Journal of Natural Sciences Research
ISSN 2224-3186 (Paper) ISSN 2225-0921 (Online)
Vol.4, No.21, 2014
www.iiste.org

Complexes of M(II)Sulphates with 4-Cyanobenzaldehyde and 4-Ethylbenzaldehyde-Cyclopropanecarboxylicacid Hydrazones

H.D. Aliyu* J.N. Nwabueze M.O. Obadare
Chemistry Department, Faculty of Science, University of Abuja, Nigeria
*E-mail: dedeji251@gmail.com

Abstract

Ten complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) sulphates with 4-cynobenzaldehydecyclopropanecarboxylicacidhydrazone (CBHN) and 4-ethylbenzaldehydecyclopropanecarboxylicacidhydrazones (EBHN) have been synthesized and characterized. The complexes have high melting points and in soluble in common solvents. Their low molar conductivity values are an indication of their non electrolytic nature in DMSO. The IR studies, shows the coordination of the ligands to the metals via the carbonyl oxygen, and the azomethine nitrogen, while the solphates is coordinated to the metals. The electronic spectral studies in DMSO suggest the octahedral symmetry for the complexes with exception of Ni(II) complexes which are square plannar. The antimicrobial activity of some of the complexes, are high against E-*col*i and *streptococcus*.

Keywords: Hdrazides, Hydrzones, Octahedral and Square-planer symmetry

Introduction

Hydrazones are useful chelating agents and are of importance biologically (Duggal H.K; AgarWala, B.V 1988, Korol, B; Multeri, et al 1967) The presence of benzyl ring system in the hydrazone causes delocalization of electrons with subsequent changes in energy level associated with the carbonyl oxygen which acts as donors. The biological activity of hydrazones and dependence of their mode of chelation on the transition metal ions present in living system have been of significant interest in recent years(Maiti, A and Ghosh S. 1989, Aggarwal R.C; et al 1981)

In this study, we attempted synthesizing, and characterized both the ligands and complexes of 4-cynobenzaldehydecyclopropanecarboxylicacidhydrazone(CBHN) and 4-ethylbenzaldehydecyclopropanecarboxylicacidhydrazones(EBHN) with Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) sulphates and their biological activity against the following microbes; *Staphylococcus aureus*, *Escherichia coli* and *streptococcus lactis*.

Experiments

All the reagents and solvents were obtained from BDH Chemical Ltd. The melting/decomposition temperature of the compounds were taken on Electrothermal 14900 series digital melting point apparatus. Infrared spectra of the ligands and complexes were recorded as nujol disc on Matson Genesis II FTIR spectrophotometer. The electronic spectra of the complexes were recorded on Brochion 4060 UV/visible Spectrophotometer in DMSO. Metal and sulphate concentration were determined gravimetrically according to standard methods(Basset, J 1964; et al)

Preparation of the ligands

Cyclopropane carboxylic acid hydrazide(CPH) was prepared by pouring slowly 33.97cm^3 (33.55g, 0.294mol) of 4-ethylcyclopropane carboxylate into 500cm^3 round bottom flask, containing 14.30cm^3 (14.73g, 0.294mol) of hydrazine hydrate in 100cm^3 of absolute ethanol. The mixture was refluxed for six hours, after which it was transferred into 400cm^3 beaker and covered with an aluminium foil. The crystals formed after it was left to stand for two weeks, were recrystalised in a little quantity of absolute ethanol, filtered and dried in a desiccators over calcium chloride (yield 66.9%).

The hydrazones were synthesized via the acid hydrazides as given below.

(CBHN)

4-cyanobenzaldehydecyclopropanecarboxylicacidhydrazones(CBHN) was prepared by adding 4.68g (0.046 mol) of (CPH) to 6.02g (0.046 mol) of 4-cyanobenzaldehyde in 100cm^3 of absolute ethanol in 500cm^3 round bottom flask, refluxed for six hours and was transferred into 400cm^3 beaker, covered and left to stand overnight. The crystals formed were recrystalised from absolute ethanol, filtered and dried over calcium chloride in a dessiccator containing calcium chloride (yield 58.50%).

(EBHN)

4-ethylbenzaldehydecyclopropanecarboxylicacidhydrazones(EBHN) was similarly prepared by refluxing 3.27 g of CPCH with 6.00cm^3 (4.30 g, 0.321 mol) of ethylbenzaldehyde in 100cm^3 of absolute ethanol, after which it was pour into 400cm^3 beaker, covered and left to stand for four days. The crystals formed were recrystallised in a little absolute ethanol dried over calcium chloride in a dessicator (yield 79.48%).

