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Studies on some metal (II) sulphates salts chelates of salicylaldehyde benzoyl acid hydrazone and acetylaldehyde benzoyl acid hydrazone

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ABSTRACT

Salicylaldehyde benzoyl acid hydrazone and Acetylaldehyde benzoyl acid hydrazone and their complexes with Metal [II] sulphates salts of Co , Ni, Cu, Pb , and Zn have been synthesized in a water – ethanol medium . The formations of the complexes are endothermic processes Complexometric titration was used to determined the stoichiometry of the formed complexes . The ligand was characterized by IR and melting point , while the complexes were characterized by melting point , elemental analysis , conductance , IR and electronic spectral studies . The complexes are non-hygroscopic, and photo stable crystalline powder with different melting point ranging from 240 – 290^{o}*C. The solubility of the metal-complexes in various solvents confirmed the diversity of the complexes as the ligands. The molar conductance values reveal a non- electrolytic nature. The coordination process takes place through the carbonyl oxygen and the amino nitrogen atom , the anionic ion is in the outer sphere of the complexes . The complexes were proposed to have the formulae* $[ML_1L_2]SO^{2-}_4 .nH_2O$ *(where M= Ni(II), Co(II) , Zn(II) , Cu(II) , Pb(II) and* L_1 *= salicyladehyde benzoyl acid hydrazone and* L_2 *= acetylaldehyde benzoyl acid hydrazone , n = 2, 6 , 7 .) . Both the ligands and complexes show no significant activities with the micro organisms tested with probably due to few nitrogen atoms attached with the compounds .*

KEY WORDS : Complexes , Hydrazones , Salicylaldehyde , Acetylaldehyde, Solubility.

INTRODUCTION

Hydrazones have been demonstrated to possess , among other , antimicrobial , anticonvulsant , analgesic ,anti-inflammatory , antiplatelet antitubercular , and antitumoral activities . For example , Epilepsy is a common neurological disorder and a collective term given to a group of syndromes that involve spontaneous , intermittent , abnormal electrical activity in the brain .

The pharmacotherapy of epilepsy has been achieved during the last decade . Furthermore , although for the last twenty years new antiepileptic drugs have been introduced into clinical practice , the maximal electroshock (MES) test and the subcutaneous pentylenetetrazole (scPTZ) test are the most widely used animal models of epilepsy to characterize the anticonvulsant activity. The biological results revealed that in general , the acetylhydrazones provided good protection against convulsions while the oxamoylhydrazons were significantly less active[1] . Fifteen new hydrazones of (2 – oxobenzoxazoline – 3-yl)acetohydrazide were synthesized and their antiepileptic activity was tested in scPTZ test . The 4 – fluoro derivative was found to be more active than the others [2] . 4 – Aminobutyric acid (GABA) is the principal inhibitory neurotransmitter in the mammalian brain . GABA hydrazones were designed and synthesized and evaluated for their anticonvulsant properties in different animal models of epilepsy such as MES , scPTZ , subcutaneous strychnine (scSTY) and intraperitonal picrotoxin (ipPIC) induced seizure tests . Some of the compounds were effective in these models [2] . Iproniazide , isocarboxazide and nialamide , which are hydrazide derivatives , exert their action by inhibiting the enzyme monoamine oxidase (MAO) . Inhibition results in increased levels of norepinephrine , dopamine , tyramine and serotonin in brain neurons and in various other tissues . There have been many reports on the antidepressants / MAO – inhibiting the activity of hydrazones derived from substituted hydrazides and reduction products . Ten new arylidenehydrazides which were synthesized by reacting 3 – phenyl- 5-sulfonamidoindole – 2-carboxylic acid hydrazide with various aldehydes , evaluated for their antidepressant activity . 3-phenyl – 5-sulfonamidoindole- 2-carboxylic acid 3,4-methylenedioy / 4-methyl / 4-nitrobenzylidene – hydrazide showed antidepressant activity at 100mg/Kg [1] .

MATERIALS AND METHODS

Methyl benzoate was obtained from Sigma – Aldrich Chemical Ltd , and used without further purification . The metal salts i.e. $CuSO_4.5H_2O$, $NiSO_4.6H_2O$, $CoSO_4.7H_2O$,$ZnSO_4.5H_2O$, and $PbSO_4$ and the carbonyl compounds were obtained from BDH Chemicals Ltd , England .

Preparation of the Ligands

Salicylaldehyde benzoyl acid hydrazide and Acetylaldehyde benzoyl acid hydrazide were prepared according to the method describe in the literature [3] . The hydrazides were later converted to the hydrazones using the following carbonyl compounds , salicylaldehyde and acetylaldehyde.

