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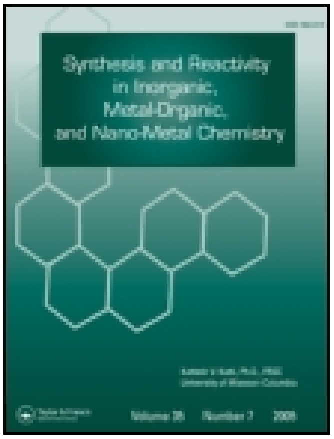

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# Synthesis and Characterization of Nickel(II) Complexes of Benzoic Acid and Methyl Substituted Benzoic Acid Hydrazides and X-Ray Structure of $Ni[C_6H_5CONHNH_2]_3Cl_2 \cdot 3CH_3OH$

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
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# Synthesis and Characterization of Nickel(II) Complexes of Benzoic Acid and Methyl Substituted Benzoic Acid Hydrazides and X-Ray Structure of $Ni[C_6H_5CONHNH_2]_3Cl_2{\cdot}3CH_3OH$

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## ABSTRACT

Nickel(II) complexes of benzoic acid hydrazides (BAH) and *o*, *m*, and *p*-substituted methylbenzoic acid hydrazides (MBAH) have been prepared and characterized by elemental analysis, room temperature magnetic susceptibility measurements, infrared and electronic reflectance spectral studies. The biological activities of the compounds and x-ray structure of $Ni[C_6H_5CONHNH_2]_3Cl_2{\cdot}3CH_3OH$ are also reported. The microanalyses showed that the hydrazides reacted with the nickel(II) salts in 1:3 (metal:ligand) molar ratio. The hydrazide ligand behaves as a

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neutral bidentate chelating ligand with coordination involving the carbonyl oxygen and the amino nitrogen of the hydrazide moiety. The effective magnetic moments ($\mu_{eff}$), infrared and electronic spectra of the compounds are consistent with a six-coordinate pseudo-octahedral arrangement of the ligands around the nickel ion. The x-ray diffraction analysis of $Ni[C_6H_5CONHNH_2]_3Cl_2 \cdot 3CH_3OH$ showed that it crystallizes as a triclinic system with a P-1 space group, $a = 10.2289(5)$, $b = 12.0707(6)$, $c = 14.0477(7)$ Å, $\alpha = 67.5540(10)^\circ$, $\beta = 69.2360(10)^\circ$, $\gamma = 73.7860(10)^\circ$. The nickel ion is coordinated by three units of benzoic acid hydrazide with the chloride ions and the methanol solvates uncoordinated in the crystal lattice. The compounds show some measurable activity against selected bacteria and fungi.

*Key Words:* Nickel; Hydrazides; Magnetic; Infrared; Electronic; X-ray; Microbiology.

## INTRODUCTION

The success of *cis*-diamminedichloroplatinum(II) (*cis*-platin) in clinical oncology not only stimulated interests in activities of platinum complexes using various bioligands; but also the screening of biological activities of various transition metal complexes.[1–5] Hydrazides and its derivatives have been known to display antitubercular, antitumour and antimicrobial activities.[6–9] Carboxylic acid hydrazides have equally been used in polymer stabilization, metal extractants and in solving ion-exchange problems.[10–14] However, there exists a scarcity structural data and structure activity relationship of hydrazides especially for their coordination compounds, and the question of the participation of the metal anion in coordination has not been satisfactorily addressed.[14–16] Gad et al.[14] in their study of poly-acryloyl benzoic acid hydrazides with some transition metals including copper(II) and nickel(II) reported coordination of chloride ions to some of these metals. In our previous studies on this system, the x-ray structure of $Cu[C_6H_5\text{-}COO]_2(NO_3)_2$ showed that nitrate anions are uncoordinated but remain in the crystal lattice.[17] It has also been established that coordination compounds exhibit a greater biological activity than the ligands themselves.[18,19]

In the present study, we present our report on the synthesis, spectral, biological and magnetic properties of nickel(II) complexes of benzoic acid hydrazides (BAH) and *ortho*-methylbenzoic acid hydrazide (*o*-MBAH), *meta*-methylbenzoic acid hydrazide (*m*-MBAH) and *para*-methylbenzoic acid hydrazide (*p*-MBAH). The nickel(II) complexes of BAH and MBAH are new and are reported here for the first time. Although, the preparation and electronic spectra of $Ni[C_6H_5COO]_3Cl_2$ have been previously reported,[16] we have obtained another composition of the compound $\{Ni[C_6H_5COO]_3Cl_2 \cdot 3CH_3OH\}$ with methanol as solvate and determined its crystal structure.

