International Journal of Theoretical & Applied Sciences, 10(2): 33-39(2018)

ISSN No. (Print): 0975-1718
ISSN No. (Online): 2249-3247

Synthesis, Characterization and Kinetic Studies of Quadri-dentate Demi-macrocyclic Complexes of Mn (II) and Cu (II) having di-aza and di-oxa Donor's

***Sajood Maqbool*[1]*, M.U Khan*[2]*, Mir Bilal Parvaiz*[3] *and H.P. Dwivedi*[1]**
[1]Department of chemistry Sanjay Ghandi Samrati Govt. Auto. P. G College Sidhi (M.P.) India
[2]Retired Principal Near Sanaskrit College Bicchia Rewa (M.P.) India.
[3]Department of Chemistry Islamia College of Science and Commerce Srinagar (J&K) India.

(Corresponding author: Sajood Maqbool)
(Received 03 August, 2018 accepted 28 September, 2018)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: Quadri-dentate demi-macrocyclic complexes of Mn (II) and Cu (II) were synthesized by refluxing their respective metal salts with desired ligand of the type $[C_{14}H_{30}N_2O_2](ClO_4)^-_2$ having di-aza and di-oxa donors in aqueous medium. The respective ligand and its complexes were characterized by conductance, elemental analysis, IR, UV-Visible, AAS, and magnetic susceptibility measurements. Kinetics of complex formation was probed by UV-visible spectroscopy at their maximum wavelengths (λ_{max}) of absorption of complexes under pseudo first condition keeping the metal ion concentration in tenfold excess while adjusting the pH from 4 - 9.60. Inverse plots of K_{obs} Vs 1 / $[M]^{2+}$ yielded a straight line with positive intercept on Y-axis while plot of pH Vs k_{obs} produces line which tapers into a curve with increase in pH.

Key words: Quadri-dentate, Demi-macrocyclic ligand, Extractants, Versatile, Bulk

I. INTRODUCTION

Demi-macrocyclic or hemi-macrocyclic ligands and their complexes are an important class of macrocyclic ligand complexes. The main difference between demi-macrocyclic or hemi-macrocyclic ligand complexes from their closed chain counterparts lies in their flexibility because of open chain type structure and shape which can be varied according to the need of researcher. Synthesis and study of macrocycles or demi-macrocyclic have undergone tremendous growth and their complexation chemistry with a wide variety of metal ions has been comprehensively studied [1]. The presence of a central cavity in macrocyclic or demi-macrocyclic ligands have long been used as selective hosts for a wide range of guest molecules and ions. Macrocyclic or demi-macrocyclic systems have been employed as selective extractants for transition and metal ions in a range of solvent extraction and bulk membrane transport studies [2]. Macrocyclic complexes find extensive biomedical applications as contrast enhancing agents in magnetic resonance imaging [3,4], as NMR shift reagents for natural systems [5] and as catalysts for the cleavage of RNA [6,7]. Demi-macrocyclic or macrocyclic ligands have received attention because of their mixed soft-hard donor character, versatile coordination behavior [8].

II. EXPERIMENTAL

All chemicals and solvents used in the present investigation were of AR-Grade and were brought into use without further purification. Ethylene-diamine (Fisher Scientific), Acetone (SRL), Perchloric acid (71-72%) Rankem brand respectively. Metal (II) Sulfate salts of Manganese and Copper were of Sigma-Aldrich brand.

1. Synthesis of the quadri-dentate demi-macrocyclic ligand : The ligand N^1,N^2,bis(2-methyl-4-oxopenten-2-yl)ethane-1,2-diamine diperchorate was prepared by reaction of ethane 1-2 diamine and acetone in equimolar ratio with direct or indirect protonation by by perchloric acid drop-wise with constant stirring. The reactions were carried in an environment cooled in ice bath because of explosive nature of the reaction and in order to obtain targeted demi-macrocyclic ligand. The yield of the reaction differed in 1:1.25 ratios in case of indirect and direct protonation. The resultant white colored crystals were decantated and excess brown color was washed by acetone. The yield was ~ 78 %. The product was vacuum dried and stored in amber colored bottle [9].

