

SYNTHESIS, PHYSICO-CHEMICAL STUDIES AND ANTIMICROBIAL EVALUATION OF NOVEL 2-(SUBSTITUTED ARYL)-1H-BENZO [D]THIAZOLES AND THEIR METAL(II)CHLORIDE COMPLEXES

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ABSTRACT

The synthesis and characterization of some new 2-(substituted aryl)-1H-benzo[d]thiazole ligands and their transition metal complexes are reported. All metal complexes were synthesized from the transition metal halide salts and 2-(substituted aryl)-1H-benzo[d]thiazoles in alcohol as a solvent at room temperature. All metal complexes have been characterized by IR spectroscopy, ESI mass spectroscopy, TGA, Electronic spectral analysis, magnetic susceptibility and elemental analysis. 2-(Substituted aryl)-1H-benzo[d]thiazole ligands and all metal complexes were evaluated for their *in vitro* antimicrobial activity against two Gram positive and two Gram negative bacteria and three fungal species. The *in vitro* study of antimicrobial activity of newly synthesized 2-(substituted aryl)-1H-benzo[d]thiazole ligands and their metal complexes of seven organisms viz., *C.Albicans*, *A.Niger* and *A.Clavatus* (Fungicidal strains), *E.Coli*, *P.Aeruginosa*, *S.Aureus*, *S.Pyogenus* (Bacterial strains), showed specific activity in inhibiting the growth of two Gram negative bacteria (*E.Coli* and *P.Aeruginosa*) and two Gram positive bacteria (*S.Aureus* and *S.Pyogenus*). It is ended from the antimicrobial results that the 2-(substituted aryl)-1H-benzo[d]thiazole compounds were active against most of the bacterial strains whereas in fungicidal activity only one compound was more active only against *C.Albicans* and the metal complexes were found most effective against bacterial and fungicidal strains than the corresponding ligands.

Keywords: Physico-chemical studies, Antimicrobial evaluation, 2-(Substituted aryl)-1H-benzo[d]thiazole ligands, Metal (II) chloride complexes.

INTRODUCTION

Small and simple benzothiazole molecules are the sulfur containing heterocyclic compounds which were found as building block for specific biological activities viz., antimicrobial and antifungal^{1,2}, cytotoxic³ and antidiabetic^{4,5}. 2-substituted benzothiazole has emerged in its usage as a core structure in the diversified therapeutically applications. The studies of structure activity relationship interestingly reveal that change of the structure of substituent group at C-2 position commonly results the change of its bioactivity. Many transition metal complexes containing benzothiazole derivatives have been investigated in past literature^{6,7}. Benzothiazole and its derivatives have great coordination interest and ability due to π -delocalized system in their structures they are capable of binding to the DNA molecules via π - π interactions, therefore benzothiazole complexes exhibits biological properties too as anti-infective, antihelmintic, antifungal and antitumor⁸.

In this research article we reported the synthesis and characterization of 2-(substituted aryl)-1H-benzo[d]thiazole ligands and their metal complexes with hydrated metal salts of Cu(II)chloride, Ni(II)chloride and Co(II)chloride. The synthesized solid complexes were investigated by the IR, ESI mass, UV-visible, TGA, magnetic susceptibility, molar conductivity and elemental analysis. All 2-(substituted aryl)-1H-benzo[d]thiazole ligands and their transition metal complexes were evaluated for *in vitro* antimicrobial activity against bacterial and fungal strains.

MATERIALS AND METHODS

Materials

The CuCl₂.2H₂O, NiCl₂.6H₂O and CoCl₂.6H₂O metal salts were purchased from Spectrochem, the organic chemicals were purchased from Merck which were used as received and the solvents were purchased from Allied Chemical Corporation and used without further purification. All melting points were determined in open capillary tube and are uncorrected. All syntheses were carried out by direct heating and continuous stirring on stirring device fitted with refluxing condenser. The pathogenic bacterial strains were procured from Institute of Microbial Technology, Chandigarh. Nutrient agar and Sabouraud's dextrose agar (SDA) were purchased from Himedial. The bacteria and fungi were sub-cultured on

Nutrient agar and Sabouraud's dextrose agar (SDA), respectively, and incubated aerobically at 37 °C.

