



Some Novel Manganese(III) Mixed Ligand Complexes and Its Decolourization Studies

DEEPIKA JAISWAL and SUDHA YADAVA*

Department of Chemistry, D. D. U. Gorakhpur University, Gorakhpur, U.P, India.

*Corresponding author E-mail: dr_sudhayadava@yahoo.co.in

<http://dx.doi.org/10.13005/ojc/340625>

(Received: August 17, 2018; Accepted: November 03, 2018)

ABSTRACT

Some novel mixed ligand complexes of Mn(III) with glycine ligand namely $[\text{Mn}(\text{gly})_2\text{Cl}(\text{en})]$, $[\text{Mn}(\text{gly})_2\text{Br}(\text{en})]$, $[\text{Mn}(\text{gly})_2\text{N}_3(\text{en})]$ and $[\text{Mn}(\text{gly})_2\text{NCS}(\text{en})]$ have been synthesized starting from $\text{Mn}(\text{gly})_2\text{Cl}$, $\text{Mn}(\text{gly})_2\text{Br}$, $\text{Mn}(\text{gly})_2\text{N}_3$ and $\text{Mn}(\text{gly})_2\text{NCS}$ respectively. These newly synthesized complexes have been characterized by UV-Vis, FT-IR and Mass spectrometry. The spectroscopic data suggest distorted octahedral geometry for all these mixed ligand complexes. The λ_{max} values of these complexes for ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$ transitions are 482 nm for $[\text{Mn}(\text{gly})_2\text{N}_3(\text{en})]$, 488 for $[\text{Mn}(\text{gly})_2\text{NCS}(\text{en})]$, 486 for $[\text{Mn}(\text{gly})_2\text{Br}(\text{en})]$ and 484 for $[\text{Mn}(\text{gly})_2\text{Cl}(\text{en})]$, all these transitions are red shifted in comparison to their parent complexes. The ligand field parameters such as 10Dq , B and β have also been calculated and suggest covalent metal ligand bonding. One peculiar finding is that the FT-IR spectra shows frequencies for both free and coordinated NH_2 group in all complexes indicating that the ethylenediamine ligand present here is non bridging in nature. The mass spectrometry results show molecular ion peaks at m/z 300, 345, 307 and 323 for $[\text{Mn}(\text{gly})_2\text{Cl}(\text{en})]$, $[\text{Mn}(\text{gly})_2\text{Br}(\text{en})]$, $[\text{Mn}(\text{gly})_2\text{N}_3(\text{en})]$ and $[\text{Mn}(\text{gly})_2\text{NCS}(\text{en})]$ respectively. The coordination of ethylenediamine to Mn(III) enhances its efficiency towards decolourization methyl red dye.

Keywords: Mn(III) mixed ligand complexes, Glycine, Ethylenediamine, Dye decolourization.

INTRODUCTION

Synthesis, characterization, and applications of Mn(III) complexes had been the focus of global research interest due to their role in the chemical and biological system¹⁻⁷. Mn(III) complexes supported on Fe_3O_4 nanoparticles had been used for selective oxidation of thiols to sulphides⁸. Mn(III) porphyrin anchored onto multiwall carbon nanotubes had been used as an efficient and reusable catalyst for heterogeneous reduction of aldehyde and ketones⁹. Mn(III)-Schiff base dicyanamide complexes had been used for checking the rhombicity effect in peroxidase studies¹⁰. The application of encapsulated Salen- and

Salhd-Mn(III) complexes in an AP- pillared clay for bicarbonate assisted epoxidation of cyclohexane had been demonstrated¹¹. Mn(III) had been found to play an important role at the redox centers of biological systems, important among those are Mn containing catalase, Mn containing ribonucleotide reductase, and the oxygen evolving center of photosystem II (PS-II)¹². Attempts had been made to mimic the active site of these enzymes also¹³⁻¹⁵. In most of the cases, Mn(III) complexes have been synthesized using potassium permanganate or Mn(II) and Mn(III) acetate¹⁶⁻¹⁹. However, most of the reported Mn(III)-complexes have octahedral or square pyramidal geometry^{15, 20-21}.



