



Synthesis and Structural Investigation of Some Transition Metals Complexes of Benzimidazolium Bromide

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The present work involves the synthesis of novel imidazolium salts of bromide in step-wise reactions which are started from preparation of 2,4-dimorpholine-6-(1*H*-benzimidazole-1-yl)-1,3,5-triazine (**1**) in potassium hydroxide and DMF solvent followed by substitution reactions with *n*-butyl bromide and *n*-octyl bromide to afford the new ligands names **L**₁ = 1-(2,4-dimorpholino-1,3,5-triazine-2-yl)-3-butyl-1*H*-benzimidazol-3-ium bromide and **L**₂ = 1-(2,4-dimorpholino-1,3,5-triazine-2-yl)-3-octyl-1*H*-benimidazol-3-ium bromide. The new ligands were recrystallized from hot chloroform and the following of reactions completion were carried out by thin layer chromatography (TLC). The formula and structures of the two salts of benzimidazolium bromide were confirmed on the basis of measurements of (CHN) elemental analyses, FT-IR, NMR and EIMS spectroscopy. Furthermore the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes were synthesized from the direct reactions of their hydrated metal salts in methanol with the solutions of the ligands in chloroform in 1:1 mole ratio and the analytical data of atomic absorption spectroscopy and elemental analyses revealed the proposed formula of the solid metal complexes. The data obtained from FT-IR, UV-Visible spectra, molar conductivity and magnetic susceptibility measurements confirmed the octahedral environment around cobalt(II) ion in [CoL(H₂O)₂Cl₂] and the tetrahedral geometry was adopted for manganese(II) and zinc(II) ions. However the square-planer structure was expected for the copper(II) and nickel(II) complexes in [MLCl₂], M = Ni(II) and Cu(II) ions and L = L₁ and L₂ ligands. As well as the suitable and favourable active sites in the two ligands L₁ and L₂ were the two nitrogen atoms of morpholine rings which has been observed from FT-IR spectra and the kinetic stability of five-member ring up on chelation with the metal ions supported the conclusion of the symmetry.

Keywords: Transition metal complexes, Benzimidazole, Triazine-imidazole.

INTRODUCTION

1,3,5-Triazine molecule is called melamine is applied as a part of the assembling of gums [1]. The derivatives of 1,2,3-triazine have widely interested many researchers due to their spectrum applications in the fields of herbicides [2], drugs and catalysis in polymers [3-5]. The chelating triazine Lewis-bases represent an important class of complex-compound due to their potential to be biologically active and mainly have been known to be antiprotozoals [6-8]. Hoog and co-workers [9] have investigated an-efficient synthesis of a novel class of multidentate polynucleating ligands through the substitution reaction of 2,4,6-trichloro-1,3,5-triazine. As well as the selective amination of cyanuric chloride in presence of 18-crown-6 has been prepared with respect of specific reactions that effected

by the type of substituent on triazine ring [10]. The neutral binuclear silver(I) complexes with symmetric triazine ligand involving imidazole moiety have reported by Poethig and Strassner [11] and the dimeric structure of Ag(I) complexes has revealed through the X-ray crystallography. The biological study of triazine derivatives have recently studied *via* effect on neuronal nicotinic receptors [12] and the results obtained that these derivatives possessed certain kinetic in transport the nicotinic receptors in living cells [13]. However the chelating *bis*-carbene rhodium(III) complexes have prepared [14] and it's role in the catalysis of imines synthesis has investigated [14]. The medicinal biochemistry of cobalt(II), nickel(II), copper(II) and zinc(II) complexes derived from Schiff base of 1,2,4-triazine derivative have reported by Sing *et al.* [15] and the identified metal complexes by NMR, FT-IR and UV-visible

spectra besides the elemental analyses have exhibited remarkable effects inhibition zones in the antimicrobial studies.

