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Spectral Characterization of Ni (II) Complexes

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ABSTRACT

The current work explains about the synthesis, spectral characterization of the complexes of few Nickel(II) complexes. The compound characterizations were performed based on the studies of infrared, elemental analysis, magnetic susceptibility and electronic spectra. Based on these studies the preliminary structures for the complexes were suggested and presented for Ni (II) complexes. The microwave method of complexes synthesis was found to be easier and convenient.

1. Introduction

Amide ligands is a significant component of many biologically important compounds and an awareness of amides formation, properties and reactions is crucial for potential development in areas such as polypeptide and protein chemistry. Most amides demonstrate pharmacological behaviour that has recently sparked interest in their chemistry.

Nickel is a hard, silver white colour metal, which occur as cubic structures and has superior strength. This is malleable, ductile and has a resistance to corrosion. This also forms a variety of complex compounds; the majority of nickel are blue or green compounds. The metal is a relatively strong heat and electricity conductor, and exhibits magnetic properties below 345° C, making it highly attractive to mix alloys with other metals (1).

Nickel is a significant manufacturing metal and is generally used in the iron and steel industry, in the automotive, architectural and chemical industries. The basic uses include: firstly, a metal substance such as stainless steel preparation, heat-proof alloy steel and various alloys is used; secondly, it is used for electrical plating, the surface layer is durable and corrosion resistant on steel and other metals as a foundation, the resistance to corrosion is greater than zinc plating; thirdly, nickel is used as a catalyst in the petrochemical hydrogenation cycle; fourthly nickel is used as a chemical source and is the raw material for the processing of nickel-hydrogen batteries and Ni-Cd batteries; fifthly, nickel is used as a new design material for the manufacture of dyes and pigments, ceramics and ferrites.

Nickel and its alloys are used in many different applications; most of which require a resistance to corrosion and/or heat. Nickel is mainly used in the preparation of alloys such as stainless steel, which accounts for approximately 65% of all nickel used in manufacturing. A nickel and copper alloy is a component of the tubing that is used to desalinate sea water. Nickel steel is used to produce armor plates and burglar-proof vessels.

Nickel is naturally found in the earth's crust, in conjunction with other elements. In the earth's crust, nickel occurs naturally, together with other elements. It is found throughout the soil, and emitted from volcanoes. Nickel is present mainly in the atmosphere in conjunction with oxygen or sulphur as oxides or as sulphides (2).

Nickel center are a common element in that hydrogenase whose function is to oxidize rather than evolve hydrogen. Nickel centers might be the active site of hydrogenase enzymes. The tetrapyrrol is intermediate in structure between porphyrin and corrin. Nickel is apparently essential for proper live function in rats (which are relatively close to human genetically) (3).

Nickel is an element that occurs in the environment only at very low levels. The role of nickel has been investigated in orthodontic induced gingival hyperplasia. Nickel is both essential and toxic for animals and humans. A nickel poor nutrition of < 0.1 mg per kg dry matter led to nickel- deficiency symptoms. Nickel is an item that occurs only at very low levels within the climate.

2. Review of work

The structural properties and antimicrobial properties of certain Co (II), Cu (II), Zn (II) and Ni (II) complexes were performed with a novel Mannich base N (1- morpholinosalicylyl) acetamide (MSA). Spectroscopic methods (IR, 1H-NMR, UV-Visible), conductometric, magnetic data and elemental analysis have defined the structure of each complex (4).

Preparation and characterization of Ni(II) complexes with N-acetyl- N'-phenylthiocarbamide have carried out by R.K. Patel and R.N. Patel (5) based on the electronic, vibrational and magnetic studies.

Satapathy et al. (6) have described the synthesis and characterization of Ni (II) complexes with thiocarbamide derivative ligand based on the elemental analysis, conductivity, magnetic and spectral data, ligand field parameters for these complexes have also been calculated.

Equilibrium study on the complex formation of Ni (II) with salicyloylamino acids have carried out by G.N. Mukherjee et al. (7), they have reported that in protonation and metallation of amide group, ligands offered bidentate (N,Q) chelation using the carboxylase oxygen and deprotonated amide nitrogen atom from the complexes.

