National Conference on Recent Trends in Synthesis and Characterization of Futuristic Material in Science for the Development of Society
(NCRDAMDS-2018)
In association with
International Journal of Scientific Research in Science and Technology

Catalytic Synthesis Of Tetraazamacrocyclic Complexes Using Silica Supported Perchloric Acid ($Hclo_4$-Sio_2) At Room Temperature

Pradip Bajirao Wagh*, Dnyaneshwar Shamrao Wankhede
School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, India

ABSTRACT

Catalytic synthesis of a series of twelve tetraazamacrocyclic complexes of first row transition metals such as Co(II), Ni(II), Cu(II) and Zn(II) was carried out using chloride, nitrate and acetate salts of metals, isatin and ethylenediamine in ethanolic medium using silica supported perchloric acid ($HClO_4$-SiO_2) as catalyst. The use of catalyst has avoided the traditional reflux method and facilitated the synthesis of complexes within shorter period of time at room temperature. The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, IR, electronic, ^{1}H-NMR, mass spectra, thermogravimetric (TGA) curve 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 tested for antimicrobial activity.

Keywords: Isatin, ethylenediamine, octahedral, powder x-ray analysis, antimicrobial activity.

I. INTRODUCTION

Synthesis of macrocyclic complexes is carried out mainly by refluxing solutions of macrocyclic ligands and respective metal salts for appropriate time period in an appropriate solvent, by maintaining pH conditions, if required. In cases where the synthesis or isolation of ligands is not possible, template method is used for such synthesis. In this method complex forming components are reacted in presence of metal ions [1-5].

Catalytic synthesis of macrocyclic complexes seems to be a neglected area, although few reports of synthesis using condensation catalysts such as DMAP, DCC and silica supported perchloric acid ($HClO_4$-SiO_2) as catalyst are available [6-8]. Silica supported acid catalysts are well known in organic chemistry synthesis. Still there use in synthesis of complexes has not been tried up to that extent yet. This fact has prompted us to undertake a study on catalytic synthesis of macrocyclic complexes using silica supported perchloric acid ($HClO_4$-SiO_2) as catalyst.

In the initial period synthesis of some already reported complexes was carried out using the catalyst and the results were compared. This paper is continuation of our study [9-10] on catalytic synthesis of macrocyclic complexes using silica supported perchloric acid ($HClO_4$-SiO_2). In present investigation we report synthesis of tetraazamacrocyclic complexes of Co(II), Ni(II), Cu(II) and Zn(II) using chloride, nitrate and acetate salts of metals, isatin and ethylenediamine in ethanolic medium using silica supported perchloric acid ($HClO_4$-SiO_2) as catalyst. The complexes were obtained by simply stirring the complex forming components at room temperature.

Synthesis of these complexes using traditional reflux method was reported by Singh et al [11]. The reaction was completed within 6-8 hours as per their report. In present investigation the time period has been reduced to a considerable extent.

The synthesized complexes have been characterized with the help of molar conductance, magnetic susceptibility measurements, IR, electronic spectra. ^{1}H-

NMR, mass spectra, thermogravimetric (TGA), and powder x-ray analysis was carried out for few selected complexes as a sample study to help to confirm the skeleton of complexes**.** 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.

II. EXPERIMENTAL

The entire chemicals used in present study were of AR grade. Isatin, ethylenediamine and metal salts were procured from S. D. fine chemicals and Spectrochem Private Limited respectively. The solvents used were distilled and dried using molecular sieves before use.

Molar conductance values of all the synthesized complexes were measured by preparing 10^{-3} M solutions in DMSO solvent using **Equiptronics** conductivity meter (**Model Eq-664**) with an inbuilt magnetic stirrer 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 on a Shimadzu UV-1600 spectrophotometer by preparing 10^{-3} M solutions of all the synthesized complexes in DMSO.

^{1}H-NMR spectrum (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 standard tetramethylsilane (TMS). Mass spectrum (for Zn(II) nitrate complex) was recorded on Q-Tof-micro instrument. TGA curve (For Ni(II) chloride complex) was recorded using SDT- 2960 (TA instrument USA) and powder x-ray diffractogram (for Cu(II) chloride complex) was recorded using and Xpert-pro XRD diffractometer.

