

# Synthesis and Characterization of New Complexes of 2-(Benzo[d]Thiazol-2-ylAmino)-2-(5-Chloro-2-Hydroxy Phenyl) Acetonitrile Ligand with Some Divalent Transition Metal Ions

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## Abstract

A series of metal ion complexes of some divalent transition metal ions having the general composition  $[ML_2Cl_2]_nH_2O$  with 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxy phenyl) acetonitrile ligand has been prepared from 5-chloro-2-hydroxy-benzaldehyde and benzo[d]thiazol-2-amine. Existence of cyanide as potassium cyanide in acidic medium was considered, characterized by elemental chemical analysis, conductance of molarity, magnetic susceptibility measurements, FTIR electronic spectral studies and mole ratio method. FTIR indicates the participation of amino and acetonitrile nitrogen which is coordinated with the central metal ion.

**Keywords:** 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxy phenyl) acetonitrile, bidentate, divalent, transition metal ions.

## Introduction

Legends and its transition metal vehicles have been of great interest to researchers since 1970s. At that time, it was found that pyridine complexes appear to be active against leukemia<sup>1</sup>. Strecker's classic reaction is a good way to prepare cyanide, amino nitrile since 1850 when Adolf Strek reacts with aldehyde, amine and hydrogen cyanide<sup>2</sup>. Adding cyanide to imines is the best way to synthesize amino nitriles.

## Material and Methods

**Materials:** All reagents types, chemicals and solvents which were used for synthesis were commercially obtained from the House of British Drug (BDH).  $MnCl_2 \cdot 4H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$  and  $CuCl_2 \cdot 2H_2O$ , salts were obtained from Fluka Company. The prepared ligand 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxyphenyl) acetonitrile has been synthesized and tagged compatible with the work being published. The spectral data of infrared of the complexes and ligands have been checked on a Shimadzu (8300) FTIR Spectrophotometer, as CsI disk. the absorption of Electronic spectra has been noticed in the range 190–1100 nm on Shimadzu (160 A) Spectrometer which recently comes from ( $10^{-3}M$ ) in ethanol free at normal temperature by using cell made from quartz (1.00) cm. Atomic Absorption technique was employed to adjust the metal inside of the compounds by using Shimadzu (A.A

680G). The analysis of elemental carbon, hydrogen nitrogen and sulfur element was done in the presence of Euro vector-EA3000A C. H. N. S. Analyzer, Italy. Gallen Kamp uses a device to set ligand fusion points and stomach complexes and to find the proportion of chlorine present gravimetrically<sup>16</sup>.

**Preparation method of the ligand:** 5-chloro-2-hydroxy-benzaldehyde (1mmol) has been added to 20 ml glacial acetic acid, p-toluene sulphonic acid, catalyst has been added in a little amount, subsequently adding (1mmol) benzothiazol-2-ylamine. The pH must be used to about 4. The reaction of mix was transferred into ice and then it was made a little alkaline with  $NH_4OH$  solution. Precipitate was washed with water and is dried by air. A group of nitrile was reported in the preparation of amino nitrile by treating a small quantity of the sample with 10% NaOH solution and ammonia released after hydrolysis of the nitrile group. The most common method to determine the purity of the compound obtained by TLC, chloroform and ethyl acetate (1: 1) was used as indicator. The product has yellow orange color and the percentage of yield was 82.55% and the degree of melting was 113-114<sup>0</sup>C.

**Preparation method of metal complexes:** A following complex  $[ML_2Cl_2]_nH_2O$  was prepared from 0.628 gm 2 mmol of (L) with 1mmol of the metal chloride 0.198 gm, 0.238 gm, 0.238 gm, 0.171 gm, 0.136 gm, 0.220 gm and 0.272 gm for  $MnCl_2 \cdot 4H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CuCl_2 \cdot 2H_2O$  and solidified in (20 ml)  $CH_3CH_2OH$  and the mixture was refluxed with stirring under the influence of anhydrous conditions by using  $Na_2SO_4$  (free from water) for 24 hours. The obtained complexes were placed after loss of alcohol and dried with diethyl ether (60-80 <sup>0</sup>C), then the products were filtered and then left in the desiccators to be dried under  $P_2O_5$ . The overall reaction was shown in equation (2).

