

Research Article

Synthesis, Characterization, and Structural Assessment of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

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The monometallic nickel(II) complexes $[\text{Ni}(\text{H}_2\text{nsh})(\text{A})_2] \cdot n\text{H}_2\text{O}$ (where A = water (H_2O), $n = 0$ (1); pyridine (py), $n = 2$ (2); 2-picoline(2-pic), $n = 0$ (3); 3-picoline(3-pic), $n = 2$ (4); and 4-picoline(4-pic), $n = 0$ (5)) and homobimetallic nickel(II) complexes $[\text{Ni}_2(\text{nsh})(\text{A})_4] \cdot n\text{H}_2\text{O}$ (where A = water (H_2O), $n = 1$ (6); pyridine (py), $n = 4$ (7); 2-picoline(2-pic), $n = 4$ (8); 3-picoline(3-pic), $n = 4$ (9); and 4-picoline(4-pic), $n = 4$ (10), resp.) have been synthesized in methanol from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh). The complexes have been characterized by elemental analyses, molar conductance, magnetic moment, and electronic and IR and TGA/DTA spectroscopic studies. The monometallic complexes (1) to (5) are found to have octahedral stereochemistry while complexes (6) to (10) are found to have distorted octahedral stereochemistry in which one of the Ni(II) centres is present in N_2O_2 coordination sphere and another Ni(II) centre is bonded to it through phenolate oxygen atoms via oxo-bridging.

1. Introduction

We have previously described the synthesis and characterization of homobimetallic Mo(VI) complexes and Ni-Zn heterobimetallic complexes derived from the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone [1, 2]. Nickel is another metal ion from the first transition series which has been selected for the synthesis of its complexes with the title dihydrazone and their characterization. Its selection is based on the consideration that a nickel or cobalt promoted molybdenum catalyst is important in industrial catalysis, particularly in the hydrosulfurization process [3], whereby organosulfur compounds in petroleum feedstocks are heterogeneously desulfurized with dihydrogen. Moreover nickel is also present in six types of metalloenzymes, namely, ureases, hydrogenases, methyl coenzyme M reductase, carbon monoxide dehydrogenase, acetyl coenzyme A synthase, and

nickel superoxide dismutases [4]. Urease, the only nickel containing metallohydrolase, catalyses the hydrolysis of urea to ammonia and carbon dioxide [5]. The microbial urease from *Klebsiella aerogenes* has been found to contain two nickel(II) ions which are 3.5 Å apart within the dinuclear active site [4]. Further nickel occurs in heterobimetallic enzymes such as jack bean urease [6] and hydrogenase enzyme [7] in which nickel is present in combination with iron.

In addition nickel plays a prominent role in several areas of material chemistry. Some topical interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials by MOCUD and sol-gel processes and in the preparation of nanoscopic dendrimers incorporating Ni and the construction of 3D hybrid inorganic-organic porous materials with Ni coordination units and the fabrication of

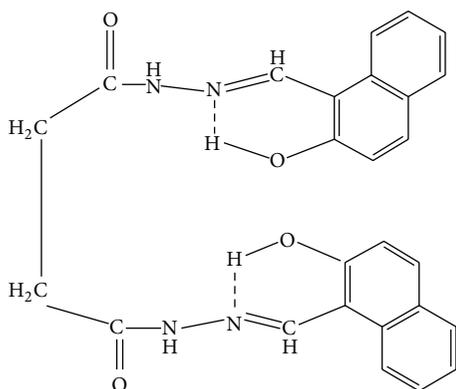


FIGURE 1: Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh).

supported Ni catalysts and Ni nanostructures through nanotechnology and paramagnetic high magnetism, culminating in the recent discovery of the first single molecule magnets based on Ni(II) centres [8].

A survey of literature has revealed that although metal complexes of monoacyl and aroyl- and pyridoyl-hydrazones have been studied in some greater detail [9–14], those of acyl-, aroyl-, and pyridoyl-dihydrazones have received attention in recent years [15, 16]. In such studies, dihydrazones have been shown to enolize to different extents depending upon the mode of the preparation of the complexes, the nature of the reaction medium, the pH of the medium, the metal salt, and the molar ratio of the metal salt and the ligand used. Further, the reported existence of homobimetallic complexes derived from dihydrazones as ligands is quite meager [1, 17–20]. Moreover, there is only a single reported existence of homobimetallic complexes of dihydrazones containing succinoyl fraction and naphthyl fragments in their molecular skeleton [1, 2].

In view of the above importance of hydrazones and their metal complexes in general and nickel complexes in particular and almost virtually negligible amount of work on homobimetallic complexes of metals with dihydrazones containing succinoyl and bulky naphthyl fragments in their molecular skeleton, the present paper aims to synthesize and characterize the monometallic and homobimetallic nickel complexes obtained from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) (Figure 1).

2. Experimental

Chemicals are as follows: nickel acetate $Ni(OAc)_2$ diethyl succinate $((CH_2)_2(CO_2Et)_2)$, hydrazine hydrate $(N_2H_4 \cdot H_2O)$, 2-hydroxy-1-naphthaldehyde $(C_{10}H_6(OH)(CHO))$, pyridine, 2-picoline, 3-picoline, 4-picoline, and methanol were procured commercially and were used without subsequent purification. Succinoyl dihydrazone and bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone were prepared by using literature method as described elsewhere [1].

