

Catalytic Studies on Schiff Base Complexes of Co(II) and Ni(II) Using Benzoylation of Phenol

Melaku Meshesha Tulu* and Ali Mohammed Yimer*

Department of Chemistry, Arba Minch University, Arba Minch, Ethiopia

*Corresponding authors: Melaku Meshesha Tulu, Department of Chemistry, Arba Minch University, Arba Minch, Ethiopia, Tel: +234-8036682351; E-mail: melechem@gmail.com

Ali Mohammed Yimer, Department of Chemistry, Arba Minch University, Arba Minch, Ethiopia, Tel: +234-8036682351; E-mail: alimohammedabc@gmail.com

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Abstract

The title metal complexes were found to be crystalline which have been characterized by elemental analysis, electrical conductivity, magnetic susceptibility measurements, and spectral techniques viz, UV-Visible, FT-IR and NMR (¹H-NMR and ¹³C-NMR). These complexes were air-stable, with high melting points and were soluble in methanol and some other organic solvents such as n-hexane, diethylether and DMSO. The molar conductance of 1×10^{-3} M solutions of the metal complexes in methanol at 27°C indicates that they behave as electrolytes. Both Cobalt(II) and Nickel(II) complexes of N-benzylideneaniline ligand show paramagnetic nature. The electronic studies along with magnetic data suggest a square planer geometry for both Co(II) and Ni(II) complexes. The peak in FT-IR spectra at 1627 cm⁻¹ confirmed the $\nu(\text{C}=\text{N})$ stretching vibration found in the free ligand. This band was shifted to a lower frequency (1603.5 cm⁻¹) in the spectra of the metal complexes and it confirms the participation of azomethine nitrogen in the coordination of metal ions. Finally, the metal complexes were screened for their catalytic activity in the phenol benzoylation reaction and found to be moderately active.

Keywords: N-benzylideneaniline; Cobalt(II) complex; Nickel(II) complex; Phenyl benzoate; Heterogeneous catalyst

Introduction

Transition metal complexes have played a significant role in the enormous growth of the field of catalysis. Metal ligand complexes found to catalyze Heck and Suzuki reactions which were tested via Palladium (II) complex of N, N, O, O-Schiff base ligand [1]. For instance, the effective oxidation of olefins using Mn(II) complexes of amino acid Schiff base [2]; the catalytic activities of transition metal complexes as it is and anchored on polymers [3]; and the catalytic activities of chiral 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) Schiff base complexes in stereoselective organic transformations [4]. Recently, there is an exponential increase in the number of publications dealing with Schiff base metal complexes as catalysts [5-8]. A survey of literature revealed that there is a paucity of a comprehensive information on industrial catalytic utility of metal complexes of cobalt (II) and nickel (II) with N-benzylideneaniline Schiff base ligand for organic transformations. The present study emphasizes the catalytic activities of Schiff base metal complexes as well as the geometry of the synthesized metal complexes. In order to explore the catalytic activities of the title metal complexes towards effective industrial catalysis; the benzoylation of phenol was carried out in particular to examine the influence of catalyst load on shape selectivity in heterogeneous phase. Both the complexes were screened as effective heterogeneous catalyst for the first time, to the best of our knowledge.

Experimental

All the chemicals used were of AR grade. Aniline (Avonchem, U.K.), Benzaldehyde (Park, U.K.) CoCl₂·6H₂O (Avonchem, U.K.) and

NiCl₂·6H₂O (Avonchem, U.K.) were used as received. Metal salt solutions were prepared in doubly distilled water. The N-benzylideneaniline ligand and metal complexes were characterized by analytical and spectral methods. The methods employed were Elemental analysis, spectral techniques like UV-vis, FT-IR, NMR, AAS and also, Gas Chromatography-Mass Selective Detector and Gram Susceptibility balance. Microanalysis of CHN in the ligand was carried out using EA 1112 Flash CHNS/O-analyzer. UV-visible spectra were recorded on a T60 UV-vis spectrophotometer. FT-IR spectra were taken on a Perkin Elmer FT-IR Paragon 1000 spectrophotometer (4000-400 cm⁻¹). NMR spectra were taken in a BRUKER ¹H-NMR, ¹³C-NMR and DEPT spectrometer with TMS as internal reference. Atomic Absorption spectroscopy (AAS-210VGP model) was employed to determine the metal ion concentration. Magnetic susceptibility was measured on a Gouy balance using Hg[Co(NCS)₄] as the calibrant.

