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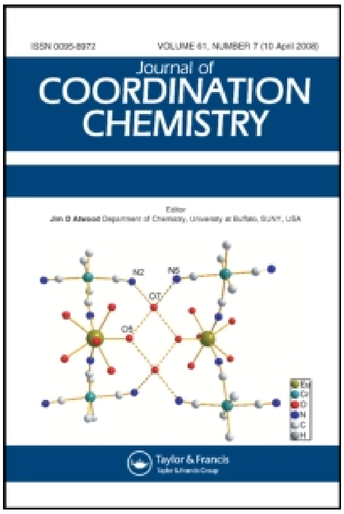

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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To cite this Article Lal, R. A. , Choudhury, S. , Ahmed, A. , Chakraborty, M. , Borthakur, R. and Kumar, A.(2009) 'Synthesis and spectral studies of nickel(II) complexes derived from disalicylaldehyde oxaloyldihydrazone', Journal of Coordination Chemistry, 62: 23, 3864 — 3874

To link to this Article: DOI: 10.1080/00958970903160972

URL: http://dx.doi.org/10.1080/00958970903160972

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Journal of Coordination Chemistry
Vol. 62, No. 23, 10 December 2009, 3864–3874

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Synthesis and spectral studies of nickel(II) complexes derived from disalicylaldehyde oxaloyldihydrazone

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(*Received 4 February 2009; in final form 16 May 2009*)

The mononuclear nickel(II) complex [Ni(H_2slox)(H_2O)$_3$] (**1**) and polymeric dinuclear complexes [Ni_2(slox)(A_4)] {A = H_2O (**2**), py (**3**), 2-pic (**4**), 3-pic (**5**) and 4-pic (**6**)} and the discrete binuclear complexes [Ni_2(slox)(NN)$_3$] {NN = bpy (**7**) and phen (**8**)} have been synthesized from disalicylaldehyde oxaloyldihydrazone (H_4slox) in methanol. All of the complexes are nonelectrolytes. Complexes **1**, **7**, and **8** are paramagnetic while binuclear **2**–**6** possess anomalously low μ_{eff} value, indicating considerable metal–metal interaction. Discrete binuclear **7** and **8** have no interaction between the two nickel(II) ions. The anomalously low magnetic moment values in **2**–**6** are explained as metal–metal interaction via phenoxide bridge. Such metal–metal interactions are less in **7** and **8** due to coordination of bipyridine and phenanthroline molecules which do not allow phenoxide bridging. The dihydrazone coordinates to the metal center as a dibasic tridentate ligand in keto-enol form in staggered configuration in **1**, while in the remaining complexes the dihydrazone is tetrabasic hexadentate in enol form in anticis configuration. The metal center has a tetragonally distorted octahedral stereochemistry.

Keywords: Nickel complex; Disalicylaldehyde oxaloyldihydrazone; Molar conductance; Magnetic moment; Spectroscopic studies

1. Introduction

Metal based therapy relies on coordination of bioactive ligands to improve their bioactivity profiles, while inactive ligands may acquire pharmacological properties [1] and metal coordination is one of the most efficient strategies in design of repository, slow release or long-acting drugs [2]. Metal complexes have gained importance as enzyme inhibitors [3]. Synthesis, structural investigation, and reactions of transition metal Schiff bases have received special attention because of their biological activities as antitumoral, antifungal, and antiviral agents [4]. Schiff-base hydrazones have antimicrobial [5], antitubercular [6], anticonvulsant [7], and antiinflammatory [8] activities. In particular, complexes of salicylaldehyde benzoylhydrazone are potent

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970903160972

inhibitors of DNA synthesis and cell growth [9]. This hydrazone also has mild bacteriostatic activity and a range of analogs has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia [10]. Antibacterial and antifungal properties of 2,6-diacetylpyridine bis(acylhydrazone) and their complexes with some first row transition metal ions were reported by Carcelli *et al.* [11]; the iron complexes were more active than the free ligand.

