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Synthesis and Characterization of Quasi-Macrocyclic Complexes using Malonyldihydrazide, Phenyl hydrazine and p-Methylbenzaldehyde at Room Temperature.

Dnyaneshwar Shamrao Wankhede*, Navashaba Tazin, and Sandip Subhanrao Chavan.

Inorganic Chemistry Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded-4316006, Maharashtra State, India.

ABSTRACT

Room temperature synthesis of a novel series of seven quasi-macrocyclic complexes of transition metal ions such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) using malonyldihydrazide, phenyl hydrazine and p-Methylbenzaldehyde have been reported. The synthesized complexes were characterized using molar conductance, magnetic susceptibility measurements, IR, electronic, $^1\text{H-NMR}$ spectra. Based on the results obtained all these complexes were proposed to have an octahedral geometry. The complexes were also screened for their *in vitro* antibacterial activities.

Keywords: Malonyldihydrazide, molar conductance, magnetic susceptibility, octahedral, antibacterial

*Corresponding author

INTRODUCTION

Quasi-macrocyclic ligands, similar to macrocyclic, are involving three or more than three potential donor atoms but are half cyclic in nature. The complexes formed utilizing these ligands are called as quasi-macrocyclic complexes.

Traditional method of synthesizing complexes includes refluxing solutions of ligands and metal salts in appropriate quantities for appropriate time period. Already prepared or available ligands are prerequisite for this method and can become troublesome where isolation of ligands is not possible. In these cases template method can be utilized. In template method solutions of complex forming components are refluxed or heated to obtain the complexes directly.

Synthesis of complexes at room temperature seems to be fascinating as it avoids refluxing of the solutions and the procedure looks easy. Present investigation deals with room temperature synthesis of quasi-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, phenyl hydrazine and p-Methylbenzaldehyde. Present paper is continuation of systematic research program going on in our laboratory in the area of synthesis and characterization of macrocyclic, quasi-macrocyclic ligands and their metal complexes [1-5].

The synthesized complexes were characterized using molar conductance, magnetic susceptibility measurements, IR, electronic and $^1\text{H-NMR}$ spectra. Based on results obtained the complexes were proposed to have an octahedral geometry. The synthesized complexes were also screened for their *in vitro* antibacterial activities.

EXPERIMENTAL

Materials and Methods

All the chemicals used in present study were of AR grade. Diethyl malonate, hydrazine hydrate, phenyl hydrazine, p-Methylbenzaldehyde and all the metal salts used 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.

Molar conductance values for all the synthesized complexes were measured by preparing their 10^{-3} M solutions in DMF solvent using Equiptronics conductivity meter with inbuilt magnetic stirrer (**Model Eq-664**) at room temperature. Magnetic susceptibility values were recorded using SES instrument's Guoy balance (**Model EMU-50**) at room temperature using copper (II) sulphate as an internal standard. These magnetic susceptibility values were utilized to calculate magnetic moments using spin only formula $\mu_{\text{eff}} = [n(n+2)]^{1/2}$ BM [6].

IR spectra were recorded as KBR pellets in the region of $4000-400\text{ cm}^{-1}$ on a Perkin Elmer Spectrophotometer. Electronic spectra were recorded in DMF solvent by preparing 10^{-3} M solutions of complexes using Shimadzu UV-1600 spectrophotometer. $^1\text{H-NMR}$ spectrum (for Mn(II) complex as a sample study) was recorded on BRUKER AVANCE II 400 NMR Spectrometer using DMSO-d_6 (spectroscopic grade) solvent. Chemical Shifts are given in ppm relative to tetramethylsilane (TMS).

Synthesis of complexes

The synthesis scheme is completed in two steps. In the first step of synthesis of malonyldihydrazide was carried out by using method reported earlier [7]. In the second step complexes were synthesized by reacting malonyldihydrazide, phenyl hydrazine and p-Methylbenzaldehyde in presence of transition metal ions in methanolic medium at room temperature. The complex forming reaction was carried out in 1:1:2:2 molar ratios of transition metal, malonyldihydrazide, phenyl hydrazine and p-Methylbenzaldehyde respectively.