EXPERIMENTAL

All the reagents and solvents were used as received. NMR spectra were obtained using Bruker Avance AMX 250, 400 spectrometer, mass spectra were obtained in electrospray (ES) mode. The analysis is performed in the laboratories of School of Chemistry of Cardiff University, United Kingdom. Melting points were measured with a Stuart Scientific melting point SMP1 apparatus, magnetic susceptibility measurements were carried out using the Faraday method with (balance magnetic susceptibility model MSB-MKI), molar conductivity ($S\text{ cm}^2\text{ mol}^{-1}$) of the complexes were recorded at 25 °C for (1×10^{-3} M) solution of the samples in a proper solvent (DMF) using a (WTW F561) Weilheim digital supercon, UV-visible spectra of the prepared ligands and complexes were measured in the region (200–800 nm) at 298 K on (Varain Cary 100 Conc. UV-visible Spectrometer, at the Department of Chemistry, College of Science, university of Mustansiriyah. The vibration spectra were recorded using the (FTIR-600) spectrophotometer in the range ($4000\text{--}400$) cm^{-1} with their cesium iodide and potassium bromide discs. As well as the structure of the prepared compounds were revealed by elemental analyses (C.H.N.S) on EuroEA-Element Analyzer 3000 at College of Education of Pure Science Ibn-Alhaithum, University of Baghdad. The percent of metals in their solid complexes were measured by flame atomic absorption by using Shimadzu Corporation Model 6809 at Ibn-Sina Center for analytical analysis and quality control.

Synthesis of 2,4-dimorpholine-6-(1H-benzimidazole-1-yl)-1,3,5-triazine (1): In a round bottom flask (100 mL) with condenser (0.588 g, 0.0105 mmol) of KOH was dissolved by (20 mL) DMF, (0.82 g, 7 mmol) of benzimidazole was added to the solution. The mixture was stirred at ambient temperature for 0.5 h (2 g, 7 mmol) of 2,4-dimorpholine-6-chloro-1,3,5-triazine was added to the reaction after dissolved with DMF. The reaction was refluxed at 120 °C for 48 h. After the reaction cooled to room temperature. 100 mL of water was added, immediately a white precipitate formed. The crude product was filtered then purified by column chromatography (silica, DCM/Et₂O 8:2) affording a white solid in yield (80 %).

Synthesis of 1-(2,4-dimorpholino-1,3,5-triazine-2-yl)-3-butyl-1H-benzimidazol-3-ium bromide (L₁): In around bottom flask provided with condenser (1.5 g, 4.1 mmol) of 2,4-dimorpholine-6-(1H-benzimidazole-1-yl)-1,3,5-triazine (1) was dissolved in (15 mL). (4.9 g, 40.1 mmol) of 1-bromo butane was added. The mixture was refluxed at 100 °C for 48 h. After cooling the volume of solution was reduced. Diethyl ether (30 mL) was added to the residue to produce the crude product as a white solid. The product was recrystallized from (CHCl₃/Et₂O) to produce a white solid in yield (85 %).

Synthesis of 1-(2,4-dimorpholino-1,3,5-triazine-2-yl)-3-octyl-1H-benzimidazol-3-ium bromide (L₂): In around bottom flask provided with condenser (1.5 g, 4.1 mmol) of 2,4-dimorpholine-6-(1H-benzimidazole-1-yl)-1,3,5-triazine (1) was dissolved in (15 mL). (7.8 g, 40.1 mmol) of 1-bromo octane was added. The mixture was refluxed at 100 °C for 48 h. After cooling the volume of solution was reduced. Diethyl

ether (30 mL) was added to produce the crude product as a white solid. The product was recrystallized by (CHCl₃/Et₂O) to produce a white solid (yield 88 %).

Synthesis of metal complexes: A solution CuCl₂·2H₂O (0.170 g, 1 mmol) in 5mL of methanol was added to the (0.480 g, 0.424 g, 1 mmol) of [L₁ or L₂] dissolved in 5 mL of hot ethanol. The resulted mixture was stirred at (room temperature) till turned the colour of solution into purple then extract with 10 mol of diethyl ether to afford pale red precipitate of CuL₁ complex. The complex was dried in air and recrystallized from hot ethanol. The metal complexes of cobalt(II), nickel(II) and zinc(II) were prepared and isolated in the solid state in the same procedure as adopted in copper(II) complexes except that the time of reactions have longed about 1-2 h.

RESULTS AND DISCUSSION

Analyses and physical measurements: All the complexes are sparingly soluble in common organic solvents but highly soluble in DMF and DMSO. The analytical data (Table-1) indicate that the complexes are mononuclear with 1:1 molar ratio of the benzimidazole ligand to metal ion. The molar conductance in DMSO is in the expected range for their neutral behaviour, indicating that no counter ions are present in the structure of all complexes and supports the formula [MLCl₂] where M = Ni, Cu and Zn(II) ions whereas the general formula for cobalt(II) and manganese(II) are [ML(H₂O)Cl₂]. The results obtained from elemental analyses (CHN) and flame atomic absorption spectroscopy were in agreement with the expected data for the structures of free ligands and their metal complexes.