Nickel (II) complexes of N, N’-ethylene bis (O-mercapto-benzamide) have been isolated by Takeshi Yamamura et al. (8). It has concluded that a square planar (S_2N_2) unit is reliable as the coordination sphere of Ni (II) complexes. The characters of the amide proton in the coordination unit have also been described.

Pyromellitic d3mide complexes of N_i (II) with di-N-phenyl pyromellitic d3mide were prepared and characterized by P. Venugopal et al. The geometries proposed for these complexes were also reported based on electronic spectra and various bonding parameters calculated from ESR spectral data. Nickel (II) amide group complexes, incorporating ligands, were isolated and characterized by B. Based on elementary research, measurement of magnetic susceptibility and vibrational, electronic spectral and thermal studies, S. Garg et al. This also studied the electrochemical actions of certain complexes.

The formation constants of Ni ternary complexes (II) with amino acids were determined by Nageswara et al. (9). They also stated that these ternary complexes are generated only in the basic pH-region.

Nickel (II) diamide ligand complexes were prepared and have been described by Hay et al. (10). They have also been reported to show octahedral geometry at these complexes. Goodgame et al. (11) documented the development of polymeric network arrays by nickel (II) complexes with alkane chain linked bis- (amide) ligands of biological relevance.

Based on the thermal analysis, Nelwamondo et al. (12) investigated the effect of the structure and the existence of the different amide ligands on the thermal stability of the nickel (II) complexes. They also stated that the steric factor plays a more important role in deciding the magnitude at set temperatures of enthalpies, peak temperature and thermal decomposition.

3. Experimental

A solution of nickel chloride (0.001 mole in 30 ml ethanol) was taken in a 250 ml circular bottom flask for the synthesis of nickel (II) complexes with amide group incorporating ligands, in this solution both amide ligand (0.003 mole) was applied gradually with continuous stirring. The reaction mixture was put at room temperature on a magnetic stirrer with steady stirring for 6-7 hours.

Additionally, a novel form of synthesis was developed in keeping with the principles of green chemistry, in which either the reaction mixture was irradiated in a 600 W domestic microwave for 2-10 minutes on the alumina bed or the reaction mixture in the solvent or the reaction mixture slurry was exposed in a 600 W microwave reactor, retaining varying time intervals on occasional and or definite inspection of TLC data.

The solid precipitate that was collected was isolated and crystallized in both ways. We cleaned and recrystalled crystals with alcohol and dried under vacuum.

➢ **Materials and Methods**

In the present work following amide group incorporating ligands have been synthesized. The synthesis of various ligands are as follows -

Synthesis of -

- N-(pyrimidin-2-yl) benzamide (N2PB) -
- N-(pyrimidin-2-yl) acetamide (N2PA) -
- N-(4,6dimethylpyrimidin-2-yl) benzamide (N46DM2PB) -
- N-(4,6dimethylpyrimidine-2-yl) acetamide (N46DM2PA)
- N-(6-hydroxy-2-mercaptopyrimidine-2-yl) benzamide (N6H2MC4PB) -
- N-(6-hydroxy-2-mercaptopyrimidine-2-yl) acetamide (N6H2MC4PA) –
- N-(2,6-dihydroxypyrimidine-4-yl)benzamide (N26DH4PB) –
- N-(2,6-dihydroxypyrimidine-4-yl) benzamide (N26DH4PA) -

All ligands have been characterized after purification with the help of physical data, UV-Visible spectra, elemental analysis, TLC, NMR and IR spectra.

➢ **Instruments Used**

- EC Double Beam UV-VIS Spectrophotometer (UV 5704SS), with quartz cell of 10 mm light path was used for Electronic spectral measurement
- IR spectra were recorded on Bruker Optic Model Alpha (FT-IR) (Zn-Se Optics, ATR) (4000-400 cm’1) using KBr disc.
- 1H-NMR spectra of the ligands at room temperature were recorded on a Bruker DRX-300(300MHz) FT NMR with low and high temperature facility (-90°C to 80°C) .
- TLC (Thin layer chromatography) of all compounds (ligands and complexes) measured by using Silica Gel.
- Microwave synthesis was conducted in a microwave oven KENSTAR-OM20ACF, 2450MHz, 800W and GMBR (Green Microwave Biochemical Reactor)
- All biological activities have been carried out with horizontal laminar. Melting point of all compounds was recorded in a Suphuric acid bath or by using Beckmann M.pt. apparatus.
- Melting point of all compounds was recorded in a Suphuric acid bath or by using Beckmann M.pt. apparatus