Preparation of catalyst:

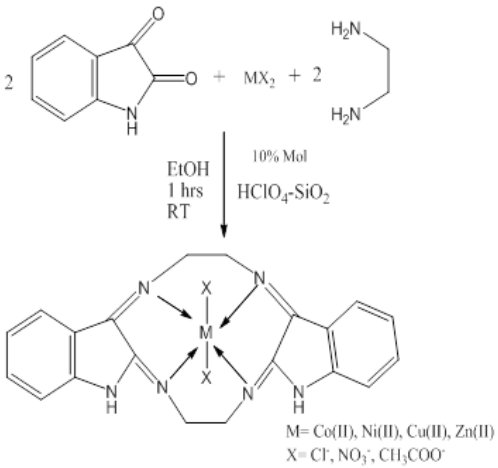
The catalyst used in present investigation was prepared using procedure reported earlier[12-13], which can be given as follows.

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 ^{o}C for 72 h under vacuum to give silica supported perchloric acid ($HClO_4$–SiO_2) (0.5 mmol/g) as free flowing powder.

Synthesis of macrocyclic complexes:

General procedure used for the synthesis of macrocyclic complexes can be given as follows:

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 isatin (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 (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.



Scheme 1. Synthesis of tetraazamacrocyclic complexes

In vitro antimicrobial activity

The synthesized complexes were screened for their antimicrobial activity 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) were 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 ^{o}C in aseptic condition. Sterile Whatmann filter paper discs were impregnated with synthesized complexes at a concentration of 1 mg/disc and were 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^{o}C for antibacterial activity and 48 h at 37 ± 1^{o}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.[14]

III. RESULTS AND DISCUSSION

General composition of the synthesized complexes can be represented as $[M(C_{20}H_{18}Cl_2N_6)]$ for chloride, $[M(C_{20}H_{18}N_8O_6)]$ for nitrate and $[M(C_{23}H_{24}N_6O_4)]$ for acetate complexes respectively and M = Co(II), Ni(II), Cu(II) and Zn(II).

Physicochemical data:
All the synthesized complexes were thermally stable and colored. Observations such as colour, melting point, % yield, solubility behavior for all the complexes were recorded. The physicochemical data recorded for all the synthesized macrocyclic complexes is represented in Table 1.

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

IR spectra:
Absence of peaks for free (NH_2) and >C=O groups in the spectra of synthesized complexes indicate towards condensation of carbonyl group of isatin with ethylenediamine.[15] Presence of single medium band at 3200-3260 cm^{-1} in the spectra of complexes may be assigned to the -NH stretching.[16]

Table 1. Physicochemical data of the synthesized macrocyclic complexes

Molecular formula	Calculated Molecular Weight (gms)	Colour	Melting Point/Decomposition Temperature (^{0}C)	Percentage Yield (%)
$C_{20}H_{18}Cl_2CoN_6$	472	Red	>250	64
$C_{20}H_{18}Cl_2NiN_6$	471	Light green	>250	68
$C_{20}H_{18}Cl_2CuN_6$	475	Green	>250	70
$C_{20}H_{18}Cl_2ZnN_6$	476	Light brown	>250	61
$C_{20}H_{18}CoN_8O_6$	525	Light red	>250	64
$C_{20}H_{18}NiN_8O_6$	524	Faint green	>250	70
$C_{20}H_{18}CuN_8O_6$	529	Green	>250	66
$C_{20}H_{18}ZnN_8O_6$	530	Faint yellow	>250	62
$C_{23}H_{24}CoN_6O_4$	507	Light red	>250	64
$C_{23}H_{24}NiN_6O_4$	506	Faint green	>250	69
$C_{23}H_{24}CuN_6O_4$	511	Green	>250	72
$C_{23}H_{24}ZnN_6O_4$	512	Light brown	>250	63

Another absorption band in the region at 1606-1690 cm^{-1} may be assigned to the (C=N) stretching vibration.[17-18] Obtained data thus provide strong evidence for formation of macrocyclic skeleton.[19] The lowest values of (C=N) observed may be due to drift of lone pair electron density of the azomethine nitrogen towards the central metal atom.[20-21] Medium intensity bands observed in the region 1500-1580 cm^{-1} may be due to aromatic stretching. The band observed in the region 1015-1355 cm^{-1} may be due to the ν(C-N) stretching vibration. The ν(M-N) stretching in complexes is observed in the region at 425-490 cm^{-1} which gives insight into the coordination of the azomethine nitrogen to the central metal.[22-23] The coordinated nitrate and acetate groups are coordinating to the metal in the range 1300-1500 cm^{-1} and 1000-1350 cm^{-1} respectively in unidentate manner.[24-25] IR spectral data recorded for all the synthesized complexes is represented in Table 2.

