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Synthesis, Characterization and Kinetic Studies of Nickel (Ii) Complex of Dibenzoyl Methane and It's Adduct

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Abstract

Nickel (II) Complex of dibenzoylmethane and the 1, 10 phenantroline adduct were synthesized using Nickel (II) acetate tetrahydrate in aqueous methanol. The resulting green Ni^{2+} compounds were characterized by elemental analysis, magnetic moments, IR and UV spectroscopy. The kinetics of the reaction for the formation of the complex was conducted. The complex and adduct were identified by coupled vibrations of Ni-O + Ni-N which were conspicuously absent in the neat ligand .The elemental and metal analysis indicates 1:2 Metal-Ligand ratio in both complex and adduct. The electronic spectral and magnetic susceptibility studies are consistent with the adoption of an octahedral geometry for the adduct. Results of the kinetic study showed that the formation of the nickel complex occurs at a rate of 1.7 x 10^3 – 9.2 x 10^3 moldm^{-3} in a 2nd order reversible reaction, which involved both the metal and the ligand with equilibrium constant K_{eq} ranging from 2.0 x 10^4 – 1.5 x 10^6. The observed rate is at variance with the rate of solvent exchange, this being typical of a tautomeric ligand.

Keywords: 1, 10-phenantroline, Dibenzoylmethane, Kinetics, Solvent-exchange.

1. Introduction

Various β-diketone metal complexes have been synthesized and their characterizations were well documented [Binnemans, 2005]. But β-diketone remains one of the ligands of choice in current researches [Arpita and Raman, 2010; Franke et al., 2009; Krishnankutty et al., 2009; and Patel, 2009]. This is primarily due to the wide range applications of β-diketonate complexes. They have biomedical applications [Kingsley, 2004], host-guest chemistry property of their metal bis β-diketonate complexes, used as NMR shift reagents [Binnemans, 2005], used as precursors for chemical vapour deposition, as catalyst and extracting agent [Syivester, 2006; Odunola et al., 2003 and Kulbinder et al., 2001]. The keto-enol property of β-diketones opened their synthesis, complex formation, known and prospective applications to kinetic and mechanistic studies not present in other ligands [Hynes and Brigid, 1979]. In the interactions of metal ions with common ligands, the loss of a water molecule from the metal ion was postulated to be the rate determining step [Hugee et al., 1993]. The first order rate constant for the reaction of nickel is $\leq 10^5$dm^{3}mol^{-1}s-^{1}. In the presence of β-diketones, values of rate constant varies with the type of diketone, difference in values obtained between complexation with the enol tautomer and the enolate ion [Mickel and Dermot, 1988]. The medium of reaction was also suspected to be a factor [Mickel and Dermot, 1988; Michael and Brigid, 1980]. In fact, it was earlier stated that many of the factors controlling the rates of reaction of metal- β-diketonate complexes were yet to be understood [Michael and Brigid, 1980]. Reported kinetic studies of nickel- β-diketonate complexes had been with few β-diketone ligands such as 4, 4, 4-Trifluoro-1-(2-thienyl) butane -1, 3-dione (Htftbd) [Mickel and Dermot, 1988], pentane-2, 4-dione [Hynes and Brigid, 1979].There had not been a good agreement between the rates obtained for the same ligands in different studies, especially with the enol tautomer. This study is aimed at investigating the synthesis, characterization of Nickel (II) complex of dibenzoylmethane and its 1-10-phenantroline adduct and the kinetic studies of its formation.

2. Materials and method

2.1 Reagents and Solvents

1, 10-phenanthroline, dibenzoylmethane were purchased from Aldrich and used as received. Solvents were purified according to literature procedures [Vogel, 1986].

