

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Studies on Some d^{10} Metal-Ion Complexes with Tellurium Containing Dithiadiazia macrocycles

Sumit Kumari, KK Verma, and Sapana Garg*

Department of Chemistry, Maharshi Dayanand University, Rohtak - 124001, India

ABSTRACT

Complexes of Zn(II), Cd(II) and Hg(II) with two quadridentate nitrogen and sulfur donor, tellurium containing dithiadiazia macrocyclic ligands have been synthesized by template condensation reactions of 2-aminoethanethiol with diaryltellurium(IV) dichlorides, R_2TeCl_2 , (R = 3-methyl-4-hydroxyphenyl and *p*-hydroxyphenyl) in presence of metal chlorides in dry methanol. Their structures have been predicted on the basis of elemental analyses, molar conductance and magnetic moment measurements, 1H NMR, Infrared and electronic absorption spectroscopy. Based on these studies the complexes, $[MLCl_2]$ (M = divalent Zn, Cd and Hg; L = 10 membered tellurium containing dithiadiazia macrocyclic ligands] have been assigned distorted octahedral geometry with the macrocycles coordinating through two S and two N atom and non-involvement of tellurium atoms. These metal complexes and their precursors have also been screened for their biocidal activities against some gram - ve and gram + ve bacteria and fungi to assess their growth inhibiting potential.

Keywords: Dithiadiazia macrocycles, 2-Aminoethanethiol, Biocidal activity, Diaryltellurium(IV) dichlorides

*Corresponding author

INTRODUCTION

Transition metal complexes containing macrocyclic ligands are of great interest in terms of coordination and structural chemistry [1] because of the presence of multiple donor atoms in the macrocycle and their flaccidity to coordinate with metal ions. The macrocyclic complexes have various applications such as in bioinorganic chemistry [2,3], biological activity [4-6], catalysts in oxidation and epoxidation processes [7,8], models for biologically important proteins and enzymes [9-13] and precursors in MOCVD processes [14-16]. Reviews show that an appreciable amount of work has been done on nitrogen and oxygen [17-19] or nitrogen and sulfur [20-22] atoms containing macrocycles.

Template synthetic route for transition metal complexes of dithiadiazia [23] and tellurium containing tetraaza [24-27] macrocycles have been reported. Due to the growing interest in macrocycles and their transition metal complexes, synthesis, spectral characterization and biocidal activities of some Cd(II), Hg(II) and Zn(II) complexes with two novel 10-membered tellurium containing dithiadiazia macrocycles (Te₂N₂S₂ system) are reported in this paper.

MATERIALS AND METHODS

The chemicals used for synthesis and recrystallization were of reagent grade. The solvents, phenol and *o*-cresol were purified and dried by standard methods [28,29] before use. All the preparations were carried out under an atmosphere of dry nitrogen as the compounds are sensitive to moisture and air.

C, H, N analyses for these metal complexes were obtained from SAIF, Panjab University, Chandigarh on a Microprocessor based Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Chlorine and tellurium contents were determined volumetrically [30]. Atomic absorption spectrophotometer (ECIL Model No.4129) was used to estimate the metal ions. IR (4000-400 cm⁻¹) and far IR (400-40 cm⁻¹) spectra were recorded using KBr and Polyethylene respectively, on a F.T. Infra-Red Spectrometer Model Nicolet IS50 (Thermo Scientific). ¹H NMR Spectra were obtained from SAIF, Panjab University, Chandigarh on BRUKER AVANCE II 400 NMR spectrometer in DMSO-d₆ using TMS as reference.

Electronic spectra were recorded on a UV-VIS-NIR Spectrophotometer; model UV-3600 Plus (SHIMADZU) in BaSO₄ at 25±2 °C. The conductance was measured in acetonitrile at 25±2°C using a dip type conductivity cell (cell constant = 0.997) on a microprocessor based conductivity bridge type MICROSIL. Magnetic mass susceptibility data were obtained from NPL, New Delhi on a Gouy's balance (model Johnson Matthey Alfa products) using glycerin as a calibrant. Melting points were determined in open capillary tube and are uncorrected.

