Substituents Effect on the Kinetics and Mechanisms of Formation of Copper (II) and Nickel (II) Complexes of Some Β-Diketones

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Abstract
Chelates of β – diketones ($R^1COCH_2COR^2$) with transition metals have been found to possess a wide range of properties and application, some of which are dependent on the substituents (R^1 and R^2). Copper(II) and Nickel(II) complexes of β – diketones in which $R^1= C_6H_5$ and $R^2 = C_6H_5$ (dbm), $R^2 = CH_3$ (bza) $R^2 = CF_3$ (tfpbd) and $R^1 = C_4H_3S$, $R^2 = CF_{3(}$tta) were synthesised and characterised using UV, IR, elemental analysis and magnetic susceptibility. The probable influence of the substituents on the kinetics and mechanisms of formation of the complexes were investigated with the aid of a Thermostated Schimadu 1800 uv-visible spectrophotometer. The reactions were studied at wavelengths characteristics of each complex. Results show the six coordinate copper(II) and nickel(II) complexes have probable distorted octahedral geometry while the four coordinate $Ni(dbm)_2$ is tetrahedral. The kinetics data suggests an influence of the diketonate substituents on the copper(II) and nickel(II) complexes in solution is in the order $C_6H_5 > CH_3 > CF_3 > C_4H_3S$ and $CF_3 > C_6H_5 > CH_3 > C_4H_3S$ respectively. Solvent influence (k_{-1}) was constant in the range 0.007 – 0.008 for fluorosubstituted complexes and least at 0.004 – 0.005 $mol^{-1}s^{-1}$ in the alkyl substituted complexes. The steady state approximation gave solvent independent rates k_1k_2 at 25°C, in the copper(II) complexes, k_2 is greater than k_1 ($k_2 > k_1$), with k_2 constant while in the nickel(II) complexes, the values of k_2 was less than k_1 and ascribed to rate determining and varies with the nickel(II) - ligand systems studied.

Keywords: β-diketones, Copper II and Nickel II Complexes, Substituents effect, Kinetics.

1.1 Introduction

β-diketones are synthetic compounds (Belova, Sliznev, Oberchammer and Girichev, 2010), important organic reagents (Wang, 2005), excellent chelates for transition metals, rare earths and actinides ions (Patel, Gundla and Patel, 2008). Several of their metal complexes possess a wide range of applications (Abu and Muhammed 2015). In most β-diketones, the substituents on the β- carbon are hydrogen atom. The substituents on the carbonyl function can be an alkyl group, a fluorinated alkyl group, an aromatic or heteroaromatic group. These substituents influence the corresponding β-diketones as well as their complexes by endowing their compounds with definite properties. β-diketones with aromatic substituents have a stronger light absorption than those with only aliphatic substituents (Zawadiak and Mrzyczek, 2012). Branched alkyl chains increase the solubility in organic solvents and volatility, perfluorinated alkyl group increases the Lewis acidity (Binnemans, 2005).

The simplest β-diketone is acetylacetone (Hacac), where the substituents on both carbonyl groups are methyl groups. All other β-diketones are considered as derived from acetylacetone by substitution of the CH_3 group (Finar, 1973). They are classified in terms of symmetry of the R – groups. In symmetric β-diketones, the substituents, $R_1 = R_2$ as in acetylacetone, dibenzoylmethane, and hexafluoroacetylacetone, where the substituents groups are CH_3, C_6H_5 and CF_3 respectively. In asymmetric β-diketones $R_1 \neq R_2$ (Kuhn, 2008) as in benzoylacetone ($R_1 = CH_3$, $R_2 = C_6H_5$), 4, 4, 4- trifluorophenylbutanedione ($R_1 = CF_3$, $R_2 = C_5H_6$) and 4, 4, 4-trifluorothenoylacetone ($R_1 = CF_3$, $R_2 = C_4H_4S$).