Physical measurements are as follows: elemental analyses (C, H, and N) were performed by Perkin-Elmer 2400

CHNS/O Analyzer II. Nickel content of the complexes was determined by literature method [21]. Infrared spectra in the range $4000\text{--}400/500\text{ cm}^{-1}$ were recorded on either BX-III/FT-IR Perkin-Elmer spectrophotometer or Nicolet-Impact 410 FT-IR Spectrophotometer with samples investigated as KBr discs. Room temperature magnetic susceptibility measurements were made on Sherwood Magnetic Susceptibility Balance MSB-Auto. All conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. A dip-type conductivity cell having platinumized platinum electrode was used. The cell constant was determined using a standard KCl solution.

2.1. Preparation of the Complexes

2.1.1. Preparation of $[Ni(H_2nsh)(H_2O)_2]$ (1). Succinoyl dihydrazone (0.90 g, 6.16 mmol) was dissolved in hot methanol-water mixture (50 mL, 90:10 v/v). A solution of $Ni(OAc)_2 \cdot 4H_2O$ (1.50 g, 6.02 mmol) in methanol (50 mL) was added to the above solution accompanied by gentle stirring for a period of 10 minutes. The resulting solution was refluxed for 15 minutes. This solution was added to a hot solution of 2-hydroxy-1-naphthaldehyde (2.70 g, 15.70 mmol) in methanol (100 mL). The reaction mixture was refluxed for 1 hour which precipitated a yellow-brown compound. The complex thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether, and dried over anhydrous $CaCl_2$. Yield is 0.72 g.

2.1.2. Preparation of $[Ni(H_2nsh)(A)_2]$, Where A = Pyridine (py, 2); 2-Picoline(2-pic, 3); 3-Picoline(3-pic, 4); and 4-Picoline(4-pic, 5). Complex $[Ni(H_2nsh)(H_2O)_2]$ (1) (1.00 g, 1.86 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at $50\text{--}60^\circ\text{C}$. To this suspension, pyridine (1.50 mL, 18.10 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 3 hrs which precipitated the light brown compound. The compound thus obtained was filtered, washed repeatedly with hot methanol and then with ether, and dried over anhydrous $CaCl_2$. Yield is 0.70 g.

Complexes (3), (4), and (5) were also prepared in the same manner using 2-picoline, 3-picoline, and 4-picoline instead of pyridine and maintaining the metal:base ratio at 1:10, respectively. Yield is 0.75 g (3); 0.77 g (4); and 0.78 g (5).

2.1.3. Preparation of $[Ni_2(nsh)(H_2O)_4]$ (6). The dihydrazone (H_4nsh) (1.00 g, 2.20 mmol) was suspended in methanol (100 mL) and stirred for 30 minutes at 60°C . To this was added a solution of $Ni(OAc)_2 \cdot 4H_2O$ (1.65 g, 6.63 mmol) in methanol (50 mL) maintaining the molar ratio at 1:3. The reaction mixture was refluxed for 3 hrs, which precipitated a brown compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether, and dried over anhydrous $CaCl_2$. Yield is 0.65 g.

2.1.4. Preparation of $[Ni_2(nsh)(A)_4]$, Where A = Pyridine (py, 7); 2-Picoline(2-pic, 8); 3-Picoline(3-pic, 9); and 4-Picoline(4-pic, 10). Complex $[Ni_2(nsh)(H_2O)_2]$ (6) (1.00 g, 1.55 mmol)

was suspended in methanol (100 mL) by gentle heating at 60°C. To this suspension pyridine (1.24 mL, 15.42 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 2 hours. The resulting precipitate was isolated in the usual way. Complexes (7) to (10) were also synthesized by essentially following the above procedure using 2-picoline, 3-picoline, and 4-picoline instead of pyridine maintaining the metal : base molar ratio at 1 : 10, respectively. Yield is 0.61 g (7); 0.65 g (8); 0.67 g (9); and 0.64 g (10).

3. Results and Discussion

The complexes described in the present paper together with their molecular formulae, colour, decomposition point, percentage yield, analytical data, magnetic moment, molar conductance, and electronic spectral data for the complexes have been shown in Table 1. The composition of the complexes has been deduced on the basis of elemental analysis as follows:

$[\text{Ni}(\text{H}_2\text{nsh})(\text{A})_2] \cdot n\text{H}_2\text{O}$ ($n = 0, 2$) ($\text{A} = \text{H}_2\text{O}$ (1), py (2), 2-pic (3), 3-pic (4), and 4-pic (5)) and $[\text{Ni}_2(\text{nsh})(\text{A})_4] \cdot n\text{H}_2\text{O}$ ($n = 1, 4$) ($\text{A} = \text{H}_2\text{O}$ (6), py (7), 2-pic (8), 3-pic (9), and 4-pic (10)). The complexes are brown, yellow, light brown, and dark yellow in colour. All of the complexes are air stable and decompose above 300°C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, chloroform, benzene, hexane, and ether. However, all of the complexes are soluble in DMF and DMSO.

3.1. Thermal/TGA/DTA Studies. None of the 1:1 (metal : ligand) complexes except complexes (2) and (4) show weight loss at 110°C ruling out the possibility of presence of lattice water in their structure. The 1:1 (metal : ligand) complexes (2) and (4) show weight losses at 110°C corresponding to two water molecules while all of the 2:1 (metal : ligand) complexes show weight losses at 110°C corresponding to four water molecules except complex (1) which shows weight loss corresponding to one water molecule at this temperature. The loss of these water molecules at this temperature suggests that they are present in the lattice structure of the complexes. Further, complexes (1) and (6) show loss of weight corresponding to two and four water molecules at 180°C suggesting the presence of two and four water molecules in their first coordination sphere around the metal centres, respectively. On the other hand, complexes (2) to (5) show weight loss corresponding to two pyridine/2-picoline/3-picoline/4-picoline molecules while complexes (7) to (10) show weight loss corresponding to four pyridine/2-picoline/3-picoline/4-picoline molecules at 220°C. The expulsion of these donor molecules at such a higher temperature indicates that they are coordinated with the metal centre.

