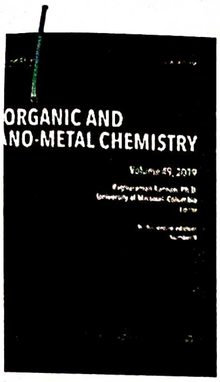

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# Facile one pot synthesis of tetraamide macrocyclic complexes using malonyldihydrazide and p-nitrobenzaldehyde at room temperature

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**ABSTRACT**

Facile one pot synthesis of a series of seven tetraamide macrocyclic complexes of first row transition metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) is carried out using malonyldihydrazide and p-nitrobenzaldehyde at room temperature using template method. The characterization and structure determination of synthesized complexes was carried out using various analytical techniques such as melting point determination, IR, UV/Visible, $^1$H NMR, Mass spectra, magnetic susceptibility and molar conductance measurements. The results obtained indicated towards the presence of an octahedral geometry of the complexes. The synthesized complexes were screened for their antibacterial activities.

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Tetraamide; macrocyclic; malonyldihydrazide; p-nitrobenzaldehyde; octahedral; antibacterial

## Introduction

Macrocyclic chemistry deals with synthesis of macrocyclic ligands, complexes and their applications in various fields of life. Synthesis and characterization of macrocyclic complexes including nitrogen donor macrocyclic ligands is a vastly explored area which includes variety of complexes such as those with polyaza, cyclidenes, porphyrins and bis-macrocyclic ligands.[1] The area of research including synthesis and characterization of tetraamide macrocyclic complexes is special owing to the presence of two possible donor atoms nitrogen and oxygen in amide group.[2] It has been established that macrocyclic complexes including amide groups possess the structural features of both macrocyclic tetraamines and oligopeptides and can stabilize higher oxidation states of the metal ions.[3–4] These observations have prompted us to undertake present study. Hence in present paper, we report facile one pot synthesis of a series of seven tetraamide macrocyclic complexes of first row transition metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) using malonyldihydrazide and p-nitrobenzaldehyde using template method. The complexes are obtained by room temperature stirring of the complex forming components for 10–12 hours. Thus we have successfully avoided the routine and traditional reflux method for synthesis of complexes.

The synthesized complexes were characterized using molar conductance, magnetic susceptibility measurements, IR and electronic spectra. $^1$H-NMR and mass spectra were recorded for some selected complexes as a sample study. Based on the results obtained all these complexes were assigned a six coordinated octahedral geometry. All the synthesized complexes were also screened for their antibacterial activities against bacterial pathogens such as *E. coli* and *S. aureus*.

## Results and discussion

The general composition of synthesized macrocyclic complexes can be represented as $[M(C_{20}H_{22}N_{10}O_8)X_2]$ for divalent metal ions [where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] and $\{[M(C_{20}H_{22}N_{10}O_8)X_2].X\}$ for trivalent metal ions [where M = Cr(III), Fe(III)] and $X = Cl^-$ in both the cases.

### Physical properties and solubility criteria

Physical properties such as color and melting points were recorded for all the synthesized complexes. The complexes showed variety of colors. Melting point values recorded were in the range 180–300 °C indicating towards thermal stability of the synthesized complexes. Solubility behavior of all the synthesized macrocyclic complexes was checked using different solvents such as water (WT), methanol (MT), ethanol (ET), chloroform (CL), dichloromethane (DCM), acetone (AC), ethyl acetate (EA), dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF). The complexes were found to be completely soluble in DMSO and DMF whereas in remaining solvents they were found to be insoluble (Table 1).

### IR spectral analysis

IR spectra for all the synthesized tetraamide macrocyclic complexes were recorded as KBr pellets in the region

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Table 1. Physical properties recorded for all the synthesized tetraamide macrocyclic complexes.

| Proposed Molecular formula | Calculated Molecular Weight, (gms) | Color | Melting Point, (°C) | Percentage Yield, (gms, %) |
|---|---|---|---|---|
| $C_{20}H_{22}N_{10}O_8CrCl_3$ | 688.50 | Green | 230 | 63 |
| $C_{20}H_{22}N_{10}O_8MnCl_2$ | 655.94 | White | 244 | 70 |
| $C_{20}H_{22}N_{10}O_8FeCl_3$ | 692.35 | Gray | 295 | 69 |
| $C_{20}H_{22}N_{10}O_8CoCl_2$ | 659.93 | Pink | 242 | 64 |
| $C_{20}H_{22}N_{10}O_8NiCl_2$ | 659.69 | Yellow | 238 | 65 |
| $C_{20}H_{22}N_{10}O_8CuCl_2$ | 664.55 | Blue | 220 | 66 |
| $C_{20}H_{22}N_{10}O_8ZnCl_2$ | 666.39 | White | 182 | 62 |