Table 2. IR spectral data recorded (cm^{-1}) of synthesized complexes

Complexes	ν (NH)	ν (C=N)	ν (C=C)	ν (M-N)
$C_{20}H_{18}Cl_2CoN_6$	3200	1644	1506	444
$C_{20}H_{18}Cl_2NiN_6$	3213	1649	1506	461
$C_{20}H_{18}Cl_2CuN_6$	3212	1619	1472	490
$C_{20}H_{18}Cl_2ZnN_6$	3250	1617	1468	425
$C_{20}H_{18}CoN_8O_6$	3200	1690	1471	489
$C_{20}H_{18}NiN_8O_6$	3221	1648	1404	490
$C_{20}H_{18}CuN_8O_6$	3224	1623	1545	460
$C_{20}H_{18}ZnN_8O_6$	3224	1621	1472	440
$C_{23}H_{24}CoN_6O_4$	3223	1620	1471	490
$C_{23}H_{24}NiN_6O_4$	3250	1639	1502	458
$C_{23}H_{24}CuN_6O_4$	3200	1610	1547	440
$C_{23}H_{24}ZnN_6O_4$	3200	1625	1547	430

Electronic spectra:

Electronic spectra of Co(II) complexes exhibit bands at 700-770 and 490-550 nm which may be assigned to $^4T_1g \rightarrow {}^4T_2g$ (F) and $^4T_1g \rightarrow {}^4T_1g$ (P) transitions. The observed data support to octahedral geometry of the complexes.[26-27]

Bands observed in the region 550-620 and 380-410 nm in electronic spectra of Ni(II) complexes may be assigned to $^3A_2g \rightarrow {}^3T_1g$ (F) and $^3A_2g \rightarrow {}^3T_1g$ (P) transitions respectively. The bands observed at 580-590 nm may be assigned to the $^3B_1g \rightarrow {}^3B_2g$ transition whereas bands observed in the region 920-980 nm may be assigned to $^3B_1g \rightarrow {}^3Eg$ transition respectively. The observed data thus supported to distorted octahedral geometry of complexes.[28]

Electronic spectra of Cu(II) complexes showed presence of two bands in the region 510-565 and 612-687 nm which may be assigned to $^2B_1g \rightarrow {}^2Eg$ and $^2B_1g \rightarrow {}^2B_2g$ transitions respectively. The observed data indicate tetragonal distortion in the molecule and thus Cu(II) complexes have distorted octahedral geometry.[28-29] The band observed at 380-440 nm in the electronic spectra of Zn(II) complexes can be attributed to LMCT transition.[30-31]

Magnetic properties:

The magnetic moment values for Co(II) complexes are in the range 4.90-4.98 BM which corresponds to three unpaired electrons.[27] The magnetic moments recorded for Ni(II) complexes in the range 2.91-2.95 BM which indicates two unpaired electrons in the nickel (II) ion towards octahedral geometry of these complexes.[28] The magnetic moment values for Cu(II) complexes are in the range 1.79-1.93 BM which corresponds to one unpaired electron in the complexes.[28] The Zn(II) complexes are diamagnetic in nature consistent with (d^{10}) configuration of Zn in complexes.[30]

Molar conductance:

The observed molar conductance values (10-22 ohm^{-1} cm^{-2} mol^{-1}) for all the synthesized complexes indicate towards their non-electrolytic behaviour.[11,32] Table 3

represents results obtained from electronic spectra, magnetic properties and molar conductance measurements for all the synthesized complexes.

^{1}H-NMR Spectra:

^{1}H-NMR spectrum recorded for Zn(II) complex spectra showed total three signals, out of which one observed at 10.20 ppm may be assigned to the -NH protons of the isatin moiety.[33] Another signal observed at 1.60 ppm may be assigned to the methyl protons. The multiplet signal observed in the region 6.80-7.70 ppm may be assigned to the aromatic ring protons of isatin moiety.[34-35]

Mass spectra:

The spectrum has shown molecular ion peak at m/z = 530 a. m. u. as [M+]. On comparison the recorded mass spectrum showed good agreement with the calculated molecular weight of the Zn(II) complex and with proposed molecular formula. Hence the same was understood for remaining complexes.