In complexes, the usual and most common mode of bonding of β-diketones are as enolate ions carrying a single negative charge (Prasad, Agrawal and Sharma, 2003, Park, Baus, Lindeman, and Fiedler, 2011), such that reaction with one or more enolate ions give either neutral or charged compounds. Monocomplexes in which the β-diketone moiety binds to the central metal atom through only one carbonyl group was obtained as intermediates in kinetically monitored reactions (Hynes and Kelly, 1988). In addition β-diketone in its neutral form does serve as a ligand where both carbonyl groups act as donor atoms (Zheng, Zhang, Zhu, Luo, Lyndoy, McMurtrie, Turner, and Wei, 2005). Infrared and N.M.R consistent Carbon and olefin bonded β-diketonate, in which the carbonyl groups do not participate in the bonding but the ligand bound to the metal through C - atom and C = C respectively have been equally obtained (Kuhn, 2008). Most synthetic studies focus on merely characterizing the final compounds (Adhikari, 2008, Patil and Prabhu, 2010, Vafazadeh et al., 2014), however, there is the need to establish a link between the complex in solution and the solid product. This study is a probe into the geometry of copper(II) and nickel(II) complexes of selected β-diketones in solution using kinetic data in addition to the usual characterisation techniques to ascertaining influence of groups bonded to the reactive atoms, and determines the probable mechanisms of the reactions leading to the formation of complexes.

1.2 Experimental

1.2.1 Synthesis

All reagents are of analytical grade and were used as purchased. The complexes were synthesised according to literature methods (Chen, Wu, Huang, Gu, and Gan, (2007), Odunola, Oladipo, Woods and Gelebe, 2003)

Copper(II) complexes of thenoyltrifluoroacetone

Thenoyltrifluoroacetone: 4.4436 g (0.020 moles) in 20 ml methanol reacted with 1.9965 g (0.01 moles) copper(II) acetate monohydrate dissolved in 50ml 40% methanol. The resulting green solution was stirred for one hour, and filtered by suction. It was washed with distilled water and 40% methanol. The green product was dried over calcium chloride. The copper(II) complexes of the other β-diketones were similarly prepared.

Nickel(II) complexes of thenoyltrifluoroacetone

Thenoyltrifluoroacetone; 4.4436 g (0.020 moles) in 80 ml methanol was stirred and heated on a magnetic stirrer until it dissolved completely to give a cream coloured solution. The heat was turned off. Nickel(II) acetate tetrahdrate; 2.4886 g (0.01 moles) dissolved in 30 ml distilled water was added dropwise to the ligand solution. 40 ml of distilled water was added to the overall solution; stirring continued for one hour. The complex formed was filtered by suction washed with distilled water and dried in a dessicator over calcium chloride. The nickel(II) complexes of the other β-diketones were similarly prepared

1.2.2 Characterisation

The solubility of the complexes in varying polarity solvents was determined. The infrared spectra of the ligands and complexes were recorded on a Nicolet 330 Fourier Transform spectrophotometer using KBr disc. Electronic spectra of the complexes were measured on Labda 3B UV/VIS spectrophotometer, absorptions of the pure solvents and the compounds were scanned at wavelengths 190 nm and 1100 nm. The solid reflectance spectra were recorded for the solid samples by grinding with nujol, making them into pasty mass spread uniformly on a whatman filter paper strip. The reference was a clean whatman filter paper strip wetted with nujol.

1.2.3 Kinetics studies

The kinetic studies were conducted using Schimadu 1800 UV/VIS double beam spectrophotometer. The baseline was run over the wavelength range for each reaction using methanol as the blank. Suitable concentration range of the ligands within which the reactions were carried out is $5 \times 10^{-5} - 1.0 \times 10^{-4}$ M for trifluorophenylbutanedione (tfpbd) and thenoyltrifluoroacetone (tta), while the range for benzoylacetone (bza) and dibenzoylmethane (dbm) is $2.0 \times 10^{-5} - 9 \times 10^{-5}$ M.

1.3 Results and discussion

Table 1.0: Solubility of the compounds in different solvents

Solvents	Water	Methanol	Ethanol	Acetone	Chloroform	DMSO	Nitrobenzene
Compounds							
[Cu(tfpbd)$_2$2H$_2$O]	IN	S	S	S	S	S	S
[Cu(tta)$_3$]	IN	S	S	S	SS	S	SS
[Cu(bza)$_2$2H$_2$O]	SS	IN	IN	S	S	S	S
[Cu(dbm)$_2$2H$_2$O]	IN	IN	IN	SS	S	SS	S
[Ni(tfpbd)$_2$2H$_2$O]	IN	S	S	S	SS	S	IN
[Ni(tta)$_2$2H$_2$O]	IN	S	SS	S	SS	S	SS
[Ni(bza)$_2$2H$_2$O]	IN	S	S	IN	S	S	IN
[Ni(dbm)$_2$]	IN	IN	SS	S	S	S	S

