

Environmentally benign synthesis and Biological evaluation of Ni(II) complexes with bi-anionic tetradentate (NOO'N) ligand

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Abstract

A facile, efficient, environmentally benign and economical method under microwave irradiation in green medium has been used for the synthesis of a series of octahedral complexes of Ni(II) with NOO'N donor ligand, o-phenylene-bis(o-hydroxy acetophenone) diamine as primary bi-anionic tetradentate ligand and quinoline, pyridine etc. different monodentate secondary ligands. All the eco-friendly synthesized complexes were characterized by elemental analysis, conductivity and magnetic moment measurements and spectroscopic analyses. The obtained results were compared with conventional methods. The anti-microbial activity of the investigated ligand and its Ni(II) complexes clearly indicates that the complexes are found to be more active than the free ligand towards the tested microbes.

Keywords: Nickel(II) complexes, microwave irradiation, octahedral geometry, anti-microbial activity

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I. Introduction

Since from about three decades, the synthetic chemists have been working for the betterment of human life by minimizing the chemical pollution. Now, much works have been going on these directions to design chemicals and chemical synthetic processes that will be less harmful to human health and the environment through using environmentally benign methodologies of chemical synthesis¹⁻³. Microwave-promoted syntheses, syntheses using catalysts and syntheses using green solvents or without solvents for the synthesis of coordination compounds are the very significant environmentally benign methods⁴⁻⁵.

Literature survey revealed that the azomethine compounds i.e., Schiff bases not only have very good complexing capacity towards transition metal ions but also have innumerable applications in the various fields and are very significant in the development of coordination chemistry⁶. The present trend in the chemical research on azomethine complexes has gyrated towards elucidation of anti-microbial and other therapeutic activities⁷⁻⁸. Consequent upon the numerous applications of Schiff bases in various fields of chemical sciences, the chemists have been greater interest in developing efficient methods for the syntheses of them and their transition metal complexes syntheses. Microwave assisted reactions are the facile, efficient and eco-friendly approach for the synthesis of various Schiff bases and their transition metal complexes⁹⁻¹⁴.

As a part of our continuing efforts to synthesize and characterize transition metal complexes using azomethine ligand under eco-friendly conditions, we now report the microwave assisted synthesis, characterization and anti-microbial activities of Ni(II) complexes of NOO'N donor ligand, o-phenylene-bis(o-hydroxy acetophenone) diamine as primary ligand and quinoline, pyridine and different monodentate secondary ligands in the present research article. The present paper presents a comparative study of the formed Schiff base and Ni(II) complexes via conventional reaction and environmentally benign methods. Although, single crystal of the investigated compounds could not be isolated from any solutions; however analytical, magnetic data and spectroscopic studies enable us to propose the possible geometry of the undertaken complexes.

II. Experimental

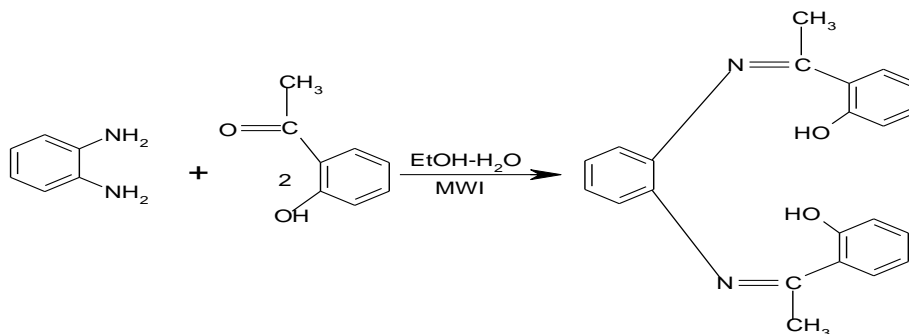
Materials & Methods

All the chemicals used for the synthesis of ligand and complexes under investigation were of analytical grade. The used solvents were purified by previously used standard methods. The melting points of the investigated compounds were determined on an Electro-thermal 9100 apparatus and are uncorrected. The conductivity measurements of the investigated complexes were done in DMF bridge model PW 9501 using Philips PW 9515/10 conductivity cell. The magnetic susceptibility of the investigated complexes was carried out by Gouy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ ($\chi_g = 16.44 \times 10^{-6}$) as a standard or reference. The elemental analyses

were recorded on a Carlo-Ebra EA1110 CHNO-S analyser. The electronic spectra in solid state as well as in solution were recorded on a Shimadzu UV-Visible spectrophotometer. The infrared spectra of the ligand and the investigated complexes were run as KBr discs in the range $4000-400\text{ cm}^{-1}$ on a Shimadzu Infrared spectrophotometer. The microwave assisted syntheses were carried out in a common but modified microwave oven model 2001 ETB with rotating tray and a power source 230 V, at output energy of 800W and 2450MHz frequency. The on/off cycling method was used to control the temperature of microwave reactions. The progress of the microwave reactions and the purity of the products were monitored by thin layer chromatography (TLC) on pre-coated silica gel GF254 plates (E-Merck) by using appropriate solvent systems. The anti-microbial activities of the ligand as well as investigated complexes was studied by disc diffusion method using nutrient agar as medium for antibacterial activity and sabraoud dextrose agar medium for antifungal activity.