## Results and Discussion

All composites stated in this work have been mentioned in table 1. Elemental analysis of all vehicles in addition to metals is signified in table 1 as well. The ligand 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxyphenyl) acetonitrile was prepared as described in the literature<sup>18</sup>. All complexes were prepared in absence of water to prevent any disintegration due to water of nitrile group to amide. Furthermore, if organic molecules are coordinated into metallic cations in coordinated organic mixtures, they will

be ready for nuclear attack such as water molecules responsible for nitrile degradation in the amide<sup>21</sup>. These complexes have stability in the solid form and were described by the common ways FTIR, UV-Visible spectroscopy, metal and elemental analysis, molar conductivity, mole ratio, chloride content and magnetic susceptibility. Because of this characterization it is possible that all assemblies have an octagonal structure with hexagonal format that contain two atoms of chlorides coordination.

The values of conductivity of the complexes ( $10^{-3}\text{M}$ ) were measured in the range 8-16 showing the nature of non-electrolytic of the complexes<sup>22</sup>. The ratio of mol to the ratio of metallic ion to ligand was used at  $\lambda_{\text{max}}=485\text{ nm}$  for  $[\text{CoL}_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  and  $\lambda_{\text{max}}=496\text{ nm}$  for  $[\text{CuL}_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$  in the presence of alcoholic solutions.

**<sup>1</sup>H-NMR:** The <sup>1</sup>H-NMR spectra for the free ligand [L] in solution of the DMSO with description were placed in table 2. The OH phenolic proton takes a signal at 9.65 ppm and the signals are related to NH and CH 4.55 and 5.82 ppm respectively<sup>23</sup>. The <sup>13</sup>C-NMR spectrum displayed the results listed in table 3.

**Infrared spectroscopy:** The IR spectral data of [L] and their complexes are presented in table 3. It was found that some ranges characterize alpha-amino nitrile like 2193-2212  $\text{cm}^{-1}$ . A shift of the range 25-55  $\text{cm}^{-1}$  was detected for  $\text{C}\equiv\text{N}$ . The red of the shift range at 15-40  $\text{cm}^{-1}$  was seen in N-H frequency bending of complexes significant to the bonded nitrogen to the metal ion. At the same time, a group of new bands appeared around 565-593  $\text{cm}^{-1}$  due to  $\nu_{\text{M-N}}$ <sup>25,26</sup>. The  $\nu_{\text{M-Cl}}$ , on the other hand could not be determined because of non-availability of far infrared data. The lattice water molecule existing in all complexes in the table 4 could be stayed by the wide band in 3430-3360  $\text{cm}^{-1}$  region of IR spectrum<sup>25</sup>.

**Magnetic studies:** The complex of  $\text{Cu}^{+2}$  shows the normality of magnetic moment of 1.77 B.M. for the  $d^9$  system having an unpaired electron<sup>28</sup>. The  $\text{Ni}^{+2}$  complexes with a magnetic moment of 3.11 B.M. detect the presence of octahedral form surfaces<sup>28</sup>. The magnetic moment of 4.55 B.M. for the  $\text{Co}^{+2}$  complexes proposed a high spin octahedral configuration<sup>27,28</sup>. Magnetic moment of  $\text{Mn}^{+2}$  complexes having 5.21 B.M value was expected to their great spin 6 coordination geometry<sup>29</sup>.

