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Spectroscopic Approach of Macrocyclic Complex of MN (II) with a New Azamacro Cyclic Tetra Dentate Ligand

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ABSTRACT
The complexes of Mn(II)) were synthesized with the new aza-macrocyclic ligand. The ligand was prepared by the reaction of 3-ethyl-2,4-pentadione and 5-bromo-2,6diamino-pyridine. All the complexes have been found to have general composition $[M(L)X_2]$ [where M = Mn(II) and X = Cl^-,& NO^-_3,]. All the complexes are characterized by the conductance measurements, magnetic susceptibility measurements, mass, I.R,EPR and electronic spectral studies. An octahedral geometry was assigned for Mn(II) complexes .

Key words EPR, Mn(II), 5-bromo-2,3-diaminopyridine, 3-ethyl-2,4-pentadione. Spectroscopic,

INTRODUCTION
Macrocyclic chemistry has been a topic of great attention to both inorganic and bioinorganic chemists all over the world due to its wider application and the unusual binding abilities. The synthesis of macrocyclic complexes has been a fascinating area of research and growing at a very fast pace owing to their resemblance with naturally occurring macrocycles and analytical, industrial, and medical applications [1–12]. In the present paper a new series of macrocyclic complexes of Mn(III) obtained by newly synthesized macrocyclic ligand has been reported. These complexes were also tested for their in vitro antibacterial activities. Some complexes showed remarkable antibacterial activities.

EXPERIMENTAL
All the chemicals used were of AR grade and procured from Fluka and Sigma Aldrich. Metals salts were purchased from Emerck and were used as received.

PREPARATION OF LIGAND
Hot ethanolic solution (20 mL) of 5-bromo-2,3-diaminopyridine (3.76 g, 0.02 mol) and the hot ethanolic solution (20 mL) of 3-ethyl-2,4-pentadione (2.56 mL, 0.02 mol) were mixed slowly with constant stirring. This mixture was refluxed at (70-90°C) for (7-9) hours (pH 4-5) in the presence of few drops of concentrated hydrochloric acid. On cooling, light-yellowish Heena green coloured precipitate was formed, which was filtered, washed and dried under vacuum over P_4O_{10}.

Preparation of Complexes
Hot ethanolic (20 mL, 60^0C) solution of ligand (0.001 mol) and hot ethanolic solution of corresponding metal salts (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5-7 hours

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at 70-90^{0}C. On cooling colored complex was precipitated out. It was filtered washed with cold EtOH and dried under vacuum over P_4O_{10}.

Physical Measurements

C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on a ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as a calibrant. Electron impact mass spectrum was recorded on JEOL-MS Route mass spectrometer. IR spectra (KBr) were recorded on Perkin Elemer FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotomer.

EPR spectra of the complexes were recorded as polycrystalline sample and at room temperature for Mn(II) complexes on E_4-EPR spectrometer using the DPPH as the g-marker.

RESULT AND DISCUSSION

Characterization of ligand has been discussed in previous paper [13-16].

On the basis of elemental analysis, the complexes were assigned to possess the composition as shown in Table 1. The molar conductance measurements of the complexes in DMSO correspond to non-electrolyte nature. Thus these complexes are formulated as $[Mn(L)X_2]$ [M = Mn(II), X = Cl^-, NO_3^- .]

The IR spectra of nitrate complexes with ligand show absorption bands in the region 1412-1428 (ν_5), 1305-1315 (ν_1) and 1018-1036 cm^{-1} (ν_2). This indicates that nitrate group is coordinated to the metal ion as an unidentate fashion**.**

MAGNETIC MOMENT AND ELECTRONIC SPECTRAL STUDIES

Electronic spectra of Mn(II) complexes, under study show absorption bands in the range of 18083-19920 (ν_1)**,** 24570-24630 (ν_2)**,** 29239-29940 (ν_3) 38620 cm^{-1} (ν_4) which is characteristics to an octahedral geometry.

The ESR spectra of the complexes were recorded as polycrystalline sample and in solution of DMSO. The spectra are shown in Polycrystalline sample gives one broad isotopic signal centered around approximately free electron 'g' value (2.0023) **[Table 3] [17-38].**

On the basis of elemental analysis, molar conductance measurements, magnetic moment susceptibility, IR, electronic and EPR spectral studies, all the complexes of Mn(II) under study were found to possess an octahedral geometry **.**

