Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(12):1153-1159

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis and characterization of tetraazamacrocyclic complexes using silica supported perchloric acid ($HClO_4$:SiO_2) as catalyst

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ABSTRACT

Silica supported perchloric acid ($HClO_4$:SiO_2) was used as a catalyst for the synthesis of twelve tetraazamacrocyclic complexes of transition metals using chloride, nitrate and acetate salts of Co(II), NI(II), Cu(II) and Zn(II). The complexes were obtained by template condensation of ethylenediamine and glyoxal in ethanolic medium in presence of above transition metal ions using silica supported perchloric acid ($HClO_4$-SiO_2) as catalyst. The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, IR, electronic, ^{1}H-NMR, Mass Spectra, TGA, and powder x-ray analysis. Based on the results obtained a six coordinated octahedral geometry has been proposed for all these complexes. The synthesized complexes were also screened for their antimicrobial activity.

Keywords: ethylenediamine; glyoxal; template method, octahedral, antimicrobial activity.

INTRODUCTION

Coordination chemistry is an important branch of inorganic chemistry. The research in the area of coordination chemistry deals with synthesis, characterization, biological activities and applications of metal complexes. Coordination chemistry comprises of many sub-areas such as macrocyclic chemistry, Schiff base chemistry and others. The area of research including macrocyclic ligands, their metal complexes and applications in various aspects of life is called as macrocyclic chemistry. The area of macrocyclic chemistry has been fascinating to the researchers all over the world and this has prompted many researchers to get engaged actively in this area [1-3].

The synthesis of macrocyclic complexes is normally carried out using two methods. The first method is the traditional one in which solutions of ligands and metal salts are refluxed for appropriate time period to obtain the complexes. An alternative method is template method [4-5] in which the solutions of ligand forming components are reacted in presence of that of metal ions to form the complexes directly. Template method is useful when isolation of the ligand is not possible and has been widely used for synthesis of macrocyclic complexes.

Synthesis of macrocyclic complexes using condensation catalysts such as DMAP and DCC is reported [6-7]. Silica supported perchloric acid ($HClO_4$-SiO_2) has been used as an efficient heterogeneous catalyst for many organic transformations and condensation because of its low cost, ease of preparation in laboratory, catalyst recycling, and ease of handling [8-10]. Although few reports are available towards the synthesis of coordination complexes using silica supported perchloric acid as catalyst [11], the area is not exposed to a proper level and thus seems to be neglected. This has prompted us to undertake this study.

In present investigation we have reported silica supported perchloric acid ($HClO_4$:SiO_2) catalyzed synthesis of twelve tetraazamacrocyclic complexes of transition metals using chloride, nitrate and acetate salts of Co(II), NI(II), Cu(II) and Zn(II). The complexes were obtained by template condensation of ethylenediamine and glyoxal in

ethanolic medium using silica supported perchloric acid as catalyst ($HClO_4$-SiO_2) in the presence of above transition metal salts. Chandra et al. [12] have reported synthesis of macrocyclic complexes using condensation reaction of ethylenediamine and glyoxal in presence of chloride salts of transition metal ions using traditional reflux method. In that paper the time period required for completion of reaction was mentioned to be of 8-10 hours. Application of silica supported perchloric acid ($HClO_4$:SiO_2) catalyst for the synthesis has not only avoided the traditional reflux method, as the complexes are obtained by simple stirring of the solutions at room temperature, but also the reaction is completed within two hours. Thus we are able to reduce the reaction completion time up to a greater extent using this acid catalyst.

The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, IR, electronic, ^{1}H-NMR, Mass Spectra, TGA, and powder x-ray analysis**.** Based on the results obtained a six coordinated octahedral geometry has been proposed for all these complexes. The synthesized complexes were also screened for their antimicrobial activity.

EXPERIMENTAL SECTION

2.1 Chemicals

All the chemicals used in present study were of AR grade. Ethylenediamine, glyoxal and metal salts were procured from S. D. fine chemicals and Spectrochem Private Limited respectively. All the solvents used were distilled and dried using molecular sieves before use.

2.2 Analytical and physical measurements

Molar conductance values of all the synthesized complexes were measured by preparing 10^{-3} M solutions in DMSO solvent using Equiptronics conductivity meter with inbuilt magnetic stirrer (**Model Eq-664**) at room temperature. Magnetic susceptibilities were determined on the SES Instrument's magnetic susceptibility Gouy's balance (**Model EMU-50**) at room temperature using copper (II) sulphate as a standard. IR spectra were recorded as KBr pellets in the region of 4000-400 cm^{-1} on a Perkin Elmer Spectrophotometer. Electronic spectra were recorded in DMSO on a Shimadzu UV-1600 spectrophotometer.

