Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(5):2429-2432

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Complex of 2-amino acetate, 6-chloro benzothiazole with some metal ions

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ABSTRACT

New metal complexes of the ligand 2- amino acetate ,6-chloro benzothiazole with some metal ions Ni(II), Cu(II) , Zn(II), Cd(II) and Sn(II) were prepared in alcoholic medium. The prepared complexes were characterized by electronic spectroscopy, FTIR spectroscopy, ^{1H}*NMR,* ^{13C}*NMR, Magnetic susceptibility and conductivity measurement. From the spectral measurement, monomer structures were proposed. The square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.*

Keywords: amino acetate, benzothiazole, metal complexes

INTRODUTION

Benzothiazoles are bicyclic ring system with multiple applications .The aromatic benzothiazole [15] nucleus is associated with variety of antihistamine activity ,pharmacological acitivities,[9,10] such as fungicidal[16], anti-inflammatory, anti- microbial,anti-convulsant ,[2]These activities are probably due to presence of the –N=C-S group[13]. Substituted benzothiazole have been reported to show diverse application as metal complexing agents and photostabliser.

The wide range of application of the ligand and its complexes aroused our interest to prepare a new series of some metal complexes [1-5].

EXPERIMENTAL SECTION

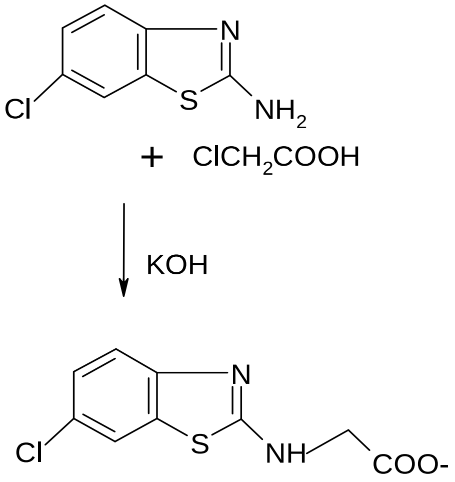
Synthesis of 2-amino acetate, 6-chloro benzothiazole:

A solution of p-chloro aniline (0.085 mol) in 95% acetic acid (50 ml) was added to a solution of KSCN (0.308 mol) in 95% acetic acid (100ml). The mixture was cooled to 0^0C & a solution of Br_2 (7.5 ml) in acetic acid (30ml) was added slowly with stirring so that temperature between 0 &10^0C. After addition was complete, the stirring was continued for 1hr. at 5^0C and then mixture was poured into water. The solid was collected & re-crystallized from ethanol. The product (0.036mol) conc. HCl (27ml) and water (50 ml) were refluxed for 2 hr. The solution was cooled and the product was filtered off, washed with water & re-crystallized from ethanol.

The steps of synthesis of 2-amino acetate, 6-chloro benzothiazole can be shown below

Preparation of complexes:

Addition of ethanol solution of the suitable metal salt (Nickel acetate tetrahydrate, Copper acetate, Cadmium acetate dihydrate, Tin chloride and Zinc acetate dihydrate) to an ethanol solution of 2-amino acetate, 6-chloro benzothiazole in 2:1(ligand: metal [3, 4] molar ratio was carried out [17]. After refluxing for half an hour, crystalline colored precipitates formed at room temperature. Washed with distilled water, dried and recrystallized from ethanol and dried at $48^0{}_{C.}$ Table 1: Shows the melting point of the prepared compounds.



INSTRUMENTATION:

The FTIR spectra in the range (4000-200) cm^{-1} were recorded as CsI disc on FTIR and the magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility Balance of Bruke Magnet B.M. 6.

The 1H nuclear magnetic resonance spectra were recorded on a Jeol 400 MHz spectrometer with tetramethyl silane (TMS) as internal standard. Melting points were recorded on a hot stage Gallen Kamp melting point apparatus.

Table 1. Physical data for ligand and metal complexes (melting point)

Compound	Melting point ^{0}C
L_H	180-185
$Ni(L_H)_2$	180
$Cu(L_H)_2$	210
$Sn(L_H)_2$	Above 300
$Zn(L_H)_2$	250
$Cd(L_H)_2$	256

L_H *- 2-amino acetate, 6-chloro benzothiazole*

RESULTS AND DISCUSSION

Infra- red spectroscopy: The ligand was prepared by the reaction of one mole of 2-amino,6-chloro benzothiazole with one mole of chloroacetic acid in presence of KOH.

Table 1 shows the physical data (m.p.) for the ligand and the prepared complexes

The FTIR spectrum of the ligand shows a characteristics stretching absorption band at 3100, 1710, 1560, and 690 cm^{-1} assigned to secondary amine, carbonyl, C=N of the thiazole ring and stretching of C-S group respectively[11].

Table 2: Characteristics absorption band of 2-amino acetate,6-chloro benzothiazole and its complexes.