Synthesis of malonyldihydrazide:

The experimental procedure used for synthesis of malonyldihydrazide was reported earlier [7] and can be given as follows:

A methanolic solution of diethylmalonate (1 mol) was taken in a round bottom flask. To it was added hydrazine hydrate (2 mol) 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-pet ether (10% + 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. (M. P. = 149 °C). Figure 1 given below represents scheme for synthesis of malonyldihydrazide.

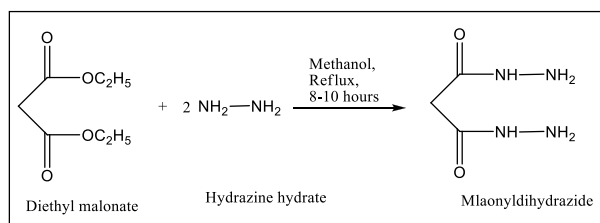


Figure 1. Synthesis of malonyldihydrazide

Synthesis of metal complexes:

General procedure used for the synthesis of metal complexes was as follows:

To a hot methanolic solution of malonyldihydrazide (2.5 mmol), a methanolic solution of dissolved transition metal salts (2.5 mmol) was added in a dropwise manner. A methanolic solution of phenyl hydrazine (5 mmol) was added to the mixture solution of malonyldihydrazide and transition metal salts with constant stirring. The resulting mixture was allowed to stir magnetically for 1 hour. After 1 hour a methanolic solution of p-Methylbenzaldehyde (5 mmol) was added to the reaction mixture. The resultant mixture was then allowed to stir for additional 10 hours. Progress of the 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 and dried in vacuo. Figure 2 represents the synthesis scheme adopted for synthesis of complexes.

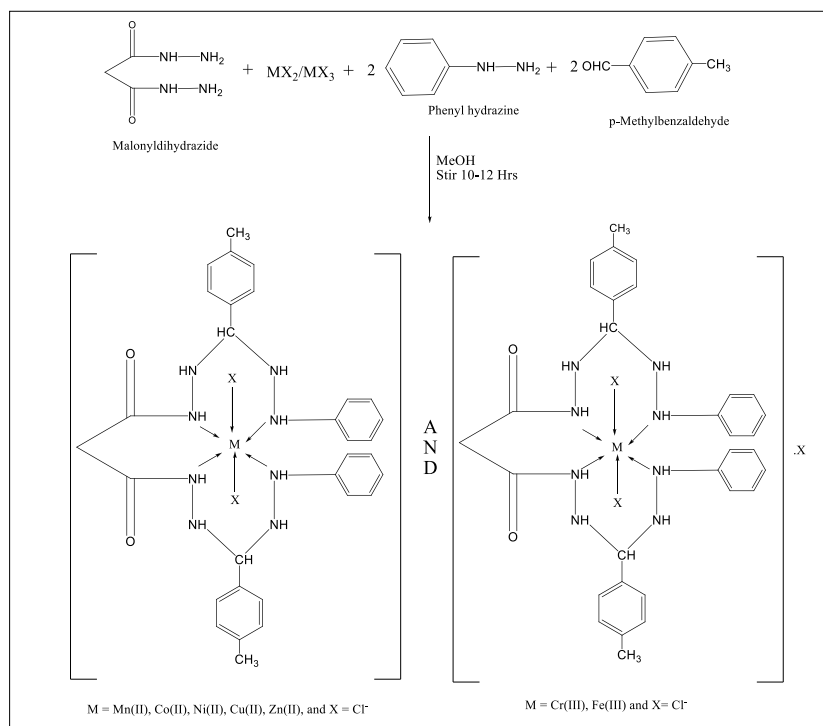


Figure 2. Synthesis of quasi-macrocyclic complexes

RESULTS AND DISCUSSION

The general composition of synthesized quasi-macrocyclic complexes can be represented as $[M(C_{31}H_{36}N_8O_2)X_2]$ for divalent metal ions (where $M = Mn(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$) and $\{[M(C_{31}H_{36}N_8O_2)X_2].X\}$ for trivalent metal ions (where $M = Cr(III)$ and $Fe(III)$) and $X=Cl$ in both the cases.

