Synthesis of Nickel(II) Complexes Using Malonodihydrazone Ligands Having Long Chain Pendent Arms

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Abstract

The Schiff base complexes of transition metals have been widely used in biological, industrial and analytical fields. The present work is synthesis and characterization of some complexes. The complexes $K_2[Ni(C_{31}H_{26}N_4O_4)_2]$, $K_2[Ni(C_{29}H_{38}N_4O_4)_2]$, and $K_2[Ni(C_{41}H_{62}N_4O_2)_4]$, have been prepared by the reaction of Schiff bases with nickel(II) acetate tetrahydrate in the presence of base (KOH) in 2:1 molar ratio. The Schiff base ligands e.g. $L'H_2$, $L''H_2$ and $L'''H_2$ were prepared from the reaction of malonodihydrazide with 4-benzyloxybenzaldehyde, 4-hexyloxybenzaldehyde and 4-dodecyloxybenzaldehyde.

Where $L'H_2$ represents

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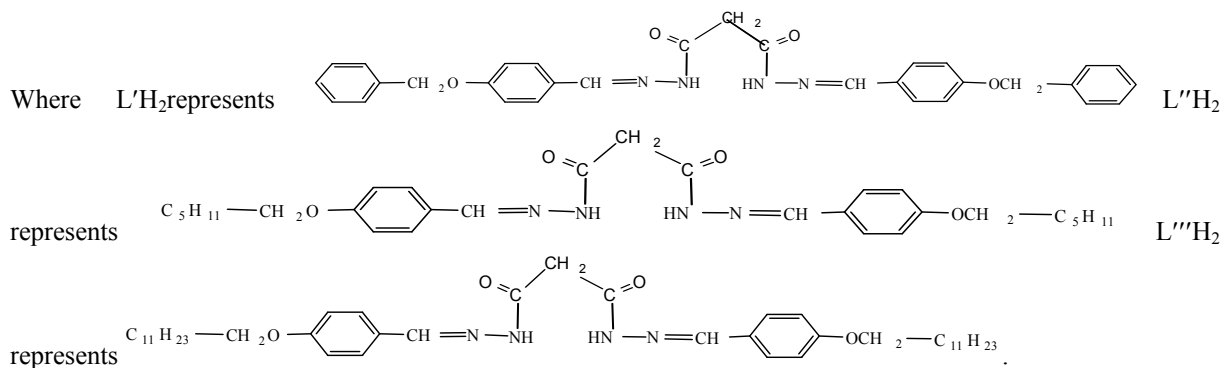
The complexes 1-3 have been characterized on the basis of elemental analysis, metal estimation, magnetic moments, conductance measurements, IR and UV-visible spectra and study of other physical properties. The suggested structures of the complexes 1-3 are square planar in nature.

Keywords: Schiff base complex, Schiff base ligand, malonodihydrazide, 4-benzyloxybenzaldehyde, 4-hexyloxybenzaldehyde, 4-dodecyloxybenzaldehyde

1. Introduction

Coordination chemistry at present stands as a land mark in the field of scientific advancement, embracing most diverse branches of science, engineering and technology. A complex has been defined as a species formed by the association of two or more simpler species capable of independent existence. (Rossotti et al., 1961). Although Jorgensen (1837-1914) started the extensive studies on the synthesis of complex compounds, it was not until 1906 when the recognition of the true nature of complexes began with Alfred Werner (1866-1919) as set out in his classic work Neuere Anschauungen ouf dem Gebiete der anorganischen chemie (Werner, 1911). For this pioneering work, Alfred Werner received the Nobel Prize in 1913. In fact he was the founder of modern coordination chemistry who postulated the first successful theory known as "Werner's coordination theory" to explain the formation, properties and stereochemistry of coordination compounds. The independent approaches of Sidgwick (1923) and Lowry (1923) are that a chemical bond required the sharing of an electron molecule with an electron pair. This led to the idea that a neutral molecule with an electron pair (Lewis base) can donate these electrons to a metal ion or other electron acceptor (Lewis acid).

Although the electron pair donor-acceptor concept of Lewis (Basdo et al., 1964) is still useful for many Lewis-acid base interactions for complex formation, it is apparent that the understanding towards the nature of bonding in metal complexes requires more detailed considerations. At the present time, four more or less distinct approaches to the theoretical treatment of the bonding and properties of coordination compounds are recognized. These theories are the Valence Bond Theory (VBT) (Bethe, 1929; Pouling, 1960), the Crystal Field Theory (CFT) (Pauling, 1960; Orgel, 1960), the Ligand Field Theory (LFT) (Figgis, 1960; Vanvleck, 1935), and the Molecular Orbital Theory (MOT) (Vanvleck, 1985; Graw, 1964).

Every Lewis acid-base reaction involving essentially the formation of coordinate covalent bond can be called a complex formation reaction. The chemistry of Schiff base complexes have attracted a great deal of attention ever since Pfeiffer carried out his Pioneer research in the 1930's. The reactivity of coordination compounds is dramatically changed on the basis of complexation. Some important interesting reactions of substituted bis-salicylaldimine chelates of copper and nickel in which the organic groups attached to nitrogen of the donors are altered have been reported.The importance and application of metal complexes in analytical Chemistry are well known (Gruses et al., 1983). The Schiff base ligands play an important role in some biological systems and their function is related, at least in part, to its chelating ability with metal. In the recent years, a considerable attention has been given to synthesis of some Schiff base complexes to study their biological activity. Therefore, the interest of the present work is to synthesis and characterization of some Schiff base complexes.

