Ain Shams University
Faculty of Education
Department of Chemistry

PHYSICO-CHEMICAL STUDIES ON COMPLEXES OF SOME HYDRAZONES BEARING THE QUINOLINE RING

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Dedication

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My God bless them all;

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Copper(II)-Complexes of an Isatinic Quinolyl Hydrazone-Anion effect

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Abstract

New heteroleptic copper(II)- complexes (1:1 or 1:2; M:L) were obtained from the reaction of an isatinic quinolyl hydrazone (H_2L) with several copper(II)- salts viz. Cl^-, Br^-, NO_3^-, ClO_4^-, SO_4^{2-} and AcO^-. The obtained complexes have O_h, square planar (D_{4h}- symmetry) and square pyramid arrangements. The complexes fulfill the strong coordinating ability of Cl^-, Br^-, NO_3^- and SO_4^{2-} anions. Depending on the type of the anion, the ligand coordinates the copper(II)- ions either through its lactam (SO_4^{2-} and ClO_4^-) or lactim forms (the others). For the copper(II)- isatinic complexes the antimicrobial activit shows a gradual change with change of the coordinated anions. Also, depending on the type of the anion, the order of the antimicrobial activity is as follows $Cl^- > SO_4^{2-} > Br^-$.

Keywords: isatinic quinolyl hydrazones, copper(II)- complexes, anion effect.

Introduction

Of the several heterocyclic rings, the importance of the quinoline ring arises from its therapeutic and biological activities[1,2]. Quinolyl hydrazones are known to function as chelating agents and have versatile modes of bonding. Recently, the biological activity of quinolyl hydrazones arises from their tendency to form metal chelates with transition metal ions[2-4]. On the other hand, the indole ring occurring in Jasmine flowers and Orange blossoms[1] exhibit a wide range of biological activity[3,4]. The incorporation of the quinoline ring with the indole ring may enhance the biological activity of such class of compounds. In continuation of our interest on the complexation of quinolyl hydrazones[3-8], this study is planned to investigate the ligational behavior of the studied hydrazone (scheme 1); 3-[2-(4,6-dimethylquinolin-2-yl) hydrazono]indolin-2-one towards several copper(II)- salts (Cl^-, Br^-, NO_3^-, ClO_4^-, SO_4^{2-} and AcO^-). In general, this study exhibit the role of the anion on the isolated copper(II)- complexes; scheme 2.

Material and Methods

Material: The chemicals used in this investigation were of the highest purity available (Merck, BDH, Aldrich and Fluka). They included $CuBr_2$, $CuCl_2.2H_2O$, $Cu(NO_3)_2.2½H_2O$, $Cu(ClO_4)_2.6H_2O$, $Cu(AcO)_2.H_2O$ and $CuSO_4.5H_2O$, *p*-toluidine, ethyl acetoacetate, phosphorus oxychloride, isatin and hydrazine hydrate (100%). The solvents used in this study were reagent grade and used without further purification.

Measurements: Microanalyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. Thermal analyses were carried out on a Shimadzu-50 thermal analyzer. Electronic spectra were recorded on a Jasco V-550 UV/VIS spectrophotometer. IR spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets. ESR spectra were recorded on a Bruker Elexsys, E 500 operated at X- band frequency. Mass spectra were recorded at 70 eV on a gas chromatographic GCMSQP 1000-EX Shimadzu mass spectrometer. ^{1}H NMR spectra were recorded as DMSO-d_6 solutions on a Varian Mercury VX-300 NMR spectrometer using TMS as a reference. Molar conductivity was measured as DMF solutions on the Corning conductivity meter NY 14831 model 441. Magnetic susceptibility of the complexes was measured at room temperature using a Johnson Matthey, MKI magnetic susceptibility balance. Melting points were determined using a Stuart melting point apparatus.

Preparation of the Isatinic Hydrazone (H_2L): The ligand; 3-[2-(4,6-dimethylquinolin-2-yl)hydrazono] indolin-2-one was prepared according to our previous publication[3-6]; an ethanolic mixture of 2-hydrazinyl-4,6-dimethyl quinoline (0.01mol) and isatin (0.012 mol) was refluxed for 15 min. The formed scarlet red compound was filtered off, washed with ethanol and crystallized from DMF; Yield: 67% and m.p 290°C. Analysis: Calcd. for $C_{19}H_{18}N_4O_2$ (334.3): C, 68.27; H, 5.38; N, 16.76. Found: C, 68.31; H, 5.15; N, 16.40.

Preparation of the metal complexes: A methanolic solution of the copper(II)- salt was added gradually to a methanolic solution of the ligand; H_2L in the mole ratio 1 : 1 ; Cu^{2+} : H_2L. The reaction mixture was refluxed for 2-4 h to ensure the complete precipitation of the formed complexes. The precipitated solid complexes (1-6) were filtered off, washed several times with methanol to remove any excess of the unreacted starting materials. Finally, the complexes were washed with ether and dried in vacuum desiccators over anhydrous $CaCl_2$. All the isolated complexes are stable at room temperature, non hygroscopic and insoluble in water, partially soluble in alcohols and completely soluble in DMSO and DMF. The molar conductances of 10^{-3}M DMF solutions of the complexes indicate non-electrolytic nature for all complexes except

complex 2. The results of elemental and thermal analyses are in good harmony with the proposed structures (table 1).

