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Manganese(II) Complexes of Pentadentate Macrocyclic Schiff-base Ligands Containing Pyridine

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Two new Schiff base macrocyclic complexes of $[MnL_1(H_2O)_2]Cl_2{\cdot}H_2O$ (1) and $[MnL_2(H_2O)_2]Cl_2{\cdot}H_2O$ (2) have been prepared *via* cyclocondensation of 2,6-diacetylpyridine and N,N′-bis(2-aminophenyl)-1,3-propandiamine and/or N,N′-bis(2-aminophenyl)-1,4-butandiamine respectively and have been characterized spectroscopically. The ligands are 16- and 17-membered pentaaza macrocycles.

Key Words: Macrocyclic, Manganese(II) complexes, Schiff base.

INTRODUCTION

Macrocyclic complexes of manganese(II) have recently been of much interest, because such systems are known to exist at the active site of some manganese-containing enzymes (*e.g.*, SOD). The manganese ion in the biosite have the ability to catalyze the disproportionation of hydrogen peroxide to dioxygen and water[1]. Moreover, the coordination chemistry of Mn has been important for the better understanding of the O_2 evolution mechanism in the photosynthetic process[2]. Mn(II) is also an effective relaxation enhancer and its complexes are important for study of contrast-enhancing agents[3]. We are taking interest in the synthesis of tetraaza macrocyclic Schiff base complexes carrying a single pendant arm derived from condensation of 2,6-diacetylpyridine with the various tripodal tetraamines[4, 5]. We extended our studies to the template synthesis of pentaaza macrocyclic complexes with two pendant arms using different branched hexaamine and other metal ions of various radius and electron configuration[6, 7]. In the present work, the aim is the preparation and characterization of a series of pentaaza Mn(II) macrocyclic Schiff base complexes by altering the size and nature of chelate rings. The Mn(II) template [1 + 1] cyclocondensation of 2,6-diacetylpyridine (DAP) and appropriate linear tetraamines, N,N′-bis(2-aminophenyl)-1,3-propandiamine and N,N′-bis(2-aminophenyl)-1,4-butandiamine, yields two new Mn(II) complexes of $[MnL_1(H_2O)_2]Cl_2{\cdot}H_2O$ and $[MnL_2(H_2O)_2]Cl_2{\cdot}H_2O$ respectively.

EXPERIMENTAL

All solvents were of reagent grade quality and purchased commercially. 2,6-Diacetylpyridine (DAP), 1,3-diaminopropane and 1,4-diaminobutane were obtained from Aldrich and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL FX90 NMR. Infrared spectra were recorded in KBr pellets using Shimadzu IR-435 spectrophotometer (4000–400 cm^{-1}).

Ligand Synthesis

N,N′-Bis(2-nitrophenyl)-1,3-propanediamine (I)

1,3-Diaminopropane 0.74 g (10 mmol), 1-chloro-2-nitrobenzene 3.15 g (20 mmol) and sodium carbonate 2.12 g (20 mmol) were mixed in a round-bottom flask and fused at 180°C for 3 h. The resulting solid was washed with 2 : 1 H_2O : EtOH. The product was recrystallised from EtOH[8]. Yield: 3.1 g (80%), m.p. = 143°C; IR (KBr, cm^{-1}) 2950 $\nu(CH_2)$, 3100 ν(CH), 3330 ν(NH), ^{1}H-NMR δ_H ($CDCl_3$, ppm): 2.1 (m, 2H), 3.4 (q, 4H), 6.7 (m, 4H), 7.3 (m, 2H), 8.1 (m, 4H); ^{13}C-NMR δ_C ($CDCl_3$, ppm): 28.59, 40.53, 113.68, 115.82, 127.11, 132.45, 136.47, 145.34.

