

IR, EPR And Electronic Spectroscopic Characterization Of A 3D Series Of Manganese And Copper Metal Complexes

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Abstract: 3d metals are generally studied as hard base and they form most stable complexes with hard acid i.e. N, O etc. Macrocyclic ligands and their transition metal complexes are great field of interest now a days. This paper deals with the synthesis and spectroscopic characterization of tetraaza-dithio macrocyclic ligands and its complexes. Template condensation of thiodiglycolic acid and diammines (2,6 diamminopyridine (L₁) and ethylene diammine (L₂)) in the presence of manganese and copper metal salts. The synthesized macrocyclic complexes have been characterized by elemental analysis, molecular weight determination, molar conductivity measurement, IR, EPR and electronic spectral studies. The magnetic moment along with IR, EPR and electronic spectral data suggested six coordinated octahedral geometry for manganese and distorted octahedral geometry for copper complexes. Conductivity data suggests that they are electrolytes. Formula of complexes have been established on the basis of chemical composition.

Keywords: Macrocyclic, distorted octahedral, conductivity, electrolytes.

I. INTRODUCTION

Macrocyclic complexes and their chemistry is a growing area of research in inorganic and bioinorganic chemistry in point of its biological significance [1]. Macrocyclic complexes have also received special attention because of their mixed soft –hard donor acceptor character and versatile coordination behavior and their pharmacological properties [2]. Macrocyclic ligands and complexes have versatile coordination behavior [3] and anti microbial, anti cancer, antiviral, anti-inflammatory, antioxidant and antitumor [4]. The formation of macrocyclic complexes depends on the size of macrocycle, nature of its donor atoms and on the complex behavior of anions involved in the coordination[5]. Transition metal ions are selective in chelation to macrocyclic ligands depending on the number, type and position of their donor atoms, the ionic radius of metal ion and coordination properties of counter ions[6]. Macrocyclic ligands and their complexes contains aza units which forms a strong chelate ring giving possible electron delocalization associated with extended conjugation that may affect the nature of the complex formed[7]. This paper describes synthesis and

characterization of macrocyclic complexes of Mn(II) and Cu(II) derived from 2,6 diammino pyridine and ethylene diammine using thiodiglycolic acid.

II. EXPERIMENTAL

All the chemicals and solvents were of analytical grade and were purchased from Aldrich and were used without further purification. Ethanol and dimethylsulfoxide (DMSO) were used as solvents. Ethanol was distilled with a good fractionating column.

PREPARATION OF COMPLEXES

One pot condensation of 1mmol of thiodiglycolic acid and 1mmol of diammines (2,6 diamminopyridine, ethylene diammine) with 1mmol of respective copper and manganese metal salts by dissolving them in the minimum quantity of ethanol at 78-86°C and refluxed for 6-7 hrs. On cooling at room temperature colored precipitates of complexes were

formed. Precipitates were washed with cold ethanol and dried under vacuum over P_4O_{10} .

PHYSICAL MEASUREMENT

IR spectra were recorded on a perkin Elmer 137 instrument in KBr pellet. Elemental analyses (CHN) of these complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Electronic spectra were recorded in the DMSO solution on a Shimadzu UV mini-1240 spectrophotometer. The molar conductance was measured on an Elico conductivity bridge (type CM82T). Magnetic moment measured on Gouy balance was made at room temperature using $CuSO_4 \cdot 5H_2O$ as calibrant. ESR spectra of complexes were recorded as polycrystalline sample in DMSO solution at liquid nitrogen temperature (LNT) on E_4 ESR spectrometer using the DPPH as the g-marker.

III. RESULT AND DISCUSSION

Mononuclear $[ML]X_2$ where $M = [Mn, Cu]$, $L = L_1$ and L_2 and $[X = NO_3]$ have been prepared. All the complexes are stable to the atmosphere. The elemental analyses [table-1] are consistent with the proposed structure of the complexes and the general composition $[M(L)]X_2$. The molar conductance values of the complexes lie in the range of $241-265 \Omega^{-1} cm^2 mol^{-1}$ in DMSO at room temperature confirm 1:2 electrolytic nature of the complexes.