Acetylaldehyde benzoyl acid hydrazone

3.04g (mol) of benzoyl acid hydrazide in 40ml of absolute ethanol was mixed with 2.36ml (3.14g , 0.07mol) of acetylaldehyde and refluxed for 4hours in a 250 ml round bottom flask . The solution was left for 3 days to crystallized . The crystals were recrystallized from ethanol and dried over $Cacl_2$ in a desiccators (yield = 67%) .

Salicylaldehyde benzoyl acid hydrazone

3.04g (0.02mol) of benzoyl acid hydrazide in 60ml of absolute ethanol was mixed with 3.50ml (4.02g , 0.09mol) of salicylaldehyde and refluxed for 4 hours, in a 250ml round bottom flask . The mixture was poured into a beaker and left for 2 days to crystallized . The resulting compound was recrystallised from ethanol , filtered and dried over $Cacl_2$ in a desiccators (yield = 54%) .

Preparation of the complexes

The complexes were prepared by the reaction between the ligands dissolved in ethanol and the M(II) sulphates in water.

$CuSO_4.5H_2O$ – Acetylaldehyde benzoyl acid hydrazone

Coper(II) – sulphate pentahydrate (4.35g , 0.017mol) in 60 ml of distilled water was added with stirring to acetylaladehyde benzoyl acid hydrazone (3.00g, mol) in 50 ml of absolute ethanol , there was an immediate precipitate of blue crystals which were filtered , washed with water , and dried over calcium chloride in a dessiccator (yield = 47%) . $CuSO_4.5H_2O$ - Salicylaldehyde benzoyl acid hydrazone was similarly prepared (yield = 63%) .

$NiSO_4.6H_2O$ – Acetylaldehyde benzoyl acid hydrazone

This was obtained by mixing nickel(II) sulphate hexahydrate (2.70 g, 0.011mol) in 50 ml of distilled water with acetylaldehyde benzoyl acid hydrazone (3.00 g , 0.012 mol) in 50ml of absolute ethanol . The metal salt solution was added with stirring to the solution of the ligand . The light blue crystals precipitated instantly . The precipitate was filtered , washed with water , then ethanol and dried over calcium chloride in a vacuum desiccators (yield = 53%) . $NiSO_4.6H_2O$ - Salicylaldehyde benzoyl acid hydrazone was similarly prepared (yield = 75%) .

$CoSO_4.7H_2O$ – Acetylaldehyde benzoyl acid hydrazone

Cobalt(II) – sulphate heptahydrate (4.89 g , 0.017mol) in 50 ml of distilled water was added with stirring to acetylaldehyde benzoyl acid hydrazone(3.oog , 0.012 mol) in 50ml of ethanol , their was in immediate precipitate of crystals which were filtered , washed with water , then ethanol and dried over calcium chloride in a vacuum desiccators (yield =86%) . $CoSO_4.7H_2O$ – Salicylaldehyde benzoyl acid hydrazone was similarly prepared (yield = 77%) .

$ZnSO_4.7H_2O$ – Acetylaldehyde benzoyl acid hydrazone

In the preparation of this complex (2.70g , 0.011mol) of zinc sulphate heptahydrate was dissolved in 50 ml of distilled water . The solution was added drop wise , with string , into a solution of (3.00g ,0.012 mol) of acetylaldehyde benzoyl acid hydrazone in 50ml of absolute ethanol , stirring was continued for some minute and left standing for some hour . The resulting crystals were filtered and dried over calcium chloride in a vacuum desiccators (yield = 34%) . $ZnSO_4.7H_2O$ – Salicylaldehyde benzoyl acid hydrazone was similarly prepared (yield = 37%) .

$PbSO_4$ – Acetylaldehyde benzoyl acid hydrazone

(1.35g , 0.005mol) of Lead(II) sulphate was dissolved in 50ml of distilled water . The solution was added to the solution of acetylaldehyde benzoyl acid hydrazone (2.00g ,0.01mol) in 50 ml absolute ethanol drop wise , with string , string was continued for a while and left standing for some minute . The resulting crystals were filtered and dried over calcium chloride in a vacuum desiccators (yield = 44%) . $PbSO_4$ – Salicylaldehyde benzoyl acid hydrazone was similarly prepared (yield = 32 %) .

Instrumental Measurements

Conductivity measurements in ethanol was made using a WTW LF340 conductivity meter . The infrared spectra of ligands and the complexes in Nujol were taken on a Unicam Scla 969 IR spectrophotometer while the electronic spectra of the complexes were recorded using 21D Milton – Roy UV – VIS spectrophotometer .

Antimicrobial Screening

Antimicrobial screening of the ligands and the complexes in aqueous ethanol was carried out using nutrient agar . Petri dishes contained already jelled nutrient agar were inoculated with some micro – organisms viz :*Escherichia coli* , *Pseudomonas aeruginosa* , *Staphylococcus aureus and Streptococcus lactis* . The petri – dishes were then impregnated with the disks containing the solutions of the ligands and the complexes . this was done in duplicate and incubated for 24 hours in an oven at 37°c .