^{1}H-NMR, mass spectra, TGA curve and powder x-ray diffractogram were recorded for some selected complexes as a sample study. Thus ^{1}H-NMR spectra (for Zn(II) chloride complex) was recorded on BRUKER AVANCE II 400 NMR Spectrometer using DMSO-d^6 (Spectroscopic grade) as a solvent. Chemical shifts are given in ppm relative to tetramethylsilane (TMS). Mass spectra (for Zn(II) nitrate complex) was recorded on Q-Tof-micro instrument. TGA curve (for Cu(II) chloride complex) was recorded using SDT- 2960 (TA instrument USA) and powder x-ray diffractogram (for Cu(II) chloride complex) was recorded using Xpert-pro XRD diffractometer.

2.3 Preparation of $HClO_4$-SiO_2 catalyst

The catalyst used in present investigation was prepared using procedure reported earlier [13-14] which can be given as follows. Seventy percent (70 %) aqueous perchloric acid (1.8 g, 12.5 mmol) was added to a suspension of SiO_2 (200–400 mesh, 23.7g) in ether (70 ml). The mixture was concentrated and the residue was heated at 100 ◦C for 72 h under vacuum to give HClO4–SiO2 (0.5 mmol/g) as free flowing powder.

2.4 Synthesis of complexes

The general procedure used for the synthesis of complexes can be given as below.

An ethanolic solution of dissolved metals salts (0.05 mol) was taken in a round bottom flask. To it was added ethylenediamine (0.10 mol) with constant stirring. Then silica supported perchloric acid ($HClO_4$-SiO_2) (10 mol %) was added as catalyst. The reaction was allowed to stir for 10 minutes. After 10 minutes glyoxal (0.10 mol) was added to the reaction mixture and then the reaction mixture was stirred at room temperature for 2 hours. The progress of reaction was checked by taking TLC in Chloroform-Methanol (90:10 %) solvent system after every 30 minutes. After two hours coloured solids were obtained, which were filtered and washed with acetone and dried with ether. The dried solid was then dissolved in 10 ml DMF/DMSO, the solid catalyst was filtered for recovery purpose. The filtrate was concentrated and the coloured complexes were obtained, which were then dried in air.

2.5 Antimicrobial activity

Antimicrobial activity of the synthesized complexes was screened using the disc diffusion method against selected pathogens such as *Bacillus Subtilis (*MTCC- 8979), *Escherichia coli* (MTCC- 443), *Candida albicans (MTCC*-227). Complexes were dissolved in DMSO and sterilized by filtering through 0.45 µm millipore filter. Nutrient agar NA (antibacterial activity) and potato dextrose agar medium PDA (antifungal activity) was prepared and sterilized by an autoclave and transferred to previously sterilized petri plates. After solidification, petri plates were inoculated with bacterial organisms in sterile nutrient agar medium at 45^{o}C and fungal organism in sterile potato dextrose agar

medium at 45°C in aseptic condition. Sterile Whatmann filter paper discs were impregnated with synthesized compounds at a concentration of 1 mg/disc was placed in the organism-impregnated petri plates under sterile condition. Standard antibiotic discs of streptomycin (100 µg/disc) and Amphotericin B (100 µg/disc) were used as positive control, while DMSO was used as negative control. Then the plates were incubated for 24 h at 37 ± 1°C for antibacterial activity and 48 h at 37 ± 1°C for antifungal activity. The zone of inhibition was calculated by measuring the minimum dimension of the zone of no microbial growth around the disc [15].