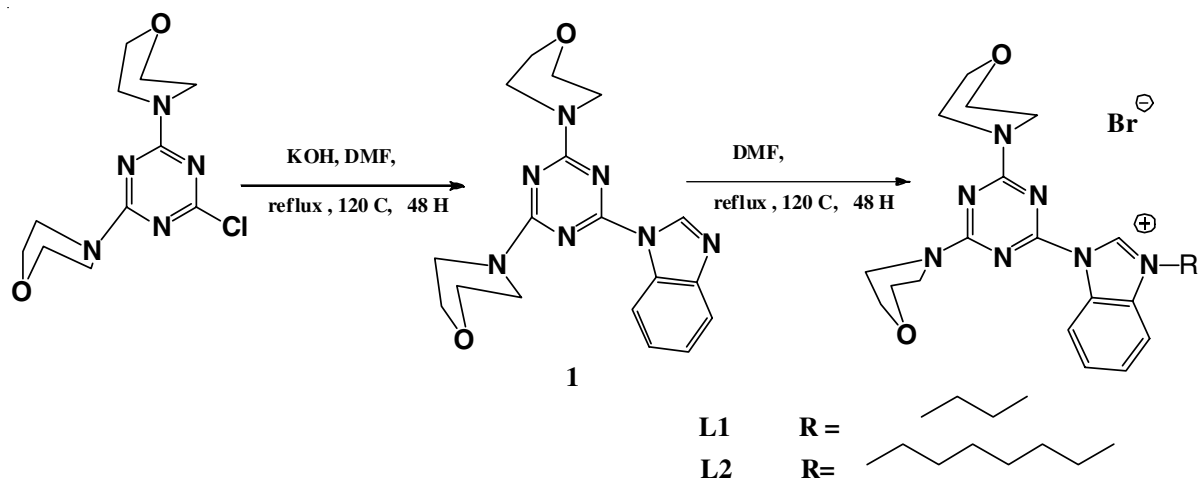
Both of benzimidazolium salts (L₁, L₂) derived from the triazine have been prepared by two steps. The first step was conducted by the reaction of 2,4-dimorpholine-6-chloro triazine which prepared according of previous literatures [16-18] and the benzimidazole in presence of DMF as a solvent at 120 °C for 48 h. KOH was used for deprotonation of the benzimidazole before substitution of third chloro atom on triazine [19]. The second step for synthesis the imidazolium salts is the reaction the previous compound with alkyl halides: 1-bromo-butan, 1-bromo octane at 120 °C for 48 h. white precipitates were obtained after purified by diffusion method (CHCl₃/Et₂O) (Scheme-I).

NMR spectra: The formation of compound 1 was confirmed by ¹H NMR and ¹³C NMR (Table-2). The proton NMR spectrum emerged multiplet peaks in ranges 3.5-3.9 ppm with integration of 16 protons of dimorpholine, which consist with previous literatures [20], in addition singlet peak at 8.9 ppm can be assigned to (NCHN), as well as doublet peaks at 8.3, 7.7 ppm can be attributed to benzimidazole protons (2H), also multiplet peak was observed at 7.3 ppm with integration 2H for benzimidazole protons. ¹³C NMR spectra showed two peaks at 165.11, 1.63.55 ppm corresponding to triazine carbon atoms. As well as two peaks for morpholine carbon atoms were observed at 66.72, 43.42 ppm. Five peaks in ranges 142.08-115.534 ppm emerged can be assigned to benzimidazole carbon atoms (Table-2). The integrals and chemical shift are consistent with attachment of the benzimidazole group at nitrogen atom.