Microwave assisted synthesis of Ligand

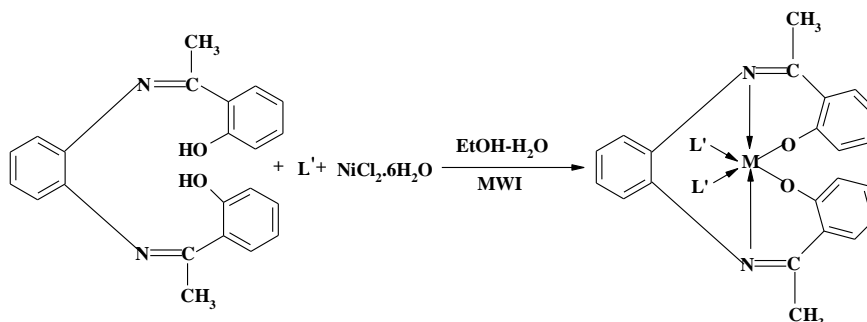
The eco-friendly, economic, enhance reaction rate, less use of hazardous chemicals, low cost and better yield, simplicity in processing and simple handling motivated us for synthesis of ligand in green solvent, e.g., 1:1 mixture of ethanol and water in a modified microwave oven. A 1:2 molar mixture of *o*-hydroxy acetophenone and *o*-phenylene diamine in aqueous-ethanolic mixture was refluxed at ambient temperature for six minutes in the microwave oven and then cooled till yellowish solid. The resultant solid product was washed with ethyl alcohol and recrystallised with acetone and finally dried under reduces pressure over anhydrous CaCl_2 in a desiccator. The reaction was completed in a short time with better yield (about 77%) than was obtained in the conventional method (schme-1). The yield and the required time for conventional and green chemical approach have been compared and the results are reported in table-1.



Scheme-1: Microwave assisted synthesis of ligand

Synthesis of Metal Complexes

The investigated Ni(II) complexes were prepared by refluxing an aqueous-ethanolic stoichiometric (1:1:2, metal:ligand L:ligand L') ratio of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, primary ligand(L) and secondary ligands (L') in the microwave oven adding a few drops of triethyl amine as a catalyst. The synthetic reactions were completed in a short time (5-12 minutes) with better yields than were obtained by the conventional method (scheme-2). The resultant coloured solid products were collected by filtration and recrystallized from DMF and washed with ethanol and finally dried under reduced pressure over anhydrous CaCl_2 in a desiccator. The progress of the microwave irradiated reaction and purity of the products were monitored by TLC silica gel G (yield: 56-70%).



Scheme-2: Microwave assisted synthesis of Ni(II)-complexes
(where, L' = H_2O , NH_3 , Quinoline, phenyl isocyanide, pyridine, picolines etc. and M=Ni)

Antimicrobial Activity

The antibacterial and antifungal activities of the investigated ligand and its Ni(II) complexes were performed by the disc diffusion method¹⁵. The *in vitro* antibacterial ligand and its Ni(II) complexes were performed against two Gram positive bacteria namely *Staphylococcus aureus* (SA) & *Enterococcus faecalis* (EF), two Gram negative bacteria namely *Escherichia coli* (EC) & *Staphylococcus mutans* (SM) and the antifungal activity was tested against fungal strains *Candida albicans* (CA) & *Aspergillus niger* (AN). The chloramphenicol was used as a standard reference in case of bacteria while griseofulvin was used as a standard for antifungal reference of the same concentration under identical conditions. The investigated compounds were dissolved in DMSO (no inhibition activity) to get concentration of 1 mg/mL. The sterile disks were soaked in test compounds and carefully placed on incubated agar surface. The petridishes were incubated for 24 hours at 643 K in case of bacteria and for 48 hours at 643 K in case of fungi. Finally, the zone of inhibition was carefully measured. Each test was performed in triplicate in individual experiments and the average is reported in table-4.