Preparation of N-benzylideneaniline ligand

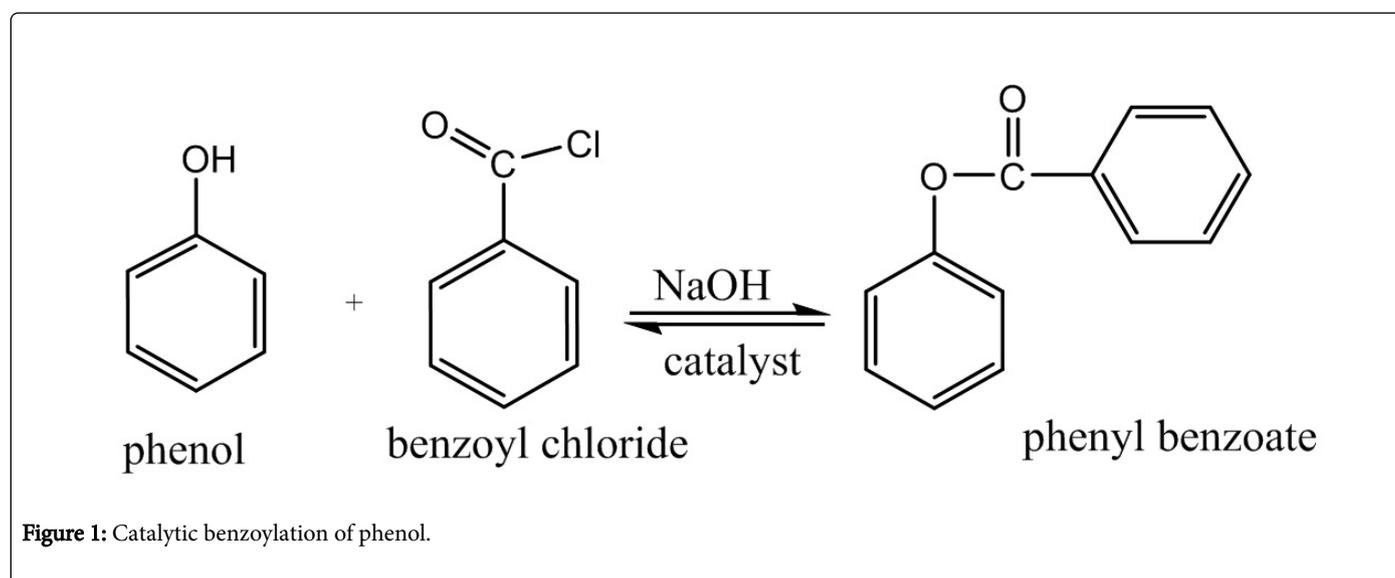
In a 250 mL florentine flask provided with stirring bar, thermometer and reflux condenser, equimolar quantity of benzaldehyde 10.143 mL and aniline 9.099 mL were added with rapid stirring. After five seconds, the reaction began, followed by evolution of heat and separation of water. The mixture was allowed to reflux for one hour and then poured with fast stirring into a 600 mL beaker containing 16.5 mL ethanol. Crystallization started in about five minutes; however more crystallization of the product was achieved by allowing the mixture further to stand in an ice bath for 30 minutes. Solid mass of the product, N-benzylideneaniline was quantitatively transferred to a Buchner funnel; suction filtered and allowed to dry in a vacuum drier. 83.986% product yield was obtained and the M.p was found to be 55-57°C.