Nickel is an important element in nature with six nickel-containing enzymes identified, CO-dehydrogenase, acetyl-CoA synthase, [Ni–Fe] hydrogenase, methyl–CoM reductase, urease, and NiSOD [12]. Some interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials MOCUD and sol-gel processes, the preparation of nanoscopic dendrimers incorporating nickel, the construction of 3-D hybrid inorganic–organic porous materials with Ni-coordination units and fabrications of supported Ni catalysts and Ni nanostructures through nanotechnology. High spin nickel(II) is important in molecular magnetism, culminating in the recent discovery of the first single molecule magnets based on nickel(II) [13].

Disalicylaldehyde oxaloyldihydrazone is a polyfunctional ligand containing amide, azomethine, and phenol in duplicate; the benzene ring of hydrazone has been replaced by another acylhydrazone. In this dihydrazone, the two hydrazones are directly bonded to one another giving better multidentate character than salicylaldehyde benzoylhydrazone. Depending on the preferred stereochemical disposition of the metal, it offers alternate modes of bonding, capable of giving mononuclear and polynuclear complexes. Further, this dihydrazone is related to 2,6-diacetylpyridine bis(acylhydrazones) in the sense that the oxaloyl-fragment of the ligand is capable of imposing planarity over the two hydrazone parts as the pyridine ring exerts in 2,6-diacetylpyridine bis(acylhydrazone).

Although a few complexes of the nickel(II) with dihydrazone derived from condensation of salicylaldehyde and related o-hydroxy aromatic aldehydes and ketones with malonoyldihydrazine and other acyldihydrazines, aroyldihydrazines, and pyridoyldihydrazines have been reported [14–17], there is no study on metal complexes of the disalicylaldehyde dihydrazone containing an oxaloyl-fragment.

The medicinal importance of hydrazones and their metal complexes and importance of nickel in biological systems and material science and absence of work on metal complexes of disalicylaldehyde oxaloyldihydrazone (H_4slox, figure 1) led to the study of nickel(II) complexes with the title ligand. This article describes the synthesis, characterization and stereochemical investigation of metal complexes derived from reaction of nickel acetate with the title ligand under different experimental conditions.

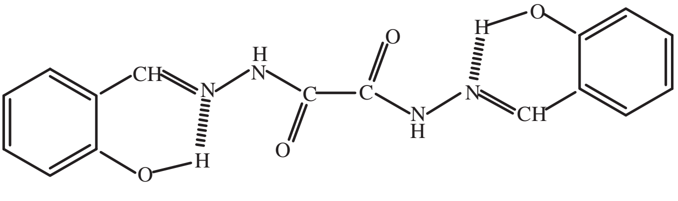


Figure 1. Disalicylaldehyde oxaloyldihydrazone (H_4slox).

2. Experimental

All reagents were commercial grade materials used without purification. The ligand disalicylaldehyde oxaloyldihydrazone (H_4L) was prepared in two steps. In the first step, oxaloyldihydrazine (ODH) was prepared by reacting diethyl oxalate (10.30 g, 7.33 mmol) in ethanol (30 mL) with hydrazine hydrate (7.70 g, 15.4 mmol). The product was recrystallized from hot water. In the second step, disalicylaldehyde oxaloyldihydrazone was prepared by reacting a warm dilute ethanol solution (100 mL) of oxaloyldihydrazine (2.00 g, 1.70 mmol) with salicylaldehyde (5.08 g, 4.24 mmol). The product was suction filtered, washed with ethanol and dried over anhydrous $CaCl_2$ [Yield: 82%] (m.p. 284°C). Anal. Calcd for $C_{16}H_{14}N_4O_4$ (%): C, 58.90; H, 4.29; N, 17.18. Found: C, 58.42; H, 4.24, N, 17.17. λ_{max}(nm) (ε_{max}) ($dm^3\,mol^{-1}\,cm^{-1}$): 293(10461), 303(10494), 340(11225).

Carbon, hydrogen, and nitrogen chemical analyses were performed using a Perkin-Elmer 240C microanalyser. The nickel content of the complexes was estimated gravimetrically as nickel dimethyl glyoximate [18]. IR spectra were recorded on either Perkin-Elmer model 983 spectrophotometer or Nicolet-Impact 410 FT-IR spectrophotometer from KBr pellets in the 4000–400 cm^{-1} range. UV-Vis spectra for the complexes from 200 to 1000 nm were recorded on a Perkin-Elmer Lambda-25 spectrophotometer. Magnetic susceptibility measurements were performed using a Sherwood Magnetic Susceptibility Balance. Molar conductances of 10^{-4} M complexes in DMSO were measured on a Direct Reading Conductivity meter-304 with a dip type conductivity cell at room temperature.