2. Experimental

Preparations of 4-alkyl/aryloxybenzaldehyde (1) were done by reflux of 4-hydroxybenzaldehyde, alkyl/arylbromide and anhydrous K_2CO_3 in acetone. Malonodihydrazide $C_3H_8N_4O_2$ (2) was prepared by the reaction of Diethylmalonate and hydrazine hydrate. To the aqueous solution of malonodihydrazide, $C_3H_8N_4O_2$, 4-alkyl/aryloxy-benzaldehyde solutions were added. Preparations of Schiff base ligands L′H$_2$, $C_{31}H_{28}N_4O_4$, L″H$_2$, $C_{29}H_{40}N_4O_4$ and L‴H$_2$, $C_{41}H_{64}N_4O_4$ (3) were completed as white powdered products. To the ethanolic solution of the ligands the nickel (II) acetate tetrahydrate solution was added and then the ethanolic solution of potassium hydroxide was added. Finally, the complexes $K_2[Ni(C_{31}H_{26}N_4O_4)_2]$, K_2 [Ni $(C_{29}H_{38}N_4O_4)_2]$, and $K_2[Ni(C_{41}H_{62}N_4O_4)_2]$ (4) are synthesised as yelloish amorphous solids.

The synthetic route of the complexes is shown in the following scheme:

(3)

(4)
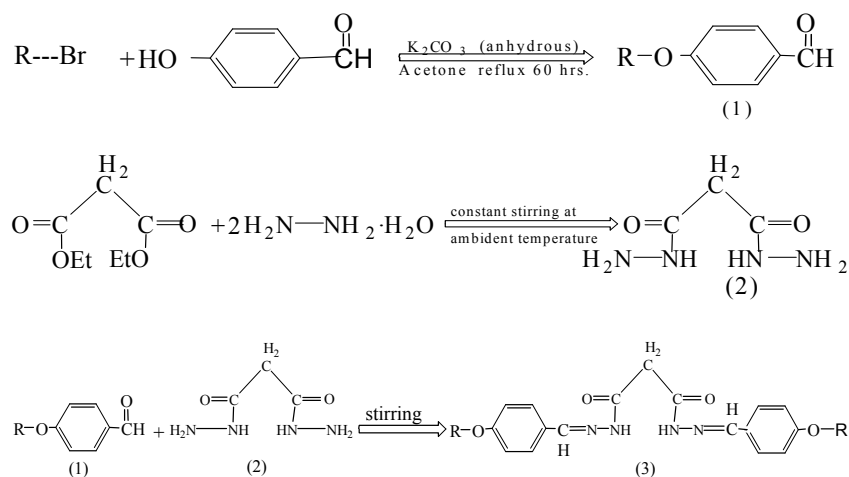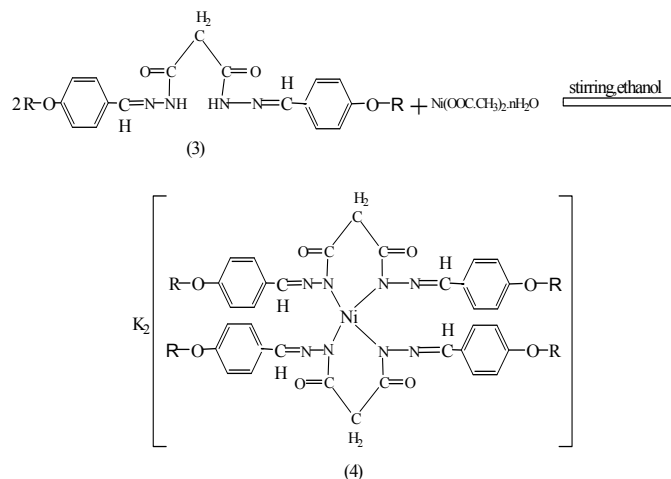
Where, $R \equiv C_6H_5\text{-}CH_2\text{-}, C_6H_{13}\text{-}, C_{12}H_{25}\text{-}$.

The characterizations of each products are done through weighing, elemental analysis, metal estimation, infrared spectra and uv-visible spectra study; conductivity, magnetic moments and melting point measurements and thin layer chromatography (TLC).