2.2 Synthesis of the Complex and adduct

2.2.1 Preparation of nickel (II) complex of dibenzoylmethane.

Dibenzoylmethane (6.73g, 0.03moles) was dissolved in 100ml of methanol, stirred and heated on a magnetic stirrer, until it dissolved completely. Nickel (II) acetate (3.73g, 0.015 moles) was dissolved in 30ml of distilled water and added dropwisely to the ligand solution. About 130ml of distilled water was added to the resulting solution and stirred continuously for about one hour. The complex formed was filtered and dried in a desiccator.

2.2.2 Preparation of the 1, 10-phenanthroline adduct of Nickel (II) dbm complex.

The organic base, 1, 10-phenantroline (0.87 g, 0.0044 moles) was dissolved in 40 ml chloroform and stirred at 60^{o}c. Slurry of the complex (1.05g, 0.0020 moles) in 40 ml of ethanol was added in drops. The resulting solution was refluxed for about three hours till precipitation occur. The product was filtered and dried in a dessicator.

2.3 Physical Measurement

Elemental analysis was determined by the analytical services division of the department of chemistry, University of the Western Cape Coast, South Africa. The Nickel was determined using a titrimetric method [Vogel, 1986]. The infra red spectra were recorded on a pye-unicam SP3-300 spectrophotometer using pressed KBr discs. The instrument was calibrated using a polystyrene film and the frequencies corrected within $\pm$ 10cm^{-1}. The electronic spectra of the compounds in chloroform were measured on the Lamda 313 UV/Visible spectrophotometer, the spectrum of the compounds were obtained at wavelengths between 900nm and 190nm. The solvent was the reference. Melting points of the compounds were determined using a Buchi (β-540) melting point apprаratus.

2.4 Kinetic Studies for [Ni (dbm)$_2$(H$_2$O)]

Kinetic measurements were made with large excess of metal (10^{-2}M) to ligand (10^{-6}M) concentrations to ensure a pseudo first order kinetic runs. The nickel acetate solution was prepared using aqueous methanol, while dibenzoylmethane was dissolved in pure methanol. U.V study was carried out to find the wavelength of maximum absorption as the products were formed. The kinetics of the reaction was conducted at the wavelength of maximum absorption (229nm). The concentration of the ligand was kept constant over a range of metal concentrations.

3. Results and Discussion

3.1 Elemental Analysis

The ratio of the ligand to the metal in the monocomplex is 2:1 and the phenantroline/dbm adduct is 2:1:1. In Table 1; %C, %H and the percentage metal affords a molecular formula of the compounds as; [Ni (dbm)$_2$ (H$_2$O)] and [Ni (dbm)$_2$phen] .

3.2 Magnetic Moment

A Nickel (II) ion with 2 unpaired electron is expected to give a spin magnetic moment of 2.83BM (Hugee et al., 1993). Octahedral nickel (II) complexes have magnetic moments between 2.9 and 3.4BM. The observed greater value is due to small but definite orbital contribution to the magnetic moment. Tetrahedral complexes, however, range from 3.0 to 4.0 BM; the larger the distortion from a regular tetrahedron, the lower the magnetic moment, hence there seems to be no clear cut distinction between the magnetic moments of tetrahedral and octahedral Nickel (II) complexes. Square planar Nickel (II) complexes were usually expected to be diamagnetic but low values of magnetic moment reported were interpreted as indicative of an equilibrium mixture of low spin/high spin Nickel (II) ions, corresponding to 15-20% paramagnetic species. The room temperature magnetic moment of Nickel dibenzoylmethane complex, and its 1, 10-phen adduct are 1.13 and 3.23 respectively. Hence, the Ni (dbm)$_2$(H$_2$O), is probably in a distorted octahedral field around the Ni^{2+} ion, while the ligands in Ni(dbm)$_2$phen, are likely octahedrally arranged. 3.42BM was obtained for Ni (II) complex of ampicillin (Guru, 2009), while 2.50 and 2.40 were reported for octahedral and tetrahedral Nickel(II) complexes respectively (Prakash et al., 2011).

