SYNTHESIS, SPECTRAL STUDIES OF METAL (II) COMPLEXES DERIVED FROM BENZOYL ACETIC ACID HYDRAZIDE

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Abstract: Benzoyl acetic acid hydrazide [BAH] were synthesized and characterized by elemental analysis, melting point, and infrared spectral studies. Their complexes with Copper (II) , Nickel (II) and Cobalt (II) were also synthesized and characterized by elemental analysis, melting point, conductance, infrared studies, and ultra violet spectroscopy . The results showed that the ligand reacted with the metal salts of nickel (II) copper (II) and cobalt (II) in 1:2 molar ratio. The infrared spectra of the of the hydrazide [BAH] showed that ν(C=O) the carbonyl stretching mode , the coupling between the in-plane bending δ(N-H) and $\square$(C-N) and the stretching frequency for the amino group $\square$(NH$_2$) . All experienced bathochromic shifts in the complexes suggesting the coordination of the moieties to the metal ions. The Infrared data also suggest that the ligands act as neutral bidentate donors ligating through the carbonyl O and the amino nitrogen of the ligand. The broad band in the region 3350-3560 cm^{-1} is accorded to $\square$(O-H) stretching vibrations, a feature indicating the presence of acid. The electronic spectra of the nickel (II) complexes showed d-d bands in the regions 24390-25000, 16528-16667, and 12987-13333 cm^{-1}. These are assigned to the spin-allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively, consistent with their well-defined octahedral configuration. All the copper(II) complexes experienced a single broad band between 13,966- 16,233 cm^{-1}assigned to a $^2T_2 \rightarrow {}^2E$ transition for a tetrahedral geometry. The absorption spectra of Cobalt (II) complexes showed $^4T_{1g} \rightarrow {}^4T_{2g}$ transitions at 14,706 -15,924 cm^{-1} with a shoulder each at 16,077 cm^{-1} 16,051 cm^{-1} and 15,924 respectively. The $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) were observed at 18,382 cm^{-1} ,18,484 cm^{-1} , and 19,230 cm^{-1} for Co[BAH]$_2$Cl$_2$, Co[BAH]$_2$Br$_2$, and Co[BAH]$_2$SO$_4$ respectively consistent with a six coordinate octahedral geometry. Further conclusive evidence of the coordination of these hydrazide with the metal(II) ions was shown by the appearance of new bands due to ν(M-N) and ν(M-O) in the metal(II) complexes, this is supported by the elemental analysis studies. The anions is in the outer coordination sphere in all the complexes.

Keywords: biological activity ; ethyl benzoyl acetate; infra-red; electronic spectral; Metal-complexes; bathochromic shift

1. INTRODUCTION

Today the study of coordination compounds has emerged as one of the major center of attraction for the inorganic chemist. It covers a comprehensive range of fascinating and theoretical applications. In synthetic work they continue to provide a challenge in the laboratory. In industry coordination compounds play key roles in homogeneous and heterogeneous catalysis, purification of water,   analytical chemistry,   solvent extraction, photography, metallurgy and electro-chemistry.[1,2,3,4,5,6] They are also used as dyes and also used for the formulation and improvement of semiconductors, superconductors,   advanced   ceramic   materials, pharmaceuticals. They are essential in many life processes such as oxygen transfer and metal   ion control.[7,8,9,]

In fact the rapidly developing field of bioinorganic chemistry is centered on the presence of metal complexes in the biological systems.[10] Moreover, the study of coordination compounds has enabled the inorganic chemist to make significant progress in refining the concept of chemical bonding and to explain the influence that bonding has on the various properties of the compounds .

Majority of the coordination compounds are those of transition elements. Among the transition elements the main transition group or d block includes the elements that have partly filled d-orbital's either in the ground state of the free atom or in one or more of their chemically important ions. The d orbital's "project well out to the

periphery of the atoms and ions so that the electrons occupying them are strongly influenced by the surroundings of the ions, and in turn are able to influence the environments very significantly".[5,6,10]

The aim of this work is to Prepare the ligands

To complex this ligands with the following metallo-elements in solutions: Copper(II)sulphate pentahydrate Nickel(II) sulphate hexahydrate and cobalt(II) sulphate hexahydrate.