Preparation of Complexes

Mn[CBHN]$SO_4.H_2O$ was prepared by adding 0.85 g (0.05 mol) manganese (II) sulphate in 50 cm^3 of deionised water, gently with stirring into a 400 cm^3 beaker containing 1.09 g (0.05 mol) of CBHCPH in 50 cm^3 of absolute ethanol.

The resultant solution was refluxed for two hours, after which it was transferred into 400 cm^3 beaker, covered and left to stand overnight. The crystals formed were filtered and dried over $CaCl_2$ in a dessicator (yield 79.0%).

The following complexes were similarly prepared. Co(CBHN)SO_4, Cu(CBHN)SO_4, Ni(CBHN)SO_4, Zn(CBHN)SO_4, Mn(CBHN)SO_4, Mn(EBHN)SO_4, Co(EBHN) SO_4, Cu(EBHN)SO_4, Ni(EBHN)SO_4, and Zn(EBHN)SO_4 using appropriate hydrazones and metal salts.

Microbial Test

The media was prepared using nutrient agar discs prepared from paper and impregnated with the solutions of the compounds in DMSO (200 mg/ cm^3). The disc were sterilized with hot air and dried at 120° C for four hours. The prepared discs were inoculated with the microbes and were observed after 48 hours(Karau, D.j; et al 2006)[6].

Results and Discussion

The ligands CBHN and EBHN were prepared with good yield, as white crystals and their melting points are high as given in table 1. This may propably be due to their polymeric nature.

The reaction of Mn(II), Co(II), Ni(II), Cu(II) and Fe(II) sulphates in ethanol with the ligands, resulted in the formation of their complexes, of; $MLnSO_4.xH_2O$ (n=1 or 2, x=3,4,5 or 6 and L= CBHN and EBHN.

The ligands and their metal complexes are soluble in DMSO. While the complexes of EBHN are also soluble in ethanol, those of the CBHN are only sparingly soluble. All the complexes are stable and can be stored for long at room temperature. The molar conductance of the complexes in DMSO at room temperature are given in Table 1, their low values suggest the non-electrolytic nature of these complexes.

Table 1. Physiochemical Properties of Ligands and Complexes

S/No	Compound	Molecular Formular	% Yield	Mpt	Colour	% M	%SO_4	Conductivity	Solubility
1	CBHN	$C_{12}H_{11}N_2O$	58.5	250	White	-	-	0.275	DMSO
2	Mn(CBHN)SO_4 $3H_2O$	$C_{12}H_{17}N_3O_8SMn$	79	245-247	White	13.71 (13.10)	22.84 (22.86)	0.281	EtOH, DMSO
3	C0(CBCHN)$_3SO_4$ $6H_2O$	$C_{36}H_{45}N_9O_{13}SCo$	93	250	Light pink	6.45 (6.53)	10.64 (10.63)	0.313	DMSO
4	Ni(CBHN)SO_4 $6H_2O$	$C_{12}H_{23}N_3O_{11}SNi$	71	199-201	Yellow	12.25 (12.33)	20.25 (20.17)	0.289	DMSO
5	Cu(CBCPCH)SO_4 H_2O	$C_{12}H_{13}N_3O_6SCu$	75	380-382	Green	16.22 (16.26)	24.72 (24.57)	0.361	DMSO
6	Zn(CBHN)SO_4 $6H_2O$	$C_{12}H_{22}N_3O_{11}SZn$	78	260-263	White	13.47 (13.55)	19.92 (19.90)	0.287	DMSO
7	EBHN	$C_{13}H_{16}N_2O$		123-125	White	--	-	0.295	EtOH DMSO
8	Mn(EBHN)SO_4 $4H_2O$	$C_{13}H_{26}N_2O_{10}SMn$	88	122-124	White	12.08 (12.00)	21.28 (21.00)	0.286	EtOH, DMSO
9	Co(EBHN)$_3SO_4$ $4H_2O$	$C_{39}H_{56}N_4O_{11}SCo$	69	114-115	Light pink	6.55 (6.73)	10.60 (10.90)	0.296	EtOH, DMSO
10	Ni(EBHN)SO_4 $5H_2O$	$C_{13}H_{26}N_2O_{10}SNi$	96	123-125	Green	12.78 (12.74)	20.94 (20.84)	0.689	EtOH, DMSO
11	Cu(EBHN)SO_4 $2H_2O$	$C_{13}H_{26}N_2O_7SCu$	61	122-123	Brown	15.52 (15.48)	23.48 (23.32)	0.292	EtOH, DMSO
12	Zn(EBHN)SO_4 $6H_2O$	$C_{26}H_{44}N_2O_{12}SZn$	73	113-115	White	9.38 (9.32)	13.60 (13.68)	0.276	EtOH, DMSO