Table 2. IR spectral data (in $cm^{-1}$) recorded for all the synthesized tetraamide macrocyclic complexes.

| Complexes | $\nu$(&Nu;-H) | Amide I band $\nu$(C=O) | Amide II band $\nu$(N-H) bending | $\nu$(M-N) |
|---|---|---|---|---|
| $C_{20}H_{22}N_{10}O_8CrCl_3$ | 3190-3420 | 1681.6 | 1515.7 | 445.3 |
| $C_{20}H_{22}N_{10}O_8MnCl_2$ | 3190-3425 | 1680.0 | 1517.3 | 445.2 |
| $C_{20}H_{22}N_{10}O_8FeCl_3$ | 3190-3450 | 1681.6 | 1515.1 | 446.4 |
| $C_{20}H_{22}N_{10}O_8CoCl_2$ | 3190-3440 | 1681.1 | 1516.13 | 446.4 |
| $C_{20}H_{22}N_{10}O_8NiCl_2$ | 3191-3421 | 1680.2 | 1516.6 | 444.3 |
| $C_{20}H_{22}N_{10}O_8CuCl_2$ | 3175-3415 | 1682.1 | 1515.1 | 446.4 |
| $C_{20}H_{22}N_{10}O_8ZnCl_2$ | 3190-3450 | 1681.0 | 1516.9 | 445.4 |

4000–400 $cm^{-1}$. The presence of absorption bands in the range 3150–3500 $cm^{-1}$ in IR spectra of all the complexes can be assigned due to $\nu$(N-H) vibrations.[5] The carbonyl absorption of amide (i.e. amide I band) was observed around 1680 $cm^{-1}$ in the IR spectra of all the complexes. The amide II band which is due to $\nu$(N-H) bending was observed around 1515 $cm^{-1}$ in the IR spectra of complexes.[5]

The position of the band arising due to coordination of amide group to the metal through nitrogen does not seem to be fixed. Researchers have reported different values[6–9] for this band ranging from 300–600 $cm^{-1}$. In present investigation the band observed around 445 $cm^{-1}$ can be assigned due to $\nu$(M-N) vibrations. Presence of $\nu$(M-Cl) band in the spectra of complexes is usually reported below 400 $cm^{-1}$ region.[10–11] The said region was not scanned for present investigation. Table 2 given below represents the results obtained from IR spectra.

### Electronic spectra analysis

Electronic spectra of all the synthesized complexes were recorded in DMF solvent and the spectra are interpreted in terms d-d transitions present.

Cr(III) complex with $d^3$ configuration is expected to show three spin allowed transitions.[12–14] The recorded spectrum of Cr(III) complex exhibited a band at 440 nm which can be assigned to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ $(\upsilon_2)$ transition, which supports to an octahedral geometry of the complex. Sharma et al.[15] and Namboori et al.[16] have confirmed the presence of similar band in the range 425–476 nm and at 457 nm respectively.

Mn(II) and Fe(III) both are having $d^5$ configuration of metal ion in the complex. Such complexes are unique, as there are no allowed (Either spin allowed or Lapporte allowed) transitions possible theoretically, still weak intensity bands are observed practically in the spectra of such complexes which can be explained according to the relaxation rules.[12–14] The spectrum of Mn(II) complex exhibited bands at 430 and 550 nm which can be assigned to $^6A_{1g} \rightarrow {}^4E_g$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) respectively indicating towards presence of octahedral geometry. Chandra et al.[17] have confirmed the presence of similar transitions in the range 442–444 nm and 537–544 nm. Similarly the spectrum recorded for Fe(III) complex exhibited a band at 500 nm which can be assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) and supports to octahedral geometry of the complex. Sharma et al.[15] and Chitra et al.[18] have confirmed the presence of similar transitions in the range 497–516 nm and 477–498 nm.

