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Synthesis, Spectral and Magnetic Properties of Ternary Nickel (II) Complexes with Acid Hydrazones and Heterocyclic Bases

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Abstract

A series of nickel(II) complexes have been synthesized by the reaction of nickel(II) acetate with some hydrazones in presences of heterocyclic bases like 2 2′-bipyridine and 1, 10- phenanthroline and characterized by analytical and other spectral techniques, like IR, far IR, and UV-Vis spectral studies and magnetic susceptibility studies.

Keywords: Ni^{II} complexes; Acid hydrazones; pseudo octahedral, magnetic susceptibility, ternary complexes.

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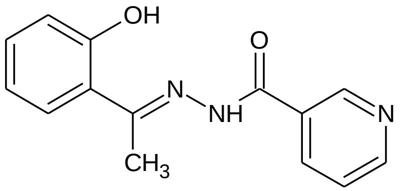
1 Introduction

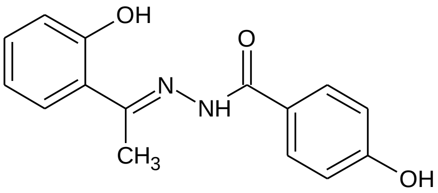
Synthesis, structural investigations and reactions of Schiff bases and their transition metal complexes have received a renewed attention in recent years. The discovery and development of new, more effective cancer medicines is the one of the main goal of present day of medicine and chemical investigation. Recently the discoveries of antitumor effects of inorganic and particularly of metal complexes and their use to cure cancer disease have received increasing attention. Metal chelation is very important process, useful both to remove toxic metals from polluted environment and to afford new chemical features to metal complexes in order to make them suitable for practical purposes, for instance practical application.

Nickel(II) has been chosen since its trace presence is now recognized to be essential for bacteria, plants, animals and human [1], and it is also known that many nickel complexes which are coordinately unsaturated, can behave as Lewis acids. Nickel (II) complexes with N_2O_2 Schiff base ligands derived from salicylaldehyde have long been used as homogeneous catalysts. [2-5]

In this work we report the syntheses, spectral and magnetic properties of ternary nickel (II) complexes containing acid hydrazones like 2-hydroxyacetophenone nicotinic acid hydrazone (H_2L^1), 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazone (H_2L^2), salicylaldehyde nicotinic acid hydrazone(H_2L^3) and 2-hydroxyacetophenone benzoic acid hydrazone (H_2L^4), and heterocyclic bases like 2, 2′ bipyridine/ 1, 10 phenanthroline, and one binary complexes of dianionic acid hydrazone. Structures of hydrazones are shown below.



H_2L^1



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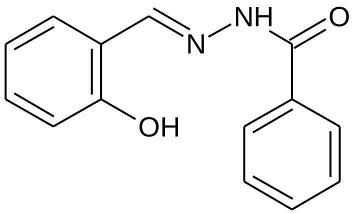
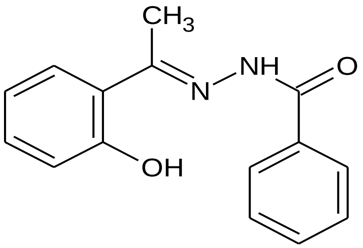


H_2L^3



H_2L^4

1.2 Results and Discussion

1.2.1 Syntheses of nickel (II) complexes

The colors and partial elemental analyses complexes are presented in Table 1. The elemental analyses data are consistent with 1:1:1 ratio of the metal ion : hydrazone : heterocyclic base for the complexes prepared except for $NiL^1.H_2O$. One or two molecules of water are also present in the complex. The ligand H_2L gets double deprotonated and coordinates as L^{2-}. The complexes are insoluble in most of the common polar and non polar solvents. They are partially soluble in DMF and DMSO. The conductivity measurements in DMF showed that all the complexes are non electrolytes.