2.1. *Preparation of the complexes*

2.1.1. Synthesis of [Ni(H_2slox)(H_2O)$_3$] (1). H_4slox (1.00 g, 3.07 mmol) was suspended in methanol (60 mL) with constant stirring for 15–20 min. To this homogeneous suspension was added slowly a solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.77 g, 3.10 mmol) in methanol (30 mL) with constant stirring over 30 min maintaining $Ni(OAc)_2 \cdot 4H_2O$ and H_4slox molar ratio at 1.01 : 1. The resulting mixture was refluxed for 1 1/2 h which precipitated a greenish yellow compound which was then suction filtered and purified by washing several times with 10 mL hot methanol, each time, followed by ether and finally dried over anhydrous $CaCl_2$. Yield: 86.5%.

2.1.2. Synthesis of [Ni_2(slox)(H_2O)$_4$] (2); [Ni_2(slox)(A)$_4$] (where A = pyridine (py, 3), 2-picoline (2-pic, 4), 3-picoline (3-pic, 5), 4-picoline (4-pic, 6)); [Ni_2(slox)(NN)$_3$] (where NN = 1,10-phenanthroline (phen, 7) and 2,2′-bipyridine (bpy, 8). Preformed H_4slox (0.50 g, 1.53 mmol) was suspended in hot methanol (30 mL) with continuous stirring. This homogeneous suspension was added to a hot solution of $Ni(OAc)_2 \cdot 4H_2O$ (1.14 g, 4.58 mmol) in methanol (40 mL) over 15–20 min accompanied by constant stirring and the mixture refluxed for about 3 h giving a greenish yellow precipitate which was suction filtered hot and purified by washing several times with 10 mL hot methanol, each time, followed by ether and finally dried over anhydrous $CaCl_2$. Yield: 82.3%.

The complexes [Ni_2(slox)(A)$_4$] (where A = pyridine (py, **3**), 2-picoline (2-pic, **4**), 3-picoline (3-pic, **5**), 4-picoline (4-pic, **6**)) were prepared by the above procedure by adding 1.82 mL of pyridine, 2-picoline, 3-picoline, and 4-picoline, respectively, to the suspension of [Ni_2(slox)(H_2O)$_4$] in methanol (30 mL) and refluxing for 1 h. Yield: 74–76%.

The complexes [Ni_2(slox)(NN)$_3$] (where NN = phen, **7** and bpy, **8**) were prepared by following the above procedure using 1.17 g (5.90 mmol) of 1,10-phenanthroline and 0.92 g (5.89 mmol) of 2,2′-bipyridine instead of pyridine, maintaining the molar ratio of [Ni_2(slox)(H_2O)$_4$] and bidentate ligand at 1 : 3. Yield: 70–72%.

3. Results and discussion

The complexes together with their colors, decomposition points, analytical, molar conductance, magnetic moment, and electronic spectral data are presented in table 1. The general compositions are: [Ni(H_2slox)(H_2O)$_3$] (**1**), [Ni_2(slox)(A)$_4$] (where A = H_2O (**2**), py (**3**), 2-picoline (**4**), 3-picoline (**5**), 4-picoline (**6**)), [Ni_2(slox)(NN)$_3$] (phen (**7**), bpy (**8**)).

These complexes are greenish yellow, yellow or brown, have a very high decomposition point and are air stable. All the complexes are insoluble in common organic solvents but soluble in DMF and DMSO.

3.1. *Thermal studies*

Complexes **1** and **2** show loss of weight corresponding to three and four water molecules at 180°C indicating that they are coordinated to nickel. Complexes **3**–**8** show weight loss at 220°C corresponding to four pyridine/substituted pyridine molecules and three 1,10-phenanthroline/bipyridine molecules. The loss of these donor molecules at such a high temperature suggests that they are present in the first coordination sphere [19].

3.2. *Molar conductance*

The molar conductivity values for all the complexes in DMSO were in the range 2.5–3.9 $\Omega^{-1}\,cm^2\,M^{-1}$ suggesting nonelectrolytes [20].