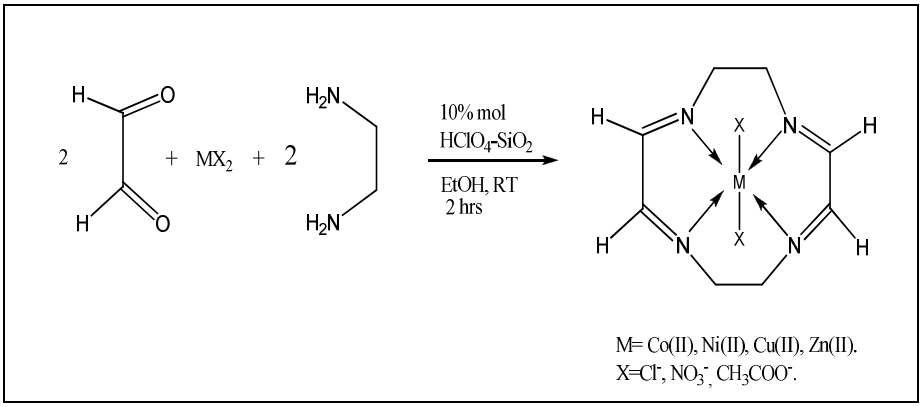

Fig. 1. Synthesis of tetraazamacrocyclic complexes

RESULTS AND DISCUSSION

The general composition of the synthesized tetraazamacrocyclic metal complexes can be represented as $[M(C_8H_{12}N_4)Cl_2]$ for chloride, $[M(C_8H_{12}N_6O_6)]$ for nitrate and $[M(C_{10}H_{18}O_4N_4)]$ for acetate salts, where M = Co(II), Ni(II), Cu(II) and Zn(II).

3.1 Physicochemical data

All the synthesized complexes were thermally stable and colored. Observations such as color, melting point, percentage yield etc. for all the synthesized complexes were recorded. The physicochemical data recorded for all the synthesized macrocyclic complexes is represented in Table 1.

3.2 Solubility behaviour

Solubility behaviour of all the synthesized complexes was checked using different solvents such as methanol, ethanol, chloroform, DCM, acetone, ethyl acetate, water, DMSO and DMF. The complexes were found to be partially soluble in water, methanol and ethanol, completely soluble in DMSO and DMF whereas in remaining solvents they were found to be insoluble.

Table 1. Physicochemical data of all the synthesized tetraazamacrocyclic complexes

Molecular formula	Calculated Molecular Weight /gms	Colour	Melting Point /°C	Percentage Yield /%
$C_8H_{12}Cl_2CoN_4$	292.98	Red	>250	60
$C_8H_{12}Cl_2NiN_4$	291.98	Light green	>250	64
$C_8H_{12}Cl_2CuN_4$	296.97	Green	>250	62
$C_8H_{12}Cl_2Zn\ N_4$	297.97	Light brown	>250	63
$C_8H_{12}N_6O_6Co$	347.15	Light red	>250	61
$C_8H_{12}N_6O_6Ni$	346.91	Faint green	>250	68
$C_8H_{12}N_6O_6Cu$	351.76	Green	>250	66
$C_8H_{12}N_6O_6Zn$	353.63	Faint yellow	>250	61
$C_{10}H_{18}O_4\ N_4Co$	317.21	Light red	>250	62
$C_{10}H_{18}O_4\ N_4Ni$	316.07	Faint green	>250	65
$C_{10}H_{18}O_4\ N_4Cu$	321.82	Green	>250	67
$C_{10}H_{18}O_4\ N_4Zn$	323.68	Light brown	>250	64

3.3 IR spectra

IR spectra for all the synthesized macrocyclic complexes were recorded as KBr pellets in the region 4000-400 cm^{-1}. Table 2 given below represents the results obtained from IR spectra of all the synthesized complexes.

IR spectra of ethylenediamine and glyoxal were compared with those of complexes. In the spectra of ethylenediamine a pair of bands with medium intensity was observed at 3230-3260 cm^{-1}, which corresponds to free amine groups (NH_2) in ethylenediamine. A strong peak observed at 1700 cm^{-1} in the spectrum of glyoxal may be

attributed to >CO groups in this compound. It is clear that absence of peaks for free (NH_2) and >C=O groups in the spectra of synthesized complexes indicate towards condensation of carbonyl group of glyoxal with amine group of ethylenediamine [16].

Table 2. IR spectral data recorded of all the synthesized tetraazamacrocyclic complexes

Complexes	ν(C-H)/cm^{-1}	ν (C=N)/ cm^{-1}	ν (C-N)/cm^{-1}	ν (M-N)/cm^{-1}
$C_8H_{12}Cl_2CoN_4$	2939	1583	1364	470
$C_8H_{12}Cl_2NiN_4$	2911	1571	1395	460
$C_8H_{12}Cl_2CuN_4$	2990	1602	1400	450
$C_8H_{12}Cl_2Zn\ N_4$	3000	1595	1397	442
$C_8H_{12}N_6O_6Co$	2917	1582	1374	450
$C_8H_{12}N_6O_6Ni$	2935	1585	1379	435
$C_8H_{12}N_6O_6Cu$	2912	1591	1400	445
$C_8H_{12}N_6O_6Zn$	3135	1594	1399	437
$C_{10}H_{18}O_4\ N_4\ Co$	2928	1583	1364	440
$C_{10}H_{18}O_4\ N_4\ Ni$	3138	1592	1400	441
$C_{10}H_{18}O_4\ N_4\ Cu$	2936	1585	1379	440
$C_{10}H_{18}O_4\ N_4\ Zn$	3169	1595	1397	442

