International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 280-285, 2017

Preparation and characterization of Manganese, Cobalt and Copper complexes of tetradentate N_6-macrocyclic ligand

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Abstract : Macrocyclic complexes of Mn, Co and Cu via Schiff base reactions. These 12-membered tetradentate N_6-macrocyclic complexes were characterized by elemental analysis, conductance, magnetic susceptibility measurements and the spectral studies like IR spectra, Electronic spectra and NMR spectra.Thus, themacrocyclic ligand coordinates through imine and secondary amine nitrogens of the macrocyclicring. The spectral data suggest that the complexes of metal chlorides have octahedral and that of metal sulphates have tetrahedral geometry.

Keywords : Synthesis, Characterization, L-glycine, Complexes of Mn^{II}, Co^{II}, $Cu^{II.}$

Introduction

A numberof nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications (1).Macrocyclic compounds and their derivatives are interesting ligand system because they are good hosts for metal anions, neutral molecules and organic cation guests (2). The macrocyclic complexes show remarkable stability (3) compared to its closed chain analogues and the metal ion is firmly held in the cavity of macrocycles.

In the present study,the preparation and characterization of Mn^{II},Co^{II} and Cu^{II} Complexes of tetradentateN_6-macrocyclic ligand are discussed. Complexes were characterized using various physico-chemical techniques, such as IR and UV/Vis spectroscopy, elemental analysis, magnetic susceptibility and conductivity measurements.

Experimental

Materials and methods

All the chemicals used for the preparation of the ligands were of BDH quality,AR grade. The microelemental analysis was carried out using CHN-Rapid Analyzer. Conductivity was measured on a Toshniwals conductivity bridge using dip type platinised platinum electrode. Molecular weights were determined by the Rast Camphor method. The magnetic susceptibilities were measured out by using Guoybalance. Proton NMR spectra were recorded on an EM 300-30MHZ NMR spectrometer in DMSO. IR spectra(KBr) of the samples were recorded on a shimadzce FTIR-8400s Spectro-Photometer. The electronic spectra(chloroform) were recorded on the Lamda 35 spectrometer.

Synthesis of ligand

The condensation reaction was carried out as follows an methanolic solution(50ml) of the trimethoprim(0.02mol) was added to a hot solution of the L-glycine (0.02 mol) in methanol. The mixture was stirred well and refluxed on a water bath. Then, concentrated hydrochloric acid(1 ml) was added and further refluxed for 6-8hrs.It was then concentrated to half of the volume and set aside for 2days.the resulting pale brown crystals were washed with methanol and ether and dried at 600C.The crude product was recrystallised from alcohol. The desired condensation product was obtained more readily 60-65% yield by the method.

{$C_{32}H_{38}N_{10}O_6$}

Yield: 95 %; color: pale brown .Anal. Calc. for $C_{32}H_{38}N_{10}O_6$ (Mw:658); C,58.34; H,5.82; N,21.26. Found: C,58.64; H,5.90; N,21.12. IR (KBr,cm-1): 3503γ(NH2),3090γ(NH), 1640(C= N),1154γas(C-C-N),1565,985(pyrimidine ring).^{1}HNMR (DMSO, ppm) δ= 2.0(4H,s,-C-CH2-); δ= 2.4(4H,t,free-NH2); δ= 3.7(18H,s,-OCH3); δ= 5.4 (2H,s,ring NH); δ= 6.6 (4H,S,Pyrimidine-CH2-Ar); δ= 7.8 (2H,d,pyrimidine –H); δ= 8.3 (4H,d,Ar-H).

Synthesis of the metal complexes

To a solution of the metal chloride(or) sulphate (0.01 mol) in methanol were added and refluxed for 5hrs. The resultant solution was cooled two days and the crystals which separated out were filtered washed with methanol-ether mixture (1:1) and dried in vacuum (4-6) over anhydrous $CaCl_2$.

{Mn (L_1)Cl_2}

Yield: 86 %; color: pale pink.Anal. Calc. for [Mn($C_{32}H_{38}N_{10}O_6$)Cl_2]: C,48.32; H,4.75; N,17.82. Found: C,48.99; H,4.88; N,17.86. IR (KBr,cm-1): 3346 γ(NH2),3050γ(NH), 1599(C= N),1115γas(C-C-N),1506,958 (pyrimidine ring),542(M-N),318(M-Cl).Λ_m/Ω^{-1} cm^2 mol^{-1}(in CH_3CN): 32.18.μ_{eff} (300K): 5.83 B.M.

