International Journal of Innovative Research and Advanced Studies (IJIRAS)
Volume 4 Issue 6, June 2017

ISSN: 2394-4404

X-Ray Powder Diffraction Of Transition Metal Complexes With Macrocyclic Ligand

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Abstract: ***Twelve membered macrocyclic complexes [MLX_2] where M = Mn(II) and X = Cl, NO_3, SCN have been synthesized by template condensation of ethylene diamine and furil. These new tetradentate ligand and its macrocyclic complexes were characterized by elemental analysis, magnetic susceptibility, molar conductance, IR, U.V.-Visible, EPR spectral studies, electrochemical properties and X-ray powder diffraction studies. g-Values are calculated for all of the complexes as polycrystalline form. All the complexes MLX_2 were found to have six coordinated octahedral geometry.***

I. INTRODUCTION

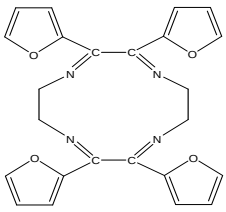

Figure 1: Structure of the Ligand

Molecular magnetism and macrocyclic compounds are two active fields of research encompassing chemistry, physics, biology and material science [1]. Recently many five, six and seven coordinate mononuclear manganese (II) complexes containing macrocyclic ligand has been prepared and studied [2].The preparation of macrocyclic polyamine ligands bearing functional pendant donor atoms and various metals ions. Transtion metal complexes with tetraazamacrocyclic ligand having controlled template synthesis of macrocyclic species [3]. The development of the field of bioinorganic chemistry has been another important factor in spurring the growth in interest in macrocyclic compounds [4]. Macrocyclic ligand systems can be turned to force metal ions and hence adopt unusual coordination geometry and unusual properties. Macrocyclic compounds and their derivatives are considerable interest in ligand system complexes of polydentate macrocyclic ligands because of the organic cation guest as well as good hosts for metal anions as variety of geometrical forms available and the possible encapsulation of the metal ion [5,6]. In this paper we report the synthesis of novel complexes of mono nuclear Mn (II) containing macrocyclic ligand.

II. EXPERIMENTAL

All the chemicals used were of AnalaR grade and procured from Aldrich. Metal salts were purchased from E.Merck and were used as received.

SYNTHESIS OF LIGAND

The reaction is carried out in 2:2 molar ratio. Hot ethanolic solution(20 mL) of furil (2 mmol, 0.38g) and a hot ethanolic solution (20mL) of ethylenediamine (2 mmol, 0.12g) were mixed slowly with constant stirring. The mixture was refluxed at ~ 78^{o}C for 10h in presence of few drops of hydrochloric acid. (It was found that few drops of hydrochloric acid increases the yield and act as good condensing agents for the condensation of primary diamine and dicarboxylic acid.) On cooling white precipitate was formed, which was filtered, washed with cold EtOH and dried over silica gel. Yield- 28%, m.pt- 190^{o}C. Elemental analysis (found 429amu): C- 67.23, H- 4.62 and N- 13.02 %. Calculated 428amu: C- 67.25, H- 4.67 and N- 13.07 %.

Since the yield of ligand is very poor, all the complexes were prepared by the template method.

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PREPARATION OF COMPLEXES

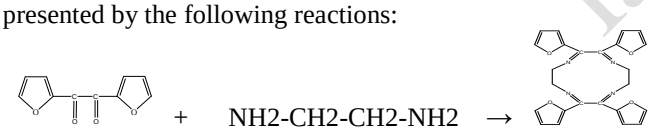
The reaction is carried out in 1:2:2 molar ratio. A mixture of metal salts (1 mmol) and ethylenediamine (2 mmol, 0.12g) was dissolved in 30 mL ethanol. The mixture was stirred with gently heating for about 10 minutes. In mixture an ethanolic solution of furil (2 mmol, 0.38g) was added. The resultant mixture was refluxed on water bath at 78°C for about 6-8 h. On cooling the reaction mixture for overnight at 0°C, the coloured crystals of the complexes precipitated out. They were filtered, washed with ethanol and dried over silica gel.

III. PHYSICAL MEASUREMENTS

IR spectra were recorded on a Perkin Elmer 137 instrument as Nujol mulls/KBr pellets.Microanalyses (C, H and N) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Shimadzu UV mini – 1240 spectrophotometer was used to take electronic spectra. Elico conductivity bridge (type CM82T) was used to measure molar conductance of the complexes. Magnetic moment measurements (Gouy balance) were made at room temperature using $CuSO_4$ $5H_2O$ as a callibrant. At room temperature a polycrystalline sample of the Mn(II) complexes was used to record EPR spectra on E_4-EPR spectrometer using the DPPH as the *g*-marker. The X-ray powder diffraction measurements were performed on Brooker (Advance Make Model D-8) with a Cu α target and operated at room temperature.