Appearance of new strong band in the range 1570-1610 cm^{-1} in the spectra of complexes may be attributed to (C=N). This peak helps to confirm the formation of azomethine group in complexes and condensation of glyoxal with amino group of ethylenediamine [17]. The medium intensity band present at 1400-1050 cm^{-1} in the spectra of complexes may be assigned to (C-N) vibration. Bands present at 2900-3150 cm^{-1} may be assigned due to the various (C-H) vibrations [1]. The band observed in the region 430-470 cm^{-1} corresponds to (M-N) vibrations in all the complexes [16]. The coordinated nitrate and acetate are coordinating to metal at 1300-1500 cm^{-1} and 1000-1350 cm^{-1} respectively in unidentate manner [18-19].

3.4 Electronic spectra

Electronic spectra for all the synthesized macrocyclic complexes were recorded in DMSO. The electronic spectra of Co(II) complexes exhibit bands at 689-700 nm and 450-490 nm which can be assigned to $^4T_1g \rightarrow {}^4A_2g$ (F) and $^4T_1g \rightarrow {}^4T_2g$ (P) transitions. This supports to octahedral geometry of Co(II) complexes [20].

The electronic spectra of Ni (II) complexes exhibited a well discernable band with shoulder on the low energy side. There are three bands observed out of two bands are in the region 930-960 nm and 600-620 nm which can be assigned to $^3A_2g \rightarrow {}^3T_1g$ (F) and $^3A_2g \rightarrow {}^3T_1g$ (P) transitions respectively. Other band observed at 395-410 nm may be assigned to LMCT transition. The observed data supports to an distorted octahedral geometry for Ni(II) complexes [21]. The electronic spectra of Cu(II) complexes exhibited two absorption bands at 980-990 nm and 530-550 nm which may be assigned to $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2B_2g$ respectively and third band observed at 360-390 nm may be due to the charge transfer. On the basis of observed data Cu(II) complexes are having distorted octahedral geometry [22-23]. Zn(II) complexes show absorption band at 360-450 nm attributed to the LMCT transition which is compatible with this complexes having octahedral geometry [24-25].

3.5 Magnetic properties

Magnetic moments for all the synthesized complexes were recorded at room temperature using copper (II) sulphate as standard. The magnetic moment values for Co(II) complexes are in the range 4.90-4.98 BM which corresponds to three unpaired electrons. The magnetic moment values recorded for Ni(II) complexes are in the range 2.85-2.90 BM which indicates presence of two unpaired electrons in the complexes. The magnetic moment values for Cu(II) complexes are in the range 1.80-1.90 BM which corresponds to one unpaired electron in the complexes [23]. The Zn(II) complexes are diamagnetic in nature consistent with (d^{10}) configuration of Zn in complexes [26].

3.6 Molar conductance

On the basis of solubility behaviour observed molar conductance values for all the synthesized complexes were measured by preparing 10^{-3} M solutions in DMSO as a solvent. The observed molar conductance values (10-25 $ohm^{-1}\ cm^{-2}\ mol^{-1}$) for complexes with divalent metal ions indicate towards their non-electrolytic behavior [27-28].

Table 3 given below represents results obtained from electronic spectra, magnetic properties and molar conductance studies for all the synthesized macrocyclic complexes.

3.7 ^{1}H-NMR Spectra

The ^{1}H-NMR spectrum for Zn (II) chloride complex was recorded as a sample for the study. The spectrum was recorded in DMSO-d^6 as a solvent against tetramethylsilane (TMS) as a standard.

The spectrum obtained showed presence of two singlet peaks. The singlet peak observed at 2.38 ppm may be attributed to the methyne proton (N-CH-CH-N) and at 3.30 ppm may be due to methylene (N-CH_2-CH_2-N) protons of macrocyclic skeleton respectively [29-30].