## EXPERIMENTAL

### Reagents and Solvents

Reagent grade $NiSO_4 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, methyl benzoate, *ortho*-, *meta*-, and *para*-methyl substituted benzoic acids were purchased from Aldrich and used as received. Solvents used were of the reagent grade or purer.

#### Preparation of the Ligands

Benzoic acid hydrazides [BAH], *ortho*-, *meta*-, and *para*-substituted methylbenzoic acid hydrazides were prepared as previously reported.[17] The purity and composition of the compounds were however established by elemental analyses, gas chromatography-mass spectrometry (GC-MS) and melting points.

### Synthesis of the Complexes

#### Preparation of $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$

$NiCl_2 \cdot 6H_2O$ (2.38 g, 10 mmols) dissolved in 15 mL hot 50% methanol was added drop-wise to 40 mL of a stirred solution of benzoic acid hydrazide (2.72 g, 20 mmols) in a 100 mL beaker maintained at 40 °C for 1 hour. During stirring, the green coloured solution gradually turned blue. The precipitates formed were filtered by suction, washed with water and methanol and then recrystallized in methanol and left at ambient temperature. A crystal suitable for X-ray measurement was found in the mother liquor. The same procedure was used to prepare $Ni[BAH]_3SO_4$, $Ni[BAH]_3(NO_3)_2$ and $Ni[BAH]_3(CH_3COO)_2$.

#### Preparation of $Ni[o\text{-}MBAH]_3SO_4$

$NiSO_4 \cdot 6H_2O$ (1.31 g, 5.0 mmols) dissolved in 15 mL of 30% methanol was added drop-wise to 30 mL of a hot methanolic solution of *o*-MBAH

(2.25 g, 15 mmols) in a 100 mL beaker while stirring at 40 °C. The volume of the mixture was reduced by one third and the mixture transferred to a 100 mL Buchner flask equipped with a condenser and stirring continued for about 2 h. The precipitates formed were filtered, washed with water and methanol and dried in vacuo over anhydrous calcium chloride. The nickel(II) chloride, nitrate and acetate derivatives were prepared similarly.

### Physical Measurements

The percent nickel in the complexes was determined using a complexometric method[20] while the elemental analyses for C, H, and N were determined using a Perkin–Elmer Series II 2400 CHNS/O analyzer. The infrared spectra were recorded on a Perkin–Elmer FTIR Spectrum 1000 spectrometer using KBr discs between 350–4000 $cm^{-1}$. Frequencies are believed to be accurate to $\pm 2\ cm^{-1}$. Electronic reflectance spectra of the ligands and the complexes in Nujol mulls were recorded on a Varian Cary 1E spectrophotometer between 190–900 nm. Melting points of the compounds were determined using a Buchi B-540 melting point apparatus. Magnetic susceptibilities were measured on powdered samples at room temperature using the Gouy method; calibration was done using mercury-tetrathiocyanatocobaltate(II) and diamagnetic corrections were calculated using Pascal's constants.[21] All the compounds were dried inside a vacuum pistol over $P_2O_5$ at 110 °C for a period between 1–2 hours.

### Experimental Details and Crystal Data for $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$

A single crystal removed from a methanolic solution of tris(benzoic acid hydrazide)nickel(II) chloride with dimensions $0.340 \times 0.255 \times 0.187$ mm was used for the x-ray measurement. The data sets were collected on a Siemens SMART CCD diffractometer ($1.63 \leq \theta \leq 22.50$ °) employing monochromated X-radiation ($\lambda = 0.71073$), MoK$\alpha$, $\omega$ scans, T = 173(2) K. A total of 3839 unique reflections were observed with $I > 2.0\sigma(I)$ out of 8879 measured reflections. The data were corrected for Lorentz and polarization effects but not for absorption. The crystal parameters are as follows: $C_{24}H_{36}Cl_2N_6NiO_6$, M = 634.20; triclinic, space group P-1, a = 10.2289(5), b = 12.0707(6), c = 14.0477(7) Å, V = 1478.03(13) $Å^3$, $\alpha = 67.5540(10)$ °, $\beta = 69.2360(10)$ °, $\gamma = 73.7860$ (10) °, Z = 2, $\rho_{calc} = 1.425$ $M\ g\ m^{-3}$.

