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Synthesis and Characterization of Nickel(II) Complexes of Various Substituted Acid Hydrazides

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Complexes of nickel(II) with *m*-chloro benzoic acid, *p*-amino benzoic acid and nicotinic acid hydrazides as ligands have been synthesized in ethanolic medium. They were characterized by elemental analyses, infrared, diffuse electronic reflectance spectroscopy and room temperature magnetic susceptibility measurements. The complexes are generally insoluble in common solvents. The results suggest octahedral coordination in which the nickel(II) is bonded to the ligands using the amide carbonyl and the amino nitrogen of the hydrazide moiety. The complexes exhibited varied antimicrobial activities against some tested organisms.

Key Words: Nickel(II), Hydrazide, Infrared, Electronic spectra, Magnetic moments.

INTRODUCTION

Hydrazides and its metal complexes have been known to display remarkable biological activities. Some of these compounds have been used in polymer stabilization, metal extractants and in solving ion-exchange problems[1-4]. While substituted benzoic acid hydrazides have received reasonable attention in the literature[4-9], the aminobenzoic and chlorobenzoic acid hydrazides have not been well studied. Most of these compounds are insoluble in common solvents, this makes it impossible to study the single crystal X-ray of the compounds and some authors have reported[10] the coordination of the anions. In our previous studies[11,12], benzoic acid is used as an entry into these substituted hydrazides and showed by its single crystal X-ray studies that the anions remain in the crystal lattice and not coordinated to the metal. In the present study, we report the synthesis, spectral, magnetic and antimicrobial study of novel *p*-amino benzoic acid (*p*-ABAH), *m*-chlorobenzoic acid (*m*-CBAH) and nicotinic acid hydrazides (NAH) and their nickel(II) complexes. The complexes derived from these electron withdrawing and electron donating substituted benzoates are new and represents the first systematic studies of the coordination chemistry of these ligands. The results are also compared with the nickel(II) complexes of nicotinic acid hydrazide-a heterocyclic acid hydrazide.

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EXPERIMENTAL

Reagent grade ethyl nicotinate, *p*-aminobenzoic acid, *m*-chlorobenzoic acid were obtained from the British Drugs House Chemicals Ltd., UK, while hydrazine hydrate, nickel(II) acetate tetrahydrate, nickel(II) chloride hexahydrate, nickel(II) sulphate hexahydrate and nickel(II) nitrate hexahydrate were purchased from Aldrich Chemicals Co., UK. All the chemicals were of the reagent grade or purer and were used without further purification. The nutrient agar used was manufactured by Antec Diagnostic Products in the UK.

Synthesis of the hydrazides

Preparation of ethyl *m*-chlorobenzoate: *m*-Chlorobenzoic acid (10.96 g; 70 mmol) was added to 20 mL ethanol and transferred into a 250 mL round-bottom flask fitted with a reflux condenser and 2 mL conc. sulfuric acid was added to the mixture. This was refluxed for 6 h and the ester obtained was extracted using ether in a separatory funnel. The ethyl *m*-chlorobenzoate ester was obtained as solid on cooling (yield 12.9 g, 80 %). This product was used for the preparation of the hydrazide.

Preparation of *m*-chlorobenzoic acid hydrazide: Ethyl *m*-chlorobenzoate (12.90 g; 70 mmol) in 20 mL ethanol was added portion wise to hydrazine hydrate (3 mL; 70 mmol) in a 250 mL round-bottom flask fitted with a reflux condenser. The yellowish suspension obtained was heated gently under reflux for 15 min, then 80 mL of ethanol was added which resulted in a clear yellowish solution. This mixture was refluxed for additional 4 h after which the solvent was distilled off leaving about one-third of the original volume which was transferred to a 250 mL beaker and left overnight at room temperature. The precipitates formed were filtered by suction, washed with deionized water, after which it was dried over calcium chloride in a desiccator (yield 23.4 g, 97 %).

Preparation of nicotinic acid hydrazide: Ethyl nicotinate (20 mL; 150 mmol) was added portion wise to hydrazine hydrate (7 mL; 150 mmol) in a 250 mL round-bottom flask. The light yellow solution obtained was heated gently under reflux for 15 min after which 70 mL ethanol was added and refluxing continued for additional 4 h. The ethanol was distilled off at the end of refluxing leaving one-third of the original volume, which was transferred into a beaker where cream coloured precipitates formed immediately on cooling to room temperature. The nicotinic acid hydrazide formed was filtered by suction, washed with deionized water and dried over calcium chloride in a desiccator (yield 14.8 g, 74 %).