Antimicrobial activity: The standardized disc- agar diffusion method[6] was followed to determine the activity of the synthesized compounds against the sensitive organisms *Staphylococcus aureus* (ATCC 25923) and *Streptococcus pyogenes* (ATCC 19615) as Gram - positive bacteria, *Pseudomonas fluorescens* (S 97) and *Pseudomonas Phaseolicola* (GSPB 2828) as Gram - negative bacteria. The antibiotics chloramphencol and cephalothin were used as standard reference in case of Gram- negative and Gram-positive bacteria, respectively. The tested compounds were dissolved in dimethyl formamide (DMF) which has no inhibition activity to get concentrations of 2 and 1 mg / mL. The test was performed on medium potato dextrose agar (PDA) which contain infusion of 200 g potatoes, 6 g dextrose and 15 g agar. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume (10 µL) from the specific concentration of dissolved tested compounds and carefully placed on inoculated agar surface. After incubation for 36 h at 27 °C, inhibition of the organisms which evidenced by clear zone surround each disk was measured and used to calculate the mean of inhibition zones.

Results and Discussion

Characterization of the hydrazone: The results of elemental analysis of the investigated hydrazone; 3-[2-(4,6-dimethylquinolin-2-yl) hydrazono] indolin-2-one are in good harmony with the proposed formula. The IR spectrum of the hydrazone (table 2) showed broad bands at 3422 / 3162 and very strong band at 1633 cm^{-1} which are assigned to ν(OH/NH) and ν(C=N), respectively. The lactam nature of the hydrazone was supported by a very strong band at 1683 cm^{-1}; ν(C=O). On the other hand, the electronic absorption spectra of the hydrazone in DMF exhibit two intense bands at 274 and 394 nm characteristic for π-π* transitions[9]. Also, a broad band at 480 nm assignable to charge transfer transition (CT) which impacts the ligand its red color. The higher energy bands are consistent with those reported for the aromatic quinoline ring[4,6,8]. The mass spectrum of the ligand showed the M^+ peak at *m/z* = 316 confirming its non hydrated formula weight (316.36) and supporting its suggested structure. Finally, the ^1H NMR spectral data of the ligand in d_6-DMSO relative to TMS; figure 1, lends a further support of the structure.

Table-1
Physical and analytical data of the copper(II)- isatinic complexes

No.	Reactants H_2L + Cu(II)- salt	Complex (F. W.)	*M.F*	Yield%	Color	Elemental Analysis; % Found/(Calcd)		
						C	H	N
1	$Cu(NO_3)_2$ .2½ H_2O	[Cu (H_2L) (HL) (NO_3)] ½ H_2O (766.01)	$C_{38}H_{32}N_9O_{5½}Cu$	63	Dark brown	59.48 (59.58)	4.03 (4.18)	16.52 (16.45)
2	Cu (ClO_4)$_2$ .6H_2O	[Cu (H_2L)$_2$ (OH_2)$_2$] (ClO_4)$_2$. ¼H_2O (935.40)	$C_{38}H_{36½}N_8O_{12¼}Cl_2Cu$	51	Yellowish brown	48.77 (48.79)	3.98 (3..90)	11.9 (11.98)
3	Cu Cl_2 .2H_2O	[Cu (HL) (Cl) (OH_2)] ½H_2O.¼MeOH (449.23)	$C_{19¼}H_{19}N_4O_{2¾}ClCu$	55	Red	51.42 (51.46)	4.20 (4. 23)	12.30 (12.47)
4	$CuBr_2$	[Cu (HL) (Br) MeOH] (490.78)	$C_{20}H_{19}N_4O_2BrCu$	60	Deep red	48.94 (48.94)	3.85 (3.87)	11.72 (11.42)
5	Cu SO_4.5H_2O	[Cu(H_2L) (SO_4) (OH_2)$_2$] 4H_2O (583.83)	$C_{19}H_{28}N_4SO_{11}Cu$	65	Reddish orange	38.99 (39.08)	4.80 (4.79)	9.62 (9.59)
6	Cu (OAc)$_2$. H_2O	[Cu L (OH_2)$_3$] 5½H_2O.¼MeOH (538.77)	$C_{19¼}H_{32}N_4O_{9¾}Cu$	60	Brick red	42.85 (42.91)	5.90 (5..93)	10.38 (10.39)

Table-2
Selected IR spectral bands (cm^{-1}) of the ligand and its complexes

Other bands	ν(C=N)	ν(C=O)	ν(OH) / ν(NH)	Complex
	1633	1683	3422 / 3162	**IsatinHQ**
ν(N – O); 1332cm^{-1}	1608	1695	3167	**1**
ν(Cl – O); 1115 cm^{-1}	1615	1705	3278 + 3191	**2**
	1610	_	3307	**3**
	1609	_	3295	**4**
ν$_3$(S – O); 1113 cm^{-1}	1604	1695	3324	**5**
	1606 1559	_	3170	**6**