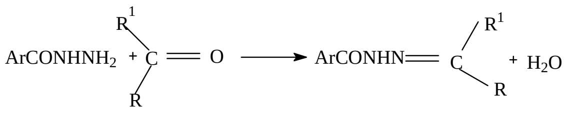
RESULTS AND DISCUSSION

The benzoyl acid hydrizide were synthesized by reacting appropriate quantity of hydrazine hydrate and methyl benzoate respectively. The acylhydrazines were obtained as a brown crystals. The preparation is as follow :

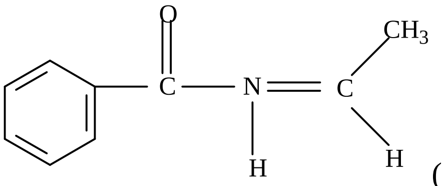
$$ArCOOCH_3 + N_2H_4.H_2O \longrightarrow ArCONHNH_2 + CH_3OH + H_2O$$

(where Ar = C_6H_5)

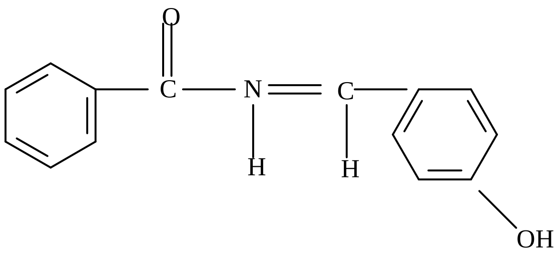
The various hydrazones were derived from the hydrazides according to the equation below :



(Where : Ar = C_6H_5 , R^1= CH_3 and R =H for Acetylaldehyde and R^1 = ArOH , R = H for Salicylaldehyde) .The structure of the ligands are shown below :



(ACBAH)



(SBAH)

The complexation reactions of the ligands and the metal sulphates to give 1:2 metal : ligand chelates are represented by the general equation :

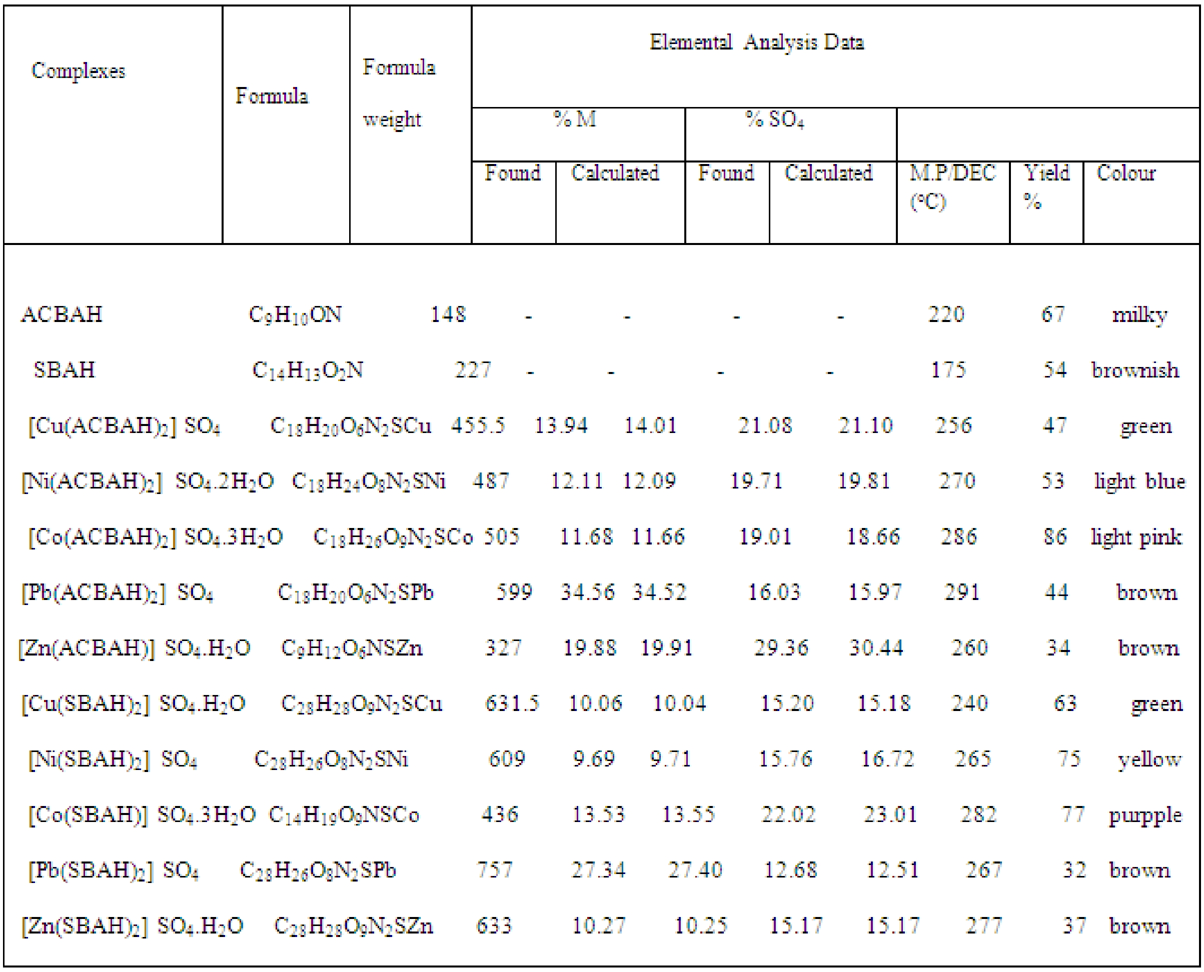
$$MSO_4.nH_2O + ArCONHNCRR^1 \rightarrow M(ArCONHNCRR^1)_2.nH_2O$$