Preparation of *p*-aminobenzoic acid hydrazide

Preparation of ethyl *p*-aminobenzoate: Ethanol (240 mL) was saturated with dry hydrogen chloride gas in 250 mL two-necked round-bottom flask equipped with a reflux condenser and a gas inlet tube. *p*-Aminobenzoic acid (36 g; 246 mmol) suspension in ethanol was added in portions to the round-bottom flask. The mixture was heated under reflux for 4 h, after which the resulting hot suspension was

dissolved in excess deionized water. Sodium carbonate was added to the acidic solution until the solution was neutral to litmus with precipitation taking place on the top of the solution. The precipitate of the ester was filtered by suction and dried in air (yield 50 g, 90 %).

Preparation of *p*-aminobenzoic acid hydrazide: Ethyl *p*-aminobenzoate (50 g; 300 mmol) suspended in 60 mL ethanol was added in portions to hydrazine hydrate (15 mL; 300 mmol) in a 250 mL round-bottom flask. The wine coloured solution obtained was refluxed with gentle heating for 15 min after which 70 mL ethanol was added and the mixture was refluxed for additional 4 h. The ethanol was distilled off leaving one-quarter of the original volume that was transferred into a 250 mL beaker where precipitation took place on cooling. The brownish crystalline precipitate of *p*-aminobenzoic acid hydrazide was filtered by suction, washed with deionized water and dried over calcium chloride in a desiccator (yield 29.5 g, 65 %).

Preparation of the metal complexes

Preparation of [Ni(*p*-ABAH)$_3$]Cl$_2$: *p*-Aminobenzoic acid hydrazide (2 g; 13 mmol) suspension in 10 mL ethanol was added in drops to $NiCl_2 \cdot 6H_2O$ (1.57 g; 6.6 mmol) in 45 mL of 20 % ethanol while stirring. Precipitation occurred immediately. It was left to stir for 1 h, after which it was filtered by suction, washed with 20 % ethanol, deionized water and dried over calcium chloride (yield 1.51 g; 53 %).

Similar procedure was used for the preparation of all the nickel(II) *p*-aminobenzoic acid hydrazide complexes except that their metal salts were dissolved in 40 % ethanol.

Preparation of [Ni(*m*-CBAH)$_3$]SO$_4$: $NiSO_4 \cdot 6H_2O$ (1.54 g; 5.89 mmol) in 30 mL 40 % ethanol was stirred while *m*-chlorobenzoic acid hydrazide (CBAH) (2.00 g; 11.7 mmol) suspension in 10 mL ethanol was added dropwisely. Precipitation occurred immediately and stirring continued for additional 1 h after which it was then filtered by suction, washed with 40 % ethanol, deionized water and was dried in a desiccator over calcium chloride (yield 2.0 g, 69 %). Similar procedure was used for the preparation of the other nickel(II) complexes except for Ni(*m*-CBAH)$_2$Cl$_2$ where nickel(II) chloride hexahydrate was dissolved in 20 % ethanol.

Similarly all the nickel(II) complexes of nicotinic acid hydrazide.

Characterization of the nickel(II) complexes: Elemental analyses were carried out using a Perkin-Elmer 240C elemental analyzer manufactured in the USA. Nickel analyses were performed using complexometric titration with EDTA[13] as the titrant. IR spectra were recorded on a Nicolet Avater 330 FT-IR spectrophotometer using KBr discs. UV-Visible spectra of the ligands and complexes were recorded in nujol using Genesys 10 UV scanning spectrophotometer made by Thermo Electron Corporation, UK. Magnetic measurements were carried out using the Faraday method on an instrument by Sherwood Scientific, Cambridge.

Biological assay: The microorganisms used are *Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus cereus*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Micrococous acidophilus*, *Pseudomonas putrifaciens* (A_1), *Streptococcus bovis*, *Proteus* sp., *Salmonella typhi*, *Pseudomonas putrifaciens* (Q), *Serratia marcescens*.

The medium was prepared by dissolving 28 g of the nutrient agar in 1000 mL deionised water. The solution was sterilized at 121 ºC for 15 min in an autoclave. Concentrations of 10, 100 and 1000 µg/mL of each of the complexes were made in dimethylsulphoxide. The dimethylsulphoxide was used as the negative control while gentamycin solution in DMSO was used as the positive control. The twelve bacterial isolates were tested for sensitivity to some of the compounds by means of a disc diffusion method[12].