Syntheses of metal complexes

The Co(II) and Ni(II) metal complexes of N-benzylideneaniline ligand were prepared by dissolving 2.379 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 2.377 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 5 mL dry methanol separate 100 mL round bottom flasks. 3.625 g of synthesized N-benzylideneaniline ligand was also dissolved in 10 mL of the same solvent (methanol) in a 100 mL round bottom flask. The above methanolic solutions of the metal chlorides and the ligand were mixed and refluxed in a 250 mL florentine flask provided with magnetic stirrer, thermometer and reflux condenser. Refluxing was continued in a petroleum oil bath for 48 hrs at 55-63°C under constant stirring. Finally, the solvent was degassed through rotary evaporator and on cooling the content, colored complexes were separated out. The complexes were filtered and washed with petroleum ether and dried under desiccator over CaCl_2 . Finally, the purity of the complexes was checked by TLC.

Catalytic benzoylation of phenol

The catalytic activity of metal complexes towards benzoylation of phenol was carried out in a 50 mL stoppered conical flask. In a typical reaction, 0.94 g of phenol and 30 mL 10% NaOH solution were mixed with 1.41 g of benzoyl chloride under the fume hood. The complex (1×10^{-5} , 2×10^{-5} , and 2.5×10^{-5} mole) was added to the reaction mixture and the reaction was considered to start at this time. The flask was shaken and periodically removed the pressure developed inside at intervals of 20, 30 and 40 minutes and the reaction mixture were heated at various temperatures (300, 313 and 318 Kelvin). The products were collected on a Buchner funnel and washed with DI-Water and air dried. The product was recrystallized from ethanol. The effects of various parameters such as concentration of catalyst, temperature and time of reaction were studied to find their effect on the product yield. The representative product was analyzed using a gas chromatograph [9] (Figure 1).



Results and Discussion

Physico-chemical characterization of n-benzylideneaniline ligand and metal complexes

The complexes were air-stable, with high melting points and were soluble in methanol and some other organic solvents such as n-hexane,

diethylether and DMSO. The molar conductivities of 1×10^{-3} M solutions of the metal complexes in methanol at 27°C indicate that the complexes behave as electrolytes [10]. The results of some physical characteristics and analytical data of the synthesized N-benzylideneaniline ligand and the metal complexes were summarized in Table 1. The obtained results are in good agreement with 1:2 mole ratio of metal to ligand.

Compound	Color	M.pt. (°C)	Λ_m (S cm ² mol ⁻¹)	Analysis (%) found (Calculated)				
				C	H	N	O	Cl
C ₁₃ H ₁₁ N (BA)	Yellow	54-56	-	84.52 (86.15)	6.29 (6.12)	7.32 (7.73)	-	-
[Co(BA) ₂ (H ₂ O) ₂ Cl ₂ ·4H ₂ O	Purple-blue	182-185	87	(52.01)	(5.70)	(4.66)	(16.00)	10.8 (11.81)
[Ni(BA) ₂ (H ₂ O) ₂ Cl ₂ ·4H ₂ O	Olive green	174-177	86	(52.03)	(5.71)	(4.67)	(16.00)	12.29 (11.81)

Table 1: Physico-chemical Characterization of N-benzylideneaniline and its Metal Complexes.

Electrical conductance measurement

The conductance of 0.2 M KCl solution was 865 Ω^{-1} . Using this value, the calculated cell constant was 3.2×10^{-6} cm⁻¹. The specific conductance of the synthesized Co(II) and Ni(II) complexes

(Co(II)=27 Ω^{-1} and Ni(II)=26.87 Ω^{-1}) were 87×10^{-6} $\Omega^{-1}\text{cm}^{-1}$ and 86×10^{-6} $\Omega^{-1}\text{cm}^{-1}$ respectively. Therefore, the molar conductivities of 1×10^{-3} molar solutions of the complexes at 27°C in methanol were 87 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Co(II) and 86 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for Ni(II) complexes. The

high values of molar conductance indicate that the complexes behave as electrolytes [11]. The electrical conductance values of the complexes are presented in Table 2.

Compound	K	k	L	Λ_m
	(10^{-6}cm^{-1})	($10^{-6}\Omega^{-1}\text{cm}^{-1}$)	(Ω^{-1})	($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
[Co(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	3.2	87	27	87
[Ni(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	3.2	86	26.87	86

Table 2: Electrical Conductance Measurement of Cobalt(II) and Nickel(II) complexes. K-Cell constant, k-Specific conductance, L-Conductance, Λ_m -Molar conductance.