{Mn (L_1)SO_4}

Yield: 81 % ; color: cream white. Anal. Calc. for [Mn($C_{32}H_{38}N_{10}O_6$)SO_4] : C,47.38; H,4.80; N,17.20. Found: C,47.47; H,4.73; N,17.29. IR (KBr,cm-1): 3405 γ(NH2), 3030γ(NH), 1589 (C= N),1129γas(C-C-N),1570, 992 (pyrimidine ring), 511 (M-N), 907 (SO_4). Λ_m/Ω^{-1}cm^2 mol^{-1}(in CH_3CN): 130.μ_{eff} (300K): 5.48 B.M.

{Co (L_1)Cl_2}

Yield: 83 % ; color: dark pink , Anal. Calc. for [Co($C_{32}H_{38}N_{10}O_6$)Cl_2] : C, 48.26; H, 4.81; N,17.66. Found: C,48.80; H,4.86; N,17.80. IR (KBr,cm-1): 3405 γ(NH2), 3008γ(NH), 1589 (C= N), 1129γas(C-C-N), 1530, 958 (pyrimidine ring), 507 (M-N), 335 (M-Cl). Λ_m/Ω^{-1} cm^2 mol^{-1}(in CH_3CN): 20.00. μ_{eff} (300K): 5.14 B.M.

{Co (L_1)SO_4}

Yield: 80 %; color: blue. Anal. Calc. for [Co($C_{32}H_{38}N_{10}O_6$)SO_4] : C,47.33; H,4.80; N,17.20. Found: C,47.23; H,4.71; N,17.21. IR (KBr,cm-1): 3404 γ(NH2), 3167γ(NH), 1422 (C= N), 1129γas(C-C-N), 1500, 909 (pyrimidine ring), 507 (M-N), 992 (SO_4). Λ_m/Ω^{-1} cm^2 mol^{-1}(in CH_3CN): 95.00. μ_{eff} (300K): 4.42 B.M.

{Cu (L_1)Cl_2}

Yield: 88 %; color: green , Anal. Calc. for [Cu($C_{32}H_{38}N_{10}O_6$)Cl_2] : C, 48.42; H, 4.88; N,17.36. Found: C,48.46; H,4.83; N,17.60. IR (KBr,cm-1): 3364 γ(NH2), 3040γ(NH), 1595 (C= N), 1154 γas(C-C-N), 1595, 959 (pyrimidine ring), 571 (M-N), 348 (M-Cl). Λ_m/Ω^{-1} cm^2 mol^{-1}(in CH_3CN): 40.19. μ_{eff} (300K): 1.95 B.M.

{Cu (L_1) SO_4}

Yield: 80 %; color: red orange. Anal. Calc. for [Mn($C_{32}H_{38}N_{10}O_6$)SO_4] : C,46.80; H,4.59; N,17.10. Found: C,46.97; H,4.68; N,17.12. IR (KBr,cm-1): 3403 γ(NH2), 3035γ(NH), 1589 (C= N), 1130γas(C-C-N), 1528, 899 (pyrimidine ring), 524 (M-N), 1042 (SO_4). Λ_m/Ω^{-1} cm^2 mol^{-1}(in CH_3CN): 120. μ_{eff} (300K): 1.26 B.M.

Results and discussion

The Schiff base macrocyclic complexes were prepared from $C_{32}H_{38}N_{10}O_6$ in the presence of MX (where M= Mn^{II},Co^{II},andCu^{II},X=Cl^-,SO_4^{2-}) produced a new series of 12-membered tetradentatemacrocyclic metal complexes of the type $M(L_1)Cl_2$ and $M(L_1)$ SO_4 as shown in Fig(1& 2).

