

Synthesis and Physicochemical Investigation of Cobalt (II) and Nickel (II) Complexes of 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone

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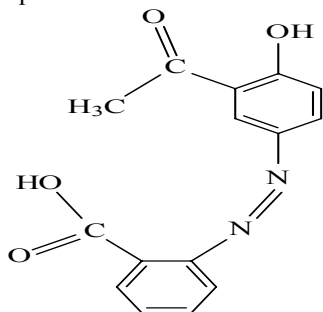
(Received on 6th May 2010, accepted in revised form 31st December 2010)

Summary: Two divalent metal complexes of Co(II) and Ni(II) ions with the 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone were synthesized and investigated by several tools such as; CHN elemental analyses, molar conductance measurements, infrared and electronic spectra. The CHN elemental analysis data showed the formation of 2:1[M:L] ratio of the formula of $[M_2L(Cl)_2(H_2O)_6]$, where, M represents Co(II) or Ni(II) ions. The molar conductance measurements indicate the existence of non-electrolytic nature. The infrared spectral data displayed the proper behavior of the synthesized 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone towards the metal ions. The electronic spectral data showed that both complexes have an octahedral geometry.

Introduction

Acetophenone compound is a bidentate ligand and it has a good ability to form several complexes with transition and non-transition metal ions [1]. Azo dye compounds [2-4] of the heterocyclic diazo component form colored complexes with many metal ions in solution [5-8]. The heterocyclic azo dyes usually react with the metal ions as tridentate ligands, forming coordinative bonds with heterocyclic moiety [9].

The 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone compound under investigation has more than one site as it contains –N=N, –COOH, C=O and –OH groups which are able to form complexes with transition metal ions.



Some metal complexes of 8-aryloxy-6-formyl-7-hydroxy-5-methoxy-2-methylchromone have been prepared and investigated. ⁽⁷⁾ Tetrahedral,

square planar and octahedral geometries were proposed for complexes based on their electronic spectra and magnetic moments.

The aim of this study is to establish the spectroscopic studies of some divalent transition metal complexes of the 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone that synthesized and investigated previously. ⁽⁸⁾

Results and Discussions

Microanalysis

The elemental analysis data of the 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone complexes are summarized in Table 1, and show the formation of 1:1 [M:L] ratio. It is found that the theoretical values are in a good agreement with the found ones.

Molar Conductance Measurements

The molar conductivity of the complexes was measured using $10^{-3}M$ $CHCl_3$ solvent, and the obtained values suggest the existence of non electrolytic nature (9).

Table-1: Elemental analysis and some physical properties of 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone complexes.

Complexes	M.Wt.	M.P °C	Color	%C		%H		%N		$\mu s(BM)$
				Calc.	Found	Calc.	Found	Calc.	Found	
$[Co_2LCl_2(H_2O)_6]$	579.00	> 300	Green	31.09	31.74	3.79	3.87	4.83	4.73	4.20
$[Ni_2LCl_2(H_2O)_6]$	578.40	> 300	Black	31.12	31.25	3.80	3.42	4.84	4.52	2.92

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Infrared Spectra

The infrared band assignments of Co(II) and Ni(II) complexes are listed in Table 1. Broad bands were observed at 3381 and 3382 cm^{-1} in the spectra of the complexes corresponded to water molecules.⁽¹⁰⁾ Meanwhile, the same spectra displayed bands at 1642 and 1662 cm^{-1} due to C=O group. The change of this group compared to its original position in the free ligands (1697 cm^{-1}) indicates its involvement in coordination through oxygen atom with the metal ion.⁽¹¹⁾ The infrared spectra showed bands at 1444 and 1446 cm^{-1} attributed to -N=N group. The change of this group to lower frequency compared to its original position in the free ligand (1490 cm^{-1}) indicates its participation in coordination through nitrogen atom.⁽¹²⁾ The additional bands observed at 315, 322, 538, 681, 757 and 760 cm^{-1} which could be assigned to $\nu\text{M-Cl}$, $\nu\text{M-N}$ and $\nu\text{M-O}$, respectively.^(13,14) The appearance of these new bands confirm the entrance of -N=N, -OH and -Cl in complexation.

Table-2: Infrared and electronic spectral data of 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone and its complexes.

Complexes	IR (cm^{-1})					UV-Vis (nm)		
	νOH	C=O	$\nu\text{N=N}$	$\nu\text{M-O}$	$\nu\text{M-N}$			
[Co2LC12(H2O)6]	3383	1642	1444	760	638	629	430	260
[Ni2LC12(H2O)6]	3381	1662	1446	757	581	682	482	388

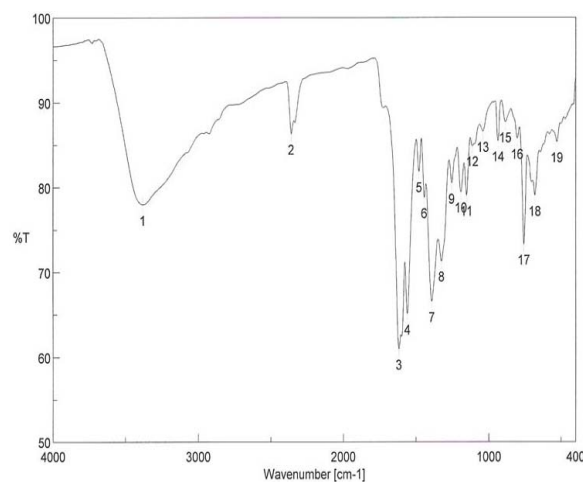


Fig. 1: IR Spectrum of Ni2-L Complex.

