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Synthesis, Characterization, and Structural Studies of Nickel(II) Complexes of Some New Substituted Acid Hydrazides

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Synthesis, Characterization, and Structural Studies of Nickel(II) Complexes of Some New Substituted Acid Hydrazides

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The syntheses, spectroscopic, magnetic, and antimicrobial and theoretical studies of a new series of hydrazides; $RCOCH_2CONHNH_2$ (R = CH₃, C₃H₇, C₆H₅) variously described as acetoacetic (AAAH), butyrylacetic (BUTAH) and benzoylacetic (BENZAH) acid hydrazides and its nickel(II) complexes are reported. Microanalyses, room temperature magnetic susceptibility measurements infrared and electronic reflectance spectra are consistent with a distorted six coordinate octahedral geometry for the complexes. The modeled compounds using semi-empirical method PM3 and density functional theory (DFT) shows a good correlation of crystallographic data. The compounds show appreciable activity against gram +ve and gram-ve bacteria.

Keywords synthesis, hydrazides, structure, spectroscopic

INTRODUCTION

The interest associated with hydrazides, its analogues and their metal complexes continue to grow due to their analytical applications, pharmaceutical properties, and ubiquitous biological activities.^[1–7] The metal complexes of hydrazides have been established from test microbes to have more enhanced biological activities than the free ligands.^[1,4] Subsequently, the syntheses of new hydrazides, their derivatives, factors influencing their isolation, varied bonding, and stereochemical possibilities offered by these compounds continue to be of interests.^[8–12] A survey of the literature shows that hydrazides-RCONHNH₂ where R = alkyl or aryl group have been studied extensively, whereas the alkyloxyl- and aryloxyl-RCOCH₂CONHNH₂ and their metal complexes have not been investigated.^[13–15] In this paper, we present our report on the syntheses, spectroscopic, magnetic and biological activities of RCOCH₂CONHNH₂(R =

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 CH_3 , C_3H_7 , and C_6H_5) and their nickel(II) complexes. These complexes are new and represent the first systematic studies on these series of hydrazides.

EXPERIMENTAL

Materials

Reagent grade ethylacetoacetate, ethylbutyrylacetate, ethylbenzoylacetate, hydrazine hydrate, nickel(II) acetate tetrahydrate, nickel(II) chloride hexahydrate, nickel(II) sulphate hexahydrate and nickel(II) nitrate hexahydrate were purchased from the British Drug House Chemicals Ltd (BDH) and Aldrich Chemicals Co., and were used without further purification. Nutrient agar was obtained from Antec Diagnostic Products, United Kingdom.

Preparation of the Ligands

Preparation of acetoacetic acid hydrazide (AAAH)

19.40 mL (400 mmoles) hydrazine hydrate in a 250 mL quick-fit conical flask fitted with a reflux condenser was stirred with gentle heating while ethylacetoacetate (400 mmoles, 51 mL) was added portion wise. The orange colored suspension obtained was refluxed for 15 min, after which 170 mL ethanol was added to give a clear yellow solution. The resultant solution was refluxed for an additional 4 hours. The ethanol was distilled off and the remaining solution was transferred into a beaker and left overnight at room temperature. The precipitates obtained were filtered by suction, washed with deionized water, and dried over calcium chloride in a desiccator. (Yield 17.2 g, 37%).

Preparation of butyrylacetic acid hydrazide (BUTAH).

9 mL (9.33 g; 190 mmoles) hydrazine hydrate was transferred to a 250 mL quick–fit conical flask fitted with a reflux condenser. 30 mL (29.5 g, 190 mmoles) ethyl butyrylacetate was added portion wise. On addition of about 20 mL of the ester, an off– white colored paste was observed. The remaining 10 mL was

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added and mixture heated under reflux for 15 min, after which 140 mL ethanol was added, which dissolved the paste and gave a faint yellow solution. Refluxing continued for an additional 4 hours after which the ethanol was distilled off. The remaining peach colored suspension was transferred to a 250 mL beaker where on cooling, formed crystalline cream precipitates. The precipitates were filtered by suction, washed with deionized water and dried in a desiccator over calcium chloride. (Yield 16.6 g, 62%).

