September 2009 *Volume 4 Issue 3*

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 4(3), 2009 [122-125]

Synthesis, characterization and antimicrobial activity of metal complexes of hydrazone derivative of 8-aceto-7-hydroxy–coumarin

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Received: 11th September, 2009 ; Accepted: 21st September, 2009

ABSTRACT

The metal complexes of Cu(II), Ni(II), Fe(II), Co(II) and Fe(III) with hydrazone derivative of coumarin have been synthesized and characterized using elemental analysis, magnetic susceptibility and IR spectra. Taking in to account, their importance in therapeutic field of research, these compounds were studied for their antimicrobial activity. The paper discs or agar diffusion technique was used. This study show net enhancement in activity on co-ordination of metals with ligand but moderate activity as compare to standard drugs.

KEYWORDS

Coumarin;
Hydrazone;
Metal Complexes;
Antimicrobial activity.

INTRODUCTION

Coumarins are nowadays an important group of organic compounds that are used as additives to food and cosmetics[1], optical brightening agents[2] and dispersed fluorescent and laser dyes[3]. The derivative of coumarin usually occurred as secondary metabolites present in seeds, root and leaves of many plant species. The usefulness of coumarins and coumarin derivatives has been shown in various areas of analysis[4].

The complex of Mn(II), Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 4-Oxo-4H-1-benzobenzyl pyran-3(carboxaldehyde-4-chlorobenzyl hydrazone) and 4-Oxo-4H-1-benzo pyran-3(carboxaldehyde-4-methyl benzyl hydrazone) have been synthesized and characterized[5]. N. M. Naik and K. R. Desai have reported the synthesis of 3-phenyl 4-methyl 7-[4'-aryl urea-6'-amino-s- triazine-2'-yl-amino] coumarin as optical whitening agent[6].

The present communication describes the synthesis and characterization of the complexes of 8-aceto-7-hydroxy-coumarin hydrazone(AHCH) with transition metal ions Cu(II), Ni(II), Fe(II), Co(II) and Fe(III).

EXPERIMENTAL

All the reagents were of AR grade. All the melting points were determined in open capillary tubes and are uncorrected. Infra red spectra (KBr)(υ max, cm^{-1}) were recorded on a Shimadzu 435 FT-IR Spectrophotometer. The metal and anions are estimated using standard procedure[7]. Molecular weight is determined by Rast's method. Elemental analyses are quite comparable with their structure. Molar conductivity were measured on

systronics conductivity meter using DMF. Magnetic susceptibility is measured by Gouy balance method.

The ligand 8-aceto-7-hydroxy-coumarin hydrazone(AHCH) is prepared[7] by condensing 8-aceto-7-hydroxy-coumarin with hydrazine hydrate, which is prepared from 7-hydroxy – coumarin by Fries migration and Acetylation. Complexes are prepared by standard procedure[8].

Synthesis of 8-aceto-7- hydroxy- coumarin hydrazone

An ethanolic solution of 7-Hydroxy-8-acetoxy coumarin (20.4 gm), Hydrazine hydrate(3.5 ml) and pyridine (1.0 ml) were mixed together in a round bottomed flask fitted with reflux condenser. The mixture was refluxed on water bath at 135° C for 1 hour then it was left to cool overnight and then it was neutralized by adding dilute KOH solution. The solid hydrazone obtained was separated and washed with absolute alcohol. Reddish crystalline needles of hydrazone were obtained. m.p. : 160° C, Yield: 72%.

Synthesis of Bis-(8-aceto-7- hydroxy- coumarin hydrazone)Copper (II)complex

1% etanolic solution of 8-aceto-7-hydroxy-coumarin hydrazone was added to a warm cupric chloride solution maintaining the pH of the mixture at pH 4.5 during the reaction. Light green precipitates were formed. Precipitates thus obtained were washed with warm ethanol. m.p.: 267° C, Yield: 61 %.

Similarly other metal complexes were prepared and characterized.

Molecular weight determination by Rast's method

The molecular weights of the metal chelates were determined by Rast's method using pure Camphor. In each case,

Weight of complex is taken 0.2 gm.

Weight of Camphor is taken 2.0 gm.