Compound	Color	Analytical data found (calculated)			μ_{eff} BM	Proposed geometry
		C%	H%	N%		
$NiL^1bipy2H_2O$	Reddish orange	56.9 (57.2)	3.99 (4.60)	13.92 (13.89)	2.76	Pseudo octahedron
NiL^1H_2O	Yellow	58.86 (59.02)	4.69 (4.45)	10.30 (10.56)	1.18	Square planar
NiL^2bipyH_2O	Reddish orange	64.28 (64.64)	4.87 (4.98)	9.67 (10.01)	3.10	Pseudo octahedron
NiL^2phenH_2O	Reddish orange	65.70 (65.59)	4.68 (4.89)	9.29 (9.56)	3.21	Pseudo octahedron
$NiL^3bipy2H_2O$	Reddish orange	56.97 (56.36)	3.65 (4.32)	14.50 (14.29)	2.91	Pseudo octahedron
$NiL^3phen2H_2O$	Reddish orange	58.50 (58.43)	4.16 (4.12)	13.26 (13.62)	3.04	Pseudo octahedron
NiL^4bipyH_2O	Orange	62.61 (61.89)	4.33 (4.57)	11.50 (11.55)	2.71	Pseudo octahedron
$NiL^4phen2H_2O$	Reddish orange	61.33 (61.51)	3.99 (4.59)	10.45 (10.63)	2.57	Pseudo octahedron

Table 1. Color, magnetic moment and elemental analyses of nickel (II) complexes

Magnetic Moment Measurements

The magnetic moment measurements were done using vibrating sample magnetometer and calculations were made using computed values of Pascal constants for diamagnetic corrections. The magnetic moment of the polycrystalline states at 300 K of the complexes were found to be 1.18-3.2 BM.

Nickel(II) complexes show diamagnetic behavior consistent with square planar environment or paramagnetic behavior consistent with an octahedral geometry and tetrahedral environment around metal atom. Five coordinate geometry is quite unusual among the nickel(II) complexes. Octahedral nickel(II) has an orbitally nondegenerate $^3A_2$ ground state and magnetic moments are in the range of 2.8-3.3 BM, which is very close to spin only value 2.8.

Tetrahedral nickel (II) has a $^3T_1$ ground state and magnetic moments are in the range of 4-4.3 BM. Both tetrahedral and octahedral have two unpaired electrons, but tetrahedral ones having higher magnetic moments. Nyholm had suggested an inverse relationship exists between magnetic moments and the distortion from tetrahedral geometry.

The magnetic moment of four coordinated $NiL^1 \cdot H_2O$ are expected to be 1.18 BM which is very low compared to the reported values for the tetrahedral complexes. Such low values are reported in the literature. Though square planar nickel (II) complexes are diamagnetic, there are some reports on weakly paramagnetic nickel(II) complexes[6]. To explain this phenomenon equilibrium between spin free and spin paired configuration is suggested. The anomalous low moments could be due to equilibrium in the solid state between the square planar and tetrahedral structures [7] or could be due to a partial population of spin triplet state close to the idealized ground state ^1A_1g for D_4h symmetry [8-9]. The low values reported for nickel (II) complexes, which are thought to arise from quenching of orbital contribution to the magnetic moment due to distortion D_3h symmetry or due to strong in plane π bonding and axial ligation as has been found in some other nickel(II) complexes [10-12].

As the consequences of interaction among nickel atom with the free electron pairs of the heteroatoms of the neighboring molecules, which leads to extension of coordination number can also leads to the paramagnetism of the square planar nickel(II) complexes [13]. The paramagnetic property of four coordinate nickel(II) systems is also because of the spin cross over phenomenon. By molecular orbital calculation, it has been shown that for planar paramagnetic nickel(II) splitting of the highest occupied molecular orbital is small and contribution of the spin free configuration to ground state should be apparent [14]. This paramagnetic behavior is because of the equilibrium between diamagnetic spin paired ground state and low lying triplet state [15]. Unfortunately, our attempts to prepare single crystals of the compound $NiL^1 \cdot H_2O$ have so far been unsuccessful; hence the confirmation of the geometry of the compound was based on the electronic spectra of the compound.

