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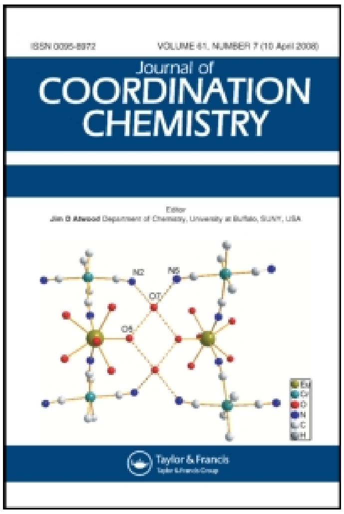

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Synthesis and characterization of heterobimetallic Ni(II)-Zn(II) complexes from bis(2-hydroxy-1 -naphthaldehyde)succinoyldihydrazone

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Synthesis and characterization of heterobimetallic Ni(II)–Zn(II) complexes from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

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Monometallic zinc(II) and nickel(II) complexes, $[Zn(H_2nsh)(H_2O)]$ (**1**) and $[Ni(H_2nsh)(H_2O)_2]$ (**2**), have been synthesized in methanol by template method from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh). Reaction of monometallic complexes with alternate metal(II) acetates as a transmetallator in 1 : 3 molar ratio resulted in the formation of heterobimetallic complexes $[NiZn(nsh)(A)_3]$ and $[ZnNi(nsh)(A')_2]$ ($A = H_2O$ (**3**), py (**4**), 2-pic (**5**), 3-pic (**6**), 4-pic (**7**)), ($A' = H_2O$ (**8**), py (**9**), 2-pic (**10**), 3-pic (**11**), and 4-pic (**12**)). The complexes have been characterized by elemental analyzes, mass spectra, molar conductance, magnetic moments, electronic, EPR, and IR spectroscopies. All of the complexes are non-electrolytes. Monometallic zinc(II) is diamagnetic while monometallic nickel(II) complex and all heterobimetallic complexes are paramagnetic. The metal centers in heterobimetallic complexes are tethered by dihydrazone and naphthoxo bridging. Zinc(II) is square pyramidal; nickel(II) is six-coordinate distorted octahedral except $[ZnNi(nsh)(A)_2]$, in which nickel(II) has square-pyramidal geometry. The displacement of metal center in monometallic complexes by metal ion has been observed in the resulting heterobimetallic complexes.

Keywords: Nickel(II); Zinc(II); Heterobimetallic; Bis(2-hydroxy-1-naphthaldehyde)-succinoyldihydrazone; Magnetic moment; Spectroscopic studies

1. Introduction

Homo and heteropolymetallic complexes containing two or more metal centers in close proximity are involved in a variety of important biochemical processes [1, 2] and are important in materials of technological and industrial significance [3, 4]. Metal ions in enzymes give rise to monometallic, homometallic, and heterometallic enzymes. For example, Mo, Zn, and Ni are present in xanthine oxidase [5], carbonic anhydrase [6],

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and bacterial hydrogenase [7], respectively, in monometallic enzymes. Copper and manganese are found in haemocyanin and tyrosinase [8] and oxygen evolving complex (OEC) [9] in photosystem II, as multimetallic enzymes. Further, Mo is found in nitrogenase [10] in combination with iron, and Zn and Cu are found together in superoxide dismutase [11] and Ni occurs in combination with iron in jack bean urease [12] and Ni–Fe hydrogenase [13]. Zn occurs in kidney bean phosphatase in combination with iron [14] and in combination with copper in proteins obtained from rat liver [15]. The efficacy of heterobimetallic complexes in asymmetric activation of carbon dioxide and related molecules has been demonstrated [16]. Further, heterobimetallic complexes have potential to mediate chemical reactions of industrial relevance either more efficiently than or, in a different manner to, isolated metal centers [17]. Heterobimetallic complexes offer an opportunity to study cooperative interaction between metal ions.

Dihydrazones derived from condensation of *o*-hydroxyaromatic aldehydes and ketones with acyldihydrazones, aroyldihydrazines, and pyridoyl dihydrazines are potential polyfunctional ligands which can bind with metal ions in various ways giving rise to monometallic, homopolymetallic, and heteropolymetallic complexes depending on the preferred stereochemical disposition of metal and the bonds formed in coordination. A survey of literature reveals that although metal complexes of monoacyl hydrazones, aroyl hydrazones, and pyridoyl hydrazones have been studied in detail [18–21], those of acyl-, aroyl-, and pyridoyl-dihydrazones have received attention in recent years only [22–25]. Heterobimetallic complexes derived from dihydrazones are quite meager [23, 26] with not a single report of heterobimetallic complexes of dihydrazones containing succinoyl and bulky naphthyl fragments in their molecular skeleton. This article describes the synthesis and characterization of heterobimetallic nickel–zinc complexes derived from bis(2-hydroxy-1-naphthaldehyde)-succinoyldihydrazone (H_4nsh) (figure 1). Monometallic zinc(II) and nickel(II) complexes have also been synthesized and characterized as precursor in the synthesis of heterobimetallic complexes.