Table 3. Electronic spectral data, molar conductance and magnetic moment values for synthesized complexes

Complexes	Absorbance (nm)	Assignment	Molar conductance ($ohm^{-1}cm^2 mol^{-1}$)	Magnetic moments μ_{eff} (BM)
$C_{20}H_{18}Cl_2CoN_6$	720 540	$^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	12	4.91
$C_{20}H_{18}Cl_2NiN_6$	620 390 920 590	$^3A_2g \rightarrow {}^3T_1g$ (F) $^3A_2g \rightarrow {}^3T_1g$ (P) $^3B_1g \rightarrow {}^3Eg$ $^3B_1g \rightarrow {}^3B_2g$	10	2.90
$C_{20}H_{18}Cl_2CuN_6$	530 670	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2B_2g$	14	1.80
$C_{20}H_{18}Cl_2ZnN_6$	440	LMCT	11	Diamagnetic
$C_{20}H_{18}CoN_8O_6$	645 540	$^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	16	4.93
$C_{20}H_{18}NiN_8O_6$	550 380 920 580	$^3A_2g \rightarrow {}^3T_1g$ (F) $^3A_2g \rightarrow {}^3T_1g$ (P) $^3B_1g \rightarrow {}^3Eg$ $^3B_1g \rightarrow {}^3B_2g$	13	2.95
$C_{20}H_{18}CuN_8O_6$	560 680	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2B_2g$	18	1.93
$C_{20}H_{18}ZnN_8O_6$	380	LMCT	15	Diamagnetic
$C_{23}H_{24}CoN_6O_4$	700 490	$^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	20	4.98
$C_{23}H_{24}NiN_6O_4$	550 410 980 580	$^3A_2g \rightarrow {}^3T_1g$ (F) $^3A_2g \rightarrow {}^3T_1g$ (P) $^3B_1g \rightarrow {}^3Eg$ $^3B_1g \rightarrow {}^3B_2g$	22	2.91
$C_{23}H_{24}CuN_6O_4$	570 690	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2B_2g$	15	1.88
$C_{23}H_{24}ZnN_6O_4$	420	LMCT	19	Diamagnetic

Thermogravimetric Analysis (TGA):

Thermogravimetric analysis was carried out for Ni(II) chloride complex as a sample and was used to determine the decomposition temperature. The TGA curve was recorded in temperature range of 10 to 500 ^{o}C. Table 4 represents the TGA data recorded for Ni(II) chloride complex.

TGA curve recorded showed first step of decomposition in the range 30-160 ^{o}C with a mass loss of 16.92 % (Calculated 16.91%). This weight loss may be attributed to decomposition of lattice water.[23] The second step of decomposition is observed in the range 200-380 ^{o}C with a mass loss of 24.35 % (Calculated 24.34 %). This weight loss may be attributed to decomposition of organic ligand and chloride. The third step of decomposition is observed in the range 390-500 ^{o}C with a mass loss of 48.42 % (Calculated 48.42 %). last step attributed to decomposition of final nickel residue.[8, 37-38]

X-ray Powder Diffraction Analysis:

As attempts to prepare single crystal of the synthesized complexes made by us resulted in failure, we decided to study powder x-ray. The X-ray powder diffraction study was done for Cu(II) chloride complex as a sample. The X-ray diffractogram was scanned in the range 5-85º at wavelength 1.54060 Aº. The diffractogram and associated data depict the 2θ value 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.

Table 4. TGA data recorded for Ni (II) complex

Complex	Temperature range ^{o}C	Percentage Weight loss (%)		Decomposition Product
		Observed	Calculated	
$C_{20}H_{18}Cl_2NiN_6$	30-160	16.92	16.91	Lattice water
	200-380	24.35	24.34	Chloride ion and ligand
	390-500	48.42	48.42	Final nickel residue

The lattice constant values a= 8.1090 Å, b=7.3670 Å, C=7.1580 Å are in concurrence with these cell parameters. The condition such as $a \neq b \neq c$ and $\alpha = \gamma \neq \beta$ required for sample to be **monoclinic** system were tested and found to be satisfactory.[37-38]

Antimicrobial activities:

The metal complexes were screened for their antibacterial activity against B. Subtilis and E. coli. A zone of inhibition of all the synthesized macrocyclic complexes was measured and compared with standard antibiotic drug streptomycin. The standard Streptomycin have shown zone of inhibition of 30 and 31 mm against B. Subtilis and E. coli respectively. Macrocyclic complexes of Co(II) and Cu(II) showed significant activity in the range of 21-28 mm, while those of Ni(II) and Zn(II) showed moderate activity in the range of 10-12 mm compared with that of the standard.

