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Synthesis and physicochemical studies of carboxylic acid hydrazide complexes of some nickel(II) β-diketonates

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Abstract

Twelve carboxylic acid hydrazide complexes of nickel(II) β-diketonates were synthesised and characterised by metal analysis, magnetic moment susceptibility, molar conductivity, solid reflectance electronic and infrared spectra measurements. The acid-hydrazide ligands were compared with their corresponding complexes. The infrared spectra bands of the complexes indicated that the oxygen atom of nickel(II) β-diketonates and the amino nitrogen were coordinated to the metal ion. The solid reflectance electronic spectral measurements displayed the three allowed transitions expected of an octahedral nickel(II) compound which are the ${}^3A_{2g} \rightarrow {}^3T_{2g}$; ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) while some showed spin-forbidden transitions. The room temperature magnetic moments obtained ranged between 1.75-4.32 B.M corroborating the electronic spectral measurements for the compounds. The molar conductivity measurements in nitromethane found in the range 1.80-7.01 $ohm^{-1}cm^{2}mol^{-1}$ showed that they are non-electrolytes which are lower than reported value of 60-118 $ohm^{-1}cm^{2}mol^{-1}$ for a 1:1 electrolyte. +9owever, the high values observed for this complexes might be suggestive of antiferromagnetism operating through a Ni-Ni bond in a dimeric structure, such that each Ni atom had a moment of 2.35 B.M.

Keywords**:** Nickel; B-Diketonates; Hydrazides; Coordination; Molar conductivity; Transitions

Introduction

Heterocyclic compounds have in recent times become one of the largest classical divisions of organic chemistry. They are of immense importance not only biologically and industrially but also to the functioning of any human society due to the properties they exhibit. The role they play in the pharmaceutical industry cannot be over-emphasised. For instance, majority of pharmaceutical products that mimic natural products with biological activity are heterocycles. In recent times, the synthesis and studies of hydrazides have attracted some attention in the field of coordination chemistry, they have been found to be more useful when they are coordinated to metals and the hydrazides acting as a ligand (Singh and

Singh, 2012). Hydrazides are a class of organic compounds with the formula R−NR^1−NR^{2}R^3 where R is acyl, sulfonyl, phosphoryl or phosphonyl, R^1, R^2, R^3 and R' are any groups-typically hydrogen (Berillo and Dyusebaeva, 2022, Majumdar *et al.,* 2014). Unlike hydrazine and alkylhydrazines, hydrazides are non-basic owing to the inductive influence of the acyl, sulfonyl, or phosphoryl substituent. A great interest to acid hydrazides and thiohydrazides is related to quality and simplicity of their synthesis and purification process as well as their high chemical reactivity (Alanine *et al*, 2004; Mathew *et al.*, 2015).

Products of hydrazides condensation with aldehydes-hydrazones revealed a wide range of antimicrobial, antiviral, antitumor, hypolipidemic, hypotensive, diuretic activities and activity against M. Tuberculosis at a relatively low toxicity (Alanine *et al*., 2004; Narang *et al*., 2012; Pillai *et al*., 2014; Karaman *et al*.,2016). The usefulness of hydrazides and their metal complexes has been manifested in the fields of medicine, engineering, polymer chemistry and plant growth but hydrazide in particular has been immensely used in biological applications. This is because of the activity of the –CONHNH$_2$ group in the compound. They are also used as antitubacular agents and the isonicotinic acid hydrazide is usually for this purpose.

Hydrazides are used as stabilizers for polymers in that they form stable high molecular weight constituents against the deteriorative activity of heavy metals (Singh and Singh, 2012). They are also used as crosslinking agents between polyamides and polyimides polymers. Water soluble monomeric hydrazides has been introduced into cigarette filters for the selective removal of aldehydes (Zhang *et al.*, 2023). Hydrazides are also used in textile industry. They have been used as textile softeners in laundering compounds containing anionic, non-ionic and amphoteric surfactants and the usual additives. They are also used as antioxidants for glycerides (Sztanke and Sztanke, 2017) and to enhance the bonding of free sulphur in rubber during vulcanization (Padakan and Radagan 2016), as anti-knock additives (Viayna, 2021), as monoamine oxidase inhibitors, stain repellant and cellulose stabilizers (Majumdar *et al*., 2014). Hydrazide complexes of transition metal ions are known to provide useful models for elucidation of the mechanisms of enzyme inhibition by hydrazine derivatives.

In this study, we report the synthesis and physicochemical studies of the new acyl hydrazides and their Ni(II) β-diketonates of 2,4-pentanedione. The major aims of this work were: (1) to prepare novel Ni(II) acetylacetonate hydrazides; (2) to evaluate and characterise the synthesised compounds.

Materials and Methods

Materials and Reagents

All the reagents and solvents used in this study were purchased from Aldrich chemicals and of analar grade; and it was ensured that all the apparatus and equipment were in a clean state and in proper working conditions.