Infrared Spectral Analyses

Compound H_2L^1, H_2L^2, H_2L^3 and H_2L^4 show a band around 3400 and 3100 cm^{-1}, which are due to -OH stretching mode and -NH stretching mode of free -OH group and -NH respectively. These bands are absent in complexes, which suggest deprotonation of the phenolic group indicating the coordination through phenolic oxygen, and enolisation of the carbonyl group, followed by deprotonation. On coordination the azomethine nitrogen shifts to a lower wavenumber by ~20 cm^{-1}. The mode of coordination of carbonyl oxygen is expected upon deprotonation of the ligand. The spectral band of -NH disappears in the complex, which indicates the enolisation followed by deprotonation and the coordination through the carbonyl oxygen. Another band which is considered to be sensitive to this coordination is the -N-N which shifts to a higher wavenumber in complex, due to the increase in the double bond character of -N-N bond. A newly formed C-O bond as the result of the enolisation gives two bands at ~1360 and ~1470 cm^{-1}. The IR spectra show a sharp band at ~1500 cm^{-1} indicating the newly formed -N=C, suggesting the coordination of hydrazone in the form of enolate rather than keto form. The spectrum of the complexes exhibit a symmetric shift in the position of the band in the region 1600-1350 cm^{-1} due to -C=C and -C=N vibrational modes and their mixing patterns are different from those present in ligands spectra.

In the case of octahedral complexes, the nitrogen atoms of the heterocyclic bases occupy the fourth and fifth positions. The heterocyclic ring breathing is observed in the finger print region, 1400-600 cm^{-1}. And the sixth position is occupied by water molecule. A broad band at ~ 3500 cm^{-1} confirms the presence of water molecule in the coordination sphere [16].

Compound	$\nu_{C=N}$	$\nu_{N=C}$	$\nu_{C\text{-}O}$	$\nu_{Ni\text{-}O}$	$\nu_{Ni\text{-}N}$
H_2L^1	1603				
NiL^1bipy	1593	1526	1357, 1466	518	490, 247
NiL^1H2O	1597	1534	1344, 1470	353	-
H_2L^2	1610				
NiL^2 bipyH_2O	1602	1497	1368, 1437	510, 353	492, 258
NiL^2phenH_2O	1599	1500	1367, 1437	353	248
H_2L^3	1609				
NiL^3 bipyH_2O	1602	1520	1359, 1447	344	482,253
NiL^3phenH_2O	1602	1517	1345, 1457	356	487, 254
H_2L^4	1609				
NiL^4 bipyH_2O	1589	1508	1364, 1430	520, 355	457, 248
NiL^4phenH_2O	1590	1504	1362, 1436		

Table 2: Selected IR frequencies of ligands and nickel (II) complexes (cm^{-1})

Electronic Spectral Analyses

The electronic spectra of the complexes were recorded in solid state and in DMF solution. All the complexes show π→π* transition in the range 40000-35714 cm^{-1} and n→π* at ~ 30000 and ~ 27000 cm^{-1}. The slight shift observed in these values of the complexes from the ligands is due to complexation. The bands observed in the range of 25000-18000 cm^{-1} are assigned to the charge transfer (CT) bands [17-18].

For the compound $NiL^1 \cdot H_2O$, absence of peaks at ~ 15000 cm^{-1} indicate absence of tetrahedral symmetry. For tetrahedral geometry the likely spin allowed transitions for the $3d^8$ nickel(II) complexes are ${}^3T_1(F) \rightarrow {}^3T_2$, ${}^3T_1(F) \rightarrow {}^3A_2$, ${}^3T_1(F) \rightarrow {}^3T_1(P)$. In most nickel (II) complexes with this stereochemistry, the ${}^3T_1(F) \rightarrow {}^3A_2$ transition occurs in the range 7000-9000 cm^{-1}, and the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition is observed in the range 14000-16000 cm^{-1} [20]. All these bands are absent in the case of $NiL^1 \cdot H_2O$ and there is no band at ~ 24000 cm^{-1}, which rules out the possibility of the tetrahedral – square planar equilibria in this compound [8]. The low energy band of this complex is broad and split in two components (at ~ 9000 and ~ 7200 cm^{-1}) indicating tetragonal distortion. The magnetic moment (~ 3 BM) lie in the region expected for octahedral complexes. The electronic spectrum of the compounds be assigned assuming that the stereochemistry pseudo-octahedral [16, 20].