4. Results and discussion

Ni (II) complexes with Amide group incorporating ligands are stable for a long period of time at room temperatures. The nickel complexes under examination were green colored powder, which was soluble in DMSO, methyl alcohol, ethyl alcohol, but partly water soluble. The estimates for elemental and metal produced adequate results as predicted. Specific physical and analytical data are. Please see Table (4.1)

➢ **Vibrational Spectra**

Vibrational spectra were reported in KBr pellets and polyethylene films in mid- and far-off IR regions and some diagnostic bands are provided in Table (4.2). An analysis of the vibrational spectrum of all complexes shows the same coordination sites given by the amide group incorporating complexation ligands as in the case of copper and cobalt complexes.

The IR bands found at 3163-3382, due to amide v (N-H) mode Cm "was changed to higher for the free amide group incorporating ligands Frequencies displaying non-participation of amide group nitrogen atoms In synchronization. Amide -I band shift negatively opposite to v(C=0).

That of V (N-H) in the carbonyl oxygen coordinating complexes (13). Pyrimidinyl nitrogen participates in bonding in complexes Figure 4.1 to 4.8, which was verified by the negative change of pyrimidinyl ring peak in complexes to Ugands comparison. Such findings provide uncertainty and support the final theoretical assumptions of the complexes and the manner in which they bond.

➢ **Measurements of Magnetic susceptibility**

The magnetic behaviour of bivalent nickel complexes is based on The essence of ligand and complex geometry. Complexes of octaeder Ni (II) show paramagnetic activity due to the presence of two unpaired electrons (14). The magnetic moment values align with the suggested nickel structure and electrical system in the complex. Such values are shown in Table V.3.B.

➢ Electronic Spectra

The nickel (II) nucleus has an optical exterior structure of 3d^1 introduces the three and single terms (in order to maximize energy) ^{3}F, ^{1}D, ^{1}P,' ^{1}G,' ^{1}S. Six octahedral nickel (II) co-ordinate complexes exhibit a simple continuum involving three spin-enabled transitions when, in an octahedral region, the ground term divides into three terms, so these three transitions are:

$$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F)\,(\nu_1)$$

$$^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)\,(\nu_2)$$

$$^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)\,(\nu_3)$$

These three transitions are observed in the regions of 9165-13000 cm^{-1} 11000-20000 cm^{-1} and 20000-28000 cm^{-1}. The absorption spectra of the amide group containing ligands show higher energy band is assigned for charge transfer and the ingle d-175 d band is assigned to $'B_{ig} \leftarrow 'A_{ig}$. However, the position of the load transfer band is uncertain, as the band could also be subject to intra-ligand transfer. Table 4.3 displays the signature absorption bands. Such results show that complexes Ni (II) is octahedral environments.

➢ Thermal Studies

The Ni (II) complexes with the ligand-containing amide group show first order kinetics in their reaction to thermal decomposition. This is based on the Coats and Redfem straight line plot (for n = 1). Activation energy (E$_a$) was measured using the goats and redfem linearisation process. The thermal studies include a summary of the complexes' thermal stability. It has been found that at room temperature no decomposition happens, and complexes remain relatively stable even above room temperature. The initial decomposition actually started more than 500 K.