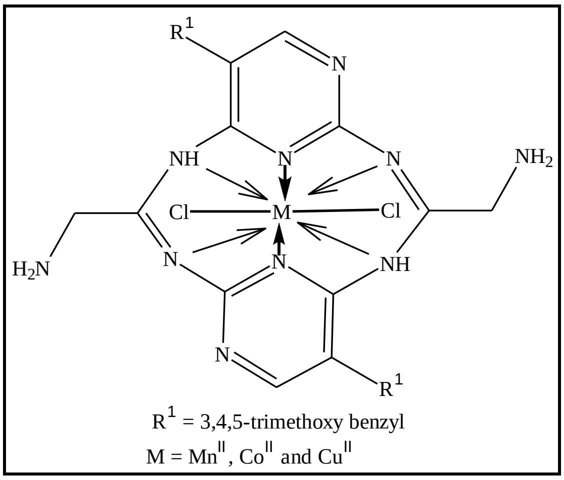

Fig (1): Proposed structure of metal(II) chloride macrocyclic complexes of L_1

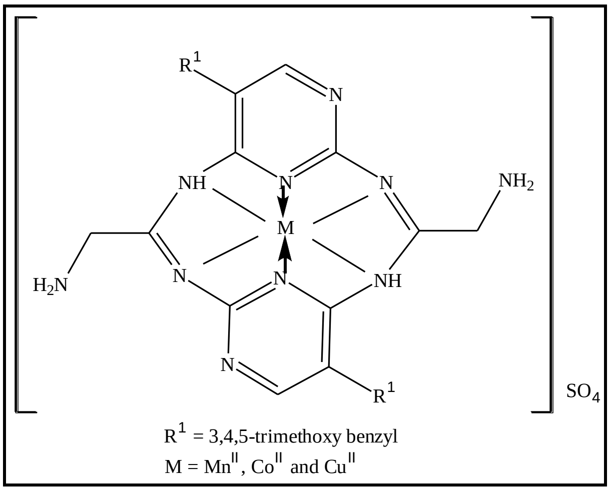

Fig (2): Proposed structure of metal(II) sulphatemacrocyclic complexes of L_1

The resulting metal derivatives are colored solids which are stable at room temperature and are non-hygroscopic. The monomeric nature of these complexes is confirmed by molecular weight determination. All the complexes are slightly soluble in methanol or ethanol but soluble in DMF and DMSO. The analytical data of the complexes are in good agreement with the calculated values,thus confirming the proposed composition for all the complexes.

Molar conductance

The molar conductance of these macrocyclic complexes of (L_1) in acetonotrile were measured and the calculated molar conductance values.

The molar conductivities of the sulphate complexes (L_1) in acetonitrile are in the range of 90-130 ohm^{-1} cm^2 mol^{-1} which is characteristic of 1:1 electrolytes,indicating that the sulphate groups are ionic in nature. The conductivities of the metal chloride complexes are in the range of 20-48 ohm^{-1} cm^2 mol^{-1} suggest that all of themnon-electrolytes (7). The presence of chloride ions is evident only after decomposition of the complexes,probably due to their presence in the coordination sphere.

IR spectra

The infrared spectra of the ligand are compared with those of the complexes to determine the bonding mode of the ligand to the metal in the complexes.The IR spectrum of the macrocyclic complexes of ligand indicate that the trimethoprim and L- glycine moieties are present.The asymmetric and symmetric stretching vibrations and deformation vibrations of theNH_2 group of amino acid observe bands at 3503 and 837 cm^{-1}respectively.This is clearly shows that primary $–NH_2$ group of amino acid do not take part in coordination (8).The free macrocyclic ligand exhibits bands at 3090 and 1640 cm^{-1} which are assigned to N-H modes of the secondary amino group and C=N mode of the imine group respectively (9-12).In all the Mn^{II},Co^{II},Cu^{II} macrcyclic complexes secondary N-H and C=N frequency of the compound was decreases to the free ligands in range 40-70cm^{-1} and 20-30cm^{-1}.Thus,the ligand coordinates through secondary amine and imine nitrogens of the macrocyclic ring (13).

There are fairly strong IR spectral bands in the region 3123 to 2965 cm^{-1} due to the C-H and C-N-C stretch of the pyrimidine ring,benzyl aromatic ring and methoxy groups also appear in the spectra of the complexes in the same region indicates that they do not take part in coordination.

The appearance of a new moderately intense band in the region 543-506 cm^{-1} assignable to (M-N) further confirms the involvement of nitrogen in coordination (14). In the sulphate complexes a broad band of strong intensity is observed near 1100cm^{-1} which is characteristic of uncoordinated SO_4^{2-} ion and confirms its presence in the outer sphere of the complex ion (15).In addition to that the frequencies of sulphate appear at 1100 and 625cm^{-1} respectively without any splitting.It shows tetrahedral symmetry for the sulphate group (16).The frequencies found at 970 and 1042cm^{-1} which are assigned to aromatic in plane deformation and aromatic out-of-plane ring deformation respectively are not at all affected indicating that ring nitrogens(pyrimidine nitrogens) are no coordinated to the metal ion.