The above studies prompted the authors' group to initiate the studies on the synthesis, characterization and application of Mn(III) complexes. In an earlier study, synthesis and characterization of novel complexes of Mn(III) with macrocyclic porphyrin ligand and ethylenediamine have been reported by this group²². The depolymerization activity of these complexes towards humic acid as coal model had also been reported earlier²³. Recently Mn(III)-porphyrin complexes with oxidation property have been reported by our group²⁴. Another work on synthesis and characterization of a novel Mn(III)-(γ -diketone) complex with catalytic and antifungal activity have also been reported from our laboratory²⁵. Tris(glycinato) Mn(III) complex has been synthesized for the first time in our laboratory²⁶. There is a report in the literature²⁷ that coordination of imidazole to Mn(III) in a Mn(III)-porphyrin complex enhances the catalytic activity of the complex towards the oxidation of benzyl alcohol to benzaldehyde in presence of sodium periodate. Considering the above report, the authors have synthesized and characterized ethylenediamine mixed ligand complexes of Mn^(III)(gly)₂Cl, Mn^(III)(gly)₂Br, Mn^(III)(gly)₂NCS, and Mn^(III)(gly)₂N₃ and have studied the decolorization potential of these novel complexes towards decolorization of methyl red dye. It has been observed that substitution of ethylenediamine in Mn(gly)₂X complex enhances its efficiency as a heterogeneous catalyst towards the decolorization of Methyl Red in presence of H₂O₂.

MATERIALS AND METHODS

Glycine was purchased from Mumbai (sigma-aldrich). All the reagents and solvents were of analytical grade and procured from Merck Ltd., Mumbai (India) and used without further purification. Milli-Q water had been used throughout the experiments.

Characterization

The purity of these complexes was checked in our laboratory by TLC method using Silica gel on glass plates. The mobile phase was dichloromethane and methanol 7:3 (v/v). Detection was made by keeping the TLC glass plates in iodine-chamber. The complexes were analyzed for C, H, and N element in Sophisticated Instrumentation Center of Cochin University of Science and Technology, Cochin. The UV-Vis spectra of the complexes were recorded on UV-Vis Spectrophotometer Hitachi (Japan) model U-2900 available in our laboratory. The FT-IR spectra of the complex were recorded on Perkin Elmer FT-IR spectrometer 2000 in KBr disk at

the Indian Institute of Technology Kanpur. Magnetic susceptibility measurement data for all these Mn (III) complexes were recorded by the instrument VSM (vibrating sample magnetometer) at IIT Kanpur. DART mass spectra of complexes were recorded on Reservoir, JMS-T100LC at the Sophisticated Analytical Instrumentation Facility, Central Drug Research Institute, Lucknow.

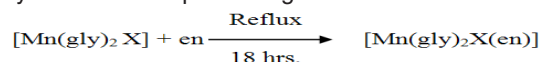
Synthesis

Preparation of ethylenediamine complexes, [Mn(gly)₂X(en)]

All these [Mn(gly)₂X(en)] complexes were prepared according to the earlier reported procedure in the literature^{26, 28} where X = Cl⁻, Br⁻, N₃⁻, NCS⁻.

For the preparation of azido complex, 0.82 g Mn(gly)₂N₃ complex was refluxed with 1 mL of ethylenediamine for 18 hours. After refluxion the obtained product was cooled for 1 h at room temperature (27°C) resulting in dark black powder of Mn(gly)₂X(en) complex, which was dried under vacuum over P₂O₅ and washed with milliQ water. The Cl⁻, Br⁻ and NCS⁻ ethylenediamine complexes were prepared analogously.

The reaction scheme for all these synthesized complexes is given below.



Where gly = glycine, X = Cl⁻, Br⁻, NCS⁻ and N₃⁻

Catalysis of methyl red by the complexes

The reaction solution (2 ml) consisted of 0.24% methyl red, 14.63% H₂O₂ and 0.5 mg of the complex in milliQ water. Since the complexes were insoluble in the reaction medium hence acted as heterogeneous catalysts. The time of 100% decolorization of the dye was recorded with the help of a stopwatch by visual observations. The UV/Vis spectra of the reaction solution before and after the decolorization of dye was recorded.

RESULTS AND DISCUSSION

The objective of this communication has been clearly stated in the introduction section. Here ethylenediamine added complexes of Mn(gly)₂Cl, Mn(gly)₂Br, Mn(gly)₂N₃ and Mn(gly)₂NCS have been synthesized to see if the catalytic properties of these novel mixed ligand complexes towards the decolorization of dye in presence of H₂O₂ is enhanced by the addition of ethylenediamine.