The structure was solved by a direct method (SHELXS-97) and refined by a full-matrix least squares procedures based on $F^2$ (SHELXL-97).[22]

Non-hydrogen atoms were refined with anisotropic displacement parameters. The coordinates of the H atoms were calculated by the SHELXL program using an appropriate riding model with varied thermal parameters. Scattering factors for atoms were taken from the International Table for Crystallography, Vol. III.[23] The refinement converged at a final $R = 0.0412$, $wR_2 = 0.1012$, GOF = 0.246. The maximum and minimum electron density peaks in the final difference map were 0.317 and $-0.370$ e.Å$^{-3}$, respectively. All calculations were performed on a Silicon Graphics Indigo 2 workstation.

The Cambridge Crystallographic Data Centre (CCDC) 182717 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via  (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

## Antimicrobial Activity

The disk diffusion method was used to investigate the antimicrobial activity of the ligands and complexes as previously reported.[17] The compounds were tested against the following bacteria: *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Klebsiella edwardsiella*, *Streptococcus faecalis*, *Bacillus cereus*, *Botridiplodia* spp. and fungi: *Rhizopus oligoporous*, *Aspergillus flavae* and *Candida albicans*.

## RESULTS AND DISCUSSION

The formation of benzoic acid hydrazides and the methyl substituted benzoic acid hydrazides proceeded in respectable yields (58–64%) from their respective methyl benzoate esters and anhydrous hydrazine as given in Eqs. 1 and 2.

$$C_6H_5COOCH_3 + H_2NNH_2 \rightarrow C_6H_5CONHNH_2 + CH_3OH \tag{1}$$

$$\begin{aligned}&(o,m,p)\text{-}CH_3C_6H_4COOCH_3 + H_2NNH_2\\ &\quad\rightarrow (o,m,p)\text{-}CH_3C_6H_4CONHNH_2 + CH_3OH\end{aligned} \tag{2}$$

The analytical data and room temperature effective magnetic moments ($\mu_{\text{eff}}$) for the complexes are given in Table 1. The reaction of the metal salts

***Table 1.*** Analytical data for the compounds.[a]

| Compound (empirical formula) | Formula weight | Colour | Yield (%) | M.p. ( °C) | Analyses, % found (calculated) | | | | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | Ni | |
| $Ni[BAH]_3Cl_2{\cdot}3CH_3OH$ ($C_{24}H_{36}Cl_2N_6NiO_6$) | 634.19 | blue | 72 | 236–238 | 45.39 (45.45) | 5.81 (5.72) | 13.28 (13.25) | 9.25 (9.26) | 3.15 |
| $Ni[BAH]_3(NO_3)_2$ ($C_{21}H_{24}N_8NiO_9$) | 591.18 | brown | 68 | 196–198 | 42.54 (42.67) | 3.99 (4.09) | 19.10 (18.95) | 9.85 (9.93) | 3.20 |
| $Ni[BAH]_3SO_4$ ($C_{21}H_{24}N_6NiO_7S$) | 563.23 | lt. blue | 64 | 342[b] | 44.66 (44.78) | 4.35 (4.30) | 14.88 (14.92) | 10.50 (10.42) | 3.05 |
| $Ni[BAH]_3(CH_3COO)_2$ ($C_{23}H_{30}N_6NiO_7$) | 561.23 | blue | 75 | 210–212 | 49.44 (49.22) | 5.45 (5.39) | 14.88 (14.97) | 10.35 (10.46) | 3.14 |
| $Ni[o\text{-}MBAH]_3Cl_2$ ($C_{24}H_{30}Cl_2N_6NiO_3$) | 580.15 | blue | 63 | 250–253 | 49.62 (49.69) | 5.24 (5.21) | 14.45 (14.49) | 10.15 (10.12) | 3.00 |
| $Ni[o\text{-}MBAH]_3(NO_3)_2$ ($C_{24}H_{30}N_8NiO_9$) | 633.26 | blue | 60 | 200–205 | 45.35 (45.52) | 4.72 (4.78) | 17.55 (17.70) | 9.17 (9.27) | 2.85 |
| $Ni[o\text{-}MBAH_2]_3SO_4$ ($C_{24}H_{30}N_6NiO_7S$) | 605.31 | blue | 68 | 230–233 | 47.58 (47.62) | 5.00 (5.00) | 13.86 (13.88) | 9.72 (9.70) | 2.96 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ni[*o*-MBAH]$_3$(CH$_3$COO)$_2$ ($C_{26}H_{36}N_6NiO_7$) | 603.32 | brown | 52 | 200–214 | 51.88 (51.76) | 5.88 (6.01) | 13.97 (13.93) | 9.54 (9.73) | 3.04 |
| Ni[*m*-MBAH]$_3$Cl$_2$ ($C_{24}H_{30}Cl_2N_6NiO_3$) | 580.15 | lt. blue | 66 | 184–186 | 49.58 (49.69) | 5.15 (5.21) | 14.39 (14.49) | 10.32 (10.12) | 2.78 |
| Ni[*m*-MBAH]$_3$(NO$_3$)$_2$ ($C_{24}H_{30}N_8NiO_9$) | 633.26 | blue | 64 | 280–282 | 45.36 (45.52) | 4.66 (4.78) | 17.86 (17.70) | 9.30 (9.27) | 2.77 |
| Ni[*m*-MBAH]$_2$SO$_4$ ($C_{24}H_{30}N_6NiO_7S$) | 605.31 | grey | 55 | 230–233 | 47.44 (47.62) | 4.96 (5.00) | 13.85 (13.88) | 9.55 (9.70) | 2.95 |
| Ni[*m*-MBAH]$_3$(CH$_3$COO)$_2$ ($C_{26}H_{36}N_6NiO_7$) | 603.32 | lt. blue | 54 | 340[b] | 51.80 (51.76) | 6.04 (6.01) | 14.14 (13.93) | 9.67 (9.73) | 3.10 |
| Ni[*p*-MBAH]$_3$Cl$_2$ ($C_{24}H_{30}Cl_2N_6NiO_3$) | 580.15 | blue | 67 | 320–324 | 49.46 (49.69) | 5.30 (5.21) | 14.57 (14.49) | 10.06 (10.12) | 2.88 |
| Ni[*p*-MBAH]$_3$(NO$_3$)$_2$ ($C_{24}H_{30}N_8NiO_9$) | 633.26 | blue | 52 | >350 | 45.72 (45.52) | 4.54 (4.78) | 17.65 (17.70) | 9.10 (9.27) | 2.97 |
| Ni[*p*-MBAH]$_3$SO$_4$ ($C_{24}H_{30}N_6NiO_7S$) | 605.31 | blue | 63 | >350 | 47.55 (47.62) | 4.96 (5.00) | 13.76 (13.88) | 9.80 (9.70) | 3.02 |
| Ni[*p*-MBAH]$_3$(CH$_3$COO)$_2$ ($C_{26}H_{36}N_6NiO_7$) | 603.32 | brown | 56 | >350 | 51.66 (51.76) | 6.13 (6.01) | 13.66 (13.93) | 9.76 (9.73) | 2.89 |