2. Experimental

2.1. *Materials*

Zinc acetate ($Zn(OAc)_2 \cdot 2H_2O$), nickel acetate ($Ni(OAc)_2 \cdot 4H_2O$), 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 used without purification.

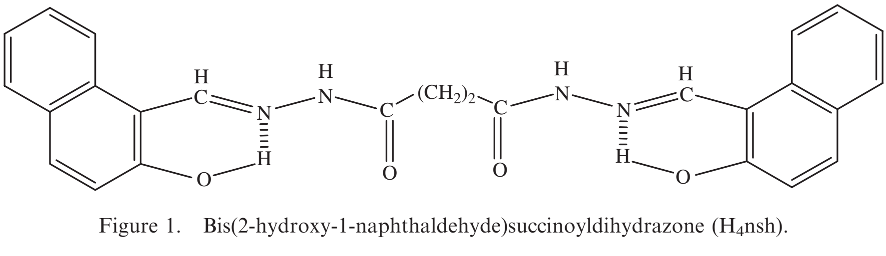

Figure 1. Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh).

2.2. *Physical measurements*

All conductance measurements were made at 1 kHz using a Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01 ns resolution and measures conductance with an accuracy of 0.05%. A dip-type conductivity cell having platinized platinum electrode was used. The cell constant was determined using a standard KCl solution. Infrared spectra from 4000 to 400/500 cm^{-1} were recorded on a BX-III/FT-IR Perkin Elmer spectrophotometer. ^1H-NMR spectra were recorded on a Bruker AC-F 300 MHz and AMX 400 High Resolution Multinuclear FT-NMR spectrometer in DMSO-d_6 with tetramethylsilane (TMS) as internal standard. Room temperature (RT) magnetic susceptibility measurements were made on Sherwood Magnetic Susceptibility Balance MSB-Auto. EPR spectra of the complexes in powdered form were recorded at X-band frequency on a Varian E-112 E-Line Century Series EPR spectrometer using TCNQ ($g = 2.0027$) as an internal field maker. Atmospheric pressure chemical ionization (APCI) mass spectra of the complexes were recorded on a Waters ZQ4000 Micromass spectrometer.

2.3. *Analysis of the complexes*

Elemental analyzes (C, H, and N) were performed on a Perkin Elmer 2400 CHNS/O Analyzer 11. Zinc and nickel contents were determined by literature method [27]. Water, ethanol, pyridine, 3-picoline, and 4-picoline were determined by heating the samples in an electronic oven for 4 h at 110°C or 180°C or 220°C each, respectively, and determining the weight loss. Water was identified by passing the vapors through a test tube containing anhydrous copper sulfate which turned blue, while pyridine, 3-picoline, and 4-picoline molecules were determined by passing the vapors through a test tube containing (1) a solution of sodium hydroxide and iodine; (2) a solution of $CHCl_3$ containing a drop of 5 M NaOH solution and (3) a test tube containing cyanogen bromide solution followed by treatment with phloroglucinol solution. The solutions turned red, green, violet, and blue [28], respectively.

2.4. *Preparation of the ligand*

Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone was prepared in two steps. In the first step, succinoylhydrazine was prepared by reacting diethyl succinate with hydrazine hydrate in 1 : 2.5 molar ratio. In the second step, bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) was prepared by reacting succinoyldihydrazine (1.0 g, 6.84 mmol) in dilute ethanol with 2-hydroxy-1-naphthaldehyde (2.59 g, 15.04 mmol) in ethanol under reflux for 30 min. The yellow precipitate, thus, obtained was purified by washing with hot ethanol and dried over anhydrous $CaCl_2$. m.p. 254°C (Found (%): C, 68.81; H, 4.80; N, 12.65). Required for $C_{26}H_{22}O_4N_4$ (%): C, 68.72;H, 4.84; N, 12.33.