3.3. *Magnetic moment*

Complex **1** has magnetic moment value of 3.10 BM, in the range for high spin octahedral nickel(II) complexes [21]. The magnetic moment values for **2**–**6** lie in the range 2.94–3.10 BM i.e. 1.47–1.55 BM per nickel(II) ion. Such a value rules out low-spin square planar stereochemistry. These values are considerably less than the values expected for two spin-free nickel(II) ions present in the same molecular unit, indicating strong metal–metal interaction in the structural unit of the complexes. Anomalous magnetic moment values in the solid state have been explained on the basis of absorption spectra by proposing mixed octahedral and square planar stereochemistry due to molecular association [22], but the electronic spectra of the complexes are consistent with their tetragonally distorted octahedral stereochemistry. Hence, it is

Table 1. Decomposition point, analytical, molar conductance, magnetic moment, and electronic spectral data for nickel(II) complexes.

			Elemental analysis: Found (Calcd)%						
No.	Complex	D.P. (°C)	M	C	H	N	Molar conductance Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$)	Magnetic Moment μ_{eff} (BM)	Electronic spectral band λ_{max} (nm) (ε_{max}) ($dm^3\,M^{-1}cm^{-1}$)
1	$[Ni(H_2slox)(H_2O)_3]$	>300	13.76 (13.44)	44.25 (43.97)	4.10 (4.12)	13.11 (12.82)	2.5	3.10	303(9053) 333(8350) 420(5720) 619(95) 932(55)
2	$[Ni_2(slox)(H_2O)_4]$	>300	22.62 (22.95)	38.00 (37.55)	3.17 (3.13)	11.15 (10.95)	3.1	2.94	297(9786) 306(8971) 432(5884) 615(69) 929(32)
3	$[Ni_2(slox)(py)_4]$	>300	15.93 (15.53)	57.41 (57.16)	3.68 (3.70)	14.66 (14.82)	2.9	2.96	295(9903) 307(8895) 431(5884) 617(69) 931(33)
4	$[Ni_2(slox)(2\text{-}pic)_4]$	>300	14.91 (14.46)	59.60 (59.12)	4.40 (4.43)	13.92 (13.79)	2.6	2.99	297(9899) 308(8746) 429(5959) 628(69) 946(31)
5	$[Ni_2(slox)(3\text{-}pic)_4]$	>300	14.82 (14.46)	58.82 (59.12)	4.47 (4.43)	14.05 (13.79)	3.0	2.98	296(9939) 307(8895) 426(5951) 633(67) 941(31)
6	$[Ni_2(slox)(4\text{-}pic)_4]$	>300	14.06 (14.46)	58.75 (59.12)	4.41 (4.43)	14.13 (13.79)	2.9	3.10	298(9898) 307(8890) 412(5947) 623(70) 940(32)
7	$[Ni_2(slox)(phen)_3]$	>300	11.81 (11.35)	60.51 (60.35)	3.04 (3.09)	13.84 (13.54)	3.7	4.95	297(7000) 307(7043) 397(4137) 629(86) 950(52)
8	$[Ni_2(slox)(bpy)_3]$	>300	13.26 (12.93)	60.32 (60.80)	3.55 (3.52)	15.17 (15.42)	3.9	4.80	297(9900) 308(8746) 426(5955) 622(69) 932(43)

Table 2. Electronic spectral bands and ligand field parameters for the nickel(II) complexes.

No.	$^3A_{2g} \rightarrow {}^3T_{2g}$ (F)		$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)		Dq	ν_2/ν_1	B	β	β°	LFSE
1	10730	932	16155	619	1073.0	1.506	607.36	0.585	41.5	36.9
2	10764	929	16260	615	1076.4	1.511	619.61	0.597	40.3	37.0
3	10741	931	16207	617	1074.1	1.509	614.75	0.592	40.8	36.9
4	10571	946	15924	628	1057.1	1.506	599.95	0.578	42.2	36.3
5	10627	941	15798	633	1062.7	1.487	564.72	0.544	45.6	36.5
6	10638	940	16051	623	1063.8	1.509	608.75	0.586	41.4	36.5
7	10526	950	15898	629	1052.6	1.510	605.42	0.583	41.7	36.2
8	10730	932	16077	622	1073.0	1.500	592.79	0.571	42.9	36.9

suggested that the lowering of magnetic moment in these complexes is due to the presence of oxo-bridged structure [23].