[a] lt. = light, M.p. = Melting point.

[b] decomposition temperature.

and the respective ligands to form the complexes can be represented as shown in Eqs. 3 and 4.

$$\begin{aligned}&\mathrm{NiX_2{\cdot}}x\mathrm{H_2O + 3C_6H_5CONHNH_2}\\&\quad\rightarrow \mathrm{Ni[C_6H_5CONHNH_2]_3X_2} + x\mathrm{H_2O}\end{aligned}\qquad(3)$$

$$\begin{aligned}&\mathrm{NiX_2{\cdot}}x\mathrm{H_2O} + 3z\text{-}\mathrm{CH_3C_6H_4CONHNH_2}\\&\quad\rightarrow \mathrm{Ni[CH_3C_6H_4CONHNH_2]_3X_2} + x\mathrm{H_2O}\end{aligned}\qquad(4)$$

where X = Cl, $NO_3$, $CH_3COO$, or 1/2 $SO_4$; $z$ = *ortho*-, *meta*-, or *para*.

The complexes were obtained as solids of various shades of green and blue. The nickel(II) complexes of benzoic acid hydrazides are fairly soluble in protic solvents like methanol and ethanol while those of the methyl substituted complexes display very poor solubility just like their copper(II) analogues.

## Infrared Spectra

The principal infrared bands and electronic reflectance spectra of the complexes in Nujol mulls are presented in Table 2. The spectral assignments have been done by critically comparing the spectra of the ligands with those of the complexes. The features observed in the infrared spectra are consistent with the structural patterns of the compounds.[24,25] Three related vibrations have been successfully used to infer coordination of ligands to the metal in the spectra of hydrazides and its metal complexes.[4,16,17,19] These are the carbonyl stretching mode $\nu(C=O)$, referred to as ‘‘amide I’’ band, the coupling between the in-plane bending $\delta(N-H)$ and $\nu(C-N)$ stretching, referred to as ‘‘amide II’’ band and the stretching frequency for the amino group $\nu(NH_2)$. The asymmetric $\nu_{as}(NH_2)$ and the symmetric $\nu_s(NH_2)$ stretching vibrations for the amino group observed as two separate bands in the ligands between 3300–3310 $cm^{-1}$ overlap in most of the metal complexes and were shifted to lower frequency at 3280–3164 $cm^{-1}$. This indicates the participation of the $NH_2$ group in coordination to the nickel(II) ion. The assignment and interpretations of the vibrations of the complexes below 1700 $cm^{-1}$ are difficult to make with certainty, because of the absorptions of the aromatic nucleus in the interval 1610–1320 $cm^{-1}$ and the differing assignments that have been made in this region.[4,5,14,19] However, since the aromatic nucleus exert relatively low influence on coordination, the vibration between 1662–1630 $cm^{-1}$ in