The purity of these complexes was checked by thin layer chromatography on silica gel glass plates. A single spot for each of the complex indicates that these complexes are pure. All the physical properties of these complexes are summarized in Table 1. The colour is black in all, it indicates that the colour of the complexes is governed by the presence of Mn(III) ion.

The UV-Vis spectra of the complexes were recorded in dimethyl sulphoxide (DMSO). One of the spectrum for Mn(gly)₂Cl(en) is shown in Fig.1 while the λ_{max} values for these four complexes are given in Table 2. The λ_{max} and the molar extinction

coefficient values for this typical spectrum are 484 nm and $2.142 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ respectively. The molar extinction coefficient value ϵ_{484} for this complex is in the range of spin allowed transition ${}^5T_{2g} \rightarrow {}^5E_g$. The λ_{max} values for all these novel mixed ligand complexes are red shifted in comparison to their parent complexes, thus showing the decrease in the crystal field stabilization energies of these complexes. The crystal field stabilization energies of Mn(gly)₂Cl(en), Mn(gly)₂Br(en), Mn(gly)₂N₃(en) and Mn(gly)₂NCS(en) have been evaluated as 23674 cm⁻¹, 23466 cm⁻¹, 23854 cm⁻¹ and 2333 cm⁻¹ respectively whereas the crystal field stabilization energies of Mn(gly)₂Cl, Mn(gly)₂Br, Mn(gly)₂N₃ and Mn(gly)₂NCS are 29,069 cm⁻¹, 28409 cm⁻¹, 25201 cm⁻¹ and 27173 cm⁻¹ respectively²⁶. In this way the ethylenediamine complexes are relatively less stable than their parent complexes. The ligand field parameters such as 10 Dq, B and β have also been calculated for these ethylenediamine Mn(III) complexes and are summarized in Table 2. The values of Racah interelectronic repulsion parameter (B) are below the free ion value for Mn(III) ion (1140 cm⁻¹)³⁰ it confirms the covalent nature of metal ligand bonds present in all four complexes while the covalency factor β is varying in the range of 0.75-0.77.

Table 2: λ_{max} values and Ligand Field Parameter of all these mixed ligand complexes

Complexes	λ_{max}	10Dq(Cm ⁻¹)	B(Cm ⁻¹)	β
Mn(gly) ₂ N ₃ (en)	482	23,854	883	0.77
Mn(gly) ₂ NCS(en)	488	23,320	863	0.75
Mn(gly) ₂ Br(en)	486	23,496	870	0.76
Mn(gly) ₂ Cl(en)	484	23,674	876	0.76

Table 1: Physical properties of Mn(III) Complexes

Complexes	color	% Yield	Analysis found (Calcd)%										F.W	Decom Temp	
			C	H	N	O	S	Cl	Br	Mn	En				
Mn(gly) ₂ N ₃ (en)	Black	52.33	15.62	2.6	22.78	20.83						17.88	19.56	307.19	302
Mn(gly) ₂ NCS(en)	Black	55.2	15.59	2.58	22.75	20.81	9.91					17.86	19.54	323.25	308
Mn(gly) ₂ Cl(en)	Black	57.67	18.56	2.47	12.99	19.79	9.93			11.79		16.99	18.59	300.62	303
Mn(gly) ₂ Br(en)	Black	59.69	18.55	2.43	12.95	19.74				14.71		16.96	18.55	345.07	305

The results of the FT-IR spectra of the complexes [Mn(III)(gly)₂Cl(en)], [Mn(III)(gly)₂Br(en)], [Mn(III)(gly)₂NCS(en)], and [Mn(III)(gly)₂N₃(en)] are summarized in Table 3. All the four complexes show a strong peak around 3400 cm⁻¹ due to NH₂ group coordinated to Mn(III). The Strong peak at 3583 cm⁻¹ is due to free amino group that is possible only when en acts as a monodentate ligand instead of bidentate or bridging ligand. These findings indicate that these mixed ligand complexes of Mn(III) are monomeric in nature and not dimeric as reported in the earlier literature for a few cases³¹. In the case of azidobis(glycinato)manganese(III)(en) one significant band is observed at 2040 cm⁻¹ showing the coordination of azido group with the Mn(III). The spectrum of thiocyanatobis(glycinato)manganese(III)(en) shows a band characteristic for coordinated NCS group $\nu(\text{Mn-N})$ at 2090 cm⁻¹ indicating the coordination of thiocyanato group to the metal through nitrogen donor atom³². These complexes are monomeric instead of dimeric this is also supported by the mass spectrophotometric studies also. One of typical mass spectrum for [Mn(III)(gly)₂N₃(en)] is shown in Fig. 2 it shows the presence of molecular ion peak at $m/z = 307$ that corresponds to the monomeric species present in this mixed ligand complex.