Physico-chemical and analytical methods

The metal ions in metal complexes were determined by gravimetric analysis. The molecular weights of metal complexes were confirmed by the Rast's Camphor method. All the synthesized compounds were micro analyzed satisfactorily for Carbon, Hydrogen, Nitrogen and Sulfur on EURO EA Elemental Analyzer, EA-3000, and RS-232; IR spectra were recorded on a SHIMADZU-FT-IR 8400 spectrophotometer using KBr discs; ¹H NMR spectra were recorded on Bruker Av-400 spectrophotometer (400 MHz) in CDCl₃ solution. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. The ESI mass spectra were recorded on Micromass Q-ToF Micro having mass Range of 4000 amu in quadruple and 20000 amu in ToF at SAIF, Punjab University. The TG analysis of all metal complexes was taken of the Diamond Thermogravimetric/ Differential Thermal Analyzer (TG/DTA) at SAIF, IIT Bombay.

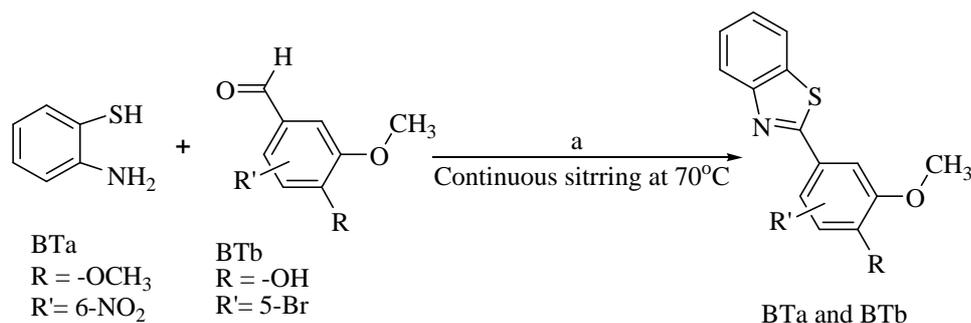
Synthesis of 2-(substituted aryl)-1H-benzo[d]thiazole ligands

Benzothiazole ligands were synthesized by the condensation of 4,5-dimethoxy-2-nitrobenzaldehyde and 3-bromo-4-hydroxy-5-methoxybenzaldehyde with 2-aminobenzenethiol respectively in equimolar amount in alcoholic media by adding ceric ammonium nitrate as a catalyst in presence of hydrogen peroxide. Reaction was monitored by thin layer chromatography by using solvent system hexane:ethylacetate (4:1). After completion of reaction the reaction mass was poured in to crushed ice, formed crude was filtered with suction and dried at room temperature.

Both aldehydes 4,5-dimethoxy-2-nitrobenzaldehyde and 3-bromo-4-hydroxy-5-methoxybenzaldehyde were prepared by previously published method^{18,19}.

2-(3',4'-Dimethoxy-6'-nitrophenyl)-1H-benzo[d]thiazole (BTa)

IR (KBr, cm⁻¹): 3072, 3009, 2935, 2845, 1670, 1600, 1577, 1518, 1467, 1392, 1224, 1028 and 756. ¹H NMR (400 MHz, CDCl₃) δ in ppm: 3.99-4.01 (m, 6H, OCH₃), 7.14 (s, 1H, Ar-H), 7.44-7.52 (t, 2H, Ar-H), 7.61 (s, 1H, Ar-H), 7.91-7.93 (d, 1H, Ar-H), 8.07-8.09 (s, 1H, Ar-H). Mass *m/z*: 316. Anal. Calcd. for C₁₅H₁₂N₂O₄S; Calcd.: C, 56.95; H, 3.82; N, 8.86; O, 20.23; S, 10.14; Found: C, 56.80; H, 3.70; N, 8.70; O, 20.03; S, 9.99 %.