IV. RESULTS AND DISCUSSION

The formation of the ligand and the complexes may be presented by the following reactions:



Furil + Ethylenediamine → L

$L + MX_2 \rightarrow MLX_2$

LIGAND

I.R spectrum of the ligand does not show any band at 3400cm^{-1} and 1700cm^{-1} corresponding to free primary diamine and carbonyl group respectively. It also supports the macrocyclic structure and complete condensation. However the IR spectrum of ligand shows new bands at 1680cm^{-1} due to the imine ν (C=N) [7] group.

A new series of mononuclear complexes MLX_2 (M=Mn and X = NO_3^-, Cl^-, SCN^-) have been prepared. The complexes were stable in atmosphere. All the complexes have high melting point (> 300°C). The result of elemental analysis (Table I1) supports the proposed macrocyclic structure. The molar conductance values of all the complexes in DMSO solution were found in the range 9-17$ohm^{-1}cm^2mol^{-1}$ suggesting that the complexes are non electrolyte[8].

I.R. SPECTRA

Bands due to anions:The unidentate NO_3 group exhibits three NO stretching bands at 1420 cm^{-1} ν_5 (NO_2), 1305 cm^{-1} (NO_2) and 1008 cm^{-1} ν_2 (NO_2). The complexes under study show IR spectral bands at 1439-1435 cm^{-1} (ν_1), 1374-1377 cm^{-1} (ν_3),1309-1308 cm^{-1} (ν_5), 1010-1013 cm^{-1} (ν_2) and 839-835cm^{-1}(ν_6). The absence of broad band at 1390 cm^{-1} indicates the coordination of both nitrate groups. The separation of ~ 125 cm^{-1} between ν_1 and ν_5 indicates that both nitrates groups act as unidentate [9]. spectra of these complexes display a strong sharp band at 2134-2139 cm^{-1}, for the C=S stretching frequency for a S-bonded thiocyanate group and a second band, relatively broad, at 2067-2070cm^{-1} for the C=N stretching frequency for a N-bonded thiocyanate group. Thus the complexes have both S-bonded and N-bonded thiocyanate groups.

S.No	Functional Groups	I.R bands in Ligand (cm^{-1})	I.R bands in Complexes (cm^{-1})
1.	>C=O	-	-
2.	$-NH_2$	-	-
3.	>C=N	1680	1620
4.	$-NO_3$	-	1439-1435, 1374-1377, 1308-1311, 1010-1013
5.	-SCN	-	2134-2139, 2067-2070

Table 1: I.R bands of ligand and complexes

ELECTRONIC SPECTRA

In the high spin octahedrally coordinated Mn^{+2} complex, the lowest configuration $(t_{2g})^3$ $(eg)^2$ gives rise to ground state $^6A_{1g}$. Eletronic spectra of the complexes display weak absorption bands at 18719 (ν_1),23310-23364(ν_2), 27933-28169(ν_3) and 38910(ν_4) cm^{-1} chracteristic of octahedral geometry in the complexes[10]. These bands may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, $^6A_{1g} \rightarrow {}^4Eg(4D)$, $^6A_{1g} \rightarrow {}^4T_{1g}(^4P)$, $^6A_{1g} \rightarrow {}^4Eg(G)$ transition respectively (Table-III).

a) EPR Spectra: In polycrystalline sample Mn^{+2} complexes usually give broad signals attributed to forbidden transitions where (m = ± 1) (m=electron spin quantum number) and Δm/o (where m=nuclear spin quantum number). The broadening of spectra in powder sample is due to immobilization of Mn^{+2} ion in the ligand results because the rotational motion of Mn^{+2} is highly restricted[10]. Another origin of line- broadening is spin relaxation which is temperature dependent. In DMSO solution, the Mn(II) complexes give EPR spectra containing the six lines arising due to the hyperfine interaction between the unpaired electrons with the ^{55}Mn nucleus (I = 5/2). The nuclear magnetic quantum number M_I, corresponding to these lines, are –5/2, –3/2, –1/2, +1/2, +3/2, +5/2 from low to high high field.The g values are given in (Table-IV). On the basis of above spectral studies, it is clear that the ligand is acting as tetradentate chelating agents having four coordination sites. The anions occupied the axial positions, thus a hexa coordinated environment for manganese has been proposed.

X-RAY ANALYSIS

X-ray diffraction analysis of the compounds $[MnLX_2]$ and $[CoLX_2]$ confirms tetragonal crystal system for these derivatives. $[MnLX_2]$ has unit cell dimensions a=2.672, b= 2.672 , c= 3.550 , $\alpha = \beta = \gamma = 90$ and $[CoLX_2]$ has unit cell dimensions a= 13.36 , b= 13.36 , c= 15.08 , $\alpha = \beta = \gamma = 90$.