2.5. *Preparation of [Zn(H_2nsh)(H_2O)] (1) and [Ni(H_2nsh)(H_2O)$_2$] (2)*

Succinoyldihydrazine (0.50 g, 3.42 mmol) was dissolved in hot methanol–water mixture (90 : 10) and a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.75 g, 3.45 mmol) in methanol (50 mL) was added accompanied by gentle stirring for 15 min. This solution was added to a solution of 2-hydroxy-1-naphthaldehyde (1.47 g, 8.54 mmol) in methanol (100 mL) drop-by-drop at 70°C over a period of 10 min accompanied by gentle stirring. The reaction mixture was refluxed for 1 h precipitating a bright yellow compound, which was filtered while hot, washed repeatedly with hot methanol, finally with ether, and dried over anhydrous $CaCl_2$.

Complex **2** was prepared by the above method using $Ni(OAc)_2 \cdot 4H_2O$ instead of $Zn(OAc)_2 \cdot 2H_2O$.

2.6. *Preparation of [NiZn(nsh)(A)$_3$] (where A = H_2O (3); pyridine (py, 4); 2-picoline (2-pic, 5); 3-picoline (3-pic, 6); 4-picoline (4-pic, 7))*

$[Zn(H_2nsh)(H_2O)]$ (1.00 g, 1.81 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 min at 60°C. This was added to a solution of $Ni(OAc)_2 \cdot 4H_2O$ (1.35 g, 5.43 mmol) in methanol (50 mL) drop-by-drop over a period of 10–15 min accompanied by gentle stirring. The reaction mixture thus obtained was refluxed for 5 h, precipitating a light brown compound, which was isolated in the usual way.

In order to prepare **4**, compound **3** (1.00 g, 1.55 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 min at 60°C and pyridine (1.30 mL, 15.52 mmol) was added maintaining $[NiZn(nsh)(H_2O)_3]$ and pyridine molar ratio at 1 : 10. The resulting reaction mixture was refluxed for 3 h, precipitating orange compound which was collected in the usual way.

Complexes **5**–**7** were prepared in a similar way using 2-picoline, 3-picoline, and 4-picoline instead of pyridine.

2.7. *Preparation of [ZnNi(nsh)(A′)$_2$] (where A′ = H_2O (8); pyridine (py, 9); 2-picoline (2-pic, 10); 3-picoline (3-pic, 11); 4-picoline (4-pic, 12))*

$[ZnNi(nsh)(H_2O)_2]$ was prepared by following essentially the same method as for $[NiZn(nsh)(H_2O)_3]$ by reaction between $[Ni(H_2nsh)(H_2O)_2]$ and $Zn(OAc)_2 \cdot 2H_2O$ instead of $[Zn(H_2nsh)(H_2O)]$ and $Ni(OAc)_2 \cdot 4H_2O$.

The remaining complexes were prepared by following essentially the same method as used for the complexes $[NiZn(nsh)(A)_3]$ using $[ZnNi(nsh)(H_2O)_2]$ instead of $[NiZn(nsh)(H_2O)_3]$.

3. Results and discussion

Synthesis of pure heterobimetallic complexes is difficult to avoid considerable quantities of undesired binuclear products. Heterobimetallic products are accessible by strategies developed by Lintvedt *et al.* [29] from monometallic complex using polyfunctional ligands and Davies *et al.* [30] *via* transmetallation beginning with a complex of discrete molecularity as target and another metal complex as transmetallator. Monometallic complexes $[Zn(H_2nsh)(H_2O)]$ (**1**) and $[Ni(H_2nsh)(H_2O)_2]$ (**2**) were synthesized by reacting metal acetate with succinoyldihydrazine in 1 : 1 molar ratio and reacting the resultant solution with excess 2-hydroxy-1-naphthaldehyde. When **1** and **2** reacted with $Ni(OAc)_2 \cdot 4H_2O$ and $Zn(OAc)_2 \cdot 2H_2O$, respectively, in 1 : 3 molar ratio in methanol, the resulting precipitates were heterobimetallic complexes $[NiZn(nsh)(H_2O)_3]$ (**3**) and $[ZnNi(nsh)(H_2O)_2]$ (**8**), respectively. Reaction of these heterobimetallic complexes with pyridine, 2-picoline, 3-picoline, and 4-picoline in 1 : 10 molar ratio led to substitution of water by pyridine and substituted pyridines.

The complexes formula, color, decomposition point, percent yield, analytical data, molar conductance, magnetic moment, and electronic spectral data are given in table 1. All of the complexes are insoluble in water, and common organic solvents, such as ethanol, methanol, acetone, chloroform, carbon tetrachloride, benzene, and ether but are soluble in DMSO and DMF. All of the complexes are air stable solid powders, decomposing above 300°C.