Physicochemical data

Observations such as colour, melting point and percentage yield for all the synthesized complexes were recorded. Physicochemical data recorded along with calculated molecular weight for all the synthesized complexes is represented in Table 1.

Table 1: Physicochemical data recorded for all the synthesized quasi-macrocyclic complexes

| Molecular formula | Calculated Molecular Weight (gms) | Colour | Melting Point (°C) | Percentage Yield % |
|----------------------------|-----------------------------------|-------------|--------------------|--------------------|
| $C_{31}H_{36}N_8O_2CrCl_3$ | 708.50 | Green | 160 | 70 |
| $C_{31}H_{36}N_8O_2MnCl_2$ | 675.94 | Yellow | 179 | 72 |
| $C_{31}H_{36}N_8O_2FeCl_3$ | 712.35 | Light Green | 200 | 73 |
| $C_{31}H_{36}N_8O_2CoCl_2$ | 679.94 | Brown | 222 | 69 |
| $C_{31}H_{36}N_8O_2NiCl_2$ | 679.69 | Light Green | 218 | 67 |
| $C_{31}H_{36}N_8O_2CuCl_2$ | 684.55 | Green | 210 | 75 |
| $C_{31}H_{36}N_8O_2ZnCl_2$ | 686.39 | Reddish | 258 | 78 |

The melting points recorded for all the synthesized complexes were in the range 160-260 °C indicating towards thermal stability of all these synthesized complexes. The percentage yield was found to be in the range 65-80 % for all the synthesized complexes.

Solubility behavior

Solubility behaviour of all the synthesized complexes was checked using different solvents such as water (WT), methanol (MT), ethanol (ET), chloroform (CL), dichloromethane (DCM), acetone (AC), ethyl acetate (EA), dimethylsulphoxide (DMSO) and dimethylformamide (DMF). The complexes were found to be completely soluble in DMF and DMSO whereas in all the remaining solvents they were found to be insoluble

IR spectra

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

Table 2: IR spectral data recorded for all the synthesized quasi-macrocyclic complexes

| Complexes | $\nu(N-H)$ cm^{-1} | Amide I band $\nu(C=O)$ cm^{-1} | Amide II band $\nu(N-H)$ bending cm^{-1} | $\nu(M-N)$ cm^{-1} |
|----------------------------|----------------------|-----------------------------------|--|----------------------|
| $C_{31}H_{36}N_8O_2CrCl_3$ | 3053.2 3310.2 | 1658.3 | 1520.2 | 506.1 |
| $C_{31}H_{36}N_8O_2MnCl_2$ | 3141.8 3396.2 | 1659.2 | 1511.2 | 516.3 |
| $C_{31}H_{36}N_8O_2FeCl_3$ | 3200.0 3418.4 | 1658.7 | 1511.4 | 516.5 |
| $C_{31}H_{36}N_8O_2CoCl_2$ | 3212.6 3338.8 | 1654.4 | 1527.1 | 502.2 |
| $C_{31}H_{36}N_8O_2NiCl_2$ | 3199.1 3421.2 | 1658.4 | 1520.2 | 508.2 |
| $C_{31}H_{36}N_8O_2CuCl_2$ | 3202.3 3448.4 | 1658.1 | 1511.4 | 516.5 |
| $C_{31}H_{36}N_8O_2ZnCl_2$ | 3163.2 3478.4 | 1654.9 | 1522.3 | 508.4 |

The close observation made at the structures of synthesized quasi-macrocylic complexes indicated the presence of amide and amine groups (-CO-NH-NH-) in the structure. Both these groups i.e. amide and amine show absorption peaks in the range of 3000-3600 cm^{-1} in the IR spectra recorded due to $\nu(\text{N-H})$ stretching vibrations [8]. In present investigation presence of absorption bands in the range 3000-3450 cm^{-1} in IR spectra recorded for all the synthesized complexes can be assigned due to $\nu(\text{N-H})$ vibrations.