**Ultra violet – visible spectroscopy:** The data of absorption spectra due to the ligand and their complexes were noted at normal temperature and solvent used was ethanol. The ligand presented two bands absorbed in the region 39528  $\text{cm}^{-1}$  and 34722  $\text{cm}^{-1}$  as a result of  $(\pi \rightarrow \pi^*)$  with  $(n \rightarrow \pi^*)$  moves separately. In other complexes, the bands were moved to higher wavelengths. The complex of  $\text{Mn}^{+2}$  does not display any d-d transitions but it showed charge transfer bands at 21277. The six coordinated electrons of  $\text{Cu}^{+2}$

complex spectrum display three bands at 14389, 22472 and 25974  $\text{cm}^{-1}$  meeting with the transitions as follow:  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g} (d_{x^2-y^2} \rightarrow d_z^2)$ , ( $\nu_1$ ),  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g} (d_{x^2-y^2} \rightarrow d_{zy})$ , ( $\nu_2$ )  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g (d_{x^2-y^2} \rightarrow d_{zy}d_{yz})$ , ( $\nu_3$ ), according to that order. As a result, the  $\text{Cu}^{+2}$  complex may be counted to own a 4 coordinated geometry around the copper ion<sup>30,31</sup>.

Though the three expected transitions are found in this case, they have similar levels of energy and usually appear in the formula of a single wide envelope<sup>31</sup>. The spectrum also displays a band at 23923  $\text{cm}^{-1}$ , that was given to a band of charge transfer. The two main bands were shown in electronic spectrum of  $\text{Co}^{+2}$  complex at 24934  $\text{cm}^{-1}$  and 15385  $\text{cm}^{-1}$ . These two d-d bands were related to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_2$ ) transitions, in that order, in an octahedral geometry around the  $\text{Co}^{+2}$  ion<sup>26</sup>.

The charge transfer band of  $\text{Co}^{+2}$  complex shows 2096  $\text{cm}^{-1}$ <sup>33</sup>. Two bands in the electronic spectrum of  $\text{Ni}^{+2}$  complex display in the region 23810 and 14493  $\text{cm}^{-1}$  which are allocated to the  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ),  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) transitions separately indicating an octahedral geometry around the  $\text{Ni}^{+2}$  ion. The complexes are also supported by the value of the  $\nu_2/\nu_1$  ratio, which are 1.60 and 1.49, separately<sup>27</sup>. Many field parameters are enlisted in table 5 such as the Racah inter-electronic repulsion parameter ( $B'$ ), splitting energy of ligand field ( $10Dq$ ), covalency factor ( $\beta$ ) and stabilization energy of ligand field ( $LFSE$ ) planned for  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  complexes.<sup>27-34</sup>

In the  $\text{Co}^{+2}$  complexes, the Racah inter-electronic repulsion parameter ( $B'$ ) was set from the following equation<sup>27</sup>:

$$B' = 1/510 \{7 (\nu_3 - 2 \nu_2) + 3 [81 \nu_3^2 - 16 \nu_2 (\nu_2 - \nu_3)]^{1/2}\}$$

when  $\text{Ni}^{+2}$  complex, ( $B'$ ) can always be obtained from the following equation<sup>26</sup>:

$$B' = \nu_2 + \nu_3 - 3 \nu_1/15$$

The ligand field splitting energy ( $10Dq$ ) was set in the following manner for the  $\text{Co}^{+2}$  complex:

$$10Dq = 1/3 (\nu_2 - \nu_3) + 15B'$$

For the  $\text{Ni}^{+2}$  complex,  $10Dq = \nu_1$

The covalence factor ( $\beta$ ) is calculated according to the following method:

$$\beta = B'/B \text{ (B is the free ion value)}$$

The ligand field stabilization energy ( $LFSE$ ) can be expressed as follows:

$$LFSE = 12Dq$$

Complexes have ( $B'$ ) values lesser than that of the freedom ion, it was considered a pointer of orbital overlap and

delocalization of the d-orbitals. Values of ( $\beta$ ) were less than unity. The ( $\beta$ ) value for the  $Ni^{+2}$  complexes is a smaller

amount than that for the  $Co^{+2}$  complexes, due to the greater covalent nature of the former.