While ¹H NMR spectra for both of imidazolium salts (L₁, L₂) showed a new peaks at 0.95, 1.45, 1.97, 4.65 ppm with

TABLE-1
 ANALYTICAL DATA OF LIGANDS (L_1 , L_2) AND THEIR COMPLEXES

Compound	m.f. (m.w., g mol ⁻¹)	Colour	Yield (%)	Elemental analysis (%): Found (calcd.)				Molar conductance (S cm ² mol ⁻¹)
				C	H	N	M	
L_1	C ₂₂ H ₃₀ N ₇ O ₂ Br (504.43)	White	80	52.45 (52.38)	6.11 (5.99)	19.55 (19.44)	–	40.5
L_2	C ₂₆ H ₃₈ N ₇ O ₂ Br (560.54)	White	85	65.25 (64.97)	9.36 (8.97)	20.65 (20.40)	–	35.9
[Cu(L_1)Cl ₂]	C ₂₂ H ₃₀ N ₇ O ₂ BrCl ₂ Cu (638.87)	Red	58	41.44 (41.36)	4.97 (4.73)	15.58 (15.35)	10.35 (9.95)	15.4
[Cu(L_2)Cl ₂]	C ₂₆ H ₃₈ N ₇ O ₂ BrCl ₂ Cu (694.98)	Red	65	45.28 (44.93)	5.85 (5.51)	14.95 (14.11)	9.65 (9.14)	15.7
[Ni(L_1)Cl ₂]	C ₂₂ H ₃₀ N ₇ O ₂ BrCl ₂ Ni (634.02)	Orange	55	41.85 (41.68)	4.95 (4.77)	15.77 (15.46)	9.68 (9.26)	17.9
[Ni(L_2)Cl ₂]	C ₂₆ H ₃₈ N ₇ O ₂ BrCl ₂ Ni (690.13)	Dark brown	65	45.55 (45.25)	5.97 (5.55)	14.77 (14.21)	8.95 (8.5)	16.4
[Co(L_1)(H ₂ O) ₂ Cl ₂]	C ₂₂ H ₃₂ N ₇ O ₂ BrCl ₂ Co (670.29)	Dark green	60	40.25 (39.42)	5.56 (5.11)	14.88 (14.63)	9.43 (8.79)	18.7
[Co(L_2)(H ₂ O) ₂ Cl ₂]	C ₂₆ H ₄₂ N ₇ O ₂ BrCl ₂ Co (726.40)	Dark green	57	43.53 (42.99)	6.21 (5.83)	14.17 (13.50)	8.69 (8.11)	18.9
[Mn(L_1)Cl ₂]	C ₂₂ H ₃₀ N ₇ O ₂ BrCl ₂ Mn (630.27)		67	42.33 (41.93)	5.21 (4.80)	15.99 (15.56)	8.97 (8.72)	19.9
[Mn(L_2)Cl ₂]	C ₂₆ H ₃₈ N ₇ O ₂ BrCl ₂ Mn (686.37)		60	45.88 (45.50)	5.98 (5.58)	14.50 (14.28)	8.85 (8.00)	19.4
[Zn(L_1)Cl ₂]	C ₂₂ H ₃₀ N ₇ O ₂ BrCl ₂ Zn (640.71)	White	55	41.55 (41.24)	4.79 (4.72)	15.57 (15.30)	10.45 (10.20)	17.9
[Zn(L_2)Cl ₂]	C ₂₆ H ₃₈ N ₇ O ₂ BrCl ₂ Zn (696.82)	White	59	45.23 (44.82)	5.90 (5.50)	14.78 (14.07)	9.98 (9.38)	18.5

Scheme-I: Synthesis of benzimidazolium salts (L_1 , L_2)
 TABLE-2
¹H NMR AND ¹³C NMR CHEMICAL SHIFTS (ppm) LIGANDS (L_1 , L_2), (400, 250, ppm, DMSO, CDCl₃)