The carbonyl absorption of amide (i.e. amide I band) can be observed in the range 1650-1690 cm^{-1} in the IR spectra of solid substances [8]. In present investigation this band was observed around 1655 cm^{-1} in the IR spectra of each of the complexes. The amide II band which is due to N-H bending in secondary amides is normally observed in the range (1570-1515 cm^{-1}) [8]. In the present investigation this band was observed around 1515 cm^{-1} in the spectra of each of the complexes.

The coordination of the amide group to the metal through nitrogen can be predicted based on the appearance of band at lower values in the IR spectra. Position of this band does not seem to be fixed and researchers have reported different values for this band ranging from 300-600 cm^{-1} [9-12]. In present investigation the band observed in the range 500-520 cm^{-1} in the IR spectra of each of the complexes can be assigned due to (M-N) vibrations.

Presence of ν (M-Cl) band in the spectra of complexes is usually reported below 400 cm^{-1} region [13-14] the said region was not scanned for present investigation.

Electronic spectra

Electronic spectra of all the synthesized complexes were recorded in DMF solvent by preparing 10^{-3} M solutions. Table 3 represents the results obtained from electronic spectra recorded.

Table 3: Electronic spectral data recorded for all the synthesized quasi-macrocylic complexes

| Complexes | Absorbance (nm) | Assignment | Molar conductance ($\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$) | Magnetic moments μ_{eff} (BM) |
|---|-----------------|---|--|--|
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{CrCl}_3$ | 570 | ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ | 65 | 3.92 |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{MnCl}_2$ | 450 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ | 16 | 5.94 |
| | 550 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ | | |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{FeCl}_3$ | 490 | ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ | 63 | 5.96 |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{CoCl}_2$ | 460 | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ | 17 | 4.90 |
| | 710 | ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ | | |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{NiCl}_2$ | 435 | ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ | 19 | 2.95 |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{CuCl}_2$ | 645 | $2\text{E}_g \rightarrow 2\text{T}_{2g}$ | 15 | 1.82 |
| $\text{C}_{31}\text{H}_{36}\text{N}_8\text{O}_2\text{ZnCl}_2$ | ----- | ----- | 10 | Diamagnetic |

The electronic spectrum recorded for Cr(III) complex exhibited two bands at 480 and 550 nm which can be assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions respectively. This observation supports to octahedral geometry of the complex. Similar observation was reported by Thirunavukkarasu et al. in which they confirmed the presence of similar band at 572 nm [15].

Spectrum recorded for Mn(II) complex exhibited bands at 450 and 550 nm which can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ transitions respectively. This supports to octahedral geometry of the complex. Chandra et al. have confirmed the presence of similar transitions in the range 442-444 nm and 537-544 nm in their research paper [16].

Spectrum recorded for Fe(III) complex exhibited bands at 490 nm which can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ transition. This observation supports to octahedral geometry of the complex. Similar observation was reported by S. Chitra et al. in which they have confirmed the presence of similar band in the range 477- 498 nm [17].

Spectrum recorded for Co(II) complex exhibited bands at 460 and 710 nm which can be assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. The presence of similar bands was reported by Omar Nasman in the range 451-457 and 714-725 nm respectively in his research paper [18].

Spectrum recorded for Ni (II) complex exhibited a band at 435 nm which can be assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition and supports to octahedral geometry for Ni(II) complex. The presence of similar band was also reported by Uma Joshi at 443 nm in her research paper [19].

Spectrum recorded for Cu(II) complex exhibited a band at 645 nm which can be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. The presence of similar band at 642 nm was reported by Rafat et al. in their research paper [20].

The electronic spectrum of Zn(II) complex did not exhibit any band due to d-d transition. As Zn(II) ion represents a d^{10} system with fully filled shell there is no scope for any electronic transition [6, 21].

Magnetic properties

Magnetic susceptibility values for all the synthesized quasi-macrocyclic complexes were recorded at room temperature using copper (II) sulphate as an internal standard.

Magnetic susceptibility value of 3.92 BM was observed for Cr(III) complex which corresponds to the presence of three unpaired electrons in the complex [14-15]. This observation supports to the octahedral geometry of the complex.