Compound	$\pi\rightarrow\pi^*$	$n\rightarrow\pi^*$	CT	$^3T_2g\leftarrow{}^3A_2g$	$^3T_1g\leftarrow{}^3A_2g$	$^3T_1(P)\leftarrow{}^3A_2g$
NiL^1bipy	40000	29850, 28571	20000, 18518	9009	-	13385
NiL^1H_2O	35741	28571, 26455	18348		-	-
$NiL^2 bipyH_2O$	37037	30303, 28818	18415	7462	11765	-
NiL^2phenH_2O	35417	29418, 28985	18518		10416	-
$NiL^3 bipyH_2O$	35714	30303, 28571	18182	7692	11764	13166
NiL^3phenH_2O	39804	30303, 28571	19804, 18182	7792	11740	13385
$NiL^4 bipyH_2O$	37258	27027	25000, 17857	7201	10926	12287
NiL^4phenH_2O	37567	29980, 27895	23580, 19345	7320	11080	12342

Table 3: Electronic spectral data of nickel (II) complexes (cm^{-1})

Experimental

Materials

Nickel(II) acetate dihydrate (Merk) Salicylaldehyde (BDH), 2-hydroxyacetophenone (BDH), benzoic acid hydrazide(Fluka), 4-hydroxybenzoic acid hydrazide (Fluka) and nicotinic acid hydrazide (Fluka) were of Analar grade and used without further purification. All the solvents were dried using standard methods before use.

Syntheses of the Complexes

All the above-mentioned complexes were synthesized using the following general method. Nickel (II) acetate dihydrate (1 mmol) was dissolved in water. To a stirred ethanolic solution of acid hydrazone (1 mmol) and 2, 2′-bipyridine / 1, 10 phenathroline (1 mmol), nickel solution was added. Resultant homogeneous brown solution was stirred for 3 h. The product formed was filtered and washed with cold ethanol, followed by ether, and dried *in vacuo* over P_4O_{10}. Unfortunately we are unable to grow single crystals suitable for single crystal XRD for any of these complexes.

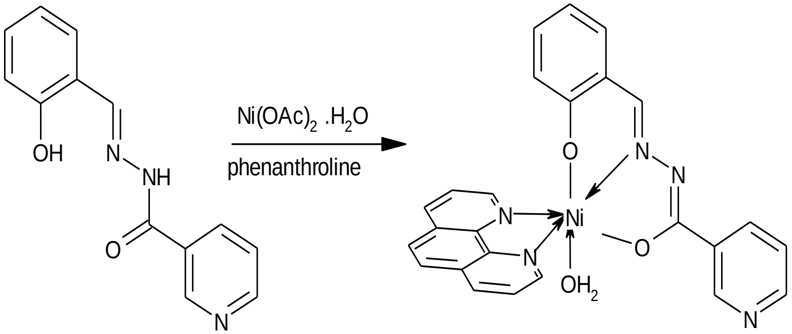


Fig. 1. Scheme of the synthesis of NiL^{3}phen

Analytical Method

Elemental analyses were carried out using a Heraeus Elemental Analyzer at RSIC, CDRI, Lucknow, India. IR spectra, in the range of 4000-400 cm^{-1} were recorded on a Shimadzu DR 8001 series FTIR instrument as KBr pellets. Solid-state reflectance spectra were recorded on Ocean Optics, Inc. SD2000 Fiber Optic Spectrometer. The magnetic moment measurements were done using vibrating sample magnetometer, Indian Institute Technology, Roorkee, India. Far-IR spectra were recorded in polyethylene matrix on an IFS 66 V FT IR Spectrometer in the range of 500-50 cm^{-1}.

Conclusion

A series of nickel(II) ternary complexes of acid hydrazones were synthesized and characterised. The coordination geometry around nickel(II) in all complexes except for $NiL^2 \cdot H_2O$ is octahedral with one dibasic tridentate ligand L^{2-}, and one bidentate heterocyclic base. A water molecule occupies the sixth position. The coordination takes place through the deprotonated hydroxyl group azomethine nitrogen and oxygen from the hydrazide moiety. All electronic transitions were assigned. The values are consistent with pseudo- octahedral structure. All the compounds were found to be paramagnetic.

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