Compd.	m.f.	¹ H NMR Chemical shift δ_H (ppm)*	¹³ C NMR Chemical shift
1	C ₂₂ H ₂₁ N ₇ O ₂	3.5-3.9 (16H, morpholine), 8.3 (d, $J = 2.8$, 1H, benzimidazole), 7.7 (d, $J = 28$, 1H, benzimidazole), 7.3 (m, 2H, benzimidazole), (s, 1H, NCHN)	165.11, 1.63.55 (3 × C, triazine), 66.72 ((4 × c, (CH ₂) ₄ , morpholine), 43.42 ((4 × c, (CH ₂) ₄ , morpholine), 142.08-115.534 (7 × c, benzimidazole ring)
L_1	C ₂₂ H ₃₀ N ₇ O ₂ Br	0.95 (t, 3H, CH ₃), 1.45 (m, 2H, CH ₂), 1.97 (m, 2H, CH ₂), 3.7-4.0 (br, 16H, morpholine), 4.65 (t, 2H, CH ₂ -N), 7.35 (m, 2H, benzimidazole), 8.35 (d, 1H, benzimidazole), 8.7 (d, 1H, benzimidazole), 10.25 (s, 1H, NCHN)	13.88 (1 × c, CH ₃), 19.58 (1 × c, CH ₂), 31.25 (1 × c, CH ₂), 44.38, 44.00 (4 × c, (CH ₂) ₄ , morpholine), 47.68 (1 × c, CH ₂ -N), 66.40, 66.19 (4 × c, (CH ₂) ₄ , morpholine), 114.64, 117.89, 127.42, 128.63, 129.23, 132.41, 143.27 (7 × c, benzimidazole ring), 160.95 (1 × c, triazine), 164.27 (2 × c, triazine)
L_2	C ₂₈ H ₃₈ N ₇ O ₂ Br	0.95 (t, 3H, CH ₃), 1.45 (m, 2H, CH ₂), 2.12 (br, 10H, (CH ₂) ₅), 3.62-4.12 (br, 16H, morpholine), 4.57 (t, 2H, CH ₂ -N), 7.72 (m, 2H, benzimidazole), 8.25 (d, 1H, benzimidazole), 8.75 (d, 1H, benzimidazole), 10.25 (s, 1H, NCHN)	14.30 (1 × c, CH ₃), 22.42 (1 × c, CH ₂), 26.18 (1 × c, CH ₂), 28.91 (1 × c, CH ₂), 29.27 (1 × c, CH ₂), 31.54 (1 × c, CH ₂), 34.54 (1 × c, CH ₂), 44.38, 44.00 (4 × c, (CH ₂) ₄ , morpholine), 47.86 (1 × c, CH ₂ -N), 66.40, 66.19 (4 × c, (CH ₂) ₄ , morpholine), 114.63, 117.90, 127.42, 128.63, 129.22, 132.38, 143.26 (7 × c, benzimidazole ring), 160.95 (1 × c, triazine), 164.67 (2 × c, triazine)

integration 3H, 2H, 2H, 2H respectively can be assigned to butyl protons. Some new peaks also observed at 0.95, 1.45, 2.12, 4.57 with integration 3H, 2H, 10H, 2H for octyl protons, in addition to previous peaks for morpholine and imidazole protons [21].

The formation for both of benzimidazolium salts (L_1 , L_2) confirmed by comparison of their ^{13}C NMR spectra with spectrum of compound (**1**), new peaks were emerged at 13.88, 19.58, 31.25, 47.68 ppm can be attributed to butyl carbon atoms for imidazolium salt (L_1), whereas new peaks at 14.30, 22.42, 26.18, 28.91, 29.27, 31.54, 34.54 and 47.86 ppm to octyl carbon atoms for benzimidazolium salts (L_2). in addition to previous peaks for morpholine and benzimidazole.

Mass spectra: Mass spectrometry of compound **1** confirmed the attachment of benzimidazole group at nitrogen by the appearance of the peak at (368) can be attributed to the molecular weight of compound [$\text{C}_{11}\text{H}_{21}\text{N}_7\text{O}_2$] [M+H].

High resolution mass spectrometry confirmed the formation of benzimidazolium salt (L_1) by the appearance of peak at 424.2452 can be assigned to molecular weight of benzimidazolium salt (L_1) [$\text{C}_{22}\text{H}_{30}\text{N}_7\text{O}_2$] $^+$ [M-Br] $^+$. While low resolution mass spectrometry for benzimidazolium salt (L_2) gave peaks at 480.29 can be attributed to molecular weight of salt (L_2) [$\text{C}_{28}\text{H}_{38}\text{N}_7\text{O}_2$] $^+$ [M-Br] $^+$ (Figs. 1-3).

