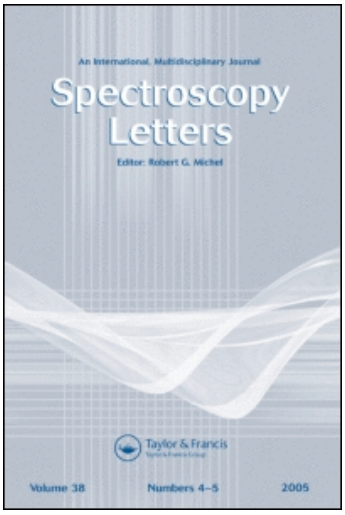


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

THE COORDINATION OF Cu(II) AND THERMAL STUDIES ON SOME QUINOXALINONE DERIVATIVE COMPOUNDS

Amina A. Soayed[a]
[a] Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

Online publication date: 31 October 2001

To cite this Article Soayed, Amina A.(2001) 'THE COORDINATION OF Cu(II) AND THERMAL STUDIES ON SOME QUINOXALINONE DERIVATIVE COMPOUNDS', Spectroscopy Letters, 34: 5, 629 — 638
To link to this Article: DOI: 10.1081/SL-100106876
URL: http://dx.doi.org/10.1081/SL-100106876

SPECTROSCOPY LETTERS, 34(5), 629–638 (2001)

THE COORDINATION OF Cu(II) AND THERMAL STUDIES ON SOME QUINOXALINONE DERIVATIVE COMPOUNDS

Amina A. Soayed

Department of Chemistry, Faculty of Science,
Alexandria University, Alexandria, Egypt

ABSTRACT

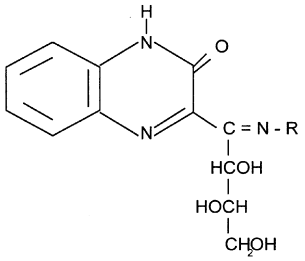
The chelates of Cu(II) ion with some quinoxalinone compounds have been prepared and characterized by elemental analysis, IR, UV-Vis, magnetic susceptibility and TGA. It is shown that the ligands behave as bi- or tridentate ligands with the coordination of one or two chloride atoms in most of the complexes. The thermal decomposition of the compounds has been used to confirm structural information.

Key Words: Cu(II) ion; Quinoxalinone; Quinoxalinone derivatives

INTRODUCTION

Hydrazines and diamines have been used to synthesize heterocyclic compounds in the carbohydrate series[1–3]. The coordination of such compounds to metal ions has not been attempted so far. The present study deals with the preparation, characterization and thermal behavior of some

quinoxalinone carbohydrate derivatives and their Cu(II) complexes of the general formula:

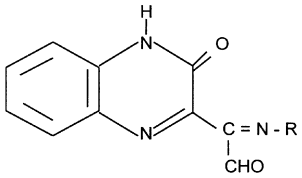


(I)

L_1 : R = -NH ph

L_3 : R = C_6H_4.COOH

L_5 : R = C_6H_4OH

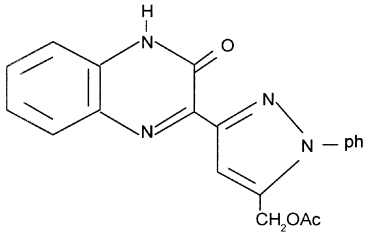


(II)

L_2 : R = -NH ph

L_4 : R = -C_6H_4COOH

L_6 : R = -C_6H_4OH



(III)

EXPERIMENTAL

Ligands of type I were prepared by mixing a suspension of L-ascorbic acid (0.1 mol) in water with an ethanolic solution of o-phenylenediamine (0.1 mol) and refluxing for one hour. To this mixture, a 0.2 molar solution of phenylhydrazine or 2-aminobenzoic acid or 2-aminophenol has been added and refluxed for another one hour giving L_1, L_3 and L_5.

Periodate oxidation of compounds (I) yielded (II)[2]. Ligand (III) (L_7) was prepared by boiling acetic anhydride together with L_1 causing the loss of two molecules of water per molecule of hydrazone[2].

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

The complexes were prepared by mixing an ethanolic solution of the Cu(II) chloride (0.01 mol) with an ethanolic solution of the ligand (0.02 mol) then being refluxed for two hours. The resulting precipitates were washed with ethanol, followed by ether and dried in a vacuum desicator over P_4O_{10}. The analytical data of the ligands and complexes are collected in Table 1.