S.N.	Complexes	Colour	m.p. (ºC)	Reaction period		Yield %		Elemental analysis Calculated(Found)%		
				C.M. hrs.	M.M. min.	C.M.	M.M.	C	H	N
1	$[Ni\text{-}(N2PB)_3]Cl_2$	Pale Yellow	235	6	2.30	40	50	54.47 (54.40)	3.71 (3.65)	17.33 (17.25)
2	$[Ni\text{-}(N2PA)_3]Cl_2$	White	210	6	2.30	35	50	39.92 (39.84)	3.88 (3.78)	23.29 (23.20)
3	$[Ni\text{-}(N46DM2PB)_3]Cl_2$	Light yellow	185	6	2.40	30	45	57.77 (57.72)	4.81 (4.74)	15.55 (15.45)
4	$[Ni\text{-}(N46DM2PA)_3]Cl_2$	Orange	168	6	2.40	40	45	46.08 (45.98)	5.28 (5.22)	20.16 (20.10)
5	$[Ni\text{-}(N6H2MC4PB)_3]Cl_2$	Light yellow	290	7	2.00	40	50	45.46 (45.40)	3.09 (3.00)	14.46 (14.42)
6	$[Ni\text{-}(N6H2MC4PA)_3]Cl_2$	Pale yellow	295	7	2.00	40	45	31.53 (31.45)	3.06 (2.96)	18.39 (18.33)
7	$[Ni\text{-}(N26DH4PB)_3]Cl_2$	Light yellow	291	7	2.00	40	50	48.11 (48.00)	3.28 (3.22)	15.30 (15.24)
8	$[Ni\text{-}(N26DH4PA)_3]Cl_2$	Yellow	290	6.5	2.00	40	55	33.90 (33.80)	3.29 (3.20)	19.78 (19.72)

Table 4.1 : Physcio-Chemical Data of Ni (II) Metal Complexes

S N	Complexes	ν_{N-H} (amide)	$(\nu_{C=O})^a$	$(\nu_{C-N+\delta N-H})^b$	$(\nu_{N-H+\delta C-N})^c$	Pyrimidinyl	ν_{M-N}	ν_{M-O}	ν_{M-cl}
1	N2PB	3382	1674	1410	1288	1621			
	$[Ni\text{-}(N2PB)_3]Cl_2$	3464	1645	1500	1360	1580	483	492	----
2	N2PA	3339	1735	1408	1288	1618			
	$[Ni\text{-}(N2PA)_3]Cl_2$	3461	1681	1475	1397	1578	482	518	----
3	N46DM2PB	3319	1673	1449	1319	1643			
	$[Ni\text{-}(N46DM2PB)_3]Cl$	3383	1671	1475	1334	1613	485	491	----
4	N46DM2PA	3318	1739	1447	1369	1642			
	$[Ni\text{-}(N46DM2PA)_3]Cl$	3384	1670	1508	1384	1560	471	545	----
5	N6H2MC4PB	3163	1706	1421	1284	1685			
	$[Ni\text{-}(N6H2MC4PB)_3Cl_2]$	3219	1645	1522	1384	1640	470	505	----
6	N6H2MC4PA	3175	1715	1340	1242	1683			
	$[Ni\text{-}(N6H2MC4PA)_3Cl_2]$	3186	1698	1558	1384	1603	478	536	----
7	N26DH4PB	3353	1714	1422	1282	1582			
	$[Ni\text{-}(N26DH4PB)_3Cl_2$	3392	1698	1457	1362	1558	473	545	----
8	N26DH4PA	3196	1716	1284	1249	1416			
	$[Ni\text{-}(N26DH4PA)_3Cl_2$	3362	1636	1360	1270	1396	472	545	----

a : - amide - I band, b: - amide - II band, c: - amide – III band

Table 4.2 : IR Vibrational frequencies of Ni(II) transition metal complexes

S N	Ligand and Complex	R_f value	μ_{eff} (BM)	Electronic Spectral Bands λ_{max} (cm^{-1})	Tentative assignments	Expected Geometry
1	$[Ni\text{-}(N2PB)_3]Cl_2$	$(.0931)^g$	2.84	9551,11376,12484,13550,15384, 18587,20491,22050,24630,27173	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
2	$[Ni\text{-}(N2PA)_3]Cl_2$	$(0.944)^g$	2.72	9153,13850,14836,16129,17006, 18315,26631	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
3	$[Ni\text{-}(N46DM2PB)_3]Cl$	$(0.900)^g$	3.10	9165,14084,14598,16103,17241, 26990,	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
4	$[Ni\text{-}(N46DM2PA)_3]Cl_2$	$(o.869)^h$	3.02	9610,14771,16863,18867,22624, 24630,	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
5	$[Ni\text{-}(N6H2MC4PB)_3]Cl_2$	$(0.930)^c$	2.96	9174,14204,16528,17667,18231, 26075,27027	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
6	$[Ni\text{-}(N6H2MC4PA)_3]Cl_2$	$(0.880)^h$	2.98	9551,14836,16077,17667,18674, 26773,27472,	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
7	$[Ni\text{-}(N26DH4PB)_3]Cl_2$	$(0.800)^h$	2.89	9541,14367,14814,15797,16313, 17985,26075	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral
8	$[Ni\text{-}(N26DH4PA)_3]Cl_2$	$(0.770)^f$	3.14	9242,13812,14814,16260,17699, 18676,26954	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Distorted Octahedral

c=ethyl acetate:carbon tetrachloride (5:5), *f*= acetone: carbon tetrachloride (5:5) ,
g= acetone: carbon tetrachloride (6:4), h= acetone: carbon tetrachloride (7:3)

