Scientific Journal for Damietta Faculty of Science 8 (1) 2018, 65-68
ISSN Print 2314-8594
ISSN Online 2314-8616

Synthesis, Spectroscopic and Thermal Analysis of Cu(II) Complexes

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Received: 2 May 2018 /Accepted: 5 May 2018

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Abstract

Copper(II) complexes of 5-(4`-derivatives phenyl azo)-8-hydroxy-7-quinolinecarboxaldehydes were synthesized and characterized by using microanalysis, IR spectra, magnetic measurements, and thermal analysis. copper(II) complexes have square planar geometry with formula $[Cu(L_n)_2].5H_2O$. The electronic spectra of all complexes exhibits a bands at ~ 17635 – 19228 and 26955-19802 cm^{-1} ranges, assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, which are the characteristic of square planar geometry.

Keywords: Complexes; Synthesis; Spectroscopic; Thermal analysis.

Introduction

Azo quinoline an important class of organic colourants which consist of at least a conjugated azo (-N=N-) chromophore and more versatile class of dye [1,2]. The azo quinoline derivatives thus obtained, has been used as prospective chelating agent for some selected d-block metal ions been examined with particular reference to the structural aspects of the ligand moieties in the metal complexes. The optical, electrical, thermal and structural properties of many 8-hydroxyquinoline derivatives and their metal complexes have been studied [3]. Quinoline compounds are one of the most prevalent ligands in coordination chemistry [4,5].

Experimental

Preparation of 5-(4`-derivatives phenyl azo)-8-hydroxy-7-quinolinecarboxaldehydes

Aniline or *p*-substituted derivatives (1 mmol) was dissolved in 30 ml of ethanol. Concentrated hydrochloric acid (10 mL) was diluted with about 40 g of crushed ice and then dropwise addition of the aniline or *p*-substituted derivatives solution to the crushed ice was carried out. To this cold solution was added 10% sodium nitrite (1 mmol) and stirred for about 1 h to complete diazotization. The coupling agent 8-hydroxy-7-quinolinecarboxaldehyde (1 mmol) dissolved in 50 ml of ethanol containing (1.0 mmol) of potasiom hydroxide was then added to the cold mixture. The resulting solution was stirred well and sodium acetate (3 g) was added for neutralization.

Preparation of complexes

To a solution of the ligands in mixture of 30 ml (2:1 v/v) of DMF and methanol and methanolic (25 mL) solution of $CuSO_4.5H_2O$ was added slowly with stirring over a period of 10 minutes. The mixed solution was stirred for another ~ 4 hrs under reflux. After reaction the solvent was removed to a half volume of the original and cooled down to room temperature.

Analytical measurements

Elemental microanalysis of the compounds were determined on Automatic Analyzer CHNS Vario ELIII. Infrared spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. The conductance was carried out by Sergeant Welch Scientific Co., Skokie, IL, USA. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy`s method. Mercury(II) (tetrathiocyanato) cobalt(II), $[Hg\{Co(SCN)_4\}]$, was used for the calibration of the Gouy tubes. Magnetic moments were calculated using the equation, $\mu_{eff.} = 2.84\ [Tc_M^{coor.}]^{1/2}$. Thermal properties of the samples were analyzed in the temperature range from 30 to 800 °C at the heating rate of 10 °C/min under dynamic nitrogen atmosphere.

Results and discussion

Characterization of copper(II) complexes

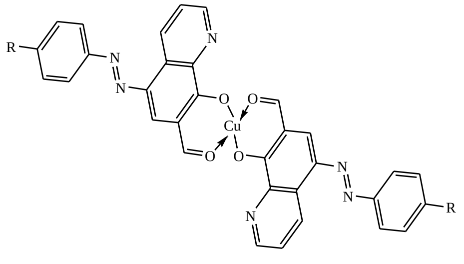
Bidentate complexes were obtained upon reaction between copper ion and ligands with molar ratio (1M:2L). The complexes $[Cu(L_n)_2]\ .5H_2O$ are soluble in DMF and DMSO. The elemental analysis of complexes are presented in Table 1. It is found that the analytical data are in a good agreement with the proposed stoichiometry of the complexes (Fig. 1). All complexes exhibited high melting points, indicating a strong bonding between the ligands and Cu(II) ion.

Table 1. Elemental analysis of Cu(II) complexes.