3.3 Infrared spectra

The hydrogen bonded enol form of the ligand was traced to the broad band at 3442cm^{-1}, which in the complex appears at 3348cm^{-1}, and it is attributed to $\nu_{OH/H2O}$. In the adduct the band was seen at 3049cm^{-1}, thus, indicating the active involvement of this site in the reaction similar to assignments reported in literature (Kumar et al., 2011). The characteristics bridging μ-acyl unit of the diketone $\nu_{c=o}+\nu_{c=c}$ were equally observed as 2 bands (1596 cm^{-1}, 1548 cm^{-1}). In the neat ligand, 3 bands (1668 cm^{-1} (w), 1595 cm^{-1} (w), 1528 cm^{-1} (w) were in the complex and 2 bands (1595 cm^{-1} (w), 1547 cm^{-1} (w) in the 1-10 phenantroline adduct. The compounds were identified by the $\upsilon_{(Ni\text{-}O)}$ bands observed at 457 cm^{-1} and 365 cm^{-1} in the complex, and coupled vibration of $\upsilon_{(Ni\text{-}O)} + \upsilon_{(Ni\text{-}N)}$, at 445 cm^{-1} and 391 cm^{-1} in the phenathroline adduct respectively which were conspicuously absent in the neat ligand (Table 2). Similar bands were assigned to $\upsilon_{M\text{-}O}$ in literature (20). The observed shifts indicates involvement of the diketonate C=O in the reactions. The C-H in plane vibrations was also distinguishing.

3.4. Electronic Spectra

In solution, Nickel (II) β-diketonates sometimes exhibit a monomer → trimer (red→green). In square-planar → octahedral equilibrium, three transitions were expected in the octahedral field. The highest energy transition; $^3A_2g\ [F] \rightarrow {}^3T_1g\ [P]\ \upsilon_1$ was obscured by a charge transfer transition while the $^3A_{2g}\ [F] \rightarrow {}^3T_{1g}\ [F]\ \upsilon_2$ was observed in the 17000 – 20000 cm^{-1} region with a lower intensity. An octahedral geometry is expected, if υ_1/υ_2 is greater than 1.5,but the absorption in the 11000– 12000cm^{-1} (υ_1) region was obscured therefore υ_1/υ_2 could not be calculated. It should be noted that coordination number five is relatively rare for Ni (II), which more often forms either octahedral high-spin or square-planar low-spin complexes. Ni (II) complexes with pentadentate ligands are often six coordinate because of addition of a solvent molecule or anion (Kryatov et al., 2002). Hence, a second water molecule or an anion is suspected on the Ni (II) dibenzoylmethane complex, but that was not explicit from the analysis.

4. Kinetic Study

The observed rate of reaction (k_{obs}) shows a general increase with increase in concentration of the ligand (dibenzoylmethane). Changes in metal concentration do not give a consistent variation with k_{obs}. From table 1 and figure 1, plots of k_{obs} against [dbm] for each [Ni^{2+}] gave straight line with a non- zero intercept, indicating a probable second order reversible reaction between Ni^{2+} and dibenzoylmethane (Odiaka, 2004).

The proposed rate law for the reaction is

$$Rate=k_1\ [Ni^{2+}][dbm]+k_{-1}[Ni^{2+}]$$

$$k_{obs}=k_1\ [dbm]\ +k_{-1}$$

Proposed mechanism of the reaction between dibenzoylmethane and nickel (II).

$$Ni^{2+}+2[dbm] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ni\ [dbm]_2$$

5. Conclusion

Nickel (II) Complex of dibenzoylmethane and it's 1,10 phenantroline adduct have been synthesized and characterized by elemental analysis, magnetic moments, IR and UV spectroscopy. The elemental analysis revealed a 1:2 metal-ligand ratio in both complex and adduct. The electronic spectral and magnetic susceptibility studies are consistent with the adoption of an octahedral geometry for the adduct. Results of the kinetic study show that the formation of the nickel complex occurs at a rate of $1.7 \times 10^3 - 9.2 \times 10^3$ $moldm^{-3}$ in a 2nd order reversible reaction, which involved both the metal and the ligand with equilibrium constant K_{eq} ranging from $2.0 \times 10^4 - 1.5 \times 10^6$. The observed rate is at variance with the rate of solvent exchange, this being typical of a tautomeric ligand.