**Table 1**  
Physical features of [L] and its metal ion complexes with their conductivity values

Formula M.wt. (gm/mole)	Elemental Analysis Calculated (Found)						Color	M.P. °C (Dec.)	Yield %	$\Omega^{-1}cm^2$ mol <sup>-1</sup>	Magnetic moment BM
	C%	H%	N%	S%	M%	Cl%					
L 315.5	57.05 (56.87)	3.17 (3.05)	13.31 (13.57)	10.14 (10.07)	-----	11.25 (11.03)	Yellow orange solid	113-114	82.55	-----	-----
[MnL <sub>2</sub> Cl <sub>2</sub> ].3H <sub>2</sub> O 810.94	44.39 (44.33)	3.21 (3.18)	10.36 (10.13)	7.89 (7.49)	6.77 (6.45)	17.51 (17.38)	Dark orange solid	212-215	72.32	13.77	5.21
[CoL <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O 796.93	45.17 (45.32)	3.01 (2.93)	10.54 (10.66)	8.03 (7.88)	7.39 (7.47)	17.82 (17.95)	Light brown solid	194-196	78.65	12.68	4.55
[NiL <sub>2</sub> Cl <sub>2</sub> ].3H <sub>2</sub> O 814.69	44.19 (45.01)	3.19 (3.13)	10.31 (10.50)	7.86 (8.03)	7.20 (7.35)	17.43 (16.88)	Greenish yellow solid	232-235	76.37	13.09	3.11
[CuL <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O 801.55	44.91 (44.75)	2.99 (2.88)	10.48 (10.66)	7.98 (8.27)	7.93 (8.02)	17.72 (17.03)	Dark yellow solid	207-210	71.45	11.89	1.77

**Table 2**  
<sup>1</sup>H-NMR data for the 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxy phenyl)  
acetonitrile in DMSO solution (ppm)  $\delta - H$

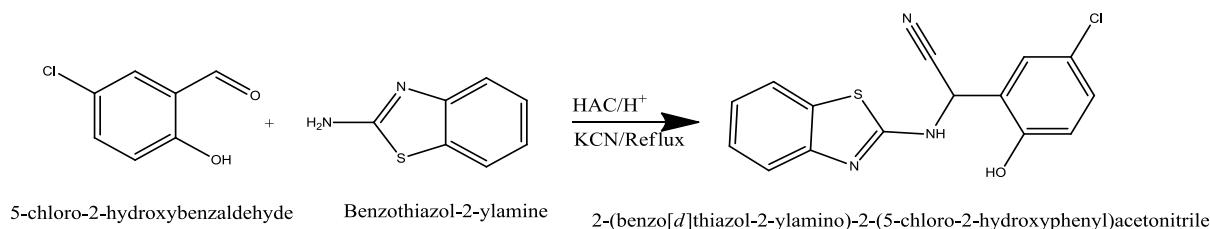
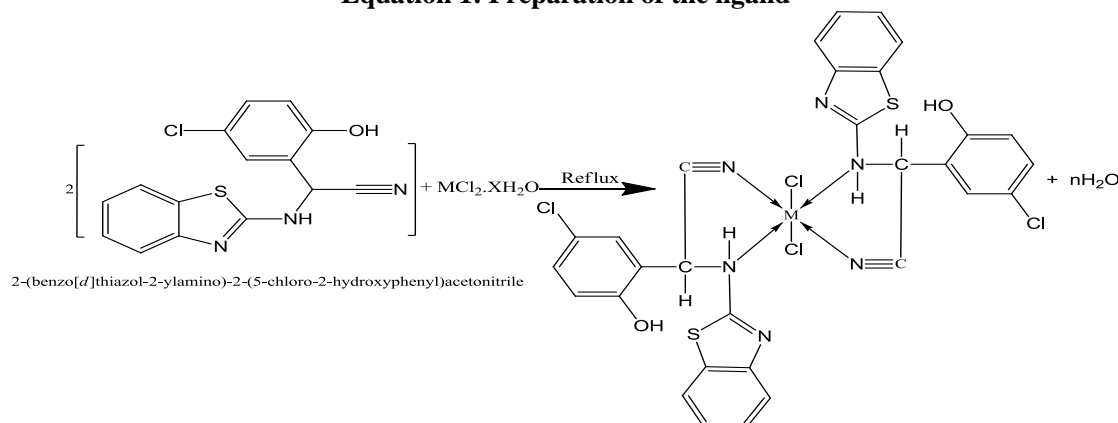
C <sub>15</sub> H <sub>10</sub> N <sub>3</sub> SOCl	Aromatic protons	Phenolic OH proton	NH proton	CH proton
	7.25 - 7.87	9.65	4.55	5.82

