

Syntheses and spectral characterization of some novel 1*H*-benzothiazole derivatives and their Cu(II) complexes

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ABSTRACT

Four novel Cu(II) complexes of the 2-(substituted 1*H*-pyrazole-4-yl)-1*H*-benzothiazole ligands (3*a-d*) have been prepared and characterized by various physico-chemical studies. The molar conductance measurements suggest that all complexes are non-electrolytes. Electronic spectral and magnetic susceptibility study indicates the distorted square planar or octahedral geometry for Cu(II) complexes. Infrared spectral study discloses the monodentate behavior of new benzothiazole ligands (3*a-d*) coordinated through tertiary nitrogen. The condensation of 2-aminothiophenol with substituted 1*H*-pyrazole-4-carbaldehydes (2*a-d*) shape ups the 2-(substituted 1*H*-pyrazole-4-yl)-1*H*-benzothiazole (3*a-d*) ligands. The formation of (3*a-d*) derivatives is explained by ¹H NMR, FT-IR and Mass spectral studies.

Keywords: Cu(II) complexes, 1*H*-benzothiazoles, Pyrazole aldehydes, Cyclocondensation, Ceric ammonium nitrate.

INTRODUCTION

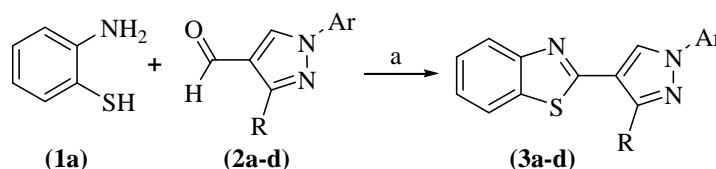
Because of the potential ability as magnetic materials and due to the various biological and physico-chemical properties, Cu(II) complexes have been widely investigated in near past [1-4]. Recently many copper complexes have been synthesized and verified to be much important in stereochemistry for the preparation of supramolecular architectures as well as various types of molecular polygons and helix or zigzag chain polymers [5]. Many antibacterial and anticancer drugs are behaved as versatile ligands [6]. Benzothiazole is *N*-heterocyclic nucleus possesses a nitrogen binding site to coordinate with metal ions. The syntheses of substituted benzothiazole derivatives have a considerable interest in organic chemistry over a long period of time because of their wide range of biological and pharmacological properties [7-10]. It has been reported that the biological properties of the ligands are enlarged after complexation with metal ions [11]. The pyrazole derivatives also has some significant biological importance and various applications in the pharmaceutical industries [12,13]. All these points about benzothiazoles, pyrazoles and copper complexes give us a reason for the synthesis of 1*H*-benzothiazole compounds and their Cu(II) complexes. Ceric ammonium nitrate is used as a catalyst for the syntheses of 1*H*-benzothiazoles because it is a versatile oxidizing reagent extensively used in organic syntheses [14]. On the basis of the use of ceric ammonium nitrate for the synthesis of azoles, it was considered as a precursor of choice in present work as its advantage to increase the rate of reaction and good yield formation. In this paper, we have reported here four novel Cu(II) complexes of benzothiazole ligands as the copper is one of the most biologically essential elements in nature [15].

MATERIALS AND METHODS

Melting points of 2-substituted-1*H*-benzothiazoles (3a-d) were determined in open glass capillaries in a paraffin bath and are uncorrected. All procedures were carried out by using standard solvents and chemicals without further purification which were commercially available and used as purchased. The IR spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer using KBR discs. The ¹H NMR spectra were measured in CDCl₃ solutions on the Bruker Av spectrophotometer (400 MHz) using TMS as an internal reference. The mass spectra were recorded on the Shimadzu GC-MS QP2010 Gas Chromatograph. The TG analysis curves were obtained on the Perkin Elmer the Diamond Thermogravimetric/Differential Thermal Analyzer (TG/DTA) model at a heating rate of 20 °C per minute. The Electronic spectra were recorded in DFM solution on a Shimadzu UV mini-1240 spectrophotometer. Molar conductance of all the complexes was performed on an Elico conductivity bridge (type CM82T). The magnetic moment of all the complexes were measured by Guoy balance at room temperature using CuSO₄·5H₂O as callibrant. All the synthesized compounds were micro analyzed satisfactorily for C, H and N on Euro EA Elemental Analyzer, EA-3000, RS-232.