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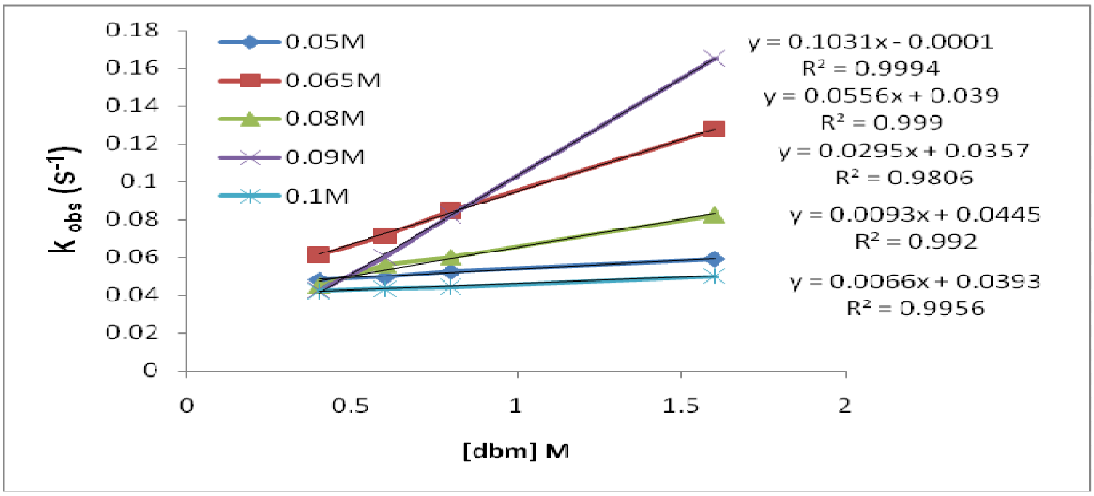

Fig 1: Plot of pseudo first order rate constant , k_{obs} against the dbm concentration,

