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Synthesis and characterization of a versatile bis(pyridylether) ligand and its complexes with Ag(I), Cu(II) and Co(II)

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Abstract

A new bis(pyridylether) ligand **L** was synthesized in 46% yield from the reaction of two equivalents of 2-pyridylethanol with α,α′-dibromo-*o*-xylene in the presence of sodium hydroxide. Ligand **L** possesses structural features that allow it to react either intermolecularly or in a chelating fashion with transition metal ions. With $AgNO_3$, ligand **L** forms a helical metallopolymer. Ligand **L**, in combination with 2-pyridylethanol, reacts with $Cu(ClO_4)_2$ to form a bridged dinuclear complex. With $Co(NCS)_2$, ligand **L** behaves as a chelating ligand to give a monomeric octahedral complex.

Keywords: Nitrogen ligands; Helical structures; Self-assembly; Supramolecular chemistry; N,O ligands

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1. Introduction

The interaction of organic multidentate ligands with transition metal ions can lead to a variety of molecular architectures, including macrocycles, polyhedra and linear and helical polymers [1–3]. As might be expected, ligand structure plays a critical role in the type of structure formed. Flexible ligands favor the formation of chelates or macrocycles, while stiff ligands often result in polymeric complexes. In recent research, we have focused on the synthesis of new bis(pyridyl) ligands in which the pyridyl groups are separated by spacer groups of varying flexibility. Depending on the spacer group, we found these ligands interact with silver(I) salts to form either chelated complexes [4] or helical polymers [5].

Supramolecular structure is also affected by the choice of metal ion. For a given ligand, the resulting complex structure is governed by the geometric preferences of the ion. As a part of our fundamental investigations in the synthesis of new multidentate heterocyclic ligands [4–6], we have sought to synthesize ligands that are flexible enough to accommodate a variety of geometric configurations, depending on the coordinated metal ion. In this report, we describe the synthesis of one such bis(pyridyl) ligand and its coordination preferences with Ag(I), Cu(II) and Co(II), metal ions that are known to exhibit a variety of coordination geometries with pyridyl ligands. This ligand reacts with Ag(I) to give a polymeric structure but reacts with Cu(II) and Co(II) to give monomeric complexes in which it is either a bridging or chelating ligand.

2. Results and discussion

The new bis(pyridylether) ligand **L** was synthesized in 46% yield from the reaction of 2-pyridylethanol with α,α′-dibromo-*o*-xylene in THF, in the presence of sodium hydroxide (Scheme 1). This reaction was not as straightforward as it may seem, as other common bases

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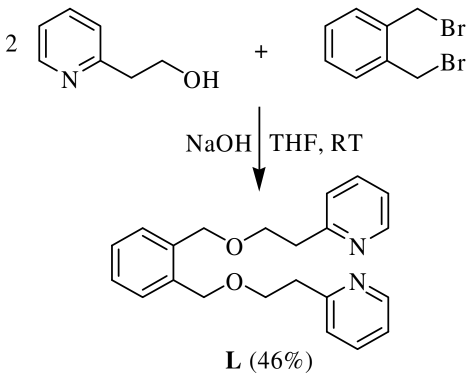

Scheme 1.

such as triethylamine, diisopropylethylamine, potassium carbonate, potassium hydroxide and lithium hydroxide were ineffective as proton acceptors. Furthermore, this reaction was unsuccessful with α,α′-dichloro-*o*-xylene as the starting material. Ligand **L**, isolated as a yellow oil, is stable under normal room conditions but hygroscopic. As can be seen from the structure of **L**, the ortho substitution pattern and the position of the pyridine nitrogen atoms suggest that this ligand can be chelating. However, the length and flexibility of the arms also allows the possibility of intermolecular complexation. Furthermore, the oxygen atoms present in the pyridyl arms may serve as additional donor atoms [7].