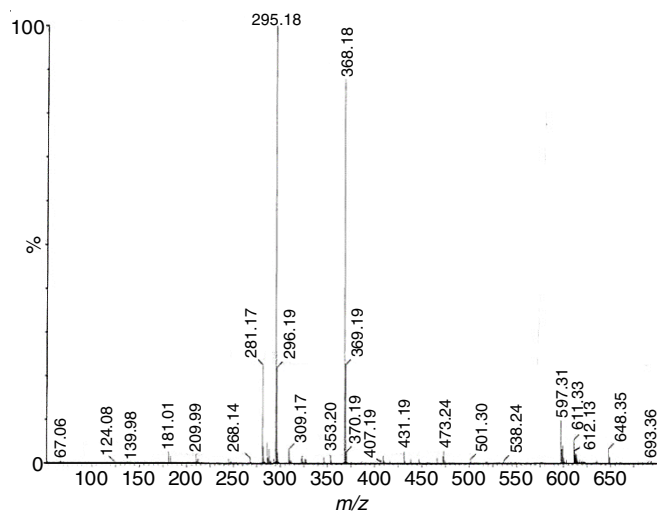


Fig. 1. Mass spectrum of compound **1**

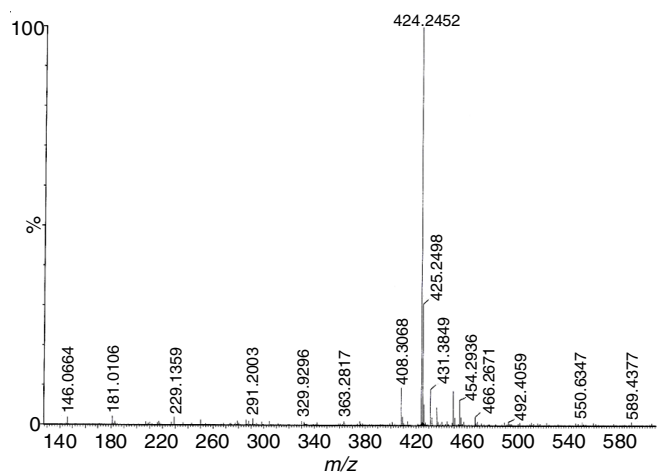


Fig. 2. Mass spectrum of imidazolium salt (L_1)

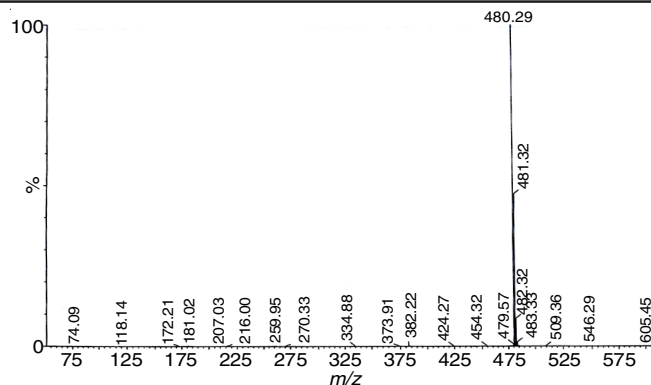


Fig. 3. Mass spectrum of imidazolium salt (L_2)

FTIR spectra of ligands L_1 , L_2 and their metal complexes:

The substitution reactions involved on the starting material of trichlorotriazine were the main reaction to enter the morpholine and benzimidazole rings in the step-wise $\text{S}_{\text{N}}2$ reactions and these products were assigned and identified by the disappearance of $-\text{C}-\text{Cl}$ bond and the new bonds of $-\text{C}-\text{N}-$ around 1390-1300 cm^{-1} may support the intermediates of bromide salts of imidazole structures [11,13]. The IR spectra of imidazole-triazine ligands show the strong absorptions arounds 1616-1566 cm^{-1} and 1394-1301 cm^{-1} are assigned to the vibration modes of $-\text{C}=\text{N}-$ and $-\text{C}-\text{N}-$ bonds respectively of triazine and benzimidazole ring [13]. As well as the bands associated with CH_2-O - and $-\text{CH}_2-\text{N}$ - of morpholine ring was observed around 1290-1242 cm^{-1} confirming the proposed structures of the two synthesized ligands. Furthermore the weak to medium absorptions around 2978-2956 cm^{-1} clearly belonged to the vibrations of aliphatic $-\text{C}-\text{H}$ bonds of the long chains of butyl and octyl groups linked to nitrogen atom of benzimidazole moiety [14,15]. The comparison of the IR spectra of the ligands with those of their metal complexes, it is noted that the less shifts in the absorptions of the main functional sites of $-\text{C}=\text{N}-$ to lower wavenumbers to 1610-1589 cm^{-1} may be remarkably associated to coordination of the copper(II), nickel(II), cobalt(II) and zinc(II) ions to the nitrogen atom of morpholine and no triazine ring. As well as the changing in the intensity and regions of $-\text{CH}_2-\text{N}$ - of morpholine ring supports strongly the binding of this active nitrogen with the empty orbitals of such transition metal ions. However, the weak to medium bands around 458-422 cm^{-1} and 570-480 cm^{-1} have ascribed to the coordination bonds of M-N-morpholine respectively. Therefore the results obtained from IR spectra assist in the confirmation of the bidentate behaviour of the two ligands *via* two nitrogen atoms of morpholine moiety with kinetic stability of six-member chelating ring [22,23]. Furthermore the presence of a broad absorptions around 3500-3400 cm^{-1} corresponding to the stretching vibration of the $-\text{OH}$ group of hydrated water molecules in manganese(II) and cobalt(II) complexes [14]. As well as the bands occurring around 1280-1236 cm^{-1} are assigned to the stretching vibration of C-N bonds of morpholine rings which have been subjected to lowering in the energy of absorptions up on coordination with the metal ions.