Co(II) and Ni(II) with $d^7$ and $d^8$ electronic configurations are expected to show the presence of three spin allowed transitions in their electronic spectrum but while recording spectra one or two bands are found to be absent in few cases.[12–14] In present investigation the spectrum of Co(II) complex exhibited a band at 430 nm which can be assigned to $^4T_1g \rightarrow {}^4A_2g$ transition which supports to octahedral geometry of the Co(II) complex. Presence of similar band was confirmed by Omar Nasman[19] in range 451–457 nm. The spectrum recorded for Ni(II) complex exhibited a band at 445 nm which can be assigned to $^3A_2g \rightarrow {}^3T_1g$ (P) transition and supports to octahedral geometry for Ni(II) complex. Ushma Joshi[20] also confirmed the presence of similar band at 443 nm.

The presence of single band is expected in an electronic spectrum of octahedral complex with $d^9$ metal ion configuration such as Cu(II).[12–14] The spectrum of Cu(II) complex exhibited a band at 660 nm which may be assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition and supports to octahedral geometry for Cu(II) complex. The presence of similar band at 642 nm was confirmed by Rafat et al.[21] The complex with $d^{10}$ electronic configuration has no scope for the presence of d-d bands as there is no scope for electronic transition. Since Zn(II) represents $d^{10}$ system, no d-d band was observed for Zn(II) complex.

### Magnetic nature

Understanding magnetic nature of complexes helps researchers to find out number of unpaired electrons present, to

Table 3. Electronic spectra, molar conductance and magnetic moments recorded for all the synthesized tetraamide macrocyclic complexes.

| Complexes | Absorbance, (nm) | Assignment | Molar conductance, (ohm$^{-1}$cm$^{2}$ mol$^{-1}$) | Magnetic moments ($\mu_{eff}$), (BM) |
|---|---|---|---|---|
| $C_{20}H_{22}N_{10}O_8CrCl_3$ | 440 | $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ | 55 | 4.20 |
| $C_{20}H_{22}N_{10}O_8MnCl_2$ | 430<br>550 | $^6A_{1g} \rightarrow {}^4E_g$<br>$^6A_{1g} \rightarrow {}^4T_{2g}$ (G) | 19 | 5.86 |
| $C_{20}H_{22}N_{10}O_8FeCl_3$ | 500 | $^6A_{1g} \rightarrow {}^4T_{2g}$ | 67 | 6.06 |
| $C_{20}H_{22}N_{10}O_8CoCl_2$ | 430 | $^4T_{1g} \rightarrow {}^4A_{2g}$ | 18 | 4.94 |
| $C_{20}H_{22}N_{10}O_8NiCl_2$ | 445 | $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ | 22 | 2.98 |
| $C_{20}H_{22}N_{10}O_8CuCl_2$ | 660 | $^2E_g \rightarrow {}^2T_{2g}$ | 20 | 1.88 |
| $C_{20}H_{22}N_{10}O_8ZnCl_2$ | —— | —— | 13 | Diamagnetic |

judge possible electronic arrangement and to shed some light on the geometry of complex. This is achieved by comparing the observed magnetic susceptibility values with those predicted theoretically. In present investigation magnetic susceptibility values for all the synthesized complexes were recorded at room temperature using copper(II) sulfate as an internal standard.

A magnetic moment value of 4.20 μB was observed for Cr(III) complex which corresponds to the presence of three unpaired electrons in the complex. The observed value supports to the octahedral geometry of the complex.[12,22] Magnetic moment values of 5.86 and 6.06 μB respectively were observed for Mn(II) and Fe(III) complexes which indicated towards high spin nature of these complexes and presence of five unpaired electrons. This observation confirms the octahedral geometry of these complexes.[12,22]

The magnetic susceptibility values of 4.94, 2.98 and 1.88 μB were recorded for Co(II), Ni(II) and Cu(II) complexes respectively which correspond to the presence of three, two and one unpaired electrons in these complexes.[12,22] The observed values represent towards octahedral geometry of these complexes. The Zn(II) complex was found to be diamagnetic in nature consistent with ($d^{10}$) configuration of Zn in complexes.[12,22]

### Molar conductance measurements

Molar conductance measurements help to find out electrolytic nature of the complexes and hence to identify the other ions (other than ligand molecules) included in the coordination sphere. Molar conductance values were measured by preparing $10^{-3}$ M solutions of synthesized complexes in DMF as a solvent. The observed molar conductance values (13–22 ohm$^{-1}$ cm$^{-2}$ mol$^{-1}$) for complexes with divalent metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) indicate towards their non-electrolytic behavior.[23] Whereas the molar conductance values (55 and 67 ohm$^{-1}$ cm$^{-2}$ mol$^{-1}$) recorded for complexes with trivalent metal ions Cr(III) and Fe(III) indicate towards their 1:1 electrolytic behavior.[24]

The results obtained from electronic spectra analysis, magnetic susceptibility and molar conductance measurements are represented in Table 3.

