Kingdom of Saudi Arabia
Al-Imam Mohammad Ibn Saud Islamic University
College of Sciences
Department of Chemistry

Title

Synthesis and Characterization of Some Metal Complexes and their Comparison with those Formed by the Heavy Metal Removal from Water

A graduation research project

Submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

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ABSTRACT

The Student will searching the University library and the known data base on the internet for previous work on Synthesis and characterization of some metal complexes and their comparison with those formed by the heavy metal removal from water under the guidance of the supervisor. The chemical will be collected according to the laboratory facilities. Some metal complexes will be prepared in ethanol and alternatively in water with different concentrations of metal salt. The tendency of the ligand to remove heavy metal would be investigated according to the laboratory resources. A comparison between the properties of the complexes formed by normal method and in the water medium will be performed. A small article will be written to be submitted to the chemistry department.

ملخص

سيقوم الطالب بالبحث في مكتبة الجامعة وقواعد البيانات المعروفة على شبكة الانترنت عن الابحاث السابقة حول تحضير وتوصيف بعض المتراكبات المعدنية المعدنية ومقارنتها مع تلك التي يتم تحضيرها عن طريق إزالة المعادن الثقيلة من المياه تحت توجيه من المشرف. سيتم جمع هذه المواد الكيميائية وفقا لامكانيات المختبرات. وسيتم إعداد بعض المتراكبات في الإيثانول ثم اعادة تحضيرها في المياء بتركيزات مختلفة من الملح المعدني. وستقاس قدرة المترابط على ازالة العناصر الثقيلة تبعا لامكانيات المختبرات. سيتم إجراء مقارنة بين خصائص المتراكبات التي حضرت بالطريقة المتبعة لتحضير هذا النوع من المتراكبات مع تلك المحضرة في الماء. سيتم كتابة مقال صغير لتقديمه إلى قسم الكيمياء.

Introduction

Schiff bases are the compounds carrying imine or azomethine (–C=N–) functional group. These are the condensation products of primary amines with carbonyl compounds and were first reported by Hugo Schiff [1, 2]. Schiff bases have also been shown to exhibit a broad range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties [3, 4]. Schiff bases have been utilized as synthons in the preparation of a number of industrial and biologically active compounds like formazans, 4-thiazolidinines, benzoxazines, and so forth, via ring closure, cycloaddition, and replacement reactions [5]. Schiff base derivatives in various processes promoted the researchers for designing of novel heterocyclic/aryl Schiff bases for development of new environmental-friendly technology [6]. In view of the importance of Schiff bases, in the present work we report the synthesis of a novel Schiff base ligands (E)-2-((2-phenylhydrazono)methyl)phenol, (Z)-2-(2-hydroxybenzylidene)hydrazine-1-carbothioamide and (E)-N-(4-nitrophenyl)-1-phenylmethanimine and their metal complexes.

Review of Literature

The first preparation of imines was reported in the 19th century by Schiff (1864). Since then a variety of methods for the synthesis of imines have been described [7]. The classical synthesis reported by Schiff involves the condensation of a carbonyl compound with an amine under azeotropic distillation. Molecular sieves are then used to completely remove water formed in the system [8]. In the 1990s an in situ method for water elimination was developed, using dehydrating solvents such as tetramethyl orthosilicate or trimethyl orthoformate [9]. In 2004, Chakraborti et al. [10] demonstrated that the efficiency of these methods is dependent on the use of highly electrophilic carbonyl compounds and strongly nucleophilic amines. They proposed as an alternative the use of substances that function as Bronsted-Lowry or Lewis acids to activate the carbonyl group of aldehydes, catalyze the nucleophilic attack by amines, and dehydrate the system, eliminating water as the final step [10]. Examples of Bronsted-Lowry or lewis acids used for the synthesis of Schiff bases include ZnCl2, TiCl4,

MgSO4-PPTS, $Ti(OR)_4$, alumina, H_2SO_4, $NaHCO_3$, $MgSO_4$, $Mg(ClO_4)_2$, H_3CCOOH, $Er(OTf)_3$,P_2O_5/Al_2O_3, HCl [10-14]. The use of microwave irradiation commenced with the independent studies of Rousell and Majetich groups [15,16]. Microwave irradiation is less environmentally problematic than other methods because it abolishes the excessive use of aromatic solvents and the Dean-Stark apparatus for azeotropic removal of water. Another feature of this technique is that the reactions achieve high efficiency in a shorter period of time. Malaria is a neglected disease that still causes serious public health problems. Every year, approximately 500 million people are afflicted by the disease, of whom around 1–3 million die, 90% of who in sub-Sahara Africa are primarily children [17]. Malaria is currently found in more than 100 countries throughout Africa, Latin America, Asia, and Oceania. Human malaria is mainly caused by four species of Plasmodium (P. falciparum, P. vivax, P. ovale, and P. malariae). The female mosquito of the Anophelesgenus is the vector of Plasmodium [18]. The search for new drugs, vaccines, and insecticides to prevent or treat this disease is clearly a priority. Schiff bases have been shown to be interesting moieties for the design of antimalarial agents. Ancistrocladidine (Figure 1) is a secondary metabolite produced by plants from the families Ancistrocladaceae and Dioncophyllaceae that present an imine group in its molecular scaffold. Compound1has been shown to be active against P. Falciparum K1 and 3D7. The minimum inhibitory concentrations (MIC values) of ancistrocladidine necessary to completely abolish P. falciparum K1 and 3D7 growth were 0.3 and 1.9lg/mL, respectively. Interestingly, compound1was 90- and 10-fold more selective to P. falciparum K1 and 3D7, respectively than to rat skeletal myoblast L-6 cells [19].

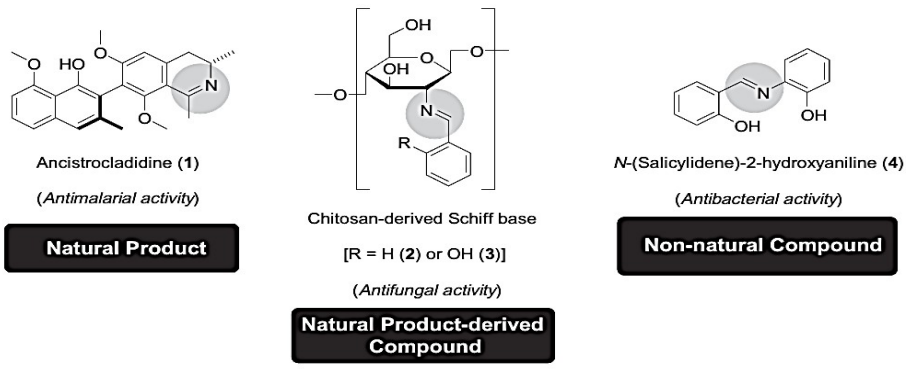
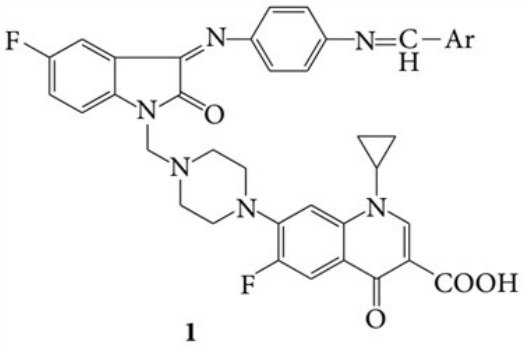