***Table 2.*** Principal infrared bands[a] and electronic transitions for the compounds.

| Compound | Infrared ($cm^{-1}$) |  | Electronic transitions ( $\times 10^3$ $cm^{-1}$) |  |  |  |  |  | ($\nu_1/\nu_2$) |
|---|---|---|---|---|---|---|---|---|---|
|  | Amide I | Amide II |  |  |  |  |  |  |  |
| BAH | 1662 vs | 1578 m | 41.15 | 37.88 sh |  |  |  |  | – |
| Ni[BAH]$_3$Cl$_2$·3CH$_3$OH | 1637 vs | 1550 m | 43.86 | 26.74 | 16.86 | 13.12 sh | 11.98 |  | (1.41) |
| Ni[BAH]$_3$(NO$_3$)$_2$ | 1648 vs | 1568 m,<br>1540 m | 48.54 | 44.84 sh | 27.17 | 21.41 | 17.10 | 11.80 | (1.45) |
| Ni[BAH]$_3$SO$_4$ | 1647 vs | 1560 m | 39.22 | 35.59 | 27.10 | 16.92 | 13.09 sh |  | – |
| Ni[BAH]$_3$(CH$_3$COO)$_2$ | 1630 s | 1580 m, | 42.02 | 27.10 | 16.89 | 13.02 sh | 11.83 |  | (1.43) |
| *o*-MBAH | 1630 vs | 1570 vs | 41.50 |  |  |  |  |  | – |
| Ni[*o*-MBAH]$_3$Cl$_2$ | 1636 s | 1560 m | 40.82 | 27.17 | 17.79 |  |  |  | – |
| Ni[*o*-MBAH]$_3$(NO$_3$)$_2$ | 1640 vs | 1560 m | 46.08 | 36.1 sh | 21.36 | 17.24 |  | – |  |
| Ni[*o*-MBAH]$_3$SO$_4$ | 1646 vs,<br>1616 sh | 1559 s,<br>1541m | 44.23 | 38.61 sh | 27.17 | 21.32 | 16.81 | 11.82 | (1.42) |
| Ni[*o*-MBAH]$_2$(CH$_3$COO)$_2$ | 1625 vs | 1555 s | 42.37 | 27.32 | 17.85 | 11.90 |  |  | (1.50) |
| *m*-MBAH | 1640 vs | 1580 vs | 40.98 |  |  |  |  |  | – |
| Ni[*m*-MBAH]$_3$Cl$_2$ | 1654 m | 1570 s | 40.32 | 26.81 | 21.23 sh | 16.78 |  |  | – |
| Ni[*m*-MBAH]$_3$(NO$_3$)$_2$ | 1645 s | 1575 s | 42.02 | 27.10 | 17.29 | 11.85 |  |  | (1.46) |
| Ni[*m*-MBAH]$_3$SO$_4$ | 1630 s | 1565 m | 39.06 | 27.10 | 17.33 | 13.08 | 11.76 |  | (1.47) |
| Ni[*m*-MBAH]$_3$(CH$_3$COO)$_2$ | 1625 vs | 1540 vs | 41.67 | 36.10 sh | 21.32 | 16.78 |  |  | – |
| *p*-MBAH | 1660 s | 1580 vs | 41.32 |  |  |  |  |  | – |
| Ni[*p*-MBAH]$_3$Cl$_2$ | 1647 vs | 1560 vs | 40.98 | 27.10 | 17.24 | 11.85 |  |  | (1.45) |
| Ni[*p*-MBAH]$_3$(NO$_3$)$_2$ | 1655 vs | 1550 s | 46.73 | 27.17 | 16.78 | 11.75 |  |  | (1.43) |
| Ni[*p*-MBAH]$_3$SO$_4$ | 1647 vs | 1560 s | 39.37 | 27.62 | 16.81 | 11.85 |  |  | (1.42) |
| Ni[*p*-MBAH]$_3$(CH$_3$COO)$_2$ | 1616 vs | 1550 vs | 41.67 | 27.40 | 17.89 | 11.86 |  |  | (1.51) |

