Synthesis, characterization and crystal structures of dipyridyl-\textit{N}-methylimine and cloro-bis (\textit{N},\textit{N}'-2,2'-dipyridyl-\textit{N}-methylimine)lithium complex

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Received September 14, 2004; accepted December 21, 2004

The preparation and characterization by X-ray crystallography and NMR spectroscopy of the 2,2'-dipyridyl-\textit{N}-methylimine (dpNmei) and the complex [cloro-bis(\textit{N},\textit{N}'-2,2'-dipyridyl-\textit{N}-methylimine)]lithium [Li(dpNmei)\textsubscript{2}(Cl)] is reported. The dpNmei was prepared from the reaction of the 2,2'-dipyridyl ketone (dpk) and methylamine and crystallizes in the monoclinic \textit{P}2\textsubscript{1}/\textit{n} space group with \(a = 6.3887(6)\), \(b = 10.1709(10)\), \(c = 16.7594(17)\) (Å), \(\beta = 100.918(2)^\circ\) and \(V = 1069.29(18)\) Å\textsuperscript{3}. The lithium complex was obtained from the reaction of dpNmei and LiCl in a molar ratio 2:1. [Li(dpNmei)\textsubscript{2}Cl] crystallizes in the orthorhombic \textit{P}bc\textsubscript{n} space group with \(a = 10.0092(12)\), \(b = 9.8201(12)\), \(c = 23.669(3)\) (Å) and \(V = 2326.4(5)\) Å\textsuperscript{3}. The crystallographic data show that the lithium ion is five-coordinated with four coordination bonds N→Li due the chelation of dpNmei and one Li–Cl bond.

KEY WORDS: 2,2'-dipyridyl-\textit{N}-methylimine; lithium complex; synthesis; crystal structures.

Introduction

Dipyridines have been extensively studied in the coordination chemistry through the synthesis of its transition-metal complexes in order to understand the formation of metal-containing extended structures that have potential magnetic properties.\cite{1,2} Dipyridines are multidentate molecules containing nitrogen atoms that may act as coordination sites. Structure of dipyridines and some derivatives may be represented by several conformers, modifying the coordination modes.\cite{1,3-5}

In particular the 2,2'-dipyridyl ketone (dpk) has been used in the synthesis of new multidentate ligands as 2,2'-dipyridylimines, usually obtained from the condensation between dpk and diamines.\cite{6} In these reactions, it is well known that aromatic ketones, as dpk, require vigorous conditions at higher temperatures, increased reaction times, the use of a catalyst and the removal of water during the reaction.\cite{7,8}

On the other hand, the formation of two 2,2'-dipyridylimine (dpi) derivatives have been reported by the condensation of dpk and aminoferrocene in reflux of THF\cite{9} and by formation \textit{in situ} in the course of the synthesis of a vanadium complex.\cite{10} In this complex the dpi moiety acts as a bidentate ligand.

In this paper we report the synthesis and structural characterization in solution and solid
state of a new iminic derivative from dpk, the 2,2′-dipyridyl-N-methylimine (dpNmei), and its coordinative behavior as bidentate ligand toward lithium ion.

**Experimental**

All manipulations of air and moisture sensitive materials were carried out under dinitrogen using Schlenk techniques. The dpk was purchased from Aldrich and used as received. Solvents were dried by standard methods. Melting points were measured on a Melt-Temp II apparatus and are uncorrected. Infrared spectra were recorded on FT-IR 200 Perkin Elmer spectrophotometer using CH2Cl2 solutions in the 4000–400 cm\(^{-1}\) range. Elemental analyses were performed on a Perkin Elmer Series II CHNS/O Analyzer 2400. NMR spectra were obtained on a Jeol GSX 400 spectrometer, \(^1\)H (399.78 MHz), \(^{13}\)C (100.53 MHz), \(^7\)Li (155.37 MHz). The chemical shifts (ppm) are relative to (CH3)4Si and LiCl. Unequivocal NMR assignment of dpNmei was made by heteronuclear and homonuclear correlation two dimensional experiments (coloc, hetcor and cosy). The single-crystal X-ray structures determination of dpNmei and [Li(dpNmei)2Cl] were performed at 291(2) K on a Bruker Smart 6000 CCD diffractometer using graphite monochromated Mo Kα radiation (0.71073 Å).