Table 3. Electronic spectral data and molar conductance and magnetic moment values recorded for all the synthesized tetraazamacrocyclic complexes

Complexes	Absorbance (nm)	Assignment	Molar conductance ($ohm^{-1}cm^2\,mol^{-1}$)	Magnetic moments μ_{eff} (BM)
$C_8H_{12}Cl_2CoN_4$	690 450	$^4T_1g\rightarrow{}^4A_2g$ (F) $^4T_1g\rightarrow{}^4T_2g$ (P)	19	4.90
$C_8H_{12}Cl_2NiN_4$	938 602 406	$^3A_2g\rightarrow{}^3T_1g$ (F)(ν_1) $^3A_2g\rightarrow{}^3T_1g$(P) ($\nu_2$) LMCT	14	2.85
$C_8H_{12}Cl_2CuN_4$	983 539 390	$^2B_1g\rightarrow{}^2A_1g$ $^2B_1g\rightarrow{}^2B_2g$ LMCT	24	1.80
$C_8H_{12}Cl_2ZnN_4$	450	LMCT	13	Diamagnetic
$C_8H_{12}N_6O_6Co$	689 480	$^4T_1g\rightarrow{}^4A_2g$ (F) $^4T_1g\rightarrow{}^4T_2g$ (P)	15	4.98
$C_8H_{12}N_6O_6Ni$	935 600 405	$^3A_2g\rightarrow{}^3T_1g$ (F)(ν_1) $^3A_2g\rightarrow{}^3T_1g$ (P) (ν_2) LMCT	17	2.92
$C_8H_{12}N_6O_6Cu$	980 540 360	$^2B_1g\rightarrow{}^2A_1g$ $^2B_1g\rightarrow{}^2B_2g$ d→d	20	1.90
$C_8H_{12}N_6O_6Zn$	360	LMCT	22	Diamagnetic
$C_{10}H_{18}O_4N_4Co$	690 487	$^4T_1g\rightarrow{}^4A_2g$ (F) $^4T_1g\rightarrow{}^4T_2g$ (P)	15	4.90
$C_{10}H_{18}O_4N_4Ni$	930 600 395	$^3A_2g\rightarrow{}^3T_1g$ (F)(ν_1) $^3A_2g\rightarrow{}^3T_1g$ (P) (ν_2) LMCT	14	2.92
$C_{10}H_{18}O_4N_4Cu$	985 545 380	$^2B_1g\rightarrow{}^2A_1g$ $^2B_1g\rightarrow{}^2B_2g$ d→d	13	1.84
$C_{10}H_{18}O_4N_4Zn$	410	LMCT	17	Diamagnetic

3.8 Mass spectra

The mass spectrum for macrocyclic complex of Zn (II) nitrate was recorded as a sample to confirm calculated molecular weights and hence to support formation of macrocyclic complexes. The mass spectrum of Zn (II) nitrate complex has shown a molecular ion peak at m/z = 353 a.m.u. as (M^{-1}). On comparison the recorded mass spectrum confirmed molecular formula and calculated molecular weight of Zn (II) nitrate complex.

3.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of Cu(II) chloride complex was done as a sample and was used to determine the decomposition temperature. The TGA curve was recorded in the temperature range of 10 to 500 ^oC. The TGA curve recorded for Cu(II) chloride complex showed first step of decomposition in the range 30-160 ^oC with a mass loss of 7.15 % (Calculated 7.14 %). This weight loss may be attributed to decomposition of lattice water [13].

The second step of decomposition is observed in the range 200-425 ^oC with a mass loss of 34.35 % (Calculated 34.33 %). This weight loss may be attributed to decomposition of coordinated Chlorine and ligand.

The third step of decomposition is observed in the range 430-500 ^oC with a mass loss of 56.71 % (Calculated 56.70 %) attributed to decomposition of final Copper residue [31]. Table 4 given below represents results obtained from TGA recorded for Cu(II) chloride complex.

Table 4. TGA data recorded for synthesized Cu(II) complex as a sample

Complex	Temperature range /^oC	Percentage Weight Loss /%		Decomposition Product
		Observed	Calculated	
$C_8H_{12}Cl_2CuN$	30-160	7.15	7.14	Lattice water
	200-425	34.35	34.33	Chloride ion coordinated and organic ligand
	436-500	56.71	56.70	CuO residue

3.10 X-ray Powder Diffraction Analysis

The X-ray powder diffraction study was done for Cu(II) chloride complex as a sample for study. The X-ray diffractogram was scanned in the range 5-85º at wavelength 1.54060 Aº. The diffractogram and associated data depict 2 theta values for each peak, relative intensity and inter-planar spacing (d-values).

