Spectroscopic Characterization Of Some Mn(II) Complexes With Nitrogen And Oxygen Containing Ligand

ArchanaKumari[#], AshishKumar[#], Ranjani Kumari[#], Amit Kumar[#] and Vijay Kumar^{*}

#ResearchScholar,P.G.DepartmentofChemistry, R.N.College,Hajipur *P.G.DepartmentofChemistry,R.N.College,Hajipur,Vaishali, Bihar E-mail- callmeashish007@gmail.com

(Received:15September2024/Revised:25September2024/Accepted:10 October2024/Published:28October2024) Abstract

Metal complexes are being continuously studied not only for their structural and bonding modes but also due to their versatile applications. The ligand 1-Phenylazo-2-naphthol(PANH) was prepared by the reported method. The prepared ligand was used for complexation with Mn(II) ion along with X. The formula of the complex has been found ML₂X₂, Where X= α -picoline, β -picoline, and pyridine.The complexes formedare characterized by physical, Chemical, and Spectroscopic methods. The mode of co-ordination of ligands through metal ions is ascertained by FTIR spectra of ligands and complexes. The geometry of complexes is found with the help of electronic spectra, magnetic moment measurement, and conductivity measurement. The geometry of complexes has been found to be distorted octahedral. It is also obvious that the ligand alongZ- the axis produced a stronger crystal field thanthe ligand onthe XY- plane.

Keywords: UV Spectra, FTIR Spectra, Distorted Octahedral Introduction

Transition metal complexes are being continuously studied not only cause of their interesting structure and bonding mode but also due to their versatile industrial application^[1-3]. The biological activities of the transition metal complexes, such as DNA binding, anti-inflammatory, anti-cancer, antibacterial, and antioxidant properties, have a significant potential for expression. Transition metal complexes have been important in a variety of industrial processes in recent years, including hydrolysis, decomposition, oxidation, reduction, epoxidation, hydrogenation, carbonylation, and polymerization reactions. These substances are more effective against a wide variety of bacterial strains, according to extensive biochemical and medical research. Additionally, they produce a range of binuclear complexes that have significant applications in food, dyes, analytical chemistry, pigment, corrosion inhibitors, magnetochemistry, binuclear reactivity, and non-enzymatic models for metabolic processes. There are several possibilities concerning the coordination of ligands containing Nitrogen, Sulphur, and Oxygen donor sites ^[4-8]. This makes our pursuit to make studies onthe structure and crystal field parameters of the steric bulk of the ligand. In the present paper we synthesis 1-Phenylazo-2- naphthol ligand as a reported method. The prepared ligand was used for complexation with Mn (II) ion along with X. Where $X = \alpha$ -picoline, β -picoline and pyridine. From the micro

analysis of complexes formed the general formula of the complex is found ML_2X_2 . The complexes formed arecharacterized by physical, chemical, FTIR spectra, and UV spectra.

Experimental

All the chemicals used were AR-grade quality. The ligand 1- Phenylazo - 2 – naphthol(PANH) was prepared by dissolving 0.01mole (1.425gm) of benzene diazonium chloride in 100 ml of ethanol. To this solution, 0.01 mole (1.44 gm) of 2- naphthol was also dissolved. The brown ppt. of 1 - Phenylazo-2-naphthol was obtained. The ligand was used for complexation with 0.01 mole (2.34 gm) of MnCl₂.6H₂O and 0.02 mole (4.96 gm) of ligand PANH. This solution was re-fluxedon a water bath with 0.01 mole (1.58 gm) of pyridine then we got yellow ppt. of [Mn(PAN)₂(py)₂], similarly prepared the complexes of [Mn (PAN)₂ (α - pico)₂] and [Mn (PAN (β - pico)₂] ^[9,13].

Result And Discussion

Table 1 presents the data of several analytical values combined. The ligand (PANH) functions as a monoanionic bidentate, according to the analytical results.^[10]Both ethanol and DMSO can dissolve the ligands and complexes. According to the molar conductance value, none of the complexes are electrolytic. The deformed octahedral geometry of Mn(II) is compatible with magnetic investigations of complexes at ambient temperature.^[11-12]The complex's general formula formed is found to be [Mn(PAN)₂X₂], where X= py, α -picoline, β -picoline.

FTIR Spectra Of Free Ligands And Complexes

The manner of ligand-to-Mn(II) ion coordination was discovered by comparing the free ligand IR spectra and its Mn(II) complexes. Three coordination sites are included in the ligand. Using the deprotonated phenolic oxygen, it can also coordinate as a monodentate anionic ligand.