[a] vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

the ligands are assigned to the ''amide I'' band. These vibrations appeared in the nickel(II) complexes at a lower frequency region at 1655–1616 $cm^{-1}$ suggesting the coordination of ν(C=O) to the nickel ion. The ''amide II'' bands in the ligands and complexes appeared in the region between 1580–1570 and 1575–1540 $cm^{-1}$, respectively. Although this vibration has been noted in previous studies not to be sensitive to coordination by metals[14–16,19], there appears to be a general lowering in the frequency of this band on coordination in the complexes studied with the exception of $Ni[BAH]_3(CH_3COO)_2$. The deformation bands $\delta(NH_2)$ between 1603–1608 $cm^{-1}$, $\tau(NH_2)$ between 1400–1300 $cm^{-1}$, $\gamma(NH_2)$ between 1040–1030 $cm^{-1}$ and δ(HNN) at~ 1240 $cm^{-1}$ do not experience significant shifts in the spectra of the complexes because of the absence of H-bonds between C=O and $NH_2$.[19] Other metal-ligand and ligand related vibrations are observed below 600 $cm^{-1}$.

## Electronic Spectra

The electronic reflectance spectra of the ligands in the UV region have similar pattern and display single bands between 41,500–40,980 $cm^{-1}$ except for BAH where an additional shoulder was observed at ~37,880 $cm^{-1}$. In the complexes, these bands are shifted to the 48,540–40,320 $cm^{-1}$ range and there appears in some cases an additional band or shoulder in the region 38,610–34,970 $cm^{-1}$. These bands are assigned to the $\pi \rightarrow \pi^*$ transition in the aromatic system overlapping with the $\pi \rightarrow \pi^*$ transition in the carbonyl group. These changes show a significant $\pi \rightarrow \pi^*$ interactions in the complexes. It can also be correlated with the involvement of N and O atoms from the ligand in coordination which strengthens the C=O and the $-NH_2$ bonds involved in the charge transfer process.[19] The appearance of the band in the 38,610–34,970 $cm^{-1}$ range has been observed in previous studies on similar system and attributed to the $\pi \rightarrow n$ transitions in the carbonyl group.[19,26]

The visible spectra of the nickel(II) complexes studied display transitions in the ranges 13,120–11,120, 21,230–16,780 and 27,620–26,740 $cm^{-1}$. These transitions have been assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$-($\nu_1$), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ($\nu_2$) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ($\nu_3$) transitions, respectively. Splitting of the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition was observed in some of the compounds. The observed transitions at 16,860 and 13,200 $cm^{-1}$ for $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$ compare favourably well with the Nujol mull spectra of $Ni[C_6H_5COO]_3Cl_2$ at 17,857 and 13,333 $cm^{-1}$, respectively. In the latter complex, an additional band was observed at ~10,500 $cm^{-1}$ in various solvents; this could not be observed in our complex due to instrumental limitations. Generally, the crystal field spectra of regular octahedral complexes are characterized by the presence of three moderately strong bands and the ratio $\nu_2/\nu_1$, the frequencies of the first and second band maxima,[27,28] lies in most cases between 1.5–1.7. The complexes displaying these two bands among those studied have this ratio observed between 1.41–1.51, suggesting the octahedral arrangement of ligands around the nickel(II) ion. The lower values obtained for this ratio is not unusual, even for octahedral nickel(II) complexes that have been structurally characterized, and indicates the degree of distortion of the compounds from the 'ideal' geometry.[29,30] In principle, it should be easy to deduce $10Dq = E[{}^3A_{2g} \rightarrow {}^3T_{2g}]$ from the spectra of the complexes. However, since the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^1E_g$ transitions are not well separated in the spectra, it is not possible to determine 10Dq accurately.[31]

## Magnetic Moments

The effective magnetic moments ($\mu_{eff}$) of nickel(II) complexes in a cubic field range between 2.8–4.2 B.M. The deviation from the expected spin-only ($\mu_{s.o.}$) value of 2.83 B.M. for two unpaired electrons are generally attributed to orbital contributions to the magnetic moments. Four-coordinated tetrahedral nickel(II) complexes have higher $\mu_{eff}$ values (3.2–4.1 B.M.) compared to the octahedral complexes (2.9–3.3 B.M.).[32] The measured values of 2.77–3.20 B.M. in the present complexes falls in the range expected for six-coordinate octahedral nickel(II). Generally, the moments of nickel(II) complexes of benzoic acid hydrazides appear slightly higher (3.05–3.15 B.M.) than those of the methyl substituted analogues (2.85–3.10 B.M.) suggesting some sort of interactions of the latter in the solid state. The position of the methyl substituents does not appear to have any influence on the magnitude of the moments.