Table 2.0: Analytical data of the compounds

Compounds	Molecular mass	Colour	%Yield	M.pt (°C)	%Carbon Expected (Observed)	%Hydrogen Expected (Observed)	%Metal Expected (Observed)
$[Cu(tfpbd)_2 2H_2O]$	531.82	Green	74.24	242-244	48.12(48.72)	2.63(2.25)	11.67(10.15)
$[Cu(tta)_3]$	730.05	Green	51.20	240-243	38.50(38.16)	2.07(1.49)	8.70(8.34)
$[Cu(bza)_2 2H_2O]$	387.88	Green	70.00	182-185	52.23(52.11)	6.13(5.90)	13.80(13.75)
$[Cu(dbm)_2 2H_2O]$	546.09	Green	56.65	270-272	65.74(65.70)	5.15(4.99)	11.58(11.54)
$[Ni(tfpbd)_2 2H_2O]$	509.01	Green	73.01	174-177	45.57(45.85)	2.75(2.91)	11.53(11.05)
$[Ni(tta)_2 2H_2O]$	521.05	Green	55.30	280-282	35.65(35.83)	1.15(2.06)	11.66(11.26)
$[Ni(bza)_2 2H_2O]$	383.07	Light Green	62.50	181-183	52.78(52.50)	6.20(6.59)	12.89(12.66)
$Ni(dbm)_2$	523.21	Green	71.44	280-284	68.64(68.20)	4.60(4.50)	11.22(11.13)

The elemental analysis of the complexes indicated that the Copper(II) and the Nickel(II) complexes were mainly bis – chelated with different number of water molecules within and outside the coordination sphere. Exception of the solid product characterised is the Copper(II) complex of thenoyltrifluoroacetone being tris – chelated: $Cu(tta)_3$, and Nickel(II) complex of dibenzoylmethane: $Ni(dbm)_2$, without associated water molecule. The complexes are soluble at varying degree in both polar and non-polar solvents except in water (Table 1.0), indicating they are electrolytes of different strength. Analytical data indicate close agreement between the expected and observed, carbon, hydrogen and metal content. All the complexes have different shades of green colour and were obtained at reasonable yield (Table 2.0).

Table 3.0: Infrared spectral data of the compounds

Compounds	υOH	υC-H	υ C-O	υC-C	υM-O
Tfpbd	3406 (s)	2351 (s)	1594 (s)	1140 (vs)	-
$[Cu(tfpbd)_2 2H_2O]$	3449 vs)	2365 (w)	1603 (vs)	1313(vs)1251(sh) 1148(vs)	693(s)
$[Ni(tfpbd)_2 2H_2O]$	3434(s)	-	1619 (s)	1297 (m)	693(s)
Tta	3390 (w)	-	1578 (s)1637 (s)	1145(vs)	-
$[Cu(tta)_3]$	3440 (s)	2353(s)	1585 (vs)	1313(vs) 1406(w) 1248(sh)	598(w)
$[Ni(tta)_2 2H_2O]$	3402 (s)	2353 (s)	1600 (vs) 1539 (sh)	1406(s) 1304(vs)	587(w)
Bza	3439 (w)	2351 (w)	1605 (s)	1264 (s)	-
$[Cu(bza)_2 2H_2O]$	3415 (s)	2354 (s)	1537 (s)	1410(w) 1292 (w)	706 (s)
$[Ni(bza)_2 2H_2O]$	3416 (s)	2353 (s)	1693(w)1516 (s)	1392 (vs)	708 (s)
Dbm	3439 (w)	2351 (s)	1635 (w)	1292 (w)	-
$[Cu(dbm)_2 2H_2O]$	3455 (s)	2351 (w)	1593(s) 1544 (s)	1484 (s) 1455 (w)	786 (s)
$Ni(dbm)_2$	3448 (s)	2368 (w)	1668(w)1595 (s) 1528 (s)	1479(s) 1392 (s) 1307 (s)	755 (s)