Preparation of benzoylacetic acid hydrazide (BENZAH).

30 mL (33.3 g, 170 mmoles) ethyl benzoylacetate solution in ethanol was added portion wise to 8 mL (8.67 g, 170 mmoles) hydrazine hydrate in a 250 mL quick–fit conical flask. The light peach solution obtained was refluxed with gentle heating for 15 min, after which 150 mL ethanol was added and refluxing continued for additional 4 hours. The ethanol was distilled off and the remaining solution was transferred to a 250 mL beaker where it was left overnight. The cream colored crystalline precipitates of the benzoylacetic acid hydrazide formed were filtered by suction, washed with deionized water and then dried in a desiccator over calcium chloride (Yield 21.5 g, 70%).

Preparation of the Nickel(II) Complexes

Preparation of Ni(BENZAH)₃(OAc)_{2.}

Ni(OAc)₂.4H₂O (2.10 g, 8.4 mmol) dissolved in 40 mL of 40% methanol was stirred while 3.00 g (16.9 mmol) benzoylacetic acid hydrazide suspension in 10 mL methanol was added dropwisely. Light green precipitates were observed immediately, and the mixture was stirred for one hour before it was filtered by suction, washed with 40% methanol, deionized water and dried over calcium chloride (Yield 2.84 g, 63%). The same procedure was used in the preparation of all the other nickel(II) benzoylacetic acid hydrazide complexes except for Ni(BENZAH)₃(NO₃)₂ where precipitation was not observed until the pH was raised to 9 with ammonia solution.

Preparation of Ni(AAAH)₃(NO₃)₂

4.37 g (15 mmol) of Ni(NO₃)₂.6H₂O was dissolved in 10 mL of 40% methanol and stirred in a 250 mL beaker while acetoacetic acid hydrazide (3.48 g, 30 mmoles) dissolved in 10 mL methanol was added dropwisely. Precipitation occurred after the pH was raised to 9. Stirring continued for additional 1hr after which the light green precipitates formed were filtered, washed with 40% methanol and deionized water and was dried over calcium chloride in a dessicator. (Yield 4.4 g, 54%). A similar procedure was used to isolate the other nickel(II) complexes of acetoacetic acid hydrazides.

The nickel(II) complexes of butyrylacetic acid hydrazides were similarly prepared as described above.

Physical Measurements

Elemental analyses for C, H, and N were determined using a Perkin- Elmer 240 C elemental analyzer. The percentage nickel in the metal complexes was determined using complexometric titration using EDTA¹⁷. Infrared spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer using KBr discs. Electronic reflectance spectra of the ligands and complexes were recorded using Genesys 10 Scanning Spectrophotometer made by Thermo Electron Corporation. 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 media was prepared by dissolving 28 g of the nutrient agar in 1000 mL deionized water. The solution was sterilized at 121°C for 15 mins in an autoclave.

Concentrations of 10 μ g/mL, 100 μ g/mL and 1000 μ g/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.^[14–15]

Computational Methods

The complexes chosen for these studies are Ni[AAAH]₃Cl₂, Ni[BUTAH]₃Cl₂ and Ni[BENZAH]₃Cl₂ since the outer- sphere ions have the least probability of interaction with the complex ion in the crystal lattice. Geometries of the Ni (II) complexes ions were initially optimized by the PM3^[18] method and the resulting structures were further optimized using hybrid functional three-parameter Becke exchange Lee-Yang-Parr correlation (DFT-B3LYP) with 6-31G* basis set because of its perceived better accuracy. All calculations were performed with the Spartan 06.^[19] The spin occupied molecular orbitals (SOMO) of the complexes ions were also displaced in order to know the effect of changing 'R' (RCOCH₂CONHNH₂: $R = CH_3$, C_3H_7 and C₆H₅) on the molecular properties as it affects electronic transitions. The calculations were carried out on a 4.0 GHz Dell PC, with 1 Gb RAM and 120 Gb HD, under the windows 2007 operational system.