IR spectra were recorded using a Perkin-Elmer 1430 spectrophotometer (200–4000 cm^{-1}). Electronic spectral measurements were done using a

Table 1. Elemental Analyses and Magnetic Moments of the Quinoxalinone Derivative Compounds and Their Cu(II) Complexes

	Found (Calcd.)%					
Species	C	H	N	Cl	M	μ_{eff} (B.M.)
L_1	59.8	5.1	15.9			
($C_{18}H_{18}N_4O_4$)	(61.0)	(5.2)	(15.8)	–	–	–
$Cu(L_1)Cl \cdot 3H_2O$	42.3	3.4	11.1	6.9	12.7	1.87
	(42.7)	(3.4)	(11.0)	(7.0)	(12.5)	
L_2	65.4	4.1	19.3			
($C_{16}H_{12}N_4O_2$)	(65.7)	(4.1)	(19.2)	–	–	–
$Cu(L_2)Cl \cdot 2H_2O$	45.0	2.6	13.4	8.2	15.3	1.88
	(45.0)	(2.6)	(13.1)	(8.3)	(14.9)	
L_3	60.0	4.3	10.8			
($C_{19}H_{17}N_3O_6$)	(59.5)	(4.5)	(10.9)	–	–	–
$Cu(L_3)H_2O$	49.2	3.8	9.1		14.0	1.85
	(49.3)	(3.7)	(9.0)	–	(13.7)	
L_4	63.5	3.5	13.0			
($C_{17}H_{11}N_3O_4$)	(63.5)	(3.5)	(13.1)	–	–	–
$Cu(L_4)Cl$	48.68	2.4	10.0	8.7	14.9	1.87
	(48.7)	(2.6)	(10.0)	(8.5)	(15.1)	
L_5	60.8	4.7	11.7			
($C_{18}H_{17}N_3O_5$)	(60.8)	(4.8)	(11.8)	–	–	–
$Cu(L_5)Cl \cdot H_2O$	45.9	3.4	8.9	7.7	12.7	1.87
	(45.8)	(3.6)	(8.9)	(7.5)	(13.4)	
L_6	65.0	3.7	13.8			
($C_{16}H_{11}N_3O_3$)	(65.5)	(3.8)	(14.3)	–	–	–
L_7	67.5	4.4	17.9			
($C_{18}H_{14}N_4O_2$)	(67.9)	(4.4)	(17.6)	–	–	–
$Cu(L_7)Cl_2 \cdot H_2O$	46.9	3.8	12.6	15.2	13.8	1.87
	(47.8)	(3.1)	(12.4)	(15.5)	(14.0)	

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

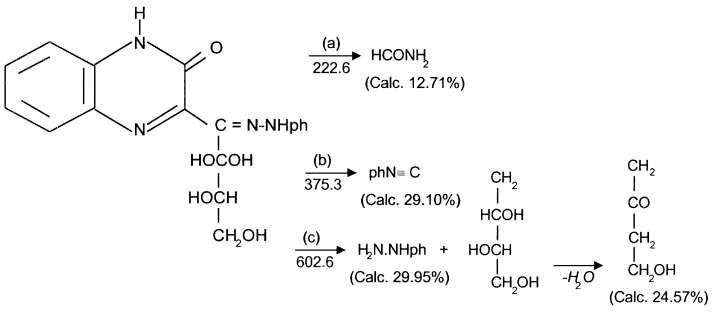
Pye-Unicam SP 1750 spectrophotometer. The molar magnetic susceptibilities were measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant. $Hg[Co(SCN)_4]$ was used as calibrant. The thermogravimetric analysis (TGA) was carried out in dynamic nitrogen atmosphere ($20\,ml \cdot min^{-1}$) with a heating rate of $10°C\,min^{-1}$ using a Shimadzu TGA-50 H thermal analyzer.

RESULTS AND DISCUSSION

Investigations of the coordination behavior of the studied ligands towards Cu(II) ion have shown that these compounds form either monohalide or dihalide adducts $CuLCl_x \cdot nH_2O(x = 1 \text{ or } 2)$, or $CuLH_2O$. The thermal and spectroscopic studies presented for the free ligands and their copper complexes confirm structural information obtained by the IR spectra related to the bonding mode of these interesting compounds which may coordinate to a metal center through several donor sites and provide important information related to the mode of their decomposition.

The nujol mull electronic spectra of the Cu(II) complexes showed absorption maxima at $(14.0–17.0) \times 10^3\,cm^{-1}$ which are in accordance with expectations for tetragonal geometry[4,5] assigned as $^2A_{1g} \leftarrow {}^2B_{1g}$[6]. The μ_{eff} values lie within the range 1.85–1.88 B.M. indicating their monomeric nature.