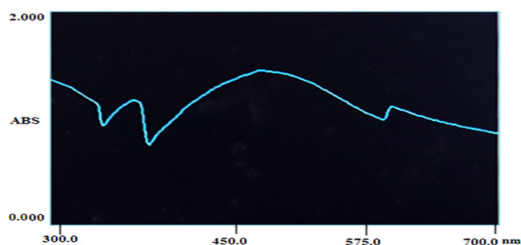


Fig. 1. UV-Visible spectra of chlorobis(glycinato)Mn(III) ethylenediamine $[Mn(gly)_2Cl(en)]$ complex

The magnetic moment values for all these manganese(III) complexes have been found in the range of 4.20-4.90 BM at room temperature. It confirms the presence of four unpaired electrons and a high-spin d^4 system in all the four novel complexes^{33, 34}. On the basis of all the above studies distorted octahedral structure has been proposed for all the novel mixed ligand complexes and it is given as in Figure 4.

Now a days oxidation and removal of synthetic dyes from the environment has become one of the important research areas to control environmental pollution. These novel complexes have been tested for their ability to decolorize Methyl red in presence of H_2O_2 . The UV spectrum of decolorization reaction of Methyl Red using the initial $[Mn(gly)_3]$ is shown in Fig. 3 here Fig. 3 (a) is the spectrum of 0.2% methyl red in 14.63% H_2O_2 in milliQ water and Fig. 3 (b) is the spectrum of the dye decolorized in presence of $[Mn(gly)_3]$ complex. In separate experiments,

relative efficiencies of $[Mn(gly)_3]$, $[Mn(gly)_2Cl]$ and $[Mn(gly)_2Cl(en)]$ have been tested towards their ability to decolorize Methyl Red dye. The composition of reaction solution and time required for complete decolorization of the dye are given in Table 4. The order of efficiency of decolorization for methyl red in presence of these complexes can be given as $[Mn^{(III)}(gly)_2Cl(en)] > [Mn(gly)_3] > [Mn^{(III)}(gly)_2Cl]$. The time required for the complete decolorization of 0.24% Methyl Red in the presence of 14.63% H_2O_2 in case of $Mn(gly)_2Cl(en)$ complex is only five second while in case of $Mn(gly)_3$ it is 10 second and in case of $Mn(gly)_2Cl$ it is 90 second. These complexes have been used for three cycles of catalysis without any apparent change, Complexes are reusable efficient heterogeneous catalysts for dye decolorization and in this way may be used on the industrial scale for the removal of environmental pollution caused by organic dyes.

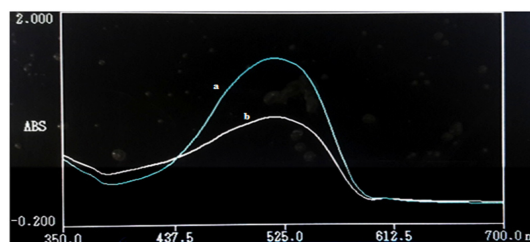


Fig. 3. Decolorization of methyl red in presence of H_2O_2 by the glycinato complex. (a) Spectrum of 0.2% methyl red in 14.62% H_2O_2 in milliQ water, (b) Spectrum of decolorized 0.2% methyl red by $Mn(gly)_3$ complex in 14.62% H_2O_2 in milliQ water

Table 3: FT-IR spectra of all these complexes

$Mn(Gly)_2N_3(en)$	$Mn(Gly)_2NCS(en)$	$Mn(Gly)_2Cl(en)$	$Mn(Gly)_2Br(en)$	Assignment
604	599	613	665	$\nu(Mn-O)$
487	497	510	486	$\nu(Mn-N)$
1385	1320	1320	1320	$\nu(CH_2)$
1648	1635	1625	1651	$\nu(COO)$
2040	-----	-----	-----	$\nu(N_3)$
-----	2090	-----	-----	$\nu(NCS)$
3400	3400	3400	3368	$\nu(NH_2)_{\text{coordinated}}$
3583	3583	3583	3583	$\nu(NH_2)_{\text{free}}$