RESULTS AND DISCUSSION

Preparation of the Compounds

Acetoacetic, butyrylacetic, benzoylacetic were prepared from their ethyl esters by refluxing equimolar amounts of the hydrazine hydrate and their respective ethyl esters for 4 hrs. The hydrazides were obtained in reasonable yields (60–70%) except acetoacetic acid hydrazides, which gave a 37% yield. The representative equation for the formation of the hydrazide is given below:

 $RCOCH_2COOR' + H_2NNH_2 \rightarrow RCOCH_2CONHNH_2 + R'OH$ R=CH₃, C₃H₇, C₆H₅andR'=C₂H₅

The nickel(II) complexes prepared by reacting the metal salts with the respective hydrazides gave a composition of 1:3 mole ratio as given below:

NiX₂. $xH_2O + 3RCOCH_2CONHNH_2 \rightarrow$ Ni(RCOCH₂CONHNH₂)₃(X)₂ where X=Cl, NO₃, CH₃COO or $\frac{1}{2}$ SO₄; R=CH3, C₃H₇ and C₆H₅

The result of the C, H, N and metal analyses showed a fairly good agreement between the observed and calculated values (Table 1). The elemental analyses showed that the acid hydrazide reacted with the nickel(II) salts in ratio 3:1. The nickel complexes display various shades of blue and green color and exhibited marked insolubility in common organic solvents making the growing of a single crystal for X-ray impossible. This is typical of acid hydrazides metal complexes.^[8,14–15]

Infrared

The selected infrared vibrational frequencies of the compounds are listed in Table 2. These vibrational frequencies are very consistent with the structural features of the compounds studied. In the studies of spectra of hydrazides and their metal complexes, three related vibrations are often used to infer coordination of the metals to the ligands.^[14,15,20] These are the carbonyl stretching frequency $[v_s(C=O)]$ or the 'amide 1', the in-plane bending deformation and stretching frequency for cyanate $[\delta(N-H) + v_s(C-N)]$ or the 'amide II' and the amino stretching vibrations $v_s(NH_2)$. In the ligands reported here, the amino stretching frequency $v_s(NH_2)$ observed between 3539- 3452 cm^{-1} became weaker and was lowered to $3195-3375 \text{ cm}^{-1}$ on coordination to the metal suggesting the participation of the amino group in the bonding. The vibrations between 1626-1618 cm^{-1} and 1600–1544 cm^{-1} in the ligands are assigned to 'amide I' and 'amide II' bands, respectively. These bands are lowered to 1618–1569 cm^{-1} and 1594–1473 cm^{-1} on coordination to nickel(II) metal ion. As expected, the highest values for the 'amide I' and 'amide II' vibrations were observed for benzoylacetic acid hydrazides (BENZAH) ligands and their complexes. This is due to the inductive (-I) electron withdrawing effect of the benzoyl group, which reduces the electron available on the hydrazide moiety resulting in increase in the force constants of the bond. Conversely, the acetoacetic acid and butyrylacetic acid hydrazides that have electron donating substituents increases the electron density on the hydrazide moiety. In this series, a bathochromic shift was observed in the 'amide' values which were more pronounced in the butyrylacetic acid hydrazide than acetoacetic acid hydrazide.

Electronic Spectra

The electronic reflectance spectra of the compounds studied (Table 2) have been assigned by critically comparing those of the ligands with the complexes and those of previous work done on similar system.^[10,12,15]

In the ultraviolet region of the compounds studied, the band observed between 45,050–51,810 cm⁻¹ have been assigned to $n \rightarrow \sigma^*$ transitions presumably due to the excitation of a nitrogen lone pair of electron to antibonding σ -orbital of the amino group. Some additional bands observed in this region between 42,200–30030 cm⁻¹ have been assigned to a combination of $\pi \rightarrow \pi^*$ and $\pi \rightarrow$ n transitions of the carbonyl groups.^[1,22] This observation shows significant $\pi \rightarrow \pi^*$ interactions in the complexes and have often been correlated with the involvement of N and O atoms from the ligand in coordination that strengthens the C=O and the –NH₂ bonds involved in the charge transfer process²².