^aReagents and conditions: Methanol, Ceric ammonium nitrate and hydrogen peroxide

Scheme 1: Reaction scheme for 2-(substituted aryl)-1H-benzo[d]thiazoles

2-(3'-Methoxy-4'-hydroxy-5'-bromophenyl)-1H-benzo[d]thiazole (BTb)

IR (KBr, cm⁻¹): 3541, 3475, 3400, 3063, 2997, 2970, 2874, 1643, 1610, 1508, 1471, 1456, 1417, 1352, 1188, 1022, 725 and 538. ¹H NMR (400 MHz, CDCl₃) δ in ppm: 4.02 (s, 3H, OCH₃), 7.46-7.50 (m, 2H, Ar-H), 7.63-7.67 (dd, 1H, Ar-H), 7.78 (d, 1H, Ar-H), 7.87-7.89 (d, 1H, Ar-H), 8.03-8.05 (d, 1H, Ar-H), 9.78 (s, 1H, OH). Mass *m/z*: 335. Anal. Calcd. for C₁₄H₁₀BrNO₂S; Calcd.: C, 50.01; H, 3.00; Br, 23.77; N, 4.17; O, 9.52; S, 9.54; Found: C, 49.89; H, 2.88; Br, 23.60; N, 4.04; O, 9.40; S, 9.40 %.

Synthesis of bis[2-(substituted aryl)-1H-benzo[d]thiazoles] metal(II)chloride complexes

The alcoholic solution of metal salt was added drop wise to a completely dissolved and stirring solution of 2-(substituted aryl)-1H-benzo[d]thiazole ligands in 100 mL conical flask. The mole ration of the reaction mixture was 1:2 of metals salt and ligands respectively. After completion of addition the mixture was stirred continuously for 72 hours at room temperature during this time product formation was observed. This was filtered off in suction and washed with methanol to get desire complex product. Yield 75-85 %.

Rast's Camphor method to determine the molecular weight of complexes

The 50 mg of the complex was weighted in a test tube and about 500 mg of camphor was added. The test tube was sealed completely and heated on water bath until it becomes a homogeneous mixture. After cooling, the melting point of the mixture was determined by using Backman thermometer. Differences between the melting of camphor and the mixture gave the depression of the melting point of pure camphor caused by addition of the complex. The molecular weight was calculated by using the following formula.

$$M = \frac{K \times w \times 1000}{t \times W}$$

Where, K = Molecular depression constant; w = Weight of complex; W = Weight of camphor; t = Depression of melting point

Antimicrobial screening

In vitro antimicrobial activity of newly synthesized 2-(substituted aryl)-1H-benzo[d]thiazoles and their metal(II)chloride complexes as minimum inhibition concentration *in vitro* by broth dilution method^{20,21} with two Gram positive bacteria *S.Aureus* and *S.Pyogenus* and two Gram negative bacteria *E.Coli* and *P.Aeruginosa* and three fungus strain *C.Albicans*, *A.Niger* and *A.Clavatus* taking ampicillin, ciprofloxacin, norfloxacin, nystatin and greseofulvin as standard drugs. The bacteria were sub-cultured on Nutrient agar and incubated aerobically at 37 °C. The solvent used for the *in vitro* antimicrobial screening for 2-(substituted aryl)-1H-benzo[d]thiazole compounds and their metal(II)chloride complexes was *N,N*-dimethyl formamide. Each compounds and standards drugs were dissolved in initially at 2000 μ g/mL and then were serially diluted to 1000, 500, 250, 100, 50, 25, 12.5 and 6.25 μ g/mL concentrations.

RESULTS AND DISCUSSION

Both 2-(substituted aryl)-1H-benzo[d]thiazole ligands were synthesized in alcoholic media by the cyclocondensation of 2-aminothiophenol and substituted aryl aldehydes using ceric ammonium nitrate (CAN as catalyst) in presence of hydrogen peroxide. All complexes were synthesized in warm alcoholic solution of the metal ions with benzothiazole ligands (BTa and BTb) in a 1:2 mole ration by conventional method. The physical data of the ligands and their metal complexes are accumulated in table 1. All complexes are soluble in coordinative solvents like Acetonitrile, *N,N*-dimethyl formamide, Dimethyl sulfoxide etc. The elemental analysis data of all complexes specify the 1:2 metal-ligand stoichiometry. The molar conductance values of the metal complexes were measured in 10⁻³ M DMF solution at room temperature suggests the non-electrolytic nature of all complexes⁹ signifying that the chloride anion is absent or situated inside of the metal coordination sphere.