### $^1$H NMR analysis

$^1$H NMR analysis helps to confirm the protonic arrangement present in the complex and in confirming structure of the complex. In present investigation $^1$H-NMR spectra were recorded for Ni(II), Cu(II) and Zn(II) complexes. The spectra were recorded in DMSO-d$^6$ as a solvent against tetramethylsilane (TMS) as a standard.

The $^1$H-NMR spectra recorded showed five to six major peaks. A singlet peak for four protons observed in the range of 1.90–2.20 ppm can be assigned to -NH- protons close to aromatic ring. Another singlet peak for four protons observed at 3.70 ppm for all complexes can be assigned to –CH$_2$- group coming from malonyldihydrazide moiety. The singlet peak for two protons observed at 4.00 ppm can be assigned to –CH- group present on the ring close to –NH- groups and coming from the aldehyde groups. The two doublet peaks observed for four protons each in the range of 7.78–7.87 and 8.08-8.15 ppm can be assigned to aromatic protons present on the ring. Finally the singlet peak observed for four protons at 11.70 ppm can be assigned for –NH- protons of amide groups which are coordinated to the metal and hence deshielded.

### Mass spectral analysis

Mass spectral analysis confirms calculated molecular weights of complexes and hence support in confirmation of formation of complexes. In present investigation mass spectrum was recorded for Co(II) complex. The spectrum recorded has shown a molecular ion peak at $m/z = 661$ a.m.u. as $(M+1)$ which confirmed molecular formula and calculated molecular weight of Co(II) chloride complex. The observation recorded thus confirmed the formation of Co(II) chloride complex and the same can be understood for remaining complexes.

### Antibacterial activity measurements

A zone of inhibition was measured for each synthesized complex and compared with standard antibiotic drug penicillin g. A zone of inhibition of 13 and 15 mm against *E. coli* and *S. aureus* respectively was observed in case of standard used (penicillin g). The complexes of Co(II), Zn(II) and Fe(III) have shown zone of inhibition values of 17, 14 and 13 mm against *E. coli* indicating significant activity. Values of 12, 11, 11 and 10 mm were recorded for Cu(II), Mn(II), Ni(II) and Cr(III) complexes indicate presence of moderate activity against *E. coli*.

Zone of inhibition values of 15, 14 and 14 mm were recorded for complexes of Fe(III), Cr(III) and Cu(II)

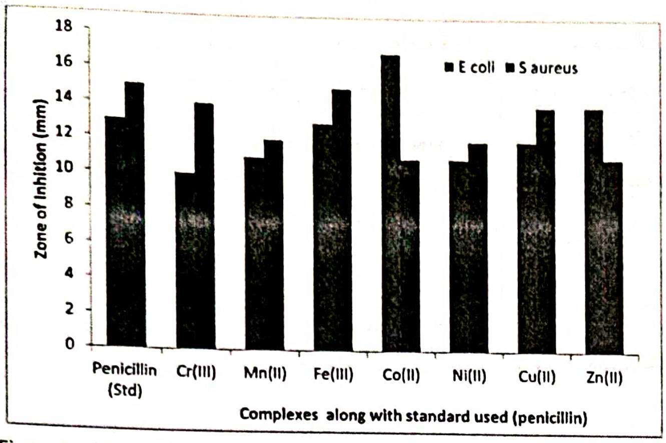

**Figure 1.** Graphical representation of antibacterial activity recorded for all the synthesized complexes against *E. coli* and *S. aureus*.

complexes respectively against *S. aureus* indicated significant activity. Mn(II), Ni(II) (12 mm each) and Co(II), Zn(II) ([illegible] mm each) complexes showed moderate activity against *S. aureus*. The results obtained from antibacterial screening of all the synthesized complexes are represented graphically as follows (Figure 1).

The results clearly indicated that the zone of inhibition area is greater for the metal complexes than the standard. Such increase in antibacterial activity can be explained based on combined activity effect of the metal and ligand. The increased activity of the metal chelates can be explained on the basis of overtone's concept and chelation theory.[25] Similar results were reported by Rajavel et al.[26] and Chandra et al.[27]

## Experimental

Diethyl malonate, hydrazine hydrate, p-nitrobenzaldehyde and transition metal salts were procured from S. D. fine chemicals and Spectrochem Private Limited respectively. All the chemicals used in present study were of AR grade. All [illegible] solvents used were distilled and dried using molecular sieves before use.

