

SPECTROSCOPIC STUDIES ON Mn (II) COMPLEXES WITH N-DONOR TETRADENATE (N₄) MACROCYCLIC LIGANDS

DR. YOGESH PANDEY, AKANKSHA SHIVHARE, CHITRANJANA KASHYAP

Deptt. of Chemistry, Bipin Bihari P.G. College, Jhansi (U.P.)

RECEIVED : 12 November, 2017

A novel family of tetraaza Macrocylic Mn(II) complex [MnLX₂] (where L = N₄ donor Macrocylic ligands) and X = [Cl, (NO₃)₂] have been synthesized. Characterization has been done on the basis of elemental analysis, molar conductance, I.R. and XPS data.

These analysis shows that the ligands behaves tetra dentate through four N atoms. The XPS data suggest the square planer geometry for Mn (II) Macrocylic complexes.

KEYWORDS : Syntheses, tetraaza Macrocylic Magnese (II) complexes.

INTRODUCTION

Magnese is the fifth element of 3d transition series. A wide range of oxidation states ranging from zero to (+8) are shown by this element, however most stable oxidation states of this element is (+II) and has electron configuration [Ar]d⁵. Transition metals play a central role in the construction of molecular materials, which display magnetic properties [1-3]. Macrocycles are a grouping class of compounds, with varying chemistry with a wide range of different molecular topologies and set of donor atoms.

In view of the above consideration in this paper, we are reporting the synthesis and spectroscopic characterization of Mn(II) complexes with a novel macrocylic tetra dentate nitrogen donor ligands.

Magnese and its compounds are widely used in analytical chemistry, metallurgical process paint and pigment industry. The complexes of magnese (II) with macrocylic schiff base ligands play an excellent role in catalytic property [4-7]. Magnese also plays an important role in many biological redox processes including disproportionation of hydrogen peroxide. Magnese alone mediate the DNA degradation in presence of oxygen in vitro. In view of the above discussion, the synthesis and characterization studied on the Mn²⁺ complexes of Macrocylic ligands are highly desirable.

MATERIALS AND METHODS

All the solvent used were of E.merck (LR grade and Ranbaxy). Solvent were used after purification and drying by conventional methods. The I.R. spectra of the complexes and ligands were recorded on perkin elmer 457 spectrometer at room temperature in KBr or CSI (for complexes) X-ray photoelectron spectra were recorded on a VG scientific ESCA-3 MK-

II electron spectrometer. The elemental analysis for C, H, & N, or S were determined on a semi-microscale.

SYNTHESIS OF LIGANDS

A solution of 3, 4 hexandione, 2, 3 hexandione or furil (2 mmol) was added dropwise with constant stirring in cyclohexane diamine or 2, 3 phenylene diamine (2 mmol) in ethanol (20 ml) solution and refluxed for 5 hrs. A white solid product appeared which was filtered, washed with C_2H_5OH and dried under vacuum. The L Macrocylic ligands was characterized by elemental analysis analysis and IR data.

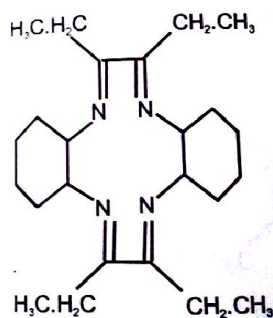


Fig. 1. Ligand = L

SYNTHESIS OF COMPLEX:

The complexes of the Mn (II) with L ligands is done by using Mn(II) salts such as $[MnCl_2 \cdot 4H_2O]$, $Mn [NO_3]_2 \cdot nH_2O$. A warm ethonolic suspension (20 ml) of ligands L (1 mmol) & hot ethanolic solution (20ml) of corresponding metal salts (1mmol) were mixed together with constant stirring. The mixture was refluxed for 8 hrs at $80^\circ C$. On cooling coloured complex was precipitated out. It was filtered washed with cold EtOH and dried under vacuum over P_4O_{10} .

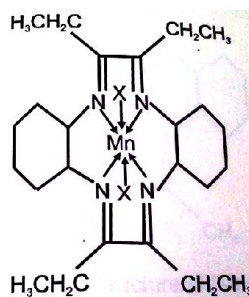


Fig. 2

RESULT AND DISCUSSION

On the basis of elemental analysis the complexes were found to have general composition $[Mn (L)X_2]$.

$X = Cl^-$, NO_3^- . The molar conductance of these complexes in DMSO corresponding to non-electrolyte in nature, thus these complexes may be formulated as $[Mn (L)X_2]$.

IR SPECTRA OF NITRATO COMPLEX

IR spectra of nitrate complex under study show absorption bands in the region of $1420-1446\text{ cm}^{-1}$, $1306-1320\text{ cm}^{-1}$ & $1005-1020\text{ cm}^{-1}$ [8].