In the visible absorption spectra of Ni(II) octahedral complexes, three spin-allowed transitions are normally observed.^[17] These absorptions are $\nu_1={}^{3}A_2g \rightarrow {}^{3}T_2g$ (F), $\nu_2={}^{3}A_2g \rightarrow {}^{3}T_1g$ (F), and $\nu_3={}^{3}A_2g \rightarrow {}^{3}T_1g$ (P), which generally fall in the range 7000–13,000, 11,000-20,000 and 19,000-27000 cm⁻¹, respectively.

The visible spectra of $Ni(AAAH)_3(NO_3)_2$, Ni(AAAH)₃(OAc)₂ and Ni(AAAH)₃SO₄, which displayed a band each between 15,773 - 15,873 cm⁻¹ region have been assigned to the ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ transition. Ni(AAAH)₃Cl₂ showed the ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)$ transitions, respectively, at 13,699 cm⁻¹ and 20,833 cm⁻¹. The butyrylacetic acid hydrazide complexes showed the ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ transition for Ni(BUTAH)₃(NO₃)₂ and Ni(BUTAH)₃SO₄ at 16,313 cm^{-1} , and 15,385 cm^{-1} , respectively. Ni(BUTAH)₃(OAc)₂ had two absorption bands at 15,385 cm⁻¹ and 25,000 cm⁻¹, which is assignable to the ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ and ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(P)$. Ni(BUTAH)₃Cl₂ had ${}^{3}A_{2}g \rightarrow {}^{3}T_{2}g$ at 9,390 and ${}^{3}A_{2}g \rightarrow$ ${}^{3}T_{1}g(P)$ at 20,661 cm⁻¹.

In the benzoylacetic acid hydrazides complex series, only the ${}^{3}A_{2}g \rightarrow {}^{3}T_{1}g(F)$ transition was observed between 15,625– 16,077 cm⁻¹. These observations and assignments of the transitions in the complexes are consistent with a six coordinate nickel(II) in an octahedral environment.^[23]

Magnetic Moment

Generally, for tetrahedral nickel(II) complexes, effective magnetic moments of (μ_{eff}) 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 B.M are attributed to orbital contributions to the magnetic moments

	Compounds μ_e (empirical form
	(B.M.)
	AAAH
	$(C_4H_8N_2O_2)$
	Ni(AAAH) ₃ SC
	$(C_{12}H_{24}N_6O_{10}S_{10}$
	Ni(AAAH) ₃ (N
	$(C_{12}H_{24}N_8O_{12}N_8O_{$
	Ni(AAAH) ₃ Cl ₂
	$(C_{12}H_{24}N_6O_6C$
	Ni(AAAH) ₃ (O
)14	$(C_{16}H_{30}N_6O_{10}N_6O_{$
50	BUTAH
bei	$(C_6H_{12}N_2O_2)$
em	Ni(BUTAH) ₃ S
lov	(C ₁₈ H ₃₆ N ₆ O ₁₀ S
4 7	Ni(BUTAH) ₃ (N
51	$(C_{18}H_{36}N_8O_{12}N_8O_{$
4	Ni(BUTAH) ₃ C
ţ O	$(C_{18}H_{36}N_6O_6C$
/] a	Ni(BUTAH) ₃ (C
sity	$(C_{22}H_{42}N_6O_{10}N_6O_{$
ver	BENZAH
Jmi	$(C_9H_{10}N_2O_2)$
le l	Ni(BENZAH) ₃
Dicl	$(C_{27}H_{30}N_6O_{10}S_{10}$
É	Ni(BENZAH) ₃
l by	$(C_{27}H_{30}N_8O_{12}N_8O_{$
dec	Ni(BENZAH) ₃
loa	$(C_{27}H_{30}N_6O_6C)$
wn	Ni(BENZAH) ₃
Do	$(C_{31}H_{36}N_6O_{10}N_6O_{$