(n = 5 ,6 , or 7)

The complexes were all obtained as coloured powdery substances . Some physical constants for the ligands and complexes are shown in Table 1.

The complexes are soluble in ethanol , but sparingly soluble in methanol ; and their insolubility in distilled water and other organic solvents such as (petroleum ether , $CHCl_3$, acetone , benzene , chloroform etc) together with their relatively high melting point /decomposition are indicative of some polymeric nature [4] . The complexes are non electrolytes in ethanol .

Table 1 : Some physical Properties and elemental analysis dataof the solid ligands and complexes prepared .



Complexes	Formula	Formula weight	Elemental Analysis Data						
			% M		% SO_4				
			Found	Calculated	Found	Calculated	M.P/DEC (°C)	Yield %	Colour
ACBAH	$C_9H_{10}ON$	148	-	-	-	-	220	67	milky
SBAH	$C_{14}H_{13}O_2N$	227	-	-	-	-	175	54	brownish
$[Cu(ACBAH)_2]\ SO_4$	$C_{18}H_{20}O_6N_2SCu$	455.5	13.94	14.01	21.08	21.10	256	47	green
$[Ni(ACBAH)_2]\ SO_4.2H_2O$	$C_{18}H_{24}O_8N_2SNi$	487	12.11	12.09	19.71	19.81	270	53	light blue
$[Co(ACBAH)_2]\ SO_4.3H_2O$	$C_{18}H_{26}O_9N_2SCo$	505	11.68	11.66	19.01	18.66	286	86	light pink
$[Pb(ACBAH)_2]\ SO_4$	$C_{18}H_{20}O_6N_2SPb$	599	34.56	34.52	16.03	15.97	291	44	brown
$[Zn(ACBAH)]\ SO_4.H_2O$	$C_9H_{12}O_6NSZn$	327	19.88	19.91	29.36	30.44	260	34	brown
$[Cu(SBAH)_2]\ SO_4.H_2O$	$C_{28}H_{28}O_9N_2SCu$	631.5	10.06	10.04	15.20	15.18	240	63	green
$[Ni(SBAH)_2]\ SO_4$	$C_{28}H_{26}O_8N_2SNi$	609	9.69	9.71	15.76	16.72	265	75	yellow
$[Co(SBAH)]\ SO_4.3H_2O$	$C_{14}H_{19}O_9NSCo$	436	13.53	13.55	22.02	23.01	282	77	purpple
$[Pb(SBAH)_2]\ SO_4$	$C_{28}H_{26}O_8N_2SPb$	757	27.34	27.40	12.68	12.51	267	32	brown
$[Zn(SBAH)_2]\ SO_4.H_2O$	$C_{28}H_{28}O_9N_2SZn$	633	10.27	10.25	15.17	15.17	277	37	brown

Note : Sulphates ions were determined using $BaSO_4$

Infrared Spectra

The diagnostic IR bands in the ligands and complexes are compared in **Table 2 .**