Electronic Spectra and Magnetic Moments

The electronic spectrum of the 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone compound showed two bands at 220 and 270 nm, these bands are assigned to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ (-N=N, C=O and -OH). The

spectrum of the Co(II) complex displayed three bands at 260, 430 and 629 nm, the first two bands are attributed to charge transfer transition and the third one is due to $4\text{T}1\text{g} \rightarrow 4\text{T}2\text{g}$, $4\text{T}1\text{g} \rightarrow 4\text{A}2\text{g}$ and $4\text{T}1\text{g} \rightarrow 4\text{T}1\text{g(P)}$ transition.⁽¹⁵⁾ Whereas, the Ni(II) complex showed three bands at 388, 482 and 682 nm, the first two bands are assigned to charge transfer transition, and the third band corresponded to $3\text{A}2\text{g} \rightarrow 3\text{T}2\text{g}$, $3\text{A}2\text{g} \rightarrow 3\text{T}1\text{g}$ and $3\text{A}2\text{g} \rightarrow 3\text{T}1\text{g(P)}$ transition.⁽¹⁶⁾ The magnetic moment values of the synthesized complexes, table-1 showed the existence of paramagnetic phenomena, this phenomena supported the geometrical structures which suggested by the electronic spectra studies.

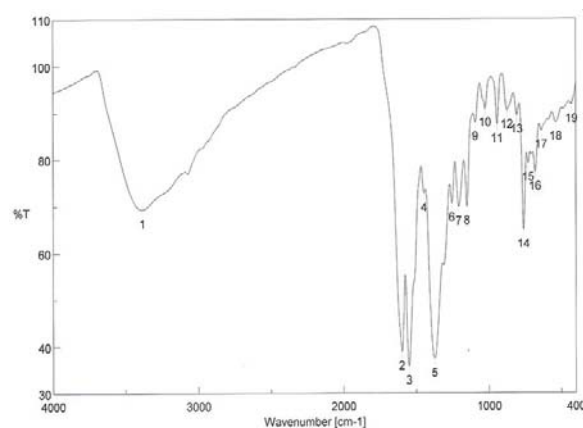


Fig. 2: IR Spectrum of Co2-L Complex

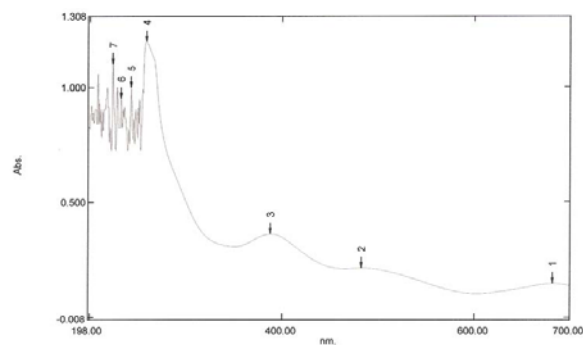


Fig. 3: Electronic Spectrum of Ni2-L Complex.

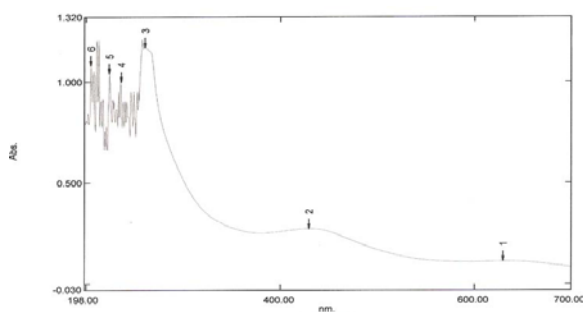
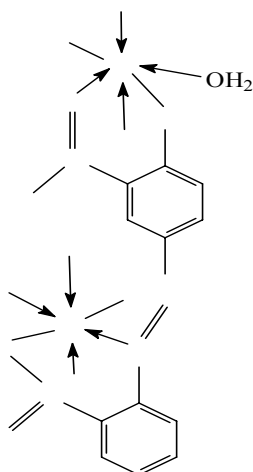


Fig. 4: Electronic Spectrum of Co2-L Complex.



Structure of complexes is $[M_2LCI_2(H_2O)_6]$
 $M = Co^{2+}$ or Ni^{2+} ions

Experimental

Materials

All reagents and chemicals used in these complexes are azo dye ($C_{15}H_{12}N_2O_4$), $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, distilled water and absolute ethanol was of AR grades (BDH).

Preparation of the Complexes

The complexes of Ni(II) and Co(II) with azodye was synthesized by mixing ethanolic solutions (50 mL) of 0.01 mole, (2.84 gm) of the ligand ($C_{15}H_{12}N_2O_4$) with the same (50 mL) of the 0.01 mol (2.38 cm³) of $CoCl_2 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ the 0.01 mol (2.37), respectively. The reaction mixtures were refluxed for three hours and left to cool and filtered by suction. The precipitates were washed several times with hot ethanol.

Physical Measurements

The synthesized 1-2-[(Z)-2-(3-acetyl-4-hydroxyphenyl)-1-diazenyl]phenyl-1-ethanone complexes were subjected to CHN elemental analyses using 2400 elemental analyzer at Micro-Analytical Center, Cairo University, Giza, Egypt. The molar conductance measurement was carried out in DMSO solvent using Conductivity meter model CMD650 digital. The magnetic moments of the complexes were measured on Johnson Mathey susceptometer devised by D.F. Evens. Infrared spectra were obtained by KBr disc technique by using IFS-25DPUS/IR Spectrometer (Bruker) in the

range of 4000-400 cm^{-1} . Electronic absorption spectra were measured in chloroform solvent using a Perkin-Elmer-Lambda β -Spectrophotometer.

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