The infrared spectral data (Table 3.0) indicates the ligands characteristics broad bands assigned to υOH in the range 3437 - 3390 cm^{-1} that varies in intensity in the order, dbm > tfpbd > bza >tta. Similar assignments had been made by Chen *et.al.* (2007), Halim, Nessa, Rahman, Chowdhury and Sallam (2005). Accompanying these are bands at 1635, 1594, 1605 and 1578 cm^{-1} observed for dbm, tfpbd, bza and tta respectively which complements the earlier band and confirming the existence of the ligands in the enolic form. Absence of any band at frequency ≥ 1700 cm^{-1} indicates nonexistence of the ligands in the diketo form. The involvement of the carbonyl functional group in chelation was evidenced by decrease intensity of the υOH bands as well as slight shifts of the carbonyl bands to lower frequencies in the complexes, except for $Cu(tfpbd)_2 2H_2O$. The coordination environment of nickel(II) complexes appears different from that of the copper(II) complexes: very strong absorption was observed at 1600 in $Ni(tfpbd)_2 2H_2O$ and 1619 cm^{-1} for $[Ni(tta)_2 2H_2O]$. The aromatic C=C – C=O in $Ni(dbm)_2$ and $Ni(bza)_2 2H_2O$ experience similar absorption with shifts to higher wavelength.

Table 4.0: Electronic spectral data of the compounds

Compounds	Charge transfer transition (cm^{-1})	Intraligand transition (cm^{-1})	d-d transition (cm^{-1})	Magnetic moment (BM)
tfpbd	-	45,454 30,487 48,780	-	
[Cu($tfpbd)_2 2H_2O$]	29,940 24,447 29940	48,780 44,843 33,222	18,382 16,233 16,000	1.88
[Ni($tfpbd)_2 2H_2O$]	29,154 28,653	48,076 45,454	18,454 16,556 15,600 14,471	3.32
Tta	29,940	48,780 31,347	-	-
[Cu($tta)_3$]	29,673 23,094	48,780 47,393 40,000	18,181 17,793 17,241	2.18
[Ni($tta)_2 2H_2O$]	29,154	51,020 46,082	17,985 17,152 16,906 16,393	3.25
Bza	-	49,454 40,000 31,645	-	-
[Cu($bza)_2 2H_2O$]	31,347	45,454 42,053 40,000	17,421 17,699 16,891 16,474	1.94
[Ni($bza)_2 2H_2O$]	26,653 27,472	50,251 40,000	19,230 18,796 15,841 15,625	3.07
Dbm	28,901	49,504 44,247 40,000	-	-
[Cu($dbm)_2 2H_2O$]	29,154	47,393 37,735	9,795 9,680 9249	1.83
Ni($dbm)_2$	29,154	46,728 37,735		3.04

Electronic spectral (Table 4.0) of the ligands indicate structural similarity with absorption at 48,780 and 49,504 cm^{-1} for the fluoro (CF_3) and the phenyl (C_6H_5) substituted ligands respectively, which are ascribed to n – σ* transitions. The n – σ* bands are accompanied by charge transfer and intra – ligand transitions observed between 30,487 – 45,454 cm^{-1}, the most prominent occurred at 30,487 - 31,645 cm^{-1} which are bands associated with electron transfer involving the carbonyl group on the ligands (Wang, Kang and Lu, 2013, Buono-Core, 1981).

In the Copper(II) complexes, ligand associated absorptions experienced varying shifts while characteristic d – d transitions due to Cu(II) were observed as broad bands within the range: 16,000 - 18, 382 cm^{-1} and 15,625 – 17,513 cm^{-1}. The magnetic moment of the complexes: Cu($tfpbd)_2 2H_2O$, Cu($tta)_3$, Cu($bza)_2 2H_2O$ and Cu($dbm)_2 2H_2O$ and are 1.88, 2.18, 1.94 and 1. 80 B.M respectively. In line with the spectral data obtained in this study, the six coordinate Copper(II) complexes: Cu($tfpbd)_2 2H_2O$, Cu($tta)_3$, Cu($bza)_2 2H_2O$ and Cu($dbm)_2 2H_2O$ have probable distorted octahedral geometry. The divalent $3d^9$ compounds of Copper(II) is subjected to Jahn - Teller distortions ruling out regular octahedron (Cotton and Wilkinson, 1987).

