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Manganese(II) complexes of pyridyl-azo-imidazoles. Single crystal X-ray structures of 3′-PyaiH and [Mn(3′- PyaiEt)$_4$](ClO$_4$)$_2$ (3′-PyaiH = 2-(3′-pyridylazo)imidazole; 3′-PyaiEt = 1-ethyl-2-(3′-pyridylazo)imidazole)

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Abstract

Pyridine and imidazole are connected by an azo group (—N=N—) to synthesize 2-[(3′-pyridyl)azo]imidazole (3′-PyaiH) and this has been confirmed by X-ray structure determination. The N(1)-alkylation gives 1-alkyl-2-[(3′-pyridyl)azo]imidazole (3′-PyaiR′) (R′ = Me (**2a**), Et (**2b**), Bz (**2c**)). The reaction between $Mn(ClO_4)_2 \cdot 6H_2O$ and 3′-PyaiR′ in methanol has synthesized [Mn(3′-PyaiR′)$_4$](ClO$_4$)$_2$ (**3**). The structure has been confirmed by single crystal X-ray diffraction study in one case, in addition to other spectral characterization. The structure reveals a tetrahedral orientation of four ligands coordinating through imidazole-N only. Cyclic voltammetry exhibits a Mn(III)/Mn(II) couple at >1.1 V along with azo reductions. However, the reaction of $MnCl_2 \cdot 4H_2O$ + 3′-PyaiR′ in the presence of NaN$_3$ or NH$_4$CNS (1:2:2 mole proportion) has synthesized Mn(3′-PyaiR′)$_2$(X)$_2$ (X = N$_3$ (**4**), NCS (**5**)).

Keywords: Pyridyl-azo-imidazoles; Manganese(II) tetrahedral; X-ray; Electrochemistry

1. Introduction

For the last decade we have been engaged in the design of several types of heterocyclic azo compounds and studies on their complexes [1–3]. This type of molecule has several advantages. To quote a few, the azo group is photochromic, redox responsive, pH-sensitive; stabilizes low valent metal oxidation states due to the presence of a low-lying azo-centred π*-molecular orbital, serves as a molecular switch, is used as a metal ion indicator in complexometric titration, dyes and pigments in textile industry [4–8]. Bi-heterocyclic azo ligands are of current interest [5,7,9] because of their photoswitching property, non-linear optical property, etc. The majority of biheterocyclic azo compounds are symmetric systems in which two identical heterocyclic units are linked by the —N=N— group. Unsymmetric biheterocyclic azo compounds are scarce. A report of thiazole —N=N— imidazole has been appeared in the literature [10]. We have reported a second example of unsymmetric bi-hetetero-cyclic azo compounds, pyridyl-azo-imidazoles (**1**) and their Cd(II) and Ag(I) complexes [11]. The ligands belong to a special case of multimodal systems [12].

In this work, we report on the manganese(II) complexes of 1-alkyl-2-[(3′-pyridyl)azo]imidazoles (3′-PyaiR′, **2**) and their derivatives. Manganese is chosen

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because of its essential structural and catalytic role in many proteins [13]. The active site involves the binding of imidazoles-N from histidine residues to Mn(II). Besides, the high local spin value of Mn(II) (d^5) enable this metal ion in the exploration of magnetic materials [14,15]. The pseudohalides, especially azide (N_3^-) and thiocyanate (SCN^-) are versatile bridging ligands [14–16] in the synthesis of transition metal complexes for improving the magnetic exchange phenomenon. This work also characterizes manganese(II)-azido/thiocyanato complexes of the pyridyl-azo-imidazole system. The X-ray structures of the free ligand, 2-(3′-pyridylazo)imidazole and tetrakis-{1-ethyl-2-(3′-pyridylazo)imidazole} manganese(II) perchlorate (**3**) are also reported herein. However, reaction of $MnCl_2$, 3′-PyaiR′ and NaN_3/NH_4CNS give Mn(3′-PyaiR′)$_2$(X)$_2$ (X = N_3(**4**), NCS (**5**)) which have been characterized by spectroscopic techniques.

