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SYNTHESIS AND CHARACTERIZATION OF METAL COMPLEXES OF SOME HYDRAZONES BEARING THE QUINOLINE RING

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جامعة عين شمس
كلية التربية
قسم الكيمياء

تحضير المتراكبات الفلزية لبعض الهيدرازونات الحاملة لحلقة الكينولين و التعرف عليها

رسالة مقدمة من

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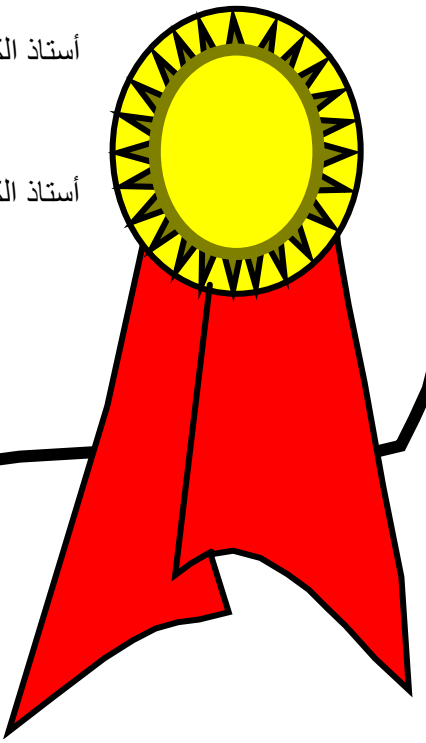

القاهرة
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Synthesis and Characterization of Metal Complexes of Some Hydrazones Bearing the Quinoline Ring

Abstract

Three series of quinolyl hydrazones were prepared and characterized. Their structural parameters (μ, E_{HOMO}, E_{LUMO}, ΔE, ΔH_f, … etc) as well as their electronic spectra in various solvents were determined. The structural parameters correlate with each other as well as with both λ_{max} and ν(C=N) to a great or less extent. The ligational behavior of only three quinolyl hydrazones (oximic, phenolic and isatinic) towards VO^{+2}, Cu(II), Ni(II) and Co(II) - ions was studied. All the isolated nickel (II) - complexes are mononuclear and have square planar geometry for the oximic hydrazone, T_d for the isatinic hydrazone and O_h for the phenolic hydrazone. This structural diversity demonstrates the great selectivity of the oximic hydrazone for Ni^{2+} ions according to the sequence;

Oximic >> Phenolic > Isatinic

On the other hand, all the VO^{+2} - complexes are binuclear or dimeric except the Oxinato (**37**) and Phen (**38**) - complexes which are mononuclear. Also, all the VO^{+2} - complexes showed an axial coordination to afford O_h structures except complexes **22** and **37** which showed a square pyramidal arrangement. However, the isolated copper (II) - complexes (mono-, bi- nuclear or dimeric) fulfill the structural diversity; O_h , T_d , square planar and square pyramidal as well as the strong coordinating ability of Cl^-, Br^-, NO_3^-, AcO^- or SO_4^{2-} compared to the non coordinating ClO_4^- anions. In general, the hydrazones showed a variety of modes of bonding and in some cases mixed modes. Structural elucidation of the isolated complexes was achieved *via* elemental and thermal analyses, magnetic susceptibility and conductivity measurements as well as spectral studies *viz*. electronic, vibrational, mass and ESR spectra.