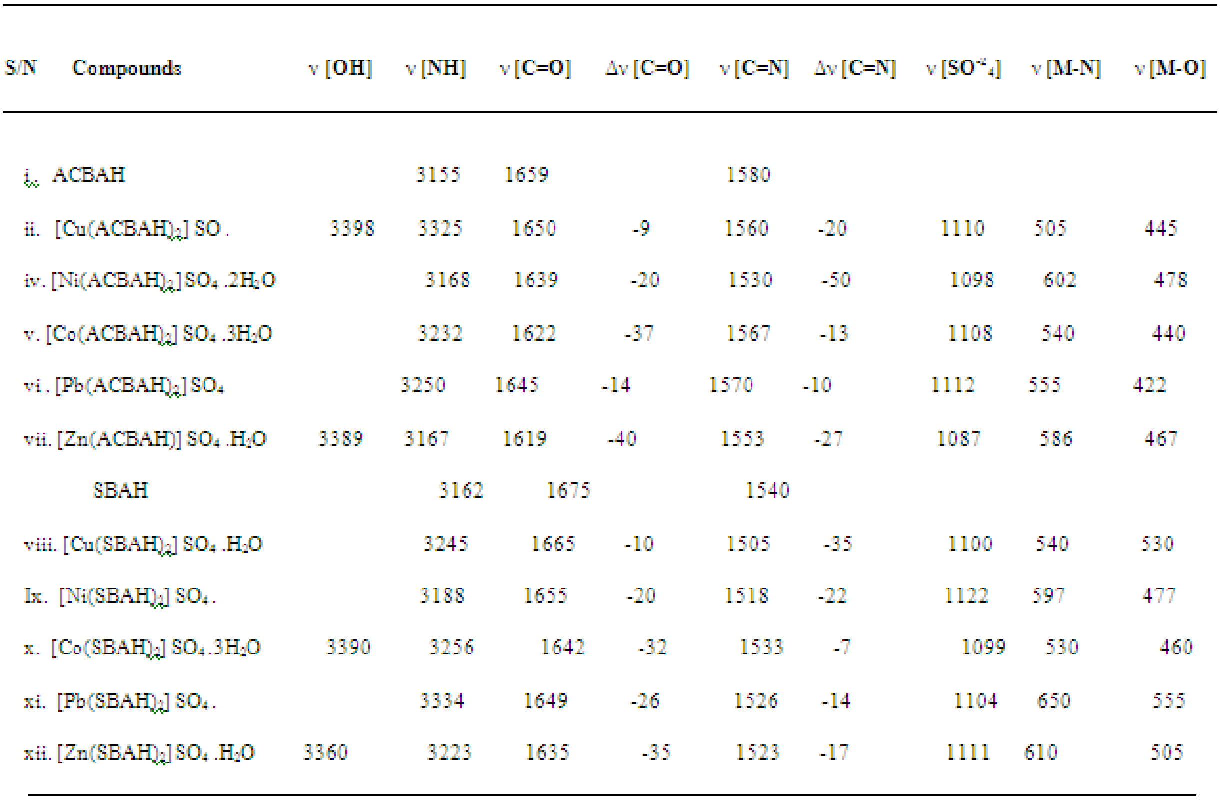
The infrared bands assignments of the complexes of Cu(II) , Pb(II) , Zn(II) , Ni(II) , and Co(II) , ions exhibits a broad band in the range of 3398-3163cm^{-1} corresponding to the presence of water molecules [5] . The bands in the range of 1580cm $^{-1}$ in the spectra of (ACBAH) ligand and 1540cm^{-1} for spectra of (SBAH) ligand due to the x(C=N) group and the change of these bands on complexation formation compared to its position in the complexes of ACBAH which is lowered by (10-50) and (7-35) in complexes of SBAH , suggesting the participation of azomethine group in coordination with the metal ions [6] . The amide □(C =O)) band which is located in the spectrum of (ACBAH) at 1659 cm^{-1} and 1675cm^{-1} for SBAH respectively undergoes a lower shift between 9 – 40 cm^{-1} in the spectra of the ACBAH and SBAH complexes due to coordination via the carbonyl oxygen [7] . As expected , N-H stretching vibrations are located at 3535– 3163 cm^{-1} .

Although the ligand are potentially multidentate . The stretching vibrations of the sulphate ion are usually observed as a sharp singlet around 1100 cm^{-1} and a medium band around 680 cm^{-1} [10]. The □(SO_4) band in all the complexes was found around 1100 cm^{1} as a singlet , this is consistent with an outer sphere sulphate group. The □$_1$mode of the sulphate group around 1100cm^{-1} is split in the spectra of all the complexes except $[Ni(ACBAH)_2]SO_4.2H_2O$, $[Zn(ACBAH)]SO_4.H_2O$, and $[Co(SBAH)]SO_4.3H_2O$. This splitting is usually associated with a decrease in the symmetry of the anion resulting from its coordination to the metals [8]. New bands in the range of 609-447cm^{-1} for complexes of ACBAH and 656-536 cm^{-1} for complexes of SBAH are assigned to the (M-N) and (M-O) vibrations [9] .

Molar Conductivity

The conductance measurements of the prepared complexes were carried out in ethanol solvent and the obtained values (Table 3) were taken as a good evidence for the existence of a non-electrolyte nature of the complexes [10] .