Since the complexes are soluble in DMSO and DMF efforts were undertaken to crystallize the complexes in both saturated and dilute solutions in CH_3CN, DMSO, DMF, DMSO–CH_3CN, DMSO–CH_2Cl_2, DMF–CH_3CN, and DMF–CH_2Cl_2. The solutions were gently evaporated either at RT or at 40, 50, and 60°C in hot air electric oven to promote crystal growth. The solutions were also kept in a freezer to grow crystals. In all our efforts, only amorphous compounds precipitated which prevented analysis of the complexes by X-ray crystallography.

3.1. *Mass spectra*

Mass spectra of **1** and **2** show m/z values of 518 and 1059.41, respectively. The m/z value of 518 for **1** is close to the value 517.38 obtained by loss of coordinated water from the complex. Hence, this signal is assigned to $[Zn(H_2nsh)]^+$ species, suggesting that **1** is monomeric. On the other hand, the m/z value 1059.4 for **2** is close to the value 1057.38 corresponding to dimer from loss of water from nickel(II). Accordingly, this signal is assigned to $[Ni(H_2nsh)(H_2O)]_2^+$ species.

3.2. *Thermal studies*

None of the complexes showed weight loss below 160°C ruling out the possibility of water in the lattice. Complexes **2** and **8** showed weight loss corresponding to two waters at 180°C, while **1** and **3** showed weight loss corresponding to one and three waters, respectively. This suggests water in the first coordination sphere around the metal in these complexes. Complexes **4**–**7** showed weight loss corresponding to three pyridine/2-picoline/3-picoline/4-picoline molecules while **9**–**12** showed weight loss corresponding to two pyridine/2-picoline/3-picoline/4-picoline molecules at 220°C. Expulsion of these neutral electron donors at high temperature indicates that they are coordinated to metal [28].

3.3. *Molar conductance*

The molar conductance values (in DMSO) for **1**–**12** lie in the range 2.81–3.21 $ohm^{-1} cm^2 mol^{-1}$ (table 1) suggesting all complexes are non-electrolytes [31].

Table 1. Complex, color, decomposition point, percentage yield, analytical, molar conductance, magnetic moment data, and electronic spectral bands for **1–12**.

S. No.	Complex and color	Yield (%)	Analysis: Found (calculations) (%) Zn	Ni	C	H	N	Molar conductance ($\wedge_M$) (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	[Zn(H_2nsh)(H_2O)] Bright yellow	33.9	12.29 (12.21)	–	58.34 (58.28)	4.12 (4.11)	10.41 (10.46)	3.1	Dia	327 (8850), 408 (14,520), 432 (12,386), 479 (2272)
2	[Ni(H_2nsh)(H_2O)$_2$] Brown	38.5	–	10.54 (10.73)	56.94 (57.07)	4.39 (4.39)	10.14 (10.24)	3.13	2.87	319 (2755), 364 (1815), 410 (1733), 564 (80), 845 (37)
3	[NiZn(nsh)(H_2O)$_3$] Orange	51.8	10.16 (10.41)	9.08 (9.35)	49.76 (49.68)	3.83 (3.82)	8.88 (8.92)	3.21	2.98	322 (12,640), 369 (11,280), 410 (15,420), 472 (1160), 615 (112), 931 (81)
4	[NiZn(nsh)(py)$_3$] Orange	48.8	8.66 (8.06)	7.08 (7.24)	60.54 (60.66)	4.09 (4.07)	12.14 (12.08)	3.12	3.03	326 (10,640), 369 (10,540), 407 (13,300), 478 (1096), 626 (112), 940 (81)
5	[NiZn(nsh)(2-pic)$_3$] Orange	45.6	7.77 (7.66)	6.52 (6.88)	61.74 (61.89)	4.61 (4.57)	11.45 (11.48)	2.98	3.10	325 (12,447), 367 (12,698), 407 (14,280), 430 (12,639), 486 (1026), 622 (108), 935 (78)
6	[NiZn(nsh)(3-pic)$_3$] Dark brown	46.3	7.76 (7.66)	6.68 (6.88)	61.78 (61.89)	4.60 (4.57)	11.47 (11.48)	2.81	2.95	326 (10,318), 369 (10,571), 408 (14,064), 477 (1082), 623 (104), 936 (78)
7	[NiZn(nsh)(4-pic)$_3$] Dark brown	47.1	7.79 (7.66)	6.55 (6.88)	61.78 (61.89)	4.59 (4.57)	11.52 (11.48)	2.92	3.15	334 (12,253), 378 (10,941), 421 (14,782), 481(1058), 621 (106), 934 (78)
8	[ZnNi(nsh)(H_2O)$_2$] Light brown	55.4	11.01 (10.72)	9.52 (9.62)	51.54 (51.14)	3.61 (3.61)	9.45 (9.18)	3.08	3.25	318 (5392), 367 (4942), 412 (4470), 966 (80)
9	[ZnNi(nsh)(py)$_2$] Light brown	52.5	8.77 (8.93)	8.52 (8.02)	59.24 (59.01)	3.84 (3.82)	11.55 (11.47)	2.98	3.35	323 (7328), 366 (7206), 410 (6946), 967 (82)
10	[ZnNi(nsh)(2-pic)$_2$] Light brown	51.2	8.77 (8.60)	7.6 (7.72)	59.74 (59.99)	4.23 (4.21)	11.15 (11.05)	3.09	3.40	324 (3643), 368 (3298), 413 (3729), 965 (78)
11	[ZnNi(nsh)(3-pic)$_2$] Light brown	51.2	8.76 (8.60)	7.67 (7.72)	59.79 (59.99)	4.23 (4.21)	11.12 (11.05)	3.13	3.42	323 (7328), 366 (7206), 414 (6946), 967 (80)
12	[ZnNi(nsh)(4-pic)$_2$] Light brown	52.42	8.81 (8.60)	7.69 (7.72)	59.78 (59.99)	4.25 (4.21)	11.16 (11.05)	3.08	3.34	342 (3874), 368 (3660), 410 (3922), 968 (81)