Preparation of Hydrazides

The hydrazides used as ligands were prepared by refluxing a mixture of 0.15 mole of the ester, 0.4 mole of hydrazine hydrate and 20 cm^3 of methanol for 2 hours before the resulting solution was distilled in vacuo. (Shono *et al.,* 1967).

Preparation of the derivatives of 2,4-Pentanedione

The derivatives were prepared by varying the substituents on the third carbon of the 2,4-pentanedione. The processes involved are described below:

Preparation of 3-methyl-2,4-pentanedione

A mixture of 66.75 cm^3 (0.65 mole) of 2,4-pentanedione, 113g (0.8 mole) of methyl iodide. 84g (0.608 mole) of anhydrous potassium trioxocarbonate (V) dried at 100 ^oC for 12 hours and 125 cm^3 of acetone were placed in a 500 cm^3 round bottom flask fitted with a reflux condenser and a calcium chloride guard tube. The mixture was heated for 4.5 hours and was allowed to cool. The work up to the reaction was improved by adding 250 cm^3 of petroleum ether (40-60%) to the cold reaction mixture before filtering and washing the solid with a 1:1 mixture of acetone and petroleum ether. The resulting mixture was concentrated on a steam bath and the residual oil was distilled (Shono *et al*., 1967).

Preparation of 3-Chloro-2,4-pentanedione

About 206 cm^3 (2 moles) of 2,4-pentadione was measured into a round-bottom flask and 161.6 (2 moles) of sulphurylchloride was added dropwise with stirring for 2 hours while the temperature was kept between 0 and 5 ^oC with the aid of ice. The resulting mixture was then poured into 200 cm^3 of water before it was extracted with ether. The organic layer in which the 3-Chloro-2,4-pentanedione was present was separated from the aqueous layer and distilled in vacuo and the 3-Cl-2,4-pentanedione was collected at a temperature range of 154-156 ^oC (Tanaka *et al*., 1959).

Preparation of Nickel (II)β-diketonate hydrazide complexes

3.56g (0.0015 mole) of Nickel chloride hexahydrate was dissolved in minimum amount of distilled water (10 cm^3) and stirred on a magnetic stirrer until the total dissolution of the nickel chloride was obtained. 3.02 cm^3 (0.03 mole) of 2,4-pentanedione was added dropwise with continuous stirring. The pH of the resulting solution was adjusted to 9 with concentrated ammonia solution after which an emergence of precipitate was observed. 0.03 mole of the hydrazide was then added with continuous stirring for another 1.5 hours. The precipitates formed were filtered and dried in a desiccator. Other nickel (II) hydrazide complexes were synthesised using the described method.

Preparation of the oxalic acid hydrazide of Nickel (II)β-diketonate

The mixture of nickel chloride, 2,4-pentanedione and the oxalic acid hydrazide that had been previously mixed with 40 cm^3 of methanol was stirred in a quick-fit conical flask fitted with a condenser for 14 hours at room temperature before the resulting precipitate was filtered off and dried in vacuo.

The described process of reaction can be expressed in the equation below

$$NiCl_2.6H_2O + 2X\text{-acac} + 2Hz \longrightarrow Ni(X\text{-acac})_2Hz_2$$

Where X: Electron releasing or withdrawing substituents.
Hz: Hydrazide

Determination of the percentage of Nickel(II) in complexes

The amount of nickel(II) present in $25cm^3$ of the standard solutions of the digested complexes was calculated bearing in mind that the number of moles of EDTA is equal to the number of moles of the nickel(II) present in each synthesized complex based on their mole ratio. The obtained results were compared with the calculated ones based on the 1:1, 1:2 and 1:3 metal to ligand ratio. The obtained results were used to predict the possible constituents and combinations of each synthesized complex.

Physical measurements

The melting points of the complexes were determined using the Gallenkamp Variable Heater melting point apparatus and the determinations were done over the smallest possible range. The solubility of the complexes was studied in various solvents to determine the extent of their interactions with the solvents. The magnetic moment susceptibilities of the complexes were determined at 25±2 ^{o}C using the Gouy method with mercury tetrathiocyanatocobaltate(II) as the calibrant. The molar conductance of the complexes soluble in nitromethane and nitrobenzene were determined using the conductivity bridge with 0.1 cell constant. The concentration of each solution was approximately 1×10^{-3} M. The diffuse reflectance spectra of the complexes were recorded on a unicam SP500 spectrophotometer equipped with a reflectance attachment, using $CaCO_3$ as a reference. The infrared spectra of the complexes and the ligands involved in the coordination with the central nickel (II) metal was carried out using a Unicam 3-300 Infrared spectrophotometer. The complexes and liquid samples were pressed on KBr disc while the infrared frequencies of the pure liquid samples were taken using NaCl.

Results and Discussion

Physical and Analytical Data

The analytical data of the prepared compounds as presented in Table 1 indicated that the colours of the complexes were mostly in various shades of green and blue while a few were grey indicating a d-d transition occasioned by the excitation of electrons from a lower energy d-orbital to a higher one (Table 1). The melting points of the synthesised compounds were observed at relatively high temperatures ranging between 155-260 ^{o}C. This indicated stronger intermolecular interactions resulting in a relatively higher stability. The % metal analysis were in good agreement with those calculated for the proposed structures.