## Crystal Structures for $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$

The ORTEP representation of the structure of $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$ is shown in Figure 1, together with the atomic numbering scheme. Interatomic distances and angles relevant to the coordination sphere around nickel are given in Table 3. The molecular structure consists of a mononuclear, six-coordinated nickel(II) complexed by three units of benzoic acid hydrazides. The coordination to the metal is through the carbonyl oxygen of the amide and the nitrogen of the amino group of each unit of the hydrazide to give essentially a $NiN_3O_3$ chromophore. The two chloride ions and three molecules of methanol are held within the interstitial spaces

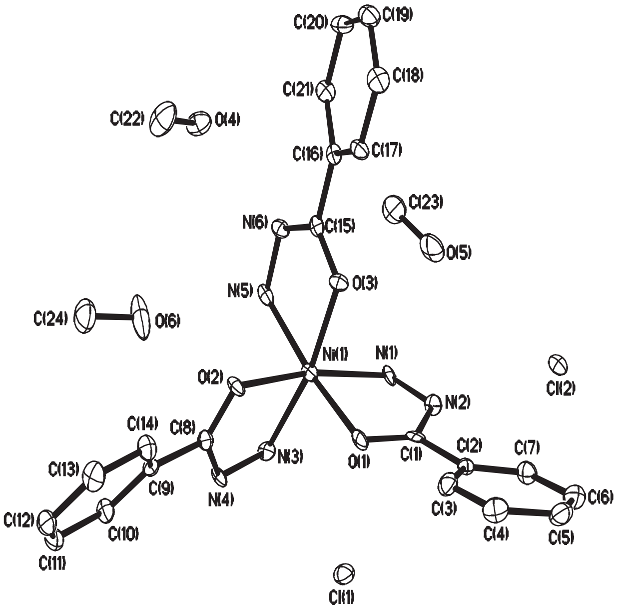


***Figure 1.*** ORTEP representation of the structure of $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$. Ellipsoids are drawn at 50% probability and protons are omitted for clarity.

of the crystal lattice. The C–O bond distances for the solvent molecules have different values; 1.367(7), 1.427 and 1.404 Å for O(4)–C(22), O(5)–C(23) and O(6)–C(24), respectively; which may indicate some measure of interaction of the solvent molecules with the monomeric complex in the crystal lattice. The geometry around the nickel(II) is best described as distorted octahedral with similarity in the bite angles; O(1)–Ni(1)–N(1) and O(2)–Ni(1)–N(3) have the same value of 78 ° while O(3)–Ni(1)–N(5) is 79 °. These angles are particularly distorted from the 'ideal' octahedral value of 90 ° probably due to chelate compression arising from the arrangement of three hydrazide units around the nickel ion. Similarly, this degree of distortion is also indicated by the *trans* octahedral angles, 169.23(15), 171.10(14), and 171.10(14) for O(3)–Ni(1)–N(3), O(2)–Ni(1)–(N1), and O(1)–Ni(1)–N(5) respectively, which, show a deviation of less than 12 ° from the 'ideal' value which should be 180 ° for this stereochemistry. The Ni–O (2.046–2.049 Å) and Ni–N (2.078–2.099 Å) bond distances in the compounds are crystallographically identical and are not unusual but compare favourably with bond distances for six-coordinate octahedral nickel(II) complexes that have been structurally