Synthesis of 2-(substituted 1*H*-pyrazole-4-yl)-1*H*-benzothiazoles (3a-d)

A mixture of 2-aminothiophenol (0.01 mole), substituted 1*H*-pyrazole-4-carbaldehydes (0.01 mole), H₂O₂ (30 %, 0.04 mole) and ceric ammonium nitrate (0.001 mole) in 30 mL alcohol was heated at 50 °C with stirring. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was dissolved in sufficient quantity of Et-OH and then poured into the ice-water, and subsequently dried.



^aReagents and conditions: Ceric ammonium nitrate, Hydrogen peroxide, Methanol
R = C₆H₅, 4-OMe-C₆H₄, 4-OH-C₆H₄, 4-NO₂-C₆H₄,

Scheme I: Reaction scheme of 1*H*-benzothiazoles

2-(1',3'-Diphenyl-1*H*-pyrazol-4-yl)-1*H*-benzothiazole (3a)

Yield: 81 %, m.p. 180 °C, IR (ν_{cm}⁻¹, KBr): 3147, 3057, 2997, 1629, 1593, 1554, 1496, 1354, 1311 and 702. ¹H NMR (400 MHz, CDCl₃) δ in ppm: 7.34-7.37 (dd, 2H, Ar-H of benzothiazole), 7.45-7.77 (dd, 10H, Ar-H of pyrazole moiety), 7.83-7.85 (d, 1H, Ar-H of benzothiazole), 7.03-7.05 (d, 1H, Ar-H of benzothiazole), 8.78 (s, 1H, pyrazole H). Mass *m/z*: 352. Anal. Calcd. for C₂₂H₁₅N₃S; Calcd.: C, 74.76; H, 4.28; N, 11.89; S, 9.07; Found: C, 74.60; H, 4.06; N, 11.74; S, 8.91 %.

2-(3'-(4"-Methoxyphenyl)-1'-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzothiazole (3b)

Yield: 78%, m.p. 155 °C, IR (ν_{cm}⁻¹, KBr): 3093, 3058, 2942, 2847, 1653, 1614, 1550, 1369, 1312, 1260, 1233, 1052 and 713. ¹H NMR (400 MHz, CDCl₃) δ in ppm: 3.89 (s, 3H, -OCH₃), 7.01-7.67 (dd, 9H, Ar-H of pyrazole moiety), 7.76-7.78 (d, 1H, Ar-H of benzothiazole), 7.84-7.86 (dd, 2H, Ar-H of benzothiazole), 8.07-8.09 (d, 1H, Ar-H of benzothiazole), 8.95 (s, 1H, pyrazole H). Mass *m/z*: 383. Anal. Calcd. for C₂₃H₁₇N₃OS; Calcd.: C, 72.04; H, 4.47; N, 10.96; O, 4.17; S, 8.36; Found: C, 71.88; H, 4.29; N, 10.83; O, 4.03; S, 8.22 %.

2-(3'-(4"-Hydroxyphenyl)-1'-phenyl-1*H*-pyrazol-4-yl)-1*H*-benzothiazole (3c)

Yield: 69 %, m.p.: 130 °C, IR (ν_{cm}⁻¹, KBr): 3456, 3375, 3078, 3057, 1680, 1620, 1587, 1518, 1350, 1298 and 692. ¹H NMR (400 MHz, CDCl₃) δ in ppm: 4.32 (s, 1H, -OH), 7.42-7.89 (dd, 9H, Ar-H of pyrazole moiety), 8.04-8.08 (dd, 2H, Ar-H of benzothiazole), 8.15-8.18 (d, 1H, Ar-H of benzothiazole), 8.29-8.35 (t, 1H, Ar-H of benzothiazole), 8.56 (s, 1H, pyrazole H). Mass *m/z*: 369. Anal. Calcd. for C₂₂H₁₅N₃OS; Calcd.: C, 71.52; H, 4.09; N, 11.37; O, 4.33; S, 8.68; Found: C, 71.39; H, 3.88; N, 11.22; O, 4.19; S, 8.50 %.