Figure 1: Ancistrocladidine

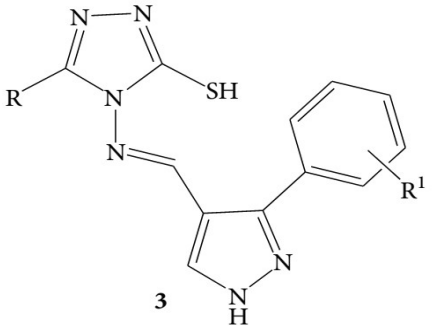
series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives, that is, 7-(4-((3-(4-(substituted benzylideneamino) phenylimino)-5-fluoro-2-oxindolin-1-yl)methyl)piperazin-1-yl)-1-cyclopropyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carboxylic acid, 1(a–l), (Figure 2) were synthesized and characterized for in vitro antibacterial activity. Antimicrobial activity of synthesized compounds was assessed by minimum inhibitory concentration (MIC) in comparison with standard antimicrobial drugs, that is, ciprofloxacin and ketoconazole. Compound 1c was reported to be more active than both of the standard drugs against tested microorganisms which proves the significance of substituted electron-donating groups in improving the antimicrobial activity [20]. A novel series of pyrazole-based Schiff bases, 3(a–j), (Figure 2) 4-[(3-substituted-1H-pyrazol-3-yl)methyleneamino]-5-substituted-4H-1,2,4-triazole-3-thiols, was synthesized and screened for antibacterial activity against the microbial strains of S. aureus, P. aeruginosa, B. subtilis, and E. coli. From the results, compound 3f was found to be equally as active as standard drug ceftriaxone against P. aeruginosa, B. subtilis, and E. coli and most active against S. aureus [21]. Synthesis of new open (4–6) (Figure 2) and macrocyclic (7) (Figure 2) Schiff bases has been done and evaluated for the antimicrobial activity. . Macrocyclic Schiff bases were reported as the condensation product of 1,6-bis(2-formylphenyl)hexane with thiocarbohydrazide. In order to test the biological activity of the synthesized compounds, four microorganisms (K. pneumoniae, E. coli, S. aureus, and S. typhimurium) were employed. All the synthesized compounds were found to be moderate to strongly active [22]. A few novel solid complexes, 8, (Figure 2) of La(III), Ce(III), Pr(III), Nd(III), Sm(III), and Gd(III) with Schiff base, that is, 9,(Figure 2) 4-hydroxy-3-(1-[2-(2-hydroxybenzylidene)-amino-phenylimino]-ethyl)-6-methyl-pyran-2-ones, were synthesized and screened for the antibacterial activity against S. aureus, E. coli, and Bacillusspecies and antifungal activity against A. niger, Trichoderma ,and F. oxysporum. Results revealed that the complexes were biologically active and have exhibited enhanced antimicrobial activity than the free ligand (Schiff base) [23]. Some novel Schiff bases, macrocyclic tetradentate nitrogen donor (N4) 6,7,14,15-tetrahydroxy-1,4,9,12-tetraazacyclohexadecane-5,8,13,16-tetrone ligand-based metal complexes, 11, (Figure 2) from10, (Figure 2) were synthesized and screened for the in vitro antifungal activity and toxicity studies. Minimum inhibitory concentration (MIC) along

with ergosterol composition assay against C. albicans (ATCC 10261), C. glabrata (ATCC 90030), and C. tropicalis (ATCC 750) was performed. The antimicrobial results indicated that all the synthesized compounds were found to be active against all fungal strains. It was observed that Ni(II) complex and Co(II) complex drastically reduced ergosterol content of cell membrane followed by the Cu(II) complex and the ligand itself [24].



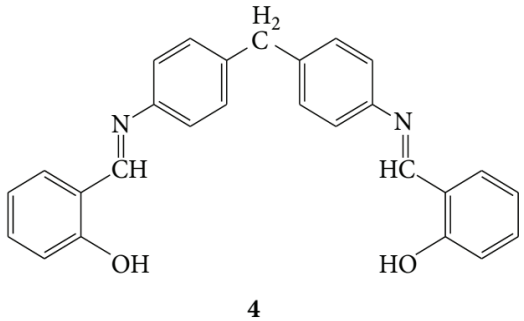
1

1	Ar	1	Ar
a	$-C_6H_5$	**g**	$-4CH_3-C_6H_4$
b	$-4Cl-C_6H_4$	**h**	$-3,4,5(OCH_3)_3-C_6H_4$
c	$-4OH-C_6H_4$	**i**	$-4OH, 5-OCH_3-C_6H_4$
d	$-4OCH_3-C_6H_4$	**j**	$-5NO_2-C_6H_4$
e	$-4NO_2-C_6H_4$	**k**	$-4N(CH_3)_2-C_6H_4$
f	$-6OH-C_6H_4$	**l**	$-CH=HC-C_6H_4$



3

3	R	R^1	3	R	R^1
a	$-C_2H_5$	H	**f**	H	H
b	$-C_2H_5$	$4-OCH_3$	**g**	H	$4-OCH_3$
c	$-C_2H_5$	4-F	**h**	H	4-F
d	$-C_2H_5$	4-Cl	**i**	H	4-Cl
e	$-C_2H_5$	$2,4-Cl_2$	**j**	$-C_3H_7$	4-F



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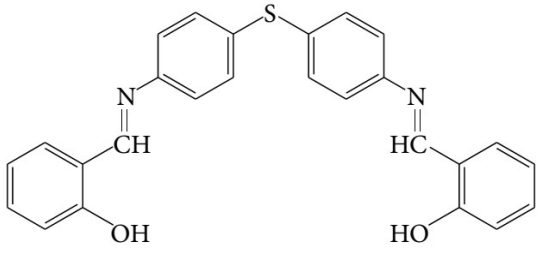

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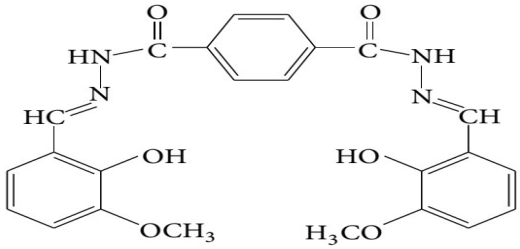

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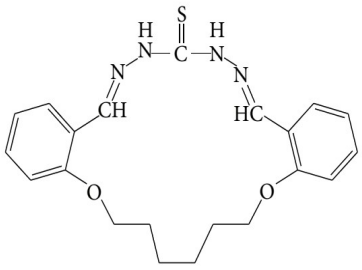
Figure 2 (Part 1) : A series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives



7

FIGURE 7

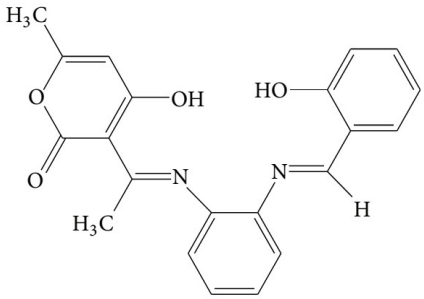


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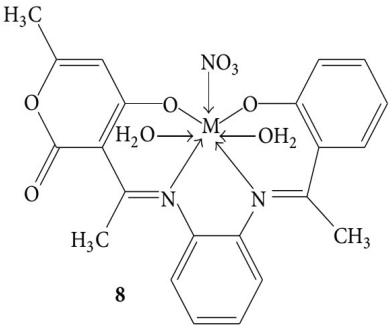
FIGURE 9



8

M = La(III), Ce(III), Pr(III), Nd(III), and Sm(III)