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| | Table -1 | | | | | | |
|---|--|---------------|---------------|---------------|---------------|--|-------------------------------|
| | | M % C/(F) | C % C/(F) | H % C/(F) | N % C/(F) | Conductivity $\lambda m(ohm^{-1} cm^{-2} mo^{-1})$ | Magnetic Moment µ (B.M) |
| 0 | Ligand PANH | | 77.41/(77.81) | 04.83/(04.00) | 11.29/(11.11) | | |
| 1 | [Mn (PAN) ₂ (py) ₂] | 07.77/(07.23) | 71.29/(71.42) | 04.53/(04.40) | 11.88/(11.70) | 16.00 | 04.89 |
| 2 | $[Mn PAN)_2 (\alpha - pico)_2]$ | 07.47/(07.00) | 71.84/(71.92) | 04.89/(04.81) | 11.43/(11.39) | 18.00 | 04.87 |
| 3 | $[Mn (PAN)_2 (\beta - pico)_2]$ | 07.47/(07.81) | 71.84/(71.96) | 04.89/(04.79) | 11.43/(11.35) | 20.00 | 04.90 |

In addition, it can coordinate as a bidentate neutral ligand by constructing a "five-membered chelate ring with phenolic oxygen and naphthalic nitrogen or a 6-membered chelate ring with phenolic oxygen and" phenylic nitrogen. Additionally, it can function as a bidentate anionic 1 coordinated by any of the two nitrogens and deprotonated naphthalic oxygen.By comparing the complex's IR spectra to those of the free ligand, the ligand coordination mode was determined.

The free ligand IR spectra displayed a broadband at 3200cm^{-1} , "which might be assigned to intra-molecular hydrogen-bonded phenolic group vibration ^[14-17]. The weak band appearing at 3000cm^{-1} in the ligand'sIR spectra that had been assigned to the $v_{\text{C-H}}$ stretching vibration of the" aromatic ring^[18-19]. The bands appearing at 1610cm^{-1} , 1525cm^{-1} , and 1840cm^{-1} may be assigned to aromatic ring vibration.

The weak and broadband at 1455 cm^{-1} might be assigned to the two condensed ring systemsring vibration that is naphthalene ring vibration ^{[22].} Thus, both benzene and naphthalene ring in ligand is confirmed by the IR spectrum of the free ligand. The aromatic azo molecule's - N = N - frequency is likewise difficult to identify in IR spectra. Le Fevre et.al^[23] have studied many aromatic compounds are made a very tentative identification of -N =N- bond in IR at 1406 ±14cm⁻¹. On this basic v-N=N- weak band is justified at 1410cm⁻¹ is assigned were0-stretching vibration ^{[24].}On the comparison of IR spectra of complexes of Mn (II) ion with that of free ligand,

severalchanges in the absorption of the frequency of the different groups of the free ligand were found. The significant changes in the absorption frequency of important groups of ligands have been given in Table2.

| Band in free ligand | Mn(PAN) ₂ (P y) ₂ | Mn(PAN) ₂ (α - Pico) ₂ | Mn(PAN)2(β - Pico)2 |
|---|--|--|---------------------|
| | 01 | 02 | 03 |
| 3200(br) | | | |
| 3000(W) | 3010 | 3005 | 3010 |
| 1610 (W, sh) | 1610 | 1615 | 1610 |
| 1525 (s, sh) | 1530 | 1525 | 1525 |
| 1480 (m, sh) | 1480 | 1480 | 1480 |
| 1455 (W, br) | 1455 | 1455 | 1455 |
| 1410 (V, W) | 1380 | 1385 | 1385 |
| 1290 (S) | 1300 | 1295 | 1300 |
| 1228 (m) | 1228 | 1230 | 1230 |
| 1110 (s) | 1110 | 1110 | 1110 |
| 1040 (m) | 1050 | 1045 | 1045 |
| 845 (w, sh) | 845 | 845 | 845 |
| 760 (s, sh) | 760 | 760 | 760 |
| New bands vC-H | | 2900 | 2905 |
| v ring vibration pyridine ring | 755 | | |
| v ring vibration of α - picoline | | 770 | |
| β - picoline | | | 775 |
| v M - N | 490 | 495 | 495 |
| v M -O | 410 | 410 | 415 |
| v M - N (py) | 650 | | |
| v M – N (pico) | | 295 | 300 |

Table-2

The deprotonation of ligand's phenolic -OH group and co-ordination through the Mn^{2+} ion is shown by the broadband that appears at 3200 cm⁻¹ in the free ligand spectra and is attributed to the intramolecular H-bonded phenolic group. This band disappears in the spectra of all the complexes. The major change in the absorption frequency in the free ligand occurs in v-N=Nstretching vibration 1410cm⁻¹ shifts to 1380-1385 cm⁻¹. This indicates the involvement in coordination with Mn (II) complexes.^[1,2,3,9,13-15]