N,N′-Bis(2-nitrophenyl)-1,4-butanediamine (II)

The compound (II) can be readily prepared by the above procedure except using 1,4-diaminobutane 0.88 g (10 mmol) instead of 1,3-diaminopropane. Yield: 2.64 g (80%), m.p. = 158°C; IR (KBr, cm^{-1}) 2948 $\nu(CH_2)$, 3097 ν(CH), 3329 ν(NH); ^{1}H-NMR δ_H ($CDCl_3$, ppm): 2.08 (p, 4H), 3.39 (t, 4H), 6.7 (m, 4H), 7.3 (m, 2H), 8.05 (m, 4H); ^{13}C-NMR δ_C ($CDCl_3$, ppm): 27.34, 39.81, 113.35, 115.62, 126.89, 132.08, 136.17, 145.22.

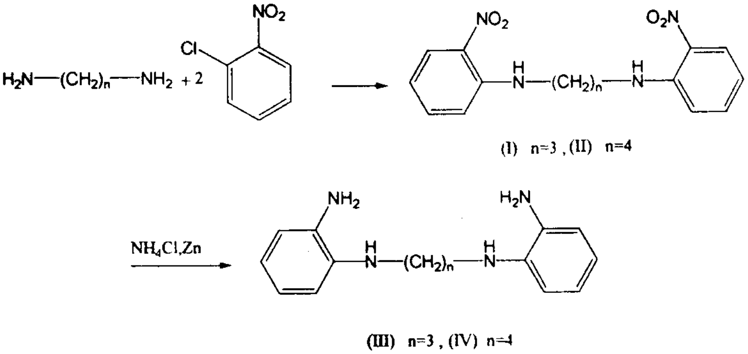
N,N′-Bis(2-aminophenyl)-1,3-propanediamine (III)

A mixture of 1 g of N,N′-bis(2-nitrophenyl)-1,3-propanediamine (I), 4 g of ammonium choloride and 2 mL of water in 30 mL of alcohol was heated to boiling and 3 g of zinc dust was added. When the solution was pale green it was filtered, and rapid stream of air was passed through the filtrate for 10 min. Upon standing the solution, deposited crystals which were recrystallized from ligroin to yield the N,N′-bis(2aminophenyl)-1,3-propanediamine **(III).**[9] m.p. = 135°C; IR (KBr, cm^{-1}): 2940 $\nu(CH_2)$, 3050 ν(CH), 3325, 3420 $\nu(NH_2)$; ^{1}H-NMR δ_H ($CDCl_3$, ppm): 1.8 (s, 2H), 3.2 (s, 8H), 6.6 (s, 8H); ^{13}C-NMR δ_C ($CDCl_3$, ppm): 23.15, 37.01, 115.05, 117.20, 117.48, 118.29, 119.56, 120.07.

N,N′-Bis(2-aminophenyl)-1,4-butanediamine (IV)

The compound (IV) can be readily prepared by the above procedure except using N,N′-bis(2-nitrophenyl)-1,3-propanediamine 1 g instead of N,N′-bis(2-nitrophenyl)-1,4-butanediamine. m.p. = 133°C; IR (KBr, cm^{-1}): 2938 $\nu(CH_2)$, 3047 ν(CH), 3325, 3419 $\nu(NH_2)$; ^{1}H-NMR δ_H ($CDCl_3$, ppm): 1.74 (p, 4H), 3.18 (m, 8H), 6.6 (m, 8H); ^{13}C-NMR δ_C ($CDCl_3$, ppm). 21.32,35.91, 114.45, 116.48, 116.08, 117.66, 118.43, 119.14.

Anal., found (calcd.) for $C_{16}H_{22}N_4$: C, 70.0 (71.0); H, 8.0 (8.1); N, 20.4 (20.7)%.