Table 2 : Diagnostic IR bands for the Ligands and complexes

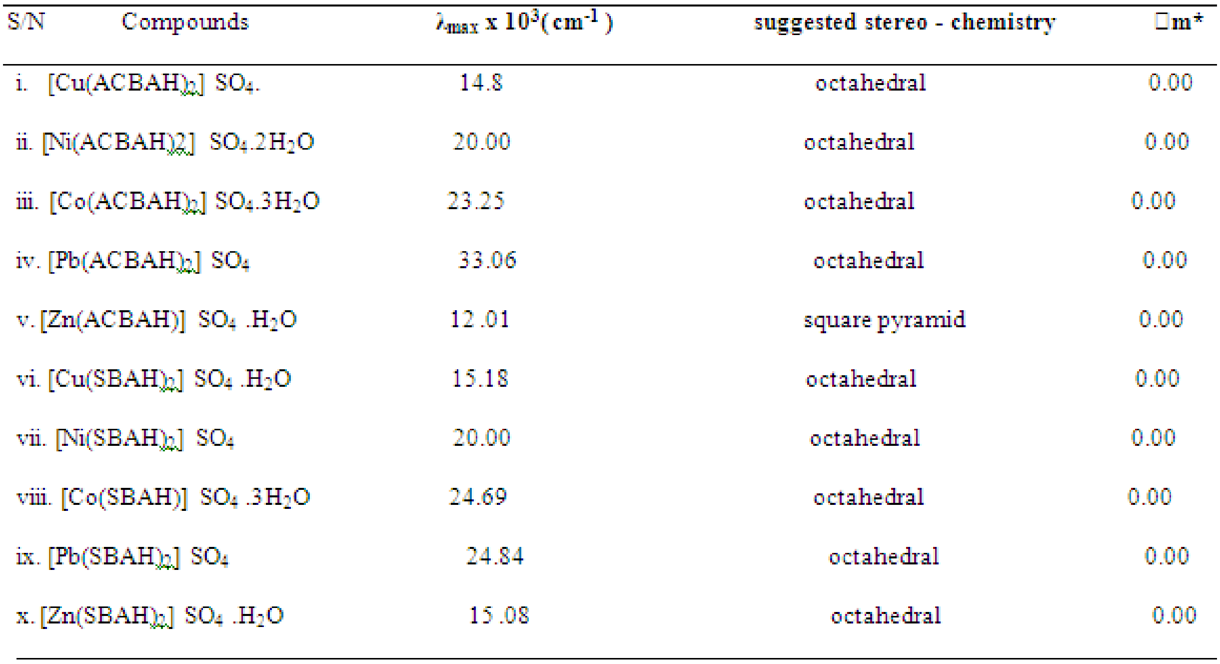


S/N	Compounds	ν [OH]	ν [NH]	ν [C=O]	Δν [C=O]	ν [C=N]	Δν [C=N]	ν [SO^{-2}_4]	ν [M-N]	ν [M-O]
i.	ACBAH		3155	1659		1580				
ii.	$[Cu(ACBAH)_2]$ SO .	3398	3325	1650	-9	1560	-20	1110	505	445
iv.	$[Ni(ACBAH)_2] SO_4 .2H_2O$		3168	1639	-20	1530	-50	1098	602	478
v.	$[Co(ACBAH)_2] SO_4 .3H_2O$		3232	1622	-37	1567	-13	1108	540	440
vi .	$[Pb(ACBAH)_2] SO_4$		3250	1645	-14	1570	-10	1112	555	422
vii.	$[Zn(ACBAH)] SO_4 .H_2O$	3389	3167	1619	-40	1553	-27	1087	586	467
	SBAH		3162	1675		1540				
viii.	$[Cu(SBAH)_2] SO_4 .H_2O$		3245	1665	-10	1505	-35	1100	540	530
Ix.	$[Ni(SBAH)_2] SO_4$.		3188	1655	-20	1518	-22	1122	597	477
x.	$[Co(SBAH)_2] SO_4 .3H_2O$	3390	3256	1642	-32	1533	-7	1099	530	460
xi.	$[Pb(SBAH)_2] SO_4$.		3334	1649	-26	1526	-14	1104	650	555
xii.	$[Zn(SBAH)_2] SO_4 .H_2O$	3360	3223	1635	-35	1523	-17	1111	610	505

Electronic Spectra

Two d → d bands located around 20,000cm^{-1} and 14,000cm^{-1}were observed in the visible spectrum of each of Ni(II) , Cu(II) , and Co(II) complexes . The ratio of the two bands is less than 1.8 and agrees with that reported for octahedral Nickel(II) complexes [12] . The positions of the bands rule out the possibility of other geometries. The bands have therefore been assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, respectively . The third spin –allowed transition to the $^3T_{2g}$ level , usually located in the near infrared region [12] , lies outside the spectral range of the instrument . The two complexes of Co(II) , however , have similar electronic spectra . The spectrum of each consists of a band located around 22,000 – 25,000cm^{-1} and a shoulder located around 19,000cm^{-1} ; this is consistent with octahedral coordination around the cobalt(II) ion [11] . This band has been assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. A broad band located around 11,000 – 17,000cm^{-1}for the Cu(II) complexes suggested a distorted octahedral copper(II) chelates .The electronic spectrum of each of the Pb(II) complexes reveals two absorption bands at 303 nm (33057cm-1) and 403 nm (24844 cm-1) due to the presence of a charge transfer transition and an octahedral geometry was suggested for this complex . The spectrum of each of theZn(II) complexes .