RESULTS AND DISCUSSION

Preparation of the compounds: The *m*-chlorobenzoic, *p*-aminobenzoic and nicotinic acid hydrazides were prepared from their respective acids. The ethyl esters of these acids were isolated from which the hydrazides were obtained in reasonable yields (66-98 %). The representative equation of reaction for the synthesis of the ligands is given below:

$$RCOOR' + H_2NNH_2 \rightarrow RCONHNH_2 + R'OH$$

where R = *m*-ClC_6H_4-, *p*-$NH_2C_6H_4$, C_5H_4N

The nickel complexes were isolated by reacting the appropriate nickel salts with the hydrazides analyzed in a 1:3 mole ratio of nickel: ligand.

$$NiX_2 \cdot xH_2O + 3RCONHNH_2 \rightarrow [Ni(RCONHNH_2)_3](X)_2$$

where X = Cl, NO_3, CH_3COO or $1/2SO_4$; R = *m*-ClC_6H_4-, *p*-$NH_2C_6H_4$, C_5H_4N.

The complexes show different shades of blue and green except $[Ni(p\text{-}ABAH)_3](OAc)_2$ and $[Ni(NAH)_3](NO_3)_2$ which are brown and purple, respectively. The result of the elemental analyses revealed a good agreement between the calculated and observed values (Table-2).

The solubility of the complexes in various donor and non donor solvents revealed varying degree of solubility. All the *m*-chlorobenzoic hydrazide complexes are soluble in DMSO while in the other solvents they were sparingly soluble. Only $[Ni(NAH)_3](NO_3)_2$ was soluble in DMSO among the nicotinic acid hydrazide series. The nickel(II) complexes of *p*-aminobenzoic acid hydrazides are sparingly soluble in nitromethane, acetone, DMSO, ethanol and methanol.

Infrared: Three related vibrations are normally used to infer coordination of hydrazide ligands to the metal. These are the carbonyl stretching frequency [ν_s(C=O)] or the 'Amide-I', the in-plane bending deformation and stretching frequency for cyanate [δ(N-H) + ν_s(C-N)] or the 'amide II' and the amino stretching vibrations $\nu_s(NH_2)$[14].

In the three ligands reported here, the $\nu_s(NH_2)$ was observed between 3351-3308 cm^{-1} as very strong bands which experienced a batochromic shift to the region between 3308-3175 cm^{-1} in the nickel complexes. This indicates the coordination of the amino group of the hydrazide moiety to the nickel(II) ion. Two bands each were reported in this region for *p*-aminobezoic acid hydrazides and its metal complexes. The bands centered at *ca.* 3419 cm^{-1} are not sensitive to metal perturbations or anion exchange in the crystal lattice and are presumably due to the $\nu_s(NH_2)$ attached to the *para*-position of the phenyl ring.

The 'amide I' band for the nicotinic acid hydrazide was observed at 1673 cm^{-1} while the amide II was found at 1600 cm^{-1}. These bands were lowered in the metal complexes on coordination to the metal to between 1660-1618 and 1575-1545 cm^{-1}, respectively. The Amide-I and Amide-II bands for *p*-aminobenzoic acid hydrazide were observed at 1682 and 1597 cm^{-1}, respectively; while those for their complexes were observed between 1680-1670 and 1594-1590 cm^{-1}, respectively. The *m*-chloro benzoic acid hydrazide had the Amide-I at 1697 cm^{-1} and the 'amide II' at 1618 cm^{-1}. The vibrations for their metal complexes were equally observed between 1693-1624 and 1624-1615 cm^{-1}, respectively. These shifts in band positions indicate that the carbonyl amides are coordinated to the nickel.

The observed vibrational frequencies of the amides recorded higher frequencies for the chlorobenzoates. This is not unexpected because of the electron withdrawing inductive (I-) effect compared with the electron donating (I+) effect of the amino-benzoates. These values are further lowered in the compounds of the nicotinic hydrazides where the heterocyclic ring provides an electron rich environment for the amide positions. These observations definitely show that the hydrazide moiety is affected by the type of substituents attached to it. Present IR results are in agreement with similar systems earlier studied[5-9,11,12].

