Synthesis and Characterization of Schiff Bases (derived from p-substituted aniline) and Their Complexes With Co(II), Ni(II) and Cu(II)

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Abstract:

The synthesis of several new coordination compounds of cobalt (II), nickel (II) and copper (II) with some Schiff bases derived from acetylacetone and p-aminophenol (L') or p-aminobonzoic acid (L") are described. The complexes have the general formulae $[M(L')_2]$ and $[M(L'')_2]$. All the complexes were characterized by molar conductance, magnetic susceptibility, IR and UV-Vis

spectra, while cobalt , nickel and copper contents were determined by standard procedures . IR and UV-Vis spectral data and magnetic properties suggest that all the complexes are square-planar. The two ligands coordinate with the metal (II) ion in a bidentate manner through the enolisable carbonyl group of acetylacetone and the azomethine nitrogen atoms.

Keywords : Schiff bases , transition metal complexes , P-substituted aniline.

Introduction:

Metal complexes of Schiff base are studied extensively due to synthetic flexibility of these compounds and their selectivity as well as sensitivity towards the central metal atom [1-5]. The ready synthesis of Schiff bases and their unique properties have contribute greatly to their uses in many biological systems. The biological activity of Schiff base is attributed to the formation of stable complexes with the transition metal present in the cell [6-9]. On the industrial scale , they have wide range of applications such as dyes and pigments [10]. Another area of application of these Schiff bases is analytical chemistry where some of these compounds are used as ligand in complexometry topic [11].

In the present study, new Schiff bases of p-substituted aniline and their complexes, which have a variety of applications in biological, clinical and analytical fields [12,13], have been synthesized and characterized. The two ligands coordinate with the metal (II) ion as a bidentate mannar through the enolisable carbonyl group of acetylacetone and the azomethine nitrogen atoms of the p-substituted aniline of the Schiff base. The structures of the Schiff bases are shown in (Fig.1).



Figure 1. Schiff bases used as ligand **Experimental:**

Materials and methods:

All the chemical used throughout these investigation were of Merck, B.D.H., Aldrich or Fluka were used as supplied without further purification.

Synthesis of the ligands:

The ligands, L' and L" were prepared by the same general method : An ethanolic(40ml) solution of p-aminobenzoic acid (1.37 g , 0.1 mol) or p-aminophenol (1.09 g , 0.1 mol) and acetylacetone (1.00 g , 0.1 mol) was taken in equimolar ratio in an ethanolic medium and the mixture was refluxed for 12h., and then cooled. The resulting precipitate was filtered off, washed with cold ethanol and air-dried (m.p⁰C for L' 143⁰C and 165⁰C for L").

Synthesis of the complexes:

All the complexes were prepared by the same general method : to an ethanolic solution containing (0.1 mol) of the metal(II) chloride was added with continuous stirring (0.2 mol) of the ligand dissolved in 30 ml ethanol. The mixture was heated under reflux for 10h. The reaction mixtures were concentrated to a small volume by evaporation. On cooling, fine precipitate of the complexes was formed. The product was filtered off, washed with cold ethanol and water and air-dried.

Analysis and physical measurements:

The metal contents were determined according to the standard procedure[18]. Melting points for the ligands and decomposition temperature measurements for the complexes were measured using Richerk-Jung Heizbank apparatus. Molar onductance measurements were carried out using a 10⁻³ M solution in dimethylformamide DMF on a LF-42 conductivity meter at room temperature. Infrared absorption spectra were recorded on Pye-Unicam SP-1100 spectrophotometer as KBr discs at 400-4000 cm⁻¹. The electronic spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10⁻³M solution of the compounds in DMF at room temperature, using a 1 cm quartz cell. The magnetic susceptibility measurements were made by the Faraday method at room temperature using a Bruker BM6 instrument. Diamagnetic corrections for the ligands were calculated using Pascal's constants [14].

Results and discussion:

The formation of the complexes and the coordination of the two ligands to copper, nickel and cobalt ions were indicated from the various chemical and spectral properties. The molar conductance values of the 10^{-3} M solutions of all the complexes suggested that they are non-electrolytes in dimethylformamide (Table 1). All the complexes are stable in air at room temperature and decompose without melting at high temperature (above

260 0 C). They are insoluble in most organic solvents. Such as acetone and chloroform. Based on the metal contents measurements have been supported the general formulae [M(L)₂] and that all the complexes act as mononuclear complexes (Table 1).

Compounds	Colour	Yield %	Conductance	% Metal		Magnetic	
Compounds			$(\mathbf{cm}^2 \mathbf{ohm}^{-1} \mathbf{mol}^{-1})$	Fond	(Calcd.)	moment (BM)	
L'	Pale brown	86.1					
L"	Yellow	80.2					
[Co(L') ₇]	Green	76.8	11	13.09	(13.42)	2.51	
[Ni (L') ,]	Brownish red	63.4	29	12.97	(13.38)	0.0	
[Cu (L') ₁]	Dark brown	62.1	7	14.87	(14.32)	1.72	
[Co(L"),]	Dark green	70.7	8	12.42	(11.90)	2.66	
[Ni (L") ጘ]	Red	63.8	17	11.54	(11.86)	0.0	
[Cu(L") ₇]	Brown	68.2	20	12.33	(12.71)	1.80	

Table (1) : Physical characteristics and analytical data of the ligands and the complexes

IR spectra:

The coordination sites of the ligands were indicated by comparison of the infrared spectra of the free ligands and their complexes (Table 2). The IR spectra of the Schiff bases L' and L'' have a broad absorption band at 3180 cm⁻¹ and 3190 cm⁻¹ respectively ; which is assigned to the enolisable OH group of the acetylacetone moiety. The breadth of this band indicates the presence of hydrogen bonds. The assignments are strengthened by the disappearance of the band in the metal chelates in which enolic proton are completely displaced by metal (II) ions. The two ligands have no absorption at the range (1670-1690) cm⁻¹, which indicates that free carbonyl groups are absent and so the ketimine structure is ruled out. The strong absorption at the range (1610-1630) cm^{-1} is assigned as the azomethine group present in the Schiff bases. In all the metal complexes, the azomethine group is Shifted to lower frequency in the region (1580-1603) cm⁻¹, which indicates that chelation takes place through

the azomethine group. The appearance of other bands due to the stretching (v) and bending (δ) vibrations at 3395 cm⁻¹ and 1318 cm⁻¹ respectively for the phenolic OH group in spectrum of L' and the appearance of a band at 1725 cm⁻¹ due to stretching vibration of unionized and un-coordinated COOH in spectrum of L" and remaining of all these bands at nearly the same frequencies in spectra of the all metal complexes suggesting the un-coordination of these groups. So, we can find out that coordination in this work take place through both azomethine nitrogen and enolic oxygen atoms. Further support for this coordination was obtained from the appearance of new bands (not observed in free ligands spectra) located at about 430-450 and 480-490 cm⁻¹ and attributed to the stretching modes of M-O and M-N, respectively [15,16].

Compounds	V(C=N)	v(OH) Phenolic	□(OH) Bending	ν (СООН)	М-О	M-N
L'	1610	3395	1318			
L"	1630			1725		
[Co(L') ₁]	1583	3391	1315		435	482
[Ni (L') ₁]	1584	3391	1316		440	481
[Cu (L') ₁]	1580	3390	1316		450	490
[Co(L"),]	1602			1721	430	489
[Ni (L") ጘ]	1603			1720	439	480
$[Cu(L'')_{\tau}]$	1600			1721	439	482

Table (2): Important IR Specral bands (cm⁻¹)

Electronic specta:

The electronic absorption spectra of the Schiff bases and their Cu(II), Co(II) and Ni(II) complexes were recorded at room temperature using DMF as the solvent. The electronic spectra of the free ligands L' and L" show a band at 32894 cm⁻¹ and 33444 cm⁻¹ respectively, which is assigned as intraligand charge transfer band. [Cu(L')₂] and [Cu(L")₂] show a d-d band in the region 20833 cm⁻¹ and 21276 cm⁻¹ respectively, due to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ transition, which supports square planar geometry

(Table3). $[Co(L')_2]$ and $[Co(L'')_2]$ show absorption in the region 17241 cm⁻¹ and 17857 cm⁻¹ respectively, corresponding to ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition, which also supports square planar geometry. $[Ni(L')_2]$ and $[Ni(L'')_2]$ show absorption in the region 20408 cm⁻¹ and 21052 cm⁻¹ respectively, assigned to ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition, which again suggests square planar geometry [19].

Compounds	Band (nm)	Position (cm) ⁻	Assignments
L'	304	32894	Intraligand C.T.
L"	299	33444	Intraligand C.T.
[Co(L') ₁]	580	17241	$^{1}A_{1g} \rightarrow ^{1}B_{1g}$
[Ni (L') ₁]	490	20408	$^{1}A_{1g} \rightarrow ^{1}B_{1g}$
[Cu (L') ,]	٤٨٠	2.72	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$
[Co(L") ₁]	560	17857	$^{1}A_{1g} \rightarrow ^{1}B_{1g}$
[Ni (L") ,]	475	21052	$^{1}A_{1g} \rightarrow ^{1}B_{1g}$
[Cu(L") ,]	470	21276	$^{2}B_{1g} \rightarrow ^{2}A_{1g}$

 Table (3): Electronic Spectral bands and their probable assignments

Magnetic moments:

The magnetic susceptibility of the complexes was measured at room temperature by using the Faraday method. Correction due to diamagnetism of the constituent elements was made by using Pascal's constants . The magnetic moments of the Cu(II) complexes lie in the region expected for square planar

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complexes (Table 1). The magnetic moment of Ni(II) complexes is zero, which indicated that the complexes have square planar structures. The magnetic moments of the Co(II) complexes lie in the region also indicative of square planar configuration [17] (Fig.2).



Figure 2. Proposed structures of the complexes

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تحضير ودراسة خصائص قواعد شيف (مشتقة من معوضات بارا- انيلين) ومعقداتها لايونات الكوبلت والنيكل والنحاس الثنائية

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الملخص:

بقياس التوصيل المولاري والحساسية المغناطيسية واطياف الاشعة تحت الحمراء وفوق البنفسجية بينما تم تقدير محتوى الكوبلت ، النيكل والنحاس في المعقدات بالطرق القياسية . دلت القياسات اعلاه على تتاسق الليكاندين بشكل ثنائي السن من خلال ذرتي اوكسجين مجموعة الهيدروكسيل الاينولية وذرتي نتروجين مجموعتي الازو ميثين وان جميع المعقددات الناتجة ذي بنية مربصع مستوي . تضمن البحث تحضير ودراسة عدد من معقدات الكوبلت والنيكل والنحاس مع ليكاندين من نوع قواعد شيف . تم اشتقاق الليكاندين من تكثيف اسيتيل اسيتون مع بارا – امينو فينول (L) و بارا – امينو حامض البنزويك (L) . تم الحصول على المعقدات من تفاعل هذين الليكاندين مع الاملاح الفلزية المناسبة في مذيب الايثانول (نسبة ١ : ٢ فلز : ليكاند) ولها الصيغة[L(L)] و[M(L)] وقد شخصت المعقدات الناتجة