FIGURE 8

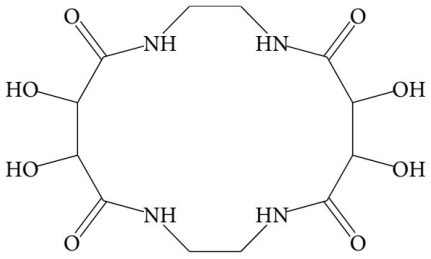


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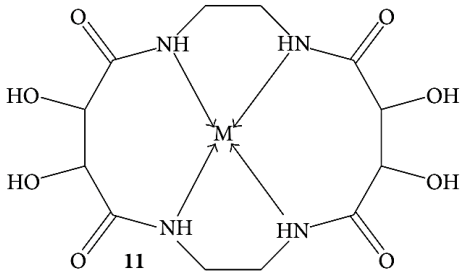
FIGURE 10



11

M = Cu(II), Co(II), and Ni(II)

FIGURE 11

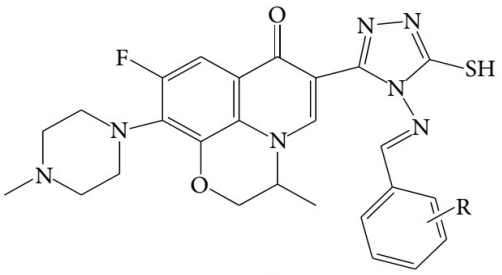
Figure 2 (Part 2) : A series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives

A novel series of fluoroquinolone C-3 heterocycles (IV), that is, s-triazole Schiff 27(a–k) (Figure 2) and mannich bases derivatives of ofloxacin was synthesized and evaluated for in vitro antitumor activity against a murine leukemia cell line (L1210), a human leukocytoma cell line (HL60), and a Chinese hamster ovary cell line (CHO) using the MTT assay. From the observed results it was concluded that a free phenol group containing compounds 27c, 27g ,and 27h exhibited more potent activity than

the other test compounds [25]. A series of thirteen quinolin-2(1H)-one-derived Schiff bases 28(a–m) (Figure 2) and their Cu(II) 29(a–m) (Figure 2) complexes was synthesized. Selected compounds were screened for their in vitro anticancer and antifungal activities. Human hepatic carcinoma cell line, Hep-G2 was employed for screening of the anticancer potential. Cisplatin was used as a standard drug for the comparison. Screened compounds were found to be active antifungal agents and compound (7E)-7-(3-ethoxy-2-hydroxybenzylideneamino)-4-methylquinolin-2(1H)-one was reported as a potent cytotoxic agent which enlightened the good potential of Cu(II) complexes of Schiff base ligands as therapeutic agents [26]. A series of three Schiff bases 4-(([3-(4-substituted phenyl)-1H-pyrazol-4-yl] methylene)amino)-5-[(substituted phenoxy)methyl]-1,2,4-triazole-3- thiol,30(a–c) (Figure 2) was evaluated for their in vivo antitumor activity against Ehrlich-ascites-carcinoma-(EAC-) bearing Swiss albino mice. Schiff bases were used in two different doses, that is, 50 mg/kg and 100 mg/kg of the body weight of mice. Mean survival time (MST) and percentage increase in lifespan (% ILS), that is, total number of days an animal survived from the day of tumor inoculation were calculated. Body weights of all animals were measured on days 0, 3, 5, 7, 10, 12, and 14 [27]. The results revealed that cisplatin (3.5 mg/kg, i.p. single dose) significantly enhanced MST of EAC-infected mice. Among the three Schiff bases 4-(([3-(4-fluorophenyl)-1H-pyrazol-4-yl]methylene)amino)-5-[(2-methylphenoxy)methyl]-1,2,4-triazole-3-thiol,30c,atthedoseof 100 mg/kg body weight was found to enhance the mean survival time of tumor-bearing mice. MST and deviated hematological parameters of infected mice were found to be normal after treatment with 30c. A series of substituted-N-[(1E)-substituted phenylmethylidene]benzohydrazide analogs, 31(a–n) (Figure 2) was synthesized and evaluated for their in vitro antioxidant, anti-inflammatory, and antimicrobial activities. The antioxidant activity of all the synthesized compounds was evaluated by the phosphomolybdenum method. Compounds 31c, 31d, and 31f were reported to show good antioxidant activity due to presence of 4-nitro, 4-methyl, and 3-nitro groups, respectively, whereas31ahaving 4-hydroxy group did not possess such activity. From the results, it can be concluded that substitutions like nitro and alkyl lead to enhancement in antioxidant activity through one-electron transfer mechanism [28]. A new Schiff base ligand N-(2-hydroxylacetophenone)-3-oxapentane-1,5-diamine (HL), 32, and its Ni complex, [Ni2 (L)2(NO3)2], 33, were synthesized and evaluated for antioxidation and DNA-binding

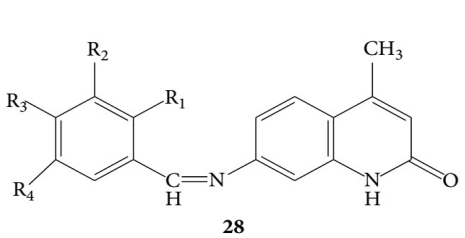
properties. The complex showed inhibitory activity and the suppression ratio of OH radical increases with increase in the concentration of the complex. Mannitol and vitamin C were employed as the standard antioxidants for comparison. According to the results the 50% inhibitory concentration (IC50) value of 33 was found to be 8.1±0.078μM whereasIC50 for mannitol was 9.6μM and 32 was devoid of antioxidant activity. Both 32and33bind to DNA in intercalation mode but the binding strength of 33was found to be better than 32 [29]. A series of 3-(benzylideneamino)-2-phenylquinazoline-4(3H)-one, 34(a–l) (Figure 2) was synthesized and evaluated for their cytotoxicity and antiviral activity. Compounds having 2-hydroxy substitution showed better antiviral activity [30]. A series of thiazolines and azetidinones was synthesized by reaction of Schiff bases, 35(a–i), (Figure 2) (intermediate reaction) with thioglycolic acid and chloral acetyl chloride, respectively. Schiff bases were evaluated for antibacterial and antiviral (against HIV-I) potential. All the compounds were found to be good HIV-I inhibitors except 35f and 35g [31]. Schiff bases of 2-phenyl-3-(amino substituted arylidene)quinazoline-4-(3H)-ones, 36(a-b) (Figure 2) were synthesized and evaluated for antihyperlipidemic activity. Hyperlipidemia was induced in rats by atherogenic diet. After 45 days, levels of serum total cholesterol (TC) and LDL cholesterol were recorded to be 231.6±1.435 mg/dL and 164.53 ±1.26 mg/dL which were comparatively higher than normal rat serum TC (71.36± 1.195 mg/dL) and LDL-C (100.66 ± 0.88 mg/dL) levels whereas serum HDL-C level was found to be lower (19.012± 0.66 mg/dL) as compared to the normal level (50.66 ± 0.88 mg/dL). Results revealed that36areduced TC and LDL-C levels to 172.41 ±41 mg/dL and 91.10±0.97 mg/dL and raised serum HDL-C level to 60.07 ±0.67 mg/dL whereas36b reduced-serumTCandLDL-Clevelsto93.63 ±1.292 and 81.35±0.81 mg/dL and raised serum HDL-C level to 59.40± 0.45 mg/dL at the dose of 200 mg/kg, p.o., once daily [32]. A series of oxovanadium complexes with mixed ligands, a bidentate NN ligand, 37, and a tetradentate ONO-donor Schiff base ligand, 38 (Figure 2) was synthesized and evaluated for protein tyrosine phosphate (PTP) inhibition. PTP1B has been identified as key enzyme related to insulin resistance. Thus the inhibition of PTP1B has emerged out as an important approach to enhance insulin sensitivity. The kinetic analysis results revealed that oxovanadium complexes displayed potent reversible competitive inhibition PTP1B with IC50 values in low nanomolar range [33]. A series of twenty-seven bis-Schiff base of isatin, 39 (i–xxvii) (Figure 2) was synthesized and evaluated

for their in vitro anti glycation activity. Compounds 39(xx) and 39 (xxi) substituted with nitro groups at para and ortho positions, respectively, were found to be the most potent antiglycation agents with IC50 (257.61 ±5.63μM) and 243.95±4.59μM better than IC50 (294.46 ±1.50μM) of rutin which was employed as standard. The 3,4-dihydroxy analog 39 (vii) was found as the third most potent antiglycationa gent with IC50 (291.14±2.53μM) [34].