Table 1: Analytical data of the carboxylic acid hydrazide complexes of nickel(II) β-diketonates

Compound	Empirical Formula	Colour	Melting Point (^{o}C)	Yield (%)	% Nickel Exp (Cal)	µeff (B.M)	Molar Conductivity ($\Omega^{-1}cm^{2}mol^{-1}$)
$[Ni(acac)_2FAHz_4]$	$C_{14} H_{32} Ni N_8 O_8$	Greenish-blue	167-169	39	11.81(11.77)	3.04	1.84
$[(Ni(acac)_2)_2EAHz_5]$	$C_{30} H_{62} Ni_2 N_{10} O_{13}$	Light-blue	165-168	23	13.19(13.23)	3.98	1.83
$[(Ni(acac)_2)_2PAHz_3]$	$C_{29} H_{56} Ni_2 N_6 O_{11}$	Blue	169-171	35	15.72(15.00)	3.90	3.03
$[Ni(acac)_2]MDHz_2$	$C_{16} H_{32} Ni N_8 O_8$	Light-brown	158-161	17	10.17(11.22)	3.59	ND
$[(Ni(acac)_2)_2SDHz_5]$	$C_{40} H_{82} Ni_2 N_{20} O_{18}$	Light-blue	169-172	19	10.66(9.41)	4.32	1.80
$[(Ni(acac)_2)_2ODHz_3]$	$C_{26} H_{50} Ni_2 N_{12} O_{14}$	Deep-blue	170_{Dec}	54	14.12(13.47)	3.57	ND
$[Ni(acac)_2BzHz]$	$C_{17} H_{22} Ni N_2 O_5$	Deep-green	155_{Dec}	10	14.67(14.80)	1.75	4.16
$[(Ni(Cl\text{-}acac)_2)_2BzHz_3]$	$C_{41} H_{52} Ni_2 N_6 O_{11} Cl_4$	Deep-blue	249-252	28	11.52(11.08)	4.07	3.14
$[(Ni(Et\text{-}acac)_2)_2BzHz_3]$	$C_{49} H_{72} Ni_2 N_6 O_{11}$	Light-grey	189-191	5	11.80(11.80)	4.03	7.01
$[Ni(acac)_2PthHz]$	$C_{18} H_{24} Ni N_4 O_6$	Light-green	240_{Dec}	37	12.96(12.90)	4.11	ND
$[Ni(Cl\text{-}acac)_2PthHz_4]$	$C_{42} H_{54} Cl_2 Ni N_{16} O_{13}$	Light-green	252-255	79	5.57(5.32)	2.89	5.35
$[Ni(Bu\text{-}acac)_2PthHz_3]$	$C_{42} H_{62} Ni N_{12} O_{10}$	Whitish-grey	260_{Dec}	79	6.84(6.16)	3.08	5.70

Key: *ND = not detected*

Magnetic Data

The effective magnetic moments of the complexes studied ranged between 1.75-4.32BM (Table 1). The spin only moment expected for Nickel (II) complexes with a d^8 configuration is 2.83 B.M. Monomeric, high spin octahedral Ni(II) complexes with octahedral geometry usually gives moments whose values ranges from 2.8-3.4 B.M. depending on the magnitude of the orbital configuration and temperature while those with tetrahedral geometry has values ranging between 3.5-4.2 B.M. (Osowole and Odutemu, 2016).

The complex $Ni(acac)_2BzHz$ gave the lowest moment of 1.75 B.M. but in the absence of the information of temperature dependence of susceptibilities of low moment complexes, it is not possible to ascertain whether the low values of the moment is due to existence of the monomers in the solids or to the effect of magnetic exchange between nickel atoms in a completely polarized solids. $Ni(Cl\text{-}acac)_2PthHz_4$ gave a moment of 2.89 B.M. which appears close to the spin only moment of nickel (II) while the complexes [Ni(acac)2FAHz4], $Ni(acac)_2MDHz_2$ and $Ni(acac)_2PthHz_3$ whose values were between 3.04-3.59 B.M. were still within the expected value for an octahedral geometry with a slight deviation which could be due to an appreciable orbital configuration arising from spin –orbit coupling (Osanai *et al.*, 2006; Raman *et al.*, 2004). The complexes $[Ni(acac)_2]_2PAHz_3$ and $[Ni(acac)_2]_2EAHz_5$ gave moments of 3.9 and 3.98 B.M. respectively while the remaining complexes gave moments ranging between 4.03 and 4.32 B.M. However, the high values observed for this complexes might be suggestive of antiferromagnetism (Osowole and Odutemu, 2016) operating through a Ni-Ni bond in a dimeric structure, such that each Ni atom had a moment of 2.35 B.M.