2. Experimental

2.1. Materials

Published methods [11] were used to prepare 1-alkyl-2-(3′-pyridylazo)imidazoles (3′-PyaiR′ where R′ = Me (**2a**), Et (**2b**), Bz (**2c**)) (Scheme 1). $Mn(ClO_4)_2.6H_2O$ was prepared by adding $MnCO_3$ to a warm $HClO_4$ solution (1:1, v/v) and then recrystallizing from water in the presence of a few drops of $HClO_4$. All other chemicals and organic solvents used for the preparation work were of reagent grade, received from SRL, India. Purification of MeCN and preparation of [*n*-Bu$_4$N][ClO$_4$] were done following the literature method [3].

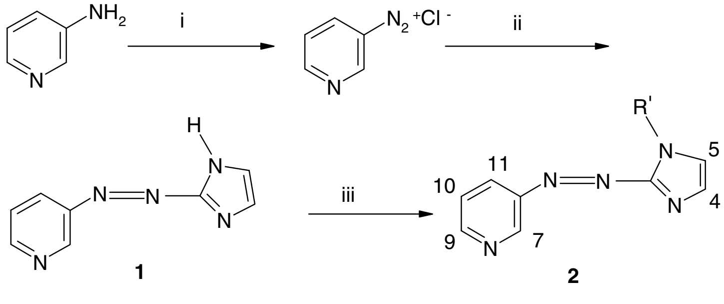
2.2. Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 CHNO/S elemental analyzer. Spectroscopic measurements were carried out using the following instruments: UV–Vis spectra, reflectance spectra, JASCO UV–Vis/NIR model V-570; IR spectra (KBr disk, 4000–200 cm^{-1}), JASCO FT-IR model 420. Molar conductances were measured by a Systronics conductivity meter, solute concentration ($\sim 10^{-3}$ M) in MeCN. Estimation of manganese was carried out by microwave digestion followed by potassium periodate oxidation to pink permanganate, which was determined by a spectrophotometric process [17]. Electrochemistry was carried out with a PAR electrochemistry system 250 potentiostat/versastat and 270 software package. In the cyclic voltametry the following conditions were used: solvent, dry MeCN; supporting electrolyte, [*n*Bu$_4$N][ClO$_4$] ($\sim$0.1 M); solute concentration ($\sim 10^{-3}$ M); working electrode, Pt-disk mili electrode; reference electrode, SCE; auxiliary electrode, Pt-wire; scan rate, 50 mV s^{-1}; formal potential, $E^0 = 0.5(Ep_a + Ep_c)$, where Ep_a and Ep_c are anodic and cathodic peak potentials, respectively; ΔEp ($|Ep_a - Ep_c|$) is the peak-to-peak separation. All experiments were done under a dry N_2 atmosphere at 295(2) K. EPR spectra were measured in MeCN solution at room temperature (298 K) and liquid nitrogen temperature (77 K) using a Bruker ESR spectrometer model EMX 10/12, X-band ER 4119 HS cylindrical resonator.

*2.2.1. Preparation of tetrakis 1-methyl-2-[(3′-pyridyl)azo]imidazole manganese(II) percholate, [Mn(3′-PyaiMe)$_4$](ClO$_4$)$_2$ (**3a**)*

A methanolic solution (15 ml) of 1-methyl-2-[(3′-pyridyl)azo]imidazole (3′-PyaiMe, 0.3 g, 1.60 mmol) was added dropwise to $Mn(ClO_4)_2 \cdot 6H_2O$ (0.2 g, 0.56 mmol) in the same solvent (20 ml) at room temperature (298 K). The mixture was stirred for 15 min and a small portion of yellow mass was filtered and rejected. The filtrate was kept undisturbed for a few days. A bright orange-red crystalline compound was filtered and washed with cold water and methanol. Finally it was dried in vacuo. The isolated yield was 0.25 g (61%).

All other complexes were prepared by the same procedure and yields varied from 60% to 70%. Microanalytical data of the complexes are as follows: [Mn(3′-PyaiMe)$_4$](ClO$_4$)$_2$ (**3a**): *Anal.* Calc. for $C_{36}H_{36}N_{20}O_8Cl_2Mn$: C, 43.11; H, 3.59; N, 27.94; Mn, 5.49. Found: C, 43.25; H, 3.65; N, 27.80; Mn, 5.65%. IR (KBr disk)



R′ = Me (**2a**), Et (**2b**), CH$_2$Ph (**2c**)

Scheme 1.