3. Results and Discussion

3.1 Synthesis of 4-benzyloxybenzaldehyde

The compound (5) was synthesized by the reaction of 4-hydroxybenzaldehyde with benzylbromide in the presence of anhydrous potassium carbonate. The infrared spectrum f the compound (5) showed a strong absorption band at 1686 cm^{-1} which is suggested for stretching frequency of $\nu(C=O)$ of aldehyde group. The band at 1601, 1576 cm^{-1} are suggested for the aromatic, $\nu(C=C)$ stretching frequencies. The bands at 1111 and 1167 cm^{-1} may be assigned to the $\nu(C\text{-}O)$ absorption. The absence of hydroxyl band at 3400-3600 cm^{-1} region indicated the formation of compound (5).
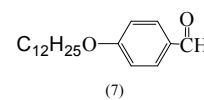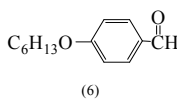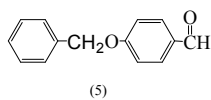
Therefore, the elemental analysis and IR spectral data suggested that the compound is the expected aldehyde, 4-benzyloxybenzaldehyde (5).

3.2 Synthesis of 4-Hexyloxybenzaldehyde

The compound (6) was synthesized by the reaction of 4-hydroxy benzaldehyde with hexylbromide in the present of anhydrous potassium carbonate. The infrared spectrum of the compound (6) showed a strong absorption band at 1686 cm^{-1} which is suggested for stretching frequency of $\nu(C=O)$ of aldehyde group. The band at 1601, 1576 cm^{-1} are suggested for the aromatic, $\nu(C=C)$ stretching frequencies. The bands at 1111 and 1167 cm^{-1} may be assigned to the $\nu(C\text{-}O)$ absorption. The absence of hydroxyl band at 3400-3600 cm^{-1} region indicated the formation of compound (6). Therefore, the elemental analysis and IR spectral data suggested that the compound is the expected aldehyde, 4-hexyloxybenzaldehyde (6).

### 3.3 Synthesis of 4-dodecyloxybenzaldehyde

The compound (7) was synthesized by the reaction of 4-hydroxy benzaldehyde with benzylbromide in the presence of anhydrous potassium carbonate. The infrared spectrum (Figure 3) of the compound (7) showed a strong absorption band at 1686 cm^{-1} which is suggested for stretching frequency of $\nu(C=O)$ of aldehyde group. The band at 1601, 1576 cm^{-1} are suggested for the aromatic, $\nu(C=C)$ stretching frequencies. The bands at 1111 and 1167 cm^{-1} may be assigned to the $\nu(C\text{-}O)$ absorption. The absence of hydroxyl band at 3400-3600 cm^{-1} region indicated the formation of compound (7). Therefore, the elemental analysis and IR spectral data suggested that the compound is the expected aldehyde, 4-dodecyloxybenzaldehyde (7).

Table 1. Elemental analysis and other physical properties of compounds 5, 6 and 7

Synthesize compounds(5-7) and their physical state	Melting point, °C	% C		% H		% O	
		Calculated	Found	Calculated	Found	Calculated	Found
5. ($C_{14}H_{12}O_2$), Yellowish powdered	72	79.25	78.80	5.09	5.01	15.09	14.48
6. ($C_{13}H_{18}O_2$), Yellowish liquid	-	75.73	74.89	8.74	8.41	15.53	15.09
7. ($C_{19}H_{30}O_2$), Reddish brown liquid	-	78.62	78.20	10.34	9.39	11.04	10.65

Table 2. Important infrared spectral bands of compounds (5, 6 and 7)

Compounds	ν(C=O)aldehyde (cm^{-1})	ν (C=C)aromatic (cm^{-1})	ν (C-O) cm^{-1}
5. ($C_{14}H_{12}O_2$)	1686	1601,1576	1111,1167
6. ($C_{13}H_{18}O_2$)	1686	1601,1576	1111,1167
7. ($C_{19}H_{30}O_2$)	1686	1601,1576	1111,1167
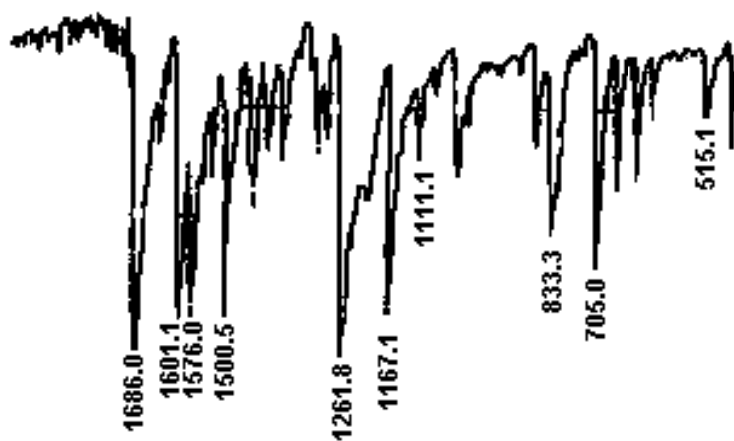
Figure 1. Infrared spectrum of compound (5), $C_{14}H_{12}O_2$
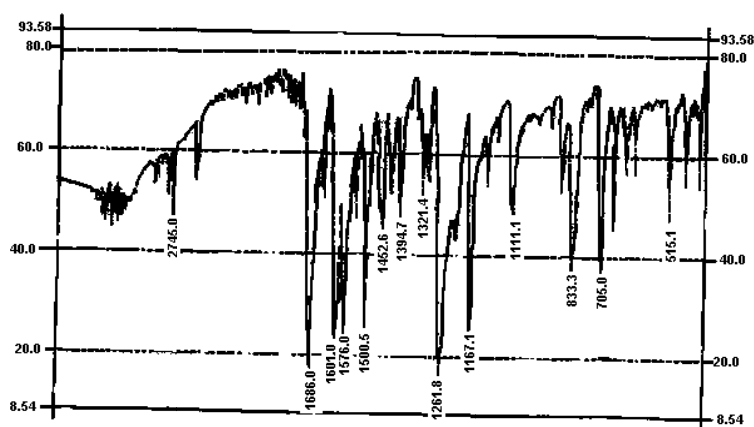
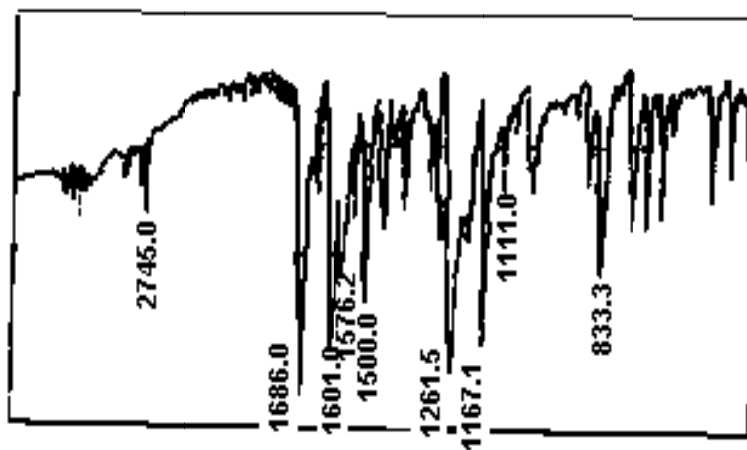Figure 2. Infrared spectrum of compound (6), $C_{13}H_{18}O_2$