The antifungal and antibacterial activity of the synthesized macrocyclic metal complexes and their precursors were tested against fungal strains: *Candida albicans* (MTCC 227), *Aspergillus niger* (MTCC 8189) and *Aspergillus fumigatus* (ITCC 4517); Gram +ve bacteria: *Staphylococcus aureus* (MTCC 2901), *Bacillus subtilis* (MTCC 2063) and *Bacillus cereus* (MTCC 7350) and Gram -ve bacteria: *Escherichia coli* (MTCC 1652) and *Salmonella typhi* (ATCC 15499) using tube dilution method [31]. The test and standard compounds were both serially diluted in Double strength nutrient broth- I.P for bacteria and Sabouraud Dextrose Broth -I.P for fungi [32]. Dilutions were made in DMSO. Fluconazole (antifungal) and Cefadroxil (antibacterial) were taken as standard drugs. Results were observed in terms of minimum inhibitory concentration (MIC).

EXPERIMENTAL

Preparation of diaryltellurium(IV) dichlorides

Bis(3-methyl-4-hydroxyphenyl) and bis(*p*-hydroxyphenyl)tellurium(IV) dichlorides were prepared by reactions of tellurium tetrachloride with *o*-cresol [33] and phenol [34] respectively as reported in the literature.

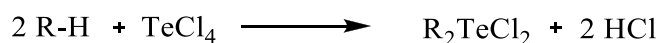
Preparations of metal complexes with 10-membered tellurium dithiadiazamacrocycles ($\text{Te}_2\text{N}_2\text{S}_2\text{M}$ system)

The metal complexes were prepared by template condensation reactions of 2-aminoethanethiol and diaryltellurium dichlorides with divalent metal chlorides in 2: 2: 1 molar ratios, as given below:

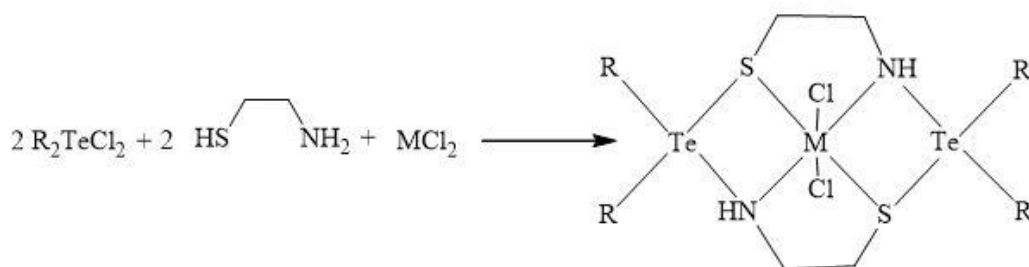
A saturated hot solution of 4.0 mmol of diaryltellurium dichloride in dry methanol was added dropwise with constant stirring to a hot methanolic (~ 10 mL) solution of 4.0 mmol of 2-aminoethanethiol taken in a round bottom flask. An immediate change in colour was observed. The contents were refluxed for 3-4 h, followed by the addition of saturated methanolic solution of metal chlorides (2.0 mmol). Again a change in colour was observed. The mixture was then further refluxed for about 8 h. The small amount of precipitated solid was filtered off and the filtrate was kept in refrigerator after concentrating it to about one third of original volume to obtain second crop of crystalline product. This was filtered, washed with petroleum ether and dried in vacuum desiccator over P_4O_{10} .

RESULT AND DISCUSSION

An electrophilic substitution reaction appears to occur when TeCl_4 is heated with *o*-cresol [33] and phenol [34](R-H) involving attack of a chlorotellurium group at a position *para* to the hydroxyl group in the aromatic rings, resulting in the formation of diaryltellurium(IV) dichlorides.