III. Results And Discussion

All the microwave assisted synthesized complexes are coloured, solid and stable towards air and moisture at room temperature. These do not possess sharp melting points and decompose on heating at higher temperature than respective melting points. The investigated complexes are not soluble in common organic solvents. All the spectral and micro-analytical results reveal that the composition of all the investigated metal complexes corresponds to $[NiL(L')_2]$ stoichiometry. The observed molar conductance values (12 to 22 $ohm^{-1} cm^2 mol^{-1}$) are too low to account for any dissociation of the investigated complexes in DMF at room temperature, which revealed their non-electrolytic nature¹⁶.

The experimental results revealed that the synthetic reactions were completed in a short time with higher yields in the microwave assisted synthetic procedure compared to the conventional thermal method. The comparison of results of conventional method and microwave irradiated method, analytical data of the investigated complexes together with their physical properties which are consistent with proposed molecular formula are shown in table-1.

Table-1: Comparison of conventional and microwave assisted method, analytical and physical data of the compounds under investigation

Compounds (Colour)	Reaction Time CM (MM)	Yield (%) CM (MM)	Mol. Weight	Melting point (in K)	Elemental analysis Calculated (Found) %				μ_{eff} (BM)	Conductance ($ohm^{-1} cm^2 mol^{-1}$)
					C	H	N	Ni		
$C_{22}H_{20}N_2O_2$ (pale yellow)	2 hrs. (6 min.)	60 (77)	344	512	76.74 (76.70)	5.81 (5.80)	8.13 (8.10)	--	--	20
$[Ni(C_{22}H_{18}N_2O_2)(H_2O)_2]$ (green)	2.5 hrs. (5min.)	57 (70)	436.69	565	60.45 (60.40)	5.03 (5.08)	6.41 (6.40)	13.44 (13.50)	3.20	22
$[Ni(C_{22}H_{18}N_2O_2)(NH_3)_2]$ (light green)	2.5 hrs. (6 min.)	40 (65)	434.69	579	60.73 (60.70)	5.52 (5.50)	12.89 (12.90)	13.50 (13.50)	3.24	15
$[Ni(C_{22}H_{18}N_2O_2)(C_5H_5N)_2]$ (faint green)	2.5 hrs. (8 min.)	41 (66)	558.69	623	68.73 (68.70)	5.01 (5.05)	10.04 (10.00)	10.51 (10.50)	3.26	12
$[Ni(C_{22}H_{18}N_2O_2)(C_9H_7N)_2]$ (greenish white)	2.5 hrs. (10 min.)	44 (67)	658.69	589	72.86 (72.80)	4.87 (4.84)	8.50 (8.50)	8.91 (8.90)	3.28	16
$[Ni(C_{22}H_{18}N_2O_2)(C_6H_5N)_2]$ (light green)	2.5 hrs. (10 min.)	53 (68)	606.69	594	67.24 (67.20)	4.62 (4.60)	9.24 (9.20)	9.67 (9.70)	3.32	13
$[Ni(C_{22}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (faint green) α -picoline	2.5 hrs. (12 min.)	41 (70)	586.69	584	69.53 (69.50)	5.46 (5.40)	9.55 (9.50)	10.00 (10.00)	3.20	12
$[Ni(C_{22}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (faint green) β -picoline	2.5 hrs. (12 min.)	33 (56)	586.69	605	69.53 (69.50)	5.46 (5.40)	9.55 (9.50)	10.00 (10.00)	3.18	18
$[Ni(C_{22}H_{18}N_2O_2)(C_5H_4NCH_3)_2]$ (faint green) λ -picoline	2.5 hrs. (12 min.)	41 (70)	586.69	595	69.53 (69.50)	5.46 (5.40)	9.55 (9.50)	10.00 (10.00)	3.20	14

CM = Conventional Method; MM = Microwave Method

IR Spectral Studies

The IR spectral data of the investigated Schiff base ligand (L) and its microwave assisted synthesized eight Ni(II) complexes are listed in table-2. The IR spectra of the investigated complexes were compared with that of free ligand in order to determine the involvement of coordination sites in coordination complexes. The

observed IR spectra of the investigated complexes contained all the absorption bands except some peculiar bands and some new absorption bands which indicated the coordination of the ligand with metal ion through N & O.

On comparing the IR spectra of the ligand precursors, o-hydroxy acetophenone and the ligand itself, the absence of the characteristic ketonic carbonyl group stretching band near 1750 cm⁻¹, and the appearance of the azomethine -C=N band at 1630 cm⁻¹ indicating the formation of the Schiff base ligand.