***Table 3.*** Selected bond distances and angles for Ni$[BAH]_3Cl_2 \cdot 3CH_3OH$.

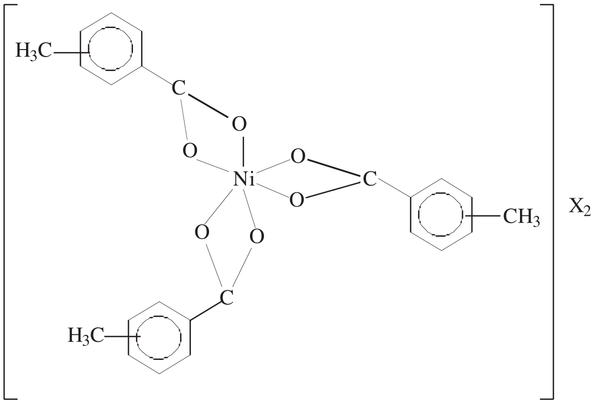
| Bond distances (Å) | | Bond angles ( °) | |
|---|---|---|---|
| Ni(1)–O(3) | 2.046(3) | O(3)–Ni(1)–O(2) | 92.65(13) |
| Ni(1)–O(2) | 2.048(3) | O(3)–Ni(1)–O(1) | 91.94(13) |
| Ni(1)–O(1) | 2.049(3) | O(2)–Ni(1)–O(1) | 89.10(13) |
| Ni(1)–N(3) | 2.078(4) | O(3)–Ni(1)–N(3) | 169.23(15) |
| Ni(1)–N(1) | 2.099(4) | O(2)–Ni(1)–N(3) | 79.47(14) |
| Ni(1)–N(5) | 2.105(4) | O(1)–Ni(1)–N(3) | 95.23(14) |
| O(1)–C(1) | 1.246(5) | O(3)–Ni(1)–N(1) | 89.06(14) |
| O(2)–C(8) | 1.238(5) | O(2)–Ni(1)–N(1) | 167.11(15) |
| O(3)–C(15) | 1.250(5) | O(1)–Ni(1)–N(1) | 78.07(15) |
| O(4)–C(22) | 1.427(7) | N(3)–Ni(1)–N(1) | 100.26(15) |
| O(5)–C(23) | 1.404(7) | O(3)–Ni(1)–N(5) | 79.18(14) |
| O(6)–C(24)#1 | 1.367(7) | O(2)–Ni(1)–N(5) | 90.59(15) |
| C(1)–N(2) | 1.352(6) | O(1)–Ni(1)–N(5) | 171.10(14) |
| C(1)–C(2) | 1.490(7) | N(3)–Ni(1)–N(5) | 93.46(16) |
| C(2)–C(7) | 1.362(7) | N(1)–Ni(1)–N(5) | 102.28(16) |
| C(8)–N(4) | 1.345(6) | C(1)–O(1)–Ni(1) | 114.0(3) |
| C(15)–N(6) | 1.331(6) | C(8)–O(2)–Ni(1) | 113.5(3) |
| C(24)–O(6)#2 | 1.367(7) | C(15)–O(3)–Ni(1) | 114.5(3) |
| N(1)–N(2) | 1.404(5) | O(1)–C(1)–N(2) | 119.6(5) |
| N(3)–N(4) | 1.420(5) | O(2)–C(8)–N(4) | 121.1(5) |
| N(5)–N(6) | 1.432(5) | O(3)–C(15)–N(6) | 121.4(5) |
| | | N(2)–N(1)–Ni(1) | 108.0(3) |
| | | C(1)–N(2)–N(1) | 117.1(4) |
| | | N(4)–N(3)–Ni(1) | 107.7(3) |
| | | C(8)–N(4)–N(3) | 116.9(4) |
| | | N(6)–N(5)–Ni(1) | 107.7(3) |

Symmetry codes (#)—x, y, z.

characterized.[26,29,33] These bond distances are shorter when compared with an average of 2.152 and 2.276 Å for Ni–O and Ni–N distances, respectively, in a hydrazonic nickel(II) complex $[Ni(H_2dapo)(OH_2)_2]Cl_2$ {dapo═2,6-diacetylpyridinebis(octanoylhydrazone)}, a seven coordinate pentagonal-bipyramidal compound.

## Microbiology

The nickel(II) complexes tested showed some measurable activities against the tested bacteria and fungi, however, they cannot be considered significant compared to those previously reported on similar systems.[7,9] It seems the activities of the hydrazide compounds are more enhanced when



where X = Cl, $NO_3$, $CH_3COO$, or $^1/_2SO_4$

***Figure 2.*** Suggested structure of the complexes.

coupled with organic groups such as oxadiazolines, furyl, thiazolidinones, and imidazoles.[7,9,34]

## CONCLUSION

Benzoic acid hydrazide (BAH) and substituted methylbenzoic acid hydrazides coordinate to nickel(II) using the C=O and the $NH_2$ groups of the hydrazides as confirmed from a comparison of the spectra of the ligands and complexes. The elemental analyses, spectral and magnetic susceptibility studies confirm a six-coordinated, distorted-octahedral arrangements of the ligands around the nickel(II) ion. There is no evidence for the coordination of the metal anions in the compound. While the compounds show some measurable activities against the tested bacteria, these activities cannot be termed significant compared to similar compounds earlier reported.[9,34] An octahedral configuration for the complexes (Figure 2) is thereby suggested similar to the crystal structure of $Ni[BAH]_3Cl_2 \cdot 3CH_3OH$ with the anions uncoordinated in the crystal lattice.

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