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Archives of Applied Science Research, 2015, 7 (4):31-36
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Synthesis and physico-chemical studies of macrocyclic ligand and its Cr(III) and Mn(II) complexes

Rajendra H. Satpute, Mahadeo A. Sakhare, Aashish O. Dhokte and Balasaheb R. Arbad*

Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad (M.S.), India

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ABSTRACT

14-membered tetraaza macrocyclic ligand and its solid complexes of Cr(III) and Mn(II) have been synthesized and characterized by elemental analysis, conductometry, magnetic susceptibility, UV–visible, FTIR, ^{1}H NMR spectra, powder X-ray diffraction and thermal analysis. From the microanalytical data, the stoichiometry of the complexes has been found to be 1:1 (metal:ligand) ratio. The TGA-DTA data suggest Cr(III) complex having one ionic nitrate ion, one water molecule and two coordinated nitrate ions and Mn(II) complex having one ionic water molecule and two coordinated chloride ions. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) complexes.

Keywords: Macrocyclic ligand complexes, Transition metal complexes, Thermal analysis, Powder X-ray diffraction etc.

INTRODUCTION

Transition metals play a central role in the construction of molecular materials, which display magnetic properties and find applications in material and supramolecular chemistry and biochemistry [1–4]. The study of macrocyclic complexes is a growing class of research [5-8]. Macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard–soft donor character and versatile coordination behavior [9,10], and for their biological activities, i.e. toxicity against bacterial growth [11], anticancerous [12] and other biochemical properties [13,14]. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments [15] as well as NMR shift reagents [16].Cr(III) complexes of macrocyclic ligands are well known for their biological importance as well as their anticarcinogenic, antibacterial, and antifungal properties [17].

The complexes of metal ions in combination to macrocyclic ligands are significant, as these resemble with natural system like porphyrin and cobalamine [18, 19]. The new macrocyclic bifunctional chelating agents are used in labeling monoclonal antibodies with radioactive metal [20-22] and for cancer diagnosis [23,24].

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

MATERIALS AND METHODS

Substituted diketone was prepared from 2-Hydroxy acetophenone and benzoic acid by Bekar Vankataraman rearrangement. Benzoic acid, phosphorus oxychloride, pyridine, potasium hydroxide, ethylene diamine of AR grade

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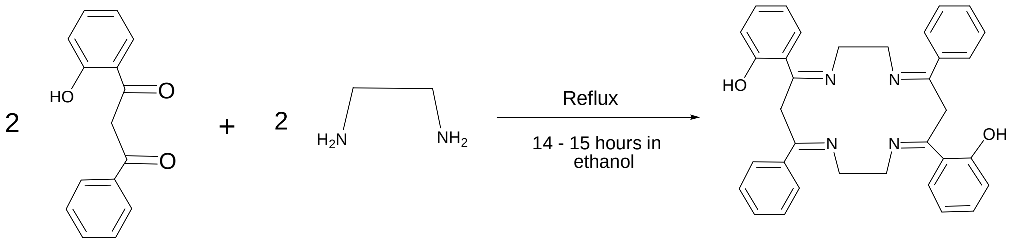
were used for synthesis of ligand. AR grade metal nitrate was used for the synthesis of complex. The carbon, hydrogen and nitrogen contents were determined on Perkin Elmer (2400) CNS analyzer. FTIR spectrum were recorded on Jasco FTIR-4100 spectrometer using KBr pellets. ^{1}H NMR spectrum of ligand was recorded in $CDCl_3$ +DMSO using TMS as internal standard. The TGA-DTA and XRD were recorded on Perkin Elmer TA/SDT-2960 and Philips 3701, respectively. The UV–visible spectra of complexes were recorded on JascoUV-530 spectrometer. Molar conductance of complexes was measured on Elico CM 180 conductivity meter using 10^{-3} M solution in DMF.

