Microwave and conventional synthesis of Co (II), Cu (II) and Ni (II) metal complexes of some acid hydrazones with their spectral characterization and biological evaluation

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Abstract: The transition metal complexes of Co(II), Ni(II), and Cu(II) derived from N'-((5-(2,5-dichlorophenyl)furan-2-yl)methylene)-2-hydroxybenzohydrazide (L24) and N'-((5-(2, 5-dichlorophenyl)furan-2-yl)methylene)benzohydrazide (L21) have been synthesized by conventional as well as microwave method being shorter time consuming, solvent less and gives improved yields as compared to the traditional conventional technique. These compounds were characterized by melting point, TLC, FTIR, ^{1}H-NMR, elemental analysis, potentiometric titration, ICP-OES and EIMS. From this analytical data it is confirmed that complexes are in octahedral structure with coordination number 6 which revealed 1:2 (metal:ligand). FTIR data shows that these synthesized hydrazone ligands have ONO donor sites and coordinate with transition metal ions in a tridentate monobasic manner. All these synthesized compounds were tested for evaluation of antibacterial activity by agar disc diffusion assay and total antioxidant activity by Phosphomolybdenum method.

Keywords: Conventional method, microwave method, hydrazone, antibacterial, antioxidants.

INTRODUCTION

Hydrazones and their derivatives having an azomethine -NHN=CH- proton, which leads to an essential class of compounds in synthetic as well as medicinal chemistry (Bharat Parashar *et al*. 2009). Interest in the research of hydrazone derivatives has been increasing day by day because of their wide applications like antimicrobial, anti-tuberculosis, antitumor and anti-inflammatory activities (P Venkateswar Rao *et al*. 2007) For example, *Isoniazid* is used in the treatment of tuberculosis (Srivsatava Ritu *et al*. 2010), 4-fluoro-N'-((5-nitrofuran-2-yl)methylene) benzohydrazide (Rollas *et al*. 2002), N'-((E)-benzylidene)-4-(2-((Z)-2-methyl-4-oxopent-1-en-3-ylidene)hydrazineyl)benzohydrazide and (E)-N-(4-(2-(4-chlorobenz-ylidene)hydrazine-1-carbonyl)phenyl)-4-methoxybenzamide show excellent antibacterial activity against two bacterial strains *Mycobacterium tuberculosis* and *Staphylococcus aureus* (Ş.Güniz Küçükgüzel *et al*. 1999, Ş.Güniz Küçükgüzel *et al*. 2002). They are additionally essential components for not only heterocycles synthesis but also used for synthesis of polymers, dyes, paints, photographic products, pharmaceutical drugs, fertilizers and pesticides (Marietta Tóth and Somsak 2001, D Perdicchia *et al*. 2003, P Chawla *et al*. 2010). Besides their biological applications, they are also used for the determination of different metals ions by spectrophotometrically and spectrofluorimetrically (Angel A. R. Despaigne *et al*. 2010, L N Suvarapu *et al*. 2012) like Pyridine-2-aldehyde-2-quinolylhydrazone is used for extractive photometric studies of first series of divalent transition metals (R. W. Frei *et al*. 1971), Cinnamaldehyde-4-hydroxybenzoyl-hydrazone used for the spectrometric determination of Co(II) in tea leaves and in vitamin B_{12} (D.Gopala Krishna *et al*. 2011). They have capacity to form stable metal complexes with high coordination numbers greater than four or six, when reaction with metals epically transition metals hence widely used in bioinorganic chemistry (A Ray *et al*. 2008, V M Naik *et al*. 2008, Sarika R.Yaul *et al*. 2009, S K Patil *et al*. 2011).

Microwave-assisted synthesis (MAS) has turned into another and rapidly developing area in organic as well as in inorganic chemistry (P Durairaj *et al*. 2015). This MAS technique is also known as green method or non-conventional technique due to less solvent usage, ecofriendly, low cost, time consuming, simplicity and better yields as compared to traditional-conventional method (Önko *et al*. 2008, AP Mishra *et al*. 2012, K Venkatesan *et al*. 2012) (R K Jain *et al*. 2012, H I Alarabi and Suayed 2014).

Keeping in view the importance of hydrazones and their transition metal complexes, we herein report the synthesis (conventional and microwave), characterization and biotic screening of some acid hydrazones and their transition metal complexes.

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MATERIALS AND METHODS

General

All chemicals and solvents used were of analytical grade from, Merck. Melting points of all the synthesized compounds were determined by GallenKamp and the given values are uncorrected. For checking the purity and progress of reactions, aluminum sheets coated with silica gel 60 F254 were used. The ^{1}H-NMR spectra were obtained using Bruker AV 400 MHz spectrophotometer in DMSO. The FTIR spectra of all compounds were recorded on Vector 22 FTIR spectrophotometer in wave number range 400-4000cm-^{1}. MAT 312 mass spectrometer was used for EIMS. For determination of carbon, hydrogen and nitrogen elemental analyzer (Flash 2000) was used while for metal estimation Thermo iCap 6300 ICP-OES was used. Halide (Cl) analysis was performed by Metrohm potentiometric autotitrator. Microwave synthesis of compounds were conducted in microwave oven DW-631. Biological studies were performed in Cholistan Institute of Desert Studies (CIDS) of The Islamia University of Bahawalpur by using incubator (B-53 IRFECO Gmbh), laminar flow cabinet (ISO 14644.1 C-4) and electric autoclave (25X Ehret D-783).