Also in the nickel(II) complexes, ligand associated absorptions experienced varying shifts while characteristic d – d transitions due to Ni(II) were observed as broad bands within the range: 15,600 - 16,556 and 16,393 – 17,985 cm^{-1}, accompanied with shoulders at 18,484 and 14, 421 cm^{-1}. However, three spin allowed transitions expected for six coordinate nickel(II) complexes having either regular or distorted octahedral geometry have energies in the range; ${}^3A_2g$ (F) → ${}^3T_2g$ (F) (υ_1), ${}^3A_2g$ → ${}^3T1g$ (F)(υ_2) and ${}^3A_2g$→ ${}^3T_1g$ (υ_3)(P) (Sallam, 2006, Ahmed et al., 2007). In line with the spectral data obtained in this study and the magnetic moment of the complexes: Ni($tfpbd)_2 2H_2O$, Ni($tta)_2 2H_2O$, Ni($bza)_2 2H_2O$ and Ni($dbm)_2$ which are 3.32, 3.25, 3.07 B.M respectively, the six coordinate nickel(II) complexes: Ni($tfpbd)_2 2H_2O$, Ni($tta)_2 2H_2O$ and Ni($bza)_2 2H_2O$ have probable distorted octahedral geometry. Although, extreme cases of distortion terminate in diamagnetic, square planar geometry, the Ni($dbm)_2$ being paramagnetic is probable tetrahedral.

Table 5.0 Wavelength at which the complexes studied gave absorptions

Copper(II) Complexes	Wavelength (nm) of Complex absorption (Frequency – cm^{-1})	Nickel(II) Complexes	Wavelength (nm) of Complex absorption (Frequency – cm^{-1})
Cu($tfpbd)_2 2H_2O$	332 (30, 140)	Ni($tfpbd)_2 2H_2O$	333 (30,030)
Cu($tta)_3$	348 (28,735)	Ni($tta)_2 2H_2O$	346 (28, 901)
Cu($bza)_2 2H_2O$	329 (30,395)	Ni($bza)_2 2H_2O$	243 (41, 152)
Cu($dbm)_2 2H_2O$	358 (27,932)	Ni($dbm)_2$	251 (39, 840)

The wavelength at which each metal – ligand system was studied (Table 5.0) indicates consistent absorptions involving π electrons of the phenyl and thioenyl rings in different environment as well as non – bonded electrons on the carbonyl oxygen. Mainly the absorptions were charge transfer transitions tailing into the visible in the range 27,900 – 30,000cm^{-1}. However, the alky substituted nickel(II) complexes: Ni($bza)_2 2H_2O$ and Ni($dbm)_2$ were studied at 39,840 – 41,152 cm^{-1} resulting from charge transfer transition.

Table 6.0: Second order rate constant (k_1), Equilibrium constant (K) at varying concentration of copper(II) ion for the formation of the compounds $Cu(tfpbd)_2 2H_2O$, $Cu(tta)_3$ $Cu(bza)_2 2H_2O$ and $Cu(dbm)_2 2H_2O$

Cu^{2+} × 10^4M	$Cu(tfpbd)_2 2H_2O$ $k_1(K_{Cutfpbd} \times 10^3)$	$Cu(tta)_3$ $k_1(K_{Cutta} \times 10^3)$	$Cu(bza)_2 2H_2O$ $k_1(K_{Cubza} \times 10^3)$	$Cu(dbm)_2 2H_2O$ $k_1(K_{Cudbm} \times 10^3)$
8.0				106.07(21.21)
9.0	22.571 (3.134)			^130.71 (36.30)
10.0	23.714 (3.204)	33.143 (5.021)		
12.0	34.571 (4.801)	28.857 (4.007)		
14.0	37.429 (5.271)	*26.571 (3.496)	35.476 (6.956)	
16.0		23.429 (3.166)	38.986 (7.217)	
18.0			39.762 (7.505)	
20.0			^51.548 (11.455)	

In formation of Cu(tfpbd)n H_2O and $Cu(tta)_3$ reactions, $k_{-1} = 0.007$ except in *, where $k_{-1} = 0.008$
In formation of $Cu(bza)_2 2H_2O$ and $Cu(dbm)_2 2H_2O$ reactions, $k_{-1} = 0.005$ except in ^, where $k_{-1} = 0.004$