Electronic spectra: The electronic reflectance bands of the ligands and complexes in Table-1 were assigned based on previous work done on similar systems[9-12,14]. In the ultraviolet region, the observed bands between 45460-51280 cm^{-1} have been assigned to $n \rightarrow \sigma^*$ transition. This is attributed to the excitation of a nitrogen lone

TABLE-1
KEY INFRARED FREQUENCIES AND ELECTRONIC SPECTRAL TRANSITIONS FOR THE COMPOUNDS (cm^{-1})

Compounds	Amide I	Amide II	$\nu(NH_2)$	Electronic bands ($\times 10^3$)
m-CBAH	1697 s	1618 s	3351 s	50.76, 49.75, 35.71
Ni(*m*-CBAH)$_3$SO$_4$	1655 s	1566 m	3199 w	16.10
Ni(*m*-CBAH)$_3$(NO$_3$)$_2$	1689 s	1618 s	3308 w	50.25, 46.73, 42.02, 33.22, 17.79, 13.05
Ni(*m*-CBAH)$_3$Cl$_2$	1693 s	1624 s	3235 m	41.49, 35.37, 14.16
Ni(*m*-CBAH)$_3$(OAc)$_2$	1624 s	1562 w	3308 s	51.02, 42.02, 35.34, 29.67, 18.80
p-ABAH	1682 s	1597 s	3419 m, 3200 m	44.84, 35.71
Ni(*p*-ABAH)$_3$SO$_4$	1682 s	1595 m	3419 m, 3205 w	45.46, 36.50, 15.48
Ni(*p*-ABAH)$_3$(NO$_3$)$_2$	1683 s	1594 s	3419 m, 3230 m	46.08, 36.50, 15.48
Ni(*p*-ABAH)$_3$Cl$_2$	1682 m	1592 s	3420 m, 3215 w	45.46, 36.50, 13.00
Ni(*p*-ABAH)$_3$(OAc)$_2$	1682 s	1596 s	3419 w, 3215 w	46.08, 36.50,16.39
NAH	1673 s	1600 w	3326 s	51.28, 45.46, 38.61
Ni(NAH)$_3$SO$_4$	1660 s	1575 w	3208 m	15.39, 13.33
Ni(NAH)$_3$(NO$_3$)$_2$	1655 s	1574 w	3175 w	35.09, 30.03, 15.92
Ni(NAH)$_3$Cl$_2$	1655 s	1545 s	3266 m	40.00, 33.33, 14.29
Ni(NAH)$_3$(OAc)$_2$	1618 s	1551 m	3247 w	47.39, 39.53, 17.36, 10.85

pair of electron to antibonding σ-orbital of the amino group. The other bands observed in this region, 30,000- 42,020 cm^{-1} has been assigned to a combination of $\pi \rightarrow \pi^*$ and $\pi \rightarrow n$ transitions of the carbonyl group.

The absorption spectra of nickel(II) octahedral complexes normally show three spin-allowed transitions variously described as $\nu_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$, $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$[15,16].

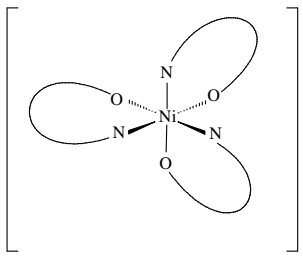
The absorption spectra of the complexes studied showed a broad band between 17,790-15,480 cm^{-1} assigned to $\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$. An additional band observed between 14,970-13,000 cm^{-1} in some of the complexes is also assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. Although all the expected transitions for the visible spectra could not be observed, the electronic spectral results obtained are similar to those in the literature for which octahedral nickel(II) compounds have been proposed[9-12,16].

Magnetic moment: The effective magnetic moment (μ_{eff}) for tetrahedral nickel(II) complexes, lie between 3.2-4.1 BM while for octahedral complexes, the values range between 2.9-3.3 BM. Deviations from the 'spin-only' magnetic moment of 2.83 BM are usually attributed to orbital contributions to the magnetic moments. The room temperature magnetic moments for the Ni(II) complexes studied were observed between 2.95-3.20 BM (Table-2) which falls in the range normally observed for octahedral nickel(II) complexes[17].

Antimicrobial activities: The acid hydrazides and their nickel(II) complexes showed appreciable activities against the test organisms. While moderate to high growth inhibitions were exhibited by some of the compounds studied, the activities cannot be compared to the standards normally employed for the studies[11].

Conclusion

The nickel(II) ion coordinates to three units of the hydrazides moiety using the amide carbonyl C=O and the amino moiety of the hydrazides. This is supported by the elemental analysis and the infrared spectral studies. The inductive effect of the substituents attached to the hydrazide moiety has pronounced effect on the vibrational modes of the hydrazides. The electronic spectral studies and room temperature magnetic moments are consistent with a plausible six coordinate octahedral geometry around the nickel ion as suggested in Fig. 1 below.