K_f of Camphor is taken 39.68° C/1000 ml.

The results are recorded in the TABLE 1.

The synthesized compounds were screened for *in vitro* antibacterial and antifungal activity against pathogens like *S. aureus*, *E. coli*, *A. niger*, *S. pyogenus* and *K. pneumoniae* by the paper discs or agar diffusion technique[9]. Their activity measured in terms of zones of inhibition, given in tabular form.

TABLE 1 : Molecular weight determination data by Rast's method

Sr. No.	Chelates with -8-aceto-7-hydroxy coumarin hydrazone	Depression in F.P.		Molecular weights	
		Theoretical (T_c)	Experimental (T_o)	Theoretical (M_c)	Experimental (M_o)
1	$Cu(C_{11}H_9O_3N_2)_2$	4.19	4.21	497.5	496.8
2	$Ni(C_{11}H_9O_3N_2)_2$	4.21	4.19	492.41	494.2
3	$Co(C_{11}H_9O_3N_2)_2$	4.27	4.27	492.94	487.0
4	$Fe(C_{11}H_9O_3N_2)_2$	8.02	7.9	272.85	274.0

TABLE 2 : Elemental data of compounds

Mol. Formula	Mol. Wt	Chelates with 8-aceto-7-hydroxy coumarin hydrazone					
		% of Elements					
		M	C	H	(O)	N	μ eff
$Cu(C_{11}H_9O_3N_2)_2$	497.5	Cu12.75 (12.76)	53.05 (53.06)	3.60 (3.62)	19.28 (19.29)	11.24 (11.25)	1.64
$Ni(C_{11}H_9O_3N_2)_2$	492.71	Ni11.96 (11.96)	53.52 (53.54)	3.64 (3.65)	19.46 (19.47)	11.33 (11.35)	-
$Co(C_{11}H_9O_3N_2)_2$	492.94	Co12.11 (12.11)	53.47 (53.46)	3.63 (3.64)	19.46 (19.44)	11.32 (11.34)	2.03
$Fe(C_{11}H_9O_3N_2)_2$	272.85	Fe20.51 (20.53)	48.34 (48.33)	3.28 (3.29)	17.55 (17.57)	10.27 (10.25)	5.09
$Fe(C_{11}H_9O_3N_2)_2$	272.85	Fe20.51 (20.53)	48.34 (48.33)	3.28 (3.29)	17.55 (17.57)	10.27 (10.25)	6.10

TABLE 3 : Antimicrobial activity of compounds

Sr. No.	Name	Zone of inhibition in mm				
		S. aureus	*E. coli*	*A. niger*	*S. pyogenus*	*K. pneumoniae*
1	$CuII(AHCH)_2$	2.10	0.72	2.90	1.80	0.08
2	$NiII(AHCH)_2$	0.36	0.36	0.72	0..36	0.11
3	$CoII(AHCH)_2$	0.50	0.36	0.21	1.80	0.10
4	$FeII(AHCH)_2$	1.20	0.74	1.40	0.74	0.09
5	$FeIII(AHCH)_2$	1.20	0.37	0.90	0.37	0.19

TABLE 4 : Zone of inhibition against standard drugs

Culture	Geramycin	Ampicillin	Penicillin	Chloromphenicol
S. Aureus	6.00	-	-	-
E.coli	-	5.00	-	-
A. Niger	-	-	5.00	-
S .pyogenus	-	-	-	6.00
K. pneumoniae	-	-	6.00	-

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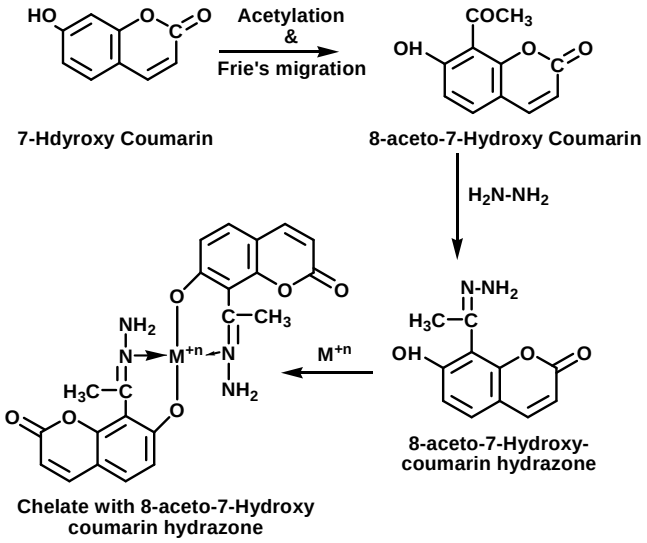