Table 7.0: Rate constant (k_1), Equilibrium constant (K) at varying concentration of nickel(II) ion for the formation of the compounds $Ni(tfpbd)_2 2H_2O$, $Ni(tta)_2 2H_2O$ $Ni(bza)_2 2H_2O$ and $Ni(dbm)_2$

Ni^{2+} × 10^2M	$Ni(tfpbd)_2 2H_2O$ $k_1(K_{Nitfpbd} \times 10^4)$	$Ni(tta)_2 2H_2O$ $k_1(K_{Nitta} \times 10^4)$	$Ni(bza)_2 2H_2O$ $k_1(K_{Nibza} \times 10^4)$	$Ni(dbm)_2$ $K_1(_{Nidbm\times} \times 10^4)$
1.0	62.000 (2.296)	23.429 (0.321)	36.000 (1.161)	37.627 (0.964)
1.2	59.714 (2.069)	46.857 (0.997)	45.000 (1.323)	60.000 (1.764)
1.4	50.000 (1.219)	28.000 (0.475)		
1.6	47.714 (0.994)	58.286 (1.766)		

In formation of $Ni(tfpbd)_2$ $2H_2O$ and $Ni(tta)_2 2H_2O$, k_{-1} varies in the range 0.003 – 0.007
In formation of $Ni(bza)_2 2H_2O$ and $Ni(dbm)_2$, k_{-1} was constant at 0.003

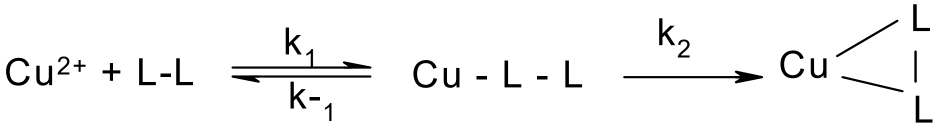
The rate constant (k_1), the equilibrium constant ($K = \frac{k_1}{k_{-1}}$) on formation of each copper(II) and nickel(II) complexes are reported in Tables 6.0 and 7.0 respectively. The results indicate an increase in k_1 with increase in concentration of the metal ion on formation of the complexes with the exception of $Cu(tta)_3$. For the formation of the copper(II) complexes investigated in this study the rate constant is in the order: $Cu(dbm)_2 2H_2O$> $Cu(bza)_2 2H_2O$ > $Cu(tfpbd)_2 2H_2O$ > $Cu(tta)_3$. However, for the nickel(II) complexes, k_1 varies in the order $Ni(tfpbd)_2 2H_2O$ > $Ni(dbm)_2$ > $Ni(bza)_2 2H_2O$ > $Ni(tta)_3$. This implies that in terms of the second order substitution rate, the electronic influence of the R – groups for the copper(II) and nickel(II) complexes is according to the order: $C_6H_5 > CH_3 > CF_3 > C_4H_3S$ and $CF_3 > C_6H_5 > CH_3 > C_4H_3S$ respectively, indicating dbm is the strongest Lewis base, while tta is least. Metal complexes of β – diketones with at least one CF_3 substituent are associated with increased thermal and chemical stability (Lai et al., 2003), however; the stabilization effect of the CF_3 group had been overwhelmed by its interaction with water (Wang, 2005). The results of the substituents behaviour within the Nickel(II) enviroment coincides with the results obtained by Kemp (2004), when the β – diketone was the leaving ligand. However, Kuhn (2008) obtained a similar order for C_6H_5, CH_3 and CF_3, in the Ti(II) complexes, where the β – diketone ligand was non – labile.

The solvent influence as measured by k_{-1}, appears constant in each complexation reaction, however, k_{-1} was highest in the fluorosubstituted complexes in which it was in the range 0.007 - 0.008 $mol^{-1}s^{-1}$ and least with the value 0.004 – 0.005 $mol^{-1}s^{-1}$ in the complexes of alkylsubstituted ligands. These observations imply that compared with the alkyl - substituted β-diketonate complexes studied, the fluoro – substituted complexes experiences greater solvent influence, also implying an inverse relationship between k_1 and k_{-1} for the complexes studied. However solvent influence was less pronounced on formation of nickel(II) complexes, thus limiting formation of a solvent intermediate and or solvent pathway, similar observation was made by Fourie *et. al.* (2010) and Dimple and Seema (2005).