Diaryltellurium(IV) dichlorides when refluxed with 2-aminoethanethiol in presence of ZnCl_2 / CdCl_2 / HgCl_2 in 2:2:1 molar ratios, yield the desired complexes as shown in Scheme-1.



where

L^1 ; R = *p*-hydroxyphenyl

L^2 ; R = 3-methyl-4-hydroxyphenyl

M = Zn(II), Cd(II) and Hg(II)

Scheme 1. Formation of Zn(II), Cd(II) and Hg(II) Complexes

These newly synthesized metal complexes are crystalline solids, stable in dry air and soluble in polar donor organic solvents. The colours, yields, melting points, elemental analyses and molar conductance of all the complexes are presented in Table 1. The analytical data are in good agreement with the proposed stoichiometry of the complexes.

Table 1: Analytical data, Physical Properties and Molar Conductance for Metal Complexes

Complex	Empirical formula (Formula weight)	Colour (Yield %)	M.P. °C	Analysis found (calculated),%						Λ_M at $ca. 10^{-3}$ M S $cm^2 mol^{-1}$ in acetonitrile
				C	H	N	Cl	Te	M	
ZnL ¹ Cl ₂	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Zn (914.19)	Yellow (81)	112-114	36.31 (36.79)	3.61 (3.31)	2.71 (3.06)	7.22 (7.76)	26.40 (27.92)	6.82 (7.15)	**
ZnL ² Cl ₂	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Zn (970.30)	Light brown (74)	130-132	39.32 (39.61)	3.72 (3.95)	2.51 (2.89)	7.14 (7.31)	26.41 (26.30)	6.56 (6.74)	31.5
CdL ¹ Cl ₂	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Cd (976.23)	Dark yellow (74)	162-164*	35.39 (35.68)	3.18 (3.41)	2.40 (2.87)	6.99 (7.26)	25.98 (26.14)	11.33 (11.51)	26.9
CdL ² Cl ₂	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Cd (1017.30)	Grey (69)	184-186*	37.32 (37.78)	3.55 (3.77)	2.51 (2.75)	7.15 (6.97)	24.80 (25.09)	10.80 (11.05)	51.0
HgL ¹ Cl ₂	C ₂₈ H ₃₀ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Hg (1049.37)	Light yellow (67)	218-220	32.35 (32.05)	2.44 (2.88)	2.30 (2.67)	6.38 (6.76)	23.99 (24.32)	18.80 (19.12)	26.8
HgL ² Cl ₂	C ₃₂ H ₃₈ Cl ₂ N ₂ O ₄ S ₂ Te ₂ Hg (1105.48)	Light yellow (61)	210-212	34.54 (34.77)	3.25 (3.46)	2.29 (2.53)	6.15 (6.41)	23.26 (23.08)	17.87 (18.15)	29.3

Λ_M reported [35] for 1:1 electrolyte in acetonitrile = 120-160 S cm² mol⁻¹, * decomposition temperature, ** insoluble in acetonitrile

Conductance Studies

Molar conductance, Λ_M values of metal complexes soluble in acetonitrile at $ca.10^{-3}$ M are presented in Table 1. The Λ_M data ($26-51 \text{ S cm}^2 \text{ mol}^{-1}$) predict non electrolyte to weak electrolyte type nature of these complexes [35], suggesting their formulation as $[\text{MLCl}_2]$.

Electronic Spectra and Magnetic Moment

Due to CT transitions [36-38] a broad and intense band in the region 232-263 nm appear in the electronic absorption spectra of these metal complexes. Sometimes the $n - \pi^*$ and $\pi - \pi^*$ bands of the ligand [37] may also be mixed with this CT band which sweeps the near UV portion and extends in the visible region with diminishing absorbance upto 500 nm which is responsible for the colour of the complexes. For these metal complexes no d-d transitions were observed consistent with their d^{10} configuration and diamagnetic nature.