2.1 Synthesis of ligand

A hot ethanolic solution (30 ml) of 1-(2-hydroxyphenyl)-3-phenylpropane-1, 3-Dione (4.80g, 0.02 mol) and a hot ethanolic solution (30 ml) of ethylene diamine (1.20 g, 0.02 mol) were mixed slowly with constant stirring. This reaction mixture was then refluxed at 80-90°C for 14–15 h in the presence of few drops of concentrated HCl. On cooling, a solid yellow precipitate was formed, which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [25-28]. (Yield: 59 %)



Scheme 1 Synthesis of ligand

2.2 Synthesis of complexes

A hot ethanolic (20 ml) solution of the ligand (0.001 mol) and a hot ethanolic (20 ml) solution of the corresponding metal salt (0.001 mol) were mixed together with constant stirring. The p^H of the reaction mixture was adjusted in the range 7-8 by adding 10% alcoholic ammonia solution. The reaction mixture was refluxed for 5–6 h at 80-90ºC.On cooling, a colored precipitate was formed. It was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10} [25-28]. (Yield 50-55%).

RESULTS AND DISCUSSION

Physical characteristics, micro analytical, molar conductance data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveals 1:1 molar ratio (metal:ligand). The presence of water molecules, chloride and nitrate ions was confirmed by TGA-DTA analysis as well as by FTIR spectroscopy. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) complexes. The metal chelate solutions in DMF shows low conductance which supports non-electrolyte nature of metal chelates.

3.1 ^{1}H NMR spectra of ligand

^{1}H NMR ($CDCl_3$-DMSO): δ= 2.6 (s, 4H, $–CH_2$), 3.8 (s, 4H, $N=C–CH_2$), 3.9 (s, 4H, $N=C–CH_2$), 5.7 (s, 2H, Ar-OH), 6.4–8.4 (m, 18H, Ar–H).

3.2 FTIR spectra

The IR spectrum of the ligand (L) shows a ν(C=N) peak at 1619 cm^{-1}, and the absence of a ν(C=O) peak at around 1700 cm^{-1} is indicative of Schiff's base condensation. The IR spectrum of ligand, appearance of a new strong absorption band at 1619 cm^{-1}, attributable to the characteristic stretching frequencies of the imino linkage ν (C=N),which provides strong evidence for the presence of cyclic product. On complex formation, the ν (C=N) shifted towards lower side by 14–19 cm^{-1}, hence the ligand is tetradentate, nitrogen donor coordinates through nitrogen of C=N group [29]. The ν(OH) vibration of the phenolic proton appears as a broad band in the region 3200-3346 cm^{-1} probably due to the overlapping of the symmetric and antisymmetric OH stretching vibrations of lattice water [30-31]. The presence of lattice water is also established and supported by TGA-DTA analysis of these complexes. Cr(III) complex exhibit absorption band in the region 355-368 cm^{-1} assigned to (Cr-N) stretching vibration and absorption bands at ~ 1500 & 1320cm^{-1} due to the ν(N=O) (ν_1) and $\nu_a(NO_2)$ (ν_5) vibrations, respectively of the coordinated nitrate ion [32-33]. Mn(II) complexes with a tetradentate macrocyclic N donor ligand and reported that infrared spectra of the complexes exhibited band in the range 440-550cm^{-1}, assigned to (Mn-N) stretching vibration [34] and 335-340 cm^{-1}, assigned to (M-Cl) stretching vibration[35]. On the basis of above discussion, a six coordinated structure is proposed for all the complexes in which the ligands coordinate *via* four azomethine nitrogens (Table 2).

3.3 Electronic spectra

The electronic absorption spectra of Cr(III) and Mn(II) complexes were recorded in DMF as a solvent. The electronic spectra of the ligand exhibits two transitions in the range 26738 and 27778 cm^{-1}, which may be attributed to the $\eta \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the imine groups. The electronic spectra of Cr(III) and Mn(II) complexes recorded in DMF solution. Electronic spectrum of Cr(III) complexes display four electronic spectral bands at 24876, 27778, 28736 and 33333 cm^{-1}. The first three bands may be assigned to transitions $^4A_2g \rightarrow {}^4T_2g$ (F), $^4A_2g \rightarrow {}^4T_1g$ (F), $^4A_2g \rightarrow {}^4T_1g$ (P) respectively and fourth one to the charge transfer [36]. Electronic spectrum of Mn(II) complex exhibit five absorption bands at 24876, 27027, 27778, 29412 and 36231cm^{-1}. These bands may be assigned to the following transitions $^6A_1g \rightarrow {}^4T_1g$ (4G), $^6A_1g \rightarrow {}^4Eg$, ^4A_1g (4G) and $^6A_1g \rightarrow {}^4Eg$ (4D), ^6A_1g (4P), respectively [36].