Table 8.0: Rate constant k_2 obtained from the extrapolation of the experimentally obtained k_1 values and the steady state approximation of solvent dependent (K_1k_2) and solvent independent rates (k_1k_2)

Copper(II) Complexes	$k_2(s^{-1}M^{-1})$	Nickel(II) Complexes	$k_2(s^{-1}M^{-1})$
$Cu(tfpbd)_2 2H_2O$	48.115 ± 0.352	$Ni(tfpbd)_2 2H_2O$	23.119 ± 5.302
$Cu(tta)_3$	48.08 ± 2.213	$Ni(tta)_2 2H_2O$	37.267 ± 7.960
$Cu(bza)_2 2H_2O$	45.873 ± 1.564	$Ni(bza)_2 2H_2O$	14.826 ± 0.899
$Cu(dbm)_2 2H_2O$	39.299 ± 6.758	$Ni(dbm)_2$	27.991 ± 2.052

The rate determining step of each reaction was ascertained with the aid of the steady state approximation; plots of k_{obs} against the square of the concentration (LL^2) of each ligand was within experimental error straight lines with slopes which equals $\frac{k_1k_2}{k_{-1}}$ (The solvent dependent rate of the complexation reaction) (Odiaka, 2004) from which k_1k_2, the solvent independent rates and subsequently k_2, the second order rate constant were obtained at 25°C. For the copper(II) complexes studied, k_2 was found to be greater than k_1 ($k_2 > k_1$), also k_2 was constant (Tables 6.0 and 8.0) within experimental error. This in addition to the first order dependence of k_1 on the concentration of each ligand and metal ion; ([LL] and [M^{2+}]) may suggests the rate measured by k_1 is of a direct interaction of the ligands with the copper(II) ion establishing an equilibrium followed by a faster process, at rate which equals k_2 which was found constant as observed in a preliminary study reported by Oladipo, Bello and Adeagbo, (2012) for the formation of the copper(II) complexes and may be ascribed to ring closure. Thus the probable mechanism for the copper(II) complexes is as in scheme 1.0



Scheme 1.0: Proposed mechanism for the formation of $Cu(LL)_2(H_2O)_n$, LL = $CF_3COCH_2COC_6H_5$ (tfpbd), $CF_3COCHCOC_4H_3S$ (tta), $CH_3COCH_2COC_6H_5$ (bza) and $C_6H_5COCH_2COC_6H_5$ (dbm)

However, for the complex $Cu(dbm)_22H_2O$, $k_2 < k_1$ in fact $k_1 \approx 2k_2$, which may be an indication that, equilibrium in forming the compound was established faster, the reverse reaction was negligible and the equilibrium is further to the transition state product than what obtains in other complexes, this assertion is confirmed by larger equilibrium constant values in the complexation process. In all the nickel(II) complexes, k_1 was found to be greater than k_2 ($k_1 > k_2$), an indication that the nickel(II) – ligand equilibrium was established faster, which encourages a probable slower process of ring closure. However, the values of k_2 vary in all the nickel(II) – ligand system studied, which may imply that the rate measured by k_2 is that associated with a probable entering of a second ligand as proposed by the steady state approximation (Odiaka, 2004). The values of k_2, probably rate determining, was influenced by the R- groups hence k_2 values varies among the nickel(II) complexes. These findings may be corroborated by lower solvent influence observed with the nickel(II) complexes. Hence the nickel(II) complex formation might proceed through the route in Scheme 2.0.

Scheme 2.0: Proposed mechanism for the formation of $Ni(LL)_2(H_2O)n$, LL = $CF_3COCH_2COC_6H_5$ (tfpbd), $CF_3COCHCOC_4H_3S$ (tta), $CH_3COCH_2COC_6H_5$ (bza) and $C_6H_5COCH_2COC_6H_5$ (dbm)

Conclusion

The infrared, electronic spectral and magnetic moment data indicate differences in the coordination environment of the Copper(II) and Nickel(II) β- diketonate complexes studied. The observations were corroborated by the kinetic data obtained. Solvent influence was more evident in the copper(II) fluoro- substituted complexes and least in the alkyl substituted copper(II) and both fluoro- and alkyl- substituted nickel(II) complexes. The second order rate constant k_2 indicates ring closure on formation of the copper(II) complexes, but in the nickel(II) and $Cu(dbm)_2$ complexes; k_2 is a measure of the coordination of a second ligand.

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