Infrared Spectra

Comparing the infrared spectra of the ligands with their M(II) sulphate complexes as given in Table 2, shows that both ligands are bidentates, with the carbonyl oxygen and azomethene nitrogen as the two coordination sites. The presence of the various ring vibration and C-H absorptions, couple with the OH absorption and that of N-H makes the spectra a little bit complicated for assignments of the individual bands.

The amide -1 band in both CBHN and EBHN ligands appears in the region 1658 and 1662 cm^{-1} respectively and are been shifted in the (C=O) of their complexes indicating a decrease in the stretching force constant of the C=O bond as a consequence of coordination through the carbonyl – oxygen atom of the free base.

The amide II bands, appears at the normal position in the N-H deformation frequency mode. In both ligands, the N-H stretching in free ligands occur in the 3208-3212 cm^{-1} region and remain unaltered after complexation. This rule out the coordination through the imine-nitrogen atom (Bethamy, L.J 1954). The band around 1587 and 1561 cm^{-1} for CBHN and EBCHN respectively which is attributed to the (C=N) mode (Agarwal, R.K and Pirakash, J 1991) are lowered in the spectra of the complexes in the range of 06-36 cm^{-1} indicating the involvement of the N-atom of the azomethine group coordination

The splitting of the (SO_4) bond around 1100-1140 cm^{-1} indicates inner coordination of the sulphates ions.

The bands below 500 cm^{-1} are tentatively assigned to vibrations of M-O and M-N bonds

Table 2: Diagnostic IR bands of the compounds (cm^{-1})

S/NO	Compound	(OH)	(NH)	(OH)	(CO)	(CN)	(CN)	(SO_4)	M-N	M-O
1	CBHN	3439	3212	1658	-	1597	-	-	-	-
2	Mn(CBHN)SO_4 $3H_2O$	3462	3210	1663	05	1561	36	1106 1171	550	495
3	Co$(CBHN)_3SO_4$ $6H_2O$	3390	2311	1661	03	1568	29	1143 1106	524	476
4	Ni(CBHN)SO_4 $6H_2O$	3440	3212	1660	02	1570	27	1143 1106	536	470
5	Cu(CBHN)SO_4 H_2O	3473	3239	1662	04	1591	08	1100 1098	508	465
6	Zn(CBHN)SO_4 $6H_2O$	3436	3213	1661	03	1592	07	1145 1106	506	477
7	EBHN	3422	3202	1652	-	1569	-	--	-	-
8	Mn$(EBHN)_3SO_4$ $4H_2O$	3414	3198	1662	10	1563	06	1128 1060	546	486
9	Co(EBHN)SO_4 $4H_2O$	3410	3195	1661	09	1564	05	1140 1106	540	459
10	Ni(EBHN)SO_4 $5H_2O$	3418	3197	1660	08	1560	09	1100 1088	547	458
11	Cu(EBHN)SO_4 $2H_2O$	3404	3201	1664	12	1560	09	1124 1106	544	475
12	Zn(EBHN)SO_4 $6H_2O$	3397	3199	1661	09	1566	13	1138 1104	524	474

Electronic spectra

The Mn(II) complexes exhibit three bands, those of Co(II) and Ni(II)complexes shows two bands while that of Cu(II) complexes gave a single band in ethanol as shown in table 3. The Mn bands are assigned to the d-d and a $^6A_{1g}$-$^4T_{2g}$ transitions of an octahedral symmetry. The Co(II) bands were assigned to $^4T_{1g}$(f)- $^4T_{1g}$(p) and $^4T_{1g}$(f) – $^4A_{2g}$, are of octahedral symmetry. The Ni(II) bands were assigned to $^3A_{2g}$-$^3T_{1g}$(f) and $^3A_{2g}$-$^3T_{2g}$(f) transition are of square –planar geometry. The single band of Cu(II) complexes were assigned to d-d transition of octahedral symmetry.