Table 1. Physical characterization, analytical and molar conductance data of ligand and its metal complexes

Ligand/complexes	F.W.	M.P. (^{0}C)	Colour	Molar conduc. Mho (cm^2 mol^{-1})	% Found (Calcd.)			
					C	H	N	M
(L)	528.25	181	yellow	3.3	77.25 (77.34)	6.10 (6.02)	10.59 (10.38)	-----
$[Cr L (NO_3)_2] NO_3 H_2O$	784.24	>300	Greenish black	56	52.30 (52.02)	4.05 (4.33)	12.38 (12.49)	6.73 (6.62)
$[Mn L(Cl)_2] H_2O$	672.18	>300	Brown	40	60.20 (60.69)	5.54 (5.05)	8.10 (8.33)	8.40 (8.17)

Table 2. FTIR spectra of ligand (L) and its complexes (cm^{-1})

Ligand/complexes	(OH)	(C=N)	(C–O)	(M–N)	Ionic nitrate	Coordinated nitrate	
						(N=O) (ν_1)	(NO_2) (ν_5)
(L)	3340	1619	1208	---	---	---	----
$[Cr L (NO_3)_2] NO_3 H_2O$	3223	1605	1260	357.9	1384	1401	1321
$[Mn L(Cl)_2] H_2O$	3346	1600	1143	522	---	---	---

3.4 Powder X-ray diffraction

The X-ray diffraction of representative metal complexes was scanned in the range 20-80° at wave length 1.540Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). The diffractogram of Cr(III) complex have 23 reflections with maxima at 2θ= 58.759° and its intensity 20.42 a.u. corresponding to d value 1.57 Å. The diffractogram of Mn(II) complex shows 18 reflection with maxima at 2θ = 36.363° and its intensity 113.89 a.u. corresponding to d value 2.4686 Å. The X-ray diffraction pattern of these complexes with respect to major peaks having relative intensity greater than 10% has been indexed by using computer programme. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. The unit cell of Cr(III) complex yielded values of lattice constants, a=15.18 Å, b = 7.10 Å, c = 6.27Å and unit cell volume V= 675.76 Å^3. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90$ required for sample to be orthorhombic were tested and found to be satisfactory [36]. Hence, it can be concluded that Cr(III) complex have orthorhombic crystal system. The unit cell of Mn(II) complex yielded values of lattice constants, a= 13.072 Å, b = 6.796 Å, c=6.891 Å and unit cell volume V =525.41 Å^3. In concurrence with these cell parameters, the conditions such as $a \neq b \neq c$ and $\alpha = \beta = 90$ $\gamma = 120$ required for sample to be monoclinic were tested and found to be satisfactory [38]. Hence, it can be concluded that Mn(II) complexes have monoclinic crystal system (fig. 1).