TABLE 1 Analytical data for the compounds

	For	mula	Yie	eld M.p.					
Compounds μ_{eff} (empirical formula)	Weight	Color	(%)	(°C)	С	Н	Ν	Ni	Analyzed (calculated)
(B.M.)									
AAAH	116.12	cream	61	217-219	41.22	6.86	23.68		
$(C_4H_8N_2O_2)$					(41.37)	(6.94)	(24.13)		
Ni(AAAH) ₃ SO ₄	503.15	lt. green	64	134	29.31	4.81	15.72	15.33	3.40
$(C_{12}H_{24}N_6O_{10}SNi)$		U			(28.65)	(4.81)	(16.70)	(11.67)	
$Ni(AAAH)_3(NO_3)_2$	531.09	lt. green	54	120	27.01	4.60	20.45	11.34	3.26
$(C_{12}H_{24}N_8O_{12}N_i)$		•			(27.14)	(4.56)	(21.10)	(11.05)	
$Ni(AAAH)_3Cl_2$	478.08	green	70	146	32.88	4.68	15.64	16.11	3.30
$(C_{12}H_{24}N_6O_6Cl_2Ni)$		-			(30.15)	(5.06)	(17.58)	(12.28)	
Ni(AAAH) ₃ (OAc) ₂	525.17	lt. green	45	130	36.39	5.66	15.83	11.04	3.16
$(C_{16}H_{30}N_6O_{10}N_i)$					(36.59)	(5.76)	(16.00)	(11.18)	
BUTAH	144.18	cream	62	218-220	49.66	8.32	19.31	_	
$(C_6H_{12}N_2O_2)$					(49.99)	(8.39)	(19.43)		
Ni(BUTAH) ₃ SO ₄	587.31	blue	69	262	36.67	6.25	14.44	10.22	3.09
$(C_{18}H_{36}N_6O_{10}SNi)$					(36.81)	(6.18)	(14.31)	(10.00)	
Ni(BUTAH) ₃ (NO ₃) ₂	615.25	lt. green	69	254	35.30	5.72	18.36	9.67	2.97
$(C_{18}H_{36}N_8O_{12}Ni)$					(35.14)	(5.90)	(18.21)	(9.54)	
Ni(BUTAH) ₃ Cl ₂	562.24	green	65	166–168	38.63	6.22	15.11	10.15	3.20
$(C_{18}H_{36}N_6O_6Cl_2Ni)$					(38.45)	(6.45)	(14.95)	(10.44)	
Ni(BUTAH) ₃ (OAc) ₂	609.33	lt. green	34	224	43.41	6.49	13.90	9.52	3.15
$(C_{22}H_{42}N_6O_{10}Ni)$					(43.37)	(6.95)	(13.79)	(9.64)	
BENZAH	178.19	white	70	156–158	60.44	5.62	15.66		
$(C_9H_{10}N_2O_2)$					(60.66)	(5.66)	(15.72)		
Ni(BENZAH) ₃ SO ₄	689.36	green	70	152	47.21	4.10	12.02	8.50	3.17
$(C_{27}H_{30}N_6O_{10}SNi)$					(47.04)	(4.39)	(12.19)	(8.52)	
Ni(BENZAH) ₃ (NO ₃) ₂	717.30	lt. green	71	148-150	45.26	4.28	15.82	8.18	3.26
$(C_{27}H_{30}N_8O_{12}Ni)$					(45.21)	(4.22)	(15.62)	(8.18)	
Ni(BENZAH) ₃ Cl ₂	664.29	green	65	156–158	49.00	4.66	12.69	8.56	3.19
$(C_{27}H_{30}N_6O_6Cl_2Ni)$					(48.82)	(4.55)	(12.65)	(8.84)	
Ni(BENZAH) ₃ (OAc) ₂	711.38	lt. green	63	160-162	52.46	5.25	11.82	8.04	2.94
$(C_{31}H_{36}N_6O_{10}Ni)$					(52.34)	(5.10)	(11.81)	(8.25)	