Mn(II) and Fe(III) complexes exhibited values of 5.94 and 5.96 BM respectively, which corresponds to the presence of five unpaired electrons in these complexes [6, 21]. This observation supports to high spin paramagnetic nature and octahedral geometry of the complexes.

Values recorded for Co(II), Ni(II) and Cu(II) complexes i.e. 4.90, 2.95 and 1.82 BM respectively correspond to the presence of three, two and one unpaired electrons respectively in these complexes. This observation supports to octahedral geometry in these complexes also [6, 21]. Zn(II) complex was found to be diamagnetic in nature consistent with (d^{10}) configuration of Zn in this complex [6, 21].

Molar conductance

Molar conductance values for all the synthesized complexes were measured by preparing their 10^{-3} M solutions in DMF as a solvent.

The observed molar conductance values ($10-20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) for complexes with divalent metal ions Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) indicate towards their non-electrolytic behaviour [22]. Whereas the values recorded (65 and $63 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) for complexes with trivalent metal ions Cr(III) and Fe(III) indicate towards their 1:1 electrolytic behaviour [23].

${}^1\text{H-NMR}$ Spectra

${}^1\text{H-NMR}$ spectrum for Zn (II) chloride complex was recorded as a sample study to confirm the protonic arrangement present in the structure of complexes. The spectrum was recorded in DMSO-d^6 as a solvent against tetramethylsilane (TMS) as a standard. The spectrum recorded showed seven major peaks as follows.

A singlet peak for four protons observed at 2.01 ppm can be assigned to **-NH-** protons close to aromatic ring. Another singlet peak for three protons observed at 2.11 ppm can be assigned to **-CH₃** group. The singlet peak for two protons observed at 3.10 ppm can be assigned to **-CH₂-** groups of malonyldihydrazide moiety. Singlet peak observed for two protons at 4.01 ppm can be assigned to **-NH-** protons close to aromatic ring in the structure.

The singlet peak observed at 5.11 ppm for single proton can be assigned to **-CH-** protons of the ring which is coming from aldehyde group. Two doublet and one multiplet peak observed in the range 6.83-7.32 ppm for 2, 2 and 5 protons can be assigned to aromatic protons (Ar-H) present in the complex structure.

Finally the singlet peak observed for two protons at 11.95 ppm be assigned for –NH- protons of amide groups which are coordinated to the metal and hence deshielded.

Antibacterial activity

All the synthesized complexes were screened for their antibacterial activities against *Escherichia coli* and *Styphyllococcus Aureus*. A zone of inhibition of all the synthesized complexes was measured and compared with standard antibiotic drugs penicillin g.

The standard used for antibacterial study penicillin g have shown zone of inhibition of 13 and 15 mm against *E. coli* and *S. Aureus* respectively. Zone of inhibition values of 17, 16, 15 and 13 mm were recorded for complexes of Cu(II), Mn(II), Fe(III) and Cr(III) respectively against *E. coli*. These complexes thus exhibited significant activity. Values of 12, 11 and 10 mm were recorded for Ni(II), Zn(II) and Co(II) complexes respectively. These complexes thus show moderate activity against *E. coli*.

Zone of inhibition values of 15, 14 and 14 mm were recorded for complexes of Cr(III), Ni(II) and Zn(II) complexes respectively against *S. aureus*. These complexes thus exhibited significant activity. Zone of inhibition values of 13, 11, 10 and 10 mm were recorded for Co(II), Fe(III), Mn(II) and Cu(II) complexes respectively which indicated that these complexes show moderate activity against *S. aureus*. The results obtained from antimicrobial screening of all the synthesized complexes are represented in Table 4 given below.