Estimation of chloride in Co(II) and Ni(II) complexes

Accurately weighed 0.2 g of each of Co(II) and Ni(II) complexes and then dissolve in two separated 400 mL beaker which contained 100 mL

Metal Complexes	Amount of Complex in (g)	AgCl(s) ppt. (g)		Mass of Cl ⁻ ion(g)		%Yield of Cl ⁻	
		Bef. dig.	Aft. dig.	Bef. dig.	Aft. dig.	Bef. dig.	Aft. dig.
[Co(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	0.2	0.0836	0.111	0.051	0.02	10.374	10.8
[Ni(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	0.2	0.097	0.099	0.024	0.025	12.027	12.295

Table 3: Mass and %yield of chloride in Co(II) and Ni(II) complexes. Bef. dig.-Before digestion, Aft. Dig.-After digestion.

The results revealed that, the percentage yield of chloride ion(s) before and after digestion of Co(II) complexes have been relatively the same. This implies that, no more chloride ion(s) act as a ligand coordinated to the central metal ion, i.e., chloride ion is found outside the coordination sphere just on the ionic sphere of the complex molecule. In the case of Ni(II) complex, the percentage yield of chloride ion(s) has no significant difference in both undigested and digested samples of the metal complex. This confirms that no chloride ion act as a ligand coordinated to the metal ion; rather they are found outside the coordination sphere of the complex molecule.

Magneto-chemical properties

Spin-only magnetic moment of cobalt(II) complex should be 3.88 B.M. However, the measured value of $\mu_{\text{eff}}=2.66$ B.M. was found to be lower than the expected value and this could be related to orbital-spin coupling. Similarly, the spin-only magnetic moment value for the complex of nickel(II) ion is supposed to be 2.83 B.M. However, the experimental value of $\mu_{\text{eff}}=1.72$ B.M. This observed deviation could be attributed to orbital-spin coupling. However, the earlier reported effective magnetic moments are in consistency with the number of unpaired electrons in both cobalt(II) and nickel(II) ions, which implies the paramagnetic nature of the complexes [12,13].

Electronic studies on n-benzylideneaniline ligand and metal complexes

The UV-Vis spectra of the ligand in DMSO solvent showed an absorption band at 251 nm. Based on the molar extinction coefficient and the maximum absorption spectral region, the observed absorption

acidified (3 mL, 6 M HNO₃) DI- water. Slowly, stirring with a glass rode, 20 mL 0.2 M AgNO₃ solution was added to the solutions of Co(II) and Ni(II) complexes. Then, the precipitated AgCl(s) was allowed to settle leaving a clear solution above the solid. The completion of precipitation was checked by adding one drop of 0.2 M AgNO₃ solution on the beaker wall and allowing the drop to run down in to the supernatant liquid, carefully watching the formation of more precipitate. Lack of further precipitation was observed after the addition of one drop of 0.2 M AgNO₃ solution to the beaker and these marks the completion of the reaction. The formed precipitate was carefully filtered and placed on a watch glass; and subsequently dried in the oven at 120°C for 2 hrs.

Chloride ion(s) found inside the coordination sphere of the complexes was determined though digestion of the complexes with conc. HNO₃ solution (15.77 M) upon heating. This mixture was kept aside until the colour of the solution changed to that of the metal salts. Then kept the solutions at room temperature and pursued the procedure for chloride ion determination. The mass and percent yield of chloride ions in both Co(II) and Ni(II) complexes are shown in Table 3.

band of the N-benzylideneaniline ligand was attributed to $n \rightarrow \sigma^*$ electronic transition. The "n" electrons (or the nonbonding electrons) were the ones located on the nitrogen of the azomethine group of benzylideneaniline ligand. Thus, the n to σ^* transition corresponds to the excitation of an electron from one of the unshared pairs to the σ^* orbital [14].