Table 4.3 : Magnetic moments and electronic Spectral data of ligands and Ni(II) metal complex

5. Conclusion

Based on the vibrational spectra, it is hypothesized that amide ligands exhibit tetradentate activity in their Ni (II) complexes by organizing amide groups by carbonyl oxygen. In complexes, the electronic spectral assignments are characteristic of the geometries implemented by metal ions. So, Ni (II) implements octahedral geometry in the amide ligand complexes. With the electronic spectral data, the magnetic moments match. Based on these studies the preliminary structures for the complexes were suggested and presented for Ni (II) complexes in Fig. 4.1 to 4.8. The complexes synthesized by the novel green method are in line with conventional synthesis and yield has been observed to be better than conventional synthesis in many cases. There are two complexes found to occur in supramolecular structure as a result of which this synthesis, observation, and analysis has been interesting and there is scope for further study.

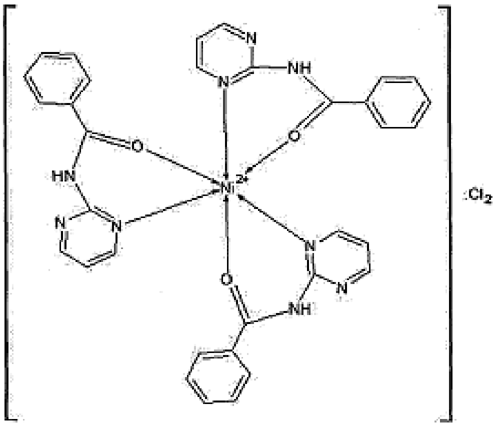

Fig. 4.1 Tentative Structure of Complex [Ni-($N_2PB)_3$]Cl_2

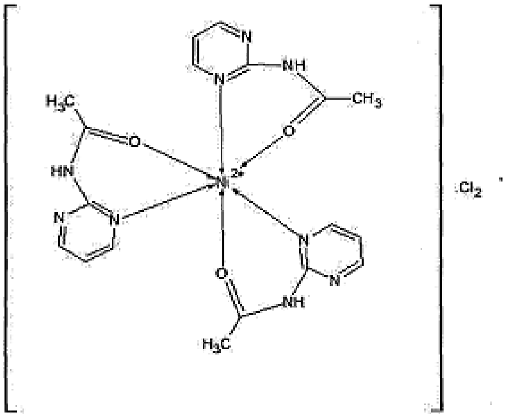

Fig. 4.2. Tentative Structure of Complex [Ni-$(N2PA)_3$]Cl_2

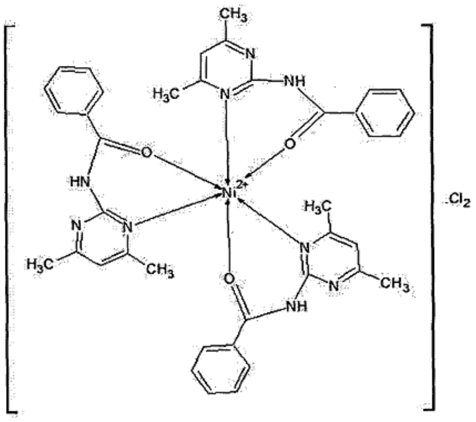

Fig. 4.3 Tentative Structure of Complex [Ni-$(N46DM2PB)_3$]Cl_2

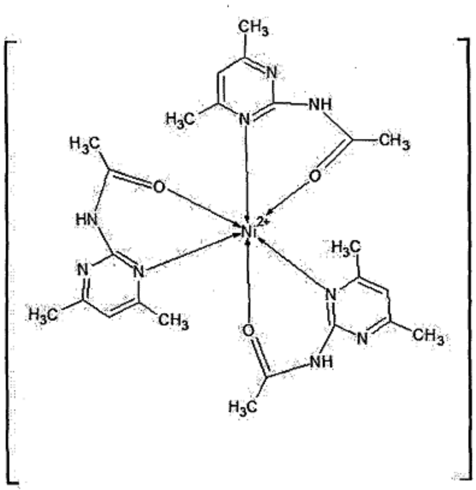

Fig. 4.4 Tentative Structure of Complex [Ni-(N46DM2PA)$_3$] Cl$_2$

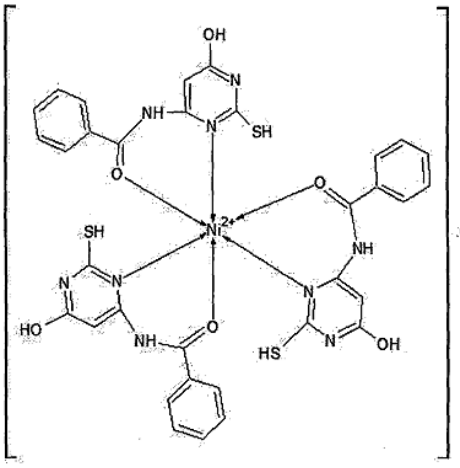

Fig. 4.5 Tentative Structure of Complex [Ni-(N6H2MC4PB)3] Cl$_2$

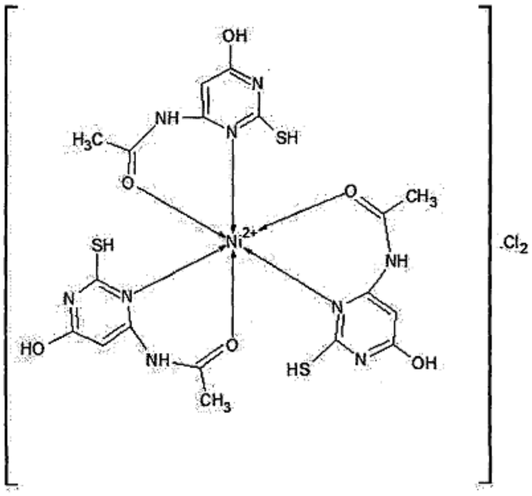

Fig. 4.6 Tentative Structure of Complex [Ni-(N6H2MC4FA)$_3$]Cl$_2$

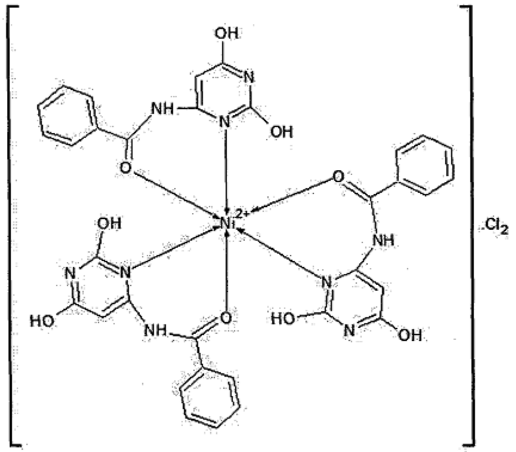

Fig. 4.7 Tentative Structure of Complex [Ni-(N26DH4PB)$_3$]Cl$_2$

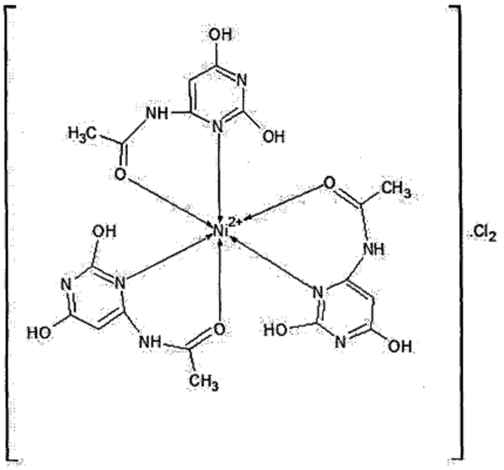

Fig. 4.8 Tentative Structure of Complex [Ni-(N26DH4PA)$_3$]Cl$_2$

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