Table 3: Electronic data of the complexes (nm)

S/NO	Compound	λ(nm)	Assignment	Stereochemistry
1	$Mn(CBHN)SO_4\,3H_2O$	310 352 360	d-d d-d ^6A_1g - $^4T_2g(f)$	Octahedral
2	$Mn(EBHN)\,SO_4\,4H_2O$	360 310 365	d-d d-d ^6A_1g - $^4T_2g(f)$	Octahedral
3	$Co(CBHN)\,SO_4\,6H_2O$	355 365	$^4T_1g(f)$ - ^4A_2g $^4T_1g(f)$ - $^4A_2g(p)$	Octahedral
4	$Co(EBHN)\,SO_4\,4H_2O$	575 500	$^4T_1g(f)$ - $^4T_1g(f)$ ^4A_2g - $^4T_1g(f)$	Octahedral
5	$Ni(CBHN)\,SO_4\,6H_2O$	560 510	^3A_2g - $^3T_1g(f)$ ^3A_2g - $^3T_1g(p)$	Octahedral
6	$Ni(EBHN)\,SO_4\,5H_2O$	405 505	^3A_2g - $^3T_1g(f)$ ^3A_2g - $^3T_1g(p)$	Octahedral
7	$Cu(CBHN)\,SO_4\,H_2O$	675	d-d	Octahedral
8	$Cu(EBHN)\,SO_4\,2H_2O$	720	d-d	Octahedral

Microbial Screening

The ligands and their metal complexes were tested against staphylococcus, Escherichia coli and streptococcus in DMSO. BCHN gave a high activity against the growth of streptococcus and its complexes with Cu(II) and Zn(II)sulphates. On the other hand, EBHN is highly active against Escherichia coli and streptococcus and its Co(II)sulphates complexes showing a moderate activity against Escherichia, While the Ni(II)sulphate complex shows a moderate activity against staphylococcus and Escherichia coli; as given in Table 4.

Table 4 Antimicrobial screening of the compounds in DMSO

s/No	Compound	Staphylococcus	Escherichia coli	Streptococcus
1	CBHN	-	-	+++
2	$Mn(CBHN)SO_4\,6H_2O$	-	-	-
3	$C0(CBHN)SO_4\,6H_2O$	-	-	-
4	$Ni(CBHN)SO_4\,6H_2O$	-	-	-
5	$Cu(CBHN)SO_4\,H_2O$	-	-	+++
6	$Zn(CBHN)SO_4\,6H_2O$	-	-	++
7	EBHN	-	++	+++
8	$Mn(EBHN)SO_4\,5H_2O$	-	-	-
9	$Co(EBHN)SO_4\,4H_2O$	-	++	-
10	$Ni(EBHN)SO_4\,5H_2O$	++	++	-
11	$Cu(EBHN)SO_4\,2H_2O$	-	-	-
12	$Zn(EBHN)SO_4\,6H_2O$	-	-	-

Key: ++ moderate activity, +++ high activity and – negative activity

Conclusion

The overall infrared spectra evidence suggests that both ligands act as bidentate ligands and coordinates through the amide-oxygen and azomethine nitrogen atom, forming a four membered chelates ring.

The result of the microbial screening against the tested microbes gave negative activity for most of the compounds and there is no evidence of enhanced activity of the ligands after complexation.

REFERENCES

Agarwal, R.K and Pirakash, J (1991) Polyhedral, 10, 2567

Aggarwal R.C; Singh, N.K. and Singh R.P (1981) Inorg. Chem. Acta 29, 2794

Basset, J; Denny, R.C; Jeffrey, G.R. and Mendam, J. Vogel Text books of qualitative Inorg. Analysi) 4th Ed. Longman, London pp 61-62

Bethamy, L.J Infrared Spectra of complexes molecules, Methuen, London 1954

Duggal H.K; AgarWala, B.V (1988) Synth React. Inorg. Met-Org. Chem. 18, 871-879

Karau, D.j; Savadog, A.j; Canini, A.j; Yameogo, S; Montesan, C.J; Simpere, J; Colizzi, V and Traore, A.S (2006)African Journal of Biotechnology 5, 95-200

Korol, B; Multeri, B.A and Brown, D (1967) Med. PHarmacol. Exp. 16, 267

Maiti, A and Ghosh S. (1989) Indian J. Chem. 28A, 980