Complexes Molecular and Emperical Formula	Molecular Wt. Found (Calc.)	Melting Temp.(°C)	Colour	Yield %	Found(Calc.%)			
					M	C	H	N
$[Mn(L)(NO_3)_2]$ $C_{20}H_{20}MnN_6O_6$	639 (639.14)	310	Light Yellow	72	8.59 (8.63)	45.05 (45.08)	3.12 (3.14)	8.76 (8.81)
$[Mn(L)(Cl)_2]$ $C_{20}H_{20}MnN_4O4Cl_2$	554 (554.05)	320	Cream	68	9.91 (9.98)	52.01 (52.09)	3.60 (3.67)	10.10 (10.17)
$[Mn(L)(SCN)_2]$ $C_{22}H_{20}MnN_6O_4S_2$	599 (599.21)	310	Off White	62	9.16 (9.21)	48.09 (48.14)	3.33 (3.39)	9.34 (9.39)

L = 2,3,8,9 tetrafuran 1,4,7,10 tetraaza cyclododeca 1,3,7,9 tetraene (N_4)

Table 2: Analytical and Physical data of the Complexes

Complexes	μ_{eff} (B.M.)	λ_{max} (cm^{-1})	ε($Lmol^{-1}cm^{-1}$)
$[Mn(L_1)(NO_3)_2]$	5.89	18720, 23,364, 28,169, 38,910	39, 41, 69,131
$[Mn(L_1)(Cl)_2]$	5.90	18,719, 23,310, 27,933, 38910	38, 42, 72, 130
$[Mn(L_1)(SCN)_2]$	5.89	18710, 23320, 27,933, 38910	37, 43, 74, 135

Table 3: Magnetic moments and electronic spectral data of the complexes

S.No	Complexes	Temperature	$g_{\parallel}$	$g_{\perp}$	g_{iso}
1.	$[Mn(L_1)(NO_3)_2]$	RT	-	-	2.0054
2.	$[Mn(L_1)(Cl)_2]$	RT	-	-	2.0099
3.	$[Mn(L_1)(SCN)_2]$	RT	-	-	2.0052

NOTE: RT- Room Temperature and LNT- Liquid Nitrogen Temperature.

Table 4: EPR Spectral data of the complexes (as polycrystalline sample)

V. CONCLUSION

The synthesized macrocyclic ligand and its complexes studied by I.R, U.V-vis, EPR, magnetic studies supports the macrocyclic structure. Comparing I.R bands of ligand and macrocyclic complexes showed that ligand coordinate to metal atom through C=N band. X-ray diffraction analysis of the compounds confirms the tetragonal crystal system for these derivatives.

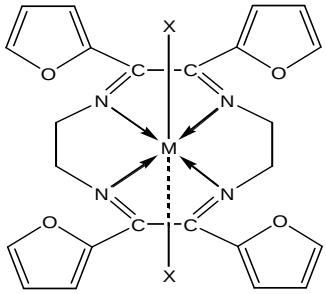


Figure 2: Structure of the complex M= Mn and (X= Cl^- , SCN, NO_3^-)

REFERENCES

[1] Chaudhary A, Rawat Ekta and Khan Sharma," Tetra aza tetraoxo Macrocyclic Complexes of Bivalent Tin as Potential Antifungal Agents", Int.J. of Applied Engg. Research; 16, 1929-1934 (2013).

[2] Al-Obaidi O.H.S and Al-Hiti R.H," Synthesis, Spectral and Theoretical Studies of Macrocyclic Cu(II), Ni(II) and Co(II) Complexes by Template Reaction of Malonic Acid with Metal(II) Chloride and Urea or Thio urea", American Chemical Science Journal; 2(1), 1-11(2012).

[3] Dubey A.K, Tiwari V.K and Dikshit S.N," Studies of Trivalent Transtion Metal Macrocyclic Complexes and its Antimicrobial Activities", Research J. of Chemical Sciences; 5(8), 35-38 (2015).

[4] Chandra S, Tyagi M and Agarwal S," Synthesis and Characterization of a tetraaza Macrocyclic Ligand and its Co(II), Ni(II) and Cu(II) Complexes", J. Serb.Chem Soc; 75(7), 935-941(2010).

[5] Chandra S and Punder M.P," Molecular and Biomolecular Spectroscopy", Spectrochimica Acta Part A; 69(1), 1-7(2008).

[6] Sellappan R, Prasad S, Jayaseelan P and Rajavel R," Synthesis, Spectral Characterization, Electrochemical and Antimicrobial Activity of Macrocyclic Schiff Base Vanadyl Complexes", Rasayan J. Chem; 3(3) 556-562 (2010).

[7] Goel V, Sonika and Malhotra R," Synthesis and studies of Tetraaza Macrocyclic Complexes of Transtion Metal ion", Scholary J. of Physical and Applied Chemistry; 1(2), 17-21(2014).

[8] Vogel, A. I," A text book of quantitative Inorganic analysis", 4th Ed.; ELBS and Longman, (1978).

[9] Nakamota, K," Sulfato, Carbonato and other complexes. Infrared and Raman spectra of Inorganic and Coordination compound", 3rd Ed; A Wiley Interscience Publication; New York. 244(1978).

[10] Figgis, B.N," Electronic spectra of complex ion", Introduction to ligand fields. Wiley Eastern Ltd. New Delhi; (1976).