Figure 3. Infrared spectrum of compound (7), $C_{19}H_{30}O_2$

3.4 Synthesis of the Schiff Bases

The Schiff base ligands (e.g. L′H₂, L″H₂ and L‴H₂) were prepared by the reaction of malonodihydrazide with 4-benzyloxybenzaldehyde, 4-hexyloxy benzaldehyde and 4-dodecyloxybenzaldehyde respectively at ambient temperature. The ligands have been characterized by IR spectra, elemental analysis and other physical properties. The infrared spectra of the ligands (L′H₂, L″H₂ and L‴H₂) are shown in Figure (1, 2 and 3) respectively. The spectral data (Table 4) of the ligands showed a strong band at (3213-3220) cm⁻¹ region suggested for the ν(N-H) stretching of amide (-CONH-) group. [The starting material malonodihydrazide[22] have three ν(N-H) bands at (3248, 3213, 3050) cm⁻¹. The bands at 3248, 3050 cm⁻¹ for the asymmetric and symmetric ν(N-H) stretching of the terminal NH₂ moiety and 3213 cm⁻¹ for amide (-CONH-) group]. The ligands showed an absorption band at (1610-1624) cm⁻¹ region suggested for the ν (C=N) stretching. This indicated the condensation between aldehyde and terminal NH₂ group of malonodihydrazide. The ligands showed a strong band at (1654-1670) cm⁻¹ for υ(C=O) stretching[24]. A broad band at (1577-1581) cm⁻¹ is due to the ν (C=C) stretching of aromatic C=C double bond.

The elemental analysis data and other physical properties (Table 3) of the ligands are consistent with their proposed formula.
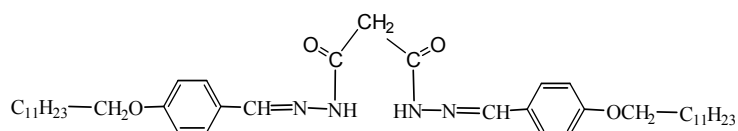
On the basis of infrared spectra, elemental analysis and other physical properties the suggested structure of the ligands (L′H$_2$, L″H$_2$ and L‴H$_2$) are shown as:
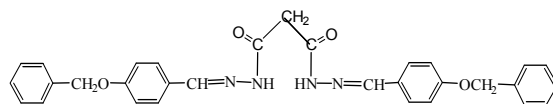
Bis[N-benzylidene(4-benzyloxy)]malonodihydrazone (C$_{31}$H$_{28}$N$_4$O$_4$) represents as L′H$_2$ ligand
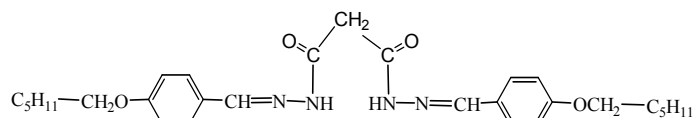
Bis[N-benzylidene(4-hexyloxy)]malonodihydrazone (C$_{29}$H$_{40}$N$_4$O$_4$) represents as L″H$_2$ ligand


Bis[N-benzylidene(4-dodecyloxy)]malonodihydrazone (C$_{41}$H$_{64}$N$_4$O$_4$) represents as L‴H2 ligand

Table 3. Elemental analysis and other physical properties of Ligands (L′H$_2$, L″H$_2$ and L‴H$_2$)