Electronic spectral and magnetic susceptibility: The electronic absorption spectra of the ligands of benzimidazole salts in chloroform show two bands around 250-310 nm and 233-295 nm with molar extinction coefficients $\epsilon_{\text{max}} = 2.57 \times$

10^2 to $1.22 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) (Table-3). These bands may be assigned to the ligand field of $-\text{C}=\text{N}-$ and $-\text{C}=\text{C}-$ associated with $\pi-\pi^*$ and $n-\pi^*$ transitions respectively [12,13]. The comparison of the electronic spectra of the ligands solutions with their metal complexes may give strong evidence for the formation of the complexes and support the proposed geometry. The red solution of copper(II) complexes in DMSO exhibited two spin-allowed transitions around (450-480) nm and (390-365)nm assigning to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transitions respectively and are consistent with the square-planer geometry of Cu(II) complexes [15,16]. The diamagnetic properties of Ni(II) complexes confirms the low-spin $3d^8$ configuration and ($t_2g^6 e_g^2$) according to crystal field model. Therefore the UV-visible spectra would have been in agreement with their expected symmetry as explained below. The orange and dark-brown solutions of nickel(II) complex NiL_1Cl_2 in DMSO showed one weak peak at 460 nm and other high-intense band around 355 nm which are reasoned from ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$ and LMCT respectively and confirms the square-planer environment around Ni(II) ion. Similarly NiL_2Cl_2 complex showed distinct $d-d$ spectra around 510 and 400 nm which are attributed to the environment of square-planer geometry around Ni(II) ion. Furthermore the dark green solutions of cobalt(II) complexes in DMSO showed three spin-allowed transitions around (650-610), (480-432) and (375-348) nm ascribing to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$, ${}^1\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ respectively [18]. The cobalt(II) complexes have magnetic moment values of 4.86 and 4.75 BM, respectively, indicating the presence of three unpaired electrons per metal ion octahedral stereochemistry is suggested [16]. For the nickel(II) complexes, the values are zero BM, respectively denoting the low-spin square-planer complexes of $3d^8$ configurations ($\mu_{\text{eff}} = 0.00 \text{ BM}$). However the spin-only magnetic

moments of copper (II) complexes were recorded expected results for spin of one odd electron for $3d^9$ electronic configurations about (1.80-1.90) BM and agrees well with the structures of square-planer geometry. The electronic spectra of manganese(II) complexes in DMSO exhibited two high intense bands around 380-290 nm and 350-275 nm assigning to LMCT and ligand field of $-\text{C}=\text{N}-$ and $-\text{C}=\text{C}-$ moiety respectively. As well as the recorded magnetic moments for manganese(II) complexes in the region 5.45-5.80 BM assisting together with UV-visible results assists us in the prediction the tetrahedral geometry around Mn(II) ion [18]. The white-off solutions of zinc(II) complexes displayed strong bands around 300-285 nm which are associated with Cl-Zn^{2+} and $\pi-\pi^*$ transitions respectively. The mainly $d-d$ spectra and ligand to metal charge transfer bands for the solutions of the synthesized complexes in continuous with their magnetic moments revealed that copper(II) and nickel(II) complexes were square-planer whereas the cobalt(II) was octahedral and Mn(II), Zn(II) complexes were suggested as tetrahedral geometry (Fig. 4).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-3
ELECTRONIC SPECTRAL DATA, MAGNETIC MOMENTS OF LIGANDS (L_1 AND L_2) AND ITS METAL COMPLEXES