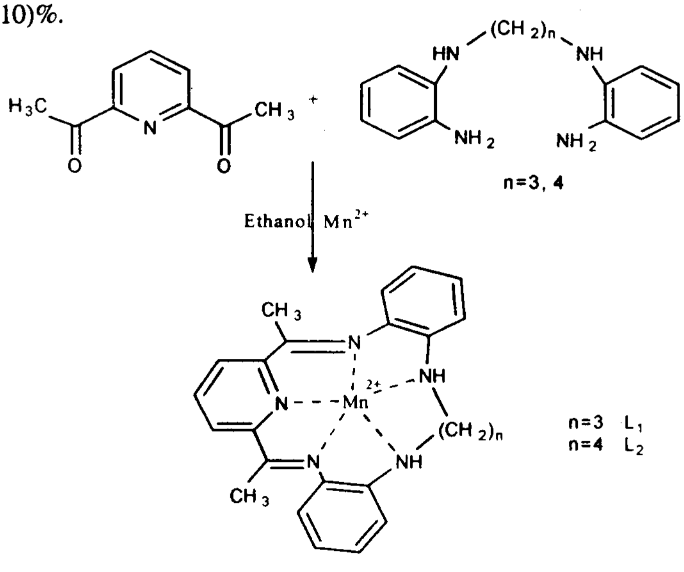
Preparation of the complexes

$[MnL_1(H_2O)_2]Cl_2 \cdot H_2O$ and $[MnL_2(H_2O)_2]Cl_2 \cdot H_2O$

To a refluxing solution of 2,6-diacetylpyridine (0.5 mmol) in absolute ethanol (25 cm^3) was added a solution of hydrated manganese chloride (0.5 mmol) in the same solvent (25 cm^3). The solution was gently refluxed with magnetic stirring for *ca.* 30 min and ethanolic solution (50 cm^3) of the amine (III) or (IV) (0.5 mmol) added dropwise.

Refluxing and stirring were maintained for *ca.* 12 h and then the solution was concentrated to half of the initial volume. Crystalline products were often obtained as needles. IR (KBr, cm^{-1}): 1450 ν(C=C), 1600 ν(C=N) py, 1637 ν(C=N), 3260 ν(NH), 3400 ν(OH). Anal., found (calcd.) for $MnC_{24}H_{31}N_5O_3Cl_2$: C, 51.60 (51.15), H, 5.60 (5.50); N, 12.00 (12.42)%.

Anal, found (calcd.) for $MnC_{25}H_{33}N_5O_3Cl_2$: C, 52.7 (52.0); H, 5.80 (5.70); N, 12.30 (12.10)%.



RESULTS AND DISCUSSION

The Schiff-base cyclocondensation of 2,6-diacetylpyridine and N,N′-bis(2-aminophenyl)-1,3-propanediamine (III) and N,N′-bis(2-aminophenyl)-1,4-butanediamine (IV) in ethanol in the presence of the appropriate hydrated Mn(II) salt and in 1 : 1 : 1 mole ratio, gave good yields of the analytically pure products $[MnL_1(H_2O)_2]Cl_2{\cdot}H_2O$ and $[MnL_2(H_2O)_2]Cl_2{\cdot}H_2O$.

The complexes are pale yellow, air-stable solids, moderately soluble in CH_3CN and DMSO. Attempts to obtain these macrocyclic compounds in presence of Mn(II) nitrate were unsuccessful. The infrared spectra of both complexes confirm the formation of the macrocyclic compounds by the absence of bands characteristic of carbonyl and primary amine groups of the starting materials. The complexes exhibit a Schiff-base $\nu(C{=}N)$ vibration in the range 1637–1633 cm^{-1} and also bands at approximately 1600 and 1450 cm^{-1} associated with a $\nu(C{=}N)$ and a $\nu(C{=}C)$ vibrations from the pyridine and aromatic rings respectively. The presence of the water molecules is confirmed by appearance of an intensive broad band centred about 3400–3300 cm^{-1} in the IR spectra of complex. The secondary amine stretches in the region 3260–3235 cm^{-1} which are split and/or shifted relative to that of free tetraamines (3400 cm^{-1}).

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