The x-ray diffraction pattern with respect to major peaks having relative intensities greater than 10 % have been indexed using computer programme. The above indexing method also yields miller indices (h k l), unit cell parameter and unit cell volume.

The unit cell of Cu(II) chloride complex yielded lattice constant values a= 15.34005 Å, b= 8.60931 Å, C = 3.63692 Å are in concurrence with these cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \beta = \gamma$ required for sample to be orthorhombic system were tested and found to be satisfactory [11, 32-33]. Hence it can be concluded that the Cu(II) chloride complex is orthorhombic.

3.11 Antimicrobial activity

All the synthesized complexes were screened for their antibacterial and antifungal activities against *Bacillus Subtilis*, *Escherichia coli*, *Candida albicans.* A zone of inhibition of all the synthesized macrocyclic complexes was measured and compared with standard antibiotic drugs streptomycin and Amphotericin B. The results obtained from antimicrobial screening of all the synthesized complexes are represented in Table 5.

Table 5. Antibacterial and antifungal activity of all the synthesized tetraazamacrocyclic complexes

Complexes	Zone of inhibition/mm, conc. (mg/ml)		
	Bacillus Subtilis MTCC-8979	*Escherichia Coli* MTCC-443	*Candida albicans* MTCC-227
$C_8H_{12}Cl_2CoN_4$	28	18	22
$C_8H_{12}Cl_2NiN_4$	10	---	20
$C_8H_{12}Cl_2CuN_4$	12	09	15
$C_8H_{12}Cl_2Zn\ N_4$	27	13	13
$C_8H_{12}N_6O_6Co$	27	22	14
$C_8H_{12}N_6O_6Ni$	10	08	18
$C_8H_{12}N_6O_6Cu$	12	10	----
$C_8H_{12}N_6O_6Zn$	24	10	10
$C_{10}H_{18}O_4\ N_4\ Co$	26	20	12
$C_{10}H_{18}O_4\ N_4\ Ni$	10	10	22
$C_{10}H_{18}O_4\ N_4\ Cu$	---	10	----
$C_{10}H_{18}O_4\ N_4\ Zn$	21	12	10
Streptomycin	30	31	----
Amphotericin B	----	----	29
DMSO	-----	-----	-----

**Activity 15-28 = Significant, activity, 8-14 = medium, ---- No activity*

The standard used for antibacterial study streptomycin have shown zone of inhibition of 30 and 31 mm against *Bacillus Subtilis*, *Escherichia coli*. Macrocyclic complexes of Co(II) and Zn(II) showed significant activity in the range of 21-28 mm against *Bacillus Subtilis*. while Ni(II) and Cu(II) complexes showed moderate activity in the range of 10-12 mm compared with that of the standard. Cu(II) acetate complex did not show any activity in this case. In case of *Escherichia coli* only Co(II) complexes showed significant activity in the range 18-22 mm while remaining complexes show less activity in the range 08-12 mm. Ni(II) chloride complex did not showed any activity.

The standard used for antifungal study Amphotericin B have shown zone of inhibition of 29 mm against *Candida albicans.* Synthesized complexes of Co(II) chloride, Ni(II) chloride, Ni(II) nitrate and Ni(II) acetate showed significant activities in the range of 18-22 mm compared with that of standard. Whereas out of remaining complexes, those of Co(II) nitrate, Co(II) acetate, Cu(II) chloride, Zn(II) chloride, Zn(II) nitrate and Zn(II) acetate showed moderate activity in the range of 10-15 mm compared with that of standard. The Cu(II) nitrate and Cu(II) acetate complexes did not show any activity. DMSO has no zone of inhibition.

CONCLUSION

Silica supported perchloric acid was used as efficient catalyst for the synthesis of twelve tetraazamacrocyclic complexes transition metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) using template condensation of ethylenediamine and glyoxal. The catalyst was found to be effective in reducing the time period for completion of reaction to an appreciable extent. Additionally the method used here avoided the traditional reflux method for complex synthesis and the complexes are obtained at room temperature by simple stirring of the solutions of

reacting components. Based on the results obtained a six coordinated octahedral geometry has been proposed for all these complexes.

Acknowledgement
Authors are also thankful to Director, SAIF, Punjab University Chandigarh for providing spectral data.

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