TGA technique was used to follow the thermal behavior of the studied ligands and some of their Cu(II) complexes in the 30–1000°C range. Thermal analytical results for L_1 reveals the decomposition to take place in three steps. The first at 222.6°C with a 12.347% weight loss, the second at 375.3°C with a 29.194% weight loss and the third at 602.6°C with a 54.800% weight loss. Thus, the pyrolysis of L_1 could be assumed as[7]:

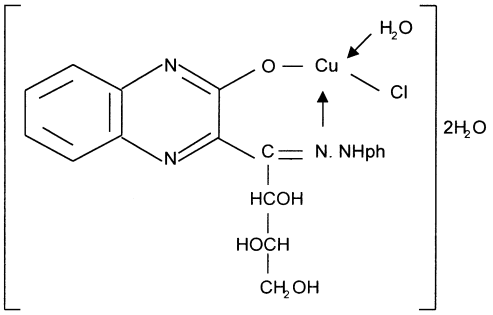


Concerning its $[Cu(L_1)Cl \cdot H_2O]2H_2O$ complex, the first decomposition step in the 24.5°C–180°C could be attributed to the loss of 3.5 water

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

molecules (found % loss 12.230; calc. 12.211). The water content is more than that resulting from the elemental analysis which can be due to hygroscopic properties[8]. The second step at 332.5°C with % weight loss 30.368 (calc. 30.060%) can be attributed to the loss of the cyanoquinoxaline moiety ($C_9H_5N_3$), whereas the third step at 429.8°C with % weight loss of 26.91 (calc. 27.56%) may be due to the loss of $phNH_2$ (18.07%) together with the elimination of a Cl (6.78%) atom and CO (2.71%) gas.

L_1 is present in a keto–enol tautomerism indicated from its IR spectrum where bands characteristic for ν N-H, ν C=O and ν OH are present but at lower frequencies than expected, Table 2. Upon complexation, the ν OH broad band between 3358–3427 cm^{-1} in the ligand transforms to a sharp band at 3437 cm^{-1} in the Cu(II) complex together with the disappearance of the ν C=O band indicating coordination through deprotonated phenolic OH group and presence of water of crystallization. Both ν NH of the hydrazone part at 2916 cm^{-1} and ν C=N (cyclic) at 1559 cm^{-1} remained in their positions in the complex indicating their non-involvement in bonding. However, the azo-methine ν C=N (1617 cm^{-1}) is shifted to 1638 cm^{-1} in the complex suggesting coordination via this group. A new band is seen at 209 cm^{-1} due to Cu-Cl bond. So, the structure of this complex is assumed to be:



The thermal behavior of $[Cu(L_2)Cl \cdot H_2O]H_2O$ shows that this complex starts losing weight at 53°C (6.373%) corresponding to the loss of 1.5 water molecule (calc. 6.338%). Again, this increase in water content than that of elemental analysis may be due to hygroscopic properties[8]. The second decomposition step at 319.25°C with a % weight loss of 34.345 is due to the loss of $C_6H_5NH \cdot N{=}CH \cdot CHO$ (calc. 34.280%). The third step at 554°C is due to the loss of NH=CHOH moiety (found 10.634%, calc. 10.564%) and the last step at 817°C corresponds to the loss of the coordinated H_2O (found 3.997%, calc. 4.22%).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table 2. IR Spectra of the Ligands and Their Complexes

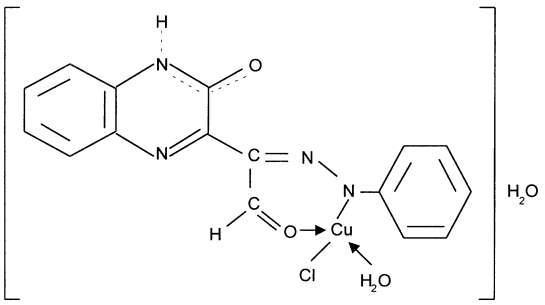
Compound	ν OH	ν NH	ν C=O	ν C=N[(a)]	ν C=N[(b)]	ν M-Cl
L_1	3358–3427	2916	1660	1559	1617	–
$Cu(L_1)Cl \cdot 3H_2O$	3437	2915	–	1559	1638	209
L_2	3427	2916 1741[(c)]	1674	1593	1652	–
$Cu(L_2)Cl \cdot 2H_2O$	3335	2975	–	1590	1655	208
L_3	3465 3361 2888[(d)]	3023	1668 1612[(e)]	1557	1583	–
$Cu(L_3) \cdot H_2O$	3428 3263 3225	–		1555	1597	
L_4	3362	2921	1679[(c)]	1578	1601	–
$Cu(L_4)Cl$	3263	–	–	1545	1588	208
L_5	3365 3292	2958	1659	1552	1601	
$Cu(L_5)Cl \cdot H_2O$	3407 3257	2960	1658	1548	1592	233
L_6	3395	2924	1636	1532	1591	–
L_7	3110,3048 3270	3296,3165	1724	1655	1619[(f)]	–
$Cu(L_7)Cl_2 \cdot H_2O$	3436		–	1660	1601	209 233