Decomposition point – all decompose above 300°C.

3.4. *Magnetic moment*

Complex **1** is diamagnetic as expected, while the remaining complexes are paramagnetic. The μ_{eff} values for **2**–**7** lie in the range 2.87–3.15 B.M. while μ_{eff} for **8**–**12** fall in the range 3.35–3.42 B.M. The μ_{eff} values for nickel(II) complexes fall in the regions 3.00–3.30, 3.00–3.45, and 3.45–4.00 B.M., respectively, for octahedral, square-pyramidal, and tetrahedral geometries [32], while square-planar nickel(II) complexes are diamagnetic. The magnetic moments rule out tetrahedral or square-planar structures. Values for **3**–**7** lie in the range 2.95–3.15 B.M. indicating distorted octahedral stereochemistry [32, 33]. Ni(II) complexes having square-pyramidal stereochemistry have magnetic moment values lying in the region 3.25–3.45 [34]; **8**–**12** at 3.35–3.43 B.M. are in the range for high-spin, square-pyramidal complexes. Hence, **8**–**12** are suggested to have square-pyramidal geometry.

3.5. *Electronic spectra*

The important electronic spectral bands along with their molar extinction coefficient are summarized in table 1. The electronic spectra of **3** and **8** are shown in "Supplementary material". The ligand exhibits bands at 311, 322, 355, and 371 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. In **1** and **2**, the ligand bands are red-shifted by 8–77 nm indicating bonding of dihydrazone to the metal. In addition to the ligand bands, complex **1** shows an additional band at 479 nm with molar extinction coefficient of 2272 $dm^3\,mol^{-1}\,cm^{-1}$; this band is assigned to ligand-to-metal charge transfer (LMCT), probably from naphtholate oxygen to zinc(II). $[Ni(H_2nsh)(H_2O)_2]$ (**2**) has absorption bands at 845 and 564 nm in addition to the ligand and charge-transfer bands, assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (υ_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (υ_2) transitions, respectively. The band due to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (υ_3) appears to be masked by strong intra-ligand/charge-transfer transition at 410 nm. The bands observed at 845 and 564 nm are characteristic of nickel(II) in distorted octahedral environment, consistent with the presence of nickel(II) with NNOO coordination [35].

+ In heterobimetallic complexes, the ligand bands are shifted to longer wavelength by 8–60 nm indicating strong bonding between dihydrazone and metal. In addition, the heterobimetallic complexes show a new band in the region 472–481 nm, similar to the charge-transfer band at 479 nm observed in **1**. Accordingly, this band is assigned to LMCT originating from naphtholate oxygen. Complexes **3**–**7** exhibit new bands at 931–940 nm (υ_1) and 615–628 nm (υ_2), respectively. The position of these bands is typical of octahedral Ni(II). A comparison of the position of the bands in the regions 931–940 and 615–628 nm with the corresponding bands in the spectra [30] of $[Ni(H_2O)_6]^{2+}$ at 1175 and 740 nm and of $[Ni(NH_3)_6]^{2+}$ at 935 and 570 nm suggests that υ_1 bears similarity with that of NH_3 while the second band, υ_2, is intermediate between those observed for H_2O and NH_3. Nickel thus may occupy NNOO coordination of the ligand, suggesting that Zn(II) is displaced by Ni(II). Hence, Ni(II) occupies NNOO coordination while zinc(II) has OOOO coordination chamber. Complexes **8**–**12** derived from $[Ni(H_2nsh)(H_2O)_2]$ exhibit only one band at 965–967 nm, similar to high-spin square-pyramidal Ni(II) [36, 37] and the band is assigned to $^3B_1 \rightarrow {}^3E(F)$. A comparison of the position of this band in the region 965–987 nm with the corresponding band in spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 (υ_1) and