General method for synthesis of acid hydrazones

Acid hydrazone ligands were synthesized by both microwave method and conventional method *(*Scheme 1) according to the reported procedure (Mussarat Jabeen *et al*. 2017).

Conventional method

According to the reported methods *5-(2', 5'-dichlorophenyl) furan-2-carbaldehyde* (A6), Benzohydrazide (H1) and Salicylhydrazide (H4) were synthesized (T Budiati *et al*. 2010, Samina Aslam *et al*. 2013). Both the reactants A6 and H1/H4 were dissolved in equimolar ratio in minimum amounts of ethanol with few drops of conc. HCl and refluxed for 3 hours. The reaction process was monitored by TLC in a solvent system of ethyl acetate and n-hexane with 1:2 ratios. After the completion of reaction, the resultant mixture was cooled at room temperature, filtered through Buchner funnel and recrystallized with dry ethanol golden yellow (L21) and pollen yellow (L24) colored target hydrazone were obtained.

Microwave method

A mixture of 10mmol A6 and 10mmol H1/H4 in 2mL ethanol with few drops of conc. HCl was exposed to microwave-irradiation of 600W for exactly 2mint. As a result, golden yellow and pollen yellow colored precipitates were formed. Purity and progress of hydrazones were confirmed by TLC with the same solvent system as mentioned above. These synthesized compounds (L21 & L24) were recrystallized with dry ethanol.

N'-((5-(2,5-dichlorophenyl) furan-2-yl)methylene)benzohydrazide (L21)

Golden yellow; Time: CM (hrs.): 03, MW(mint.): 02; Yield: CM: 2.52g (70%), MW: 3.1g (86%); Solubility: Soluble in ethanol, DMF, DMSO, ethyl acetate; m.p.: 165°C; Anal. Calculations for $C_{18}H_{12}Cl_2N_2O_2$ (*Mr*= 358): Calculated % (Found %): C, 60.2 (60.19); H, 3.37 (3.37); Cl, 19.74 (19.74); N, 7.80 (7.80): MS (EIMS): m/z: 360 [M$^+$+2], 358 [M$^+$], 356 [M$^+$-2], 295 [M$^+$-C_5H_4], 240 [M^{+2}-C_7H_6NO], 185 [$C_8H_3Cl_2O$], 113[C_5H_2ClO], 69 [C_4H_4O]; FTIR (cm-^{1}): (N-H), 3217.7; (C=O), 1649.5; (C=N), 1550.4; (C-O-C), 1286.0; (C-N), 1142.8; (N-N), 1026.7; (C-Cl), 796.6; ^{1}H-NMR (DMSO) δ: 12.0 (N-H, *s*,1H), 8.442 (CH=N, *s*,1H), 7.928-7.914 (H-2',6', *d*, 2H), 7.714-7.70 (H-4', *d*, 1H), 7.685-7.55 (H-3',5',6, *m*, 3H), 7.507-7.457 (H-3,4, *m*, 2H), 7.40-7.392 (H-2 furan ring, *d*, 1H), 7.064-7.056 (H-1 furan ring, *d*, 1H).

N'-((5-(2,5-dichlorophenyl)furan-2-yl)methylene)-2-hydroxybenzohydrazide (L24)