To characterised these complexes by the following: I.R and UV-VIS spectral studies, conductivity measurement, melting point/decomposition, and elemental analysis.

To study possible geometry and coordination of these metallo-elements to the ligands.

To study the position / coordination point of the sulphate ions to the metal.

To study the antimicrobial screening for both the ligands and the complexes with some known bacteria.

In this report we present the results of our investigations on the synthesis, and spectral studies of Ni (II), Co(II) and Cu(II) complexes of benzoyl acetic acid hydrazides [BAH].

2.   Experimental

2.1 Synthesis of the Ligand

The hydrazide [BAH] were prepared by adding the ester, ethyl benzoyl acetate 25ml (0.019 mol) was added to hydrazine hydrate 10 ml (0.019 mol) , with about 120 ml ethanol . The mixture was refluxed on a water bath for 6hrs in a 250 cm^3 round bottom flask. The mixture was concentrated to half it's volume and left to crystallize. The resulting crystals gave a crystalline cream precipitate which were filtered, washed with deionised water, and recrystallised from ethanol. The pure crystals were then dried over $CaCl_2$ in a vaccum dessicator for 3 days (% yield= 84.63, 20.7g).

2.2 Preparation of the complexes

$Cu[BAH]_2SO_4.5H_2O$:   1.148g   (0.0046   moles)   of $CuSO_4.5H_2O$ in 15ml of distilled water was added, with stirring to 1.00g (0.0056 moles) of benzoyl acetic acid hydrazide in 40ml of hot absolute ethanol. There was immediate precipitation of green crystals, which were filtered, washed with ethanol and dried over $CaCl_2$ in a vaccum dessicator (% yield = 65, 27.43g.)
The other complexes were similarly prepared using the same procedure and equimolar quantities of the metal salt and the respective ligands.

2.3 Instrumental measurements and Analytical Estimations

The conductivity measurement for the complexes were taken at room temperature in DMF using Meter Toledo MC   126   conductivity   meter.   Melting   point /decomposition temperatures of the ligands and complexes were determined using a Gallenkamp melting point apparatus. The magnetic susceptibilities of the complexes were taken on a Sherwood Scientific Magnetic Moments Balance Model No MKI using $Hg[Co(SCN)_4]$ as calibrant. The Percentage of metals in the complexes was determined by complexometrically titration standard methods using EDTA. Elemental analysis for C, H, and N were determined using a Perkin-Elmer 240C elemental analyzer. Infrared spectra of the ligand were recorded as Nujol mulls while those of the complexes were recorded as pressed KBr discs on an FT-IR spectrophotometer. The electronic spectra of the complexes were recorded on a unicam UV-VIS spectrophotometer.

3.   Results and Discussion

The ligand used in this work are prepared as follow :
The preparation of the hydrazide from the ester and hydrazine hydrate is represented by the equation below :

$$RCOCH_2COOR' + H_2NNH_2.H_2O \rightarrow RCOCH_2CONHNH_2 + R'OH + H_2O$$

The reaction of the metal salts and the respective ligand to form complexes can be represented as follow :

$$MX.xH_2O + yRCOCH_2CONHNH_2 \rightarrow M[RCOCH_2CONHNH_2]n + xH_2O$$

M = Cu , Ni and Co and y =2, n = 2. x = 2-7 X = SO_4 , Br, Cl

The analytical data and some physical constants for the complexes are shown in Table 1. The complexes were of different colours ranging from purple, brown or greenish in colour, high melting and insoluble in water and organic solvents except DMF and DMSO an indication that they may be polymeric . They are non-electrolytes in DMF[11] indicating low ionic character (Table 3).