Conductance Measurements

The nickel(II) complexes behaved as non-electrolytes in nitromethane and nitrobenzene as shown by their molar conductivities (Λm) of 1.80-7.01 $\Omega^{-1}cm^2mol^{-1}$ (Table 1) which were much lower than expected value for 1:1 electrolyte at 60-118 $\Omega^{-1}cm^2mol^{-1}$ (Osowole and Daramola, 2012).

Solubility Test

The solubility of the Carboxylic Acid Hydrazide ligands and their Complexes of Nickel(II) β-Diketonates of the complexes in ten different polar and non-polar solvents which are water, methanol, ethanol, acetone, dimethylsulphoxide, dimethylformamide, nitromethane, nitrobenzene, trichloromethane and benzene showed that the complexes were insoluble in the non-polar solvent benzene but most were completely soluble in nitrobenzene and nitromethane. Hence, they displayed non-electrolytic property in those solvents.

Infrared Spectral

The infrared spectral and data (Figs.1-4 and Table 2) showed different absorption bands and were assigned by comparing those of the synthesised hydrazides with their nickel(II) β-diketonates complexes. The bands in the region 3500-3000cm^{-1} assigned to ν(N-H) were observed for the compounds and a lower frequency shift was displayed from the prepared hydrazides and the complexes. This trend was also displayed for ν(C=O) absorption bands for all the synthesised compounds. The ν(C=O) bands were observed in the region 1785-1620 cm^{-1} for the ligands and 1665-1575cm^{-1} for the nickel(II) β-diketonates.

Two sets of carbonyl vibrational modes were observed in the hydrazide complexes and a general hypsochromic shifts were observed when compared with those of the ligands and nickel (II) β-diketonates. The lowest values of the two sets can be assigned to the ν(C=O) of the β-diketonates in which the possibility of linkage to the central metal is assumed (Osowole, A.A., 2008; Osowole, A.A., 2012). This can be explained by the fact that electrons are withdrawn from the carbonyl group thus lengthening the bond and lowering the absorption frequency. Therefore, the lowering of the ν(C=O) in the amide group can be said to be due to the possibility of H-bonding due to the presence of the N-H group. The vibrational frequencies between 695-400 cm^{-1} are assigned to the metal-ligand vibrations, ν(M–L) modes, evidence for the formation of M–O/M–N bonds (Omoregie and Woods, 2011; Olanrewaju *et al.*, 2018).

Table 2: Infrared spectral data of the carboxylic acid hydrazide complexes of nickel (II) β-diketonates

Compound	**Absorption Bands (cm^{-1})**					
	ν(N-H)	**ν(O-H)**	**ν(C=O)**	**δ(NH_2)**	**ν(CN) Keto +NH_2**	**ν(M-L)**
FAH_Z	3490w		1620m, b		1530vw	
$Ni(acac)_2.H_2O$			1665sh, 1622vs			
$[Ni(acac)_2FAHz_4]$	3260s		1590s, 1570w	1140m	1510s	650w, 610w, 550m, 420m
EAH_Z	3400w, b; 3300w		1650m, br		1540w	
$[(Ni(acac)_2)_2EAHz_5]$	3500vw, 3225s		1600m, 1565m	1149w	1500s	650w, 640w 600w, 410m

PAHz	3490w, b		1670w, b 1600w, b			
[(Ni(acac)$_2$)$_2$PAHz$_3$]	3480w,br, 3270s, 3210w,sh		1585s, b	1190w, 1160m, 1130w	1510m	650m, 620m, 560m, 400m
MDHz	3520vw, 3400vw, 3280w, 3020vw		1680w	1150vw	1530w	
[Ni(acac)$_2$MDHz$_2$]	3480w, b, 3200m, 3210w,s			1190w, 1140w	1505m	660w, 620vw, 570w
SDHz	3480vw, 3400w, 3300m, 3200w, 3000w		1625m	1175m, 1120vw	1530m	
[(Ni(acac)$_2$)$_2$SDHz$_5$]	3285s, b		1590m, 1565s	1140m	1510s	650w, 610w, 550m, 420m, 350w
ODHz	3400vw, 3280m, 3180w, 3000w		1700vw, 1600vw	1100m	1530s	
[(Ni(acac)$_2$)$_2$ODHz$_3$]	3200br		1620,1570m	1160m	1525w	650w, 540w, 420w
BzHz	3400w		1670vw, b	1190vw, 1150vw, 1130vw	1540vw	
[Ni(acac)$_2$BzHz]	3540w, 3400w	3400br	1700vw, 1690vw, 1540m	1180w, 1100vw	1535m	600w, 530w
[[(Ni(Et-acac)$_2$)$_2$].2H$_2$O		3403b	1585w,b			653vw, 418vw
[(Ni(Et-acac)$_2$)$_2$BzHz$_3$]	3500w		1620m, 1590w, 1550m	1190m	1540w	580w, 530w, 440w
[Ni(Cl-acac)$_2$]		3352vb	1575b			599vw, 455w, 417vw
[(Ni(Cl-acac)$_2$)$_2$BzHz$_3$]	3400vw			1225w	1530w	695w, 550vw
PthHz	3440w, 3400w, b		1785w	1160vw	1540vw	
[Ni(acac)$_2$PthHz]	3280s, b		1690w, 1580w	1155m	1535vw	645w, 560w, 485w, 420w
[Ni(Cl-acac)$_2$PthHz$_4$]	3490vw, 3400vw, 3260vw, 3120w		1640w, 1580w	1145vw	1515w,br	680m,645w, 495w, 380w
[Ni(Bu-acac)$_2$].H$_2$O		3420vb	1695vw, b;1570s,b			440w, b
[Ni(Bu-acac)$_2$PthHz$_3$]	3505vw, 3220m, 3120w		1650m, 1600w, 1560w		1515vw	