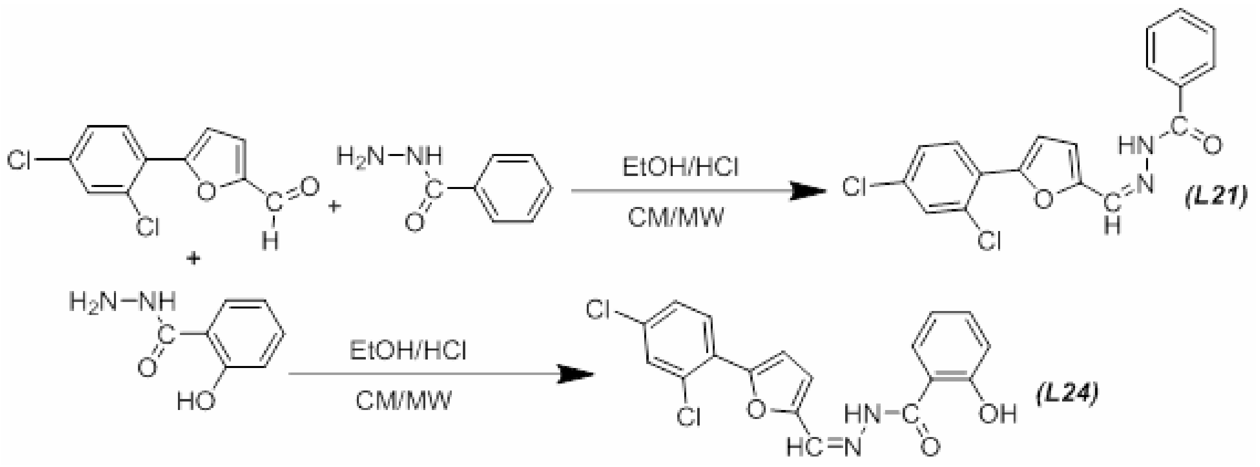
Pollen yellow; Time: CM (hrs.): 03, MW(mint.): 02; Yield: CM: 2.68g (72%), MW: 3.27g (87%); Solubility: Soluble in ethanol, DMF, DMSO, ethyl acetate; m.p.: 195°C; Anal. Calculations for $C_{18}H_{12}Cl_2N_2O_3$ (*Mr*=374): Calculated % (Found%): C, 57.62 (57.81); H, 3.22 (3.18); Cl, 18.90 (18.97); N, 7.47 (7.37); MS (EIMS): m/z: 376 [M$^+$+2], 374 [M$^+$], 335 [M^{+2}-C_2H_3O], 305 [M$^+$-2Cl], 254 [M$^+$-$C_4H_2Cl_2$], 145 [M$^+$- $C_{12}H_9N_2O_3$], 135 [M$^+$-$C_{11}H_6Cl_2NO$], 121 [M$^+$-$C_{11}H_7Cl_2N_2O$], 93 [C_6H_5O], 85 [M^{+2}- $C_{13}H_9Cl_2N_2O_2$], 69 [M$^+$-$C_{14}H_9Cl_2N_2O_2$]; FTIR (cm-^{1}): (N-H), 3234.4; (O-H), 3083.4; (C=O), 1619.4; (C=N), 1538.0; (C-O-C), 1228.3; (C-N), 1140.6; (N-N), 1024.2; (C-Cl), 790.4; ^{1}H-NMR (DMSO) δ: 11.96 (N-H, *s*, 1H), 11.74 (O-H, *s*, 1H), 8.441 (CH=N, *s*, 1H), 7.917-7.866 (H-6,6', *m*, 2H), 7.666-7.65 (H-3, *d*, 1H), 7.508-7.441 (H-4,4', *m*, 2H), 7.417-7.408 (H-2 furan ring, *d*, 1H), 7.183-7.175 (H-1 furan ring, *d*, 1H), 7.017-6.958 (H-3',5', *m*, 2H).

Synthesis of metal complexes

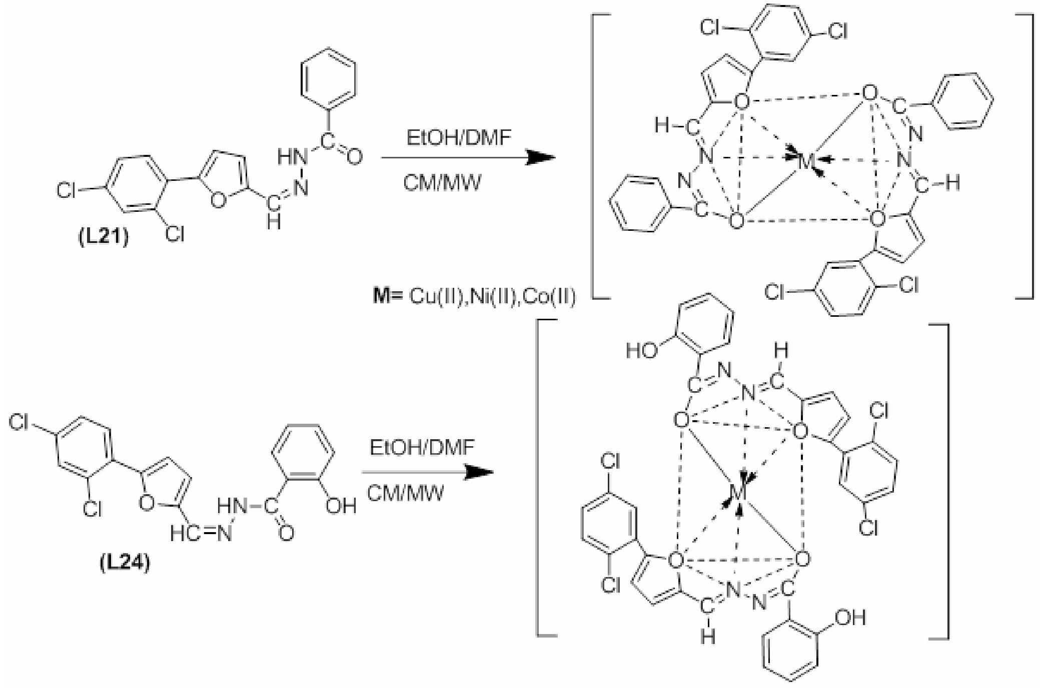
Like synthesis of hydrazone ligands, transition metal (II) complexes with synthesized hydrazone ligands (L21 & L24) were prepared by conventional and microwave method according to the reported procedure *(Scheme 2)* (Mussarat Jabeen *et al*. 2017). Details of both methods are given below,