3.1 Infra-red Spectra

The relevant infrared bands for the ligands and complexes are shown in Table II. The ν(C=O) vibration which appears in the spectra of the ligands at ca 1794 cm$^-$^{1} which was lowered in the spectra of the complexes ; this indicates ligation via the carbonyl O[12]. The ν(NH), ν(NH$_2$) and ν(OH) vibrational bands appear above 3000 cm^{-1} as unresolved bands. It is therefore difficult to unambigously assign these bands and ascertain the ligation profile of the amino nitrogen[12]. The anion bands of a free sulphate, bromate and chloro ion appears at ca 1110 cm^{-1} . Upon coordination the Td symmetry is lowered giving rise to a splitting of the band.[13] In all the complexes, this band is found around this region. Indicating that the anions does not involve in the coordination to the metal ions[14]. In the low-frequency

region, spectra of the metal(II) complexes(Table 11) exhibited[12,13] new bands which are not present in the spectra of the ligand. These bands are located at 625 and 470 cm^{-1}, which are attributed to v(M−O) and v(M−N). The spectral features observed are consistent with the structural patterns of the compound and those of the hydrazides already reported in the literature [15,16].

3.2 1H and 13C NMR spectra

The 1H-NMR spectrum of the ligand exhibits a multiplet signal at 7×3–7×8 d (m, Ar-H) and 10×1 d (s, N–H). In Metal (II) complex, the N–H proton is shifted slightly downfield at 10×3 d which reveals the bonding of the azomethine nitrogen to metal (II) ion. The 13C-NMR spectra of metal (II) complex was recorded by employing TMS as internal reference and DMSO as solvent at ambient temperature. The number of signals of sharp peaks represent the number of carbons of the compound which are chemically non-equivalent. The spectra exhibit the azomethine, C=N carbon at 178 ppm.

3.3 ESR spectra

The ESR spectra of copper complex provide information of importance in studying the metal ion environment. The X-band ESR spectra of the Cu(II) complex, recorded in DMSO at liquid nitrogen temperature and at room temperature (300 K). The spectrum of the copper complex at room temperature shows one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. However, this complex in the frozen state shows four well resolved peaks with low field region. The copper complex exhibits the $g\parallel$ value of 2×31 and g value of 2×16. These values indicate that the ground state of Cu(II) is predominantly dx_2–y_2. The spin-orbit coupling constant, $\Box$ value (− 486 cm^{-1}) calculated using the relations, $g_{av} = 1/3[g\parallel + 2g$] and $g_{av} = 2(1–2\Box / 10Dq)$, is less than the free Cu(II) ion (−832 cm^{-1}) which also supports covalent character of M–L bond in the complex. The G values of 3×82 indicates negligible exchange interaction of Cu–Cu in the complex. The covalency parameter α^2 is calculated ($\alpha^2 = 0\times82$) using the following equation :

$$\alpha^2_{Cu} = \ - (A\parallel/0\times036) + (g\parallel - 2\times0023) + 3/7(g \ - 2\times0023) + 0\times04.$$

If the value of $\alpha^2 = 0\times5$, it indicates complete covalent bonding, while the value of $\alpha^2 = 1\times0$ suggests complete ionic bonding. The observed value of α^2 (0×82) of the complex is less than unity, which indicates that the complex has some covalent character in the ligand environment.

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3.5 Magnetic and Electronic spectral properties

The Co(II) complexes exhibited well-resolved bands at 14,706–15,924 cm^{-1} with a shoulder band at 16,077, 16,051 and 15,924 cm^{-1} (Table 1V) and are assigned[17] to the transitions $^4T_{1g}(F)\rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F)\rightarrow {}^4T_{1g}(P)$ for a high-spin octahedral geometry[18]. A high-intensity band at 28565– 29215 cm^{-1} was assigned to the metal to ligand charge transfer. The magnetic susceptibility measurements (4.2–4.5 BM) for the solid Co(II) complexes are also indicative of three unpaired electrons per Co(II) ion suggesting[6,7,9] consistency with their octahedral environment.

The magnetic moment of copper (II) complexes are usually in the range 1.7 – 2.2B.M. irrespective of stereochemistry.[17] The observed moment are in the range 1.73 – 1.90 B.M. The electronic spectral bands occur as broad in the region 600 – 900nm. Values close to 600nm are often taken to be indicative of square plannar geometry.[12] In this instance both the spectral and magnetic data suggest octahedral coordination.