Melting points for all the synthesized complexes were recorded using open glass capillary method in the laboratory. IR spectral (Perkin Elmer, KBR pellets, 4000–400 cm$^{-1}$) analysis was used to obtain information about chemical bonds and functional groups present in synthesized complexes. UV/Visible (Shimadzu, UV 1600 spectrophotometer) spectral analysis was used to study electronic transitions present in the synthesized complexes. $^1$H-NMR spectra (Bruker Avance II 400 NMR) were recorded for Ni(II), Cu(II) and Zn(II) complexes to confirm the protonic arrangement in the synthesized complexes. Mass spectrum (Q-tof-micro instrument) was recorded of Co(II) complex to confirm the molecular weight of synthesized complex as a sample study. Magnetic susceptibility measurements (SES Instrument's Magnetic Susceptibility Guoy balance, Model EMU-50) were done to predict number of unpaired electrons present in the synthesized complexes and their magnetic nature. Molar conductance measurements (Equiptronics conductivity meter with an inbuilt magnetic stirrer, Model Eq-664) were used to check the electrolytic behavior of synthesized complexes.

### Preparation of malonyldihydrazide

Malonyldihydrazide was prepared using the procedure reported earlier,[28] which can be given as follows:

A methanolic solution of diethylmalonate (1.3213 g, 10 mmol) was taken in a round bottom flask. To it was added hydrazine hydrate (0.0641 g, 20 mmol) in methanol. The reaction mixture was refluxed for 8–10 hours. Progress of the reaction was checked by thin layer chromatographic technique using solvent system ethyl acetate (10%) + Pet ether (90%). After complete disappearance of starting material the reaction mixture was allowed to cool for one hour. After cooling for one hour white crystalline product was obtained. It was filtered, washed with methanol and recrystallized from ethanol. Melting point was checked. (Yield = 0.9909 g, 75%, M. P. = 152 °C) (Figure 2).

### Synthesis of tetraamide macrocyclic complexes

General procedure used for synthesis of complexes was as follows:

A methanolic solution of dissolved transition metal salts ($CrCl_3.6H_2O$-0.6660 g, $MnCl_2.4H_2O$-0.4948g, $FeCl_3.6H_2O$-0.6758 g, $CoCl_2.6H_2O$-0.5948 g, $NiCl_2.6H_2O$-0.5942 g, $CuCl_2.2H_2O$-0.4262 g and $ZnCl_2$-0.3407g, 2.5 mmol each) was taken in a round bottom flask and allowed to stir magnetically. Malonyldihydrazide (0.6605 g, 5 mmol) was dissolved in an appropriate quantity of methanol by warming and was added to the solution of transition metal salts with constant stirring. The resulting mixture was allowed to stir magnetically for 1 hour. After 1 hour methanolic solution of p-nitrobenzaldehyde (0.7566 g, 5 mmol) was added to the reaction mixture. The resultant mixture was then allowed to stir for additional 10 hours. The progress of reaction was checked by taking TLC in Chloroform-Methanol (90% + 10%) solvent system after every 30 minutes. After 10 hours the stirring was stopped. The obtained solid product was filtered off, washed with methanol, recrystallized in ethanol and dried in vacuo (Figure 3).

### Antibacterial activity measurements

Disc diffusion method was used for the screening of all the synthesized complexes against bacterial pathogens such as *E. coli* and *S. aureus*. Complexes were dissolved in DMSO and sterilized by filtering through 0.45 µm Millipore filter. Nutrient agar (NA) 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 NA medium at 45 °C. Sterile Whatmann filter paper discs impregnated with synthesized compounds at a concentration of 1 mg/disc was placed in the organism-impregnated Petri plates under sterile condition. Standard antibiotic disc of streptomycin (100 µg/disc) was used as positive control while DMSO was used as negative control. Then the plates were incubated for 24 h at

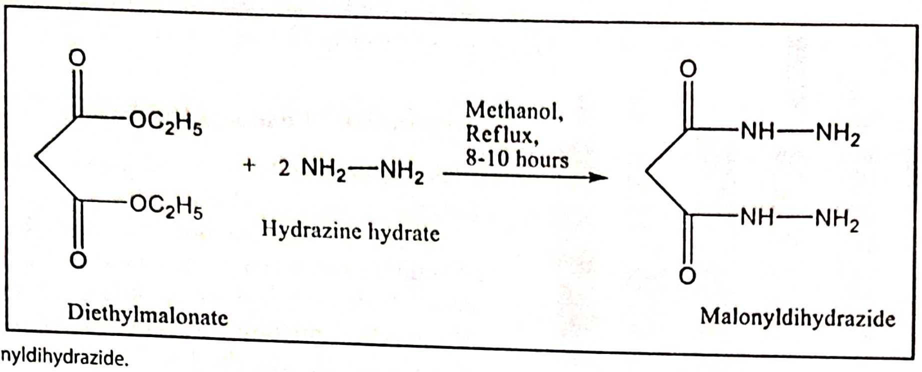

Figure 2. Synthesis of malonyldihydrazide.