Table 1: Physical and analytical information of ligands and their metal complexes.

Compound	Color	Elemental analysis Cacl.(Found) %							m.p. °C	
		C	H	N	S	O	Br	M		Cl
BTa	Pale yellow	56.95 (56.80)	3.82 (3.70)	8.86 (8.70)	10.14 (9.99)	20.23 (20.03)	-	-	-	120
BTb	Light yellow	50.01 (49.89)	3.00 (2.88)	4.17 (4.04)	9.54 (9.40)	9.52 (9.40)	23.77 (23.60)	-	-	150
[Cu(BTa) ₂ Cl ₂]	Greenish black	46.97 (46.86)	3.15 (3.11)	7.30 (7.18)	8.36 (8.23)	16.69 (16.57)	-	8.28 (8.15)	9.24 (9.11)	230
[Ni(BTa) ₂ Cl ₂]	Dark brown	47.27 (47.14)	3.17 (3.06)	7.35 (7.22)	8.41 (8.29)	16.79 (16.66)	-	7.70 (7.58)	9.30 (9.19)	195
[Co(BTa) ₂ Cl ₂]	Green	47.26 (47.13)	3.17 (3.04)	7.35 (7.21)	8.41 (8.30)	16.79 (16.65)	-	7.73 (7.61)	9.30 (9.17)	235
[Cu(BTb) ₂ Cl ₂]	Brown	41.68 (41.55)	2.50 (2.38)	3.47 (3.34)	7.95 (7.82)	7.93 (7.80)	19.81 (19.68)	7.88 (7.76)	8.79 (8.66)	200
[Ni(BTb) ₂ Cl ₂]	Dark orange	41.93 (41.82)	2.51 (2.40)	3.49 (3.35)	8.00 (7.87)	7.98 (7.84)	19.93 (19.81)	7.32 (7.19)	8.84 (8.70)	210
[Co(BTb) ₂ Cl ₂]	Dark pink	41.92 (41.80)	2.51 (2.38)	3.49 (3.36)	7.99 (7.87)	7.98 (7.85)	19.92 (19.79)	7.35 (7.21)	8.84 (8.71)	198

Gravimetric estimation of metal ions

Each complex was broken down in 60 % analar perchloric acid on heating till the clear solution was obtained. By using this solution, copper(II), nickel(II) and cobalt(II) ions were gravimetrically estimated as CuO^{10} , Ni(DMG)_2^{11} and $\text{Co(anthranilate)}^{12}$ respectively.

IR spectra of complexes

All newly synthesized ligands and their metal complexes were characterized by their IR bands in solid state with potassium bromide; the bands appearing at 3500 cm^{-1} reasonably assigned as ν OH stretching of the ligand (BTb). The characteristic stretching bands displays at 1260 cm^{-1} and 1040 cm^{-1} assigned as ν_{as} C-O-C and ν_{s} C-O-C respectively of methoxy group in both ligands. Aromatic ring ν C-H, ν C=N and ν C-S-C stretching were obtained at $3069\text{--}3086\text{ cm}^{-1}$, $1600\text{--}1670\text{ cm}^{-1}$ and $720\text{--}760\text{ cm}^{-1}$ respectively for both benzothiazole (BTa and BTb) ligands.

On complexation with metal ions, the characteristic changes occur in the vibrational spectra of the free ligands are mounted up below.

The stretching vibration of ligands ν C=N were shifted to the lower frequency region on complex formation which indicates the involvement of the nitrogen atom of the benzothiazole moiety during complexation. The far IR studies of representative complexes appear the bands in the range of $440\text{--}350\text{ cm}^{-1}$ and $290\text{--}250\text{ cm}^{-1}$ which have been attributed to ν M-N and ν M-Cl stretching respectively¹³.

ESI mass spectra of complexes

The ESI mass spectra of represented metal(II) complexes of 2-(substituted aryl)-1H-benzo[d]thiazole ligands shows molecular ion peaks with respect to their molecular weight (with +5 to +9 and -5 to -9 peak variations) corresponding with the 2:1 stoichiometry of ligands and metals respectively. All metal complexes display the fragmented molecular ion peak of their corresponding ligands and

complexed ions with metals as ML_2 and ML (Where, M = Cu(II), Ni(II) and Co(II); L = BTa and BTb).