The new band appearance at 755cm⁻¹, 770cm⁻¹, and 775cm⁻¹ in the spectra of the complex is indicative of the coordinated pyridine presence, α -picoline, and β -picoline respectively in their coordination spheres. ^[25-27]

Magnetic Moment And Electronic Spectra Of Complexes

Mn (II) is d^5 system. The ground state term for d^5 system is ⁶S which is Octahedral symmetry transformed into ⁶A₁g symmetry. This is orbitally degenerate and hence no orbital

contribution is expected for the present complexes. The Experimental value of μ and $\lambda_m Mn$ (II). Complexes have been given in Table – 3

| Sl.No. | Complexes | μ (in B.M) | λm (in ohm ⁻¹ cm ⁻² mol ⁻¹) |
|--------|---|------------|--|
| 1 | Mn (PAN) ₂ (py) ₂ | 04.89 | 16.00 |
| 2 | Mn (PAN) ₂ (α - pico) ₂ | 04.87 | 18.00 |
| 3 | Mn (PAN) ₂ (β - pico) ₂ | 04.90 | 20.00 |

Spin-free octahedral compounds are indicated by these magnetic moment values.^[28-29] The value of molar conductivities in DMF solution is indicative of the Mn (II) complexes non-electrolytic nature in the present study.

Electronic Spectra Of Mn (II) Complexes

For d⁵ system of Mn (II), following are the Terms = ${}^{6}S$, ${}^{4}G$, ${}^{4}F$, ${}^{4}D$, ${}^{4}P$, ${}^{2}H$, ${}^{2}G$, ${}^{2}F$, ${}^{2}D$, ${}^{2}P$ and ${}^{2}S$ which corresponds to its total 252 micro states. Out of these terms, ${}^{6}S$ is the ground term, which being singly degenerate doesn't split and in an octahedral crystal field undergoes symmetry transformation into ${}^{6}A_{1g}$. The next higher state ${}^{4}G$ goes splitting in an octahedral field as below.



| SI.No. | Compelexes | Electronic bands in | Assignment |
|--------|---|--|---|
| | | cm ⁻¹ | |
| 1 | [Mn (PAN) ₂ (py) ₂] | $v_1 = 15,000 \text{cm}^{-1}$ $v_2 = 19,950 \text{cm}^{-1}$ $v_3 = 23,650 \text{cm}^{-1}$ $v_4 = 25,100 \text{cm}^{-1}$ | ${}^{4}T_{1g} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{2g} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}E_{g} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}A_{1g} ({}^{4}D) \leftarrow {}^{6}A_{1g} $ |
| 2 | [Mn PAN) ₂ (α - pico) ₂] | $v_1 = 15,300 \text{cm}^{-1}$ $v_2 = 20,470 \text{cm}^{-1}$ $v_3 = 23,800 \text{cm}^{-1}$ $v_4 = 25,000 \text{cm}^{-1}$ | ${}^{4}T_{1g} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}T_{2g} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}E_{g'} ({}^{4}G) \leftarrow {}^{6}A_{1g} \\ {}^{4}A_{1g} ({}^{4}D) \leftarrow {}^{6}A_{1g} $ |

| 3 | [Mn (PAN) ₂ (β - pico) ₂] | $v_1 = 15,800 \text{cm}^{-1}$ $v_2 = 20,850 \text{cm}^{-1}$ $v_3 = 23,500 \text{cm}^{-1}$ $v_4 = 25,500 \text{cm}^{-1}$ | ${}^{4}T_{1g} ({}^{4}G) \leftarrow {}^{6}A_{1g}$ ${}^{4}T_{2g} ({}^{4}G) \leftarrow {}^{6}A_{1g}$ ${}^{4}E_{g} ({}^{4}G) \leftarrow {}^{6}A_{1g}$ ${}^{4}A_{1g} ({}^{4}D) \leftarrow {}^{6}A_{1g}$ |
|---|--|--|--|
| | | | |

Table – 4

The assignments of bands are in fair agreement with the reported values for Mn(II) spin free octahedral complexes. The tentative structure of complexes is shown below:-



X = Pyridine, $\alpha\text{--picoline}$ and β - picoline

Conclusion

The Mn(II) complexes with ligand PANH (1-phenylazo-2-naphthol), α -picoline, β -picoline and pyridine form spin free distorted octahedral geometry. The ligand PANH act as bidentate monoanionic in these complexes.

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