and depends very much on the stereochemistry. Thus, the tetrahedral and octahedral Ni(II) complexes have no clear-cut distinction in the magnetic moments, and unusual moments of 2.97 B.M and 3.78 B.M, respectively, have been reported.^[24] The room temperature magnetic moments for the Ni(II) complexes studied were observed between 2.94-3.40 B.M. (Table 1), which falls in the range normally observed for octahedral nickel(II) complexes.^[24]

Antimicrobial Activities

The acid hydrazides and their nickel(II) complexes showed measurable activities against the test organisms by the moderate to high growth inhibition exhibited by some of the compounds.^[25] Ni[BUTAH]₃(OAc)₂ displayed a very high inhi-

bition against Staphylococcus aureus and Pseudomonas putrifaciens (A1), while NI[BENZAH]₃Cl₂ showed moderate growth inhibition against Serratia Marcescens. The other complexes displayed very low inhibition against the tested bacteria. Generally, the activities of the acid hydrazides were enhanced by coordination to the nickel(II) ions.

Computational Studies

Geometries and structural data

The modeled molecular structures consist of a mononuclear, six-coordinated Ni(II) complexed with three units of 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. The geometry around the nickel(II) is best

	-	-		· · · ·		
Compounds	amide I	amide II	νNH_2	Electronic bands ($\times 10^3$)		
AAAH	1612(m)	1544(w)	3539(w)	51.28, 37.18		
Ni(AAAH) ₃ SO ₄	1570(s)	1556(w)	3345(w)	15.87		
Ni(AAAH) ₃ (NO ₃) ₂	1570(s)	1556(w)	3557(w)	40.00, 36.50, 34.96, 15.77		
Ni(AAAH) ₃ Cl ₂	1569(m)	_	3375(w)	20.83, 13.70		
Ni(AAAH) ₃ (OAc) ₂	1570(s)	1513(w)	3339(w)	48.78, 40.49, 36.50, 32.57, 15.77		
BUTAH	1618(m)	1592(w)	3460(m)	45.05		
Ni(BUTAH) ₃ SO ₄	1570(s)	1476(s)	3356(w)	15.39		
Ni(BUTAH) ₃ (NO ₃) ₂	1570(s)	1473(s)	3356(m)	42.02, 35.34, 33.22, 16.31		
Ni(BUTAH) ₃ Cl ₂	1572(m)	1505(s)	3195(w)	20.66, 9.39		
Ni(BUTAH) ₃ (OAc) ₂	1572(s)	1476(s)	3206(w)	25.00, 15.39		
BENZAH	1626(m)	1600(s)	3452(w)	49.75, 41.49, 38.61		
Ni(BENZAH) ₃ SO ₄	1612(w)	1579(w)	3369(m)	51.81, 37.31, 33.22, 15.63		
Ni(BENZAH) ₃ (NO ₃) ₂	1594(s)	1553(m)	3357(w)	35.09, 30.03, 15.92		
Ni(BENZAH) ₃ Cl ₂	1618(m)	1594(s)	3235(m)	48.78, 36.90, 33.56, 16.08		
Ni(BENZAH) ₃ (OAc) ₂	1618(s)	1594(s)	3326(m)	51.02, 36.90, 31.65, 15.70		