[(a)] C=N in the quinoxalinone ring
[(b)] azomethine C=N
[(c)] C=O of the aldehydic group
[(d)] OH of the aldehydic group
[(e)] νs (COO^-)
[(f)] C=N of pyrazole ring

IR shows that L_2 is present in keto–enol tautomerism depicted from the presence of ν OH and ν C=O at 3427 and 1674 cm^{-1}, respectively. Upon complexation, a band at 3335 cm^{-1} suggests the presence of a water molecule together with a band at 820 cm^{-1} assigned to the out-of-plane deformation vibrations of a coordinated water molecule[9]. The ν N-H of the hydrazone moiety at 2916 cm^{-1} is shifted in the complex to 2975 cm^{-1} and ν C=O of the aldehydic group at 1741 cm^{-1} in the ligand, completely vanished

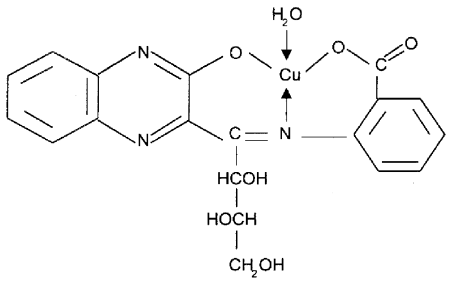
MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

upon complexation suggesting the coordination to occur via these two groups. A new band located at 208 cm^{-1} depicts a Cu-Cl bond. Thus $[Cu(L_2)Cl \cdot H_2O]H_2O$ could be in the following form:



L_3 sublimes in one step at 230.24°C. However, its $[Cu(L_3)H_2O]$ undergoes three thermal decomposition steps. The first at 295°C corresponding to the loss of $C_6H_5 \cdot N{=}CH \cdot CHOH \cdot CHOH \cdot CH_3$ moiety (found 45.038%; calc. 44.876%). The second step at 382°C due to the decomposition of the cyanoaniline part ($C_7H_6N_2$) (found 29.424%; calc. 29.580%) and the last at 521°C with % loss 4.795 attributed to the loss of a coordinated water molecule (calc. 4.510%).

The IR spectra, Table 2, are in concordance with these results and a band at 811 cm^{-1} confirms the presence of the coordinated water[9] and supports the following structure for the complex:

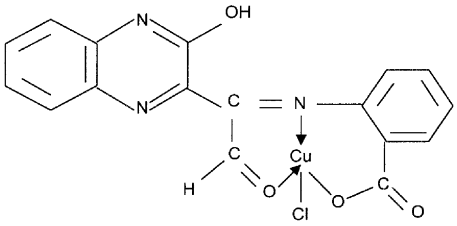


In the case of the aldehyde derivative (L_4), the first decomposition step was a multi step starting from 40°C up to 416°C with a % weight loss of 35.019 corresponding to the loss of a cyanoaniline moiety (calc. 35.515%). The second step at 462.5°C is due to the decomposition of C_6H_5COOH (found 38.279%, calc. 38.009%) and at last, a step at 834.5°C due to the decomposition of $NH{=}C \cdot CHO\text{-}CH\text{-}$ group (found 20.922%, calc. 21.495%).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

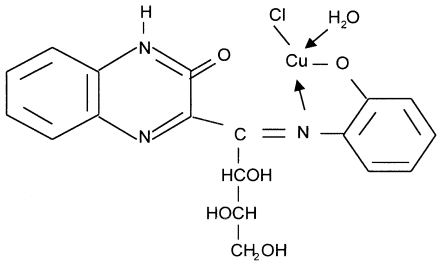
The TGA of $Cu(L_4)Cl$ shows only two decomposition steps where the weight decrease amounts 39.885% and 39.836% and these are possibly due to the loss of $OHC \cdot HC{=}N \cdot C_6H_5$ and the escape of a Cl atom[10] in a step (calc. 40.258%) and the loss of $CH_2{=}NH \cdot C_6H_4NH_2$ together with CO_2 in a another step (calc. 39.39%) and the formation of CuO.