Conventional method

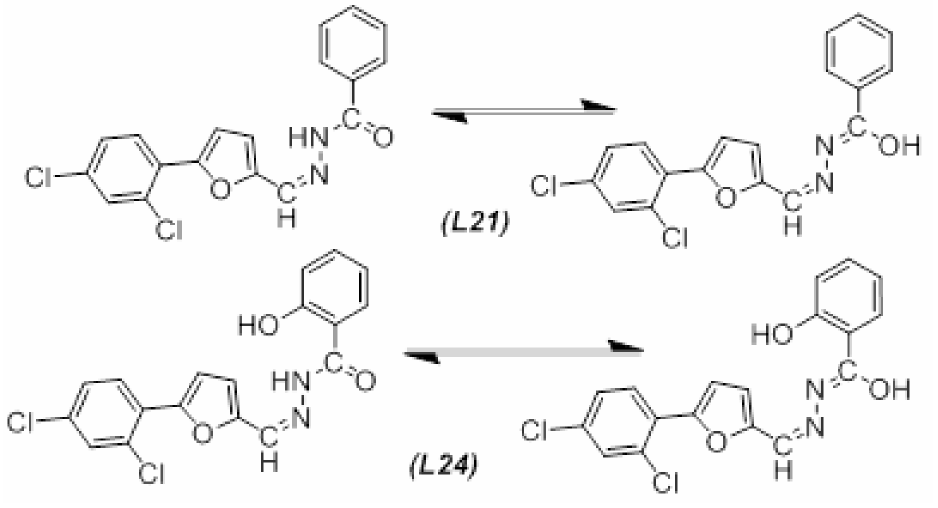
Ethanoic solution of transition metal chloride was slowly added to the 50mL warmed solution (DMF and ethanol) of hydrazone with 1:2 molar ratios and refluxed for 0.5-9.0 hrs. The reaction's progress was scrutinized by TLC in ethyl acetate and n-hexane (1:1). The synthesized colored precipitates were washed several times with ethanoic DMF.