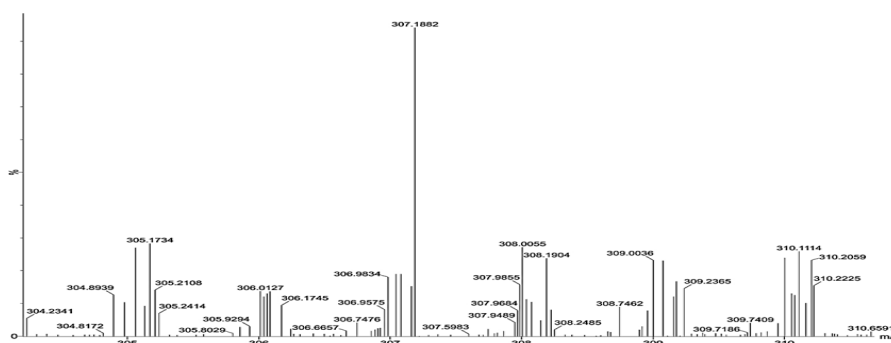


Fig. 2. DART Mass spectra of azidobis(glycinato)Mn(III)ethylenediamine $[Mn(gly)_2N_3(en)]$ complex

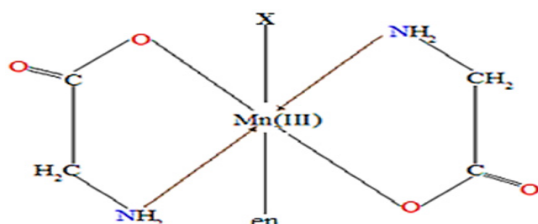


Fig. 4. Structure for all these synthesized complexes, $[\text{Mn}(\text{gly})_2\text{X}(\text{en})]$ Where $\text{X} = \text{Cl}^-$, Br^- , N_3^- , NCS^-

Table 4: The results of decolourization of methyl red by the complexes

S.No.	Complexes	Quantity	Decolourization Time
1.	$\text{Mn}(\text{gly})_3$	0.5 mg	10 sec
2.	$\text{Mn}(\text{gly})_2\text{Cl}$	0.5mg	90 sec
3.	$\text{Mn}(\text{gly})_2\text{Cl}(\text{en})$	0.5mg	5 sec

CONCLUSION

Four novel complexes $[\text{Mn}^{(\text{III})}(\text{gly})_2\text{Cl}(\text{en})]$, $[\text{Mn}^{(\text{III})}(\text{gly})_2\text{Br}(\text{en})]$, $[\text{Mn}^{(\text{III})}(\text{gly})_2\text{NCS}(\text{en})]$, and

$[\text{Mn}^{(\text{III})}(\text{gly})_2\text{N}_3(\text{en})]$ have been synthesized and characterized by UV-Visible, FT-IR, Mass spectrophotometry and magnetic susceptibility measurements. Their tentative structure has been proposed to be octahedral. These ethylenediamine mixed ligand complexes of Mn(III) are better reusable heterogeneous catalysts for the decolourization of Methyl Red in presence of H_2O_2

ACKNOWLEDGMENT

The authors are thankful to CSIR New Delhi for the financial support through the grant no. 02(0261)/16/EMR II dated 28/04/16. The authors are also thankful to the Head Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur for administrative support. The authors acknowledge the services rendered by the Sophisticated Analytical Instrument Facility (SAIF), Cochin and Central Drug Research Institute (CDRI), Lucknow for recording FT-IR and DART Mass of the samples and IIT Kanpur (ACMS Department) for magnetic susceptibility measurements.