The loss of neutral molecules at such a high temperature may indicate their presence in the coordination sphere around the metal centre but the classification of solvent molecules on the basis of TGA alone as being held in the lattice or being coordinated with the metal centre needs utmost caution in view of the fact that the loss of solvent

molecules at considerable high temperature might occur due to hydrogen bond network in the solid state of the complexes that might permeate the lattice.

The vapours evolved at temperatures 110°C, 180°C, and 220°C in all complexes have been identified except complexes (3) and (8) by passing through a trap containing anhydrous copper sulfate and test tubes containing solution of sodium hydroxide and chloroform, I₂ and sodium hydroxide and cyanogen bromide, respectively [22, 23]. The vapours evolved at 110°C in complexes (2), (4), and (6) to (10) and at 180°C in complex (1) and in both temperature ranges in complex (6) turned anhydrous copper sulfate blue confirming that they originate from water molecules. The vapours evolved in complexes (2) and (7) at 220°C turned the CHCl₃ and NaOH solution red [24]. This confirmed that they originate from pyridine molecules. Similarly, the vapours evolved from complexes (4), (5), (9), and (10) at this temperature turned the colour of cyanogens bromide solution to green violet and blue, respectively, on treatment with phloroglucinol solution. This suggests the presence of 2-picoline and 4-picoline molecules in complexes (4), (5), (9), and (10), respectively. The weight loss corresponds to two pyridine/3-picoline/4-picoline molecules in complexes (2), (4), and (5) and to four pyridine/3-picoline/4-picoline molecules in complexes (6), (9), and (10) lending credence to the suggested number of pyridine/3-picoline/4-picoline molecules in the first coordination sphere of these complexes.

Thermal properties of the mononuclear complex $[\text{Ni}(\text{H}_2\text{nsh})(\text{H}_2\text{O})_2]$ (1) and the binuclear complexes $[\text{Ni}(\text{nsh})(\text{A})_4] \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{H}_2\text{O}$ (6), py (7), and 2-pic (8)) were investigated as representative samples by thermogravimetric analysis and differential thermal analysis. Figures 7–10 (Supplementary Data in Supplementary Material available online at <http://dx.doi.org/10.1155/2015/121895>) present the recorded TGA/DTA curves of the four metal complexes under dinitrogen atmosphere. The essential common feature of all the complexes is that once they start losing weight, they give no indication of their stability at any point of their decomposition unless they are converted into metal oxide in the final stage. It can be seen that the TGA curves of complex (1) show no weight loss up to 200°C indicating absence of water molecules and any other absorptive solvent molecules in the complex. At a temperature of 200°C, a weight loss process commences and weight loss (exp.: 6.0%) equal to two water molecules (theo.: 6.59%) is completed up to a temperature of about 290°C. The water molecules lost in this temperature range indicate that they are coordinated with the metal centre. The most important decomposition step in the complex occurs in the temperature range 295–650°C in which weight loss of about 78.27% is observed. The ultimate product of the decomposition reaction is metallic oxide. The thermogram shows that once the decomposition of the complex has commenced at 200°C, it continues until the complex is converted into metallic oxide at a temperature of about 650°C. The loss of coordinated water molecules and ligand occurs in a single simultaneous step.

Complex $[\text{Ni}_2(\text{L})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (6) shows essentially two decomposition steps in the temperature range 85–730°C. The TGA curve of the complex starts showing mass loss

TABLE I: Analytical data and physical properties of Ni(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