KEY: *s= sharp, vs= very sharp, m= medium, w= weak, vw= very weak, b= broad, vb= very broad*

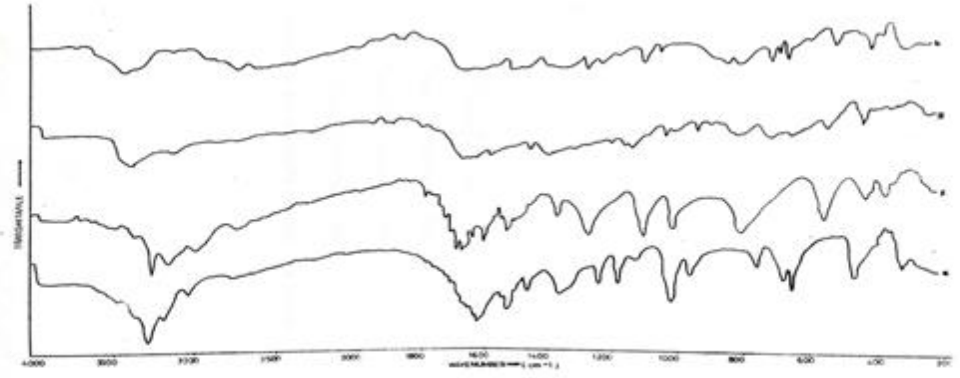


Figure 1: Infrared Spectral of the Carboxylic acid Hydrazides, (a) FAHz, (b) EAHz, (c) PAHz, (d) MD

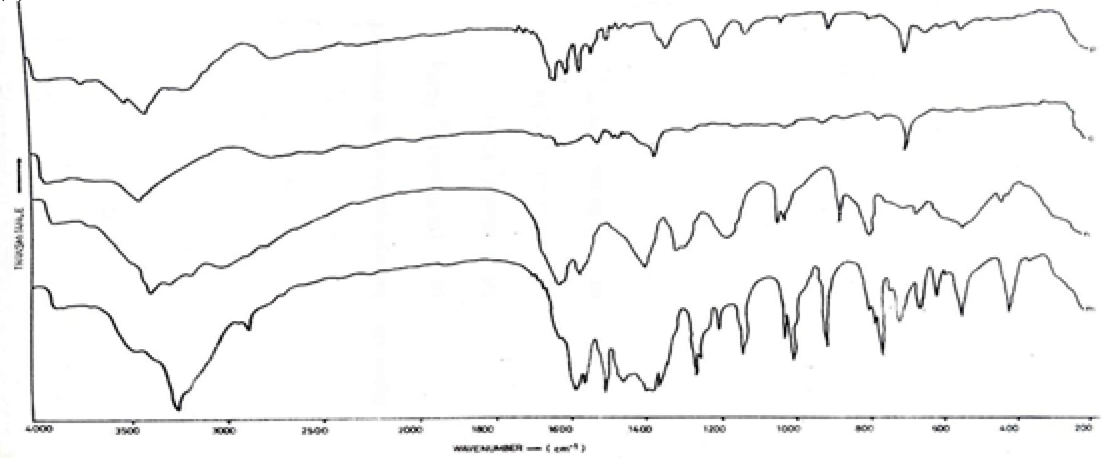


Figure 2: Infrared Spectral of the Carboxylic acid Hydrazides,(e) SDHz,, (f) ODHz, (g) BzHz, (h) PthHz