During the complexation with Co(II) and Ni(II) metal ions, the absorption band of the ligand shifted to the longer wavelength (lower energies) implying, bathochromic type of shift [15]. The UV-Vis absorption spectra of Co(II) complex in DMSO solvent exhibited a weak absorption band at 291 nm which was attributed to the LMCT band. Thus, on the basis of electronic spectra, magnetic moment value ($\mu_{\text{eff}}=2.66$ B.M.) and the blue color of the complex, a square planar coordination may be suggested for the Co (II) complex. The electronic spectra of Ni(II) complex in DMSO solvent showed a weak absorption band at 286 nm which was assigned to the LMCT band. The magnetic moment value ($\mu_{\text{eff}}=1.72$ B.M.) indicates paramagnetic nature, which along with the spectral data and the olive green color of the complex suggest, a high-spin square planar geometry for the Ni (II) complex.

FT-IR spectra and mode of vibrational frequencies

The IR spectra of N-benzylideneaniline ligand shows stretching and out-of-plane bending vibration for ($\text{sp}^2\text{-C-H}$ hydrogen) at 3061 and 693.5 cm^{-1} respectively, showing the presence of aromatic ring in the schiff base ligand [16]. This extremely intense absorption of out-of-plane C-H bending vibration resulting from strong coupling with adjacent hydrogen atom validate, the presence of monosubstituted alkyl-(methine group) attached to the aromatic ring (Ar-CH). The

methine hydrogen furnish only one weak C-H stretching at 2890 cm^{-1} . The spectrum of the schiff base free ligand also shows stretching vibration of the azomethine nitrogen with the aromatic ring at 1193.5 cm^{-1} Ar-N [17].

The IR spectra of the complexes were compared with the free ligand in order to determine the coordination sites that may be involved in chelation. There were some guide peaks in the spectra of the ligand, which were helpful in achieving this goal. The position and/or the intensities of these peaks were expected to change upon chelation. The new peaks generated also act as guide peaks, as water is in chelation. These guide peaks were shown in Table 4.

Compound	$\nu\text{C=N}(\text{cm}^{-1})$	$\nu\text{O-H}(\text{cm}^{-1})$	$\nu\text{M-O}(\text{cm}^{-1})$	$\nu\text{M-N}(\text{cm}^{-1})$
$\text{C}_{13}\text{H}_{11}\text{N}$ (BA)	1627 (sh)	-	-	-
$[\text{Co}(\text{BA})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	1603.5 (sh)	3412 (br)	1101.5 (sh)	754.5 (m)
$[\text{Ni}(\text{BA})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$	1603.5 (sh)	3399 (br)	1042 (sh)	748 (m)

Table 4: FT-IR data (4000-400 cm^{-1}) of N-Benzylideneaniline ligand and its metal complexes. Sh-sharp, m-medium, br-broad.

Upon comparison, it was found that the ν (C=N) stretching vibration existed in the free ligand at 1627 cm^{-1} . This band was shifted to lower frequency (1603.5 cm^{-1}) in the spectra of the complexes, which confirms the participation of the azomethine nitrogen of the C=N moieties in the coordination of the metal ions [18]. At the lower frequency, the spectra of Co(II) and Ni(II) complexes exhibited new bands at 754.5 and 748 cm^{-1} respectively, which could be assigned to (M-N) vibration modes and bands to the right of 582 cm^{-1} , could be assigned to (M-O) stretching vibrations of H_2O molecule in the metal complexes. Due to the larger dipole moment change for M-O compared to M-N, the (M-O) usually appears at higher frequency than the (M-N) band [19]. The IR spectra of the complexes showed a broad band at 3412 and 3399 cm^{-1} that can be assigned to the $\nu_a(\text{OH})$ and $\nu_s(\text{OH})$ vibration modes from water molecules in Co(II) and Ni(II) complexes respectively. Therefore, from the IR spectra, it was concluded that the N-benzylideneaniline behaves as a neutral monodentate ligand coordinated to the metal ions via azomethine nitrogen.