27

27	R	27	R
a	H	**g**	3-OH, 4-CH_3O
b	4-CH_3O	**h**	4-OH, 3-CH_3O
c	2-OH	**i**	4-Cl
d	2-CH_3O	**j**	4-F
e	3,4-OCH_2O	**k**	4-NO_2
f	3,4,5-$(CH_3O)_3$		



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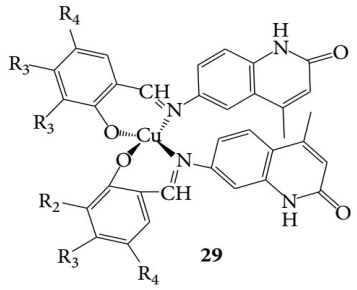
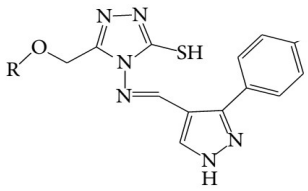


29

28, 29	R_1	R_2	R_3	R_4
d	OH	OC_2H_5	H	H

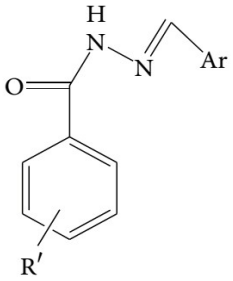
FIGURE 28



30

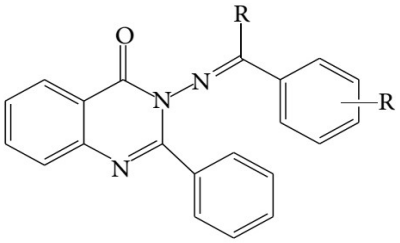
30	R	R_1
a	4-Methylbenzene	Cl
b	4-Methylbenzene	F
c	2-Methylbenzene	F

Figure 2 (Part 3): A series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives



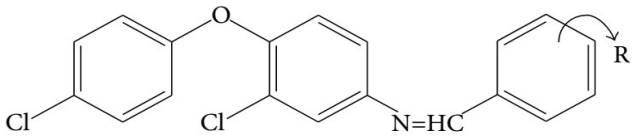
31

31	R′	Ar	31	R′	Ar
a	4-Cl	2-OHC_6H_4	**g**	2-COC_6H_5	-C_6H_4
b	4-Cl	3-OCH_3, 4-OHC_6H_3	**h**	2-COC_6H_5	4-ClC_6H_4
c	4-Cl	4-$NO_2C_6H_4$	**i**	2-COC_6H_5	4-$NO_2C_6H_4$
d	4-Cl	4-$CH_3C_6H_4$	**j**	2-COC_6H_5	4-$CH_3C_6H_4$
e	4-Cl	2-$OHC_{10}H_6$	**k**	2-COC_6H_5	3-OCH_3, 4-OHC_6H_3
f	4-Cl	3-$NO_2C_6H_4$	**l**	2-COC_6H_5	4-OHC_6H_4
			m	2-COC_6H_5	2-$NO_2C_6H_4$
			n	2-COC_6H_5	2-OHC_6H_4



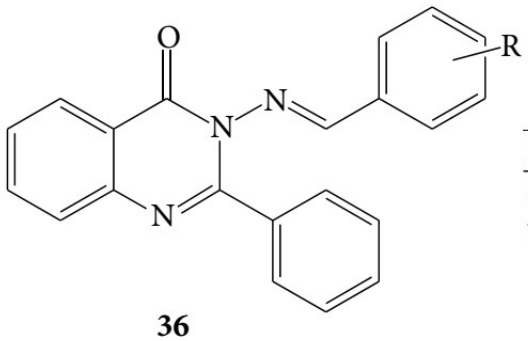
34

34	R	R′	34	R	R′
a	H	2-OH	**g**	H	4-OH
b	H	2-NO_2	**h**	CH_3	H
c	H	4-OCH_3	**i**	CH_3	4-OH
d	H	4-$N(CH_3)_2$	**j**	H	4-Cl
e	CH_3	4-Cl	**k**	H	3-OH, 4-OCH_3
f	H	H	**l**	H	2-OCH_3



35

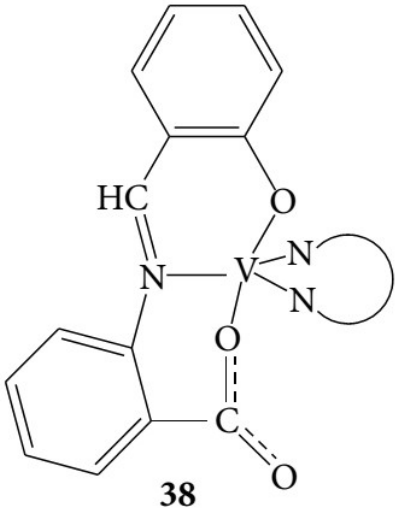
35	R
a	H
b	2-OH
c	4-OH
d	4-OH, 3-OCH_3
e	-CH=CH-C_6H_5
f	4-Cl
g	4-NO_2
h	4-OCH_3
i	3,4,5-$(OCH_3)_3$



36

36	R
a	2-OH
b	4-OH, 3-OMe

Figure 2 (Part 4): A series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives



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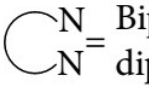
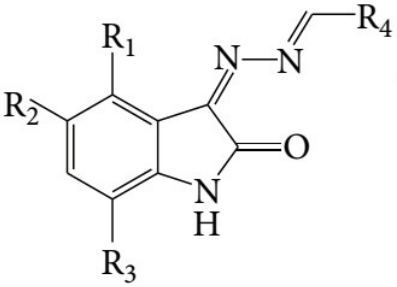


Bipyridine, phenanthroline, dipyridoquinoxaline, dipyridophenazine, and methyldipyridophenazine



39

39	R_1	R_2	R_3	R_4
xx	H	H	H	4-$NO_2C_6H_4$
xxi	H	H	H	2-$NO_2C_6H_4$
vii	H	H	H	3,4-$(OH)_2C_6H_3$

Figure 2 (Part 5): A series of some novel 5-substituted Schiff and Mannich bases of isatin derivatives

Experimental

Experimental Part

In this part the student started to learn by the synthesis of an already prepared ligand and its metal complexes for comparison reasons [35] then the new methodology was used to prepare the complexes and to test the ability of the ligand to remove heavy metal from water.