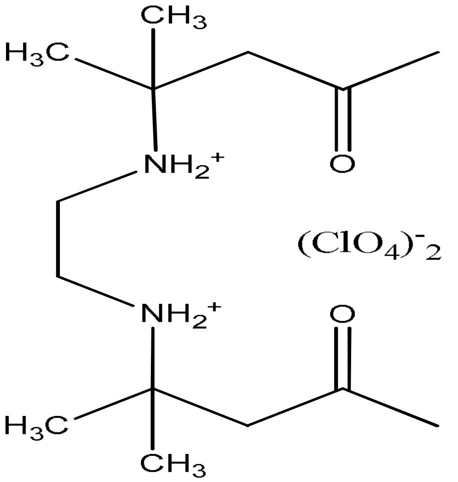


Fig. 1. Proposed structure of the Quadri-dentate demi-macrocyclic ligand having di-aza and di-oxa donors.

2. Synthesis of the desired quadri-dentate demi-macrocyclic - metal complexes of Mn (II) and Cu (II): The respective metal complexes were synthesized by refluxing the ligand and metal sulfate salts of Mn (II) and Cu (II) in equimolar ratios in aqueous medium. The mixtures were refluxed for several hours on a heating mantle until the reacting species changed their color from white and blue to brown and reddish green color respectively for Mn (II) and Cu(II).The resultant solutions were evaporated and crystallized on hot water baths for several days, there after they were scratched and vacuum, oven dried at ambident temperatures.

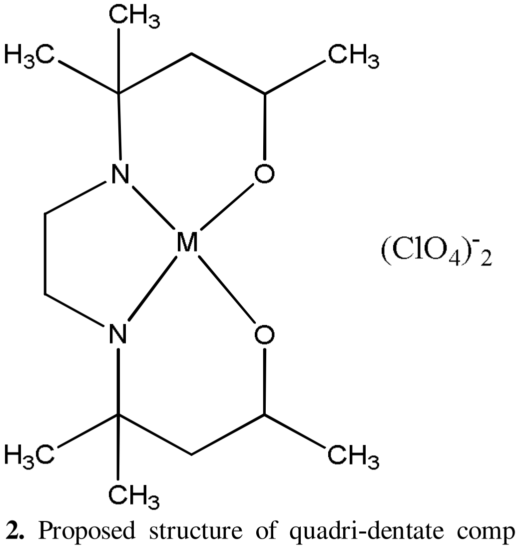


Fig. 2. Proposed structure of quadri-dentate complex having di-aza and di-oxa donors where M= Mn(II) and Cu(II).

III. RESULTS AND DISCUSSION

A. UV-visible Spectra of Ligand

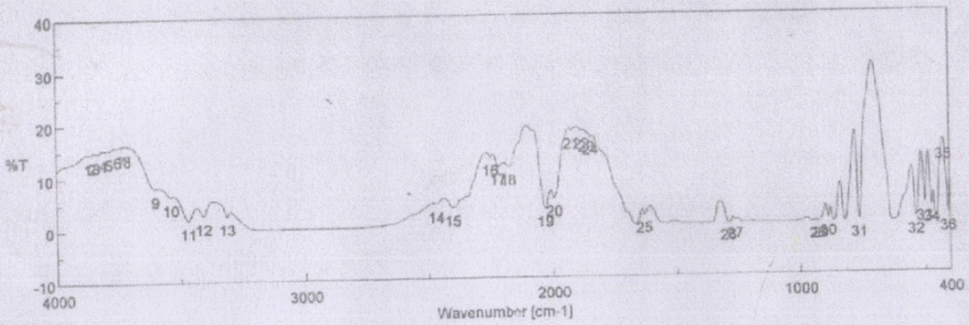
The UV-visible spectrum of the desired quadri-dentate demi-macrocylic ligand was recorded in an entire range from near IR to extreme ultraviolet region i.e. 1020-190 nm. The visible spectrum of the ligand does not show much absorption in visible region due to the absence of most of the chromophores while it does little characteristic absorption in the ultraviolet region from 270-300 nm particulars of ketonic group due to the $\pi - \pi *$ and $n - \pi *$ transitions of the ketonic group which become more intense in extreme ultraviolet region. The ligand does not show transitions for saturated secondary amine (Fig. 3).

