19231cm^{-1} can be represent transition ^2Eg→ ^2T_2g, all these results indicate the octahedral geometry for copper complex[20], Through all the measurements and analytical spectral geometry expected for all the complexes in Figure(1).

Table (3): Electronic spectra, Molar conductivity and Megnetic moment data of the Schiff base and its metal complexes

Compounds	Wave number (cm^{-1})	Assignment	Molar conductivity Ohm^{-1} cm^2 mol^{-1}	Magnetic moment B.M	Suggested structure
L	45454 38610	π → π* n→π*	- -	- -	
$[MnL(H_2O)_2].H_2O$	19048 18018	$^6A_1g_{(S)}$ → $^4g_{(G)}$ $^6A_1g_{(S)}$ → $^4g_{(G)}$	27	5.8	octahedral
$[Co\ L(H_2O)_2].H_2O$	27472 15037 12285	$^4T_{1g(F)}$ → $^4g_{(P)}$ $^4T_{1g}$ → ^4g ^4T_1g , ^4T_2g	25	4.29	octahedral
$[Ni\ L(H_2O)_2].H_2O$	27777 19920 13071	^3A_2g , $^3T_1g_{(P)}$ ^3A_2g , $^3T_1g_{(F)}$ ^3A_2g , ^3T_2g	29	3.46	octahedral
$[Cu\ L(H_2O)_2]H_2O$	39370 27548 19231	C.T C.T ^2Eg,^2T_2g	28	1.71	octahedral

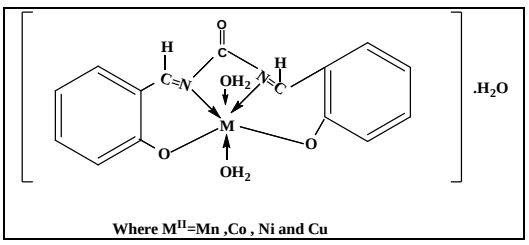


Fig.(1): Suggested structure of prepared complexes

Conclusion:

The ligand 2-hydroxybenzaldine urea prepared by heat refluxing. The ligand behaves as multidentate ligand through (O,N) atoms. From the FT-IR sprctrum and UV-Visible study this complexes have octahedral geometry.The

conductivity measurements showed all the complexes have nonionic nature.

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تحضير ودراسة الفحوصات الفيزيائيه والكيميائيه لمعقدات الايونات Mn(II)، Co(II)،Ni(II) وCu(II) مع الليكاند 2- هيدروكسي بنزيلدين يوريا

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الخلاصه :-

تم تحضير بعض المركبات الفلزيه من الليكاند المحضر من تفاعل ماده الديهايديه وهي السلسلديهايد مع ماده اخرى مثل اليوريا ومن خلال تحليل مكونات الفلز وجد ان القيم النظريه تطابق القيم العمليه وهذا يشير الى ان نسبة الفلز الى الليكاند هي نسبة [1:1]، شخصت هذه المعقدات بأستخدام طيف الاشعه تحت الحمراء وطيف الاشعه فوق البنفسجيه –المرئيه وتم قياس الحساسيه المغناطيسيه للمعقدات المحضره ومن خلال التوصيليه الكهربائيه للمعقدات وجد ان جميع المعقدات تمتلك طبيعه غير ايونيه ، ومن خلال النتائج تم اقتراح الشكل ثماني السطوح للمعقدات المحضره.

الكلمات المفتاحيه : معقدات قواعد شيف ، عناصر انتقاليه والتركيب الكيميائي ثمانية السطوح