Materials

All the reagents employed for the preparation of the ligand and its complexes were of the best grade available and used without further purification. Preparation of ligands:

Preparation of ligands

The Ligand, H2L1

Ethanol solution (10 mL) of 2-hydroxybenzaldehyde (1.00 g, 8.19 mmol) was added dropwise to ethanol solution (10 mL) of phenylhydrazine (0.89 g, 8.19 mmol) over 15 min with stirring and continue stirring for 0.5 h. The yellow precipitate (Figure 3) was then filtered off, washed with methanol, and dried in a vacuum desiccator over P4O10 (1.23 g, 71% yield). 1H NMR (400 MHz, DMSO): δΔ10.61 ppm [s, 1H, H(8)], 10.40 ppm [s, 1H, H(10)], 820 ppm [s, 1H, H(7)], 7.55 ppm [d, 1H, H(6)], 7.28 ppm [pst, 1H, H(2)], 720 ppm [t, 2H, JD7.6, H(12) and H(16)], 7.01 ppm [t, 2H, JD7.6, H (13) and H(15)], 690 ppm [m, 2H, H(1) and H(3)], 6.80 [t, 1H, J D 7.6, H(14)]. 13C NMR (300 MHz, DMSO, 300 K): 155.67 C(8), 144.70 C(7) and C(11), 137.36 C(2) and C(5), 129.35 C(6), 129.26 C(15) and C(13), 120.41 C(14), 119.35 C (1), 115.98 C(3), 111.70 C(12) and C(16). IR (KBr): n(OH) 3291 (br), n(NH) 3281(Sh), n(CHN) 1622(s), n(C-O) 1250 (m). Elemental analysis for C13H12N2O (212.25): Anal. Calcd. C 73.56, H 5.70, N 13.20; Found C 73.61, H 5.92, N 13.09.

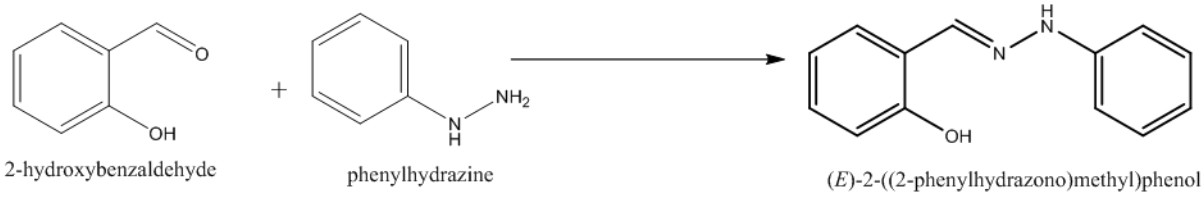


Figure 3: Preparation of the ligand H_2L^1

Preparation of metal complexes

Complexes 1 and 2:

A hot (60° C) methanol solution of the copper (lI) acetate or cobalt acetate was added to a hot (60° C) ethanol solution of the ligand with molecular ratios 1:1 L/M (ligand /metal). The reaction mixture was then refluxed for a 2 h. The precipitates formed were filtered, washed with ethanol, then with diethyl ether and dried under vacuum over anhydrous $CaCl_2$.

Complex 3:

(150 mL) of distilled water and (0.472 g) of copper (11) acetate monohydrate was added with stir until melted (blue color) to (0.5 g) of the ligand with stir and molecular ratios 1:1 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed (brown color) were filtered, and dried in oven (3.912 g), (the solution green color).

Complex 4:

(150 mL) of distilled water and (0.944 g) of $(CH_3COO)_2Cu.H_2O$ was added with stir until melted (blue color) to (0.5 g) of the ligand with stir and molecular ratios 1:2 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed (brown color) were filtered, and dried in oven (4.031 g), (the solution green color).

Complex 5:

(150 mL) of distilled water and (1.888 g) of $(CH_3COO)_2Cu.H_2O$ was added with stir until melted (blue color) to (0.5 g) of the ligand with stir and molecular ratios 1:4 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed (brown color) were filtered, and dried in oven (4.70 g), (the solution green color).

Complex 6:

(150 mL) of distilled water and (3.776 g) of $(CH_3COO)_2Cu.H_2O$ was added with stir until melted (blue color) to (0.5 g) of the ligand with stir and molecular ratios 1:8 L/M . The reaction mixture was then refluxed for a 2 h (bluish green color). The precipitates formed (brown color) were filtered, and dried in oven (4.142 g), (the solution blue color).

Complex 7:

(150 mL) of distilled water and (4.72 g) of $(CH_3COO)_2Cu.H_2O$ was added with stir until melted (blue color) to (0.25 g) of the ligand with stir and molecular ratios 1:20 L/M . The reaction mixture was then refluxed for a 4 h (bluish green color). The precipitates formed (brown color) were filtered, and dried in oven (3.892 g), (the solution blue color).

Complex 8:

(150 mL) of distilled water and (0.561 g) of nickel chloride extra pure was added with stir until melted (green color) to (0.5 g) of the ligand with stir and molecular ratios 1:1 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed white color) were filtered, and dried in oven (3.997 g), (the solution green color).

Complex 9:

(150 mL) of distilled water and (1.122 g) of $NiCl_2.6H_2O$ was added with stir until melted (green color) to (0.5 g) of the ligand with stir and molecular ratios 1:2 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed white color) were filtered, and dried in oven (4.152 g), (the solution green color).

Complex 10:

(150 mL) of distilled water and (2.244 g) of $NiCl_2.6H_2O$ was added with stir until melted (green color) to (0.5 g) of the ligand with stir and molecular ratios 1:4 L/M . The reaction mixture was then refluxed for a 2 h (green color). The precipitates formed white color) were filtered, and dried in oven (4.272 g), (the solution green color).

Complex 11:

(150 mL) of distilled water and (0.588 g) of Cobalt(ll) Acetate tetrahyrate was added with stir until melted (pink color) to (0.5 g) of the ligand with stir and molecular ratios 1:1 L/M . The reaction mixture was then refluxed for a 2 h (pink color). The precipitates formed white color) were filtered, and dried in oven (3.942 g), (the solution pink color).

Complex 12:

(150 mL) of distilled water and (1.176 g) of Cobalt(ll) Acetate tetrahyrate was added with stir until melted (pink color) to (0.5 g) of the ligand with stir and molecular ratios 1:2 L/M . The reaction mixture was then refluxed for a 2 h (pink color). The precipitates formed white color) were filtered, and dried in oven 4.020 g), (the solution pink color).

Complex 13:

(150 mL) of distilled water and (2.352 g) of Cobalt(ll) Acetate tetrahyrate was added with stir until melted (pink color) to (0.5 g) of the ligand with stir and molecular ratios 1:4 L/M . The reaction mixture was then refluxed for a 2 h (pink color). The precipitates formed white color) were filtered, and dried in oven (4.104 g), (the solution pink color).

Results and Discussion

Results and Discussion

In case of complexes 3-13, the addition of the ligand to the metal salt solution formed to phases. After vigorous stirring the color of the solution changed to pale and the yellow ligand started to become brown indicating the formation of complex. After filtrations, the precipitate formed was brown and resemble the formed complexes in case of complexes 1 and 2. The samples formed were send for IR and elemental analysis (we did not obtain the results yet). The remaining solutions will be investigated for metal concentration using ICP. Since the ligand and tow of its complexes are already published [35] by the supervisor the results may Be summarized as:

All the synthesized compounds are colored, solid, stable at room temperature, non-hygroscopic, insoluble in water and parhly soluble in common organic solvents such as $CHCl_3$, but soluble in MDF and DMSO. The proposed structure for complexes are summarized in figure 4.