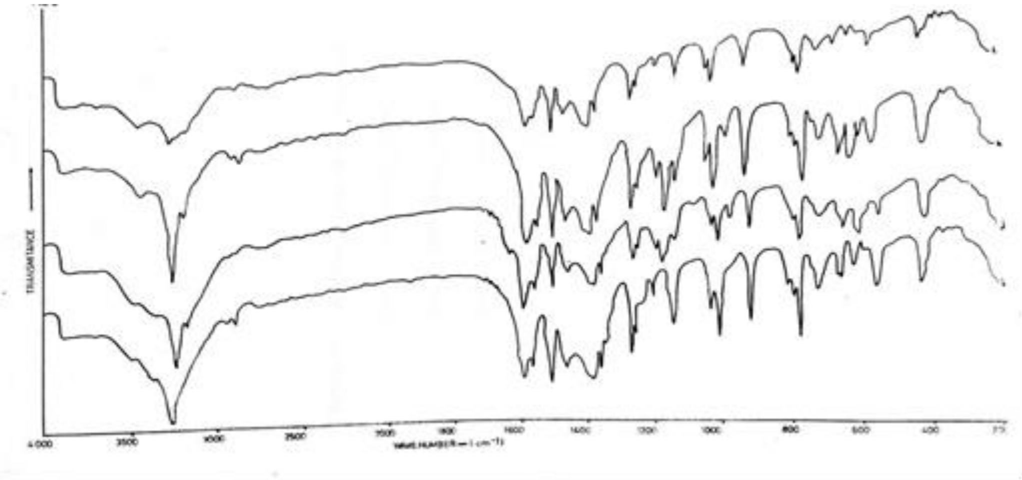


Figure 3: Infrared Spectral of the Complexes: (i) [Ni(acac)$_2$FAHz$_4$], (j) [(Ni(acac)$_2$)$_2$EAHz$_5$],

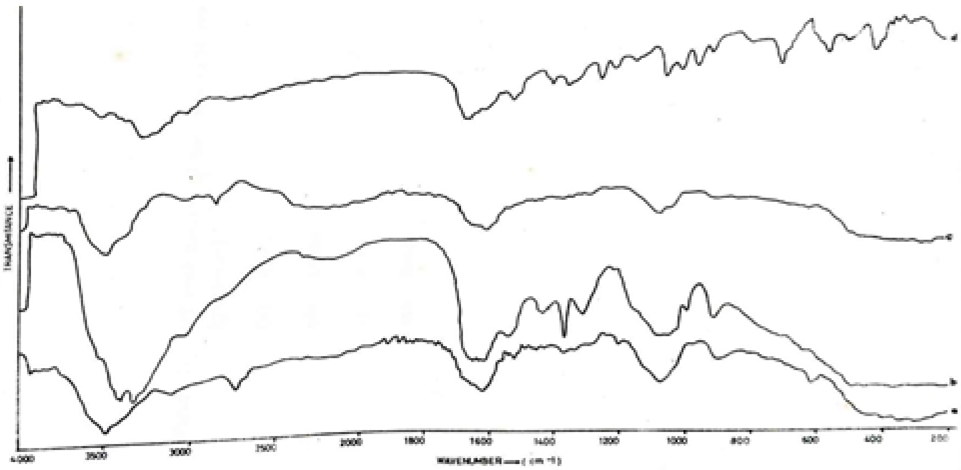


Figure 4: Infrared Spectral of the Complexes: (m) [(Ni(acac)$_2$)$_2$SDHz$_5$], (n) [(Ni(acac)$_2$)$_2$ODHz$_3$], (o) [Ni(acac)$_2$BzHz], (p) [(Ni(Cl-acac)$_2$)$_2$BzHz]

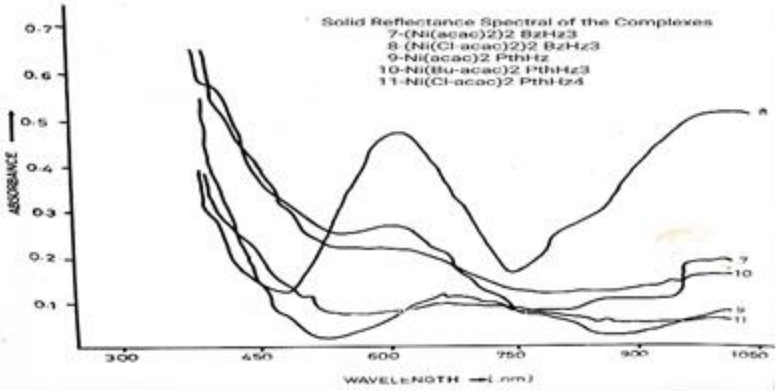
Electronic Spectra Data

The absorption spectra bands obtained for the complexes (Table 3; Fig. 5a-c) showed the expected transitions of Nickel (II) (Cotton and Wilkinson, 1988). For complexes with octahedral geometry, three basic transitions are expected from the ground state term, $^3A_{2g}$. They are $^3A_{2g} \rightarrow {^3T_{2g}}$; $^3A_{2g} \rightarrow {^3T_{1g}}$ (F) and $^3A_{2g} \rightarrow {^3T_{1g}}$ (P) which are observed between 7000-13000 cm^{-1}, 11000-20000 cm^{-1} respectively. Two additional spin forbidden bands $^3A_{2g} \rightarrow {^1E_g}$ and $^3A_{2g} \rightarrow {^1T_{2g}}$ are also observed at times. (Osowole and Daramola, 2012). A typical spectra of a tetrahedral nickel(II) complex have multiple visible bands at 8000 cm^{-1} and 16000 cm^{-1} which has been assigned to the $^3T_1 \rightarrow {^3A_2}$ and $^3T_1 \rightarrow {^3T_1}$ (P) transitions respectively. In certain circumstances, the $^3T_1 \rightarrow {^3T_2}$ is also observed. Weak bands on the low and high energy sides have been assigned to transitions to the ^1D and ^1G levels. Square planar nickel(II) complexes are distinguished from the octahedral and tetrahedral complexes in that there is usually no electronic transition occurring below 10000cm-1 but two prominent bands are observed at 15000-25000cm^{-1} and 23000-30000cm^{-1} and these are for the $^3T_1 \rightarrow {^3A_2}$ and $^3T_1 \rightarrow {^3T_1}$ (P) transitions respectively.