REFERENCES

- Maxwell, J. G.; Peter, T. *Coord. Chem. Rev.*, **1991**, *108*, 115-161.
- Jelle, B.; Minze, T. R.; Ronald, H.; Ben, L. F. *Inorg Chim Acta.*, **2002**, *337*, 75-82.
- Sumitra, M.; Sanjay, K.; Mandal, S. B.; William, H. A. *Chem. Rev.*, **2004**, *104*, 3981-4026.
- Suzana, C.; Caslav L.; Goran, N.; Jakov S.; Milos. R.; Miladin, G. M. *Sensors.*, **2006**, *6*, 1708-1720.
- Donald, J. D.; Eric B. F. *Inorg. Chem.*, **2007**, *46*(15), 5967-5978.
- Qian, P.; Shi, Z.; Hao, S.; Nian, Li.; Yu-Ping, T.; Wei, Li.; Hao T.; Wei-Z.; Min-Zhe S.; Jin, A. D. *Curr. Organ. Chem.*, **2013**, *17*, 2936-2970.
- Chetan, K.; Modi, P.; M. Trivedi. *J. Coord. Chem.*, **2014**, *67*(22), 3678-3688.
- Mojtaba, B.; Mohammad, M. H.; Firouz, M. J. *Coord. Chem.*, **2013**, *66*(17), 3025-3036.
- Saeed, R.; Elaheh, B.; Saeed, Z. *J. Coord. Chem.*, **2016**, 638-649.
- Manuel, R. B.; Rocio, C.; Fernandez, G.; M, Isabel.; Ana, M.; G, N.; Gustavo, G. R.; Marcelino, M.; Laura, R. S. *J. Chem.*, **2017**, 1-10.
- Garcia, A. M.; Moreno, V.; Delgado, SX.; Ramirez, AE.; Vargas, LA.; Vicente, MA.; Gil, A. *J. Molec. Catal A-Chemical.*, **2016**, *416*, 10-19.
- Dismukes, G. C.; *Bioinorganic Catalysis*, J. Reedijk, (Ed) First edition, Marcel Dekker Inc, New York., **1993**, 317.
- Faulkner, K. M.; Stevens, R. D.; Fridovich, I. *Arch Biochem Biophys.*, **1994**, *2*, 341-346.
- Christian, R.; Goldsmith, A. P.; Cole, T. Daniel; P.S. *J. Am. Chem. Soc.*, **2005**, *127*(27), 9904-9912.
- Arpan, D. S.; Biswas, M. D.; Bikash, K. S.; Abhishake, M.; Shyamal, K. S.; Mahammad A. *RSC Advances.*, **2015**, *5*, 23855-23864.
- Hosseini, A.; Gus, J. P., *Inorg. Chem.*, **1982**, *21*, 3903-3907.
- Shalaby, M. S.; Abdallah, H., *Front. Chem. Sci. Eng.*, **2013**, *7*(3), 329-337.
- Iffet, S.; Necla, G.; Turgut G., *Synth. React. Inorg. Met.-Org. Chem.*, **2001**, *31*(7), 1175-1187.
- Altan, Guvenç.; Karabacakoglu, B., *Turk J Chem.*, **2000**, *24*, 101-108.
- Bhagwan, S. G.; Asha, L. D.; Ranjina, D., *Transition. Met. Chem.*, **1988**, *13*, 351-355.
- Laurence, J. B.; Victor, W. Day.; *Inorganic Chemistry.*, **1977**, *16*, 1360-1667.
- Sudha, Y.; Shashi. L. B. *J. Coord. Chem.*, **2011**, *64*, 3950-3959.
- Shashi, L. B.; Sudha, Y. *J. Coord. Chem.*, **2012**, *65*, 3492-3501.
- Niharika, A.; Sudha, Y. *J. Coord. Chem.*, **2018** (accepted).
- Preeti, D.; Sudha, Y. *J. Coord. Chem.*, **2018** (accepted).
- Deepika, J.; Sudha, Y., *Inorg. Chim. Acta.*, (communicated).
- Jelle, B.; Minze T.; Ronald, H.; Ben, L. F. *Inorg. Chim. Acta.*, **2002**, *337*, 75-82.
- Manabendra, N. B.; Mihir, K. C.; Darlando, T. K., *Dalton Trans.*, **1982**, 669-670.
- Patel, I. A.; Bharat, T. T., *Indian. J. Chem.*, **1999**, *38*, 422-433.
- James, E. H.; Ellen, A. K.; and Richard, L. K. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th Edn, *Pearson Education, Singapore.*, **2005**, 445.
- Stults, B. R.; Robert, S. M.; Victor, W. D. *Inorg. Chem.*, **1975**, *14*(4), 722-730.
- Brahim, B.; Ali, O.; Djouhra, Aggoum.; Ramiro, R. R.; Yasmina, O.; Emilia, M. *Res. Chem. Intermed.*, **2016**, *42*(5), 4839-4858.
- Behere, D. V.; Samaresh, M. *Inorg. Chem.*, **1980**, *19*, 992-995.
- Fleischer, E. B.; Palmer, J. M.; Srivastava, T. S.; Chatterjee, A. *J. Am. Chem. Soc.*, **1971**, *93*, 3162-3167.