Complexes **7** and **8** have higher magnetic moment values of 4.95 and 4.80 BM, respectively, 2.48 and 2.40 BM per metal ion. The μ_{eff} value per metal ion is again less than the value required for two unpaired electrons, suggesting some antiferromagnetic interaction between the two metal centers. The antiferromagnetic interaction in these complexes is less than those in **2**–**6** which may be attributed to coordination of phen and bpy preventing oxo-bridging.

3.4. *Electronic spectra*

Important electronic spectral bands for the ligand and complexes are presented in table 1, along with their molar extinction coefficients.

All the complexes show two weak bands in the regions 907–946 and 617–650 nm, in addition to ligand bands, described as $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transitions, respectively. The positions of these bands suggest that these complexes have tetragonally distorted octahedral stereochemistry.

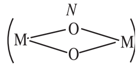
The ligand field parameters [24], namely, Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10 Dq), covalency factor (β) and ligand field stabilization energy (LFSE) have been calculated for **1**–**8** (table 2).

Values of ν_2/ν_1 for tetragonal complexes are 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 [25] gradually lowers the ratio ν_2/ν_1 from the theoretical value 1.80–1.50–1.70 and values 1.60–1.70 are common for nickel(II) complexes of octahedral symmetry. In the present complexes the ν_2/ν_1 values lie in the range from 1.49 to 1.51, slightly lower than usual octahedral complexes but within the range reported for octahedral complexes [26]. These low values indicate a strong interaction between $^3T_{1g}$ (P) and $^3T_{1g}$ (F) states of nickel(II). The ligand field stabilization energies for **1**–**8** lie in the range 36.2–37.0 kcal mol^{-1}.

3.5. *Infrared spectra*

Comparison of the IR spectra of the free dihydrazone (H_4slox) with those of the complexes suggests that it is present in keto-enol form in **1** and enol form in the remaining complexes (table 3).

Table 3. Infrared spectral data for **1**–**8**.

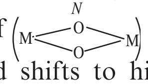
Compound	N(OH) + N(NH)	ν(C=O)	ν(C=N)	Amide II + ν(C–O)	ν(NCO$^-$)	ν(C–O)	ν(N–N)	N(M–O) (phenolic)	ν(M–O) (carbonyl)	
H_4slox	3278(s) 3204(s) 3050(s)	1667(s)	1627(s) 1603(s)	1534(s)	–	1262(s)	1035(m)	–	–	–
1	3400(s) 3279(s) 3200(s)	1668(m)	1608(s)	1537(s)	–	1304(s)*	1042(w)	581(w)	469(w)	–
2	3374(s)	–	1625(s) 1600(s)	1551(s)	1533(s)	1306(s)*	1048(w)	592(m)	461(w)	810(w)
3	3415(s)	–	1600(s)	1557(s)	1530(s)	1304(s)*	1040(w)	596(m)	464(w)	812(w)
4	3367(s)	–	1626(s) 1600(s)	1551(s)	1533(s)	1307(s)*	1047(w)	599(m)	463(w)	818(w)
5	3392(s)	–	1622(s) 1600(s)	1553(s)	1532(s)	1307(s)*	1049(w)	598(m)	476(w)	816(w)
6	3410(s)	–	1618(s) 1599(s)	1551(s)	1503(s)	1299(s)	1040(w)	597(w)	493(m)	814(w)
7	3379(s)	–	1609(s) 1588(s)	1555(s)	1516(s)	1277(s)	1045(w)	565(w)	441(w)	–
8	3375(s)	–	1610(s) 1598(s)	1558(s)	1513(s)	1275(s)	1024(m)	560(w)	434(w)	–

*Merged with ligand band.

Bands at 3278, 3204, and 1667 cm^{-1} in the free ligand arise due to the stretching of phenolic –OH, secondary –NH and >C=O, respectively, in accord with literature reports [27–34]. The IR spectrum of **1** shows these bands in almost the same position as the uncoordinated dihydrazone but considerably reduced in intensity, indicating that half of the ligand remains unbonded. IR spectra of **2**–**8** do not show any band in these regions. The absence of band due to phenolic –OH in the IR spectra of the complexes indicates deprotonation and involvement in bonding to the metal while the absence of band due to stretching vibration of secondary –NH group and >C=O group indicates that the secondary –NH and carbonyl groups are absent upon complexation with metal, probably from enolization [27, 29, 34].