TABLE 2 Some infrared frequencies and electronic spectral transitions for the compounds (cm^{-1})

s = strong; m = medium; w = weak

described as distorted octahedral. The calculated bite angles for Ni(AAAH)₃Cl₂using B3LYP/6-31G* for O(1)-Ni-(N1), O(2)-Ni-N(3) and O(3)-Ni-N(5) are 90.17, 94.46, and 92.86°, respectively. While the same bite angles for Ni(BUTAH)₃Cl₂and Ni(BENZAH)₃Cl₂ are 90.81, 92.47, 92.53, and 90.95, 93.43, 92.35, respectively. While the two methods of calculations are closer in this respect, there is a small variation of less than 4° from the 'ideal value' of 90° for a nickel complex under-

going no distortion. For the three complexes, there is a larger deviation from 'an ideal 180° ' for the trans octahedral angles of O(1)-Ni-N(3), O(2)-Ni-N(5), and O(3)-Ni-N(1), which experienced a variation of between ± 18 in the three complexes using both calculation methods. These observations are similar to those obtained experimentally from our previous studies.^[15] The bond distances for Ni-O and Ni-N are affected by changing 'R' (from acetyl, butyl and benzyl), although the differences



FIG. 1. Graphical representation of the SOMO orbitals for (a) $Ni[AAAH]_3^{+1}$ ion, (b) $Ni[AAAH]_3Cl_2$, (c) $Ni[BUTAH]_3Cl_2$ and (d) $Ni[BENZAH]_3Cl_2$.

	Ni[AAAH] ₃ Cl ₂ Ni[BUTAH] ₃ Cl ₂		BUTAH] ₃ Cl ₂	Ni[BENZAH] ₃ Cl ₂			
Numbering PM3		B3LYP/6-31G*	PM3	B3LYP/6-31G*	PM3	B3LYP/6-31G*	
Ni-O ₁	1.888	1.922	1.887	1.942	1.881	1.932	
Ni-O ₂	1.845	1.925	1.845	1.926	1.836	1.945	
Ni-O ₃	1.867	1.942	1.868	1.941	1.898	1.968	
Ni-N ₁	1.872	1.956	1.871	1.955	1.858	1.937	
Ni-N ₃	1.871	1.985	1.871	1.987	1.874	1.988	
Ni-N ₅	1.854	1.955	1.855	1.954	1.851	1.954	
$C_1 - O_1$	1.284	1.297	1.285	1.296	1.283	1.295	
C_2-O_2	1.351	1.356	1.349	1.352	1.365	1.376	
$C_{3}-O_{3}$	1.337	1.346	1.335	1.344	1.256	1.246	
$C_1 - N_2$	1.357	1.381	1.357	1.381	1.365	1.392	
C_2-N_4	1.470	1.478	1.468	1.474	1.476	1.484	
$C_3 - N_6$	1.514	1.526	1.512	1.533	1.422	1.441	
$N_1 - N_2$	1.455	1.479	1.454	1.477	1.462	1.468	
N_3-N_4	1.440	1.442	1.441	1.439	1.435	1.423	
$N_5 - N_6$	1.344	1.352	1.345	1.350	1.382	1.386	
O ₁ -Ni-O ₂	83.89	86.06	83.77	85.19	81.38	83.59	
O ₁ -Ni-O ₃	83.82	89.42	83.71	90.06	82.38	90.06	
O ₂ -Ni-O ₃	82.05	89.15	82.22	89.92	83.72	89.71	
N_1 -Ni- N_3	91.14	91.89	91.09	91.82	91.43	91.34	
N ₁ -Ni-N ₅	88.05	91.97	87.98	90.99	88.36	92.78	
N ₃ -Ni-N ₅	90.89	86.42	90.63	86.47	90.86	87.02	
O ₁ -Ni-N ₁	91.75	90.17	91.78	90.81	92.37	90.95	
O ₁ -Ni-N ₃	175.65	170.67	175.46	171.21	173.49	171.28	
O ₁ -Ni-N ₅	92.44	89.70	92.98	89.24	94.53	92.91	
O ₂ -Ni-N ₁	97.18	102.08	97.32	100.94	97.09	101.38	
O ₂ -Ni-N ₃	92.54	94.46	92.38	92.47	92.90	93.43	
O ₂ -Ni-N ₅	173.69	169.30	173.85	172.80	173.30	169.59	
O ₃ -Ni-N ₁	175.56	198.93	175.49	197.88	174.52	198.44	
O ₃ -Ni-N ₃	93.25	91.55	93.41	92.97	93.94	90.66	
O ₃ -Ni-N ₅	92.47	92.86	92.26	92.53	90.50	92.35	
C ₁ -O ₁ -Ni	106.42	107.19	106.80	107.05	108.01	108.58	
C ₂ -O ₂ -Ni	107.89	106.45	107.93	109.44	107.43	109.78	
C ₃ -O ₃ -Ni	107.38	112.66	107.39	110.32	106.45	112.01	
$O_1 - C_1 - N_2$	118.64	119.91	118.68	119.14	117.23	119.93	
$O_2 - C_2 - N_4$	112.23	115.03	112.36	116.04	112.57	117.21	
$O_3 - C_3 - N_6$	114.09	121.56	113.93	121.18	119.80	120.87	
N ₂ -N ₁ -Ni	100.06	103.07	100.20	102.75	101.04	102.74	
N ₄ -N ₃ -Ni	99.45	101.01	99.20	103.80	98.81	102.15	
N ₆ -N ₅ -Ni	106.58	108.77	106.54	108.74	105.79	109.53	
$C_1-N_2-N_2$	119.76	120.63	119.69	121.01	119.53	121.31	
$C_2-N_4-N_3$	112.77	114.87	119.52	119.29	112.93	116.03	
C ₃ -N ₆ -N ₅	115.74	116.62	115.52	117.82	115.85	116.98	