Ligands and physical state	Melting point, °C	% C		% H		% N		% O	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
L′H$_2$(C$_{31}$H$_{28}$N$_4$O$_4$), White Powdered	196	71.51	55.80	5.43	6.71	10.76	23.65	12.30	13.48
L″H$_2$(C$_{29}$H$_{40}$N$_4$O$_4$), White Powdered	182	68.46	69.89	7..93	5.41	11.02	15.45	12.59	8.79
L‴H$_2$ (C$_{41}$H$_{64}$N$_4$O$_4$), White Starfish like crystal	190	72.73	51.20	9.53	8.39	8.28	23.21	9.46	13.25

Table 4. Important infrared spectral bands of ligands (L′H$_2$, L″H$_2$ and L‴H$_2$)

Ligands	ν (N-H) cm^{-1}	ν (C-H) cm^{-1}	ν (C=O) cm^{-1}	ν (C=N) cm^{-1}	ν (C=C) cm^{-1}
L′H$_2$(C$_{31}$H$_{28}$N$_4$O$_4$)	3216	2931	1660	1614	1577
L″H$_2$(C$_{29}$H$_{40}$N$_4$O$_4$)	3220	2920	1670	1624	1581
L‴H$_2$(C$_{41}$H$_{64}$N$_4$O$_4$)	3213	2931	1654	1610	1575
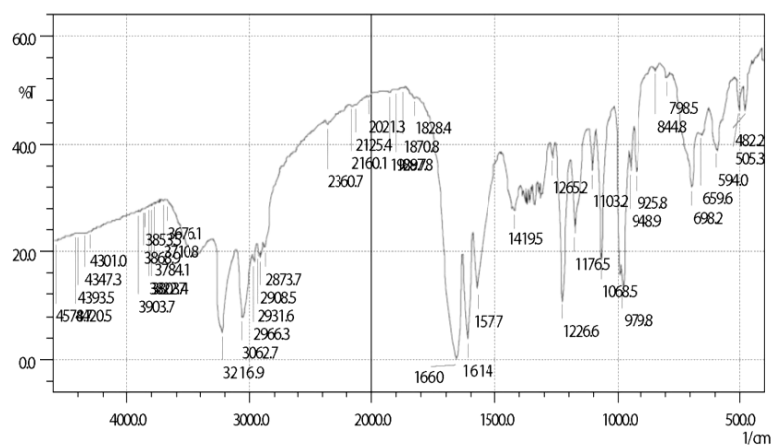
Figure 4. Infrared spectrum of L′H$_2$ Schiff base
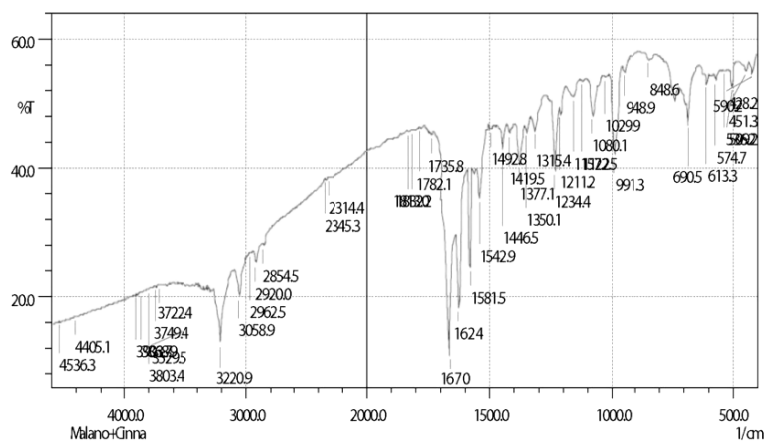
Figure 5. Infrared spectrum of L″H$_2$ Schiff base
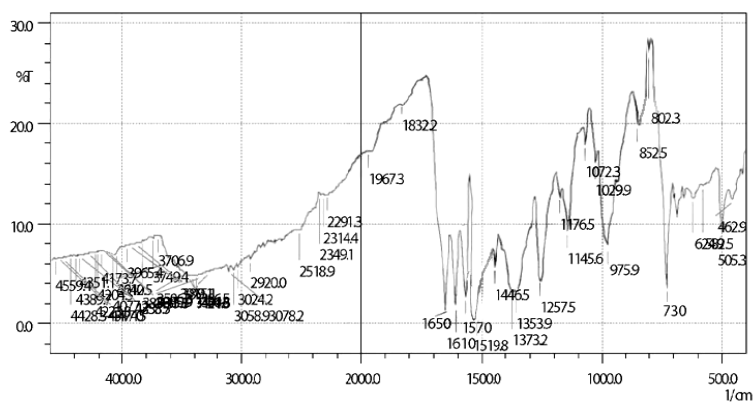
Figure 6. Infrared spectrum of L‴H$_2$ Schiff base ligand

3.5 Reactions of Schiff Bases (e.g. L′H₂=C₃₁H₂₈N₄O₄, L″H₂=C₂₉H₄₀N₄O₄ and L‴H₂=C₄₁H₆₄N₄O₄) with Nickel(Ii) Acetatetetrahydrate in the Presence of Base (KOH): Synthesis of Complexes 1-3

The complexes 1-3 were prepared by the reaction of Schiff bases (e.g. L′H₂, L″H₂ and L‴H₂) with nickel(II) acetatetetrahydrate in the presence potassium hydroxide. The complexes have been characterized by elemental analysis, metal estimation, magnetic moments and conductance measurements, IR and UV-visible spectra and study of other Physical properties. The elemental analysis (Table 6) and metal estimation (Table 5) of the complexes 1-3 are consistent with the proposed formula. The conductance values (Table 5) of the complexes 1-3 reveal that they are 2:1 electrolytic in nature.