$[Ni(NH_3)_6]^{2+}$ at 935 (υ_1) and those in **3**–**7** suggests that the υ_1 band in these complexes is shifted away from position of υ_1 in complexes with nitrogen donors and toward the position of υ_1 with oxygen donors. Thus, nickel in **8**–**12** is probably coordinated to carbonyl oxygen in enol form, suggesting that Ni(II), which originally occupies NNOO coordination, is displaced by Zn(II) in the heterobimetallic complexes. Thus, it is suggested that in these complexes the nickel(II) occupies OOOO coordination chamber, while zinc(II) occupies NNOO coordination chamber. Various ligand field parameters, namely Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10 Dq), covalence factor (β) and ligand field stabilization energy for **3**–**7** are provided in "Supplementary material". Calculated values of υ_2/υ_1 (1.49–1.51) lie in the range reported for an octahedral environment around Ni(II) [38].

3.6. *EPR spectra*

EPR spectra of **3** and **8** have been recorded as representative examples of the geometry of the nickel(II) in heterobimetallic complexes. EPR spectra of **3** at 9.1 GHz show a single signal at $g = 2.004$ in polycrystalline form both at RT and liquid nitrogen temperature (LNT), while those of **8** are featureless. The signal at $g = 2.004$ is attributed to arise from the double quantum transition [39]. In the Ni(II) complex, the zero-field splitting (ZFS) ranges from a few [40] to some tens of wave numbers [41]. Consequently, the conventional X-band and Q-band EPR spectroscopy using electromagnetic quanta around 0.3 and 1.5 cm^{-1}, respectively, find it difficult to excite transitions between the states of the spin-triplet manifold [42]. Four-coordinate square-planar/five-coordinate nickel(II) centers are present in hydrogenase enzyme [43, 44] and the reduced states of C-cluster in the bacterial carbon monoxide dehydrogenase [45]. The nickel(II) centers are EPR silent in these biological systems, while four-coordinate tetrahedral and six-coordinate octahedral complexes are EPR active. The fact that **3** shows an intense signal with $g = 2.004$ suggests that nickel(II) has octahedral geometry, while the featureless spectrum of **8** suggests that the nickel(II) is five-coordinate square-pyramidal. Further, the g-value for nickel complexes depends on the donor set as well as on the coordination geometry of the complex. Complexes with oxygen donors (donor set NiO_6) have g-values greater than 2.2, whereas those with the nitrogen donors (donor set NiN_6) generally have g value either equal to 2.2 or less than this. The g value in **3** is less than 2.2, as is expected for NiN_2O_4 donor set [46, 47]. The intensity of the signal at $g = 2.004$ in **3** remains unchanged at RT as compared to LNT, ruling out the possibility of impurity [48].

3.7. *^{1}H-NMR spectra*

The ligand shows two proton doublets at δ 11.61 and 12.73 ppm assigned to δ(OH) protons (Supplementary material). These doublets appear as singlets at 12.21 and 12.80 ppm in the ^{1}H-NMR spectrum of **1** with downfield shift by 0.60 and 0.07 ppm, respectively, showing coordination of naphtholic –OH group to zinc. δ(NH) signal, which appears at δ 9.99 and 11.14 ppm in the free dihydrazone disappears in **1** indicating the collapse of amide structure of the dihydrazone and coordination to zinc in the enol form. This is also supported by IR spectroscopy which does not show any band characteristic of $>C=O$. The azomethine proton signals at δ 8.60 and 9.05 ppm as doublets in the free dihydrazone appear at δ 8.99 and 9.13 ppm as doublets, showing coordination of azomethine nitrogen to zinc. Azomethine proton signals in the uncoordinated dihydrazone and **1** as two resonances only suggests that the dihydrazone is coordinated to zinc in the *anti-cis* configuration [49].

3.8. *Infrared spectra*

Some of the structurally significant IR spectral bands for the free dihydrazone, the precursor Zn(II) and Ni(II) complexes and the heterobimetallic Ni–Zn and Zn–Ni complexes are listed in "Supplementary material". Comparison of IR spectra of the monometallic, heterobimetallic, and uncoordinated dihydrazone suggests that the dihydrazone is coordinated to the metal center in the enol form in all of the complexes.

