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ONE POT TEMPLATE SYNTHESIS AND CHARACTERIZATION OF TRIVALENT TRANSITION METAL ION COMPLEXES DERIVED FROM DIAMINOPYRIDINE AND GLYOXAL

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ABSTRACT

A new series of hexaazamacrocyclic complexes of type $[M(TML)X_2]$ *where M = Cr(III), Mn(III) and Fe(III); TML is tetradentate macrocyclic ligand and X =* Cl^-, NO_3^-, CH_3COO^-, *has been prepared from 2,6-diaminopyridine and glyoxal by template method. The complexes are formulated as:* $[M(TML)X]X_2$ *due to 1:2 electrolytic nature of these complexes. The ligand coordinates through all four azomethine nitrogens but pyridine nitrogens do not take part in coordination as confirmed by absence of (M-Py) vibrations. These complexes have been characterized with the help of various physico-chemical techniques like IR, far-IR, elemental analyses, electronic spectra, conductance and magnetic susceptibilities. The distorted square pyramidal geometry has been proposed for all of these complexes.*

Keywords: *Macrocyclic complex, template, infrared, magnetic moment.*

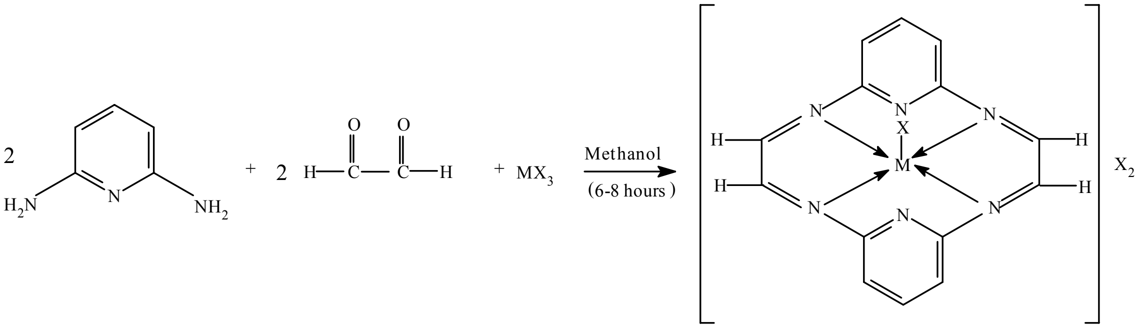
INTRODUCTION

The design and study of metal containing macrocycles is an interesting field of chemistry[1]. Over the last few years, very active research in macrocyclic chemistry has attracted the interest of inorganic chemists[2]. The chemistry of tetraimino macrocyclic complexes is of considerable interest because of their applications for modeling bioinorganic systems, catalysis and analytical practice[3]. Spontaneous self assembly reactions have been considered as vehicles for reliable and economical preparation of macrocyclic complexes. Hence these reactions hold a fascination for chemists to mimic anabolic reaction without enzymes. Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems[4]. Macrocyclic ligands form more stable complexes as compared to analogous open chain ligands[5]. *In-situ* one pot template synthesis is the most widely adopted method for preparation of macrocyclic complexes[6]. A number of nitrogen donor macrocyclic derivatives have been used for a long time in analytical, industrial and medical applications[7]. Macrocyclic metal complexes are of great importance due to their resemblances with many natural systems such as porphyrins and cobalamines[8]. Macrocyclic nickel complexes find use in DNA recognition and oxidation[9] while macrocyclic copper complexes find use in DNA binding and cleavage[10]. Macrocyclic metal complexes of lanthanides *e.g.* Gd^{+3} are used as MRI contrast agents[11,12]. Macrocyclic metal chelating agents (DOTA) are useful for detecting tumor lesions[13]. The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments[14] as well as NMR shift reagents[15]. Some macrocyclic complexes have been found to exhibit potential antibacterial activities[16,17]. Prompted by these, in the present paper synthesis and characterization of trivalent chromium, manganese and iron macrocyclic complexes derived from 2,6-diaminopyridine and glyoxal have been discussed.

EXPERIMENTAL

Materials: *2*,6-diaminopyridine was purchased from Koch-Light, England and glyoxal was obtained from SRL Pvt. Ltd Mumbai. All other chemicals used were of AnalR grade.