Infrared Spectra

The important IR data alongwith their assignments are presented in Table 2. The spectra of the metal complexes are quite complex and thus an attempt has been made to identify the donor sites by comparing the spectra of the complexes with those of corresponding constituents; 2-aminoethanethiol and diaryltellurium dichlorides. The metal complexes under study did not show any band corresponding to free amino group; instead a new single sharp band appeared in the region $3090-3142 \text{ cm}^{-1}$ (sometimes mixed with O-H) assignable to $\nu_{\text{N-H}}$ vibration [22,27,38,39], provide an evidence for the skeleton of the macrocyclic moiety. This contention finds support from the appearance of medium to strong intensity band at $\sim 1600 - 1667 \text{ cm}^{-1}$ and $809-826 \text{ cm}^{-1}$ attributed to N-H deformations coupled with N-H out of plane bending vibrations [39].

Table 2: Important IR Data (cm^{-1}) for Metal Complexes

Complex	$\nu_{\text{N-H}}$	N-H def.	N-H out of plane bending	$\nu_{\text{C-N}}$	$\nu_{\text{C-S}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	$\nu_{\text{M-Cl}}$	$\nu_{\text{Te-N}}$
$[\text{ZnL}^1\text{Cl}_2]$	3142 mb	1591 m	825 s	1173 s	692 sh	464 w	323 w	288, 325 m	418 w
$[\text{ZnL}^2\text{Cl}_2]$	3120 s	1627 s	811 s	1176 m	723 m	455 w	324 w	294, 324 w	419 w
$[\text{CdL}^1\text{Cl}_2]$	3117 s	1636 s	826 s	1173 s	720 m	462 w	325 w	*	418 w
$[\text{CdL}^2\text{Cl}_2]$	3120 m	1610 s	809 m	1180 m	759 m	459 w	328 w	*	423 w
$[\text{HgL}^1\text{Cl}_2]$	3118 s	1667 s	824 m	1174 m	682 m	466 w	330 w	286, 330 m	426 w
$[\text{HgL}^2\text{Cl}_2]$	3090 mb	1620 s	809 s	1174 m	761 m	456 w	334 w	287, 334 w	416 w

m= medium, b= broad, s= strong, w= weak, sh= shoulder, *very weak bands

Medium to weak intensity bands at $\sim 1174 \text{ cm}^{-1}$ and $455-466 \text{ cm}^{-1}$ may be assigned to C-N stretching vibration [26,40,41] and M-N stretching [26,42,43] respectively. The tellurium containing macrocyclic ring [26,27,42] is also favoured by appearance of new weak intensity bands at $426-416 \text{ cm}^{-1}$ due to Te-N vibrations. These complexes show complete absence of the band at around 2400 cm^{-1} due to S-H stretching vibration which appears in the spectra of 2-aminoethanethiol. Two new medium intensity bands in the region $323-334 \text{ cm}^{-1}$ and $682-761 \text{ cm}^{-1}$ assigned to $\nu(\text{M-S})$ and $\nu(\text{C-S})$ vibrations respectively [19,43,44] are consistent with metal-sulfur co-ordination. Further, presence of medium to weak intensity bands in the region $286-334 \text{ cm}^{-1}$ may be assigned to $\nu(\text{M-Cl})$ vibration [40,45-49].

Proton Magnetic Resonance Spectra

The proton chemical shifts for the metal complexes in DMSO- d_6 are presented in Table 3. In the metal complexes, the phenyl protons resonate at slightly upfield side (6.63-7.66 δ ppm) as compared to the parent diaryltellurium dichlorides [33,34] due to replacement of 2 Chlorine by 2 Nitrogen atoms and hence increase in electron density at the tellurium atom. 2-Aminoethanethiol, $H_2N-CH_2-CH_2-SH$, exhibits proton chemical shifts at 1.45 (2H), 2.50 (1H), 2.75 (2H) and 2.87 (2H) δ ppm due to amino, thiol, methylene (adjacent to N) and methylene (adjacent to S) groups respectively [22,50,51].