The synthesized complexes were also screened for their antifungal activities against C. albicans and their zone of inhibitions were compared with Amphotericin B. Amphotercin B have shown zone of inhibition of 29 mm against C. albicans. Macrocyclic complexes of Co(II) and Ni(II) showed signigicant activities in the range of 18-28 mm compared with that of the standard. Whereas out of remaining complexes those of Cu(II) and Zn(II) nitrate showed moderate activity in the range of 10-15 mm and remaining those of Cu(II) and Zn(II) chloride and Zn(II) acetate did not show any activity. DMSO has no zone of inhibition. Table 5 represents the antimicrobial activities recorded for all the synthesized complexes.

Advantages of catalyst:

On comparison with the results reported earlier[11], the catalyst ($HClO_4$-SiO_2) used in present study was found to be efficient in following aspects:

The complexes were obtained simply by stirring the ethanolic solutions of complex forming components at room temperature. Thus tradition reflux method was avoided. Synthesis of complexes using reflux method requires at least 6-8 hours while catalytic synthesis has completed the reaction in two hours only. Thus reducing the time required for completion of reaction has been reduced to a greater extent. Work up of the reaction was easy and the catalyst can be removed from simple filtration.

Table 5. Antimicrobial activities of synthesized complexes

Complexes	Zone of inhibition in mm, conc. (1.0 mg/ml)		
	Bacillus Subtilis MTCC-8979	**Escherichia Coli MTTC- 443**	**Candida albicans MTTC-227**
$C_{20}H_{18}Cl_2CoN_6$	19	22	28
$C_{20}H_{18}Cl_2NiN_6$	11	08	20
$C_{20}H_{18}Cl_2CuN_6$	16	10	----
$C_{20}H_{18}Cl_2ZnN_6$	11	---	----
$C_{20}H_{18}CoN_8O_6$	15	16	22
$C_{20}H_{18}NiN_8O_6$	11	09	18
$C_{20}H_{18}CuN_8O_6$	19	00	10
$C_{20}H_{18}ZnN_8O_6$	10	08	08
$C_{23}H_{24}CoN_6O_4$	16	13	20
$C_{23}H_{24}NiN_6O_4$	12	10	18
$C_{23}H_{24}CuN_6O_4$	11	08	10
$C_{23}H_{24}ZnN_6O_4$	12	09	----
Streptomycin	30	31	---
Amphotericin B	----	----	29
DMSO	----	----	----

*Range of activity: 16-28 = Significant, 8-15 = medium, --- No activity

IV. CONCLUSION

Silica supported perchloric acid ($HClO_4$-SiO_2) has been used as efficient catalyst for the synthesis of macrocyclic complexes. The use of catalyst has avoided the traditional reflux method and allowed the synthesis of complexes by simple stirring method at room temperature. Moreover the synthesis of complexes has been achieved in two hours. Thus the time required for completion of reaction has been reduced to a greater amount which represents the advantage of the method used.

V. ACKNOWLEDGEMENTS

We are grateful to Director, SAIF, Punjab University, Chandigarh for providing spectral data.

VI. REFERENCES

[1]. Kalam, A., Tripathi, V., Srivastav, S., Pandey, Y., Kumar, A., Gupta, A., and Purohit, A., Turk. J. Chem., 2010, vol. 34, p. 147.

[2]. Singh, D. P., and Kumar, R., Transition Met. Chem., 2006, Vol. 31. p. 970.

[3]. Singh, D. P., and Kumar, R., J. Serb. Chem. Soc., 2007, vol. 72, p. 1069.

[4]. Rathi, P., and Singh, D. P., Der Pharma Chemica, 2014, vol. 6, p. 203.

[5]. Singh, D. P., Malik, V., Kumar, R., and Kumar, K., Russian J. Coord. Chem., 2010, vol. 36, p. 220.

[6]. Shakir, M., and Verkey, S. P., Polyhedron, 1995, vol. 14, p. 1117.