R = *m*-ClC_6H_4, *p*-$NH_2C_6H_4$, C_4H_3N; X = Cl, NO_3, CH_3COO, or $1/2SO_4$

= $RCONHNH_2$

Fig. 1. Suggested structures for the complexes

TABLE-2
ANALYTICAL DATA FOR THE COMPOUNDS

Compounds (e.f.)	f.w.	Colour	Yield (%)	m.p. (ºC)	Elemental analysis (%): Found (Calcd.)				μ_{eff} (BM)
					C	H	N	Ni	
m-CBAH ($C_7H_7N_2OCl$)	170.65	Off-white	98	122-124	49.01 (49.27)	3.89 (4.14)	16.25 (16.42)	–	–
Ni(*m*-CBAH)$_3$SO$_4$ ($C_{21}H_{21}N_6O_7SCl_3Ni$)	666.72	Light blue	69	146-148	37.99 (37.83)	3.31 (3.17)	12.73 (12.61)	8.51 (8.81)	2.95
Ni(*m*-CBAH)$_3$(NO$_3$)$_2$ ($C_{21}H_{21}N_8O_9Cl_3Ni$)	694.67	Pale blue	36	148	36.30 (36.31)	3.15 (3.17)	15.87 (16.13)	8.33 (8.45)	3.10
Ni(*m*-CBAH)$_3$Cl$_2$ ($C_{21}H_{21}N_6O_3Cl_5Ni$)	641.65	Light green	66	142	39.22 (39.31)	3.14 (3.30)	13.06 (13.10)	9.25 (9.15)	3.13
Ni(*m*-BAH)$_3$(OAc)$_2$ ($C_{25}H_{27}N_6O_7Ni$)	688.74	Pale blue	46	134	43.66 (43.60)	3.74 (3.95)	12.11 (12.20)	8.66 (8.52)	3.05
p-ABAH ($C_7H_9N_3O$)	151.17	Off-white	66	58-60	55.63 (55.62)	5.89 (6.00)	28.01 (27.80)	–	–
Ni(*p*-ABAH)$_3$SO$_4$ ($C_{21}H_{27}N_9O_7SNi$)	608.29	Light green	44	74-76	41.60 (41.47)	4.56 (4.47)	20.66 (20.72)	9.96 (9.65)	3.11
Ni(*p*-ABAH)$_3$(NO$_3$)$_2$ ($C_{21}H_{27}N_{11}O_9Ni$)	636.23	Lt. green	39	78-80	39.26 (39.64)	4.41 (4.28)	24.32 (24.22)	9.86 (9.23)	3.20
Ni(*p*-ABAH)$_3$Cl$_2$ $C_{21}H_{27}N_9O_3C_{12}Ni$)	583.22	Green	37	66-68	43.22 (43.25)	4.69 (4.67)	21.42 (21.62)	10.38 (10.07)	2.98
Ni(*p*-BAH)$_3$(OAc)$_2$ ($C_{25}H_{33}N_9O_7Ni$)	630.31	Brown	43	68-70	47.33 (47.64)	5.41 (5.28)	20.34 (20.00)	9.25 (9.31)	2.96
NAH ($C_6H_7N_3O$)	137.14	Off white	74	160-162	52.49 (52.55)	5.08 (5.15)	30.49 (30.64)	–	–
Ni(NAH)$_3$SO$_4$ ($C_{18}H_{21}N_9O_7SNi$)	566.21	Blue	55	200-202	38.55 (38.18)	4.03 (3.74)	22.36 (22.26)	10.82 (10.37)	3.18
Ni(NAH)$_3$(NO$_3$)$_2$ ($C_{18}H_{21}N_{11}O_9Ni$)	594.15	Purple	81	148	36.26 (36.39)	3.66 (3.56)	25.81 (25.93)	9.78 (9.88)	3.20
Ni(NAH)$_3$Cl$_2$ ($C_{18}H_{21}N_9O_3Cl_2Ni$)	541.14	Blue	71	180-182	39.64 (39.95)	3.82 (3.91)	23.56 (23.30)	10.82 (10.85)	3.06
Ni(NAH)$_3$(OAc)$_2$ ($C_{22}H_{27}N_9O_7Ni$)	588.23	Green	45	148	44.37 (44.92)	4.61 (4.63)	21.73 (21.43)	9.94 (9.98)	3.11

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