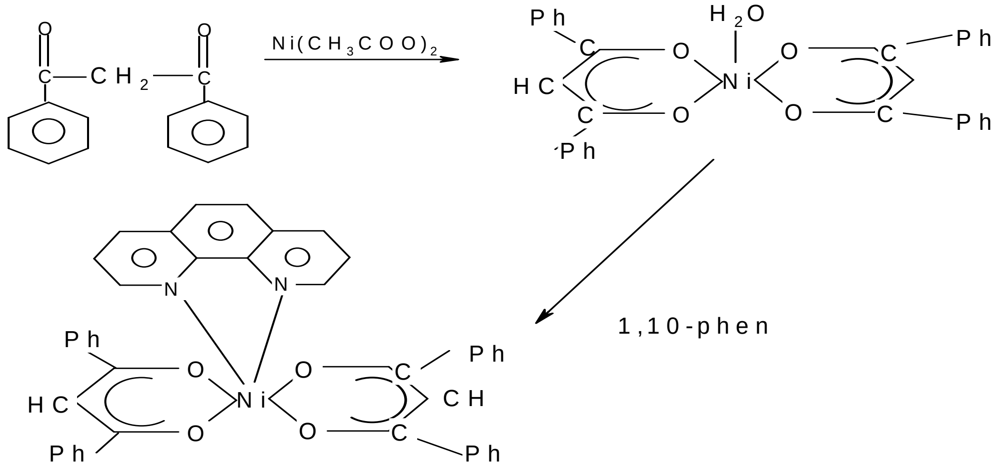

Fig. 2: Proposed reaction paths

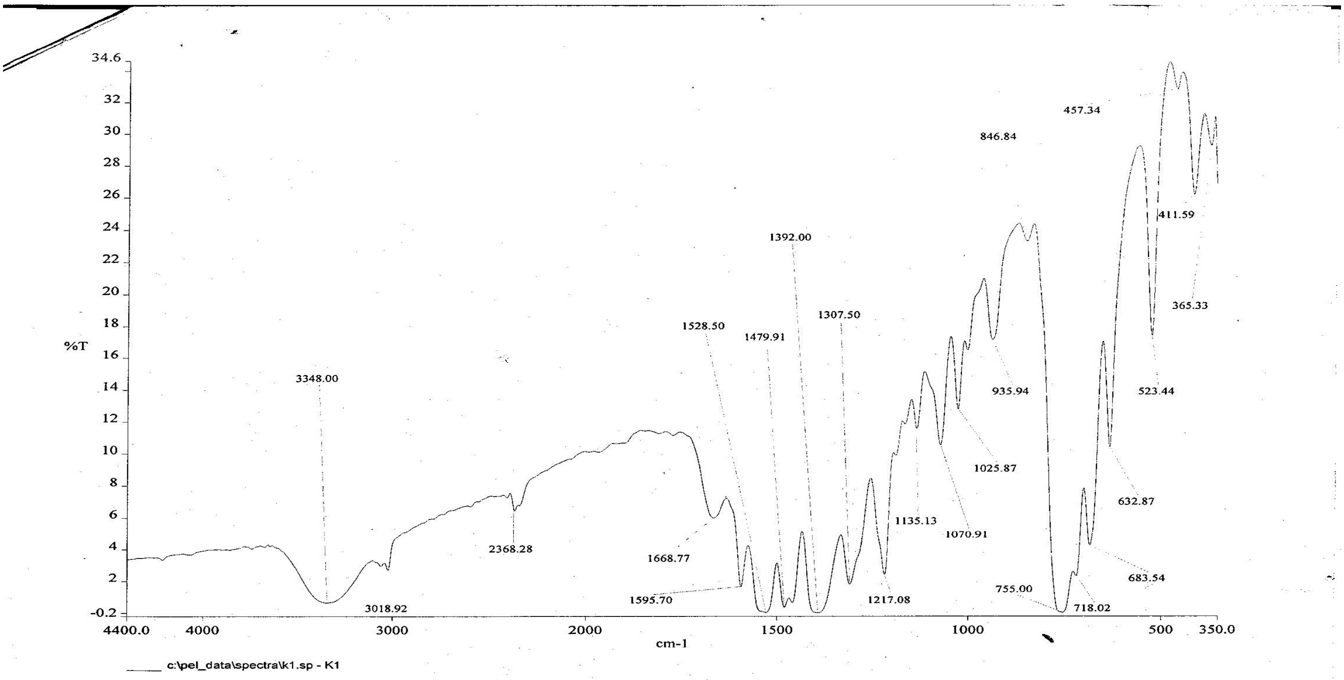

Fig 2a: Infra red spectrum of Ni$[C_6H_5COCH_2COC_6H_5]_2(H_2O)$

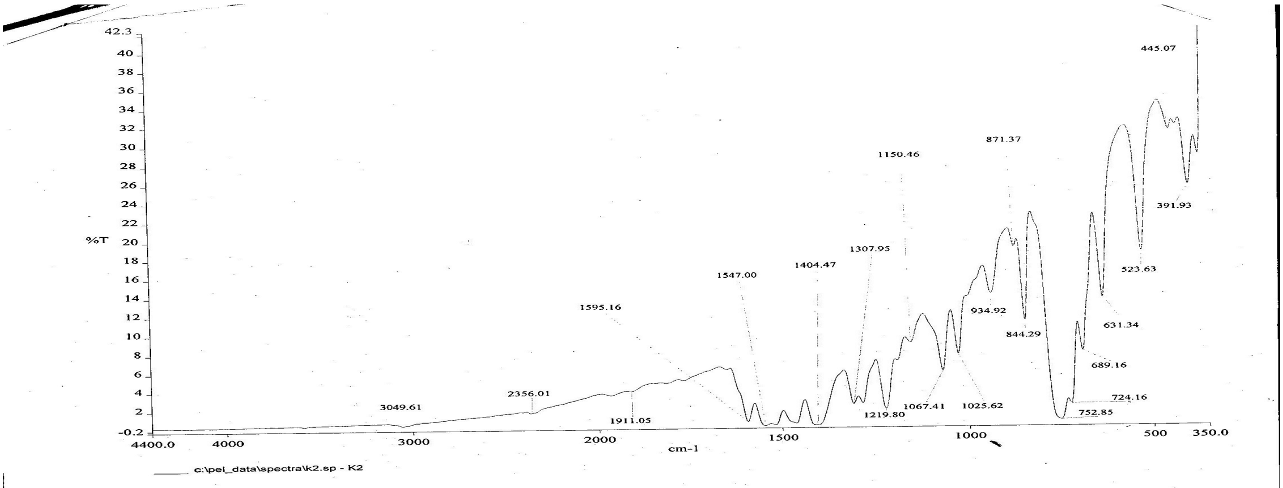

Fig 2c: Infra red spectrum of Ni $[C_6H_5COCH_2COC_6H_5]_2[C_{10}H_8N_2]$

Table 1: Analytical data for the compounds.

Compound	M.F	M.M	Colour	% Yield	M.Pt.	% metal		%C		% H	
						Exp.	Obs.	Exp.	Obs.	Exp.	Obs.
$Ni(dbm)_2(H_2O)$	$Ni[C_6H_5COCH_2COC_6H_5]_2(H_2O)$	525.213	Green	83	178-180	11.17	11.35	68.87	68.91	4.62	4.70
$Ni(dbm)_2phen$	$Ni[C_6H_5COCH_2COC_6H_5]_2[C_{10}H_8N_2]$	705.413	Green	37	d68 -70	8.32	8.50	68.04	68.09	4.42	4.46

Table 2: IR Data (cm^{-1}) for ligand, complex and adduct

	$\upsilon_{OH/H2O}$	$\nu_{c=o}+\nu_{c=c}$	ν_{c-o}	ν_{C-N}	ν_{Ni-O}	ν_{Ni-N}	ν_{C-H}
Ligand	3442	1596 1548	1228	-	-	-	927-680
Complex	3348	1668 1595 1528	1217	-	457	365	935-632
Adduct	3049	1595 1547	1219	1307	445	391	934-631

Table 3: Observed rate constant at different [dbm] and nickel concentrations

$[dbm]x10^{-6}$ M	$[Ni^{2+}]$ $x10^{-2}$M				
	5.0	6.5	8.0	9.0	10.0
	$k_{obs}(s^{-1})$				
0.4	0.0482	0.0613	0.0449	0.0426	0.0422
0.6	0.0496	0.0616	0.0560	0.0731	0.0433
0.8	0.0525	0.0847	0.0691	0.0823	0.0443
1.6	0.0592	0.1277	0.0823	0.1652	0.050

Table 4; the slope (k_1), the pseudo first order rate constant (k_{-1}) for the reverse reaction and equilibrium constant (K_{eq}) for the reaction.

$k_1 x\ 10^{-2}\ (s^{-1})$	$k_{-1}\ x\ 10^{-2}(s^{-1})$	$K_{eq}= k_1/k_{-1}$
0.93	4.45	0.21
5.50	3.90	1.40
2.90	3.57	0.80
10.30	0.01	1030
0.66	3.93	0.16

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