Table 3: 1H -NMR Spectral Data (δ ppm) for the Metal Complexes in DMSO- d_6

Complex	Chemical Shift, δ ppm
[ZnL ¹ Cl ₂]	1.92 (s, 2H, -NH-), 2.98 (t, 4H, -CH ₂ -S-), 3.12 (t, 4H, -CH ₂ -N-) 6.64 ^d & 7.63 ^d (16H, phenyl), 9.8 (s, 4H,OH)
[ZnL ² Cl ₂]	1.99 (s, 2H, -NH-), 2.97 (t, 4H, -CH ₂ -S-), 3.13 (t, 4H, -CH ₂ -N-), 2.49* (s,12H, phenyl-CH ₃) 6.63 ^d , 7.55 ^d & 7.66 ^s (12H, phenyl), 8.08 (s, 4H,OH)
[CdL ¹ Cl ₂]	1.88 (s, 2H, -NH-), 2.99 (t, 4H, -CH ₂ -S-), 3.15 (t, 4H, -CH ₂ -N-) 6.68 ^d & 7.64 ^d (16H, phenyl), 8.9 (s, 4H,OH)
[CdL ² Cl ₂]	2.01 (s, 2H, -NH-), 2.99 (t, 4H, -CH ₂ -S-), 3.13 (t, 4H, -CH ₂ -N-) 2.53 (s, 12H, phenyl -CH ₃) 6.69 ^d , 7.53 ^d & 7.61 ^s (12H, phenyl), 8.99 (s, 4H,OH)
[HgL ¹ Cl ₂]	1.98 (s, 2H, -NH-), 2.98 (t, 4H, -CH ₂ -S-), 3.16 (t, 4H, -CH ₂ -N-) 6.65 ^d & 7.61 ^d (16H, phenyl), 9.9 (s, 4H,OH)
[HgL ² Cl ₂]	2.05 (s, 2H, -NH-), 2.94 (t, 4H, -CH ₂ -S-), 3.14 (t, 4H, -CH ₂ -N-) 2.50* (s, 12H, phenyl -CH ₃) 6.66 ^d , 7.55 ^d & 7.65 ^s (12H, phenyl), 7.87 (s, 4H,OH)

(s= singlet, d= doublet, t= triplet, m= multiplet); * may be mixed with solvent peak.

The synthesized metal complexes do not show any signal due to free amino group. Instead, a broad singlet at 1.88-2.05 δ ppm assignable to coordinated secondary amino group [19,24,26] confirms the formation of macrocyclic skeleton. All the complexes show presence of triplets (slightly downfield side) at 2.94-2.99 and 3.12-3.16 δ ppm corresponding to (S-CH₂; 4H) and (N-CH₂; 4H) respectively, of the 2-aminoethanethiol Moiety.

However, no band could be assigned for free amino or thiol protons, suggesting that proposed macrocyclic complexes are formed by the condensation reaction. Further, the independence of chemical shifts of aryl protons on the metal ions, hints at non-participation of Te atoms of the macrocycle in coordination with the metal ions. Thus, proton NMR studies support the formation of 10-membered tellurium containing dithiadiazia macrocycles and their quadridentate behavior as predicted by IR studies. Based on elemental analyses, conductance, magnetic, infrared, electronic and proton magnetic resonance spectral studies, a distorted octahedral geometry involving two N and two S of the dithiadiazia macrocycle and 2 Cl may be proposed for these metal complexes as shown in Figure 1.