[7]. Singh, R. V., and Chaudhary, A., J. Inorg. Biochem., 2004, vol. 98, p. 1712
[8]. Kamble, V. T., and Ibatte, S. N., Int. J. Chem. Sci., 2013, vol. 11, p. 1858.
[9]. Wankhede, D. S., and Wagh, P. B., Russian J. Gen. Chem., 2016, vol. 86, p. 696.
[10]. Wankhede, D. S., Wagh, P. B., and Hangirgekar, S. P., J. Chem. Pharma. Res., 2015, vol. 7, p. 1153-1159.
[11]. Singh, D. P., Kumar, R., Kambhoj, M., Grover, V. and Jain, K., Russian J. Coord. Chem., 2008, vol. 34, p. 233.
[12]. Shukla, P. K., Verma, A., and Pathak, P., Archives Appl. Sci. Res., 2014, vol. 6, p. 18.
[13]. Kantevari, S., Vuppalapati, S. V. N., Biradar, D. O., and Nagarapu, L., J. Mol. Catalysis A: Chemical, 2007, vol. 266, p. 109.
[14]. Bauer, A. W., Kirby, W. M. M., Sherris, J. C., and Truck, M., Ame. J. Clinical Pathology, 1966, vol. 45, p. 493
[15]. Nivasan, S. S., Athappan, P. A., and Rajagopal, G., Trans. Met. Chem., 2001, vol. 26, p. 588.
[16]. Casas, J. S., Castellano, E. E., Garcia, M. S., Tasende, A., Sachez, Sordo, J., Inorg. Chim. Acta, 2000, vol. 304, p. 283.
[17]. Singh, A. K., Singh, R., and Saxena, P., Trans Met. Chem., 2004, vol. 29, p. 867.
[18]. Dey, K., Bandyopadhyay, D., Nandi, K. K., Poddar, S. N., Mukhopadhay, G., and Kauffman, G. B., Synth. React. Inorg. Met-Org Chem., 1992, vol. 22, p. 1111.
[19]. Mohamed, A. K., Islam, K. S., Hasan, S. S., and Shakir, M., Trans. Met. Chem., 1999, vol. 24, p. 198.
[20]. Zeng, Q., Sun, J., Gou, S., Zhou, K., Fang, J., and Chen, H., Trans. Met. Chem., 1998, vol. 23, p. 371.
[21]. Lodeiro, C., Bastida, R., Bertolo, E., Macias, A., and Rodriguez, A., Trans. Met. Chem., 2003, vol. 28, p. 388.
[22]. Chandra, S., and Pundir, M., Spectrochim. Acta A, 2007, vol. 68, p. 883.
[23]. Rana, V. B., Singh, D. P., and Teotia, M. P., Trans Met. Chem., 1982, vol. 7, p. 174.
[24]. Chandra, S., and Gupta, L. K., Spectrochim. Acta A, 2004, vol. 60, p. 2767.
[25]. Singh, D. P., Malik, V., Kumar, R., Kumar, K., and Dhiman, S. S., J. Serb. Chem. Soc., 2010, vol. 75, p. 1369.
[26]. Rana, V. B., Singh, D. P., and Teotia, M. P., Trans. Met. Chem., 1981, vol. 6, p. 36.
[27]. Rana, V. B., Singh, D. P., Teotia, M. P., Polyhedron, 1982, vol. 1, p. 377.
[28]. Lever, A. B. P., Inorganic Electronic Spectroscopy, 2nd Ed. Amsterdam: Elsevier, 1968.
[29]. Singh, D. P., Grover, V., Kumar, K., and Jain, K., J. Serb. Chem. Soc., 2011, vol. 76, p. 385.
[30]. El-Boraey, H. A., Emam, S. M., Tolan, D. A., and El-Nahas, A. M., Spectrochim. Acta A, 2011, vol. 62, p. 360.
[31]. Raman, N., Ravichandran, S., and Thangaraja, C., J. Chem. Sci., 2004, vol. 116, p. 215.
[32]. Singh, D. P., Parveen, R., Kumar, R., Surain, P., and Aneja, K. R., J. Incl. Phenom. Macro. Chem., 2014, vol. 78, p. 363.
[33]. Labisbal, E., Sousa, A., Castineiras, A., Garcia-Vazquez, J. A., Romero, J., and West, D. X., Polyhedron, 2000, vol. 19, p. 1255.
[34]. Nisari, M. S., and Amiri, A., Trans. Met. Chem., 2006, vol. 31, p. 157.
[35]. Khan, T. A., and Shagupta, M., Trans. Met. Chem., 1999, vol. 24, p. 669.
[36]. Kareem, A., Zafar, H., Sherwani, A., Mohammed, O., and Khan, T. A., J. Molecular. Struct., 2014, vol. 1075, p. 17.
[37]. Shaikh, R. A., Wani, M. Y., Shreaz, S., and Hasmi, A. A., Arabian J. Chem., 2012, (In press).
[38]. Munde, A. S., Jagdale, A. N., Jadhav, S. M., and Chondhekar, T. K., J. Serb. Chem. Soc., 2010, vol. 75, p. 349