Electronic spectra and magnetic susceptibility

The electronic spectra of ligands and their metal complexes were measured on Shimadzu UV mini-1240 spectrophotometer. During the electronic absorption measurement of benzothiazole ligands in DMF, exhibits two bands at 36363 cm^{-1} and 35587 cm^{-1} for (BTa) ligand and 32051 cm^{-1} and 31746 cm^{-1} for (BTb) ligand owing to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively.

The electronic spectra of the Cu(II) complexes displays the intense bands at 24096 cm^{-1} and 22371 cm^{-1} respectively because of ligand metal charge-transfer transitions. The Cu(II) complexes exhibits a bands at (13089 cm^{-1} , 13263 cm^{-1} and 14368 cm^{-1}) and (12987 cm^{-1} , 13349 cm^{-1} and 15021 cm^{-1}) due to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$, ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$ transitions suggesting the square planar formation of both complexes of ligand BTa and BTb respectively^{14,15}. The magnetic moment statistics of the copper(II) complexes at room temperature gives (1.77 BM for complex of BTa ligand and 2.07 BM for complex of BTb ligand) con signing to their geometry. The electronic spectra of nickel(II) complexes display ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$, ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2$ and ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transitions at 12987 cm^{-1} , 13369 cm^{-1} and 14085 cm^{-1} respectively of (BTa) and 13205 cm^{-1} , 14023 cm^{-1} and 16528 cm^{-1} of (BTb) proposing a tetrahedral geometry for both Ni(II) complexes; closely related to magnetic susceptibility measurement (3.92 BM for complex of BTa ligand and 3.48 BM for complex of BTb ligand) for both nickel(II) complexes signifying tetrahedral geometry. Cobalt(II) complexes of both benzothiazole ligands (BTa and BTb) have electronic spectral bands at (13055 cm^{-1} and 14286 cm^{-1}) and (13482 cm^{-1} and 15384 cm^{-1}) assignable to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ transitions suggesting a tetrahedral stereochemistry around cobalt ions¹⁶. The magnetic values of both cobalt complexes (4.48 BM for complex of BTa ligand and 5.13 BM for complex of BTb ligand) shows good agreement with reported values for the tetrahedral environment around Co(II) ions. (Table 2).

Table 2: Electronic spectral and magnetic moment values of the complexes

Complex	Electronic spectral bands (cm^{-1})		Assignment	μ_{eff} BM	Geometry	Molar conductance $\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$
	LMCT	d-d bands				
[Cu(BTa) ₂ Cl ₂]	24096	13089	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$,	1.77	Square planar	15.89
		13263	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$,			
		14368	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$			
[Ni(BTa) ₂ Cl ₂]	25126	12987	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$,	3.92	Tetrahedral	18.00
		13369	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2$,			
		14085	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$			
[Co(BTa) ₂ Cl ₂]	25000	13055	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$,	4.48	Tetrahedral	15.58
		14286	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$			
[Cu(BTb) ₂ Cl ₂]	22371	12987	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$,	2.07	Square planar	14.23
		13349	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$,			
		15021	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$			
[Ni(BTb) ₂ Cl ₂]	24271	13205	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$,	3.48	Tetrahedral	12.85
		14023	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{A}_2$,			
		16528	${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$			
[Co(BTb) ₂ Cl ₂]	22471	13482	${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$,	5.13	Tetrahedral	12.01
		15384	${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$			

Thermal analysis

TGA of [M(BTa)₂Cl₂] (M = Cu(II), Ni(II) and Co(II))