NMR spectral data

$^1\text{H-NMR}$ spectrum of the Schiff base (BA) shows highly deshielded singlet absorption at δ (9.941 ppm, ^1H) which can be attributed to the azomethine proton (H-C=N-). Multiple signal absorptions in the region of δ (6.503 - 8.520 ppm, 10 H) were assigned to chemically nonequivalent aromatic protons (Ar-H) [20]. The strong signal which appeared in the region between δ (3.5-4.5 ppm, 2 H) can be attributed to unreacted/excess droplets of phenyl amine protons during ligand synthesis. The solvent (DMSO- d_6) which was not 100% isotopically pure, it contains some trace of DMSO-(CH_3) $_6$ that gave peaks at δ (2.5 ppm) and the doublet arises due to coupling of a proton with deuterium [21]. $^{13}\text{C-NMR}$ spectra of N-benzylideneaniline ligand was recorded in DMSO- d_6 of δ (100.63 MHz). The signal which appeared at δ of 194.02 ppm in $^{13}\text{C-NMR}$ spectra of the N-benzylideneaniline ligand was assigned to azomethine carbon atom (CH=N). Chemically nonequivalent aromatic ring carbon atoms of the ligand furnished

resonance peaks at chemical shifts of 116.70, 126.60, 129.12, 129.31, 129.74, 129.95, 132.07, 135.15, 136.14, 136.43, 151.56, 161.30 ppm, and quaternary carbon atoms which were parts of the aromatic rings and adjacent to the azomethine carbon and nitrogen as well, provided low intensity signals at δ of 136.43 and 151.56 ppm. Due to the absence of Carbon-13 to proton spin-spin splitting, there were no such peaks in DEPT-135 spectra. Trace of phenyl amine droplets which were found in the ligand show peaks at 114.65, 121.37, 129.60, 148.59 δ ppm.

Metal ion determination

A known weight (3 g) of the metal complexes was treated with 5 mL concentrated sulphuric acid followed by 20 mL concentrated nitric acid. The mixture was kept aside until clear solution was formed. It was then evaporated on a water bath. After cooling, 15 mL concentrated nitric acid was added and again evaporated on a water bath. The residue was diluted with DI-water in 100 mL volumetric flask to make solution of known volume [22,23]. These solutions were used for estimation of metal ions using a series of standard solutions of the corresponding metal ions. Five series of standard solutions were prepared from 1000 ppm stock solution with DI-water containing 1.5 mL conc. HNO_3 . The experimentally found percentage compositions of both Co(II) and Ni(II) complexes of the respective benzylideneaniline ligand were 10.235% and 10.024% respectively, and the calculated percentage composition of cobalt(II) complex was 9.816% and that of nickel(II) complex was 9.779% as per the proposed formula of the metal complexes. The experimentally found percentage compositions of metals in the complexes were in good agreement with the calculated percentage composition of the metal complexes. The structural formula of the metal complexes shown in Figure 2 was consistent with the above-mentioned data.

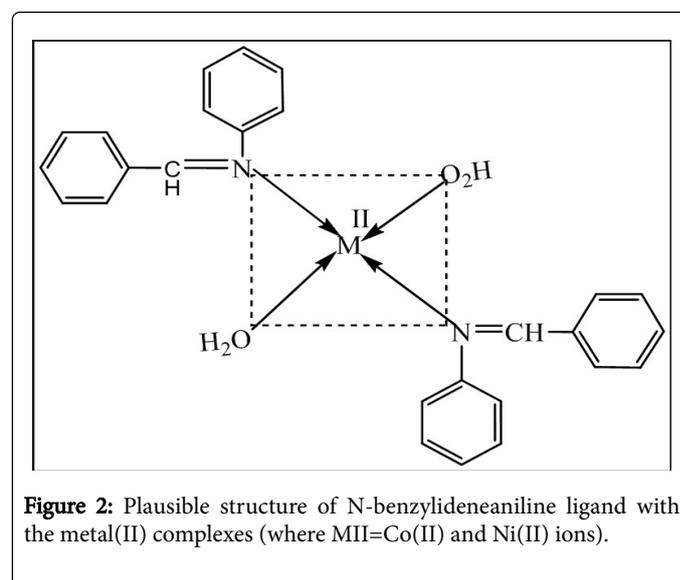


Figure 2: Plausible structure of N-benzylideneaniline ligand with the metal(II) complexes (where MII=Co(II) and Ni(II) ions).