**Synthesis of 2,2′-dipyridyl-N-metilimine (dpNmei)**

A solution of 2,2′-dipyridyl ketone (dpk) (0.100 g, 0.540 mmol) in 5 mL of dry methanol was added to a solution of methylamine 2.0 M (1.0 mL, 0.062 g, 2.00 mmol). The mixture was refluxed for 24 h using a Dean-Stark trap. The excess of solvent and methylamine were evaporated to dryness in vacuum to give a moisture sensitivity yellow solid. Yield: (0.105 g) 98%. mp.: 67–68°C. Microanalysis: Found (Calc.): C, 72.93 (73.07); H, 5.81 (5.62); N, 20.93 (21.30)%; \(^1\)H NMR: \(\delta\) 8.52 (d, H-3, \(J = 4.40\) Hz), 8.30 (d, H-8, \(J = 4.40\) Hz), 7.85 (d, H-11, \(J = 8.10\) Hz), 7.56 (td, H-5, \(J = 7.70, 1.83\) Hz), 7.49 (td, H-10, \(J = 7.70, 1.46\) Hz), 7.08 (m, 2H, H-6 and H-4), 7.00 (td, H-9, \(J = 6.0, 1.10\) Hz), 3.14 (s, Me-12); \(^{13}\)C \(^1\)H NMR: \(\delta\) 167.9 (C-1), 156.7 (C-7), 154.7 (C-2), 149.7 (C-3), 148.7 (C-8), 136.3 (C-10), 136.0 (C-5), 124.0 (C-9), 123.6 (C-4), 123.0 (C-6), 122.1 (C-11), 41.3 (Me-12). IR data (CH2Cl2): \(\nu\) (C=\(\text{N}\)) 1683 cm\(^{-1}\); MS: 197 m/z [M]+.

**Synthesis of [Li(dpNmei)2(Cl)]**

**Method A:** A mixture of dpk (0.118 g, 0.641 mmol) in 5.0 mL of dry methanol and 30.0 mL of dry benzene was added to a solution of methylamine 2.0 M (1.0 mL, 0.062 g, 2.00 mmol) and LiCl (0.014 g, 0.330 mmol). The mixture was refluxed for 48 h using a Dean-Stark trap. The excess of solvent and methylamine were evaporated to dryness in vacuum to give an amber solid. Yield: 95% (0.265 g). mp: 119–121°C. The complex easily changes color from amber to brown in the presence of traces of moisture and satisfactory elemental analysis were not obtained. \(^1\)H NMR: \(\delta\) 8.72 (d, 1H, H-3, \(J = 4.80\) Hz), 8.45 (d, 1H, H-8, \(J = 4.80\) Hz), 7.75 (td, 1H, H-5, \(J = 7.70, 1.46\) Hz), 7.58 (td, 1H, H-10, \(J = 7.70, 1.46\) Hz), 7.34 (d, 1H, H-11, \(J = 7.70\) Hz), 7.28 (td, 1H, H-4, \(J = 6.20, 1.10\) Hz), 7.20 (d, 1H, H-6, \(J = 8.10\) Hz), 7.17 (td, 1H, H-9, \(J = 6.40, 1.28\) Hz), 3.16 (s, Me-12); \(^{13}\)C \(^1\)H NMR: \(\delta\) 167.6 (C-1), 155.0 (C-7), 154.0 (C-2), 150.3 (C-3), 149.5 (C-8), 137.1 (C-10), 136.7 (C-5), 124.8 (C-6), 123.7 (C-11, C-9 and C-4), 41.3 (Me-12); \(^7\)Li NMR \(\delta\) 2.23; IR data (CH2Cl2): \(\nu\) (C=\(\text{N}\)) 1679 cm\(^{-1}\).

**Method B:** A solution of dpNmei (0.120 g, 0.609 mmol) in 30.0 mL of dry benzene was added to a solution of LiCl (0.013 g, 0.306 mmol) in 3.50 mL of dry methanol. The mixture of reaction was refluxed for 48 h with a Dean-Stark trap. The excess of solvents were evaporated to dryness in vacuum to give an amber solid. Yield: 95% (0.252 g).