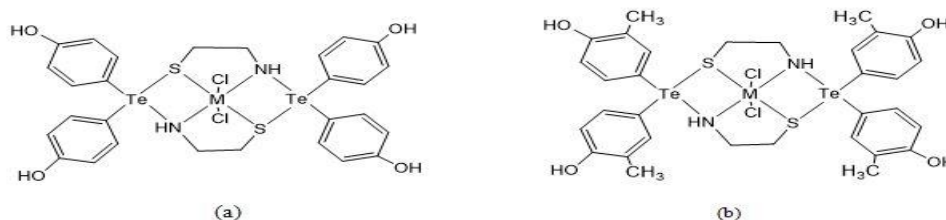


Figure 1. Proposed Structure of the Ditellurium Dithiadiazia Macrocyclic Metal Complexes of the Type [ML¹Cl₂] (a) and [ML²Cl₂] (b)

Antimicrobial Studies

The results (Table 4 and 5) indicate that some of the complexes possess very good antimicrobial activity as compared to the standard bactericide and fungicide. All the complexes show better antimicrobial

activity than their precursors and thus indicated that complexation to metal enhances the activity of the ligand. Among all the synthesized metal complexes; $[\text{HgL}^1\text{Cl}_2]$ ($\text{MIC} = 6.25\text{-}12.5 \mu\text{g ml}^{-1}$) and $[\text{HgL}^2\text{Cl}_2]$ ($\text{MIC} = 3.12\text{-}6.25 \mu\text{g ml}^{-1}$) complexes are found to be more powerful and potent bacteriostatic and fungistatic agent. Also, the metal complexes containing 3-methyl 4-hydroxyphenyl moiety in their ligand framework show better activity.

Table 4: Minimum Inhibitory Concentration (MIC) of Metal Complexes Against Test Bacteria

Complex	MIC($\mu\text{g ml}^{-1}$)				
	<i>Salmonella typhi</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Bacillus cereus</i>	<i>Staphylococcus aureus</i>
$\text{NH}_2(\text{CH}_2)_2\text{SH}$	12.5	12.5	25	12.5	12.5
R_2TeCl_2 (<i>p</i> -hydroxyphenyl)	25	25	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5	25	25
$[\text{ZnL}^1\text{Cl}_2]$	12.5	12.5	12.5	6.25	12.5
$[\text{ZnL}^2\text{Cl}_2]$	12.5	6.25	12.5	12.5	12.5
$[\text{CdL}^1\text{Cl}_2]$	12.5	12.5	25	12.5	12.5
$[\text{CdL}^2\text{Cl}_2]$	12.5	12.5	12.5	6.25	12.5
$[\text{HgL}^1\text{Cl}_2]$	12.5	6.25	6.25	6.25	6.25
$[\text{HgL}^2\text{Cl}_2]$	6.25	6.25	3.12	3.12	6.25
Cefadroxil	3.12	1.56	3.12	1.56	3.12

Table 5: Minimum Inhibitory Concentration (MIC) of Metal Complexes Against Test Fungi

Complex	MIC($\mu\text{g ml}^{-1}$)		
	<i>Aspergillus niger</i>	<i>Aspergillus fumigatus</i>	<i>Candida albicans</i>
$\text{NH}_2(\text{CH}_2)_2\text{SH}$	12.5	12.5	25
R_2TeCl_2 (<i>p</i> -hydroxyphenyl)	25	25	25
R_2TeCl_2 (3-methyl-4-hydroxyphenyl)	25	25	12.5
$[\text{ZnL}^1\text{Cl}_2]$	12.5	12.5	6.25
$[\text{ZnL}^2\text{Cl}_2]$	12.5	12.5	12.5
$[\text{CdL}^1\text{Cl}_2]$	12.5	12.5	25
$[\text{CdL}^2\text{Cl}_2]$	12.5	12.5	12.5
$[\text{HgL}^1\text{Cl}_2]$	6.25	6.25	6.25
$[\text{HgL}^2\text{Cl}_2]$	3.12	6.25	3.12
Fluconazole	3.12	3.12	1.56

CONCLUSION

Zn(II), Cd(II) and Hg(II) complexes have been prepared by template condensation of diaryltellurium(IV) dichlorides with 2-aminoethanethiol in presence of divalent metal chlorides. These newly synthesized complexes have been characterized by elemental analyses, conductance measurements, electronic absorption, IR and proton magnetic resonance spectral studies. Based on these studies, a distorted octahedral structure has been assigned to these complexes. Hg(II) complexes show very good antimicrobial activity against some pathogenic bacteria and fungi while others are moderately active.