The infrared spectra (Figure 7, 8 and 9) of the complexes 1-3 showed (Table 7) absorption band at (1610-1620) cm^{-1} region suggested for υ (C=N) stretching. There is no band at (3100-3300) cm^{-1} region indicated the absence of (N-H) group of the complexes. This also indicated the deprotonation of amide (-CONH-) proton. The complexes showed a strong band at (1650-1666) cm^{-1} which represents the υ (C=O) stretching.[24] A broad band at (1570-1580) cm^{-1} is due to the υ(C=C) double bond. A new band arises at (730-748) cm^{-1} is due to the υ (M-N) stretching[26], which indicates the coordination of ligand to the metal through the nitrogen atom.

The magnetic moment data of the complexes 1-3 are shown in Table 7. The magnetic moment of the complexes 1-3 showed negative value. These values corresponds that Ni(II) d^8-system has no unpaired electron, suggested the diamagnetic complexes.

The UV-visible spectra of the complexes 1-3 are shown in Figure (10, 11 and 12). The complexes showed (Table 10) a single broad band at 400 nm 1, at 430 nm 2, and at 420 nm 3, represent the d-d transition of $^1A_{1g} \rightarrow {}^1B_{1g}$ which suggested the square planar geometry of the Ni(II) complexes. The band observed below 400 nm assigned due to the $\pi \rightarrow \pi^*$ transition of the ligands.

On the basis of elemental analysis, magnetic moment, conductance measurements, metal estimation, IR and UV-visible spectra and other physical properties the suggested structure of complexes 1-3 are square planar in nature as shown in Figure (A), (B) and (C) respectively.
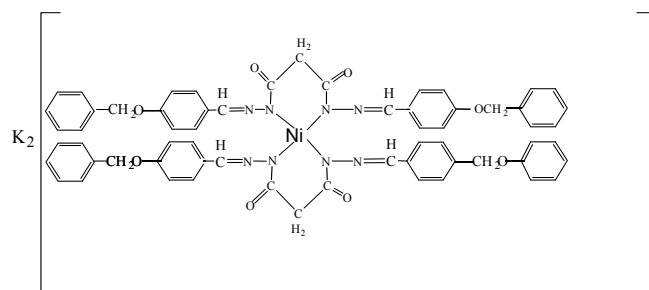

Figure (A). Square planar structure of K₂ [Ni(L′)₂] for complex 1, L′ represents C₃₁H₂₆N₄O₄

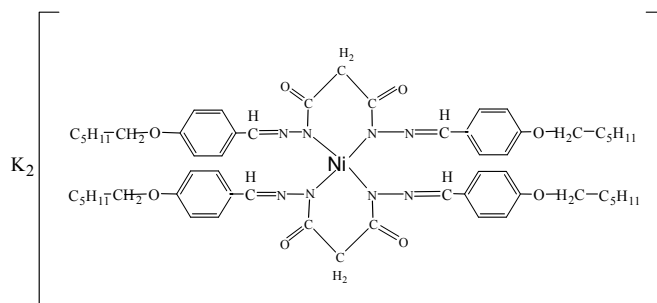Figure (B). Square planar structure of K₂ [Ni(L″)₂] for complex 2, L″ represents C₂₉H₃₈N₄O₄
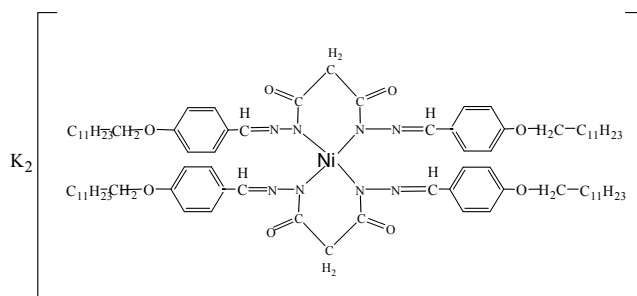
Figure (C). Square planar structure of $K_2 [Ni(L''')_2]$ for complex 3, L''' represents $C_{41}H_{62}N_4O_4$

Table 5. Analytical data and other physical properties of complexes 1-3

No	Complexes	Colour	Melting point °C	% M Calculated	% M Found	Molar conductance Ohm^{-1} cm^2 mol^{-1}	yield%
1	$K_2 [Ni(L')_2]$	Yellow	260 (d)	5.00	4.6	70.29	40
2	$K_2 [Ni(L'')_2]$	Pale yellow	250 (d)	5.12	5.01	67.22	48
3	$K_2 [Ni(L''')_2]$	Greenish yellow	238 (d)	3.95	3.89	72.69	45

Note: Here d = decomposition temperature.