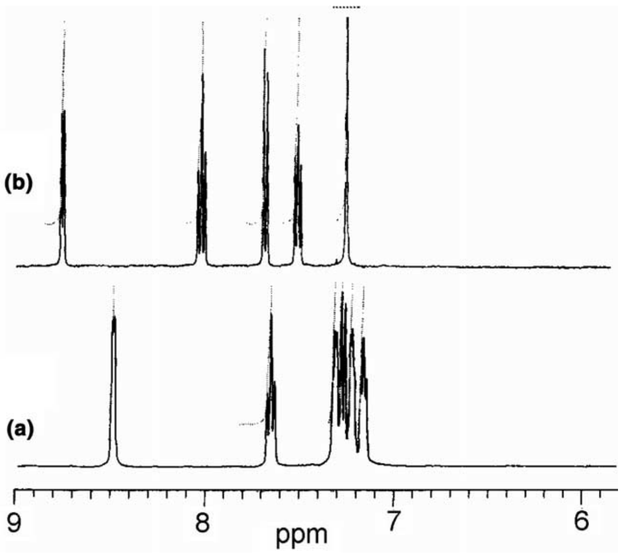

Fig. 1. ^{1}H NMR spectra (aromatic region) in [D$_6$]acetone of (a) **L**, and (b) **Ag**–**L**.

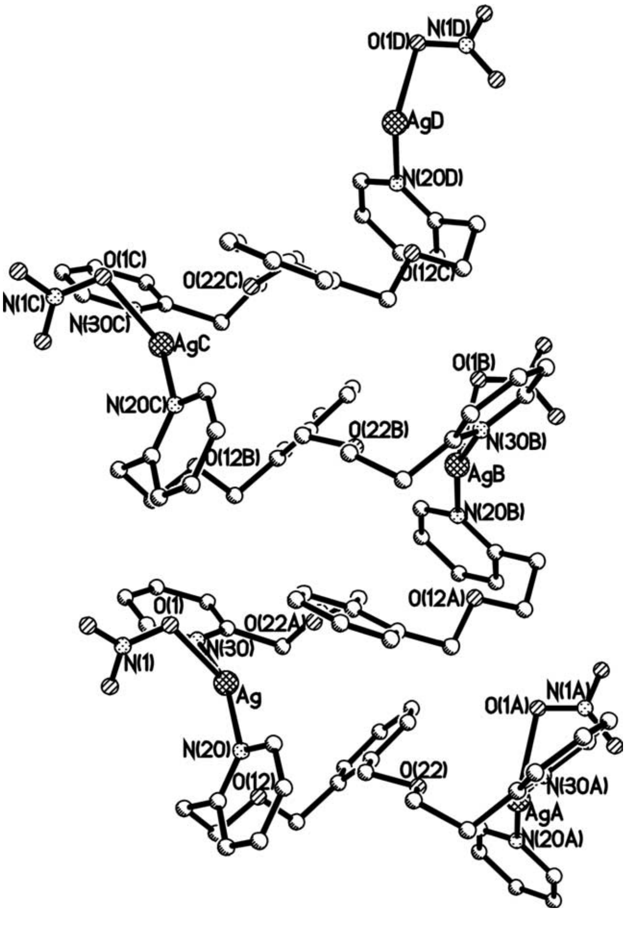

Fig. 2. Subsection of **Ag**–**L** (hydrogen atoms omitted for clarity).

When an aqueous solution of silver nitrate was added to an acetone solution of **L** (1:1 ratio), a cloudy solution resulted which cleared within seconds. The solution was stored in the refrigerator and fine needle-like crystals formed in approximately 3 days.[1] After redissolving the crystals in methanol and adding water, orange block crystals (**Ag**–**L**) formed in 58% yield from the refrigerated solution after approximately one week. The ^{1}H NMR spectrum of **Ag**–**L**, which itself dissolved slowly into acetone-D$_6$, showed the pyridine proton signals to be spread out and shifted downfield compared to the spectrum of ligand **L**, suggesting Ag–L complexation in solution (Fig. 1). X-Ray crystal analysis of **Ag**–**L** revealed that **L** reacted intermolecularly with Ag(I) to give a one-dimensional helical polymer (Fig. 2). Structurally related bis(pyridylether) ligands such as 1,4-bis(2-pyridyloxymethyl)benzene and 1,4-bis(2-pyridylmethoxy)benzene have been reported to give π–π stabilized zigzag metallopolymers on interaction with AgNO$_3$ [8]. Each helical repeat unit of **Ag**–**L** consists of two ligands and two silver ions. The N–Ag–N bond angle of 160.49(14)° is distorted from linearity due to additional coordination of a nitrate ion oxygen atom (Ag–O(1) 2.591(4) Å), and weaker coordinations from two oxygen atoms of two separate ligands (Ag–O(12) 3.343(3) Å; Ag–O(22A) 2.748(3) Å). We observed no evidence for π–π interactions within each helical strand, as the stacked aryl rings are separated by 8.508(1) Å.

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[1] We did not obtain X-ray quality crystals from reactions of **L** with silver triflate or silver tetrafluoroborate.