Infrared spectra:

IR spectra of the complexes were recorded to confirm their structures. The assignments of the characteristic vibrational frequencies of the complexes were made by comparison with the vibrational frequencies of the free ligand. The ligand behaved as neutral or monobasic bidentate ligand coordinating through the imine nitrogen and the phenolic oxygen. In some complexes the signal of the imine group was shifted to lower wave number accompanied by a decrease in its intensity while the signal due to phenolic C-O were shifted to higher wave number, indicating they are involved in complex formation. The two new signals in the 430–457 and 539–573 cm^{-1} ranges may be assigned to ν(M-N) and ν(M-O) respectively. IR spectral studies reported on metal aceto complexes indicated that the acetate ligand may coordinate to a metal center in either a monodentatc, bidentate or bridging manner. The $\nu_{asym.}(CO_2)$ and $\nu_{sym.}(CO_2)$ of the free acetate ions are at 1560 cm^{-1} and 1416 cm^{-1}, respectively. In monodcntatc coordination ν(C=O) is found at higher energy than $\nu_{asym.}(CO_2)$ and ν(C-O) is lower than $\nu_{sym.}(CO_2)$. As a result, the separation between the two ν(CO) bands is much larger in monodentate complexes than the free ion. The opposite trend is observed in bidentate aceto coordination; the separation

between ν(CO) is smaller than for the free ion. [36-37] Both complexes showed two new bands in 1554-1566 cm^{-1} and 1344 cm^{-1}, which may be attributed to $n_{asym.}$(COO) and $n_{sym.}$ (COO), respectively, with D > 210 indicating monodentate acetates. [36]

Electronic Spectra

The copper complex showed two bands at 540 nm and 610 nm, which can be assigned to the 2B1g→ 2B2g and 2B1g→ 2Eg transitions, respectively indicating that copper(II) have tetragonal distorted octahedral geometry. [37-38] Its magnetic moment was 1.95 B.M., which falls within the range normally observed for octahedral copper complexes. [39] The magnetic moments of the complex 3 is 598 BM, which is closer to the spin only value indicating an octahedral structure for this complex [40] which was further supported by the appearance of very week signals at 540, 650 and 834 nm ranges which can be assigned to the transitions 6A1g→ 4A1g(G), 6A1g→ 4T2g(G), and 6A1g→ 4T1g(G) in an octahedral geometry. [40,41]

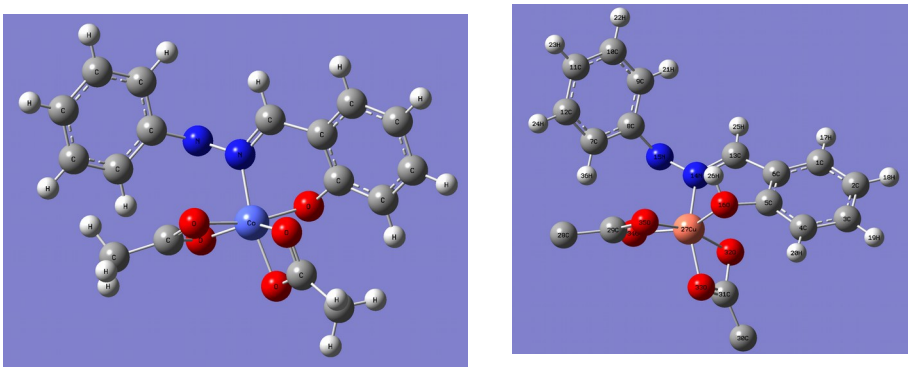
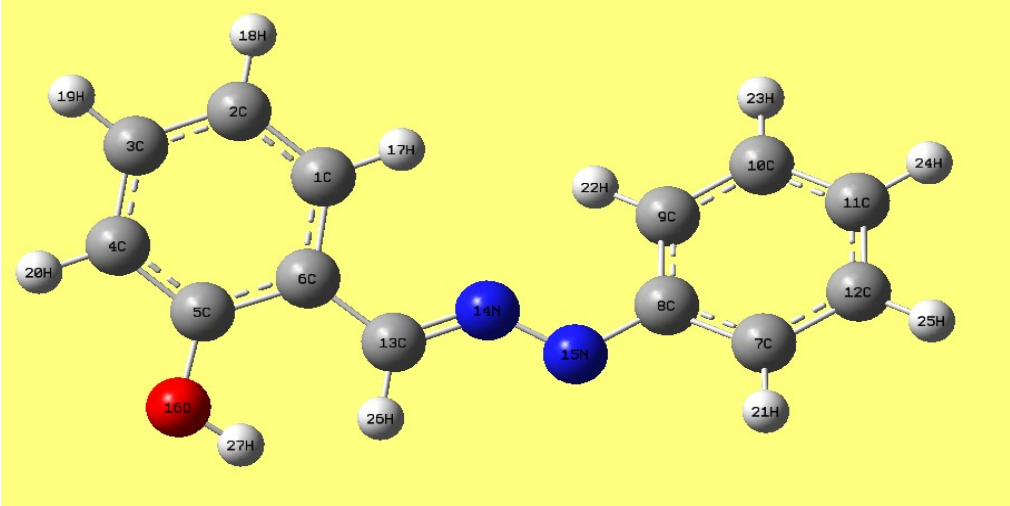


figure 4: The proposed structure for some complexes

Molecular Modeling

The Results of modeling the ligand are summarized as follow:

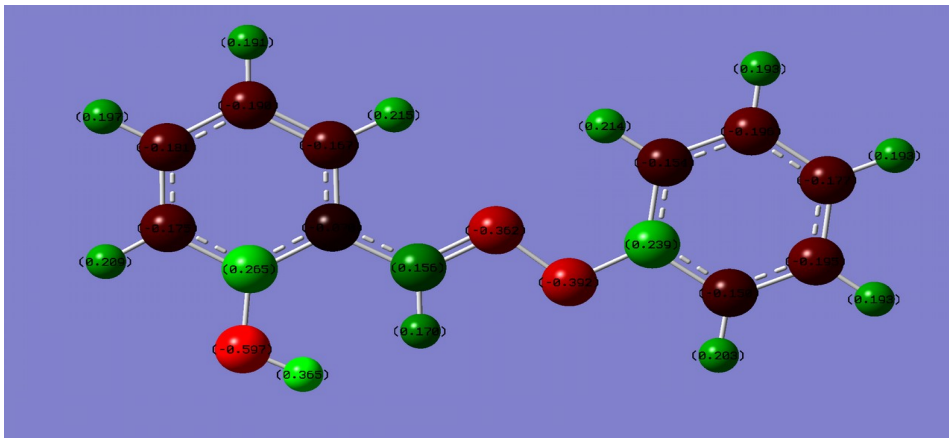


1- Atomic Charges optimization:

Center		Spin Dipole Couplings 3XX-RR	3YY-RR	3ZZ-RR
1	Atom	-0.034282	-0.033962	0.068243
2	Atom	0.017242	0.013740	-0.030982
3	Atom	-0.039368	-0.042688	0.082056
4	Atom	0.017588	0.017966	-0.035554
5	Atom	-0.039864	-0.043439	0.083304
6	Atom	0.021996	0.016925	-0.038920
7	Atom	-0.084346	-0.087638	0.171983
8	Atom	0.057354	0.045842	-0.103196
9	Atom	-0.085891	-0.084137	0.170028
10	Atom	0.042890	0.034035	-0.076925
11	Atom	-0.093363	-0.100834	0.194197
12	Atom	0.039741	0.039341	-0.079082
13	Atom	-0.140403	-0.145735	0.286138
14	Atom	0.119487	0.100633	-0.220120
15	Atom	-0.520812	-0.532347	1.053159
16	Atom	-0.045825	-0.049650	0.095475
17	Atom	0.002522	0.000077	-0.002599
18	Atom	0.002198	-0.000817	-0.001382
19	Atom	0.004458	-0.003420	-0.001038
20	Atom	0.000770	0.000706	-0.001477
21	Atom	-0.007144	0.012172	-0.005028
22	Atom	0.002644	0.001085	-0.003729
23	Atom	0.005044	-0.002410	-0.002634
24	Atom	0.012142	-0.010109	-0.002033
25	Atom	0.000900	0.001784	-0.002684
26	Atom	-0.010742	0.017832	-0.007090
27	Atom	0.004364	-0.000240	-0.004124

