



Synthesis and Characterisation of Nickel Metal Complexes Derived From Novel Hydrazone Derivatives

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ABSTRACT The nickel(II) complexes were prepared from nickel sulphate and hydrazone derivatives. The hydrazone ligands were synthesized by the condensation of 2-hydroxy benzoyl hydrazide with various aldehydes viz. p-methoxybenzaldehyde, benzaldehyde, p-methylbenzaldehyde, p-bromobenzaldehyde and α -naphthaldehyde. These hydrazone derivatives and nickel(II) metal complexes have been characterized by elemental analysis and various physicochemical techniques such as IR, ¹H-NMR, mass spectroscopy, electronic absorption, molar conductance, magnetic susceptibility and TG-DTA analysis.

KEYWORDS

Nickel sulphate; 2-hydroxy benzoyl hydrazide; Aldehydes; characterization.

INTRODUCTION

Transition metal complexes with hydrazone derivatives have been amongst the widely studied co-ordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemicals, analytical and antimicrobial fields¹. The Ni(II) complexes of hydrazone derivatives are known for their versatile coordination. The ligands exhibit keto-enol tautomerism and containing donor atoms like N, O are important to prepare metal complexes which shows biological activity. The presence of functional group, usually hydroxyl, azomethine, sufficiently near the site of coordination in the hydrazone ligands, gives a five or six membered chelate ring on reaction with metal ion, which shows structural variations depending upon the type of substituent present on aromatic ring².

EXPERIMENTAL

Materials and Methods

All the chemicals used were of the analytical grade (AR) and of highest purity. The 2-hydroxy benzoyl hydrazide was prepared by the method reported³ in the Vogel. The ester like methyl salicylate and hydrazine hydrate 80% were obtained from HIMEDIA while aldehydes such as p-methoxybenzaldehyde, benzaldehyde, p-methylbenzaldehyde, p-bromobenzaldehyde, α -naphthaldehyde and nickel sulphate were obtained from THOMAS BAKER. Solvents like ethanol whenever used were distilled and purified according to standard procedures³.

Melting point of ligands was taken in open capillary and was uncorrected. The UV-Vis spectra were recorded on Chemito uv 2600 Double Beam UV-Vis spectrophotometer. IR spectra of all the ligands were recorded in KBr on a Perkin-Elmer Precisely Spectrum 100 FT-IR Spectrometer in the region 4000-400 cm⁻¹. ¹H-NMR spectra was recorded in DMSO on a Bruker 300MHz Spectrometer, Mass spectra were recorded on a GCMS.

The 10⁻³M solution in DMSO of each of the complexes was prepared to measure molar conductance using EQUIPTRONICS conductivity meter model no. EQ-660A with a dip-type conductivity cell fitted with platinum electrode (cell constant = 1.0 cm⁻¹). The magnetic susceptibility at room temperature were measured using Gouy's method and diamagnetic corrections for the ligand component applied using Pascal's constant to calculate effective magnetic moments⁴. The Rigaku Thermo Plus-8120 TG-DTA instrument was used for TG-DTA.

Preparation of 2-hydroxy benzoyl hydrazide from corresponding ester

A mixture of methyl salicylate (1.3 ml, 10 mmol) and hydrazine hydrate 80% (1.2 ml, 20 mmol) were refluxed in ethanol for 3hrs on water bath. The resulting reaction mixture was allowed to cool to room temperature. The separated product was filtered washed with ethanol and purified by recrystallisation from ethanol (yield 85%).

Synthesis of hydrazones with various aldehydes

The solution (0.01 M) of 2-hydroxy benzoyl hydrazide in ethanol was taken in a two neck round bottom flask fitted with water condenser. Stirred for 10 min and heated gently on heating mantle to get clear solution. The solution of substituted aromatic aldehyde (0.01 M) in ethanol was added slowly to this stirred solution. This reaction mixture was further reflux on water bath for 3hrs. When this solution was cooled to room temperature, precipitate formed was separated by filtration and purified by recrystallization from ethanol (yield 80%).

Synthesis of nickel complexes

To a hot suspension of ligand (0.01M) in ethanol, an ethanolic solution (0.01M) of the metal salt nickel sulphate was added dropwise with constant stirring with the help of rotametal and refluxed for 3hrs. The resulting reaction mixture was cooled to room temperature and pH adjusted to 7.8 to 7.9 by aq. NH₃ and then refluxed it further for 30min. The resultant product was filtered, repeatedly washed with ethanol and dried at room temperature.