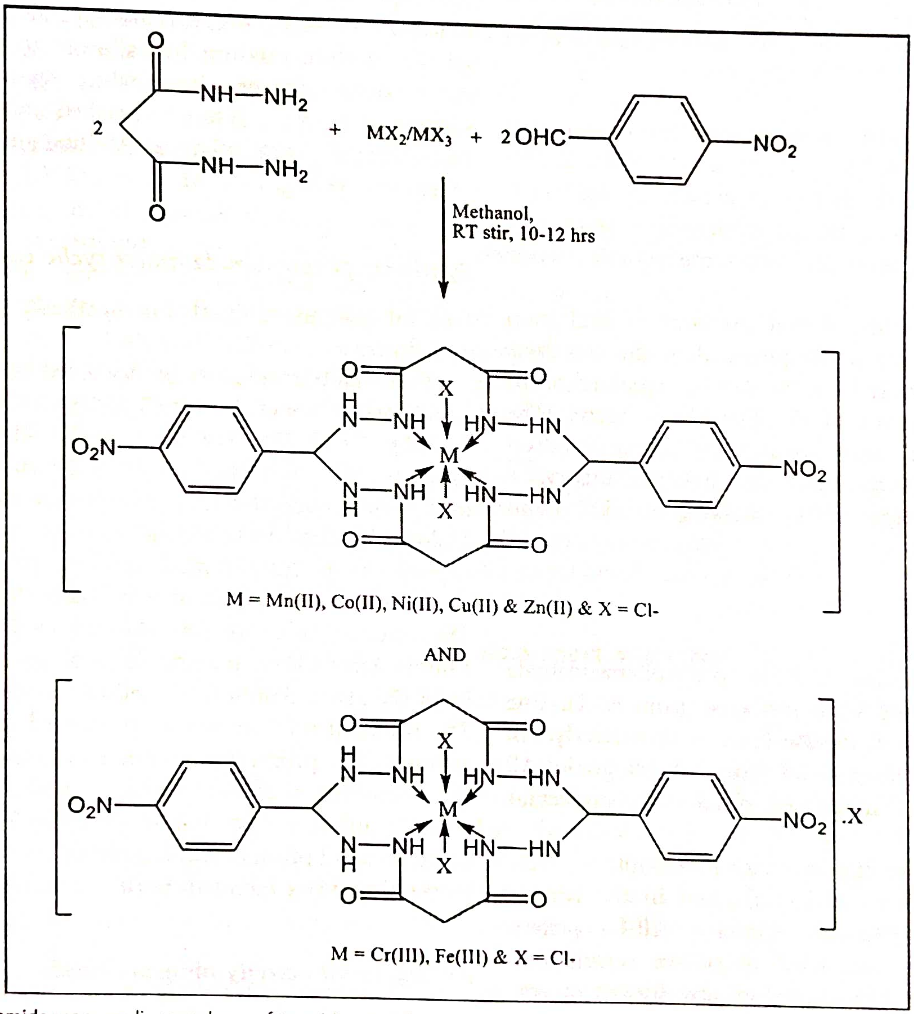

Figure 3. Synthesis of tetraamide macrocyclic complexes of transition metals using malonyldihydrazide and p-nitrobenzaldehyde.

37 ± 1 °C for antibacterial activity. The zone of inhibition was calculated by measuring the minimum dimension of the zone of no microbial growth around the disc.[29]

## Conclusion

A series of seven tetraamide macrocyclic complexes of first row transition metals have been synthesized using malonyldihydrazide and p-nitrobenzaldehyde by template method. The complexes were obtained at room temperature using simple stirring of methanolic solutions of complex forming components instead of the traditional reflux method. This can be considered to be an advantage as we have avoided the traditional reflux method successfully. Based on the results obtained all the complexes were proposed to have an octahedral geometry.

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