B. IR Spectra of ligand

The IR spectrum of ligand shows typical absorption band at 2960cm^{-1} principally owing to asymmetric stretching mode in which two C-H bonds of the methyl group are extending while the third one is contracting at 2904cm^{-1} due to symmetrical stretching (v_sCH_3) in which all the three C-H bonds extend and contract in phase. The peak at 2985 and 3007 are attributed to the asymmetrical stretching ($v_{as}CH_2$) and symmetrical stretching (v_sCH_2). The high energy shifting of these peaks depict strain in the chain caused. The symmetrical bending vibration ($\delta s CH_3$) causes peak at 1348cm^{-1}, while the sharp peak at 1445 cm^{-1} is attributed to asymmetrical bending ($\delta as CH_3$). Strong absorption band at 1473cm^{-1} is of ($\delta s CH_2$) of methylene group. Absorption bands between 1313cm^{-1} to 1156cm^{-1} are endorsed to the twisting and wagging vibrations of methylene group. Strong absorption peak at 1685cm^{-1} is due to ketonic stretching vibration. The slight shift in ketonic stretching vibration towards higher energy end is due the shielding of ketonic group. Overlapping band peaks at 3019, 3007, 3266 cm^{-1} and 3370 cm^{-1} are due to the N-H stretching vibration. Strong bands due to ionic pechlorate occur at 1105cm^{-1} and 655cm^{-1}.

Elemental Analysis of the quadri-dentate demi-macrocyclic ligand having di-aza and di-oxa donors [$C_{14}H_{30}N_2O_2$] ($ClO4)^-_2$. The C,H,N,O analysis of the ligand was done on Elementar(Vario El-III) CHNOS elemental analyzer.

The elemental analysis for Carbon, Hydrogen, Nitrogen and Oxygen for desired quadri-dentate ligand after calculating by established methods and recording were almost in close conformity with the properties of the ligand (Table 1).



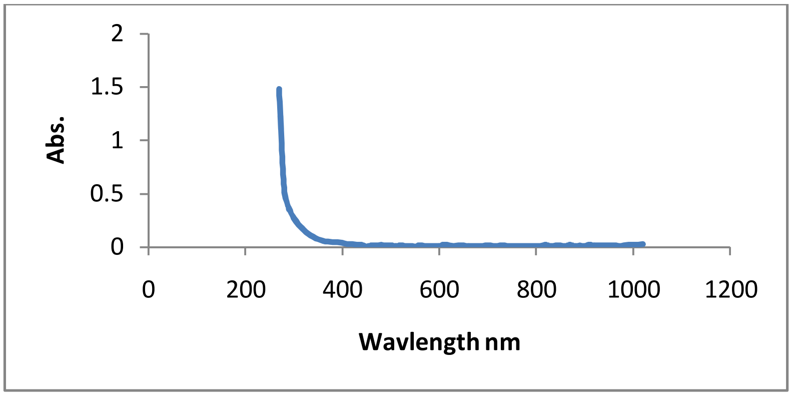


Fig. 3. UV-visible spectrum of quadri-dentate demi-macrocyclic having di-aza di-oxa donors.

Table 1: A comparison of the calculated and recorded percentage of the constituent elements of the quadri-dentate demi-macrocyclic ligand having di-aza and di-oxa donors.