TABLE 3
Selected bond distances (Å) and bond angles (°) of Ni[AAAH] ₃ Cl ₂ , Ni[BUTAH] ₃ Cl ₂ , and Ni[BENZAH] ₃ Cl ₂ calculated at PM3
and B3LYP/6-31G* levels



R = CH₃CO, C₃H₇CO, C₆H₄CO; X = Cl, NO₃, CH₃COO, or 1/2SO₄

FIG. 2. Suggested structures for the complexes.

ranged from 0.002Å to 0.024Å. Generally, the Ni-Nand Ni-O calculated at PM3 are shorter than that of B3LYP/6-31G*. The correct values may be in between the two values perhaps closer to the one calculated using B3LYP/6-31G*. In our previous studies on the single crystal X-ray structure of Ni[C₆H₅CONHNH₂]₃Cl₂.3CH₃OH,^[15] the calculated bond distances are shorter than that of the experimental data; however, as expected, the results from B3LYP/6-31G* are closer to the X-ray data due to level theory and parameterizations. The data for the different bond angles and bond distances are also compared in Table 3.

These studies show in the absence of experimentally obtained X-ray data glaring distortions from the perfect octahedral geometry around the nickel(II) ions of the complexes modeled, although both theories gave different variations. In spite of different calculation methods being used to obtain the data presented here for the modeled complexes, a comparison between these results at PM3 and DFT showed that the spin occupied molecular orbitals (SOMO) participations are predominantly from two hydrazide units on Ni[AAAH]₃Cl₂ compound with one chlorine involved. For Ni[BUTAH]₃Cl₂and Ni[BENZAH]₃Cl₂ complexes, the SOMO are on one unit each of BUTAH and BENZAH, respectively (Figure 1).

CONCLUSION

These complexes coordinate to the nickel(II) ion using the amide carbonyl C=O and the amino moiety of the hydrazides as evident from a critical comparison of the spectra of the ligands and complexes. The elemental analysis, electronic spectral studies, magnetic susceptibility measurements and theoretical studies are consistent with a six-coordinate, distorted octahedral arrangements of three hydrazide units around the nickel(II) ion. Some of

The complexes also showed measurable activities against the tested fungi and bacteria. An octahedral configuration of the complexes (Figure 2) is proposed similar to the crystal structure of Ni[BAH]₃Cl₂.3CH₃OH¹⁶ with the anions in the outer coordination sphere.

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