The ligand shows very strong bands at 1627 and 1603 cm^{-1} due to >C=N stretching. This band is a single strong band at 1608 cm^{-1} in **1** while as a couple of strong intensity bands in the region 1626–1588 cm^{-1} in the remaining complexes [34–36]. The average position of ν(C=N) shifts to lower frequency by 2–7 cm^{-1} in all of the complexes except **7** and **8**, where the shift to lower frequency is 17 and 11 cm^{-1}, respectively. The shift of ν(C=N) to lower frequency indicates coordination of the dihydrazone through azomethine. The appearance of ν(C=N) as a single band in **1** suggests that the dihydrazone coordinates to nickel in staggered configuration, while the splitting of ν(C=N) into two bands in **2**–**8** suggests that the dihydrazone is bonded to nickel in anticis configuration [29, 37].

Free dihydrazone has a strong band at 1534 cm^{-1} assigned to mixed contribution of the amide II and ν(C–O). This band shifts to higher frequency by 3 cm^{-1} in **1**. Such a small positive shift indicates coordination of phenolate to the metal center but precludes the possibility of bridging phenolate [38]. A positive shift of about 17–24 cm^{-1} is observed for this band in **2**–**6**, indicative of involvement of phenolate bridging [39]. The shift of ν(C–O) (phenolate) by about 17–24 cm^{-1} indicates phenolate oxygen bonding to the metal. A new strong intensity band at 1503–1533 cm^{-1} in all of the complexes except **1** is assigned to stretching of the newly created NCO$^-$ [40]. The ν(NCO$^-$) confirms the presence of dihydrazone in enol form in **2**–**8**. The intensity of the band at 1537 cm^{-1} has considerably increased in **1** as this band has contribution due to ν(C-O) (phenolate) and ν(NCO$^-$); suggesting involvement of phenolate C–O and enolate C–O in bonding via enolization of half of the dihydrazone.

Complexes **2**–**6** show a weak band at 810–820 cm^{-1}, observed in neither the IR spectra of the uncoordinated ligand nor in **1**, **7**, and **8**. Hence, this band is assigned to stretching vibration of  [41]. The weak band at 1035 cm^{-1} in the ligand is assigned to ν(N–N) and shifts to higher frequency by 5–14 cm^{-1} in the complexes indicating involvement of only one nitrogen of N–N in coordination [42]. New weak to medium bands in the region 560–599 cm^{-1} and a weak band at 434–476 cm^{-1} in **1**–**8** are assigned to stretch of Ni–O (phenolic) and Ni–O (enolized carbonyl) [43].

Free pyridine absorbs around 604 cm^{-1} due to in-plane ring deformation mode [43]. In the complexes a weak band is observed in the region 600–620 cm^{-1}, assigned to in-plane deformation of pyridine and substituted pyridine indicating their coordination to the metal. In **7** strong intensity bands are observed at 726 and 848 cm^{-1} assigned to out-of-plane motion of the hydrogens on the heterocyclic rings and the hydrogens on the center ring of 1,10-phenanthroline, respectively [44]. In the bipyridine complex only one band is observed at 736 cm^{-1} due to out-of-plane motion of the hydrogens as expected for two identical groups of four hydrogens [45].

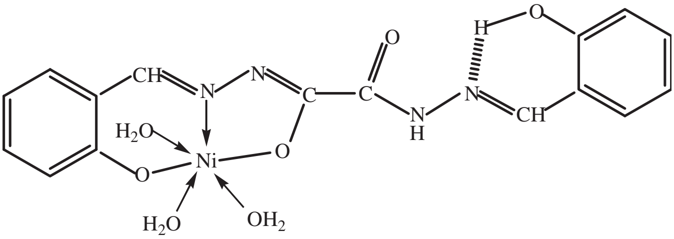


Figure 2. Tentative structure for $[Ni(H_2slox)(H_2O)_3]$ (**1**).