| Complexes | M.Wt. Calc. (Found) | Molar cond. $\Omega^{-1} cm^2 mol^{-1}$ | Colour | Yield % | M.Pt. °C | Elemental analysis Calc. (Found) | | | |
|---------------------------------|---------------------|---|--------------|---------|----------|----------------------------------|---------------|-------------|---------------|
| | | | | | | Cu/Mn | C | H | N |
| $[CuL_1](NO_3)_2 \cdot 2O_{10}$ | 536 (535.29) | 262 | Green | 66 | 129 | 11.94 (11.99) | 26.86 (26.92) | 3.73 (3.78) | 15.67 (15.74) |
| $[CuL_2](NO_3)_2 \cdot 2O_{10}$ | 633 (632.19) | 243 | Green | 58 | 170 | 10.11 (10.16) | 34.12 (34.19) | 2.84 (2.93) | 17.69 (17.73) |
| $[MnL_1](NO_3)_2 \cdot 2O_{10}$ | 601 (599.54) | 242 | Straw | 78 | 241 | 11.62 (11.64) | 30.44 (30.51) | 4.22 (4.29) | 11.83 (11.91) |
| $[MnL_2](NO_3)_2 \cdot 2O_{10}$ | 527 (524.870) | 251 | Light yellow | 62 | 263 | 11.23 (11.00) | 30.51 (33.64) | 4.84 (4.87) | 11.83 (11.29) |

Table 1: Molar conductance and elemental analysis data of mononuclear Cu(II) and Mn(II) complexes

IR spectra: IR spectra of both the metal complexes of nitrates display one absorption band at $1380-1384 cm^{-1}$ suggests that both nitrate ions are uncoordinated to metal ion. The appearance of a lower intensity band in the region of $524-505 cm^{-1}$ corresponds to the $\nu(M-N)$ vibration and a band at $754 cm^{-1}$ in the spectrum corresponds to the $\nu(C-S)$ stretching vibration supports the fact that the ligands coordinate to the metal ions through the nitrogen and sulphur of C=N and C-S group in all the complexes [8]. The macrocyclic Cu(II) complexes contain a broad band in the region $3375-3498 cm^{-1}$ due to the presence of lattice water molecules [9]. In the IR spectra of complexes with L_2 ligand two extra medium to strong bands at $1593-1591 cm^{-1}$ and $1499-1497 cm^{-1}$ are expected for the two highest energy pyridine ring vibrations it supports the macrocyclic nature of the ligand [table-4].

Electronic spectra: Electronic spectra of six coordinated Cu^{+2} complexes have D_{4h} or C_{4v} symmetry and E_g and T_{2g} levels of 2D free ion term will split into B_{1g} , A_{1g} , B_{2g} and E_g level

$${}^2B_{1g}, {}^2A_{1g}, {}^2B_{1g}, {}^2B_{1g}, {}^2B_{1g}, {}^2E_g$$

The energy level sequence will depend on the amount of tetragonal distortion due to ligand field and Jahn-Teller effect [10]. The electronic spectra show characteristic bands at $13400-13750$ and $18500-18900 cm^{-1}$. Manganese (II) complexes have d^5 electronic configuration. The lowest electronic configuration for the high spin octahedral coordinate manganese (II) complexes, gives rise to ground state ${}^6A_{1g}$. All the lowest absorption bands therefore, must be spin forbidden transitions. Electronic spectra of the manganese complexes display four weak intensity bands in the range $\sim 18051-20132 cm^{-1}$ (ν_1), $\sim 22050-24631 cm^{-1}$ (ν_2), $\sim 27993-29961 cm^{-1}$ (ν_3) and $\sim 33003-38610 cm^{-1}$ (ν_4) characteristic for an octahedral environment around the manganese(II) ion [table-2]. These bands may be assigned to the following transitions: ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)\nu_1$, ${}^6A_{1g} \rightarrow {}^4E_g(4A_{1g})(4G)\nu_2$, ${}^6A_{1g} \rightarrow {}^4E_g(4D)\nu_3$, ${}^6A_{1g} \rightarrow {}^4T_{1g}(4P)\nu_4$.