Calculated %	Observed/Found %
Carbon = 36.73	Carbon = 35.56
Hydrogen = 6.61	Hydrogen = 5.90
Nitrogen = 6.12	Nitrogen = 5.84
Oxygen = 34.96	Oxygen = 33.55

C. Atomic Absorption Spectroscopy

Atomic absorption measurements for the respective complexes were recorded on Perkin Elmer A.A.S-800. The complexes were digested in DMSO by preparing their molar solutions. The instrument was calibrated by preparing standard solutions of two metals i.e. Mn (II) and Cu (II) obtained individually from SRL. A series of 5%, 10%, 15% and 1%, 2%, 3% standard solutions were prepared respectively

The recorded percentages obtained in terms of ppm for Mn (II) and Cu (II) were 300.9 and 266.5 ppm respectively

D. UV-Visible spectra

The UV-Visible spectra of complexes were recorded on UV-1601 Shimadzu spectrophotometer in an entire range of near IR to far UV region i.e 1000- 200nm in DMSO. The possible transitions of Mn(II) are

$^4T_{1g} \rightarrow {}^4T_{2g}$ E 17050 – 23000, $^4T_{2g} \rightarrow$ $^4A1g, {}^4Eg$ E 23000 - 2680

The electronic spectra of the copper complex show a band 10869-10752 cm^{-1} corresponding to $^2E \rightarrow {}^2T_2$ indicating an octahedral geometry around the metal ion. These assignments are further supported by a close agreement between observed and calculated values of the λ_{max} for the ν2 transition.

The band at 35010 → CT is the charge transfer band of copper complex. The Dq parameter evaluated for copper complex is 1081. The nephelauxetic parameter, β evaluated for these complexes suggest a low degree of covalency in the metal ligand bond.

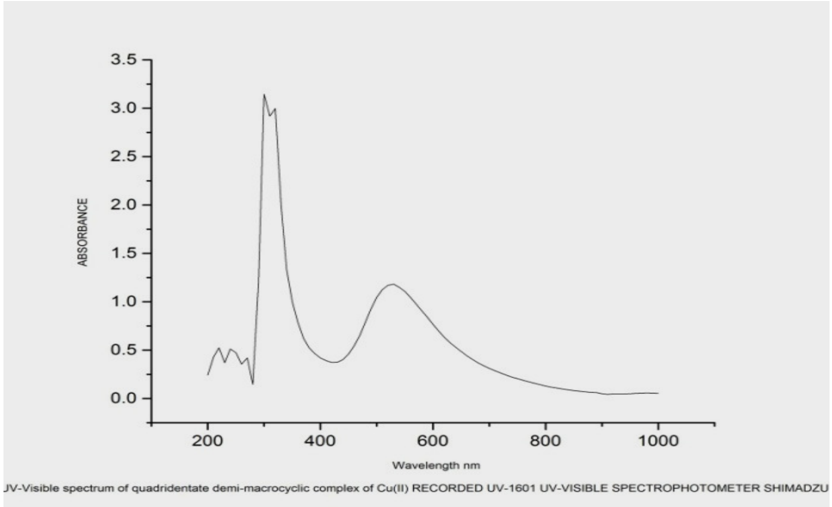


Fig. 5. UV-Visible spectrum of Cu (II) quadri-dentate demi-macrocyclic complex.

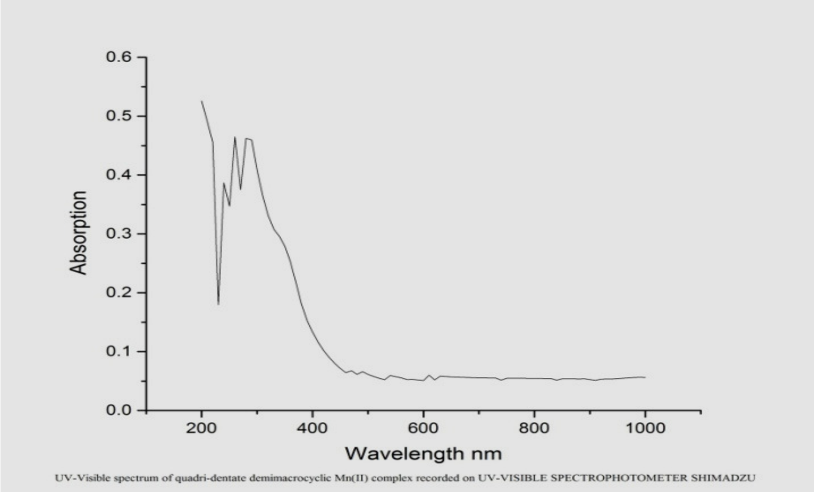


Fig. 6. UV-Visible spectrum of Mn (II) quadri-dentate demi-macrocyclic complex having di-aza and di-oxa donors.