Compound	Exp. (calcd.)%		
	C	H	N
$[Cu(L_1)_2]\ .5H_2O$ **(1)**	53.18 (53.30)	3.03 (3.14)	11.26 (10.97)
$[Cu(L_2)_2]\ .5H_2O$ **(2)**	55.44 (55.62)	3.10 (3.27)	11.36 (11.45)
$[Cu(L_3)_2]\ .5H_2O$ **(3)**	54.26 (54.43)	2.82 (2.84)	12.34 (11.91)
$[Cu(L_4)_2]\ .5H_2O$ **(4)**	49.43 (49.58)	2.22 (2.32)	10.78 (10.85)
$[Cu(L_5)_2]\ .5H_2O$ **(5)**	48.12 (48.27)	2.18 (2.26)	14.33 (14.08)

Infrared spectra

The IR spectroscopy is known to be a powerful tool for structural determinations of the ligand and metal chelates. The assignments of fundamental functional groups are basic for such purposes. The infrared spectra of the ligands (HL_n) show a broad hydroxyl group band. The intensity of this band is considerably greater than that of the free OH vibration frequency. The broad sharp can be attributed to the fact that the OH group is involved in hydrogen bonding.



R = OCH_3 (HL_1), R = CH_3 (HL_2), R = H (HL_3), X = R (HL_4) and R = NO_2 (HL_5)

Fig. 1. The structure of copper(II) complexes

The characteristic band of the CN_{py} ring, observed at ~1585 cm^{-1}, is little changed indicating the nitrogen atom of the quinoline does not take part in coordination [2,3], while the observed at ~ 1570 cm^{-1} is assigned to the stretching vibration of -N=N-. In the infrared spectra of the complexes, the band observed at 1575 cm^{-1} due to the υ(N=N) mode remain more or less at the same position in complexation indicating that it is not a center of chelation.

The ligands exhibit broad and weak absorption bands in the region ~3315-3325 cm^{-1} υ(OH) and strong bands at ~ 1280-1295 cm^{-1} δ(OH). This later is replaced by at a higher frequency ~ (1340-1350 cm^{-1}) in the complexes indicating that the ligands coordinate to the Cu(II) ion as deprotonated.

In addition to above bands, the IR bands due to phenyl ring systems between 1555-1565 cm^{-1} which are almost unaffected in the complexes have been assigned to aromatic υ(C=C) vibration, indicating non-participation of π-electron cloud in the M-L bond formation [6]. The position of the bands is influenced to a small extent by the nature of substituent groups. However, they depend on a rather greater degree, on the way in which the latter are arranged around the ring.

The bands at ~ 1655 cm^{-1} of carbonyl group υ(C=O) occurs at higher frequency in the ligands [7-11] than in the respective complexes by 10-15 cm^{-1}, revealing its involvement in Cu(II) complexes. In this case, the decrease of electronic density of the ring may be correlated with the donor character of the oxygen atom in the M-O bond. There is also another correlation, observed when comparing the position of the υ(C=O) band in the free ligand and in the corresponding complexes. In these cases, the higher shift corresponds to higher electronegativity. Evidently, the presence of electronegative groups in the ring affects the donor capacity of the O and N atoms. These comparisons show that the electronegativity of the ring substiituents produces not only a decrease of the electronic density over the ring, generating a diminution in the υ(C=N) stretching frequency, but also causes a lowering of the donor character of the N atom.

Thermogravimetric analysis

Thermal analysis is useful in determining the thermal stability and the water molecules content in the complexes [12-15]. Thermogravimetric analysis (TGA) of copper(II) complexes are shown in Fig. 2 and the thermal analysis data are listed in Table 2.

Table 2. Thermal analysis data of Cu(II) complexes**.**

Complexes	Temp. range (ºC)	Found mass loss (calc.) (%)	Assignment
(1)	50-113	11.43 (11.76)	Loss of $5H_2O$ molecules in outside of the coordination sphere
	113-406	16.85 (16.72)	Loss of $C_3H_{12}O_5$
	406-800	55.33 (54.86)	Loss of of $C_{27}H_{12}N_6$
	> 800	16.39 (16.66)	CuO residue + 4 carbon atoms
(2)	50-120	11.71 (12.27)	Loss of $5H_2O$ molecules in outside of the coordination sphere
	120-800	77.76 (76.89)	Loss of $C_{34}H_{24}N_6O_3$
	> 800	10.53 (10.84)	CuO residue
(3)	50-120	13.28 (12.76)	Loss of $5H_2O$ molecules in outside of the coordination sphere
	120-800	67.34 (67.47)	Loss of $C_{27}H_{20}N_6O_3$
	> 800	19.38 (19.77)	CuO residue + 5 carbon atoms
(4)	50-118	10.77 (11.62)	Loss of $5H_2O$ molecules in outside of the coordination sphere
	118-800	74.95 (73.46)	Loss of $C_{29}H_{18}N_6Cl_2O_3$
	> 800	14.28 (14.92)	CuO residue + 3 carbon atoms
(5)	50-120	11.41 (11.31)	Loss of $5H_2O$ molecules in outside of the coordination sphere
	120-409	20.94 (20.87)	Loss of $C_2H_2N_2O_7$
	409-800	50.01 (50.28)	Loss of $C_{25}H_{16}N_6$
	> 800	17.64 (17.54)	CuO residue + 5 carbon atoms