It was observed that the frequencies obtained due to the vibrations of (O-H), (C=N) and (C-N) groups in ligand have been appreciably changed during the complexation. In all the investigated complexes, it is clear that the hydroxyl group band at 3360 cm⁻¹ of the ligand was disappeared indicating deprotonation of the ligand and conforming coordination of the phenolic oxygen atom to the metal center. The deprotonation of phenolic (-OH) group of ligand has been supported by the shifting of phenolic (C-O) frequencies from 1420-1430 cm⁻¹ to high frequencies 1450-1460 cm⁻¹ in the investigated complexes. The reduction of frequency of (C=N) group in the ligand (1630 cm⁻¹) to 1580 cm⁻¹ suggests the participation of nitrogen atom of azomethine group in the bond formation with metal center. The reduction in the frequency of C-N group in the ligand from 1240 cm⁻¹ to 1220 cm⁻¹ indicated the coordination of aldimino nitrogen of ligand with the metal center¹⁷. The comparison of IR spectra of the ligand and the investigated complexes, it is concluded that the ligand behaves as bi-anionic tetradentate (NOO'N) donor molecule.

Due to overlap of $\nu(\text{OH})$ & $\nu(\text{NH})$ vibrations in case of aqua-complex, separate band for coordinated H₂O was not obtained. However, a band at 750 cm⁻¹ is attributed due to rocking mode of coordinating water with metal center. The amino complex displays one broad and strong band around 3460 cm⁻¹ assignable to (NH) stretching vibration of coordinated NH₃. In case of phenyl isocyanide complex, there is an increase in the $\nu(\text{C}=\text{N})$ vibration of the ligand (2170 cm⁻¹) and the complex (2220 cm⁻¹) indicating the involvement of isocyanide (N=C) group in the coordination. In quinoline complex, the medium and broad band around 1680 cm⁻¹ obtained due to ring vibration indicates the involvement of N-atom of the quinoline in the complex formation. The pyridine and picoline complexes display bands in the finger print and far infrared region. The IR bands at 1000-1100 cm⁻¹ in the complex is regarded as the characteristic vibrations of the coordinated pyridine molecule and different picoline molecules display bands at 790, 770 and 750 cm⁻¹ respectively¹⁸.

A sharp and medium band obtained in the range of 420-435 cm⁻¹ in the investigated complexes due to $\nu(\text{M}-\text{N})$ vibrations further confirms the coordination of aldimino N-atoms in the bond formation with the metal center. A sharp and medium band obtained in the range of 450-475 cm⁻¹ in the complexes due to $\nu(\text{M}-\text{O})$ further confirms the coordination of phenolic oxygen atom in the bond formation with the metal center. The frequency obtained due to the vibrations of (M-O) bond is greater than that of (M-N) bond because (M-O) bond is more ionic than the (M-N) bond¹⁹.

Table-2: Observed IR bands (cm⁻¹) of Ligand and their Ni-complexes

Bands (cm ⁻¹) of Ligand	Bands of complexes	Probable assignment
--	3480	$\nu(\text{N}-\text{H})$
3360		$\nu(\text{O}-\text{H})$
1630	1580	$\nu(\text{C}=\text{N})$
1420	1450	$\nu(\text{O}-\text{H})$ phenolic
1240	1220	$\nu(\text{C}-\text{N})$
	1680	$\nu(\text{C}=\text{N})$ Quinoline
	2220	$\nu(-\text{NC})$
	1050	Due to pyridine ring
	790	α -picoline
	750	β -picoline
	760	λ -picoline
	450-475	$\nu(\text{M}-\text{O})$
	420-435	$\nu(\text{M}-\text{N})$

Electronic Spectral Studies & Magnetic Properties

The electronic spectra of ligand and its investigated nickel complexes were recorded in order to assign the plausible geometry around the central metal ion in the complexes. The electronic spectra of the ligand and its nickel complexes in DMF were scanned in the region 200-1000 nm and their tentative assignments are presented in table-3.