| Complexes | Spectral bands in cm^{-1} | μ_{eff} (B.M.) |
|-------------------|-----------------------------|--------------------|
| $[CuL_1](NO_3)_2$ | 13425, 18504 | 1.92 |
| $[CuL_2](NO_3)_2$ | 13587, 18749 | 1.95 |
| $[MnL_1](NO_3)_2$ | 19297, 23200, 27993, 33003 | 5.95 |
| $[MnL_2](NO_3)_2$ | 18052, 22050, 28739, 38022 | 5.91 |

Table 2: Electronic Spectral bands (cm^{-1}) of Mononuclear Cu(II) and Mn(II) complexes

EPR: All the complexes show anisotropic EPR spectra characteristic of tetragonal Cu^{+2} . G-values are calculated by using: $g_{\parallel} = [2-8\lambda/\Delta E_2]$, $g_{\perp} = [2-2\lambda/\Delta E_3]$ Where $\lambda = 823 cm^{-1}$ and $\Delta E_2 = {}^2B_{1g} - {}^2B_{1g}$, $\Delta E_3 = {}^2B_{1g} - {}^2E_g$. Mn(II) is a d^5 odd electron system whose ground state is a Kramers' doublet and degeneracy is only completely removed by a magnetic field [11]. The broad signal in the polycrystalline EPR spectra of the Mn(II) complexes is attributed to forbidden transitions [table-3]. Broadening is due to immobilization of Mn(II) ion in the ligand and also due to spin relaxation, which is temperature dependent.

| Complexes | g_{\parallel} or g_3 | g_2 | g_{\perp} or g_1 | G |
|-------------------|--------------------------|-------|----------------------|------|
| $[CuL_1](NO_3)_2$ | 2.26 | 2.23 | 2.06 | 5.41 |
| $[CuL_2](NO_3)_2$ | 2.40 | 2.20 | 2.06 | 8.79 |
| $[MnL_1](NO_3)_2$ | 2.44 | 2.20 | 2.04 | 6.78 |
| $[MnL_2](NO_3)_2$ | 2.46 | 2.22 | 2.06 | 7.88 |

Table 3: ESR Spectral data of Mononuclear Cu(II) and Mn(II) complexes

| Complexes | $\nu(N-H)$ | Amide-I | Amide-II | Amide-III | Amide-IV | $\nu(M-N)$ | Anion |
|-------------------|------------|---------|----------|-----------|----------|------------|-------|
| $[CuL_1](NO_3)_2$ | 3291 | 1660 | 1532 | 1227 | 548 | 410 | 1383 |
| $[CuL_2](NO_3)_2$ | 3295 | 1667 | 1531 | 1243 | 549 | 420 | 1383 |
| $[MnL_1](NO_3)_2$ | 3278 | 1662 | 1537 | 1241 | 535 | 417 | 1384 |
| $[MnL_2](NO_3)_2$ | 3286 | 1659 | 1534 | 1232 | 538 | 418 | 1383 |

Table 4: IR Spectra bands of Mononuclear Cu(II) and Mn(II) complexes

IV. CONCLUSION

On the basis of IR spectral study it was concluded that ligand coordinated to the metal ion in hexadentate manner i.e. through N_4S_2 donor atoms. IR, UV, EPR spectroscopic characterization study revealed that Mn(II) complexes possessed an octahedral geometry and Cu(II) complexes possessed distorted octahedral geometry. (Fig 1-2).

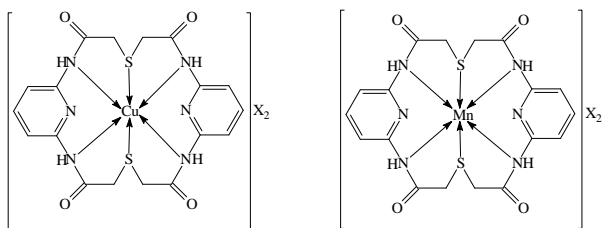


Figure 1: Complexes of Cu and Mn with L_1

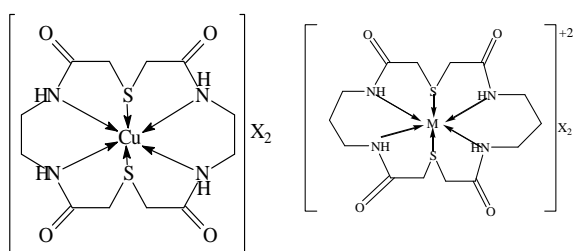


Figure 2: Complexes of Cu and Mn with L_2

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