RESULTS AND DISCUSSION

All nickel metal complexes are brown, yellow solids (Table-1), soluble in DMSO. The complexes are non-hygroscopic and thermally stable having decomposition temperature more than 250°C indicating a strong metal-ligand bonding. The value observed for molar conductance of all complexes fall between 0.004 to 0.010 mhos.cm²mol⁻¹ in 10⁻³ M DMSO solution indicating^{5,6} the complexes are non-electrolytic in nature.

Table 1: Physical and analytical data of the complexes:

Complexes	Molecular Formula (Formula Wt.)	Yield %	Color	% Elemental analysis Found (calculated)				μ_{eff} (B.M.)
				Ni	C	H	N	
N1	[C ₁₅ H ₁₂ O ₂ N ₂ ·Ni·2H ₂ O] (633.2858)	80	Brown	9.27 (9.21)	56.90 (56.54)	4.77 (4.74)	8.85 (8.79)	2.94

N2	$[C_{28}H_{22}O_4N_4Ni \cdot 2H_2O] \cdot n$ (573.2342)	81	Brown	10.24 (10.17)	58.67 (58.26)	4.57 (4.54)	9.77 (9.71)	2.92
N3	$[C_{30}H_{26}O_4N_4Ni \cdot 2H_2O] \cdot n$ (601.2878)	79	Brown	9.76 (9.70)	59.93 (59.53)	5.02 (5.01)	9.32 (9.26)	2.93
N4	$[C_{30}H_{26}O_4N_4BrNi \cdot 2H_2O] \cdot n$ (651.1224)	78	Brown	9.01 (8.96)	51.65 (51.33)	3.71 (3.69)	8.60 (8.55)	2.97
N5	$[C_{36}H_{30}O_4N_4Ni \cdot 2H_2O] \cdot n$ (673.3498)	80	Yellow	8.72 (8.66)	64.22 (63.83)	4.49 (4.46)	8.32 (8.27)	2.91

Infrared Spectra

The FTIR spectra of the metal complexes (Table-2) were recorded in KBr over the range 4000-400 cm^{-1} . The FTIR spectrum of the free ligands show four characteristics bands at around 3260-3300, 3404, 1653 and 1607 cm^{-1} assignable to (-N-H), free (-O-H) stretching phenolic moiety, amide carbonyl (-C=O) and azomethine (-C=N), stretching mode respectively. The absence of a weak broad band in 3260-3300 cm^{-1} region, noted in the spectra of the metal complexes indicates^{7,8} deprotonation of bonded (-NH) group during complex formation and subsequent coordination of the oxygen of amide carbonyl to metal ion.

The ν (C=N) band is shifted to lower wavenumber with respect to free ligand, indicating that the nitrogen of azomethine group is coordinated to the metal ion, which was further confirmed by observation of the red shift in the ν (N-N) stretching frequency from 830 to 981 cm^{-1} region. New bands observed in the complexes at 2046 and 2218 cm^{-1} are attributed^{9,10} to the >C=N-N=C< group. The spectra of metal complexes showed a new band at around 500 cm^{-1} and 425 cm^{-1} for ν (Ni-O) and ν (Ni-N) vibrations respectively. Hence, coordination takes place via oxygen of amide and nitrogen of azomethine group of ligand molecule.

Table 2: Important IR spectral bands (cm^{-1}) of the complexes

Assignment	N1	N2	N3	N4	N5
ν (C=N)	1599	1589	1589	1587	1595
ν (N=C-O)	1507	1525	1529	1528	1508
ν (Ni-O)	509	552	493	494	510
ν (Ni-N)	430	423	431	423	430

Magnetic Susceptibility Measurement

The magnetic susceptibility measure for all the nickel(II) complexes at room temperature by the Gouy's method using $[Ni(en)_2]SO_4$ as a calibrant. The effective magnetic moments were calculated after applying diamagnetic corrections for the ligand components using Pascal's constants⁴. The room temperature μ_{eff} value for the nickel(II) complexes were found in the range 2.91-2.97 B.M., these magnetic susceptibilities of the complexes are consistent with octahedral geometry around the central Ni(II) metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

Electronic spectra

The electronic spectra of the metal complexes in DMSO (10⁻⁴ M) was recorded. The ground state nickel(II) in an octahedral coordination is $^3A_{2g}$. The electronic spectra of nickel(II) complexes display three absorption bands in the range of 11494-11415 cm^{-1} , 15037-14925 cm^{-1} and 27777-27397 cm^{-1} due to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ respectively, which indicates¹¹ the octahedral geometry of the nickel(II) complexes.