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List of Abbreviations

2-hyrazinyl-4,8-dimethylquinoline	**HQ**
(*Z*)-2-((2-(4,8-dimethylquinolin-2-yl)hydrazono)methyl)phenol	**2-OH BzHQ**
(*Z*)-3-((2-(4,8-dimethylquinolin-2-yl)hydrazono)methyl)phenol	**3-OH BzHQ**
(*Z*)-4-((2-(4,8-dimethylquinolin-2-yl)hydrazono)methyl)phenol	**4-OH BzHQ**
(*Z*)-4-((2-(4,8-dimethylquinolin-2-yl)hydrazono)methyl)benzene-1,3-diol	**2,4-OH BzHQ**
(*Z*)-2-(2-(2-chlorobenzylidene)hydrazinyl)-4,8-dimethylquinoline	**2-Cl BzHQ**
(*E*)-2-(2-(2-methoxybenzylidene)hydrazinyl)-4,8-dimethylquinoline	**2-OMe BzHQ**
(*Z*)-4,8-dimethyl-2-(2-(1-phenylethylidene)hydrazinyl)quinoline	**AHQ**
(*Z*)-2-(1-(2-(4,8-dimethylquinolin-2-yl)hydrazono)ethyl)phenol	**2-OH AHQ**
(*Z*)-4,8-dimethyl-2-(2-(1-(4-nitrophenyl)ethylidene)hydrazinyl)quinoline	**4-NO_2 AHQ**
(*Z*)-4,8-dimethyl-2-(2-(1-*p*-tolylethylidene)hydrazinyl)quinoline	**4-NH_2 AHQ**
(*Z*)-2-(2-(1-(4-chlorophenyl)ethylidene)hydrazinyl)-4,8-dimethylquinoline	**4-Cl AHQ**
(*Z*)-2-(2-(1-(4-methoxyphenyl)ethylidene)hydrazinyl)-4,8-dimethylquinoline	**4-OMe AHQ**
(*E*)-3-(2-(4,8-dimethylquinolin-2-yl)hydrazono)butan-2-one	**Biacetyl HQ**
(*E*)-3-(2-(4,8-dimethylquinolin-2-yl)hydrazono)butan-2-one oxime	**Oxime HQ**
(*E*)-2-(2-(4,8-dimethylquinolin-2-yl)hydrazono)-1,2-diphenylethanone	**Benzil HQ**
2-(2-(4,8-dimethylquinolin-2-yl)hydrazono)-1,2-diphenylethanol	**Benzoin HQ**
(*Z*)-3-(2-(4,8-dimethylquinolin-2-yl)hydrazono)indolin-2-one	**Isatin HQ**
1,10-phenanthroline	**Phen**
N,N,N`,N`-tetra-methylethylenediamine	**Tmen**
triethylamine	**NEt_3**

8-hydroxy-quinoline	**Oxine**
charge transfer	**CT**
dielectric constant	**D**
Kosower's parameter	**Z**
Reichardt's parameter	**E_T**
donor number	**DN**
acceptor number	**AN**
Kamlet - Taft's parameter	**(α, β, π^*)**
Octahedron	**O_h**
Tetrahedron	**T_d**
Square planar	**D_{4h}**

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Aim of the work

The importance of the isatinic and phenolic quinolyl hydrazones arises from incorporating the quinoline ring with the indole ring and the phenolic compounds. Quinoline ring has therapeutic and biological activities whereas, the indole ring occurs in Jasmine flowers and orange blossoms. Also, phenols have antiseptic and disinfectants activities and are used in the preparation of dyes, bakelite and drugs. On the other hand, the importance of the oximic quinolyl hydrazones arises from: i) Their versatile bonding modes; the oximato group (=N-O$^-$) can function as a bridge to bind two metal ions in various ways. Thus, it can form a $\mu_{1,2}$(N,O) oximato-bridged extended network. ii) The ability of the oximato group to stabilize higher oxidation states of metals. iii) The design of selective receptors for the Ca(II) and Ba(II) ions. iv) The development of new oxygen activation catalysis. v) The mechanistic study of corrosion inhibition on iron surfaces and vi) The employment of oximato ligands in the synthesis of homometallic and heterometallic clusters, and coordination polymers with interesting magnetic properties. All these reasons stimulated our interest to isolate and characterize VO^{+2}, Cu(II), Ni(II) and Co(II) - complexes of the oximic, isatinic and phenolic quinolyl hydrazones as well as to study the role of the counter ions on the formed complexes. In general, this study is an extensive one to investigate the ligational behavior of the studied hydrazones towards VO^{+2}, Cu(II), Ni(II) and Co(II) - ions. Also, this study concentrate on correlation of the structural parameters for a large number of hydrazones as well as the dependence of λ_{max} and ν(C=N) of the hydrazone linkage on both the structural parameters and the Hammett's constant (σ_p).