ACKNOWLEDGEMENT

The authors are thankful to M. D. University, Rohtak for providing the necessary facilities. One of the authors (SK) is also thankful to M. D. University, Rohtak for providing University Research Scholarship. We also thank SAIF, Panjab University Chandigarh for providing the CHN analyses and spectral data.

REFERENCES

- [1] Wang Q, Tang K Z, Liu W S, Tang Y and Tan M Y, J. Solid State Chem., 2009; 182: 31.

- [2] Chaudhary A, Bansal N, Fahmi N and Singh R V, *Indian J. Chem.*, 2004; 43A: 320; Chandra S, Gupta R, Gupta N and Bawa S S, *Transition Met. Chem.*, 2006; 31: 147.
- [3] Lindoy L F (Ed.), *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989; Salavati-Niasari M, Amiri A, *Trans. Met. Chem.*, 2005; 30: 720–725.
- [4] Chandra S and Gupta L K, *Trans. Met. Chem.*, 2007; 32: 558.
- [5] Nishat N, Rahis-Ud-Din and Dhyani S, *J. Coord. Chem.*, 2009; 62(6): 996-1004.
- [6] Veggel F C J M van, Verboom W and Reinhoudt D N, *Chem. Rev.*, 1994; 94: 279.
- [7] Ren Y W, Guo H, Wang C, Liu J J, Jiao H, Li J and Zang F X, *Trans. Met. Chem.*, 2006; 31: 12.
- [8] Salavati-Niasari M, Adaryni M R and Heydarzadeh S, *Trans. Met. Chem.*, 2005; 30: 445.
- [9] Gange R R, Alison J L, Gall S and Kovac C A, *J. Am. Chem. Soc.*, 1999; 99: 7170.
- [10] Martin J W L, Johnston J H and Curtis N F, *J. Chem. Soc., Dalton Trans.*, 1978; 68.
- [11] Hughes M N, *Inorganic Chemistry of Biological Processes*, 2nd Edn., Wiley, New York, 1981.
- [12] Casella L, Gullotti M, Gioia L D, Monzani E and Chillemi F, *J. Chem. Soc., Dalton Trans.*, 1991; 2945.
- [13] James S R and Margerum D W, *Inorg. Chem.*, 1990; 19: 2784.
- [14] Steigerwald M L, Sprinkle C R, *J. Am. Chem. Soc.*, 1987; 109: 7200.
- [15] Hirpo W, Dhingra S, Sutorik A C, Kanatzidis M G, *J. Am. Chem. Soc.*, 1993; 115: 1597.
- [16] Vander Pleog A F M J, Vander Kolk C E M and Van Koten G J, *J. organomet. Chem.*, 1981; 212: 283.
- [17] Gasperov V, Galbraith S G, Lindoy L F, Rumbel, B R, Skelton B W, Taskker P A and White A H, *J. Chem. Soc., Dalton Trans.*, 2005; 139.
- [18] Saraj M R A, Saadeh S M and Latif S A, *Z. Naturforsch*, 2003; 58b: 658.
- [19] Nasman O S M, *Transition Met. Chem.*, 2008; 33: 285.
- [20] Shakir M, Varkey S P and Hameed P S, *J. Chem. Res.*, 1993; 11: 2964.
- [21] Ismael A A A, Baraka R M and Nasman O S M, *Polyhedron*, 2001; 20: 455.
- [22] Shakir M and Varkey S P, *Polyhedron*, 1994; 13: 791.
- [23] Nasman O S M, *Phosphorus, Sulfur and Silicon*, 2008; 183: 1541-1551.