The electronic spectra of the Ni(II) complexes showed d-d bands in the regions 24390– 25000, 16528–16667, and 12987–13333 cm^{-1}. These are assigned to the spin-allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively, consistent with their well-defined octahedral configuration. The band at 29815–30335 cm^{-1} was assigned to metal $\rightarrow$ ligand charge transfer. The magnetic measurements (3.0–3.3 BM) showed two unpaired electrons per Ni(II) ion suggesting[17,18] also an octahedral geometry for the Ni(II) complexes.

Table 1: Analytical data of ligand and complexes

Metal Chelates		FW	Colour	% yield	Mpt/Dec ^{0}C	% Metal Observed (Calculated)			
						Metal	C	H	N
[BAH]	$C_9H_{10}O_2N_2$	178.19	white	84.63	230-232	-	60.58 (60.61)	5.60 (5.61)	15.76 (15.71)
Cu[BAH]$_2$SO$_4$.H$_2$O	$C_{18}H_{22}CuO_9N_4S$	533.5	Brownish	65	217-219	12.02 (11.90)	40.52 (40.49)	4.14 (4.12)	10.45 (10.50)
Cu[BAH]$_2$Cl$_2$	$C_{18}H_{20}CuO_4N_4Cl_2$	490.5	Reddish- brown	73.11	220-222	12.94 (12.95)	44.05 (44.04)	4.07 (4.08)	11.45 (11.42)
Cu[BAH]$_2$ Br$_2$	$C_{18}H_{20}CuO_4N_4Br_2$	579.3	Dirty –green	55.67	215-218	10.94 (10.96)	37.30 (37.29)	3.46 (3.45)	9.67 (9.67)
Ni[BAH]$_2$ SO$_4$.H$_2$O	$C_{18}H_{22}NiO_9N_4S$	528.6	Dull-green	52	199	10.97 (11.09)	40.88 (40.86)	4.12 (4.16)	10.60 (10.59)
Ni[BAH]$_2$ Cl$_2$	$C_{18}H_{20}NiO_4N_4Cl_2$	485.6	Dark-green	59	220	12.02 (12.06)	44.48 (44.48)	4.10 (4.12)	11.72 (11.53)
Ni[BAH]$_2$ Br$_2$.H$_2$O	$C_{18}H_{22}NiO_5N_4Br_2$	592.4	Dark-green	87	200-202	9.92 (9.89)	54.60 (54.50)	4.45 (4.16)	10.50 (10.60)
Co[BAH]$_2$ SO$_4$ .H$_2$O	$C_{18}H_{22}CoO_9N_4S$	528.9	Purple	65.67	213	11.12 (11.14)	40.79 (40.84)	4.17 (4.16)	10.49 (10.59)
Co[BAH]$_2$ Cl$_2$.H$_2$O	$C_{18}H_{22}CoO_5N_4Cl_2$	502.9	Purple	67	227-229	11.76 (11.71)	42.90 (42.95)	4.86 (4.37)	11.14 (11.14)
Co[BAH]$_2$ Br$_2$	$C_{18}H_{20}CoO_4N_4Br_2$	574.7	Purple	75.43	215	10.20 (10.25)	37.58 (37.58)	3.49 (3.48)	9.70 (9.74)

Table II. Diagnostic IR bands for the ligands and complexes (cm^{-1})

Metal chelates	(OH)	Amide I	Amide II	(C=O)	(NH$_2$)	(M-N; M-O)
[BAH]		1628m	1590w	1794w	3477m	- -
Cu[BAH]$_2$SO$_4$.H$_2$O	3254m	1546w	1551w	1545w	3177w	564, 464
Cu[BAH]$_2$Cl$_2$		1528s	1495m	-	3256m	556,413
Cu[BAH]$_2$Br$_2$		1565w	1440s	1727m	3078w	617, 570
Ni[BAH]$_2$ SO$_4$.H$_2$O	3443	1550s	1487w	1557w	3222m	567,459
Ni[BAH]$_2$ Cl2		1544s	1451m	1534s	3302w	512 , 463
Ni[BAH]$_2$ Br$_2$.H$_2$O	3427br	1550w	1487w	-	3169m	612,479
Co[BAH]$_2$SO$_4$ .H$_2$O		1544 w	1444s	1707m	3217m	510 , 486
Co[BAH]$_2$Cl$_2$ .H$_2$O		1550s	1492w	-	3331w	601, 510
Co[(BAH]$_2$Br$_2$		1519w	1436m	1577w	3190w	563, 465