**Table 3**  
<sup>13</sup>C- NMR data for 2-(benzo[d]thiazol-2-ylamino)-2-(5-chloro-2-hydroxy phenyl) acetonitrile

Structure	C <sub>1</sub>	C <sub>2</sub>	C <sub>8</sub>	C <sub>9</sub>	C of all aromatic
	117.5	56.5	155.5	168.5	120-130

**Table 4**  
The Special character bands for FTIR spectra of the ligand and its metal ion complexes in (cm<sup>-1</sup>)

Compound	$\nu$ O-H cm <sup>-1</sup> Lattice water	$\nu$ N-H cm <sup>-1</sup>	$\nu$ C $\equiv$ N Nitrile	$\delta$ N-H	$\nu$ M-N
L	-----	3332	2237	1640	-----
[MnL <sub>2</sub> Cl <sub>2</sub> ].3H <sub>2</sub> O	3396	3305	2193	1625	575
[CoL <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	3430	3310	2198	1612	578
[NiL <sub>2</sub> Cl <sub>2</sub> ].3H <sub>2</sub> O	3402	3317	2182	1619	570
[CuL <sub>2</sub> Cl <sub>2</sub> ].2H <sub>2</sub> O	3360	3318	2205	1613	593

**Equation 1: Preparation of the ligand****Equation 2: Preparation method of metal complexes**

**Table 5**  
**Electronic spectra in very pure ethanol for the ligand (L) and its metal ion complexes**

Compound	$\lambda$ nm	$\nu$ $\text{cm}^{-1}$	Transition	$\text{B} \cdot \text{cm}^{-1}$	$\text{Dq}/\text{B}^*$	$\beta$	$15\text{B}^*$ $\text{cm}^{-1}$	Suggested structure
L	253 288	39526 34722	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-----	-----	-----	-----	-----
$[\text{MnL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	248 272 470	40323 36765 21277	Ligand Field Ligand Field C.T	-----	-----	-----	-----	O.h
$[\text{CoL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	246 295 415 ---- 650 401	40650 33898 24096 9625* 15385 24934	Ligand Field Ligand Field C.T ${}^4\text{T}_{1g}(\text{F}) \rightarrow$ ${}^4\text{T}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \rightarrow$ ${}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F})$ $\rightarrow {}^4\text{T}_{1g}(\text{P})$	787	2.15	0.801	11660	O.h
$[\text{NiL}_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	260 295 405 --- 690 420	38462 33898 24691 9760* 14493 23810	Ligand Field Ligand Field C.T ${}^3\text{A}_{2g}(\text{F}) \rightarrow$ ${}^3\text{T}_{2g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F}) \rightarrow$ ${}^3\text{T}_{1g}(\text{F})$ ${}^3\text{A}_{2g}(\text{F})$ $\rightarrow {}^3\text{T}_{1g}(\text{P})$	631	1.582	0.603	9315	O.h
$[\text{CuL}_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	268 293 418 695 445 385	37313 34130 23923 14389 22472 25974	Ligand Field Ligand Field C.T ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	-----	-----	-----	-----	O.h

\*Calculated value

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