



Copper(I) and silver(I) coordination assemblies of imino-pyridyl and azino-pyridyl ligands: Syntheses, crystal structures, spectroscopic and photophysical properties



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ABSTRACT

Six coordination polymers, $[\text{Cu}(\mu\text{I})(\text{L}^1)]_n$ (**1**), $[\text{Cu}(\mu\text{I})(\text{L}^2)]_n$ (**2**), $[\text{Cu}(\mu\text{I})(\text{L}^3)]_n$ (**3**), $[\text{Cu}(\mu\text{I})(\text{L}^4)]_n$ (**4**), $[\text{Ag}(\text{L}^4)(\text{NO}_3)]_n$ (**5**) and $[\text{Ag}(\text{L}^5)](\text{ClO}_4) \cdot 4\text{CH}_3\text{CN}$ (**6**) based on coinage metals Cu(I)/Ag(I) and a set of five imino-pyridyl ligands (L^1 – L^5) have been synthesized. The self-assembling behaviour of the metals and the ligands and photo-physical properties of these coordination polymers have been described. Cu_2I_2 secondary building unit (SBU) is a robust feature of the Cu and Iodine self-assembly. This SBU along with the ligands provides 1D coordination polymers in **1**, **2** and **4** and 2D coordination polymer in **3**. The Ag(I) complex **5** is a helical coordination polymer and **6** is a 2D coordination polymer with (4, 4') net architecture with rhombic grids.

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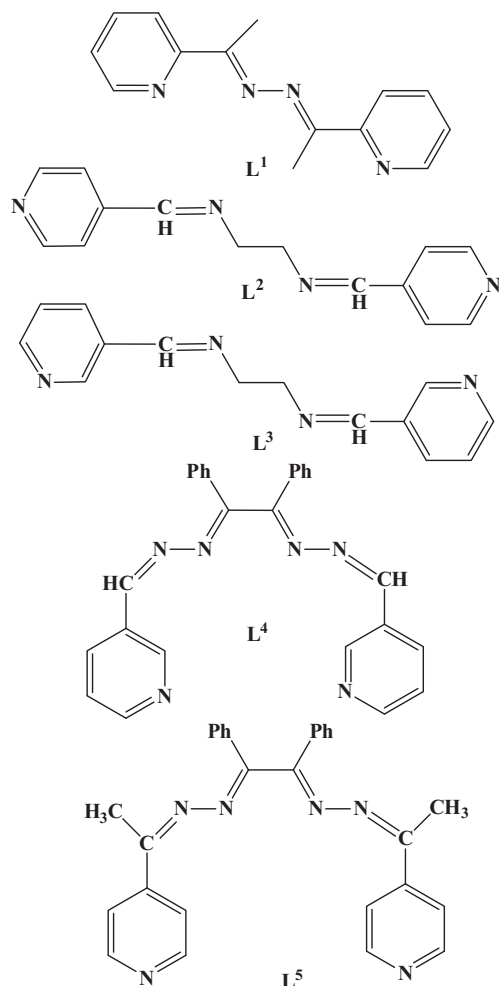
1. Introduction

Studies of coordination polymers have assumed a phenomenal growth during recent past. This class of complexes can be synthesised in a controlled manner by adopting crystal engineering methodology [1]. In designing higher dimensional coordination polymers one utilises the stereo-chemical as well as electronic information encoded in metal nodes and various N, O, S donor ligands as spacers to direct coordination assembly with particular architectures/topologies [2] and desired functional properties [3]. It is the functional property of the resultant coordination polymer that is of practical interest but the topology of the architecture in many cases is responsible for the functional behaviour [4]. In this respect semi-rigid imino pyridyl ligands have been utilised by different groups to design coordination assembly of various transition metals yielding materials with diverse topologies such as helicates, 1D and 2D coordination polymers [5]. The N donor ligands are easily customizable due to the relative ease with which the length at the central part of the ligand can be tailored and also various substituents can be easily incorporated. Also the relative positioning of N atoms both on the terminal pyridyl rings and in central part of

the ligand can easily be modified as is needed in designing. In the shortest imine-based bis-pyridyl ligand, 2-pyridine ketazine (pyridylmethylketazine), L^1 (Scheme 1) two pyridyl units are linked directly through the imine nitrogen atoms. This apparently simple ligand exhibits rich coordination modes toward metal ions and particularly suitable for preparing helicates [5]. The imino-pyridyl ligands L^2 and L^3 are excellent building blocks for the preparation of various architectures. The azino-pyridyl ligands L^4 and L^5 have been synthesized for the first time and in designing these ligands it has been kept in mind how the effect of substituents and the donor atoms' position on the ligand frame would affect coordination mode towards metal ions. Though ligand L^1 can chelate metal ions due to close proximity of pyridyl N atom and imine N atom on the ligand body, other ligands are expected to be incapable of chelation due to wider spacing of N atoms and steric congestion due to phenyl and methyl substituents on the ligand frame. It is expected that L^2 – L^5 would generally act as spacer for metal ions by coordinating them through the pyridyl terminals. Herein we report six new coordination assemblies of coinage metals Cu(I) and Ag(I) with imino-pyridine ligands L^1 – L^5 . As precursor of Cu(I) ion we have chosen Iodide salts of Copper with a preconception that the self-assembling behaviour of Cu^+ and I^- can lead to the robust Cu_2I_2 – secondary building unit (SBU). In the design of coordination polymer the SBU approach [6] is very useful one, which generally utilised to design robust and strong coordination polymers having

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Scheme 1. Ligands used in this study.