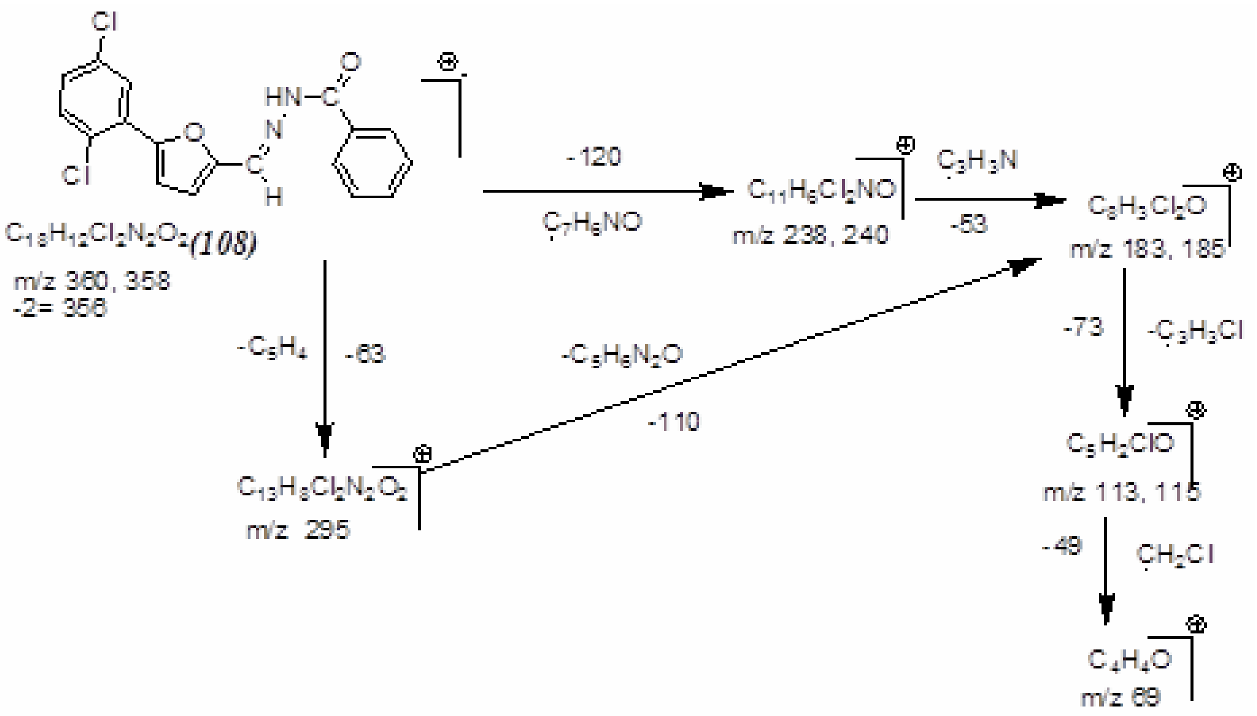
Scheme 1: Synthesis of Hydrazones



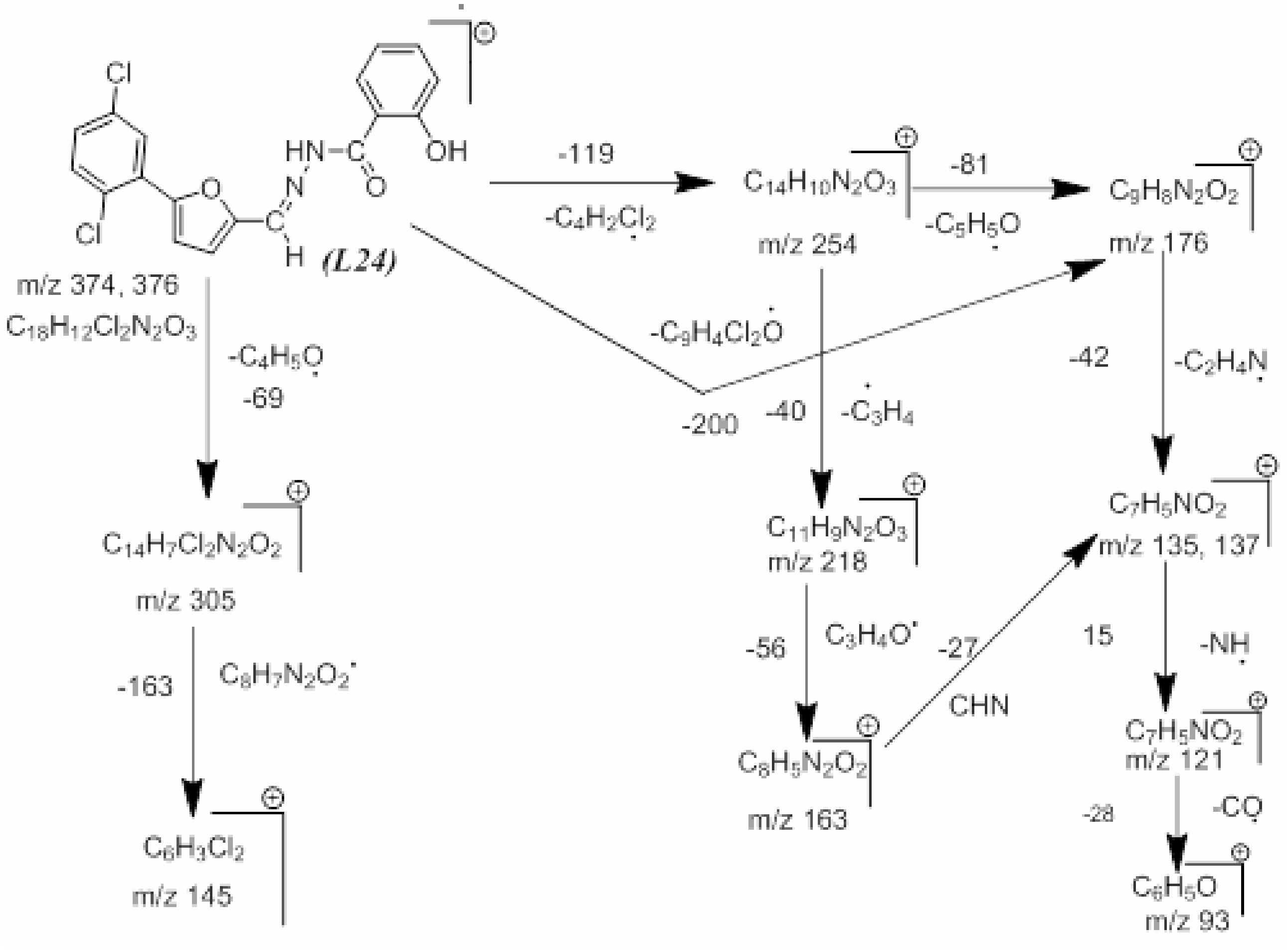
Scheme 1: Synthesis of Hydrazone metal (II) complexes



Scheme 3: *Keto-Enol tautomerism of hydrazones* L21 & L24



Scheme 4: Fragmentation pattern of hydrazone ligand L21



Scheme 5: Fragmentation pattern of hydrazone ligand L24

Microwave method

Divalent transition metal chloride and hydrazone ligand with molar ratios 1:2 were subjected to microwave radiations of 600W for 1.0-7.0 mints in the presence of 1mL DMF and 1mL ethanol. The completion of reaction was checked by TLC with the same solvent system mentioned above. The resulting solid colored metal complexes were washed several times with DMF and ethanol mixture (1:2) to get pure colored precipitates of metal complexes.

[Cu(L21)$_2$]

Yellowish green; Time: CM (hrs.): 0.5, MW (mint.): 01; Yield: CM: 79%, MW: 84%; Solubility: Soluble DMSO; m.p (decomposed): 132°C; Analytical Calculations for $[Cu(C_{18}H_{11}Cl_2N_2O_2)_2]$ (*Mr*=779.94): Calculated % (Found%): C, 55.44 (55.39); H, 2.84 (2.88); Cl, 18.18 (18.11); N, 7.18 (7.07); Cu, 8.15 (8.11); FTIR (cm-^{1}): (C=N-N=C), 1514.2; (C-O-C), 1392.5; (N-N), 1027.6; (C-Cl), 799.4; (M-N), *582.5;* (M-O), 451.7.

[Ni(L21)$_2$]

Yellowish Orange; Time: CM (hrs.): 04, MW (mint.): 02; Yield: CM: 60%, MW: 77%; Solubility: Soluble DMSO; m.p (decomposed): 194-196°C; Analytical Calculations for $[Ni(C_{18}H_{11}Cl_2N_2O_2)_2]$ (*Mr*= 775.09): Calculated % (Found%): C, 55.79 (55.58); H, 2.86 (2.78); Cl, 18.30 (18.24); N, 7.23 (7.15); Ni, 7.57 (7.69); FTIR (cm^{-1}): (C=N-N=C), 1507.1; (C-O-C), 1387.8; (C-O), 1098.4; (N-N), 1022.5; (C-Cl), 794.7; (M-N), 590.0; (M-O), 458.1.