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REFERENCES

1. R. D. Guy and C. L. Chakrabarti, Can. J. Chem., 1976, **54,** 2600.
2. J. Havel, Research Report, "Modeling and Experimental Verification Transport Mechanism of Pollutants and Evaluation of Risks" Grant GA 1487/ 93, Prague, 1994.
3. S. E. Bailey, T. J. Olin, R. M. Bricka and D. D. Adrin, Water Res., 1999, **33,** 2469.
4. J. W. Hamaker and J. M. Thompson, "Adsorption in Organic Chemicals in the Soil Environment" Vol. Ed. C. A. Marcel Dekker, New- York, pp. 49-143, 1972.
5. P. Merdy, E. Guillon and M. Aplincourt, New. J. Chem., 2002, **26,** 1638.
6. H. A. Schroeder, J. J. Balassa and I. H. Tipton, J. Chron. Dis., 1966, **19,** 545.
7. World Health Organization (WHO), Trace Elements in human nutrition and health, Geneva, Chapter 10, pp. 163-167.
8. R. M. Leach and E. D. Harris, Ed. Manganese, In : B.L. O'Dell and R. A. Sunde, eds. Handbook of Nutritionally Essential Mineral Elements, Marcel Dekker Inc, New –York, Basel, Hong- Kong, pp. 335-355, 1997.
9. H. J. Schneider and M. Anke, Arch. Exp. Vet. Med. 1971, **25,** 787.
10. R. M. Leach and M. S. Lilburn, World Rev. Nutr. Diet, 1978, **32,** 123.
11. C. R. K. Rao and P. S. Zacharias, Polyhedron, 1977, **16,** 1201.
12. M. Shakir, S. P. Varkey and P. S. Hameed, Polyhedron, 1993, **12,** 2775.
13. S. Chandra and L. K. Gupta, Spectrochim. Acta A, 2004, **60,** 2767.
14. K. Nakamoto, Infrared and Raman Spectra of the Coordination Compounds, Wiley Interscience, New- York, 1970.
15. E. Q. Gao, H. Y. Sun, D. Z. Liao, L. H. Jiang, S. P. Yan, Polyhedron, 2002, **21,** 359.
16. L. F. Lindoy, "The Chemistry of Macrocyclic ligand Complexes", Cambridge University Press, UK, 1989.
17. S.Chandra Anupma and.D.Jain, **J. Ind. chem. soc., vol 86,2009,p 220-224.**
18. S.Chandra Anupma and.D.Jain and Anupma, **J. Ind. chem. soc., vol 87 2010, p 1245-1249.**
19. S.Chandra and Anupma and.D.Jain, , IJPAC, Vol.**4,**2009, issue 3.
20. S.Chandra and Anupma and.D.Jain,IJCC,Vol2,2011
21. P. S. Kalsi Spectroscopy of Organic Compounds, Fourth ed., New Age International, New Delhi, India, 2001.
22. R. K. Rao, P. S. Zacharias, Polyhedron, 1997, **16,** 1201.
23. K. Nakmoto, Infrared spectra of Inorganic and Coordination compounds, Wiely, Interscience, New York, 1970.
24. A. B. P Lever, Crystal Field Spectra, Inorganic Electronic Spectroscopy, First ed., Elsevier, Amsterdam,1968, 249 .
25. M. Shakir, O. S. M. Nasman, A. K. Mohamed, S. P. Varkey, Ind. J. Chem., 1996, **25 A,** 710 .
26. A. G. Tomilnson, B. J. Hathway, D. E. Billing and P. Nicholls, J. Chem. Soc.,1965, 65.
27. S. Chandra, K. Gupta. S. Sharma, Synth. React. Inorg. Met. Org. Chem.,2001, **31,** 1205.
28. W. G. Hanna, M. M. Moawad, Trans. Met. Chem., 2001, **26,** 644.
29. M. Sakai, A. Hara, S. Anjo, M. Nakamura, J. Pharm. Biomed. Anal.,1999, **18,** 1057.
30. P. Kopel, Z. Travnicek, J. Marek, M. Korabik, J. Mrozinski, Polyhedron, 2003, **22,** 411.
31. S. Chandra and L. K. Gupta, Spectrochim. Acta , 2004, **60 A,** 3079 (2004).
32. S. Chandra and S. Sharma, Trans. Met. Chem., 2007, **32,** 150.
33. S. Chandra, L. K. Gupta and D. Jain, Spectrochim. Acta., 2004, **60 A.**
34. M. Shakir and S. P. Varkey, polyhedron, 1995, **14 ,** 1117.
35. K. Anuradha and R. Rajavel., IJPT,2011, Vol.3, Issue-2.
36. S.Chandra Anupma and.D.Jain, **J. Ind. chem. soc., vol 86,2009,p 220-224.**
37. S.Chandra Anupma and.D.Jain and Anupma, **J. Ind. chem. soc., vol 87 2010, p 1245-1249.**
38. S.Chandra and Anupma and.D.Jain, , IJPAC, Vol.**4,**2009, issue 3.
39. S.Chandra and Anupma and.D.Jain,IJCC,Vol2,2011
40. R.A Sheikh ,I Ab Rahman Int .J.Electrochem.Sci. 2013, Vol.**8** 6972-6987.
41. M.Razaeivala and H .Keypour, Coordination Chemistry Reviews, 2014 Vol.**280**, ,p203-253
42. S.Chandra and Ruchi . Spectrachim acta, 2013 Vol.**(103),** p338-348

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Table – 1

Molar Conductance and Elemental Analysis

Complexes	Color	Molar Conductance	Yield (%)	m.p. (^{0}C)	Elemental analysis data found (calculated) (%)			
					C	H	N	M
$[Mn(L)Cl_2]$ $[MnC_{24}H_{28}N_6Br_2Cl_2]$	Brown	12	55	270	8.06 (8.00)	41.81 (41.98)	4.04 (4.08)	12.18 (12.24)
$[Mn(L)(NO_3)_2]$ $[MnC_{24}H_{28}N_8O_6Br_2]$	Light Brown	10	52	278	7.45 (7.48)	36.95 (38.97)	3.67 (3.78)	11.34 (11.36)

Table 2

Magnetic Moment and Electronic spectral data of the complexes

Complex	μ eff (B.M.)	λ max (cm^{-1})
$[Mn(L)Cl_2]$	5.98	19920,24570,29940
$[Mn(L)(NO_3)_2]$	5.92	18083,24630,29239,38610

Table 3

EPR Spectral data of the Mn(II) Complexes

	$g_\perp$	g_{II}	g_{iso}
$[Mn(L)Cl_2]$	2.1673	2.2420	2.1922
$[Mn(L)(NO_3)_2]$	2.1387	2.2734	2.1836

Table4

Ligand Field Parameters Of Mn(II) Complexes

Complexes	Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	F_4	F_2	h_x
[Mn(L)Cl2]	1992	767.14	0.9760	3379.72	96.56	1249.94	0.3427
[Mn(L)(NO3)2]	1808	658.42	0.8376	3609.16	103.11	1173.97	2.3200

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