The IR spectral bands due to complex formation suggests the formation of the complex through the oxygen and aldehydic group, OH of the carboxylate moiety and azomethine C=N groups. This proposes the following structure:



L_5 decomposed first in a multistep from 95°C–232°C with weight loss of 22.747%, which corresponds to the loss of a water molecule together with a methanol molecule (calc. 23.10%). Next, a % weight loss of 43.015% was obtained at 325.4°C attributed to losing o-OH-C_6H_4-N=CH · CH_2OH (calc. 42.54%) and a last step at 575.7°C with % loss of 40.057% due to the loss of the quinoxalinone ring ($C_8H_5N_2O$) (calc. 40.845%).

The IR of the $Cu(L_5)Cl \cdot H_2O$ complex suggests the mode of bonding to occur between Cu(II) ion with the azomethine C=N and the deprotonated phenolic group assigned from their being shifted, whereas NH and C=O groups did not participate assuming the complex structure to be as follows:

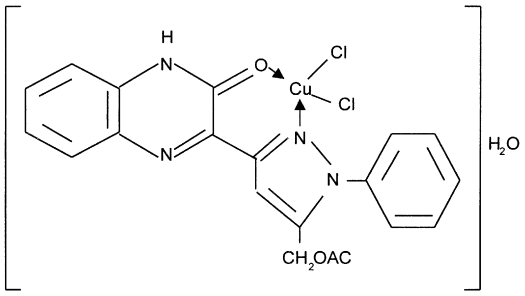


L_6 started to decompose at 88.46°C by the loss of an OH group (found 5.607%, calc. 5.978%) followed by the decomposition of

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

$C_6H_5N{=}CH \cdot CHO$ at 342°C (found 44.635%, calc. 45.39%) and at 624.5°C, the rest of the compound decomposes (found 50.325%, calc. 49.83%). Trials were done to prepare its copper complex but they were unsuccessful.

L_7 was found by TGA to decompose in a three step process. At first, $C_6H_5NH_2$ is probably lost at 340°C (found 29.75%, calc. 29.347%), then $CH_3 \cdot CH_2 \cdot CH_2OH \xrightarrow{-H2O} CH_3CH{=}CH_2$ which is lost at 440°C (found 12.978%, calc. 13.260%) and at 598°C, the rest of the compound decomposed. The IR spectral bands of this ligand and its Cu(II) complex are shown in Table 2. The appearance of a band at 3436 cm^{-1} in the complex is due to the presence of a water molecule. ν C=N of quinoxalinone ring at 1655 cm^{-1} didn't suffer a considerable change on complexation, whereas that of the pyrazole ring is blue shifted by 18 cm^{-1} indicating its participation to the metal ion. Two new bands at 233 cm^{-1} and 209 cm^{-1} are indicative of terminal chlorides. Thus the proposed structure for $[Cu(L_7)Cl_2]H_2O$ is:



REFERENCES

1. ElAshry, E.S.H.; Abdel Rahman, M.M.; Nassr, M.; Amer, A. Carbohydr. Res. **1978**, *67*, 415.
2. ElAshry, E.S.H.; Abdel Rahman, M.M.; Rashed, N.; Amer, A. Carbohydr. Res. **1978**, *67*, 423.
3. ElAshry, E.S.H.; ElKholy, I.E.; El-Kilany, Y. Carbohydr. Res. **1978**, *67*, 495.
4. Lever, A.B.P. *Inorganic Electron Spectroscopy*; Elsevier: Amsterdam, 1968.
5. Hathaway, B.J.; Billing, D.E. Coord. Chem. Rev. **1970**, *5*, 143.
6. Procter, I.M.; Hathaway, B.J.; Nicolls, P. J. Chem. Soc. (A) **1968**, 1678.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

7. Bahr, U.; Schulten, H.R. Journal of Analytical and Applied Pyrolysis **1983**, *5*, 27.
8. Yongmin, L.; Guosheng, H.; Yongxiang, M. Polyhedron **1993**, *12* (9), 1043.
9. Mashaly, A. Polyhedron **1993**, *12* (7), 745.
10. Garcia, A.B.; Diez, M.A.D.; Barros, F.J.G.; Rolando, F.J.H. Transition Met. Chem. **1996**, *21*, 197.
11. Stefan, S.L. Journal of Thermal Analysis **1994**, *42*, 1299.

Received August 17, 2000
Accepted June 15, 2001

Request Permission or Order Reprints Instantly!