[Co(L21)$_2$]

Dull green; Time: CM (hrs.): 09, MW (mint.): 07; Yield: CM: 43%, MW: 51%; Solubility: Only soluble in DMSO on heating; m.p (decomposed): 151-153°C; Analytical Calculations for $[Co(C_{18}H_{11}Cl_2N_2O_2)_2]$ (*Mr*=775.33): Calculated % (Found%): C, 55.77 (55.62); H, 2.86 (2.81); Cl, 18.29 (18.31); N, 7.23 (7.26); Co, 7.60 (7.5); FTIR (cm^{-1}): (C=N-N=C), 1505.7; (C-O-C), 1373.6; (N-N), 1019.1; (C-Cl), 782.7; (M-N), 557.1; (M-O), 450.2.

[Cu(L24)$_2$]

Lime green; Time: CM (hrs.): 01, MW (mint.): 02; Yield: CM: 68%, MW: 82%; Solubility: Soluble DMSO; m.p (decomposed): 143°C; Analytical Calculations for $[Cu(C_{18}H_{11}Cl_2N_2O_3)_2]$ (*Mr*= 811.94): Calculated % (Found%): C, 53.25 (53.34); H, 2.73 (2.69); Cl, 17.47 (17.35); N, 6.90 (6.81); Cu, 7.83 (7.73); FTIR (cm-^{1}): (O-H), *br*, 3081.7; (C=N-N=C),1506.7; (C-O-C), 1254.6; (C-O), 1099.4; (N-N), 1048.2; (C-Cl), 805.3; (M-N), 532.3; (M-O), 476.6.

[Ni(L24)$_2$]

Coral; Time: CM (hrs.): 04, MW (mint.): 02; Yield: CM: 66%, MW: 77%; Solubility: Soluble DMSO; m.p (decomposed): 182°C; Analytical Calculations for $[Ni(C_{18}H_{11}Cl_2N_2O_3)_2]$ (*Mr*=807.09): Calculated % (Found%): C, 53.57 (53.51); H, 2.75 (2.58); Cl, 17.57 (17.60); N, 6.94 (7.80); Ni, 7.27 (7.28); FTIR (cm-^{1}): (O-H), *br*, 3065.4; (C=N-N=C), 1513.9; (C-O-C), 1253.9; (C-O), 1096.2; (N-N), 1050.5; (C-Cl), 804.4; (M-N), 535.4; (M-O), 457.4.

[Co(L24)$_2$]

Greenish brown; Time: CM (hrs.): 08, MW (mint.): 07; Yield: CM: 48%, MW: 65%; Solubility: Soluble in DMSO on heating; m.p (decomposed): 96°C; Analytical Calculations for $[Co(C_{18}H_{11}Cl_2N_2O_3)_2]$ (*Mr*=807.33): Calculated % (Found%): C, 53.56 (53.66); H, 2.75 (2.71); Cl, 17.57 (17.5); N, 6.94 (7.02); Co, 7.30 (7.4); FTIR (cm-1): (O-H), *br*, 3061.4; (C=N-N=C), 1501.2; (C-O-C), 1246.0; (C-O), 1097.4; (N-N), 1038.1; (C-Cl), 805.7; (M-N), 588.2; (M-O), 452.6.

RESULTS

In this study, initially we prepared hydrazone ligands L21 and L24 (Scheme 1) which were then coordinated with different transition metals like copper, nickel and cobalt to give following complexes $[Cu(C_{18}H_{11}Cl_2N_2O_2)_2]$, $[Ni(C_{18}H_{11}Cl_2N_2O_2)_2]$, $[Co(C_{18}H_{11}Cl_2N_2O_2)_2]$, $[Cu(C_{18}H_{11}Cl_2N_2O_3)_2]$, $[Ni(C_{18}H_{11}Cl_2N_2O_3)_2]$, $[Co(C_{18}H_{11}Cl_2N_2O_3)_2]$ by conventional and microwave assisted method (Scheme 2). All the compounds were obtained in a yield 43-79% in conventional method and give better yields 51-84% in microwave method. Hydrazone ligands are soluble in almost all ordinary organic solvents but complexes are only soluble only in DMSO.

For structural confirmation of all the synthesized ligands and complexes, FTIR, elemental analysis, EIMS, NMR, ICP-OES and potentiometric titration were performed and data is presented above.

To check the antibacterial activity, compounds were tested by agar disc diffusion method against three gram-positive and six gram-negative bacterial strains (table 1, fig. 1). Furthermore, total antioxidant activity was checked by Phosphomolybdenum method (table 1, fig. 2).

DISCUSSION

In the present study, the main purpose was to synthesize some furfuraldehyde-based acid hydrazones and their divalent transition metal complexes by both traditional conventional and microwave method. The microwave technique is supposed to be a green route in synthetic chemistry due to less quantity of solvents.

All the synthesized compounds were characterized by several physico-chemical and spectral techniques. Over the span of microwave-assisted synthesis, it was watched that the response time was diminished from hours to minutes and the products were acquired in same or better yield as compared to regular conventional techniques.