All complexes show isothermic degradation with two or more steps of decomposition. The copper(II) complex have 27% weight degradation at $130\text{--}320\text{ }^\circ\text{C}$ may be due to loss of chloride ions and methoxy groups, second decomposition start at $320\text{ }^\circ\text{C}$ and finished at $920\text{ }^\circ\text{C}$ showing 89% weight loss may be according to loss of both coordinated ligands. The nickel(II) complex decomposed into two stages, the first decomposition start from $90\text{ }^\circ\text{C}$ and end at $180\text{ }^\circ\text{C}$ displays 9 % weight loss due to removal of chloride ions, the second stage of decomposition shows continual 70% weight loss between $180\text{--}1000\text{ }^\circ\text{C}$ which may be due to removal of all organic parts from the compound. The 70% weight at $50\text{--}1000\text{ }^\circ\text{C}$ of the cobalt(II) complex was remove in the first step of decomposition may be loss of both coordinated ligands. Ni(II) and Co(II)

complexes are not stable upto $1000\text{ }^\circ\text{C}$ they need more thermal energy to convert themselves into metal oxide.

TGA of [M(BTb)₂Cl₂] (M = Cu(II), Ni(II) and Co(II))

All metal complexes of (BTb) ligand displays little bit non isothermic degradation behavior in compare to the metal complexes of (BTa) ligand. It has been clearly seen that the (BTb) metal complexes are more stable than (BTa) complexes. The same pattern of decomposition in two steps observed in the TGA graph of all three complexes, first stage of decomposition between $120\text{--}400\text{ }^\circ\text{C}$ showing 49-52% weight loss according to removal of one molecule of ligand, second step of decomposition start within $400\text{--}900\text{ }^\circ\text{C}$ with respect to 39-41% weight loss. At the end of undergo total decomposition compounds convert in to their corresponding metal oxide¹⁷.

Antimicrobial screening

All the synthesized organic and coordination compounds were screened for antimicrobial activity against two Gram (+) and two Gram (-) bacterial strains and three fungal strains (Table 3). It can be seen that the new benzothiazole metal complexes exhibit better

inhibition activity for antibacterial and antifungal strains than benzothiazole ligands (BTa and BTb). Most of compounds show more active against Gram (+) bacteria *S.Aureus* and *S.Pyogenus*. Only three complexes, nickel(II) and copper(II) complexes of ligand (BTa) and copper(II) complex of ligand (BTb) are active against fungicidal *C.Albicans*.

Table 3: Antibacterial and antifungal screening data of 2-(substituted aryl)-1H-benzo[d]thiazole ligands and their metal complexes ($\mu\text{g mL}^{-1}$).

Compound	Antibacterial activity (MIC value) (concentration in $\mu\text{g mL}^{-1}$)				Antifungal activity (mycelia growth inhibition) (concentration in $\mu\text{g mL}^{-1}$)		
	<i>E.C.</i> MTCC 442	<i>P.A.</i> MTCC 441	<i>S.A.</i> MTCC 96	<i>S.P.</i> MTCC 443	<i>C.A.</i> MTCC 227	<i>A.N.</i> MTCC 282	<i>A.C.</i> MTCC 1323
BTa	125	200	500	500	1000	500	500
[Cu(BTa) ₂ Cl ₂]	200	100	200	62.5	500	1000	1000
[Ni(BTa) ₂ Cl ₂]	200	250	100	100	500	>1000	>1000
[Co(BTa) ₂ Cl ₂]	100	125	100	250	>1000	>1000	>1000
BTb	200	200	200	200	>1000	500	500
[Cu(BTb) ₂ Cl ₂]	250	250	100	200	250	1000	1000
[Ni(BTb) ₂ Cl ₂]	100	125	100	200	1000	>1000	>1000
[Co(BTb) ₂ Cl ₂]	200	62.5	100	100	1000	>1000	>1000
Standard bactericide							
Ampicillin	100	100	250	100	-	-	-
Ciprofloxacin	25	25	50	50	-	-	-
Norfloxacin	10	10	10	10	-	-	-
Standard fungicide							
Nystatin	-	-	-	-	100	100	100
Griseofulvin	-	-	-	-	500	100	100

CONCLUSIONS

Spectroscopic data and elemental analyses (Table 1) of the metal complexes designate that the nitrogen atom of benzothiazole ligands are monodentately coordinated to the metal ions and all complexes have 1:2 metal-ligand ratio represented in following figure 1. A square planar geometry observed for both copper(II) complexes, whereas, tetrahedral geometry observed for all nickel(II) and cobalt(II) complexes. Thermogravimetric analysis of all metal complexes gives agreement about the absence of water molecules in the coordination sphere. The antimicrobial activity of all compounds shows that benzimidazole metal complexes are more active than those of ligands.