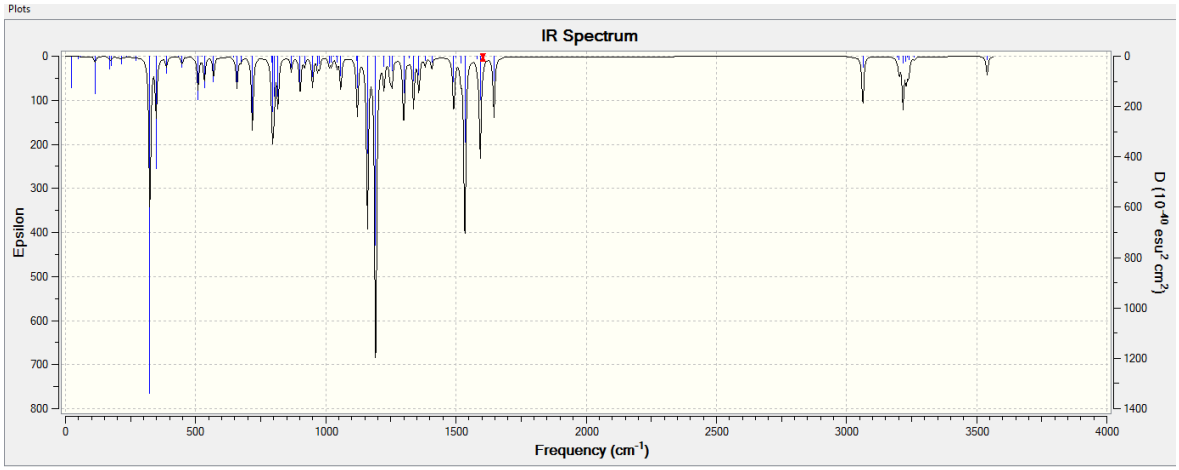
		XY	XZ	YZ
1	Atom	-0.000746	0.000009	0.000007
2	Atom	-0.000870	-0.000007	-0.000009
3	Atom	-0.002242	0.000021	0.000031
4	Atom	-0.002142	-0.000007	-0.000007
5	Atom	-0.000397	0.000011	0.000005
6	Atom	-0.003457	-0.000006	-0.000012
7	Atom	0.000205	-0.000047	-0.000061
8	Atom	0.015224	0.000019	0.000031
9	Atom	0.000205	-0.000064	-0.000037
10	Atom	0.000218	0.000021	0.000026
11	Atom	0.003939	-0.000043	-0.000074
12	Atom	0.004700	0.000019	0.000030
13	Atom	-0.006217	0.000155	0.000190
14	Atom	0.001045	-0.000063	-0.000204
15	Atom	-0.001449	-0.000115	-0.000527
16	Atom	-0.000276	0.000128	-0.000026
17	Atom	0.003657	0.000000	-0.000001
18	Atom	-0.000252	0.000000	0.000000
19	Atom	-0.005800	0.000000	0.000002
20	Atom	-0.002030	0.000000	0.000000
21	Atom	-0.000566	-0.000001	0.000005
22	Atom	-0.011844	0.000001	-0.000003
23	Atom	-0.000593	0.000001	0.000000
24	Atom	0.011481	0.000005	0.000000
25	Atom	0.003940	0.000001	0.000002
26	Atom	0.002044	0.000002	-0.000005
27	Atom	-0.000295	-0.000005	0.000003

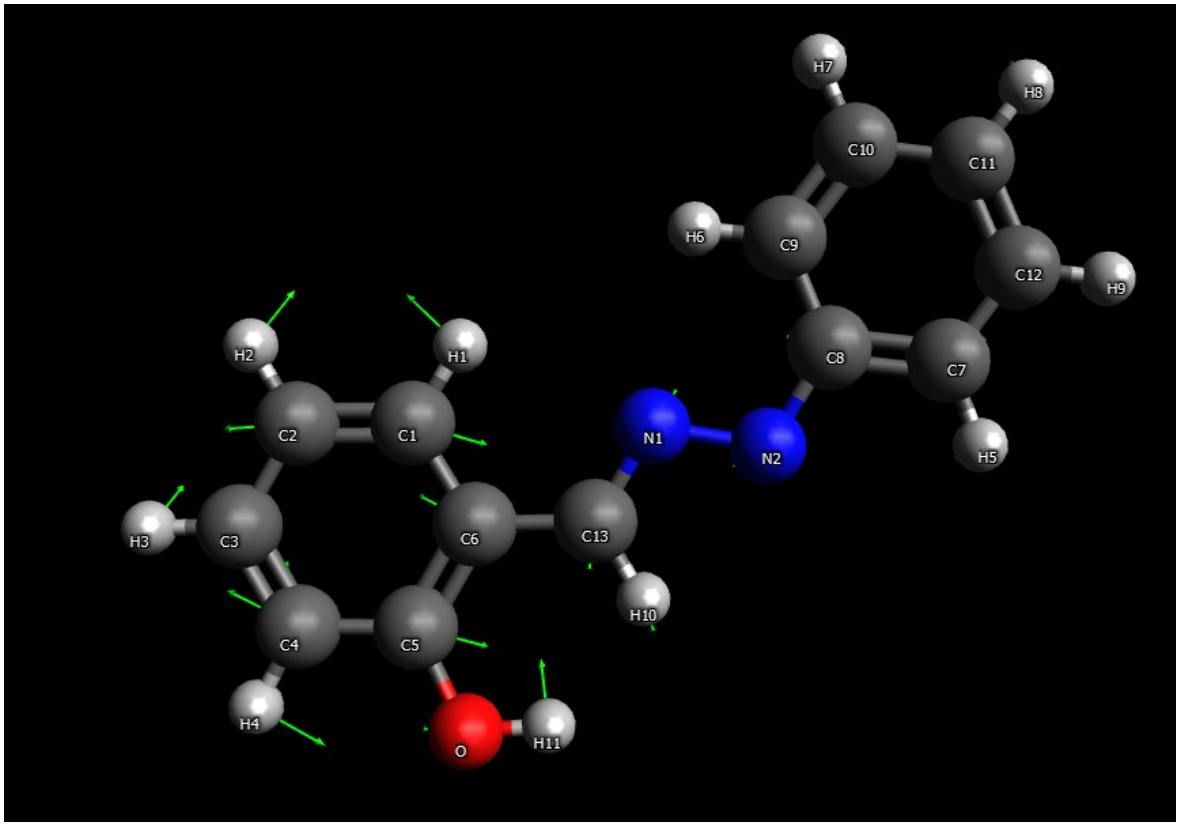
2- Charge Distribution



3- Infrared:

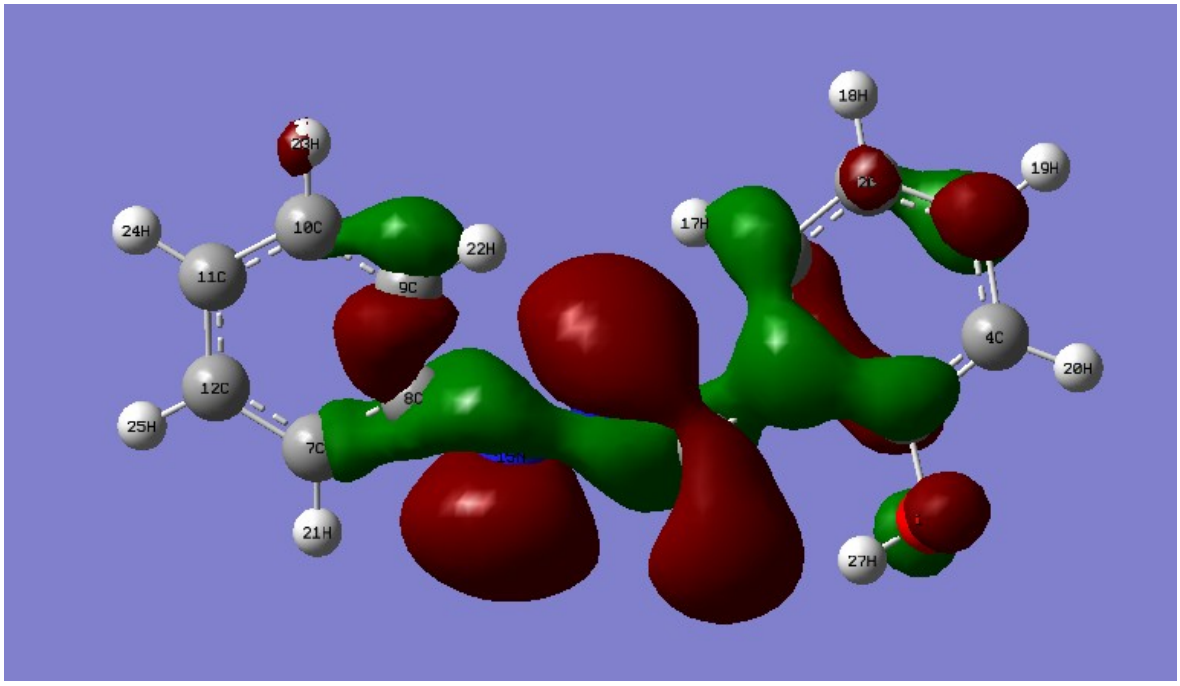
The resulted spectrum was almost identical to that obtained from the analysis. The spectra can even by explained and assigned theoretically and also display force vector.



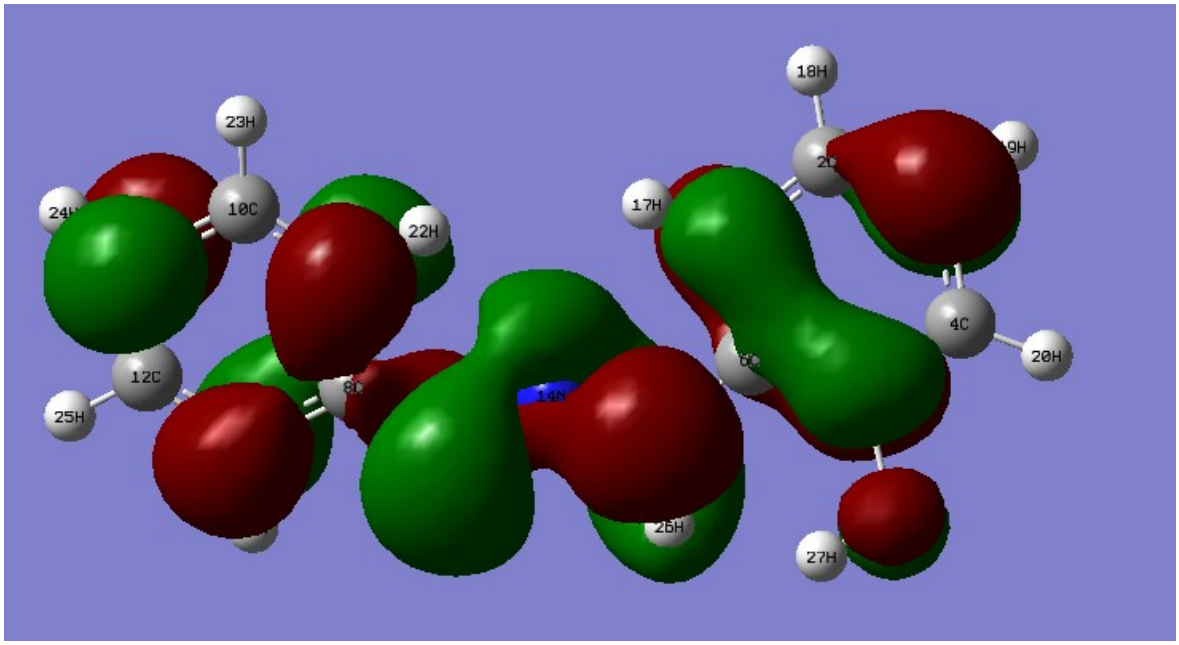


The signal at 1646 cm^{-1} is due to the vibration

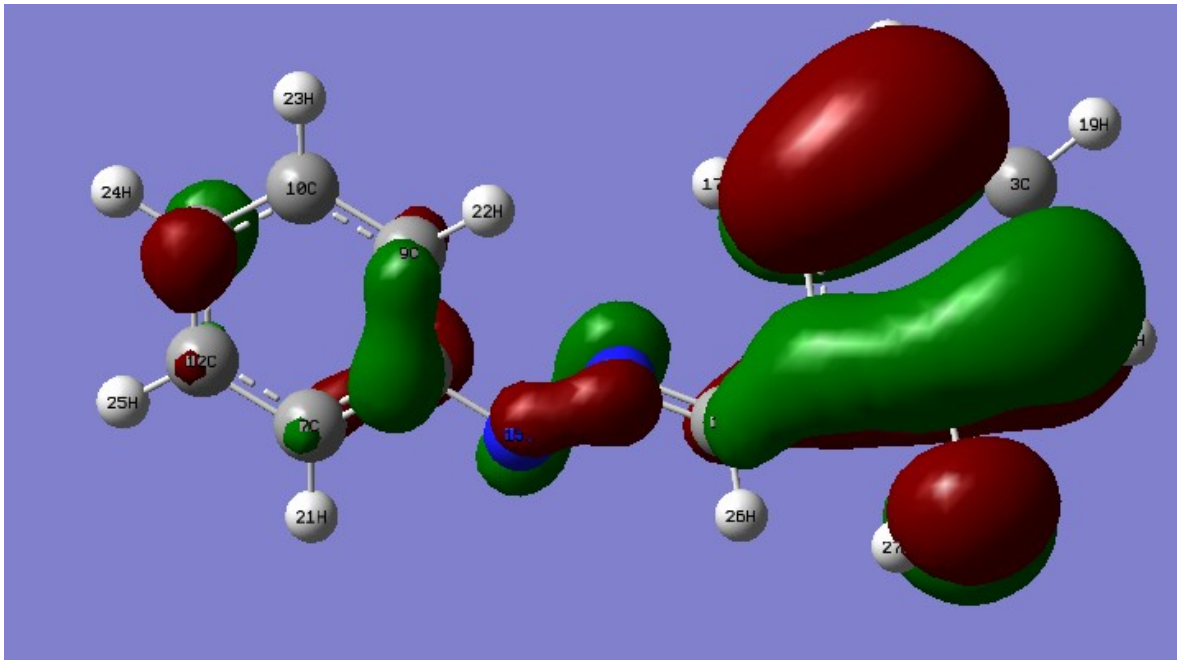
4- HOMO Molecular Orbitals



5- LUMO Molecular Orbitals



6- Occupied Molecular Orbitals



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