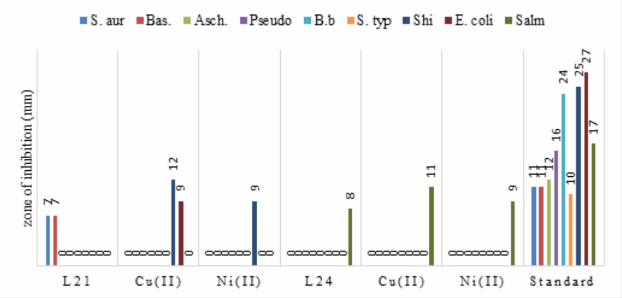


Fig. 1: Graphical representation of Antibacterial activities of Ligands and their metal complexes

All synthesized compounds including ligands and metal complexes are colored, solids and stable. These synthesized compounds were affirmed by elemental analysis, proton NMR, mass spectra, FTIR, ICP-OES and potentiometric titration. Both of the synthesized hydrazone ligands displayed keto-enol tautomerism (A Ray *et al*. 2008) (Scheme 3) and are mono anionic with ONO donor sites, which form octahedral complexes with Cu(II), Ni(II) & Co(II) metals with coordination number six. OH group in hydrazone ligand L24 do not take part in formation of metal complexes, and was confirmed by FTIR having broad absorption peak at 3061-3083 cm^{-1}.

^{1}H-NMR of the Acid Hydrazones (L21 & L24)

The structure of L21 was confirmed by the presence of two singlet peaks N-H at 12.0 ppm and azomethine proton's 8.442 ppm. Two doublets of three protons (H-4' and H-2', 6') appeared at 7.928-7.914 ppm and 7.714-7.70 ppm with same J-vale 5.6 Hz. Two protons (H-3 & H-4) should give two doublets but these peaks immerged to give a multiplet at 7.507-7.457 ppm. Similarly, a multiplet of three protons (H-6 & H3', 5') appeared at 7.685-7.55 ppm. Two doublets of two furan protons appeared at 7.40-7.392ppm and 7.064-7.056 ppm with same J-value 3.2 Hz (Terence N Mitchell and Costisella 2013).

^{1}H NMR spectrum of L24 showed two singlets at 11.96 ppm 11.74ppm relative to H-N-CO and O-H respectively, while the signal of the azomethine proton appeared as a singlet at 8.441ppm. Two doublets of two furan protons appeared at 7.417-7.408ppm and 7.183-7.175 ppm with very close J-values 3.6 Hz and 3.2 Hz (Terence N Mitchell and Costisella 2013).

Mass spectra of ligands

The mass spectrum of hydrazone ligand L21 showed molecular ion peaks [M^{+}] and [M^{+2}] at 358 and 360 respectively. Base peak appeared at 240 representing [$C_{11}H_6Cl_2NO$]$^{+}$ ion. Further important fragmentation peaks appear at 295, 185, 115 and 69 (D L Pavia *et al*. 2008). The detailed fragmentation pattern is given below.

Mass spectrum of hydrazone ligand (L24) indicated the molecular ion peak [M^{+}] and [M^{+2}] at 374 and 376. Base peak and main fragmentation peaks including isotopic peaks appear at 305, 254, 218, 176, 135, 121 and 93 (D L Pavia *et al*. 2008).

IR spectra of ligands and their metal complexes

FTIR spectral not only very helpful for determination of mode of bond formation but also useful for structure determination of synthesized compounds. The data showed that the hydrazone ligands exist in ketonic form due to the presence of N-H and C=O absorption bands at 3217-3234 and 1619-1649 cm^{-1}. The detailed spectral data is given below.

FTIR spectrum of hydrazone ligand L21 showed different absorption bands at 3217.7, 1649.5, 1550.4, 1288.0, 1142.8, 1026.7 and 796.6cm^{-1} indicating N-H, C=O, C=N, C-O-C, C-N, N-N and C-Cl respectively. Sharp band of mono-substituted benzene appear at 691.4 cm^{-1} while a small band at 898.1 cm^{-1} indicate tri-substituted benzene (Lambert 1987, Stuart 2004).

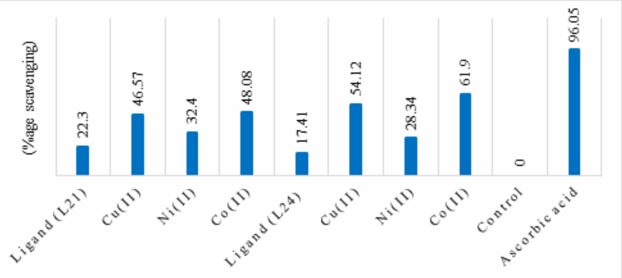


Fig. 2: Graphical representation of total antioxidant activity of ligands and metal complexes

FTIR spectral data of metal complexes of L21 showed that N-H and C=O absorption bands disappear and new absorption band appear at 1514-1507 cm^{-1} indicating C=N-N=C(Muhammad Nasrullah *et al*. 2013). Position and intensity of C-O-C absorption peaks change from 1286cm-1 to 1392-1387 cm^{-1} indicating bonding through oxygen. M-N and M-O absorption bands appear at low wave number at 582-590cm^{-1} and 451-458cm^{-1} respectively (Abdul-Ghany M.Al-Daher and Al-Qassar 2011).