Serial number	Complex and colour	DP (°C)	Yield (%)	Analysis: found (calc.) (%)	Molar conductance (Λ_M) Ohm ⁻¹ cm ² mol ⁻¹	Magnetic moment μ_B (BM)	Electronic spectral bands λ_{max} (nm) (ϵ_{max} dm ³ mol ⁻¹ cm ⁻¹)
1	[Ni(H ₂ nsh)(H ₂ O) ₂] Brown	>300	70.00	Ni 10.54 (10.73) C 56.94 (57.07) H 4.39 (4.42) N 10.14 (10.24)	3.13	2.87	319 (2755), 364 (1815), 410 (1733), 564 (80), 845 (37)
2	[Ni(H ₂ nsh)(py) ₂]-2H ₂ O Brown	>300	68.00	Ni 8.24 (8.32) C 61.12 (61.30) H 4.85 (4.86) N 11.86 (11.91)	2.81	3.45	319 (3938), 364 (2579), 413 (2214), 562 (80), 842 (36)
3	[Ni(H ₂ nsh)(2-pic) ₂] Yellow	>300	65.00	Ni 8.04 (8.41) C 64.94 (65.44) H 4.89 (4.91) N 11.94 (12.05)	2.62	2.98	319 (1428), 366 (1265), 411 (1777), 429 (1386), 564 (37), 847 (33)
4	[Ni(H ₂ nsh)(3-pic) ₂]-2H ₂ O Brown	>300	63.00	Ni 7.95 (8.00) C 62.17 (62.23) H 5.21 (5.22) N 11.41 (11.46)	2.91	3.09	319 (3930), 366 (2534), 410 (2216), 563 (80), 846 (37)
5	[Ni(H ₂ nsh)(4-pic) ₂] Dark brown	>300	65.00	Ni 8.11 (8.41) C 65.03 (65.44) H 4.89 (4.91) N 11.98 (12.05)	2.85	3.30	319 (1838), 362 (1131), 409 (1047), 561 (80), 842 (36)
6	[Ni ₂ (nsh)(H ₂ O) ₄]-H ₂ O Brown	>300	69.00	Ni 17.73 (17.84) C 47.38 (47.47) H 4.27 (4.29) N 8.47 (8.52)	2.97	1.73	325 (6874), 369 (6653), 420 (8649), 562 (50), 843 (29)
7	[Ni ₂ (nsh)(py) ₄]-4H ₂ O Light brown	>300	62.00	Ni 12.19 (12.27) C 57.66 (57.78) H 4.83 (4.85) N 11.67 (11.72)	2.81	1.14	326 (3345), 368 (3442), 421 (5091), 564 (81), 848 (35)
8	[Ni ₂ (nsh)(2-pic) ₄]-4H ₂ O Brown	>300	65.00	Ni 11.44 (11.59) C 59.27 (59.32) H 5.36 (5.38) N 11.02 (11.07)	2.72	1.54	326 (2987), 421 (4006), 565 (79), 849 (29)
9	[Ni ₂ (nsh)(3-pic) ₄]-4H ₂ O Brown	>300	64.00	Ni 11.46 (11.59) C 59.28 (59.32) H 5.36 (5.38) N 11.04 (11.07)	2.64	1.39	326 (5030), 421 (7445), 568 (79), 850 (29)
10	[Ni ₂ (nsh)(4-pic) ₄]-4H ₂ O Light brown	>300	65.00	Ni 11.45 (11.59) C 59.29 (59.32) H 5.37 (5.38) N 11.03 (11.07)	2.81	1.29	348 (5058), 420 (7123), 563 (79), 844 (29)

at 85°C which continues up to 152°C. In this temperature range the complex shows mass loss equal to 2.80% which corresponds to one water molecule (theo.: 2.74%) signifying that it is present in the lattice structure of the complex. After this, another decomposition step commences which lasts up to 370°C. The mass loss in this temperature range corresponds to loss of four water molecules (exp.: 10.70%; theo.: 10.95%). The loss of water molecules in this temperature range suggests that they are coordinated with the metal centre. The loss of lattice and coordinated water molecules occurs in a single continuous step which suggests that those water molecules are hydrogen bonded to ligand as well as to one another which permeates the lattice. The last step which commences after 370°C corresponds to the loss of coordinated ligand molecule devoid of two oxygen atoms (exp.: 64.77%; theo.: 63.89%). The weight loss in the temperature range 370–510°C is equal to 38.47% which corresponds to loss of two-naphthaldehyde fraction (theo.: 38.33%) of the coordinated ligand. The remaining part of the ligand decomposes after 510°C until it is converted to metal oxide at 731°C. The percentage weight of the final residue is 21.67% which corresponds to two NiO molecules (theo.: 22.72%). Complexes (7) and (8) show almost similar decomposition behavior. The thermograms of the complexes show three decomposition steps within the temperature range 100–694°C. In complex $[\text{Ni}_2(\text{L})(\text{py})_4]\cdot 4\text{H}_2\text{O}$ (7) the first step of decomposition occurs in the temperature range 200–410°C which corresponds to four water and two pyridine molecules (exp.: 24.75%; theo.: 24.07%) in the temperature range 200–400°C while, in complex $[\text{Ni}_2(\text{L})(2\text{-pic})_4]\cdot 4\text{H}_2\text{O}$ (8), the first stage in the temperature range 100–400 [Ni₂(L)(py)₄].4H₂O (7) corresponds to the loss of four water molecules and one 2-picoline molecule (exp.: 16.85%; theo.: 16.39%). The next stage involves the loss of two pyridine molecules (exp.: 16.42%; theo.: 16.59%) in complex (7) and three 2-picoline molecules (exp.: 27.85%; theo.: 27.59%) in the temperature range 400–440°C in complex (8). The last step involves the decomposition of the coordinated ligand (exp.: 43.79%; theo.: 43.96%) devoid of two oxygen atoms in complex (7) in the temperature range 440–630°C. In fact the water molecules are lost in the temperature range 200–275°C in complex (7) (exp.: 7.85%; theo.: 7.54%) and in the temperature range 1230–235°C in complex (8) (exp.: 6.45%; theo.: 7.12%). The complexes show endothermic peaks centred at 265 and 210°C, respectively, signifying that these water molecules are present in the lattice of the complexes. The two pyridine molecules and one 2-picoline molecule are lost subsequently in the temperature range of 275–410°C and 235–400°C, respectively. The loss of pyridine and 2-picoline molecules and the coordinated ligand are characterized by broad exothermic peaks in the DTA curve of the complex.

3.2. Molar Conductance. The molar conductance values of complexes (1) to (10) in DMSO solution at 10⁻³ M dilution fall in the range 2.62–3.13 ohm⁻¹cm²mol⁻¹ suggesting that they are nonelectrolytes in this solvent [25].