The uncoordinated dihydrazone shows medium intensity bands at 3423 and 3244 cm^{-1} assigned to υ(OH) vibration of 2-hydroxy-1-naphthaldehyde of the dihydrazone and υ(NH) of secondary –NH, respectively. IR spectra of **1** and **2** show a medium intensity band in the region 3000–3500 cm^{-1} attributed to water absorbed by KBr during pellet preparation and contribution from coordinated water in the complexes. The band at 3000–3500 cm^{-1} in **1** and **2** also appears to have contribution from the stretching vibration of naphtholic –OH. Neither complex shows υ(NH) at 3244 cm^{-1} or $\upsilon(C=O)$ vibration at 1672 cm^{-1} in the uncoordinated dihydrazone, suggesting enolization of the ligand in the complexes.

The $\upsilon(C=N)$ is a couple of bands at 1622–1602 cm^{-1} similar to that in the uncoordinated dihydrazone in which these bands appear at 1633 and 1593 cm^{-1}. The average negative shift of 2-3 cm^{-1} indicates coordination of dihydrazone through azomethine nitrogen to metal [50]. The existence of two $\upsilon(C=N)$ bands shows that the two azomethine nitrogens are inequivalent, suggesting that the two $M \leftarrow N$ bonds are not the same; the differences between $\upsilon(C=N)$ stretching frequencies of the order of 13–18 cm^{-1} fall in the range for *anti-cis* configuration [49, 51]. Thus, dihydrazone exists in the *anti-cis* configuration in the complexes as also deduced from ^{1}H-NMR spectroscopy of **1**.

A band of medium intensity at 1540 cm^{-1} in the infrared spectrum of the free dihydrazone is attributed to joint contribution of amide II + υ(C–O) (naphtholic). This band splits into two bands in IR spectra of the complexes and at 1540 and 1508 cm^{-1}, respectively. The position of the band at 1540 cm^{-1} remains almost unchanged in **2**–**7** and shifts to higher frequency by 19-40 cm^{-1} in the remaining complexes. The intensity of this band is considerably increased in **8**–**12**. A new intense band at 1508 cm^{-1} in IR spectra of the complexes is attributed to stretching vibration of newly created NCO produced as a result of deprotonation of the enolic form of the ligand [52]. The complexes show new weak bands at 528 and 558 cm^{-1} [53] due to coordinated naphtholic –OH. The IR spectra of the heterobimetallic complexes **3**–**12** are almost the same as those of **1** and **2** suggesting the mode of coordination of dihydrazone remains essentially the same as in **1** and **2**. Complexes **4**–**7** and **9**–**12** show a new but very weak band at 1012–1014 and 1051–1072 cm^{-1}, respectively, assigned to ring breathing mode of pyridine and substituted pyridine in the complexes [54]. A new band at 773–780 cm^{-1} in spectra of all heterobimetallic complexes, which is observed neither in the IR spectrum of the uncoordinated dihydrazone nor in **1** and **2**, is assigned

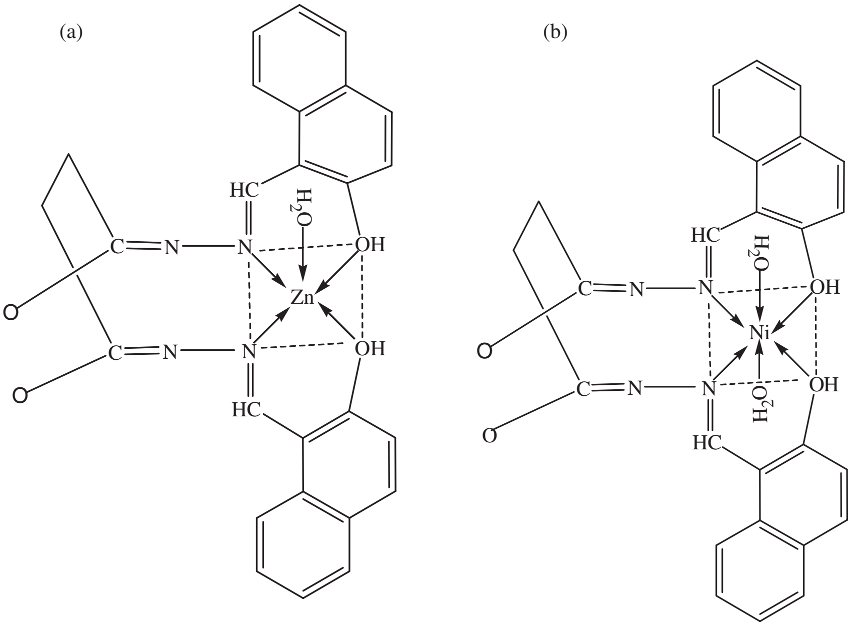

Figure 2. Tentative structure of (a) $[Zn(H_2nsh)(H_2O)]$ (**1**) and (b) $[Ni(H_2nsh)(H_2O)_2]$ (**2**).