E. IR Spectra of complexes

The IR spectra of quadri-dentate complexes were recorded on Jasco model-4100 FTIR spectrophotometer using KBr discs.The IR spectra of Mn (II) complex exhibit a strong sharp to medium intensity peak at 509.115 cm^{-1} which may be assigned to (Mn-O) stretching vibration. The peak at 424.27 cm^{-1} for manganese complex may be attributed to (Mn-N) stretching.

The IR spectra of Cu (II) complex exhibits a medium intensity peak at 524.66 cm^{-1} which may be assigned to (Cu-O) extending vibration. The medium range peak at 492.77 cm^{-1} is probably due to the (Cu-N) extending vibration.

The ν (M-O) and also ν (M-N) stretching frequencies are in the order of Cu >Mn. Upon complex formation some of the vibrations are decreased which may be due to hindered vibration. The characteristic ν (C-O) absorption frequencies undergo a negative shift of 55 cm^{-1} to 65 cm^{-1} particularly due to reclining effect of lone pair donation of oxygen atom towards metal ion. The non appearance of ν_s (N-H), ν_{as} (N-H) and δ (N-H) Vibrations in the complexes confirm the coordination of the metal ion by the de-protonation of internal protons.

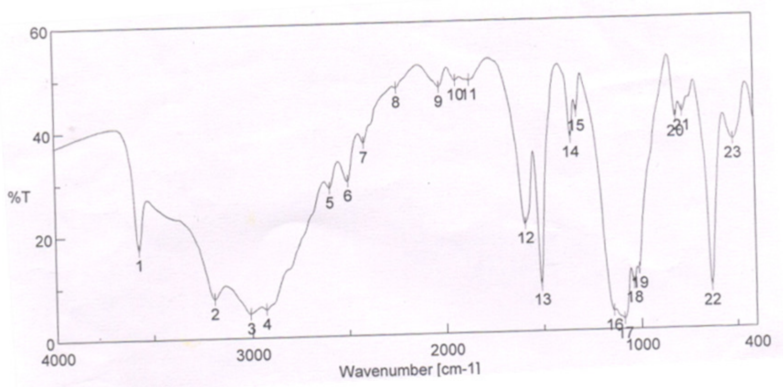


Fig. 7. IR Spectrum of the Mn(II) Quadri-dentate Demi-macrocyclic Complex having di-aza di-oxa donors.

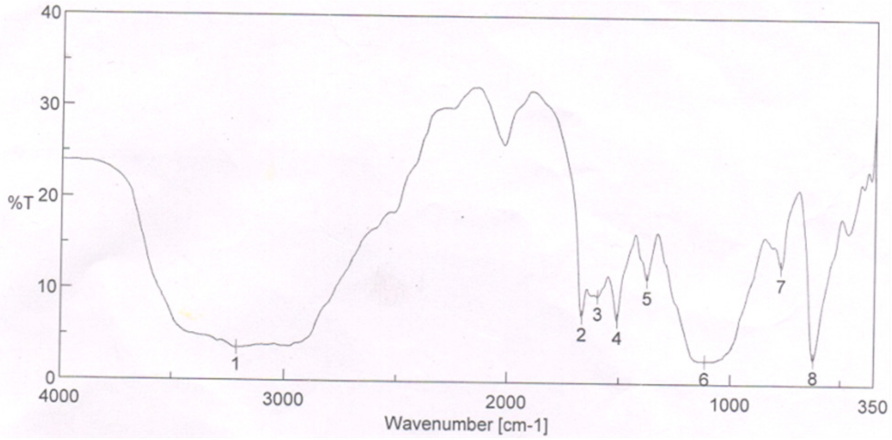


Fig. 8. IR Spectrum of the Cu (II) Quadri-dentate Demi-macrocyclic Complex having di-aza and di-oxa donors.