Table 6. Elemental analysis data of complexes 1-3

No	Complexes	% C Calculated	% C Found	% H Calculated	% H Found	% N Calculated	% N Found	% O Calculated	% O Found
1	$K_2[Ni (L')_2]$	63.43	63.02	4.46	4.25	9.54	8.98	10.91	10.45
2	$K_2[Ni (L'')_2]$	60.55	59.02	6.66	6.51	9.74	9.12	11.13	10.90
3	$K_2[Ni (L''')_2]$	66.22	66.06	8.41	7.27	7.54	7.15	8.61	8.41

Table 7. Magnetic moment data of the complexes 1-3, T = 300K

No	Complexes	Sample length, 'l' in cm	Weight of the sample 'm' in g	Susceptibility of the empty tube 'R$_0$'	Susceptibility of sample with tube 'R'	Mass susceptibility, χ_g ×10^{-6} C.G.S unit	Molecular weight, M	Molar susceptibility χ_m ×10^{-3} C.G.S unit	Diamagnetic correction χ_g ×10^{-6} C.G.S unit	χ_m^{corr} ×10^{-3} C.G.S unit	μ_{eff} in B.M
1	$K_2[Ni(L')_2]$	1.9	0.0331	-15	-19	-0.478	1172.893	-0.561	-	-	Dia.
2	$K_2[Ni(L'')_2]$	1.7	0.04	-35	-40	-0.443	1149.501	-0.509	-	-	Dia.
3	$K_2[Ni(L''')_2]$	1.6	0.0423	-21	-29	-0.631	1485.885	-0.938	-	-	Dia.

Table 8. Important infrared spectral bands of complexes 1-3, (as KBr disc)

No	Complexes	ν (C=N) cm^{-1}	ν (C=C) cm^{-1}	ν (M-N) cm^{-1}	ν (C=O) cm^{-1}
1	K$_2$[Ni (L')$_2$]	1615	1575	740	1654
2	K$_2$[Ni (L'')$_2$]	1620	1580	748	1666
3	K$_2$[Ni (L''')$_2$]	1610	1570	730	1650

Table 9. UV-visible spectrum of complexes 1-3

No	Complexes	λ max (nm)
1	K$_2$[Ni (L')$_2$]	400
2	K$_2$[Ni (L'')$_2$]	430
3	K$_2$[Ni (L''')$_2$]	420
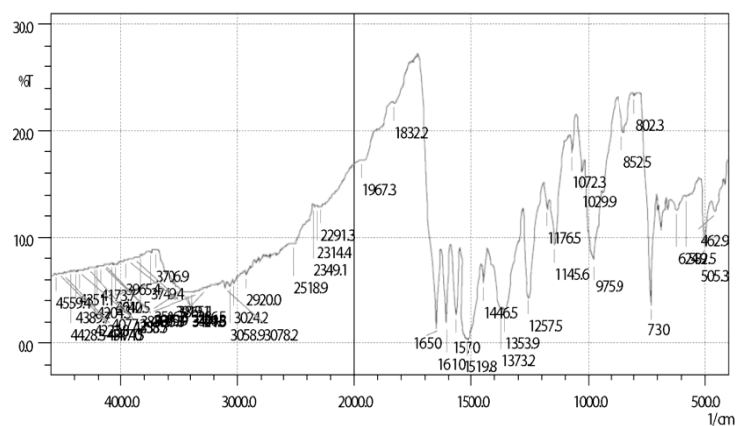
Figure 7. Infrared spectrum of K$_2$[Ni(C$_{31}$H$_{26}$N$_4$O$_4$)$_2$] complex 1
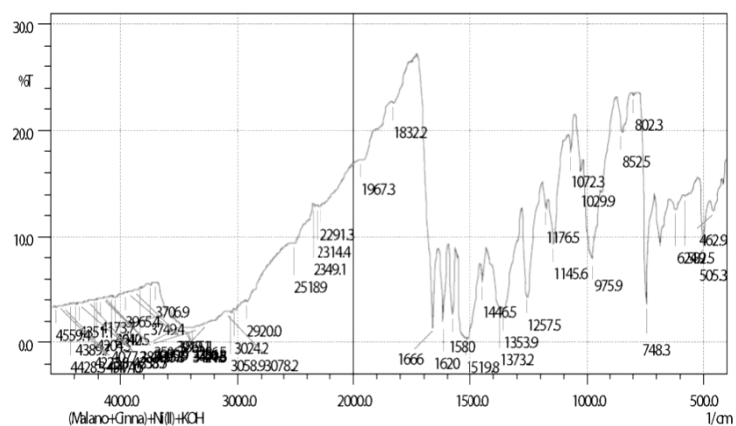
Figure 8. Infrared spectrum of K$_2$[Ni(C$_{29}$H$_{38}$N$_4$O$_4$)$_2$] complex 2
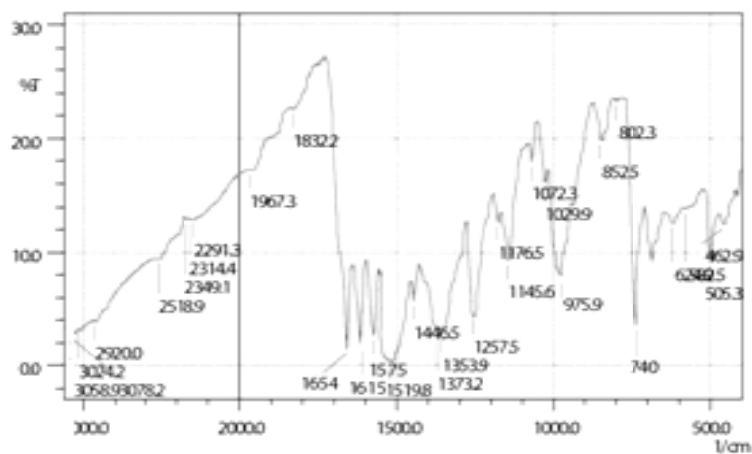
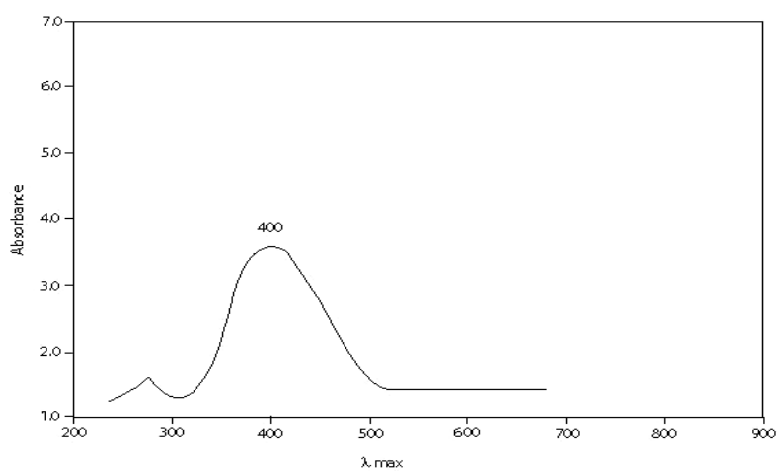Figure 9. Infrared spectrum of $K_2[Ni(C_{41}H_{62}N_4O_4)_2]$ complex 3