to the stretching vibration of the tetraatomic species $[\mathrm{M}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{M}]$ resulting from bridging naphtholate oxygen [55]. A new non-ligand band at 500–525 cm^{-1} is assigned to υ(M–O)(naphtholate) [56] and the band at 420–482 cm^{-1} is assigned to υ(M–O)(carbonyl) [57], indicating coordination of naphtholate oxygen and enolized carbonyl oxygen to the metal. On the basis of results obtained from various physico-chemical and spectral studies, structures for the complexes have been suggested as shown in figures 2–4.

4. Conclusion

This article describes two monometallic zinc(II) and nickel(II) complexes and 10 heterobimetallic nickel(II)–zinc(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone. The dihydrazone is coordinated in enol form in all of the complexes in *anti-cis* configuration. In monometallic complexes **1** and **2**, the dihydrazone is a dibasic tetradentate ligand coordinating through two azomethine nitrogens and two protonated naphtholic –OH groups. One and two waters are coordinated to zinc(II) and nickel(II), respectively. The zinc(II) and nickel(II) in **1** and **2** are proposed to have square-pyramidal and distorted-octahedral stereochemistry, respectively. In all heterobimetallic complexes, the dihydrazone is a tetrabasic hexadentate ligand coordinating to the metals in enol form in *anti-cis* configuration. On reaction of monometallic complexes with the alternate metal salts, the first metal center is displaced by the transmetallating metal. In $[NiZn(nsh)(A)_3]$, nickel(II) is

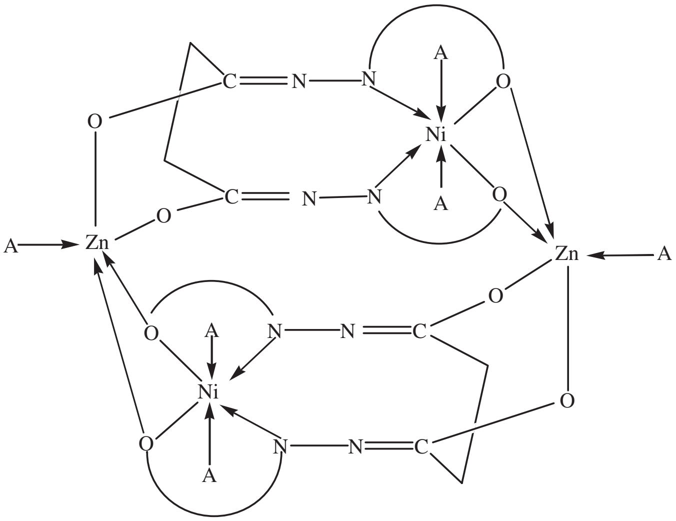

Figure 3. Tentative structure of [NiZn(nsh)$(A)_3$] where A = H_2O (**3**), pyridine (**4**), 2-picoline (**5**), 3-picoline (**6**), and 4-picoline (**7**).

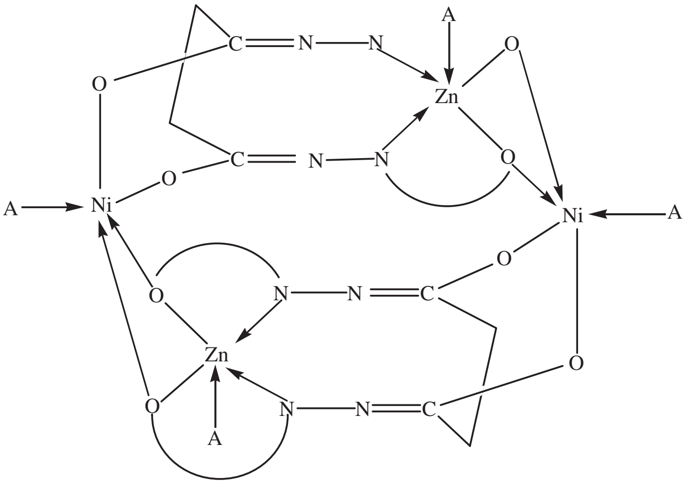

Figure 4. Tentative structure of [ZnNi(nsh)$(A)_2$].

six-coordinate, while zinc(II) is five-coordinate. In [ZnNi(nsh)$(A)_2$], both metal centers have square-pyramidal geometry.

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