3.3. Magnetic Moment. The μ_B (BM) values for complexes (1) to (10) are set out in Table 1. The effective electronic

configuration of nickel(II) is 3d⁸ and exhibits a magnetic moment higher than that expected for two unpaired electrons in an octahedral and a tetrahedral environment, whereas diamagnetism of the nickel(II) complexes leads to square planar stereochemistry. The effective magnetic moment reported for high-spin octahedral Ni(II) complexes is in the range 3.00–3.50 BM, while for the tetrahedral complexes it ranges from 3.5 to 4.0 BM. The reason for this deviation is attributed to spin-orbit coupling which causes an orbital contribution in the quenched ³A_{2g} ground state of Ni(II) ion in an octahedral environment and not due to contribution from the orbital angular momentum of the electrons because the orbital angular momentum does not affect ³A_{2g} state. On the contrary, in case of a tetrahedral Ni(II) complex, the orbital angular momentum contributes strongly to the magnetic moment leading to magnetic moment values as high as 4.0 BM. The paramagnetism of nickel(II) complexes (1) to (5) rules out the possibility of square planar structure and tetrahedral structure can be discarded on the basis of the magnitude of the magnetic moment. Complexes (1) to (5) have magnetic moment values in the region of 2.85–3.45 BM which is typical of an octahedral Ni(II) compound [26, 27].

In homobimetallic Ni(II) complexes (6) to (10), two Ni(II) ions are present for each ligand molecule and the resulting complexes have magnetic moment values in the region of 1.14–1.73 BM, that is, 0.5–0.87 BM per metal(II) ion. Such low values of magnetic moment in complexes (6) to (10) certainly rule out low-spin square planar stereochemistry for the complexes. But these values are considerably less than the values reported for spin-free nickel(II) complexes indicating a strong metal-metal interaction in the structural unit. Anomalous magnetic moment values in the solid state have been explained on the basis of absorption spectra by proposing a mixed octahedral and square planar stereochemistry in the solid state due to molecular association [28–31], but the electronic absorption spectra of the complexes described in this paper are consistent with the tetragonally distorted octahedral stereochemistry. Since the hydrazine bridges do not cause any lowering of the magnetic moment [21], therefore it is still reasonable to believe that the lowering of the magnetic moment is due to the presence of oxo-bridged structure and as a result of this Ni(II) complexes attain a tetragonally distorted octahedral stereochemistry.

3.4. Electronic Spectra. The electronic spectra of the ligand and its Ni(II) complexes were recorded in DMF solution because of poor solubility of the ligand and the complexes in common organic solvents. The important electronic spectral bands for the dihydrazone ligand (H₄nsh) and the monometallic and homobimetallic Ni(II) complexes along with their molar extinction coefficient are presented in Table 1. The free ligand H₄nsh exhibits a couple of bands in the region of 317 nm and 363 nm. The band at 317 nm is assigned to intraligand $\pi \rightarrow \pi^*$ transition while the band at 363 nm is assigned to $n \rightarrow \pi^*$ transition [32–34].

The electronic spectra of the complexes exhibit two to four bands in the region of 300–450 nm. The bands appearing in the region of 319–370 nm are attributed to intraligand transitions which exhibit red shift on complexation. The red

TABLE 2: Ligand field parameters for Ni(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

Serial number	Complex	${}^3A_{2g} \rightarrow {}^3T_{2g} (F)$ (ν_1)		${}^3A_{2g} \rightarrow {}^3T_{1g} (F)$ (ν_2)		Dq (cm^{-1})	ν_2/ν_1	B (cm^{-1})	β	β° (%)	LFSE (kcal mol^{-1})
		nm	cm^{-1}	nm	cm^{-1}						
1	[Ni(H ₂ nsh)(H ₂ O) ₂]	845	11834	564	17730	1183.4	1.498	653.57	0.6278	37.22	40.66
2	[Ni(H ₂ nsh)(py) ₂].2H ₂ O	842	11876	562	17794	1187.6	1.4983	656.09	0.6302	36.98	40.80
3	[Ni(H ₂ nsh)(2-pic) ₂]	847	11806	564	17730	1180.6	1.5017	659.79	0.6338	36.62	40.56
4	[Ni(H ₂ nsh)(3-pic) ₂].2H ₂ O	846	11820	563	17762	1182	1.5027	662.63	0.6365	36.35	40.61
5	[Ni(H ₂ nsh)(4-pic) ₂]	842	11876	561	17825	1187.6	1.5009	661.81	0.6357	36.43	40.80
6	[Ni ₂ (nsh)(H ₂ O) ₄].H ₂ O	843	11862	562	17794	1186.2	1.5001	659.18	0.6332	36.68	40.75
7	[Ni ₂ (nsh)(py) ₄].4H ₂ O	848	11792	564	17730	1179.2	1.5035	662.95	0.6368	36.32	40.51
8	[Ni ₂ (nsh)(2-pic) ₄].4H ₂ O	849	11779	565	17699	1177.9	1.5025	660.07	0.6341	36.59	40.47
9	[Ni ₂ (nsh)(3-pic) ₄].4H ₂ O	850	11765	566	17606	1176.5	1.4964	645.98	0.6205	37.95	40.42
10	[Ni ₂ (nsh)(4-pic) ₄].4H ₂ O	844	11848	563	17762	1184.8	1.4991	656.37	0.6302	36.98	40.70

shift of the ligand bands gives good evidence of chelation of dihydrazone to the metal centre. All of the complexes show new band in the region of 410–440 nm which has very high molar extinction coefficient. In view of very high molar extinction coefficient of this band, it is assigned to have its origin in the ligand-to-metal charge-transfer transition. This band arises most probably from charge-transfer transition from naphtholate oxygen atoms to the metal centre [16, 35, 36]. This ligand-to-metal charge-transfer band is strongly influenced by the chemical nature of the ligand within a given stereochemistry and is responsible for the appearance of orange colour of the complexes.