Table III. Solubility data for ligand the complexes

SOLVENTS

Metals chelates	water	methanol	ethanol	pet. Ether	DMF	ether	DMSO	$\Omega^{-1}cm^2mol^{-1}$
[BAH]	IS	IS	IS	IS	S	SS	S	-
Cu[BAH]$_2$SO$_4$.H$_2$O	IS	SS	IS	IS	S	IS	S	11.6
Cu[BAH]$_2$Cl$_2$	IS	IS	IS	IS	S	IS	S	18.9
Cu[BAH]$_2$Br$_2$	IS	IS	IS	IS	S	IS	S	14.7

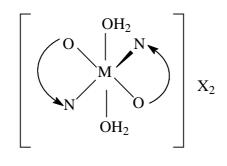|								
Ni[BAH]$_2$ SO$_4$.H$_2$O	SS	IS	IS	IS	S	IS	S	7.8
Ni[BAH]$_2$ Cl$_2$	SS	IS	IS	IS	S	IS	S	8.0
Ni[BAH]$_2$ Br$_2$.H$_2$O	IS	IS	IS	IS	S	IS	S	13.5
Co[BAH]$_2$SO$_4$ .H$_2$O	IS	IS	IS	IS	S	IS	S	16.5
Co[BAH]$_2$Cl$_2$ .H$_2$O	IS	IS	IS	IS	S	IS	S	18.9
Co[(BAAH]$_2$Br$_2$	IS	IS	IS	IS	S	IS	S	22.6

Note : IS : insoluble , SS : sparingly soluble , S : soluble

Table IV. Electronic and magnetic data for the complexes

Metal chelates	μeff(B.M)	$\square_{max}$ (cm^{-1})	Assignment	Geometry
Cu[BAH]$_2$SO$_4$. H$_2$O	1.73	16,233	d → d	Octahedral
Cu[BAH]$_2$Cl$_2$	1.80	15,384	d → d	Octahedral
Cu[BAH]$_2$Br$_2$	1.84	13,966	d →d	Octahedral
Ni[BAH]$_2$SO$_4$. H$_2$O	3.2		24,390-2500	^{3}A$_{2g}$ (F) →^{3}T$_{2g}$ (F) Octahedral
Ni[BAH]$_2$Cl$_2$	3.1	16,528-16,667	^{3}A$_{2g}$ (F) →^{3}T$_{1g}$ (F) Octahedral	
Ni[BAH]$_2$Br$_2$. H$_2$O	3.3	12,987-13,333	^{3}A$_{2g}$ (F) →^{3}T$_{1g}$ (P) Octahedral	
CO[BAH]$_2$SO$_4$. H$_2$O		4.2	18,382	^{4}T$_{1g}$ (F) → ^{4}T$_{2g}$ (F) Octahedral
Co[BAH]$_2$Cl$_2$. H$_2$O		4.5	18,484	^{4}T$_{1g}$ (F) → ^{4}T$_{1g}$ (P) Octahedral
Co[BAH]$_2$Br$_2$		4.4	19,230	^{4}T$_{1g}$ (F) → ^{4}T$_{1g}$ (P) Octahedral

4. Conclusion

The metal (II) ions coordinates to two units of the hydrazides moiety respectively 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 electronic spectral bands observed are consistent with an octahedral geometry Fig (a) .

$$R = C_6H_5COCH_2 ,$$

$$\curvearrowright = RCONHNH_2 ,\ X = Cl , Br , {}_{1/2} SO_4$$

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