Cobalt(II) and Nickel(II) Complexes of N-benzylideneaniline Ligand as Catalyst for the Benzoylation of Phenol

Catalytic studies on the metal complexes towards phenol benzoylation

The catalytic activities of synthesized Co(II) and Ni(II) complexes were studied for activity towards phenol benzoylation reaction. Both complexes showed good catalytic activity. The activities of the cobalt(II) complex was somehow higher than that of nickel(II) complex. In order to arrive at suitable reaction conditions for maximum transformation to phenyl benzoate, an optimum catalyst load was employed. Also, the effect of reaction temperature and time on the conversion efficiency was studied.

Reaction kinetics of phenol benzoylation

Effect of catalyst quantity: The effect of amount of catalyst on the yield of phenyl benzoate was showed in Table 5. Three different concentrations of catalyst (1×10^{-5} , 2×10^{-5} , and 2.5×10^{-5} mol) were studied. The catalyst load which showed the highest activity during the test reaction was used for the fixed amount of phenol (0.01 mol, 0.94 g) and benzoyl chloride (0.01 mol, 1.41 g) later. An amount of 2.5×10^{-5} mol gave comparable results in both cases with ca. 55.35% and 34.83% conversion to phenyl benzoate in 30 minutes of reaction time at 313 K for cobalt(II) and nickel(II) complexes respectively. Lower catalyst load results in poor conversion. The conversion increases linearly with catalyst concentration but eventually it decreases at elevated temperatures.

%yield of phenyl benzoate		
Catalyst load (mol)	[Co(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	[Ni(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O
1×10^{-5}	26.13	29.83
2×10^{-5}	40.84	31.83
2.5×10^{-5}	55.35	34.84

Table 5: The effect of catalyst quantity on conversion. Reaction temperature 313 K, reaction time 30 minutes.

Effect of temperature: Three different temperatures (300, 313 and 318 K) were studied to find the effect of reaction temperature on phenol benzoylation and the results are shown in Table 6, keeping other parameters same for the catalytic activity evaluation. Below 313 K, conversion to phenyl benzoate was drastically reduced. At the same time, above 313 K, the decomposition of product was found, which was not advantageous for phenol benzoylation.

%yield of phenyl benzoate		
Temperature (K)	[Co(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	[Ni(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O
300	40.84	31.83
313	91.99	36.13
318	44.55	34.03

Table 6: The effect of temperature on conversion. Reaction time 30 minutes, catalyst load 1×10^{-5} mol.

Effect of time: The catalytic benzoylation of phenol, using benzoyl chloride was studied as a function of time. Too much of extended reaction time appears to result in poor product yield. Table 7 shows that the favorable reaction time was thirty minutes. There was no significant change in the conversion to phenyl benzoate beyond the specified time of reaction.

%yield of phenyl benzoate		
Reaction Time (minutes)	[Co(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O	[Ni(BA) ₂ (H ₂ O) ₂]Cl ₂ .4H ₂ O
20	40.84	31.83
30	76.58	55.96
40	42.44	46.65

Table 7: The effect of reaction time in catalytic efficiency. Reaction temperature 313 K, catalyst load 1×10^{-5} mol.

Conclusion

The FT-IR spectral studies on the complexes revealed that, N-benzylideneaniline ligand was involved in coordination only through the azomethine nitrogen. This illustrates the monodentate behavior of the ligand. In addition, the vibrational bands provide evidence for coordination of water molecule to the central metal ions. The tentative structure of both complexes shown in Figure 2 suggests planer geometry. The electronic studies on both complexes demonstrate their transition in LMCT mode. In order to explore effective industrial applications, both cobalt(II) and Nickel(II) complexes were evaluated for their catalytic activities towards benzoylation of phenol. The conversion to phenyl benzoate was enhanced by increasing the catalyst load. The conversion data showed that, both complexes have only mild conversion efficiency as heterogeneous catalyst in the benzoylation of phenol.

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