In FTIR spectrum of L24, a broad band of O-H appear at 3083.4 cm^{-1}. Sharp signals of N-H and C=O at 3234.4 and 1619.4 respectively indicating *ketonic nature* of the ligand. Some other characteristic bands of C=N, C-O-C, C-N, N-N, C-O-H and C-Cl appears at 1536.0, 1228.3, 1140.6, 1024.2, 1301.3 and 790.4cm^{-1}. Further the substituted phenyl rings confirmed by the signals of 1, 2, 5 tri-substituted benzene at 873.1cm^{-1} as a weak signal and 1, 2 di-substituted benzene at 752.7cm^{-1} as a medium signal (Lambert 1987, Stuart 2004).

In metal complexes of L24 absorption bands for C=N-N=C appears at 1501-1513cm^{-1} (Muhammad Nasrullah *et al*. 2013). In complexes M-O and M-N weak absorption bands appears at low wave number 452-476cm^{-1} and 532-

Table 1: Antibacterial activity of hydrazone ligands and their metal complexes

Comp'd.	Zone of inhibition in diameter (mm)									Total antioxidant activity (%age scavenging)
	Gram-positive			Gram-negative						
	s.aur	*Bas*	*Asch*	*Pseudo*	*B.b*	*S.typ*	*Shi*	*E.coli*	*Salm.*	
L21	7	7	---	----	----	----	----	---	----	22.30±0.11
$[Cu(L21)_2]$	----	----	----	----	----	----	12	9	----	46.57±0.10
$[Ni(L21)_2]$	----	----	---	----	----	----	9	----	----	32.40±0.17
$[Co(L21)_2]$	---	---	---	---	---	---	---	---	---	48.08±0.03
L24	----	----	----	----	----	----	----	----	8	17.41±0.15
$[Cu(L24)_2]$	----	----	----	----	----	----	----	----	11	54.12±0.07
$[Ni(L24)_2]$	----	----	----	----	----	----	----	----	9	28.34±0.12
$[Co(L24)_2]$	---	---	---	---	---	---	---	---	---	61.9±0.05
+ve Control	11	11	12	16	24	10	25	27	17	96.05±0.05
-ve Control	---	---	---	---	---	---	---	---	---	-----

588cm^{-1} respectively (Abdul-Ghany M.Al-Daher and Al-Qassar 2011). OH occur at 3081-3061cm^{-1} which indicates that the OH functional group does not take part in complex formation.

Antibacterial activity of hydrazone ligands and their metal complexes

The antibacterial activity of synthesized acid hydrazones and their metal complexes was studied by agar disc diffusion method against three gram +ve bacteria *Staphylococcus aureus* (s.aur), *Bacillus subtilis* (Bas) and *Actinobaculumschaalii* (Asch) and six gram -ve bacteria *Pseudomonas aerugenosa* (Pseudo), *Escherichia coli* (E.coli), *Salmonella typhimurium* (S.typ.), *Bordetellabronchiseptica* (B.b), *Shigella* (Shi) and *Salmonella* (Salm) with concentration 500 µg /disc whereas standard drug (*Ampicillin*) used with concentration 50µg/disc. The detailed procedure is already reported (Mussarat Jabeen *et al*. 2017). The results are tabulated in table 1. Majority of the synthesized compounds were inactive.

Antioxidant activity of hydrazone ligands and metal complexes

Phosphomolybdenum method was used to calculate the total antioxidant capacity of all synthesized compounds including hydrazone ligands and metal complexes, spectroscopically by the formation of Phosphomolybdenum complex. The method based on the reduction of Mo(IV) to green colored Mo(V) complex by the sample analyte in acidic medium (Mansoor Ahmad *et al*. 2013, Md. Nur Alam *et al*. 2013). The detailed procedure is reported already (Mussarat Jabeen *et al*. 2017) and results are given in table 1.

Hydrazone metal complexes especially cobalt complexes showed good antioxidant activities as compared to their ligands with inhibition activities 48.08 and 61.9 %.

CONCLUSION

In summary, hydrazone ligands derived from 5-(2', 5'-dichlorophenyl) furan-2-carbaldehyde and benzohydrazide or salicylhydrazide with their metal complexes were prepared by microwave strategy in higher yields, in quicker time, and with less chemical waste related to conventional techniques. From all these prepared compounds copper complexes showed extreme yields up to 87% and 83% respectively. All these compounds were characterized by various spectroscopic and analytical techniques. The hydrazone ligands have ONO donor sites and can act as tridentate mono-basic ligands. As a result, the metal complexes give octahedral structures. The antibacterial activity was checked by agar disc diffusion method against different bacterial strains while antioxidant activity was calculated by Phosphomolybdenum method.

As a result of antibacterial studies, copper and nickel metal complexes act as moderate antibacterial agents against *Shigella*, *Escherichia coli and Salmonella.* While cobalt complexes are inactive against all strains. Total antioxidant capacity of cobalt complexes is higher than ligands and other complexes with percentage inhibition 61.9±0.05% which concluded that cobalt complexes may act as good antioxidants.

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