ELECTRONIC SPECTRA AND XPS SEPCTRA

The high spin six coordinated Mn (II) complexes has d^5 electronic configuration *i.e.* t_{2g}^3 , e_g^2 give rise to ground state ${}^6A_{1g}$. It is derived from the free ion 6S state, which is orbitally non-degenerate [9].

MAGNETIC MOMENT

The ground state term of Magnese (II) is ${}^6A_{1g}$, as there is only possible configuration for five unpaired electrons. This correspond to half filled d-shell electron and is spherically symmetrical.

There is no temperature independent paramagnetic effect. IR spectra of these N_4 complexes of all ligands show that the shifting in $V_c = N$, to lower side in all the complexes which confirms that the coordination takes place through the nitrogen of $V_{c=N}$ group [10].

Data is mentioned in Table-1, 2 and 3.

Table 1. Molar conductance and elemental analysis of Mn (II) complexes.

S. No.	Complexes	Elemental analysis found (Calc.%)				Molar conductance $\pi^{-1}\text{ cm}^2\text{ mol}^{-1}$
1.	[Mn L Cl ₂]	57.2 (57.0)	7.0 (7.1)	11.2 (11.0)	-	20
2.	[Mn L (NO ₃) ₂]	51.4 (51.5)	6.2 (6.4)	15.2 (15.0)	-	22

Table 2. Magnetic movement and electronic spectral data of Mn (II) complexes.

S.No.	Complexes	μ_{eff} BM	λ_{max} cm^{-1}
1.	[Mn L Cl ₂]	5.88	18206, 24610, 26315
2.	[Mn L (NO ₃) ₂]	5.85	18600, 24552, 27548

Table 3. Mn $2P_{1/2, 3/2}$ binding energies (eV) in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ salt their metal complexes.

S.No.	Salt and their complexes	Mn^{+2}	
		$2P_{1/2}$	$2P_{3/2}$
1.	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	654.2	643.2
2.	MnL Cl_2	653.2	642.2
3.	$\text{Mn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	654.8	643.8
	$[\text{MnL}^1(\text{NO}_3)_2]$	653.8	642.8

CONCLUSION

On the basis of elemental analysis magnetic susceptibility, molar conductance measurement, I.R., electronic EPR spectral studies and the subsequent discussion for the complexes given above, the structure may be proposed for these complexes as shown in fig. 1, and their geometry is shown below.

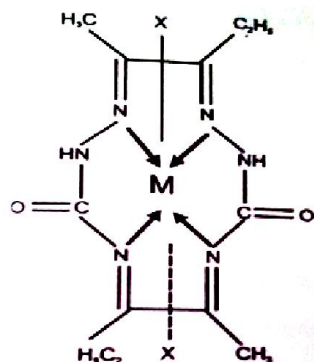


Fig. 3. Structure of complex, where,
[M = Mn(II)] (X = Cl, NO₃) [Mn (L) X₂]

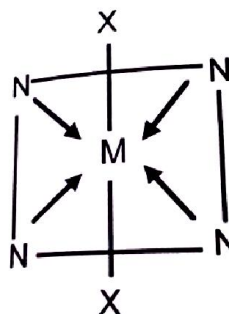


Fig. 4. [Mn (L) X₂] square planar geometry

REFERENCES

1. Chiswell, B., Mckenzie, E.D. and Lindog, L.F., *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R.D. Gillard and J.A. MC. Cleverty), Vol. 4, 1 Pergamon Press, Oxford (1990).
2. McCann, M., Cesey, R.M.T., Devereux, M., Curran, M. and Mekee, V., *Polyhedron*, **5** (14), 2321 (1996).
3. Youngs, H.L., Gelpke, M.D.S., Sundaramoorthy, D.L.M. and Gold, M.H., *Biochemistry*, **16**, 5664 (1977).
4. Temel, H. and Hosgorem, H., *Trans. Met. Chem.*, **27**, 609 (2002).
5. Lopez, J., Liang, S.D. and BU, X.R., *Tetrahedron. Lett.*, **39**, 4199 (1998).
6. Kureshy, R.I., Khan, N.H., Abdi, S.H.R., Polyer, Patel, S.I., Iyer, P., Suresh, E. and Dastidar, P., *Mol. Catal. A.*, **160**, 217 (2000).
7. Kureshy, R.I., Khan, N.H., Abdi, S.H.R., Iyer, P. and Patel, S.T., *Polyhedron*, **18**, 1773 (1999).
8. Heidt, C.J., Kostre, G.F. and Johnson, A.N., *J. Am. Chem. Soc.*, **80**, 6471 (1958).
9. Chandra, S. and Gupta, L.K., *J. Indian Chem. Soc.*, **82**, 454 (2005).
10. Zhang, Xiaofeng, Chen, Hui, Ma, Chengbiang, Chen, Chengneng, *Qiuion Liu*, **10**, 1039 (2006).

□