Scheme 1 : Stepwise preparation of hydrazone and their chelates

RESULT AND DISCUSSION

The structure of the synthesized compounds are confirmed by elemental analyses, IR spectral, conductivity and magnetic studies. The observed molecular weight by Rast's method is in the conformity of the metal-ligand ratio1:2 for Cu(II), Ni(II) and Co(II) but it is 1:1 for Fe(II) and Fe(III) metal chelates.

IR Studies

A broad band observed in ligand spectra at 3420 cm^{-1} is broadened and has shifted to a lower frequency region at 390 cm^{-1} on the complexation with metal ion suggesting coordination of alcoholic oxygen[10] by deprotonation. The linkage with alcoholic oxygen is further supported by the appearance of a band in far IR region at 550-535 cm^{-1} which may be assigned[11] to M-O. The next IR spectra of the ligand exhibit a strong and broad band at 1600 cm^{-1} which may be assigned[12] to C=N. This band is shifted to a lower frequency region on complexation which suggest involvement of azomethine N in bonding with metal ion. The linkage with azomethine N is further confirmed by the appearance of a band in the far IR region at 425-395cm^{-1} which may be assigned[13] to M-N. The peak at 1720 cm^{-1} is attributed to δ-lactone ring of coumarin. A broad band observed at 3250cm^{-1} which can be assigned[14] to N-H. This band remains unchanged on complexation indicating non involvement of secondary amino group in the coordination with metal ion. In short, most of the bands appeared in the spectra of corresponding ligand are observed at the similar position in the IR spectra of metal complexes TABLE 5.

TABLE 5 : IR spectral data of compounds

Sr. No.	COMPOUND	OH	NH	CH	C=N	C-O	M-O
1	AHCH	3420	3252	2930	1605	1050	-
2	$CuII(AHCH)_2$	-	3253	2960	1680	1180	555
3	$NiII(AHCH)_2$	-	3250	2975	1690	1055	510
4	$CoII(AHCH)_2$	-	3240	2980	1650	1285	550
5	$FeII(AHCH)_2$	-	3256	2930	1660	1130	545
6	$FeIII(AHCH)_2$	-	3290	2970	1610	1140	540

Magnetic studies

The magnetic susceptibility measurements of the complexes were obtained at room temperature using Gouy balance. Pure $Hg[Co(SCN)_4]$ was 4 used as calibration standard[15].

The Copper, Cobalt, Ferrous and Ferric complexes are paramagnetic in nature, while Nickel complex is diamagnetic in nature. The Cu(II), Ni(II), Co(II),Fe(II) and Fe(III) metal chelates are of tetrahedral geometry.

Conductivity measurements

Molar conductance data of the complexes were measured in the solvent DMF and the complexes were found to be non electrolytic[16] in nature. Conductivity value of the complexes are lie in the range 8.1-10.8 $Ohm^{-1}cm^2\ mol^{-1}$.

ANTIMICROBIAL ACTIVITY

The result of antimicrobial activity is given in TABLE 3. The zones of inhibition is less as compare to standard drugs. Among all these compounds Cu(II) metal chelate has shown highest activity against all strains of micro organisms. Fe(II) metal chelate has shown good activity against *S aureus* and *A. niger*, Fe(III) metal chelate also possesses good activity against *S. aureus*. Co(II) and Ni(II) metal chelates possess moderate activity as compare to other compounds. All the compounds are very less active against *K. pneumoniae*.

ACKNOWLEDGEMENT

The authors express their gratitude to Dr. Judas Franco, the research guide for providing the necessary research facilities and research guidance

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