high thermal stabilities. Silver(I) ions have also been utilised in the design of organic–inorganic hybrid materials, since as soft acids they favour stable coordination to soft bases (like unsaturated nitrogen atom containing ligands and have been widely utilised in the context of azino-pyridine ligands), most of the cases producing helical assemblies [7]. Targeted synthesis of helical coordination polymer still remains a great challenge in the field of crystal engineering as helical topology is important for designing optical materials and is also associated with the molecules of life [8,9]. In the present report we have studied the self-assembling behaviour of pyridine-ethylene base ligands **L**² and **L**³ with Cu(I). Whereas **L**² gives rise to a 1D coordination polymer **L**³ gives rise to a 2D coordination polymer effected by a change in the pyridine N atom position. This study also reveals that the azino-pyridyl based ligands **L**¹, **L**⁴ and **L**⁵ (Scheme 1) are predisposed for helical architecture in combination with coinage metals. Whereas **L**¹, **L**², **L**³ and **L**⁴ were studied in combination with Cu(I) to see the effect of ligand flexibility and spacer length; **L**⁴ and **L**⁵ in combination with Ag(I) were studied to explore the effect of pyridyl N-atoms' position and substituent effects.

2. Experimental

2.1. Materials and physical measurements

All the reagents were procured commercially from Aldrich. Microanalyses were performed by Perkin-Elmer 2400II elemental

analyzer. The melting point was determined by an electro-thermal IA9000 series digital melting point apparatus and is uncorrected. IR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV–Vis spectra on a Shimadzu UV-160A spectrophotometer, ¹H and ¹³C NMR spectra by a Bruker DPX200 spectrometer. EI mass spectra on a VG Autospec M-250 instrument. Fluorescence spectra were recorded on a Perkin Elmer LS55 Luminescence Spectrometer.

Caution! Though while working with the perchlorate complex described here we have not met with any incident, care should be taken in handling them as perchlorates are potentially explosive. They should not be prepared and stored in large amounts.

2.2. Preparation of ligands

2.2.1. Synthesis of ligand **L**¹

The ligand **L**¹ was prepared by refluxing 2-acetyl pyridine and hydrazine hydrate in 2:1 M ratio in methanol, following a reported procedure [10].

2.2.2. Synthesis of ligand **L**²

The ligand **L**² was prepared in good yield by refluxing 4-pyridine carboxaldehyde and ethylenediamine in 2:1 M ratio in methanol, following a reported procedure [11].

2.2.3. Synthesis of ligand **L**³

The ligand **L**³ was prepared as a yellow solid by refluxing 3-pyridine carboxaldehyde and ethylenediamine in 2:1 M ratio in methanol, following reported procedures [12].

2.2.4. Synthesis of ligand **L**⁴

To a 25 mL of anhydrous methanol solution of benzil dihydrazone (0.714 g, 3 mmol), freshly distilled 3-pyridine carboxaldehyde (0.642 g, 6 mmol) was added. The colour of the resulting solution turned yellow immediately. The solution was refluxed for 6 h, maintaining dry conditions. Then it was slowly cooled to room temperature to yield a yellow crystalline solid which was filtered off, washed with 5 mL of water and dried in air. Yield, 0.94 g (75%); mp 135 °C. *Anal. Calc.* for C₂₆H₂₀N₆: C, 74.97; H, 4.84; N, 20.18. Found: C, 74.88; H, 4.89; N, 20.12%. EI-MS: *m/z* 416.93 (MH⁺, 100%). FTIR/cm⁻¹ (KBr): 3435(wb), 3026(m, split), 1610(vs), 1568(m), 1543(w), 1487(s), 1443(s), 1414(vs), 1323(s), 1305(m), 1240(m), 1188.7(m), 1078(w), 1024(s), 999(m), 953(m), 866(m), 820(m, split), 777(s), 748 (s), 713(m), 690(vs), 627(w), 571(m). ¹H NMR (200 MHz, CDCl₃, TMS): δ 8.76 (s, 2 H), 8.60(s, 2 H), 7.88 (d, 4 H), 7.84 (dd, 2 H), 7.51–7.26 (m, 10 H). ¹³C NMR (200 MHz, CDCl₃, TMS): δ 165.99, 157.87, 150.33, 140.89, 133.44, 131.47, 128.90, 127.85, 122. UV-Vis λ_{max}/nm (ε/dm³ mol⁻¹ cm⁻¹) (CH₃OH): 334 (36900); 272 (41500).

2.2.5. Synthesis of ligand **L**⁵

To a 25 mL of anhydrous methanol solution of benzil dihydrazone (0.714 g, 3 mmol), 4-acetyl pyridine (0.726 g, 6 mmol) was added. The resulting pale yellow mixture was refluxed for 8 h, under dry condition. Then it was slowly cooled to room temperature. Yellow crystalline solid separated out, which was filtered off and dried in air. Yield, 0.96 g (72%); mp 122 °C. *Anal. Calc.* for C₂₈H₂₄N₆: C, 75.65; H, 5.44; N, 18.91. Found: C, 75.68; H, 5.58; N, 18.83%. EI-MS: *m/z* 444.97 (M⁺, 100%). FTIR/cm⁻¹ (KBr): 3346(w), 3205(w), 3029(w), 1950(w), 1655(w), 1599(vs) (C=N), 1562(s), 1490(m), 1442(m), 1407(s), 1365(m), 1321(m), 1300(m), 1254(w), 1215(w), 1175(w), 1138(w), 1095(w), 1062(m), 1022(w), 993(m), 952(w), 927(w), 824(s), 767(m), 740(m), 692(s), 655(w), 576(m), 503(w), 430(w). ¹H NMR (200 MHz, CDCl₃, TMS): δ 8.56 (d, 4 H), 7.87 (d, 4 H), 7.44–7.33 (m, 10 H), 2.24 (s, 6 H). ¹³C NMR (200 MHz, CDCl₃, TMS): δ 160.61, 159.42, 149.51,

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