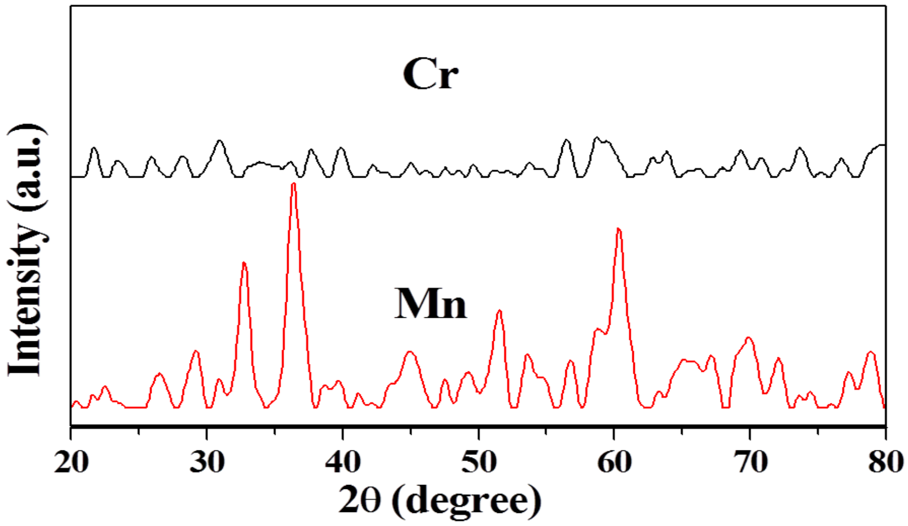


Fig. 1. X-ray diffractogram of Mn(II) and Cr(III) complexes

3.5 Thermal analysis

The simultaneous TGA-DTA analysis of metal complexes was studied from ambient temperature 50 to 1000 °C in nitrogen atmosphere using α-Al_2O_3 as reference. The Cr(III) and Mn(II) complexes of ligand were chosen for thermal study. Themogravimetric analysis shows that the Cr(III) and Mn(II) complexes of ligand exhibit high thermal stability. The lattice water is removed in the temperature range of 55–110 °C and the ionic nitrates are removed in the 178–360 °C range. The macrocycle is lost in the temperature range of 361– 825 °C along with the coordinated nitrate [39]. Mandalik et al [40] reported that themal study of Mn(II) and Cr(III) Schiff base complexes and shows weight loss in between 80-150 ºC indicates that presence of lattice water.

Cr(III) complexes of L in which one lattice water and one ionic nitrate ion are removed with mass loss of 9.53 % (calcd.10.15%) between 50-190 ºC and two coordinated nitrate ions are removed with loss of 15.59% (calcd.15.77 %) between 190-310 ºC. An endothermic peak in the range 135-145 ºC (δmax 140 ºC) in the DTA curve corresponds to the dehydration and denitration step and second endothermic peak in the range 270-280ºC (δmax 280 ºC) corresponds to the denitration step. The macrocycle is lost in the temperature range of 310–820 ºC. An endothermic peak in the range 380-390 ºC (δmax 385 ºC) in the DTA curve corresponds to the loss of macrocycle step. The mass of final residue corresponds to stable Cr_2O_3.

Mn(II) complexes of L in which one lattice water is removed with mass lose of 2.62 % (calcd.2.69 %) between 50-100 ºC and two coordinated chloride ions are removed with loss of 9.83% (calcd.10.53%) between 100-310 ºC. An endothermic peak in the range 90-100 ºC (δmax 100 ºC) in the DTA curve corresponds to the dehydration and second endothermic peak in the range 300-320ºC (δmax 310 ºC) corresponds to the dechlorination step. The macrocycle is lost in the temperature range of 310–820 ºC. An endothermic peak in the range 400-410 ºC (δmax 410 ºC) in the DTA curve corresponds to the loss of macrocycle step. The mass of final residue corresponds to stable MnO.

CONCLUSION

Based on analytical, conductance, magnetic, infrared, electronic spectral data, TGA and X-ray powder pattern, all these complexes exhibit six coordination number. A tentative, general structure of Cr(III) and Mn(II) macrocyclic ligand complexes is given in Fig.2. The FTIR spectral data suggest that the ligand behaves as a tetradentate ligand with N donor atoms towards central metal ion. The X-ray diffraction data suggest orthorhombic crystal system for Cr(III) and monoclinic crystal system for Mn(II) complexes. Analytical data obtained from thermal studies reveals that these complexes are thermally stable.

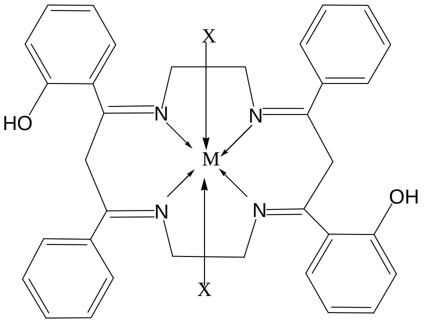


Fig. 2. Proposed structure of metal complexes
Where M =Cr(III)and Mn(II)
X=NO₃ for Cr(III) and X=Cl for Mn(II)

Acknowledgement
The authors are grateful to the Head, Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad for providing the laboratory facilities and UGC-BSR FF and UGC-SAP Programmes for financial help.

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