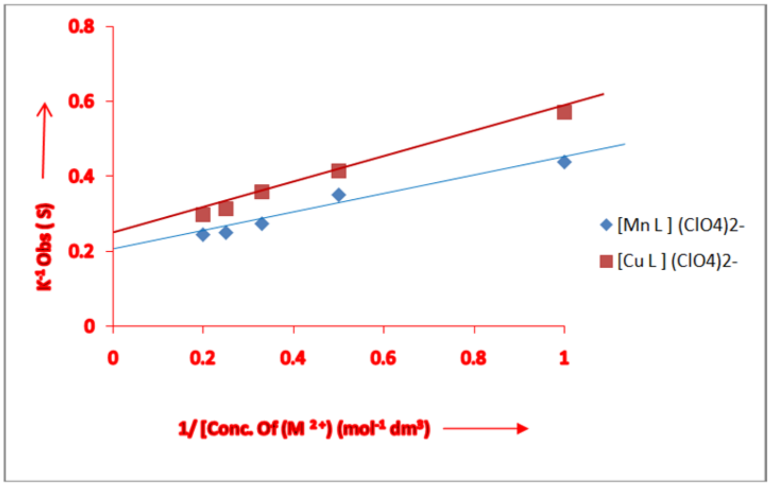
Conductance measurements. The conductance measurements were carried in DMSO at room temperature i.e. 298K on Systronics digital Conductivity meter (304). The extreme low molar conductance values i.e. (Λ_m = 3-7 ohm^{-1} cm^2 mol^{-1}) for quadri-dentate demi-macrocyclic complex of Mn (II) and (Λ_m = 5- 12 ohm^{-1} cm^2 mol^{-1}) respectively for quadri-dentate demi-macrocyclic complex of Cu (II) in aqueous medium indicate their non-electrolytic nature.

Magnetic Susceptibility. Magnetic susceptibility measurements were carried on Sherwood Magnetic susceptibility balance (Auto).The magnetic moment values for Mn (II) and Cu (II) were μ_{eff} = 6.04 and μ_{eff} = 2.08 respectively. The higher value's of magnetic susceptibility for manganese and copper complex's is probably due to the octahedral nature of complexes.

Kinetics of formation of Complexes. The kinetics of formation of complexes was followed by UV-Visible using Lasany double beam spectrophotometer at maximum wavelengths (λ_{max}) of absorption of the complexes keeping the metal ion concentration in tenfold excess employing jobs methods of continuous variation[10] by preparing a series of solutions. The formation of complexes follows first order kinetics obeying Beer-Lamberts law in which absorption decreases with time and corresponding decrease in concentration. The first order rate k_{obs} was in order of 10^4 to 10^5 s^{-1}.The kinetics of exchange of water by the respective metal [M(II)] ions nearly followed Gray and Langford classification of class II metals [11].

Table 2: Dependence of rate on n$[M]^{2+}$ ion concentration.

Sr.No	n$[M]^{2+}$X10^2 (mol dm^{-3})	10^4 k_{obs} (S^{-1})	
		Q-DT Demi-macrocyclic complex of Mn(II)	**Q-DT Demi-macrocyclic complex of Cu (II)**
1.	1	2.21	1.76
2.	2.00	2.82	2.47
3.	3.00	3.63	2.83
4.	4.00	3.74	3.41
5.	5.00	3.94	3.07



λ_{max} = 200nm [Mn (II)], 300nm [Cu(II)], Temp = 298

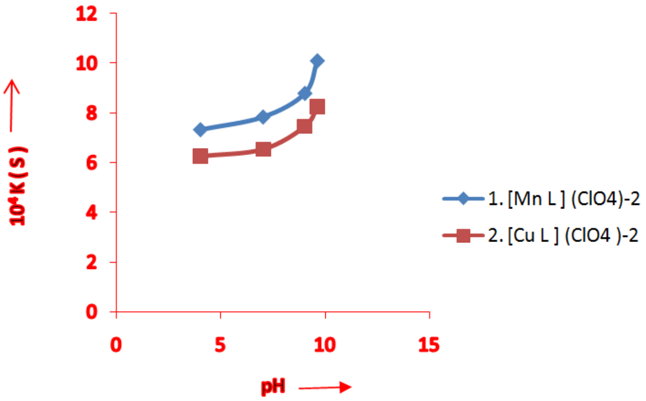
Fig. 9. Plot of 1/Kobs Vs 1/n $[M]^{2+}$.