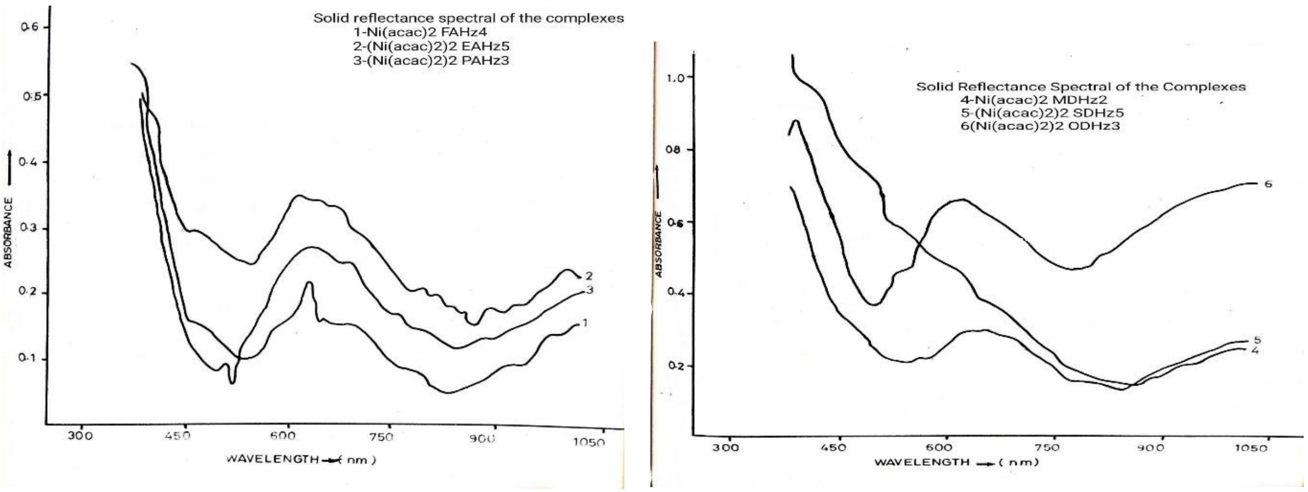
Most of the complexes studied showed three allowed transitions of an octahedral geometry with some spin forbidden transitions except for Ni(acac)$_2$ MDHz$_2$, [Ni(acac)$_2$]$_2$ SDHz$_5$, Ni(acac)$_2$ PthHz and Ni(Bu-acac)$_2$ PthHz$_3$ in which only two allowed transitions at 9900-10204 and 15385-16667 cm^{-1}. Spin forbidden transitions were not observed in [Ni(acac)$_2$]$_2$EAHz$_5$, [Ni(acac)$_2$]$_2$PAHz$_3$, Ni(Cl-acac)$_2$PthHz$_4$ and Ni(acac)$_2$BzHz (Chaudhary *et al.*, 2005, Agarwal and Prasad, 2008).

Table 3: Electronic spectra data of the complexes

	Tentative band assignments and transitions (cm^{-1})				
Compound	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^2A_{2g} \rightarrow {}^3T_{1g}$(F)	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	$^3A_{2g} \rightarrow {}^1Eg$	$^3A_{2g} \rightarrow {}^1T_{1g}$
[Ni(acac)2FAHz4]	9900	15873	27027		21739
[(Ni(acac)$_2$)$_2$EAHz$_5$]	10101	16393	21739	14286	
[(Ni(acac)$_2$)$_2$PAHz$_3$]	9900	15873	19608		
[Ni(acac)$_2$]MDHz$_2$	9900	-	24390	15873	20000
[(Ni(acac)$_2$)$_2$SDHz$_5$]	9900	16129	-	12500	
[(Ni(acac)$_2$)$_2$ODHz$_3$]	10000	16393	25641		18868
[Ni(acac)$_2$BzHz]	10526	15152	22222		
[(Ni(Cl-acac)$_2$)$_2$BzHz$_3$]	10204	16393	25000	12500	
[(Ni(Et-acac)$_2$)$_2$BzHz$_3$]	10204	16393	25000	13699	
[Ni(acac)$_2$PthHz]	9900	15385	-	13889	
[Ni(Cl-acac)$_2$PthHz$_4$]	10204	14706	20000	12346	
[Ni(Bu-acac)$_2$PthHz$_3$]	10000	16667	-		24390