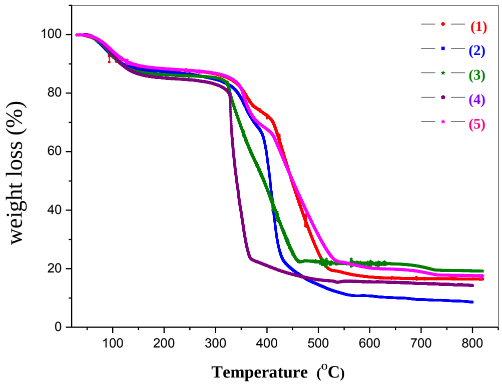


Fig. 2.TGA curves of copper(II) complexes

Magnetic and electronic spectra

The magnetic susceptibilities and the electronic absorption bands of HL_n and their Cu(II) complexes, in Nujol mull, are listed in Table 3. The electronic spectra of all complexes exhibits a bands at ~ 17635 – 19228 and 26955-19802 cm^{-1} ranges, assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, which are the characteristic of square planar geometry. The magnetic moments values of the Cu(II) complexes are normal within the range reported for one unpaired electron in a square planar geometry [16].

Table 3. Magnetic susceptibility and electronic spectra of the complexes**)**.

Complexes	μ_{eff} (B.M.)	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$
(1)	1.82	19228	27395
(2)	1.83	18048	26955
(3)	1.84	17635	27777
(4)	1.85	18587	20207
(5)	1.85	18315	19802

Conclusion

Copper(II) complexes of 5-(4`-derivatives phenyl azo)-8-hydroxy-7-quinolinecarboxaldehydes were synthesized and characterized. The electronic spectra of all complexes exhibits a bands at ~ 17635 – 19228 and 26955-19802 cm^{-1} ranges, assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, which are the characteristic of square planar geometry.

References

Sh.M. Morgan, N.A. El-Ghamaz, M.A. Diab, J. Mol. Struct. 1160 (2018) 227-241

N.A. El-Ghamaz, M.A. Diab, A.A. El-Bindary, A.Z. El-Sonbati, S.G. Nozha, Spectrochim. Acta A 143 (2015) 200–212.

N.A. El-Ghamaz, M.A. Diab, A.Z. El-Sonbati, O.L. Salem, Spectrochim. Acta A 83 (2011) 61–66.

M. Saçmacı, H.K. Çavuş, H. Arı, R. Şahingöz, T. Özpozan, Spectrochim. Acta A 97 (2012) 88–99.

K.H. Lam, R. Gambari, K.K.H. Lee, Y.X. Chen, S.H.L. Kok, R.S.M. Wong, F.Y.

K. Laxma Reddy, S. Sri Hari and P. Lingaiah, Ind. J. Chem. 24A (1985) 318.

M.I. Abou-Dobara, A.Z. El-Sonbati, Sh.M. Morgan, World J. Microbiol. Biotechnol. 29 (2013) 119–126.

Sh.M. Morgan, A.Z. El-Sonbati, M.A. El-Mogazy, *Appl. Organomet. Chem.* https://doi.org/10.1002/aoc.4264

Sh.M. Morgan, M.A. Diab, A.Z. El-Sonbati, *Appl. Organomet. Chem.* https://doi.org/10.1002/aoc.4281

Sh.M. Morgan, M.A. Diab, A.Z. El-Sonbati, *Appl. Organomet. Chem.* https://doi.org/10.1002/aoc.4305

A.Z. El-Sonbati, M.A. Diab, Sh.M. Morgan, J. Mol. Liq. 225 (2017) 195–206.

Sh.M. Morgan, A.Z. El-Sonbati, H.R. Eissa, J. Mol. Liq. 240 (2017) 752–776.

A.Z. El-Sonbati, M.A. Diab, Sh.M. Morgan, A.M. Eldesoky, M.Z. Balboula, *Appl. Organomet. Chem.* https://doi.org/10.1002/aoc.4207.

A.Z. El-Sonbati, M.A. Diab, Sh.M. Morgan, H.A. Seyam, J. Mole. Struct. 1154 (2018) 354-365.

M. A. Diab, A. Z. El-Sonbati, Sh. M. Morgan, M. A. El-Mogazy, Appl. Organometal. Chem. 2018, https://doi.org/10.1002/aoc.4378.

A.Z. El-Sonbati, M.A. Diab, Sh.M. Morgan, M.Z. Balboula, *Appl. Organomet. Chem.* https://doi.org/10.1002/aoc.4059.