Compound	λ_{max} (nm)	ν (cm^{-1})	Assignment	μ_{eff} (B.M.)	Geometry
L_1	250	40000	$n-\pi^*$	–	–
	310	32258	$\pi-\pi^*$	–	–
L_2	233	42918	$n-\pi^*$	–	–
	295	33898	$\pi-\pi^*$	–	–
$[\text{Cu}(\text{L}_1)\text{Cl}_2]$	450	22222	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	1.8	Square planer
	390	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	–	–
$[\text{Cu}(\text{L}_2)\text{Cl}_2]$	450	22222	${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$	1.9	Square planer
	390	25641	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	–	–
$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	460	21739	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	0.00	Square planer
	355	28169	LMCT	–	–
$[\text{Ni}(\text{L}_2)\text{Cl}_2]$	510	19607	${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$	0.00	Square planer
	400	25000	LMCT	–	–
$[\text{Co}(\text{L}_1)(\text{H}_2\text{O})_2\text{Cl}_2]$	650	15384	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$	4.86	Octahedral
	480	20833	${}^1\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$	–	–
	375	26666	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$	–	–
$[\text{Co}(\text{L}_2)(\text{H}_2\text{O})_2\text{Cl}_2]$	610	16393	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$	4.75	Octahedral
	432	23148	${}^1\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$	–	–
	348	28734	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$	–	–
$[\text{Mn}(\text{L}_1)\text{Cl}_2]$	290	34482	$\pi-\pi^*$	5.45	Tetrahedral
	380	26315	LMCT	–	–
$[\text{Mn}(\text{L}_2)\text{Cl}_2]$	275	36363	Ligand field	5.80	Tetrahedral
	350	28571	LMCT	–	–
$[\text{Zn}(\text{L}_1)\text{Cl}_2]$	300	33333	$\pi-\pi^*$	0.00	Tetrahedral
$[\text{Zn}(\text{L}_2)\text{Cl}_2]$	285	35714	$\pi-\pi^*$	0.00	Tetrahedral
	360	27777	LMCT	–	–

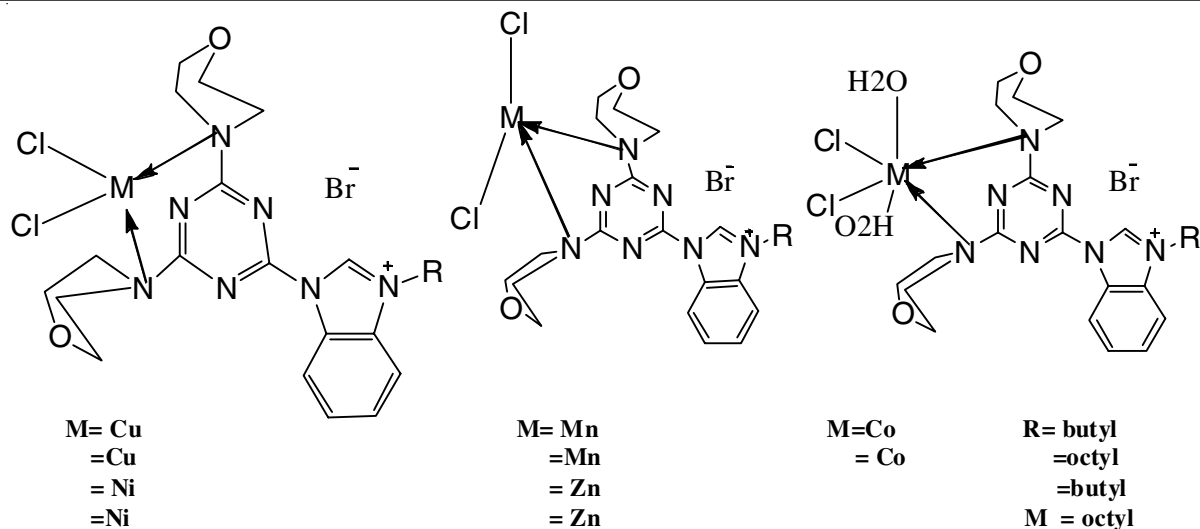


Fig. 4. Proposed structures of synthesized complexes

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