Table 3 : Electronic Data for the Complexes



S/N	Compounds	λ_{max} x 10^3(cm^{-1})	suggested stereo - chemistry	□m*
i.	$[Cu(ACBAH)_2]$ SO_4.	14.8	octahedral	0.00
ii.	$[Ni(ACBAH)2]$ $SO_4.2H_2O$	20.00	octahedral	0.00
iii.	$[Co(ACBAH)_2]$ $SO_4.3H_2O$	23.25	octahedral	0.00
iv.	$[Pb(ACBAH)_2]$ SO_4	33.06	octahedral	0.00
v.	$[Zn(ACBAH)]$ SO_4 $.H_2O$	12 .01	square pyramid	0.00
vi.	$[Cu(SBAH)_2]$ SO_4 $.H_2O$	15.18	octahedral	0.00
vii.	$[Ni(SBAH)_2]$ SO_4	20.00	octahedral	0.00
viii.	$[Co(SBAH)]$ SO_4 $.3H_2O$	24.69	octahedral	0.00
ix.	$[Pb(SBAH)_2]$ SO_4	24.84	octahedral	0.00
x.	$[Zn(SBAH)_2]$ SO_4 $.H_2O$	15 .08	octahedral	0.00

The result of the antimicrobial screening of both the ligands and complexes was shown in Table 5 . They show no significant activities probably because of the few nitrogen atoms attached to the compounds [12]

Table 4. Solubility test of the ligands and complexes in some selected solvents

Ligands / Complexes	Ethanol	Methanol	Benzene	Petroleum ether	Acetone	Distilled water
SBAH	S	SS	NS	NS	NS	NS
ACBAH	S	SS	NS	NS	NS	NS
$[Cu(ACBAH)_2] SO_4$	S	SS	NS	NS	NS	NS
$[Ni(ACBAH)_2] SO_4$ .2H2O	S	SS	NS	NS	NS	NS
$[Co(ACBAH)_2] SO_4.3H_2O$	S	SS	NS	NS	NS	NS
$[Pb(ACBAH)_2] SO_4$	S	SS	NS	NS	NS	NS
$[Zn(ACBAH)] SO_4 .H_2O$	S	SS	NS	NS	NS	NS
$[Cu(SBAH)_2] SO_4 .H_2O$	S	SS	NS	NS	NS	NS
$[Ni(SBAH)_2] SO_4$	S	SS	NS	NS	NS	NS
$[Co(SBAH)] SO_4 .3H_2O$	S	SS	NS	NS	NS	NS
$[Pb(SBAH)_2] SO_4$	S	SS	NS	NS	NS	NS
$[Zn(SBAH)_2] SO_4 .H_2O$	S	SS	NS	NS	NS	NS

Note : S : Soluble , SS : Slightly Soluble , NS : Not Soluble

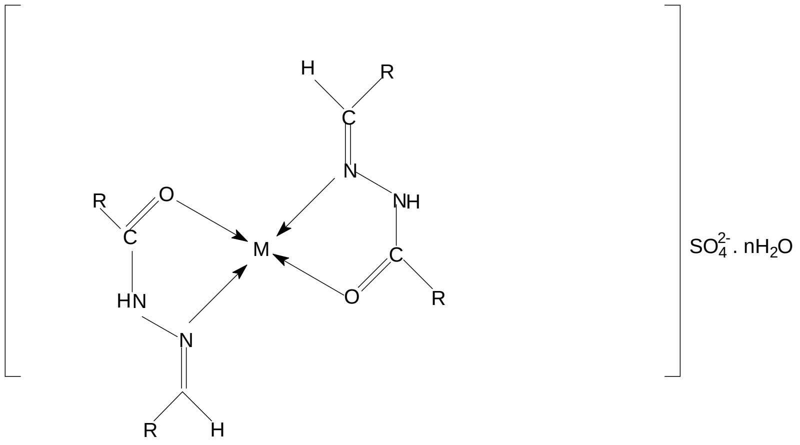
Table 5 : antimicrobial screening test results