2-(3'-(4''-Nitrophenyl)-1'-phenyl-1H-pyrazol-4-yl)-1H-benzothiazole (3d)

Yield: 73 %, m.p.: 170 °C, IR ($\nu_{\text{cm}^{-1}}$, KBr): 3124, 3090, 3063, 1683, 1597, 1531, 1348, 1313 and 684. ^1H NMR (400 MHz, CDCl_3) δ in ppm: 6.70-7.72 (d, 1H, Ar-H of benzothiazole), 6.80-6.98 (t, 4H, Ar-H of pyrazole moiety), 7.09-7.11 (d, 1H, Ar-H of benzothiazole), 7.43-7.47 (dd, 2H, Ar-H of benzothiazole), 7.57-7.74 (dd, 5H, Ar-H of pyrazole moiety), 8.31 (s, 1H, pyrazole H). Mass m/z : 398. Anal. Calcd. for $\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_2\text{S}$; Calcd.: C, 66.32; H, 3.54; N, 14.06; O, 8.03; S, 8.05; Found: C, 66.16; H, 3.39; N, 13.89; O, 7.94; S, 7.90 %.

Synthesis of dichloro-bis[2-(substituted 1H-pyrazole-4-yl)-1H-benzothiazole]Cu(II) complexes ($\text{Cu}(\mathbf{3a-d})_2\text{Cl}_2$)

The 2-(substituted 1H-pyrazole-4-yl)-1H-benzothiazoles (**3a-d**) (1.0 mM) were dissolved in hot Et-OH (20 ml) and the resulting solution was treated with hydrated copper salt (0.5 mM) dissolved in Et-OH (10 ml) with continuous stirring at 90 °C to separate the products ($\text{Cu}(\mathbf{3a-d})_2\text{Cl}_2$) from the reaction mixtures after several days in the specific way depending on the complex.

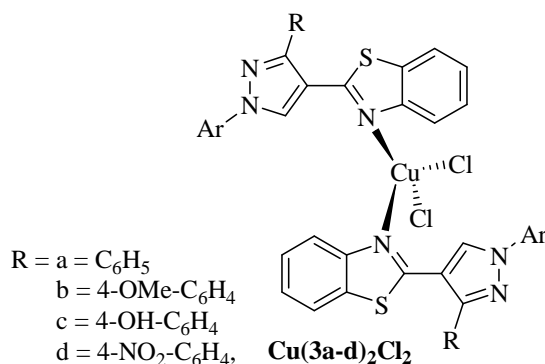


Figure I: Proposed structure for dichloro-bis(3a-d**)Cu(II) complexes**

RESULTS AND DISCUSSION

Four novel 2-(substituted 1H-pyrazole-4-yl)-1H-benzothiazole ligands (**3a-d**) were synthesized by the cyclocondensation of 2-aminothiophenol with substituted 1H-pyrazole-4-carbaldehydes, using ceric ammonium nitrate as a catalyst in presence of hydrogen peroxide. 1H-pyrazole-4-carbaldehydes were prepared according to previously published method [16]. The use of ceric ammonium nitrate is to accelerate the rate of reaction and formation of yields of benzothiazole compounds in the good approach. The Cu(II) complexes were synthesized in hot ethanolic solutions of ligands and metal salt with continuous stirring and heating until the product separate out from the reaction mass. Complexes were characterized by elemental analyses, magnetic susceptibility measurements, thermogravimetric analyses, FT-IR spectra and Electronic spectra.

 ^1H NMR spectra

Only benzothiazole ligands were characterized by ^1H NMR spectroscopy and the data obtained in agreement with their chemical structures. The ^1H NMR spectral data of ligands show the characteristic singlet of pyrazole ring proton at 8.31-8.95 δ ppm and the aromatic ring protons at 6.70-8.35 δ ppm. The sharp singlet for the $-\text{OCH}_3$ group and $-\text{OH}$ group of compounds (**3b**) and (**3c**) were observed at 3.89 δ ppm and 4.32 δ ppm respectively.

Table I: Analytical, magnetic moment and conductivity data of the Cu(II) complexes

Comp ^d	Elemental data Found (Calc.)				Λ	μ_{eff} BM
	Cu	C	H	N		
$\text{Cu}(\mathbf{3a})_2\text{Cl}_2$	7.55(7.41)	62.81(62.67)	3.59(3.46)	9.99(9.86)	9.13	1.70
$\text{Cu}(\mathbf{3b})_2\text{Cl}_2$	7.05(6.91)	61.29(61.16)	3.80(3.67)	9.32(9.19)	20.00	1.69
$\text{Cu}(\mathbf{3c})_2\text{Cl}_2$	7.28(7.16)	60.51(60.38)	3.46(3.34)	9.62(9.49)	9.22	1.71
$\text{Cu}(\mathbf{3d})_2\text{Cl}_2$	6.82(6.70)	56.74(56.61)	3.03(2.96)	12.03(11.92)	15.11	1.69

Λ = Molar conductance ($\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$) in 10^{-3} M solution of DMF

Elemental analyses and molar conductivity

The presence of chloride atoms in the complexes were determined by peroxide fusion of the sample, followed by volumetric estimation using Volhard's method [17]. The analytical results indicate 1:2 (M:L) stoichiometry for all complexes, the complexes are soluble in DMF, DMSO and 1,4-dioxane. The molar conductance values for 1×10^{-3} M solution of the complexes in DMF show them to be non-electrolytes ($2\text{--}20 \Omega \text{ cm}^2 \text{ mol}^{-1}$) (Table I).