In an octahedral environment, Ni(II) complexes exhibit three bands which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g} (F)$ (ν_1); ${}^3A_{2g} \rightarrow {}^3T_{1g} (F)$ (ν_2); and ${}^3A_{2g} \rightarrow {}^3T_{1g} (P)$ (ν_3) transitions, respectively. Since the transition ${}^3A_{2g} \rightarrow {}^3T_{1g} (P)$ (ν_3) generally occurs in the region of 330–400 nm in which the bands due to organic fraction of the complexes arise as well, hence, this region is not useful from the point of view of drawing any conclusion about the stereochemistry around the Ni(II) centre. However, the first two low energy bands observed in the region of 500–900 nm in all of the complexes are characteristic of nickel(II) in octahedral environment. The octahedral geometry of Ni(II) complexes is further supported by the value of ν_2/ν_1 ratio which lies in the region of 1.498–1.504 [26, 37].

Various ligand field parameters (Table 2), namely, Racah interelectronic repulsion parameter (B), ligand field splitting energy (10 Dq), covalency factor (β), and ligand field stabilization energy (LFSE), have been calculated for the Ni(II) complexes.

The ligand field splitting energy (10 Dq) and the Racah interelectronic repulsion parameter (B) were calculated by the equations given by Lever [38]. Consider

$${}^3A_{2g} \longrightarrow {}^3T_{2g} (F), (\nu_1) = 10 \text{ Dq} \quad (1)$$

$${}^3A_{2g} \longrightarrow {}^3T_{1g} (F), (\nu_2) = 7.5B + 15 \text{ Dq} \quad (2)$$

$$- \frac{1}{2} (225B^2 + 100 \text{ Dq}^2 - 180 \text{ Dq}B)^{1/2}$$

$$\begin{aligned} & {}^3A_{2g} \longrightarrow {}^3T_{1g} (P), (\nu_3) \\ & = 7.5B + 15 \text{ Dq} \\ & + \frac{1}{2} (225B^2 + 100 \text{ Dq}^2 - 180 \text{ Dq}B)^{1/2}. \end{aligned} \quad (3)$$

The Racah interelectronic repulsion parameter (B) was also calculated by the following equation [39] and the values obtained were found to be the same as calculated from the equations given by Lever:

$$B_{\text{Complex}} = \frac{(2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)}{(15\nu_2 - 27\nu_1)}. \quad (4)$$

The covalency factor (β) was obtained by the following equation:

$$\beta = \frac{B}{B'} \quad (B' \text{ is the free ion value} = 1038 \text{ cm}^{-1}). \quad (5)$$

The ligand field stabilization energy (LFSE) is expressed by the following equation:

$$\text{LFSE} = 12 \text{ Dq}. \quad (6)$$

The percentage lowering of energy of “P” state in the complexes as compared to its value in the free gaseous ion (β°) is obtained by the following equation:

$$\beta^\circ = 100 - (\beta \times 100). \quad (7)$$

The energy of first transition for complexes (1) to (10) lies in the range of 11765–11876 cm^{-1} which is equal to 10 Dq. The evaluation of Racah interelectronic repulsion parameter “ B ” from the expression of ν_1 gave values which lie in the range of 645–662. These values are very low as compared to the free ion value (1038 cm^{-1}). This indicates that all of the complexes have considerable covalent character. The nephelauxetic ratio, β , for the complexes lies in the range of 0.62–0.64. The obtained β value being less than unity suggests the presence of considerable amount of covalent character in the metal-ligand bonds. The percentage lowering of energy of “P” state

in the complexes as compared to its value in the free gaseous ion, that is, β° , lies in the range of 36.32–37.95% which shows a high degree of covalency.

The ν_2/ν_1 values for tetragonal complexes are found significantly higher than the usual range for octahedral complexes and sometimes greater than the theoretical limit of 1.80 for octahedral symmetry. The interaction between ${}^3T_{1g}$ (P) and ${}^3T_{1g}$ (F) states [40] gradually lowers the ratio of ν_2/ν_1 from the theoretical value of 1.80 to 1.50–1.70 and values in the range of 1.60–1.70 are common for nickel(II) complexes of octahedral symmetry. In the present complexes ν_2/ν_1 values lie in the range of 1.49–1.50 which are slightly lower than the lower limit of usual octahedral complexes but are within the range reported for octahedral nickel(II) complexes [41]. These low values indicate a strong interaction between ${}^3T_{1g}$ (P) and ${}^3T_{1g}$ (F) states of the complexed nickel(II) ion. The value of ligand field stabilization energy for the complexes lies in the range of 40.42–40.80 kcal mol⁻¹.

3.5. Infrared Spectra. The uncoordinated dihydrazone shows a medium intensity broad band centred at 3423 cm⁻¹ and a medium intensity band at 3244 cm⁻¹ (Table 3). The band at 3423 cm⁻¹ has been assigned to $\nu(\text{OH})$ vibration of 2-hydroxy-1-naphthaldehyde part of the dihydrazone, while the band at 3244 cm⁻¹ is assigned to arise from secondary –NH group. The IR spectra of the complexes show a weak-to-medium intensity band in the region of 3000–3500 cm⁻¹. This band is attributed to stretching vibrations of water molecules absorbed by KBr during pellet preparation. However, these bands appear to have contribution from coordinated water molecules in complexes (1) and (6). The band in the region of 3000–3500 cm⁻¹ in complexes (1) to (5) also appears to have contribution from the stretching vibration of coordinated naphtholic –OH group. Further, the spectral features of complexes (6) to (10) conspicuously indicate the coordination of naphtholic –OH group via deprotonation to the metal centre in these complexes.