Isolation of complexes: Our several attempts to isolate the free macrocyclic ligand were unsuccessful. Hence, all the complexes were obtained by template synthesis. To a stirring methanolic solution (~50 cm^3) of 2,6 diaminopyridine (10 mmol) was added trivalent chromium, manganese and iron salt (5 mmol) dissolved in minimum quantity of methanol (20 cm^3). The resulting solution was refluxed for 0.5 h. After that glyoxal (10 mmol) was added in the refluxing mixture and again refluxed for 6-8 h. On overnight cooling dark coloured ppt. formed which was filtered, washed with methanol, acetone, diethylether and dried *in vacuo* (Yield ~45%). The complexes were found soluble in DMF and DMSO, but were insoluble in common organic solvents and water. They were found thermally stable up to ~240°C and then decomposed.
The template syntheses of the complexes may be represented by the following scheme-1:



Where M = Cr(III), Mn(III), Fe(III)
X = Cl^{-1}, NO_3^{-1}, CH_3COO^{-1}
Scheme-1

Analytical and physical measurements: The microanalyses of C, H, and N were carried out at Sophisticated Analytical Instrument Facility, CDRI, Lucknow. The metal contents were determined by standard EDTA methods[18]. Electronic spectra (DMF) were recorded on Cary 14 spectrophotometer. The magnetic susceptibility measurements were carried at IIT Roorkee. The IR spectra were recorded on Infrared spectrophotometer in the range 4000-667 cm^{-1} using KBr pellets. The conductivity was measured on digital conductivity meter (HPG System, G-3001).

RESULTS AND DISCUSSION

The analytical data show the formula of macrocyclic complexes as: $[M(C_{14}H_{10}N_6)X]X_2$; where M = Cr(III), Mn(III), Fe(III) and X=Cl^{-1}, NO_3^{-1}, CH_3COO^{-1}. The test for anions is positive before and after decomposing the complexes with conc. HNO_3, indicating their presence inside as well as outside the coordination sphere. Conductivity measurements in DMSO indicated them to be electrolytic in nature (140-150 $ohm^{-1}cm^2$ mol^{-1})[19]. All compounds give satisfactory elemental analyses results and magnetic moment as shown in the Table-1.

IR Spectra

It was noted that a pair of bands are present in the spectrum of 2,6-diaminopyridine at 3250-3400 cm^{-1} corresponding to $\nu(NH_2)$ but are absent in the infrared spectra of all the complexes. Further, no strong absorption band was observed near 1700-1710 cm^{-1} indicating the absence of >C=O of glyoxal. This confirms the condensation of carbonyl groups of glyoxal and amino groups of 2,6-diaminopyridine[20,21]. These results provide strong evidence for the formation of macrocyclic frame[22]. A strong absorption band in the region ~1595-1615 cm^{-1} may be attributed to the C=N group[23,24]. The lower values of ν(C=N) may be explained on the basis of drift of lone pair density of azomethine nitrogen towards metal atom[21,25]. The bands present at ~3040 cm^{-1} may be assigned due to ν(C-H) vibrations of glyoxal moiety. The bands present in the range ~1350-1000 cm^{-1} are assigned due to ν(C-N) vibration. The IR spectra of the complexes do not show any change in the pyridine ring vibrations and interestingly enough, it appears that in these complexes pyridine nitrogen does not take part in coordination[26,27]. Moreover, the coordination through pyridine nitrogen does not take place, as it will result in the formation of unstable four membered rings.

Far IR spectra

The far IR spectra show bands in the region ~430-450 cm^{-1} corresponding to ν(M-N) vibrations[28-30]. The presence of bands in all complexes in ~430-450 cm^{-1} region originate from (M-N) azomethine vibrational modes and gives idea about coordination of azomethine nitrogens[31]. The bands present at 300-315 cm^{-1} may be assigned as being due to ν(M-Cl) vibrations[28,30]. The bands present at 225-255 cm^{-1} in all nitrato complexes are assignable to ν(M-O) vibrations[28]. However, the absence of various (M-py) vibrations supports the non-involvement of pyridine nitrogens in coordination.

Magnetic measurements and electronic spectra

Chromium complexes: Magnetic moment of chromium complexes were found in the range of 4.20-4.50 B.M. The electronic spectra of chromium complexes show bands at ~9020-9300, 13040-13330, 17470-18310, 27430-27840 and 34810 cm^{-1}. However, these spectral bands cannot be interpreted in terms of four or six coordinated environment around the metal atom. In turn, the spectra are consistent with that of five coordinated Cr(III) complexes, whose structure have been confirmed with the help of X-ray measurements[32]. Thus keeping in view, the analytical data and electrolytic nature of these complexes, a five coordinated square pyramidal geometry may be assigned for these complexes. Thus, assuming the symmetry C_{4V} for these complexes 33, the various spectral bands may be assigned as: 4B1 → 4Ea, 4B1 → 4B2, 4B1 → 4A2 and 4B1 → 4Eb.