FT-IR spectra

Selective FT-infrared and electronic spectral bands of the Cu(II) complexes are given in table II. The infrared spectrum of ligands shows a characteristic peaks around $3147\text{--}2997 \text{ cm}^{-1}$, which has been attributed to a $\nu\text{C-H}$ of aromatic ring stretching modes. In the IR spectrum of ligands two sharp bands in the range of $1683\text{--}1629 \text{ cm}^{-1}$ and $713\text{--}684 \text{ cm}^{-1}$ are assigned to $\nu\text{C=N}$ and $\nu\text{C-S-C}$ stretching of thiazole ring respectively. The intensities of the thiazole $\nu\text{C=N}$ bands has been decreased at about $5\text{--}20 \text{ cm}^{-1}$ in down field after complexation of tertiary nitrogen of benzothiazole ring with Cu(II) ion, which are observed in the range of $1666\text{--}1617 \text{ cm}^{-1}$ [18].

Table II: FT-IR and electronic spectral data

Comp ^d	IR frequencies (cm^{-1})			Electronic bands (nm)		
	C=N	C-S-C	N-Cu	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	d \rightarrow d
3a	1629	702	-	251	259	-
3b	1653	713	-	250	276	-
3c	1680	692	-	239	262	-
3d	1683	684	-	245	261	-
Cu(3a) ₂ Cl ₂	1617	683	475	253	278	710, 790
Cu(3b) ₂ Cl ₂	1651	690	468	255	320	620, 760, 780
Cu(3c) ₂ Cl ₂	1662	681	501	255	293	680, 775
Cu(3d) ₂ Cl ₂	1666	668	464	259	300	730, 772

Magnetic susceptibility and electronic spectra

All Cu(II) complexes are found to be paramagnetic. The μ_{eff} values of all Cu(II) complexes fall in the range of 1.69–1.71 BM, which are very less in compare to reported values for Cu(II) ions, this low spin values of Cu(II) complexes recommend the square planar configuration around metal center [19].

The electronic spectral data of the complexes are given in Table II. The band at 620 nm and 680 nm in Cu(3b)₂Cl₂ and Cu(3c)₂Cl₂ complexes assigned to $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transitions respectively with two weak bands in the range of 730–780 nm proposed the octahedral or distorted square planar geometry for both Cu(II) complexes [19]. Rest of two Cu(II) complexes of (3a) and (3d) benzothiazole ligands displays bands in the range of 710–790 nm according to $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$ and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$ transitions reveals a distorted square planar structure for Cu(II) complexes [20]. The observed geometry for all complexes is in good agreement with the measured magnetic susceptibility values of the complexes.

Thermo gravimetric analyses

The thermo gravimetric analyses of the Cu(II) complexes shows that complexes doesn't contain coordinated or lattice water molecules. TGA graphs show three step decomposition for all complexes; the weight loss of complexes at $250\text{--}445^\circ\text{C}$ are in good agreement of one molecule of ligand. Second molecule of ligand gets decomposed in the range of $450\text{--}650^\circ\text{C}$. Finally all complexes convert in to the metal oxide (CuO) as a product from which the metal content was calculated. The TG analyses values of elimination of molecules are neared to their calculated values.

CONCLUSION

Newly synthesized Cu(II) complexes are non-electrolyte and have empirical formula Cu(3a-d)₂Cl₂, confirmed from the elemental analyses. The spectral study provides that the benzothiazole ligands were coordinated with Cu(II) ion through nitrogen atom and behave as monodentate ligands. The distorted octahedral of square planar geometry is confirms for all Cu(II) complexes by electronic spectral data and magnetic susceptibility values.

Acknowledgements

The authors are thankful to Department of Chemistry, Saurashtra University, Rajkot for necessary support for this work. Minaxi Maru is grateful to the RGNFS, UGC, New Delhi, INDIA for the financial support as Junior Research Fellow.

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