None of the complexes shows the band characteristic of νNH vibration. This suggests the destruction of –NH group as a result of enolization of the ligand in the complexes and its coordination with the metal centre in the enol form.

The $\nu(\text{C}=\text{O})$ stretching vibration appears as a very strong band at 1672 cm⁻¹ in the infrared spectrum of the uncoordinated dihydrazone. In the infrared spectra of all the complexes, the amide I band disappears indicating destruction of amide structure of the ligand and its coordination through carbonyl oxygen atoms (in enol form) to the metal centre.

The $\nu(\text{C}=\text{N})$ band appears as a couple of bands in the region of 1622–1602 cm⁻¹ in the IR spectra of the complexes similar to that in the uncoordinated dihydrazone. This band registers an average downward shift of 2–3 cm⁻¹ indicating coordination of dihydrazone through azomethine nitrogen atom with the metal centre [42, 43]. This downward shift of $\nu(\text{C}=\text{N})$ band is attributed to the drainage of electron density from azomethine nitrogen atom to the metal centre. The existence of two $\nu(\text{C}=\text{N})$ bands in the complexes shows that the two azomethine nitrogen groups are inequivalent

suggesting that the strengths of the two M←N bands are not the same. Further, the differences between the two $\nu(\text{C}=\text{N})$ stretching frequencies are of the order of 13–18 cm⁻¹ which is the reported range of absorption for molecules with *anti-cis* configuration. [44]. This suggests that the dihydrazone exists in the *anti-cis* configuration in these complexes.

A weak but intense band at 1508 cm⁻¹ in the IR spectra of the complexes is attributed to stretching vibration of newly created NCO⁻ group produced as a result of enolization of the ligand [42, 43].

The medium intensity band at 1281 cm⁻¹ due to $\nu(\text{C}-\text{O})$ shifts to higher frequency by 21 cm⁻¹ in complexes (1) to (5) and appears as ~1303 cm⁻¹ as a medium intensity band. On the other hand this band splits into two bands in complexes (6) to (10). One of the bands remains almost at the same position in the complexes as compared to that in the free ligand while the other band shifts to higher position by ~21 cm⁻¹ and appears around 1303 cm⁻¹ as a medium intensity band. Such a feature associated with $\nu(\text{C}-\text{O})$ band indicates bonding through C–O oxygen atoms to the metal centre [42, 43].

It has been found that the $\nu(\text{N}-\text{N})$ band appears in the region of 1040–970 cm⁻¹ in the metal complexes derived from N,N-diacyl hydrazines [44]. Eliminating the bands due to C–H in-plane deformation in the region of 1050–900 cm⁻¹, a weak band at 1029 cm⁻¹ in the present ligand has been assigned to $\nu(\text{N}-\text{N})$. This band shifts to higher frequency by 14–27 cm⁻¹ in all of the metal complexes. This indicates the involvement of nitrogen atom of N–N group in coordination with the metal centre [45]. Complexes (6) to (10) show an additional band in the region of 861–897 cm⁻¹ and it is assigned to have contribution from the band arising from “ $\nu_{\text{C}=\text{O}}^{\text{M}}$ ” which resulted from the involvement of naphtholate oxygen atoms in bridge formation [46, 47].

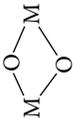
Complexes (2) to (5) and (7) to (10) show a new but very weak intensity band in the region of 1076–1045 cm⁻¹. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline, and 4-picoline molecules. The presence of this band in the IR spectra of complexes (2) to (5) and (7) to (10) indicates coordination of pyridine, 2-picoline, 3-picoline, and 4-picoline with the metal centre [48].

The antisymmetric and symmetric –OH stretching modes of lattice water appear in the region of 3500–3000 cm⁻¹, while the H–O–H bending mode appears in the region of 1630–1610 cm⁻¹. Coordinated water molecules besides showing the above two bands also show wagging and rocking modes in the region of 900–750 cm⁻¹ which are activated by coordination with the metal centre [49].

4. Conclusion

Monometallic and homobimetallic Ni(II) complexes have been studied in the paper. The monometallic complexes (1) to (5) possess μ_{eff} value in the range of 2.85–3.45 BM consistent with their octahedral stereochemistry while in complexes (6) to (10) μ_{eff} values lie in the range of 1.14–1.73 BM, that is, 0.57–0.87 per Ni(II) ion, which are less than the values reported for spin-free Ni(II). These values rule out the possibility of any

TABLE 3: Structurally significant infrared (IR) bands (in cm^{-1}) for bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Ni(II) complexes.