(a)



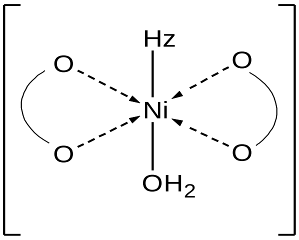
(b) (c)

Figure 5a-c: Electronic spectral of the synthesised nickel (II) complexes

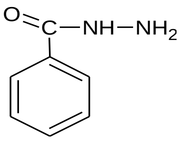
Conclusions

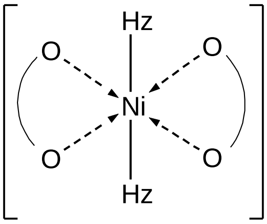
From the results obtained from the series of experiments carried out on the hydrazides complexes of nickel (II) β-diketonates, it can be assumed that the complexes may probably have an octahedral geometry. This was corroborated by the electronic spectra and magnetic moments susceptibility values observed for all the synthesized compounds. The coordination to the central metal can also be assumed to be through the carbonyl oxygen of the β-diketonates and the amino nitrogen as suggested by the infrared spectra of the complexes and their ligands.

The Proposed Structures



where H_z =





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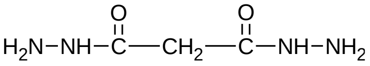
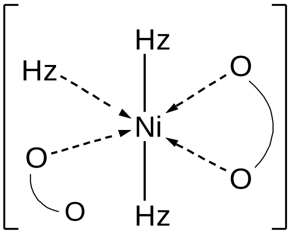


$H_2N-NH-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-NH-NH_2$



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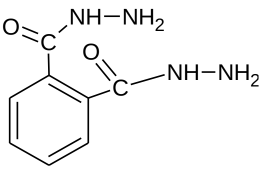

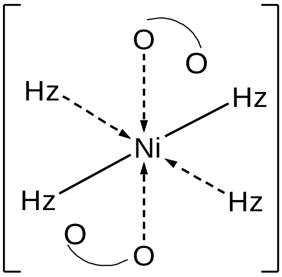

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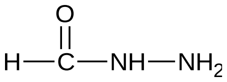
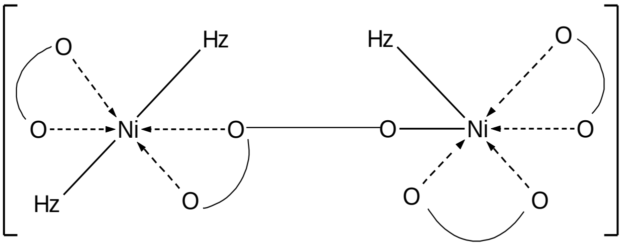


$H-\overset{O}{\overset{\|}{C}}-NH-NH_2$



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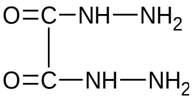

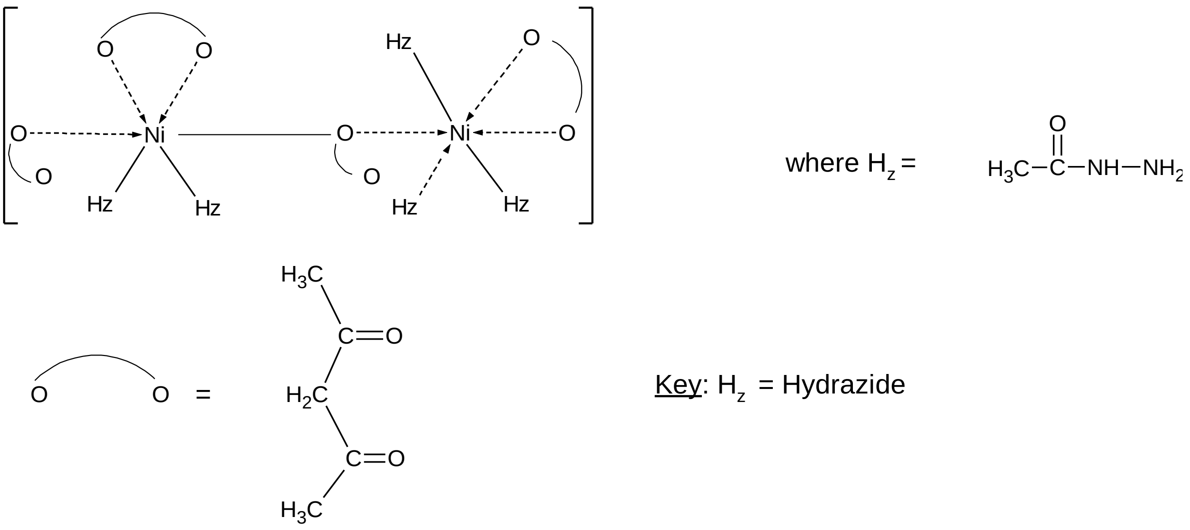

Key: H_z = Hydrazide

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