Table 4: Antibacterial activity recorded for all the synthesized quasi-macrocyclic complexes

| Complex | Zone of inhibition (in mm) | |
|----------------------------|----------------------------|------------------|
| | <i>E. coli</i> | <i>S. aureus</i> |
| $C_{31}H_{36}N_8O_2CrCl_3$ | 13mm | 15mm |
| $C_{31}H_{36}N_8O_2MnCl_2$ | 16mm | 10mm |
| $C_{31}H_{36}N_8O_2FeCl_3$ | 15mm | 11mm |
| $C_{31}H_{36}N_8O_2CoCl_2$ | 10mm | 13mm |
| $C_{31}H_{36}N_8O_2NiCl_2$ | 12mm | 14mm |
| $C_{31}H_{36}N_8O_2CuCl_2$ | 17mm | 10mm |
| $C_{31}H_{36}N_8O_2ZnCl_2$ | 11mm | 14mm |
| Std (penicillin g) | 13mm | 15mm |

CONCLUSION

Room temperature synthesis of seven quasi-macrocyclic complexes of transition metals was carried out using malonyldihydrazide, phenyl hydrazine and p-methylbenzaldehyde. The method adopted is advantageous in the sense that it avoids the use of traditional reflux method and the complexes are obtained with room temperature stirring only. The synthesized complexes were proposed to have an octahedral geometry. All the synthesized complexes exhibited moderate to significant activity against the tested bacterial pathogens.

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REFERENCES

- [1] Wankhede DS, Wagh PB, Shankarrao O. Asian J Biochem Pharma Res 2012; 2(4): 126-134.
- [2] Wankhede DS, Wagh PB, Rajput SB, Karuppayil SM, Satare SS. Int J Pharma Res Scholars 2014; 3(2): 766-774.
- [3] Wankhede DS, Wagh PB. Russian J Gen Chem 2016; 86(3): 696-701.
- [4] Wankhede DS, Wagh PB, Hangirgekar SP. J Chem Pharma Res 2015; 7(12): 1153-1159.
- [5] Wankhede DS, Tazeen N. J Chem Pharma Res 2015; 7(10): 135-141.
- [6] Cotton FA, Wilkinson G. Advanced Inorganic Chemistry, 5th Edition. John Wiley, Singapore, 1988.



- [7] Rajavel R, Vadivu MS, Anitha C. E-J Chem 2008; 5(3): 620-626.
- [8] Kalsi PS. Spectroscopy of Organic Compounds. New Age International Publishers, India, 2004.
- [9] Abdussalam AM, Faten SA, El-Ajaily MM, Abdunnaser ME. Green and Sustain Chem 2014; 4: 103-110.
- [10] Gaber M, El-Hefnawy GB, El-Borai MA, Mohamed NF. J Therm Ana Calori 2012; 109: 1397-1405. .
- [11] Thakur GA, Shaikh MM. Acta Polo Pharma & Drug Res 2006; 63(2): 95-103.
- [12] Patel KB, Kharadi GJ, Vyas KB, Nimavat KS. Int J Pharma Res Scholars 2012; 1(2): 474-480.
- [13] Chandra S, Kumar R. Trans Met Chem 2004; 29: 269-275.
- [14] Prasad S, Jayaseelan P, Rajavel R. Int J Chem Sci 2011; 9(4): 1711-1724.
- [15] Dhaveethu K, Padmavathy S, Ramachandramoorthy T, Thirunavukkarasu K. World J Pharmacy Pharma Sci 2014; 3(7): 1381-1401.
- [16] Chandra S, Ruchi. Spectrochimical Acta Part A 2013; 103: 338-348.
- [17] Nagajothi A, Kiruthika A, Chitra S, Parmeswari K. Research J Chem Sci 2013; 3(2): 35-43.
- [18] Nasman OSM. J Al Azhar University-Gaza (Natural Sciences) 2007; 9: 53-59.
- [19] Joshi U. J Chem Pharma Res 2013; 5(9): 96-99.
- [20] Rafat F, Siddiqi MY, Siddiqi KS. J Serb Chem Soc 2004; 69(8-9): 641-649.
- [21] Lee JD. Concise Inorganic Chemistry, 4th Edition. ELBS Chapman and Hall, 1995.
- [22] Chandra S, Verma S. Spectrochimica Acta Part A 2008; 71: 458-464.
- [23] Rafat F, Siddiqi KS. J Korean Chem Soc 2011; 55(6): 912-918.