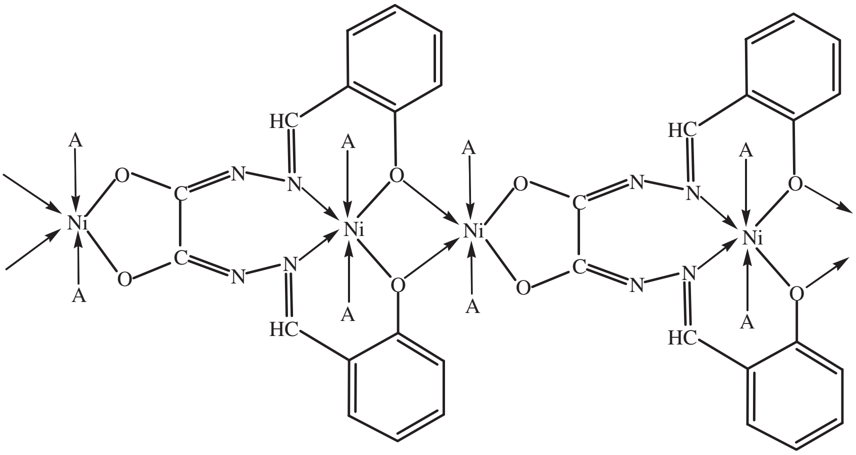


Figure 3. Tentative structure for $[Ni_2(slox)(A)_4]$ (where $A = H_2O$ (**2**), py (**3**), 2-pic (**4**), 3-pic (**5**), 4-pic (**6**)).

Complexes **7** and **8** also show a medium broad band at 648 and $652\,cm^{-1}$ assigned to in-plane ring deformation of 1,10-phenanthroline and 2,2′-bipyridine indicating coordination to the metal.

4. Conclusion

We have described mononuclear, binuclear, and polynuclear complexes and characterized them from physico-chemical and spectroscopic studies. The dihydrazone is bonded in **1** as a dibasic tridentate ligand through phenolate oxygen, enolate oxygen, and azomethine nitrogen. In the remaining complexes, the dihydrazone coordinates tetrabasic hexadentate through both phenolate oxygens, both enolate oxygens, and both azomethine nitrogens. In **2**–**8**, one metal is bonded to two phenolate oxygens and two azomethine nitrogens with NNOO coordination while the other metal is bonded to two enolate oxygens. In **2**–**6**, the metal bonded to enolate oxygens is tethered to another metal through phenoxide bridging leading to extended structure giving rise to polynuclear complexes. In **7** and **8**, no bridging is present, due to coordination of bipyridine and phenanthroline. The dihydrazone coordinates in staggered configuration in **1** and anticis configuration in **2**–**8**. Water, pyridine, substituted pyridine, bipyridine,

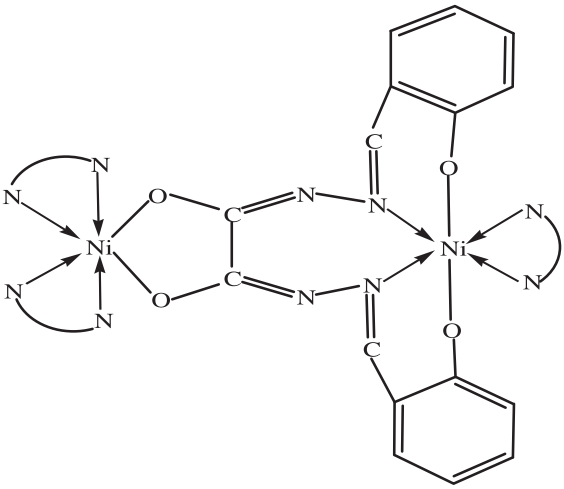


Figure 4. Tentative structure for [Ni_2(slox)(NN)$_3$] (where NN = phen (**7**) and bpy (**8**)).

and phenanthroline are coordinated to the metal. Complex **1** is normal paramagnetic corresponding to one high-spin nickel(II) while **7** and **8** possess magnetic moment values for four unpaired electrons corresponding to two nickel(II) ions per dihydrazone with no metal–metal interaction. Complexes **2**–**6** possess anomalously low values of magnetic moment indicating metal–metal interaction. All the complexes possess distorted octahedral stereochemistry around the metal. The tentative structures for the complexes are shown in figures 2–4.

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