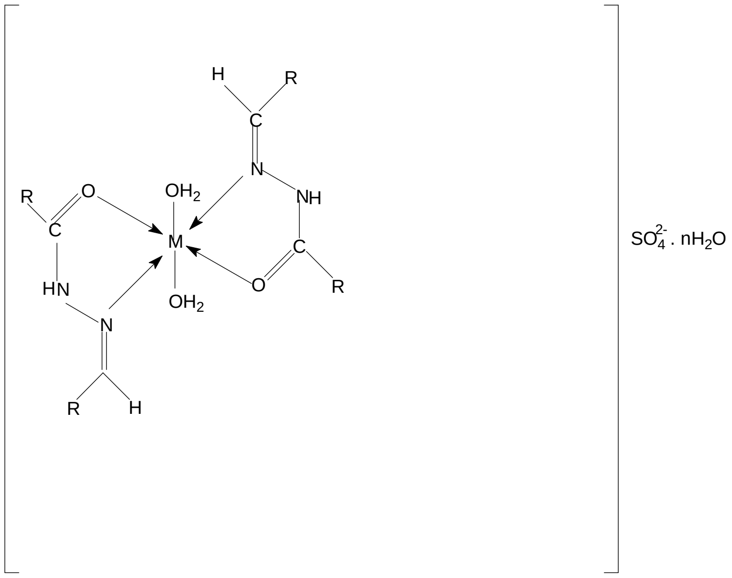
S /N	**Compounds**	***E. coli***	***Staphy. A***	***Strep. L***	***Pseudo. A***
i.	SBAH	-	+	+	+
ii .	ACBAH	-	-	-	+
iii .	$[Cu(ACBAH)_2] SO_4$	-	-	-	-
iv .	$[Ni(ACBAH)_2] SO_4 .2H_2O$	-	-	-	+
v .	$[Co(ACBAH)_2] SO_4 .3H_2O$	+	-	+	-
vi .	$[Pb(ACBAH)_2] SO_4$	-	-	-	-
vii .	$[Zn(ACBAH)] SO_4 .H_2O$	-	-	-	-
viii .	$[Cu(SBAH)_2] SO_4 .H_2O$	-	-	-	-
ix .	$[Ni(SBAH)_2] SO_4$	-	-	-	-
x .	$[Co(SBAH)] SO_4 .3H_2O$	-	+	+	-
xi .	$[Pb(SBAH)_2] SO_4$	-	-	-	-
xii .	$[Zn(SBAH)_2] SO_4 .H_2O$	-	-	-	-

key : ***+ :*** *Fairly active ,* *- : No active*

CONCULUSION

The ligands act as neutral bidentate donors coordinating via the carbonyl oxygen and the azomethine nitrogen . Some of the complexes adapt a square plannar geometry while some complexes are octahedral . Both the ligands and the complexes are not active against the test microbes . On the basis of their physiochemical properties , the following structures are proposed for the chelates .





REFERENCES

[1] Rollas.S., Gulerman.N; Erdeniz . H; *Farmaco* , **(2002)** . 57, 171 – 174 .
[2] Kucukguzel .S.; Rollas. S .; Kucukguel . I; and Kiraz . M ; . *Eur* . *J. Med* . *Chem* . **(1999)** ; 34 , 1093 – 1100 . .
[3] 3 . Nwabueze . J.N ; Salawu. O .W. ; *J. Chem* . *Soc* . *Nigeria* , **(2007)**, 32. No.2 , 254-259
[4] Kucukguel .S.G., Oruc .E.E. ; Rollas .S. ; Sahin. F. ; and Ozbek . A.; *Eur. J* . *Med* . *Chem* (2002) .37 , 197 – 206 .
[5] Kaymakcioglu.K.B., Oruc. E.E . ; Unsalan. S. ; Kandemirli . F. ; Shvets. N. ; Rollas . S. and Anatholy. D. . *Eur* . *J* . *Med* . *Chem* . **(2006)** ; 41 , 1253 – 1261 .
[6] Ragavendran.J., Sriram. D. ; Patel. S. ; Reddy. I . ; Bharathwajan. N. ; Stables. J. and Yogeeswari. P. . *Eur* . *J* . *Med* . *Chem* . **(2007)** . 42 , 1461 – 151 .

[7] Todeschini.A.R., Miranda. A.L.P. ; Silva. C.M. ; Parrini. S.C. ; and Barrerio. E.J ; *Eur . J . Med . Chem* . **(1998)** . 33 , 189 – 199 .
[8] Lima.P.C., Lima. L.M. ; Silva. K.C. ; Leda. P.H. ; Miranda. A.L.P. ; Fraga. C.A.M. ; and Barreiro. E.J. ; . *Eur . J . Med .Chem* . **(2000)** . 35 .187 – 203 .
[9] Abd el wahed .M.G., Abd el wanes. S., gamel . M.El and Abd el halem. S., *J.Serb.Chem.Soc* . **(2004)** ; 69(4) , 255 – 264 .
[10] Alcock .J.F., Baker . R.J. and Diamantis. A.A. ; *Aust. J. Chem*. **(1972)** . 25 , 289 – 302 .
[11] Nwabueze .J.N; Ikewere . P.O. ; Patel. K.S. ; *Synth. React. Inorg. Met .Org .Chem*. **(1989)** 19(9) , 893 – 907.
[12] Nwabueze.J.N.; *Transition Met. Chem*., **(1996)** . 21 , 258 – 261 .