Thermal measurements

The simultaneous TG-DTA studies of the complexes (Table-3) was recorded on Rigaku Thermo Plus-8120 TG-DTA instrument in nitrogen atmosphere by increasing the temperature from room temperature up to 900°C at the heating rate of 10°C/min. All the complexes investigated shows similar behavior in their thermogram. In the first step the complex losses two water molecule in the temperature range between 100°C to 180°C indicates¹²⁻¹⁵ that the complex is thermally stable up to nearly 100°C above which it loses the water molecule.

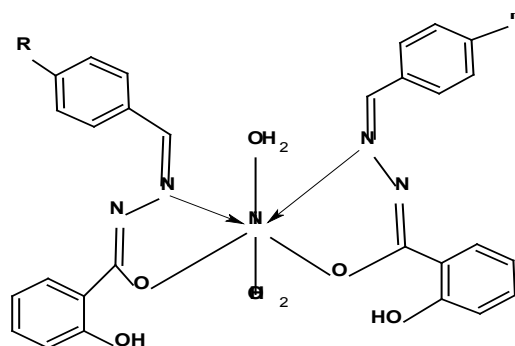
The DTA curve of complex displays an endothermic peak at 100°C, which is attributed to the loss of two water molecules. The dehydrated product is stable up to 180°C above that temperature the second step starts; complex loses some moiety C_6H_5CHON in the temperature range between 180°C to 360°C. The complex loses another moiety in the temperature range 360°C to 560°C which could be attributed due to loss of $C_6H_5O_2N$. Further decomposition occurs in the temperature range of 560°C to 680°C corresponds to the final residue as nickel oxide the ultimate product of heating.

Conclusion

Based on the above results the following conclusion may be drawn. The higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes respectively. Room temperature magnetic studies are indicative of paramagnetic nature and an octahedral geometry of the Ni(II) complexes which is supported by the electronic spectra. The IR spectra show bonding of the metal through N- and O- donor atoms of the two ligands (Figure-1).

Table 3: Thermal data for vanadium metal complexes

Complex	Temperature Range (°C)	% Weight loss		Decomposition product
		Found	Calculated	
N1 $[C_{30}H_{26}O_4N_4Ni \cdot 2H_2O]$	100-180	5.63	5.69	$[C_{30}H_{26}O_4N_4Ni]$
	180-360	41.13	41.10	C_6H_5CHON
	360-560	41.39	41.41	$C_6H_5O_2N$
	560-680	11.85	11.80	NiO
N2 $[C_{28}H_{22}O_4N_4Ni \cdot 2H_2O]$	100-180	6.54	6.29	$[C_{28}H_{22}O_4N_4Ni]$
	180-360	35.18	34.93	C_6H_5CHN
	360-560	45.99	45.75	$C_6H_5O_2N$
	560-680	12.29	13.03	NiO
N3 $[C_{30}H_{26}O_4N_4Ni]$	100-180	6.42	5.99	C_6H_5CHN
	180-360	38.40	37.97	$[C_{30}H_{26}O_4N_4Ni]$
	360-560	44.05	43.62	$C_6H_5O_2N$
	560-680	11.13	12.42	NiO
N4 $[C_{28}H_{22}O_4N_4BrNi \cdot 2H_2O]$	100-180	5.78	5.53	$[C_{28}H_{22}O_4N_4BrNi]$
	180-360	49.11	48.86	C_6H_5NCHBr
	360-560	34.38	34.14	$C_6H_5O_2N$
	560-680	10.73	11.47	NiO
N5 $[C_{36}H_{30}O_4N_4Ni \cdot 2H_2O]$	100-180	5.61	5.35	$[C_{36}H_{30}O_4N_4Ni]$
	180-360	44.85	44.61	C_6H_5CHN
	360-560	39.19	38.95	$C_6H_5O_2N$
	560-680	10.35	11.09	NiO



Where R = -OCH₃, -H, -CH₃, -Br, -Ph

Figure-1 :Proposed structure of the nickel metal complexes

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