Magnetic measurements and Electronic spectra

Manganese complex: The magnetic moment of the manganese(II) complex was found to be 5.9 B.M.,which indicates a high spin(d^5) system.The magnetic moment of manganese(II) chloride and sulphate complexes are 5.83 B.M and 5.48 B.M.So,this may suggest octahedral or tetrahedral coordination for the metal ion (17).The electronic spectra of the manganese(II)chloride complexexhibits to a very weak bands at 10204cm^{-1}which are assigned to $^6A_1g \rightarrow {}^4T_1g(G)$ transition. This observation reveal that the stereochemistry of this complex is consistent with six coordinate octahedral geometry.The electronic spectrum of manganese(II)sulphate complex exhibit bands do not show narrow d-d transitions are over shadowed by stronger charge transfer transitions(18,19).

Cobalt complex: The magnetic moment of the cobalt (II) sulphate is 4.42 B.M suggesting tetrahedral(20) and Cobalt(II) chloride register magnetic moment value of 5.14 B.M.,which indicates the octahedral geometry (21).The electronic spectra of the Cobalt(II) chloride complex shows three bands at 10193,11248 and 19763 cm-1 which can be assigned to $^4T_1g(F) \rightarrow {}^4T_2g(F)$,$^4T_1g(F) \rightarrow {}^4A_2g(F)$, and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ transitions respectively, in a octahedral geometry (22-24).The electronic spectrum of the Cobalt(II) sulphate complex also found in the range 18793cm^{-1} in thenear infrared region is due to $^4A_2g(F) \rightarrow {}^4T_1g(P)$ transition.These transitions are characteristic of cobalt(II)sulphate in a tetrahedral environment.

Copper complex: The magnetic moment of the copper (II) chloride complex at room temperature is found to be 1.95 B.M., corresponding to the presence of one unpaired electron which offers the possibility of octahedral geometry (21). The copper (II) sulphate complex exhibit magnetic moment value of 1.26 B.M., indicating one unpaired electron showing paramagnetic character with tetrahedral geometry (25). The electronic spectrum of the copper (II) chloride complex shows a broad band in the range 12107 cm^{-1}in the visible region is due to $^2Eg – {}^2T_2g$ transition, which in good agreement with a distorted octahedral geometry for copper (II) ion (26-28). The electronic spectrum of copper (II) sulphatecomplex shows two electronic absorption bands, a low energy and less intense one at 10616 cm^{-1} and a relatively high energy and less intense at 14535 cm^{-1}. Tetrahedral complexes of copper (II) are known (29) to have a band assigned to dx^2-y^2-dyz transition has been reported for certain copper (II) complexes with a pseudo tetrahedral geometry.

NMR spectra

The proton magnetic resonance (30,31)spectra of the ligand $C_{32}H_{38}N_{10}O_6$are recorded in DMSO solvent using TMS as internal standard. The spectral data gives some important information to conclude the formation of ligand. The spectrum shows seven signals which are observed at seven different regions from the TMS. This indicates that there are seven different types of protons.^{1}H-NMR spectrum of the macrocyclic ligand display peaks at δ= 2.0 (4H,s,-C-CH2-); δ= 2.4 (4H,t,free-NH2); δ= 3.7 (18H,s,-OCH3); δ= 5.4 (2H,s,ring NH); δ= 6.6 (4H,S,Pyrimidine-CH2-Ar); δ= 7.8 (2H,d,pyrimidine –H); δ= 8.3 (4H,d,Ar-H) and thus the ^{1}H-NMR spectrum confirms the presence of trimethoprim and L-glycine moieties in the macrocyclic condensedproduct. From the ratio of the intensities of the peak the number of protons can be calculated as 38.

Conclusion

In the present work, incorporation of pyrimidine moiety into the macrocyclic frame work is found to potentially enhancing the rigidity and binding ability of the ligands towards the transition metal ions. The electrical conductance values for the complexes in acetonitrile indicate that the chloride complexes are non-electrolytic and sulphate complexes are ionic in nature. The IR spectral studies reveal that the coordination site of the complexes by comparing with the ligand. The magnetic moments of the complexes indicate that they are all of high spin with paramagnetic in nature. The magnetic and electronic spectral studies support that all the complexes have octahedral and tetrahedral geometry. ^{1}H-NMR spectral studies were carried out for the complexes to ascertain the mode of coordination as proposed by IR spectrum.

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