The double reciprocal plot (Fig. 9) of k_{obs} Vs conc. of M^{2+} ions gives a straight line with positive intercept on Y-axis. The plot clearly indicates that the order of quadri-dentate complex formation with respect to Mn(II) and Cu(II) having di-aza and di-oxa donors is one at lower concentration of M(II) ions and zero order at higher concentration of M(II) ions respectively.

Effect of pH on kobs. As indicated in Fig. 10 increase in pH increases the k1 for the concerned metal(II) ion as suggested by data in the table. As a general rule the complexation of metal ions by a ligand increases with decreasing hydrogen ion concentration that is with increase in pH with respect to M(II) concentration.

Table 3: pH dependence of K_{obs} for the complexation of QD-DMC having di-aza and di-oxa donors.

Sr. No	pH	[Mn(II) L] $(ClO_4)^-_2$	[Cu (II) L] $(ClO_4)^-_2$
		K_{obs} x 10^4 (S^{-1})	
1.	4.00	7.31	6.24
2.	7.00	7.82	6.62
3.	9.00	8.63	7.57
4.	9.60	10.08	8.79



10^3 [QDMC] (mol^{-1}dm^3) = 5.0 ; [M(II) x 10-2 (mol^{-1} dm^3) = 5.0 , λ_{max} = 200nm Mn(II) and 300 nm Cu (II) , Temp = 298 K.

Fig. 10. Plot of kobs Vs pH.

IV. CONCLUSION

Quadri-dentate ligand and its respective complexes i.e. Mn(II) and Cu (II) were synthesized and characterized by various methods. The kinetic studies of their formation was also studied. The effect of pH was also observed and discussed.

ACKNOWLEDGEMENT

The authors are grateful to USIC Kashmir University for providing A.A.S facilities and also to Department of Pharmacy Jamia Hamdard University New Delhi for providing elemental analysis facilities.

REFERENCES

[1]. S. Chandra and R. Kumar, (2009). Spectrochim. Acta A, **66**, 74.

[2]. Y. Dong, S. Farquhar, K. Gloe, L. F. Lindoy, B. R. Rumbel, P. Turner and K. Wichmann, (2003). *J. Chem. Soc., Dalton Trans.,* 1558.

[3]. F. Touti, A. K. Singh, P. Maurin, L. Canaple, O. Beuf, J. Samarut, and J. Hasserodt, (2011). *J. Med. Chem.*, **54**, 4274.

[4]. K.H. Jung, H.K. Kim, G. H. Lee, D.S. Kang, J.A. Park, K. M. Kim, Y. Chang, and T. J. Kim, (2011). *J. Med. Chem.*, **54**, 5385.

[5]. A. D. Sherry, C. F. G. C. Geraldes, in: J.C. G. Bunzli, G. R. Choppin (1989). (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, chap. 4, Elsevier, Amsterdam.

[6]. K. Nwe, C. M. Andolina and J. R. Morrow, (2008). *J. Am. Chem. Soc.,* **130**, 14861.

[7]. C. S. Rossiter, R. A. Mathews and J. R. Morrow, (2007). *J. Inorg. Biochem.,* **101**, 925.

[8]. L. K. Gupta and S. Chandra, (2007). Spectrochim. *Acta A*, (2007), **68**, 839.

[9]. M. Sajood, Dwivedi A.P, Khan M.U, Diwivedi H.P, (2018). *Int. Jour. Eng. Inf. Syst.,* **2**, 1-4.

[10]. Job, Paul (1928). "Formation and Stability of Inorganic Complexes in Solution". *Annali di Chimica Applicata.* **9**: 113–203.

[11]. C.H. Langford and H.B. Gray, (1973). Ligand Substitution Dynamics, Benzamin, New York.