Manganese complexes: The magnetic moment of manganese complexes lay in the range 4.85-4.90 B.M. The electronic spectra of manganese complexes show three d-d bands which lay in the range 12260-12580, 16060-18910 and 35430-35740 cm^{-1}. The higher energy band at 35450-35750 cm^{-1} may be assigned due to charge transfer transitions. The spectra resemble to those reported for five coordinate square pyramidal manganese porphyrins[31,33]. This idea is further supported by the presence of the broad ligand field band at 20400 cm^{-1} diagnostic of C_{4V} symmetry, and thus the various bands may be assigned as follows: ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5B_2$, and ${}^5B_1 \rightarrow {}^5E$, respectively. The band assignment in single electron transition may be made as: $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively in order of increasing energy. However, the complexes do not have idealized C_{4V} symmetry.

Iron complexes: The magnetic moment of iron complexes lay in the range 5.82-5.90 B.M. The electronic spectra of iron (III) complexes show various bands 9830-9960, 15520-15575, 27620-27720 cm^{-1} and these bands do not suggest the octahedral or tetrahedral geometry around the metal atom. The spectral bands are consistent with the range of spectral bands reported for five coordinate square pyramidal iron (III) complexes[34]. Assuming C_{4V} symmetry for these complexes, the various bands can be assigned as: $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{z^2}$. Any attempt to make accurate assignment is difficult due to interactions of the metal-ligand л-bond systems lifting the degeneracy of the d_{xz} and d_{yz} pair.

CONCLUSIONS

Based on various physicochemical studies such as elemental analyses, conductivity, magnetic, electronic, and IR spectral studies a distorted square pyramidal geometry may be proposed for all of these complexes as shown in Fig. 1

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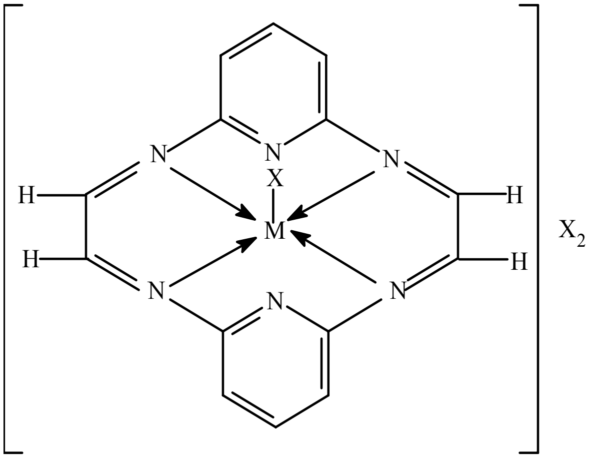

Where M = Cr(III), Mn(III), Fe(III)
X = Cl^{-1}, NO_3^{-1}, CH_3COO^{-1}

Figure-1

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Table-1: Analytical data of trivalent chromium, manganese and iron complexes derived from 2,6-diaminopyridine and glyoxal.

Sr. No.	Complexes	Found (calcd.) % M	C	H	N	Colour	Mol. Wt.
1.	$[Cr(C_{14}H_{10}N_6)Cl]Cl_2$	12.03(12.35)	39.76(39.90)	2.34(2.37)	19.65(19.95)	Yellowish Brown	421
2.	$[Cr(C_{14}H_{10}N_6)(NO_3)](NO_3)_2$	10.35(10.40)	33.48(33.60)	1.93(2.00)	25.11(25.20)	Brown	500
3.	$[Cr(C_{14}H_{10}N_6)(OAc)](OAc)_2$	10.27(10.59)	48.72(48.87)	3.69(3.86)	17.08(17.10)	Light Brown	491
4.	$[Mn(C_{14}H_{10}N_6)Cl]Cl_2$	12.88(12.97)	39.54(39.62)	2.30(2.35)	19.73(19.81)	Dark Brown	424
5.	$[Mn(C_{14}H_{10}N_6)(OAc)](OAc)_2$	10.95(11.13)	48.34(48.58)	3.49(3.84)	16.86(17.00)	Brown	494
6.	$[Fe(C_{14}H_{10}N_6)Cl]Cl_2$	12.97(13.17)	39.41(39.52)	2.22(2.35)	19.53(19.76)	Yellowish brown	425
7.	$[Fe(C_{14}H_{10}N_6)(NO_3)](NO_3)_2$	10.93(11.11)	33.21(33.33)	1.77(1.98)	24.83(25.00)	Light Brown	504
8.	$[Fe(C_{14}H_{10}N_6)(OAc)](OAc)_2$	11.19(11.31)	48.37 (48.48)	3.65(3.83)	16.90(16.96)	Light Brown	495