Compound	ν(C=O) cm^{-1}	ν (C-O) cm^{-1}	ν (M-O) cm^{-1}
L_H	1700	1020	
$Ni(L_H)_2$	1580	1000	430
$Cu(L_H)_2$	1665	980	410
$Sn(L_H)_2$	1630	975	408
$Zn(L_H)_2$	1550	990	425
$Cd(L_H)_2$	1565	970	428

L_H *- 2-amino acetate, 6-chloro benzothiazole*

The reaction between this ligand with Ni(II), Cu(II), Sn(II), Zn(II) and Cd(II)Gave different types of complexes[14,19]. In the free ligand, the band at 1710 and 1033 cm^{-1} were assigned to the stretching of C=O and C-O of the carboxylate group. On complexation these bands were shifted to a lower frequency region.

The shift is probably due to the complexation of the metal to the ligand [6].through oxygen of the carbonyl group. Stretching of metal –oxygen bands of the complexes appeared in low frequency region (408-430) cm^{-1} [12]. The IR data of the complexes are shown in table 2

The table lists of stretching frequency (**ν**) for some the group exhibited by ligand and complexes [18].

Magnetic Susceptibility and conductivity measurement:
The experimentally determined value of magnetic moment for each complexes is listed in Table 3. Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in partially filled d-orbital in outer shell of the metal ion in the complex.

The magnetic moment for Ni (II) complexes is approximately 3.16 B.M.this value refers to high spin tetrahedral structure, while the value of Cu (II) is approximately 1.60 led to suggest the square planar structure. Other complexes have no magnetic moment because its diamagnetic. Molar conductivity measurement in DMF solvent at 25 ^{0}C showed that complexes were non –electrolyte.

Table 3: Magnetic moment, conductivity measurement in DMF solvent

Symbol	Name	Conductivity (ohm^{-1} cm^{2} mol-^{1})	Magnetic moment (B.M.)	Suggested Structure
L_H	2-amino acetate, 6-chloro benzothiazole			
$Ni(L_H)_2$	Bis(2-amino acetate, 6-chloro benzothiazole) nickel(II)	13	3.16	Tetrahedral
$Cu(L_H)_2$	Bis(2-amino acetate, 6-chloro benzothiazole) copper(II)	20	1.60	Square planar
$Sn(L_H)_2$	Bis(2-amino acetate, 6-chloro benzothiazole) tin(II)	09	0.00	Tetrahedral
$Zn(L_H)_2$	Bis(2-amino acetate, 6-chloro benzothiazole) zinc(II)	11	0.00	Tetrahedral
$Cd(L_H)_2$	Bis(2-amino acetate, 6-chloro benzothiazole) cadmium(II)	16	0.00	Tetrahedral

NMR Spectroscopy:
The data of 1H NMR of the 2-amino,6-chloro benzothiazole and its complexes shows good solubility in DMSO. The proton nuclear magnetic resonance spectral data gave additional support for the composition of the complexes [7].Table 5

The δ 7.35-8.14 ppm resonance signal protons of the aromatic ring shifted to higher field upon complexation. While proton of the CH_2 aliphatic group shifted to higher field also.

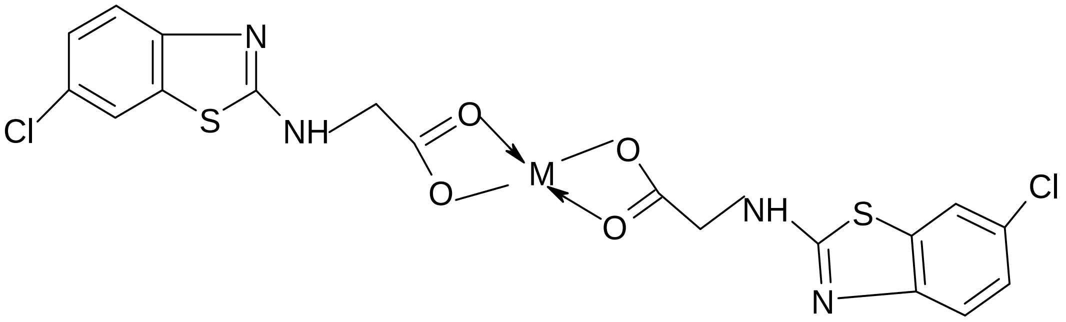
Table 4 ^{1H}NMR spectral data (δ ppm) of the ligand and complexes

Symbol	$-CH_2$ aliphatic	Aromatic
L_H	4.14	7.35-8.14
$Ni(L_H)_2$	4.12	6.40-7.12
$Cu(L_H)_2$	4.20	6.43-7.89
$Sn(L_H)_2$	4.16	6.65-7.83
$Zn(L_H)_2$	4.22	6.30-7.93
$Cd(L_H)_2$	4.21	6.60-7.80

Study of Complex formation in solution:
Mole ratio [M/L] in the complex was determined using **Mole ratio method** [8]. The complexes of L_H with metal ions were studied in solution using ethanol as a solvent.

The [M/L] ratio was determined from absorbed light [A]for metal salt and ligand.

The result of complexes in ethanol, suggestion that metal to ligand ratio was [1/2] for all complexes. On the basis of preceding discussion, the structure of the complexes suggested as follows



CONCLUSION

The ligand 2-amino acetate, 6-chloro benzothiazole were successfully synthesized by condensation method. The ligand was treated with different metal salts to formed corresponding complexes. Square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

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