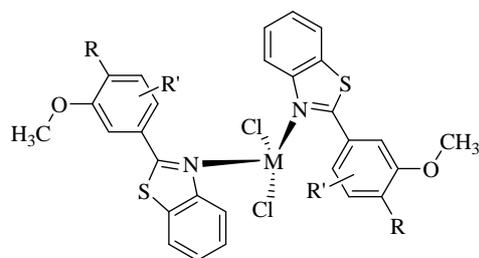


Fig. 1: Proposed structure of bis[2-(substituted aryl)-1H-benzo[d]thiazole]metal(II)chloride complexes

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REFERENCES

- Messina F, Botta M, Corelli F, Paladino A. Tetrahedron: Asymmetry. 2000; 11: 4895.
- Abdel-Wahab BF, Abdel-Aziz HA, Ahmed EM. European Journal of Medicinal Chemistry. 2009; 44: 2632.

- Kaniwa K, Ohtsuki T, Yamamoto Y, Ishibashi M. Tetrahedron Letters. 2006; 47: 1505.
- Di Nunno L, Franchini C, Scilimati A, Sinicropi MS, Tortorella P. Tetrahedron: Asymmetry. 2000; 11: 1571.
- Moreno-Díaz H, Villalobos-Molina R, Ortiz-Andrade R, Díaz-Coutiño D, Medina-Franco JL, Webster SP, Binnie M, Estrada-Soto S, Ibarra-Barajas M, León-Rivera I, Navarrete-Vázquez G. Bioorganic & Medicinal Chemistry Letters. 2008; 18: 2871.
- Lindoy LF, Livingstone SE. Coord Chem Rev. 1967; 2: 173.
- Cesar Lozano M, Osvaldo Cox, Mariel Muir M, Johara Morales D, Jorge Rodriguez-Caban L, Pablo Vivas-Mejia E, Fernando Gonzalez A. Inorganica Chimica Acta. 1998; 27: 137-144.
- Gordana Pavlovic, Zeljka Soldin, Zora Popovic, Vesna Tralic-Kulenovic. Polyhedron. 2007; 26: 5162-5170.
- Geary WJ. Coord Chem Rev. 1971; 7(1): 81-122.
- Cumming and Kay. Quantitative Chemical Analysis, (Oliver and Lyod, London), 1956; 257.
- Vogel AI. A Text Book of Quantitative Inorganic analysis, London, 1968; 527.
- Vogel AI. Ibid. 1968; 527.
- Mani G, Scapacci G. Inorg Chimica Acta. 1976; 16: 163 (b) Vos JG, Groeneveld W. Inorg Chimica Acta. 1977; 24: 123.
- Gao EQ, Bu WM, Yang GM, Liao DZ, Jiang ZH, Yan SP, Wang GL. J Chem Soc Dalton. 2000; 1431-1436.
- Hathaway BJ In: Wilkinson G, Gillard RD, McCleverty JA (Eds.). Comprehensive Coordination Chemistry, Pergamon, Oxford, 1987; 5: 533-594.
- Goodgame M, Cotton FA. J Am Chem Soc. 1962; 84: 1543.
- Yasodhai S, Sivakumar T, Govindarajan S. Thermochim Acta. 1999; 338: 57.
- Afanaseva VL, Lyubeshkin AV, Kovaleva SS, Bagreeva MR, Anisimova OS, Glushkov RG. Khimiko-Farmatsevticheskii Zhurnal. 1987; 21(11): 1367-71.
- Fletscher, Charles A. Organic Syntheses. 1953; 33: 65-7.
- Barry AL, Thornsberry C. In: Lennette EH, Balows A, Hausler WJ, Shadomy HJ (Eds.). Manual and Clinical Microbiology, ASM, Washington DC, 1985; 978.
- Jones RN, Barry AL, Govan TT, Washington JA. In: Lennette EH, Balows A, Hausler WJ, Shadomy HJ (Eds.). Manual and Clinical Microbiology, ASM, Washington DC, 1985; 972.