Serial number	Ligand/complex	$\nu(\text{OH} + \text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Amide II + $\nu(\text{C}-\text{O})$ (naphtholic)	$\nu(\text{NCO}^-)$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$		$\nu(\text{M}-\text{O})$	Other bands
	H_4nsh	3423 m 3244 m 3051 m	1672 vs	1633 vs 1593 m	1540 m	—	1281 m	1029 w	—	—	—
1	$[\text{Ni}(\text{H}_2\text{nsh})(\text{H}_2\text{O})_2]$	3410 m 3291 m	—	1622 s 1604 m	1540 s	1508 w	1306 m 1282 w	1084 w 1039 w	—	555 w 521 w	—
2	$[\text{Ni}(\text{H}_2\text{nsh})(\text{py})_2] \cdot 2\text{H}_2\text{O}$	3419 m 3286 m	—	1618 s 1604 m	1540 s	1507 w	1303 m 1282 w	1038 w	—	521 w	1052 w
3	$[\text{Ni}(\text{H}_2\text{nsh})(2\text{-pic})_2]$	3421 m	—	1617 s 1602 m	1540 s	1508 w	1303 m	1038 w	—	521 w	1053 w
4	$[\text{Ni}(\text{H}_2\text{nsh})(3\text{-pic})_2] \cdot 2\text{H}_2\text{O}$	3420 m	—	1616 s 1602 m	1540 s	1506 w	1303 m	1038 w	—	521 w	1070 w
5	$[\text{Ni}(\text{H}_2\text{nsh})(4\text{-pic})_2]$	3435 s	—	1617 s 1604 m	1540 m	1508 w	1303 m	1036 w	—	522 w	1045 w
6	$[\text{Ni}_2(\text{nsh})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$	3401 m 3055 m	—	1618 s 1602 w	1540 vs	1508 w	1302 m 1282 w	1030 w	897 w	569 w 525 w	—
7	$[\text{Ni}_2(\text{nsh})(\text{py})_4] \cdot 4\text{H}_2\text{O}$	3419 m 3051 m	—	1617 vs 1602 s	1540 vs	1508 w	1303 m 1283 w	1093 w	882 w	595 w 528 w	1069 w
8	$[\text{Ni}_2(\text{nsh})(2\text{-pic})_4] \cdot 4\text{H}_2\text{O}$	3421 m 3055 m	—	1617 vs 1602 vs	1540 vs	1508 w	1302 m 1281 w	1093 w 1032 w	883 w	589 w 567 w	1076 w
9	$[\text{Ni}_2(\text{nsh})(3\text{-pic})_4] \cdot 4\text{H}_2\text{O}$	3409 m 3051 m	—	1617 vs 1602 vs	1541 vs	1508 w	1302 m 1282 w	1049 w 1003 w	862 w	585 w 532 w	1061 w
10	$[\text{Ni}_2(\text{nsh})(4\text{-pic})_4] \cdot 4\text{H}_2\text{O}$	3398 m 3050 z	—	1617 vs 1602 vs	1541 vs	1508 w	1302 m 1282 w	1094 w 1030 w	861 w	570 w 528 w	1070 w

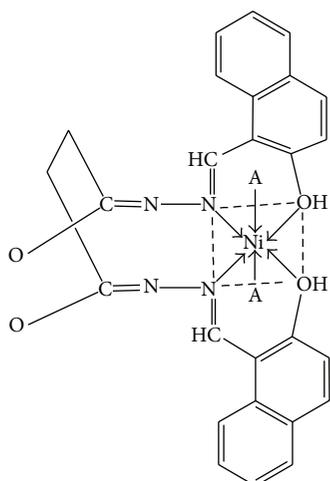


FIGURE 2: Tentative structure of $[\text{Ni}(\text{H}_2\text{nsh})(\text{A})_2] \cdot n\text{H}_2\text{O}$ (where A = water (H_2O), $n = 0$ (1); pyridine (py), $n = 2$ (2); 2-picoline(2-pic), $n = 0$ (3); 3-picoline(3-pic), $n = 2$ (4); and 4-picoline(4-pic), $n = 0$ (5)).

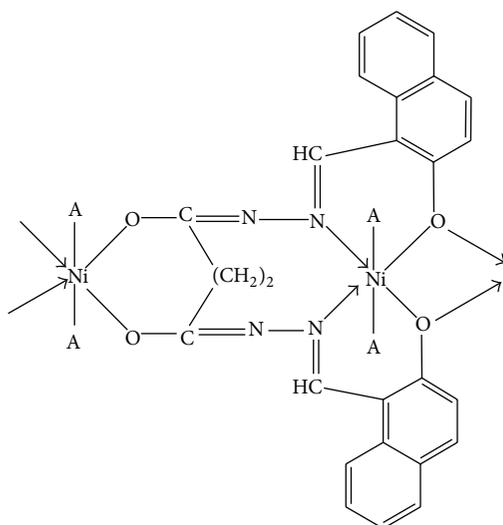


FIGURE 3: Tentative structure of $[\text{Ni}_2(\text{nsh})(\text{A})_4] \cdot n\text{H}_2\text{O}$, where A = water (H_2O), $n = 1$ (6); pyridine (py), $n = 4$ (7); 2-picoline(2-pic), $n = 4$ (8); 3-picoline(3-pic), $n = 4$ (9); and 4-picoline(4-pic), $n = 4$ (10).

metal-metal interaction in monometallic complexes while the values suggest strong metal-metal interaction in complexes (6)–(10). The dihydrazone (H_4nsh) coordinates with the metal centre as a dibasic tetradentate ligand in enol form through azomethine nitrogen atoms and deprotonated naphtholic oxygen atoms in complexes (1)–(5). In these complexes, (1)–(5), the dihydrazone donor atoms are arranged around the Ni(II) centre in the equatorial position while the axial positions are occupied by the coligands H_2O /pyridine/2-picoline/3-picoline/4-picoline molecules. Electronic spectral studies suggest that all of the homobimetallic complexes (6)–(10) have distorted octahedral stereochemistry. In these complexes the ligand coordinates with the metal centre as

a tetrabasic hexadentate ligand. One of the Ni(II) centres is present in N_2O_2 coordination sphere and another Ni(II) centre is bonded to it through phenolate oxygen atoms via oxo-bridging.

The tentative structures for the complexes have been shown in Figures 2 and 3.

Conflict of Interests

Authors declare that there is no conflict of interests regarding the publication of this research work.

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