- [24] Nitu and Verma K K, *J. Chem. Pharm. Res.*, 2010; 2(4): 793.
- [25] Nitu and Verma K K, *Int. J. Chem. Sci.*, 2011; 9(1): 229.
- [26] Rathee N and Verma K K, *J. Serb. Chem. Soc.*, 2012; 77(3): 325-333.
- [27] Srivastava S, Kalam A, *J. Indian Chem. Soc.*, 2006; 83: 563.
- [28] Vogel AI, *A Text Book of Organic Chemistry*, 3rd Edn., Longman, London, 1975.
- [29] Weissberger A, Ed., *Technique of Organic Chemistry*, Vol. 7, 2nd Edn., Interscience Publishers, Inc. N. Y., 1967.
- [30] Vogel A I, *A Text Book of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, Longman, London, 1975; 3: 266, 324.
- [31] Cappuccino JC, Sherman N, *Microbiology- A Laboratory Manual*, Addison Wesley, California, 1999; 263.
- [32] *Pharmacopoeia of India*, Volume 1, Controller of Publications, Ministry of Health Department, Government of India, New Delhi, 2007; 37.
- [33] Khandelwal B L, Kumar K and Raina K, *Synth React Inorg Met Org Chem.*, 1981; 11(1): 65.
- [34] Khandelwal B L, Kumar K and Berry F J, *Inorg Chim Acta*, 1981; 47: 135-137.
- [35] Geary W J, *Coord Chem Rev.*, 1971; 7: 81-122.
- [36] Sonmez N M, Levent A and Sekerci M, *Synth. React. Inorg. Met.-Org. Chem.*, 2003; 33: 1747.
- [37] Mukhopadhyay R, Bhattacharjee S and Bhattacharya R, *J. Chem. Soc.*, 1944; 2799.
- [38] Rathee N and Verma K K, *Der Pharma Chemica*, 2011; 3(1): 97.
- [39] Rana V B, Singh P, Singh D P, Teotia M P, *Polyhedron*, 1982; 1: 377.
- [40] Srivastava S, Kalam A, *Synth. React. Inorg. Met.– Org. Chem.*, 2004; 34: 1529.
- [41] Panda A K, Panda A, Sutar S, Mishra P, Pradhan S, Ghos S and Pany S, *J. Indian Chem. Soc.*, 2009; 86: 908.
- [42] Kulkarni Y D, Srivastava S, *Indian J. Chem.*, 1985; 22: 710.
- [43] Shakir M, Kumar D and Varkey S P, *Polyhedron*, 1992, 11(22): 2831.
- [44] Chandra S, Gautam S, Rajor H K and Bhatia R, *Spect. chim. acta part A: molecular and biomolecular spectroscopy*, 2015; 137: 749.
- [45] Nasman O S M, *Asian J. Chem.*, 2014; 16: 471-475.
- [46] Patil S A, Kamble U V and Badami P S, *Main Group Chemistry*, 2009; 8: 189-206.
- [47] Khan S, Nami S A A and Siddiqi K S, *Spect. chim. Acta part A*, 2007; 68: 269-274.
- [48] Singh D, Kumar K, Kumar R and Singh J, *J. Serb. Chem. Soc.*, 2010; 75: 217-228.
- [49] Shakir M, Islam K S, Mohamed A K, Shagufta M and Hasan S S, *Trans. Met. Chem.*, 1999; 24: 577-580.



- [50] Silverstein R M, Spectrometric Identification of Organic Compounds, 4th Edn. John Wiley, New York, 1981.
- [51] Pavia D L, Lampman G M, Kriz G S and Vyvyan J R, Spectroscopy, 2007.