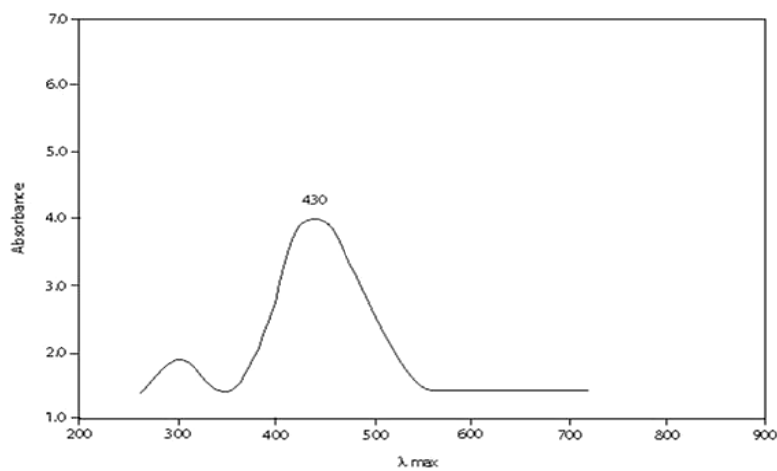Figure 10. UV-visible spectrum of $K_2[Ni(C_{31}H_{26}N_4O_4)_2]$ complex 1

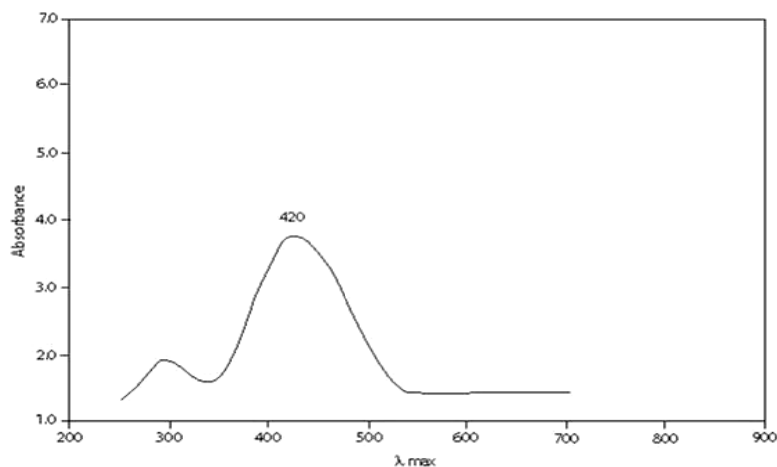Figure 11. UV-visible spectrum of $K_2[Ni(C_{29}H_{38}N_4O_4)_2]$ complex 2

Figure 12. UV-visible spectrum of $K_2[Ni(C_{41}H_{62}N_4O_4)_2]$ complex 3

Acknowledgements

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