Table-3: Data of electronic spectra of the ligand (L) and its Ni(II) complexes

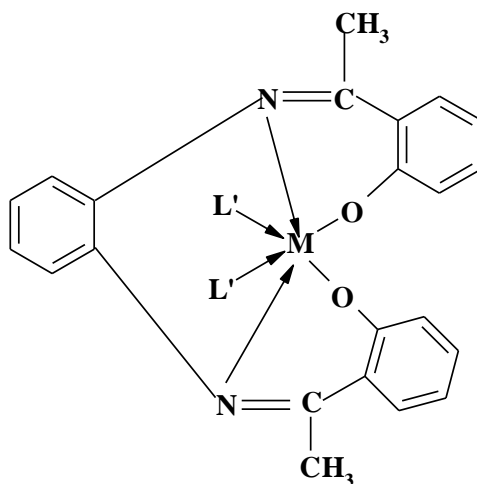
Complexes	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	Charge Transfer Band
C ₂₂ H ₂₀ N ₂ O ₂	13850	--	--	28300
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(H ₂ O) ₂]	8210	16400	22640	29600
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(NH ₃) ₂]	8150	16200	21750	31300
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₅ N) ₂]	8090	16200	21420	32700
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₉ H ₇ N) ₂]	8100	21250	21250	33100
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₆ H ₅ NC) ₂]	8130	15700	21930	33900
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	8110	16000	21840	33500
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	8130	15600	22630	33200
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	8100	16000	21610	34100

All the investigated complexes [Ni(L)(L')₂] show an intense band around 28300-34100 cm⁻¹ which has been assigned as charge transfer band from the ligand to the metal center. Further, three bands were obtained in which the first obtained in the range of 8090-8210 cm⁻¹ and is broad and unsymmetrical due to J.T. distortion and due to ³A_{2g}(F) → ³T_{2g}(F) transition. The second sharp and symmetrical band obtained in the range of 15400- 16400 cm⁻¹ due to ³A_{2g}(F) → ³T_{1g}(F) transition which is spin as well as symmetry allowed transition. The third sharp and symmetrical band obtained in the range of 21250- 22640 cm⁻¹ due to ³A_{2g}(F) → ³T_{1g}(P) transition which is spin as well as symmetry allowed transition. The electronic transitions revealed the spin free octahedral geometry for all the investigated nickel complexes²⁰⁻²¹.

The values of the magnetic moments obtained for all the investigated nickel complexes in the range of 3.18 to 3.32 B.M. indicates their octahedral geometry²².

Proposed Geometry of Ni(II) Complexes

On the basis of above spectral and magnetic properties observations, it is tentatively suggested that the investigated Ni(II) complexes show octahedral geometry [figure-1] in which the primary ligand (L) acts as dibasic tetradentate (NO O'N) donor and the elemental analysis data and molecular weight determination of investigated complexes show their mono-meric nature.


Figure-1: Proposed octahedral geometry of investigated Ni-complexes

Studies of Antimicrobial Activities

The difference in the antimicrobial activities of the ligand and its investigated Ni(II) complexes were studied and the results are presented in table-4. The comparison of MIC (minimum inhibitory concentration) values of investigated ligand and its nickel complexes indicates that generally all complexes have a better activity than the free ligand which may be probably due to their lipophilic nature and it can be explained on the basis of chelation theory²³. Further, the antimicrobial results show that the activity of ligand has increased on coordination to the central metal ion of the investigated Ni(II)-complexes.

Table-4: In vitro Antimicrobial Activity of the ligands and their Co-complexes (in µgmL⁻¹)

Compound	MIC(µg/mL)					
	Bacteria				Fungi	
	Gram positive		Gram negative		CA	AN
SA	EF	EC	SM			
C ₂₂ H ₂₀ N ₂ O ₂	13	11	13	12	19	20
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(H ₂ O) ₂]	9	8	10	8	16	13
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(NH ₃) ₂]	8	9	10	9	14	16

[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₅ N) ₂]	10	8	11	9	15	14
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₉ H ₇ N) ₂]	11	8	9	10	18	17
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₆ H ₅ NC) ₂]	9	10	10	11	14	15
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	10	9	12	10	12	16
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	9	10	11	8	14	12
[Ni(C ₂₂ H ₁₈ N ₂ O ₂)(C ₅ H ₄ NCH ₃) ₂]	11	9	10	9	17	15
Chloramphenicol	0.25	1.5	2.3	1.7	3.2	3.5
Griseofulvin	--	--	--	--	8	11

IV. Conclusions

An efficient and facile synthesis of a new biologically active ligand in single step by treating *o*-hydroxy acetophenone with *o*-phenylene diamine in aqueous-ethanol as a green solvent and its Ni(II) complexes carrying potential pharmacophore have been prepared in an environmentally benign microwave protocol. The yields of the products formed under MWI were high in comparison to conventional method and time required for completion of these reactions was also less in comparison to classical method.

The synthesized ligand coordinated with the Ni(II) ion in a tetradentate (NO O'N) manner. On the basis of elemental analysis, molar conductance, magnetic susceptibility measurements, electronic, IR spectral observations, octahedral geometry has been proposed for the Ni(II) complexes. Antimicrobial data suggests that the investigated metal complexes possess comparatively better antibacterial and antifungal activities than the ligand.

Conflicts of interest

The authors declare no conflict of interest.

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