

Novel organic–inorganic composite coordination polymers generated from new multidentate schiff-base ligand and Ag(I) salts†

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Two novel organic–inorganic hybrid coordination polymers were synthesized based on a new multidentate Schiff-base ligand and Ag(I) salts

Design and synthesis of organic–inorganic composite coordination polymers exhibiting novel structures and properties have provided exciting new prospects.^{1–2} In contrast to the well developed bipyridine-type ligand chemistry, efforts on bipyrazine-type spacers are still unusual, although pyrazine or substituted pyrazine compounds have been used as bridging spacers in the preparation of coordination polymers. Recently, we have design and synthesized a new bipyrazine-Schiff-base ligand (L1, Scheme 1). Compared to the known bipyridine-Schiff-base ligands,³ L1 is more flexible and could be used as a multidentate ligand. Herein, we wish to report the synthesis, X-ray single crystal structures, and luminescent properties of two novel coordination polymers, namely [Ag₅(L1)₃(NO₃)₃][Ag(NO₃)₃]₃·3CHCl₃ (**1**) and [Ag₂(L1)₂](SbF₆)₂·CH₂Cl₂ (**2**) based on it.

X-ray crystallography† shows that **1** is made up of a novel non-interpenetrating 3-D coordination network. There are five different Ag(I) centers in **1**. Four are part of the 3-D polymeric framework, one is part of the triangular anion [Ag(NO₃)₃]²⁻. Two N_{pyrazinyl} donors together with two N_{Schiff-base} donors on L1 chelate two Ag(I) centers (Ag(2) and Ag(3)), and the remaining terminal N-donors are monodentate to two Ag(I) centers (Ag(1) and Ag(4)). So L1 reported herein might be described as a bis-bidentate and bis-monodentate ligand. In the solid state, four Ag(I) (Ag(1)–Ag(4)) centers are connected to each other by L1 through all six N-donors into novel metal–organic tubes (crystallographic dimensions, ca. 6 × 6 Å)⁴ extending along the crystallographic *b* axis, in which the CHCl₃ guest molecules are located (Fig. 1). In addition, Ag(1) and Ag(4) are further linked by coordinated NO₃⁻ counter ions into 1-D inorganic chains along the crystallographic *a* axis. The uncoordinated triangular [Ag(5)(NO₃)₃]²⁻ counter ions are located between these chains. When viewed down the crystallographic *b* axis, a very regular inorganic “honeycomb-like” arrangement (crystallographic dimensions, ca. 13 × 13 Å)⁴ is found in **1** (Fig. 2). Remarkably, the

inorganic silver nitrate “honeycomb” encapsulates Ag(I)–L1 metal–organic tubes, and connects them through three sets of Ag(I)–N coordination bonding systems, including Ag(1)–N(1), Ag(1)–N(7) and Ag(4)–N(6), into a novel non-interpenetrating 3-D network (Fig. 3). It is well known that silver nitrate can generate hollow inorganic networks in the solid state and encapsulate some guest moieties. For example, the zeolite-like [Ag(NO₃)] network in C₆₀{Ag(NO₃)₅} encapsulates fullerene guests through Ag(I)–C₆₀ π–π interactions into an interesting inorganic host–organic guest complex.⁵ Compared to C₆₀{Ag(NO₃)₅}, the hollow silver nitrate network in **1** encapsulates polymeric organic–inorganic hydride tubes instead of a molecular organic guest. Moreover, the metal–organic tubes themselves also serve as the host frameworks in which small CHCl₃ molecules are located in a nearly linear arrangement. The CHCl₃ molecules in the intrachannel [···CHCl₃···CHCl₃···] columns are distant from one another, with the shortest intermolecular Cl···Cl distances of 3.51(3) Å. The remarkable feature of **1** is its chemical species arrangement, as shown in Fig. 3, the organic–organic/inorganic hybrid–inorganic species arrange successively from the center to the edge. Self-

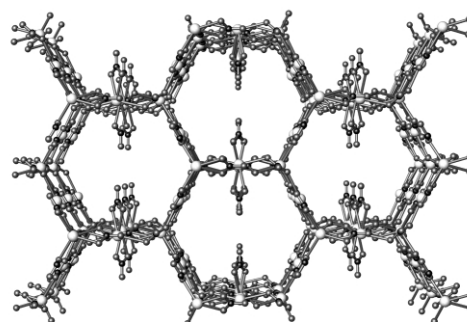
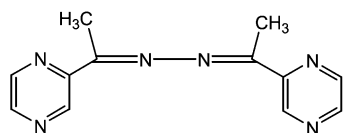


Fig. 2 Inorganic Ag–NO₃ honeycomb-like net.



Scheme 1 New Schiff-base ligand.

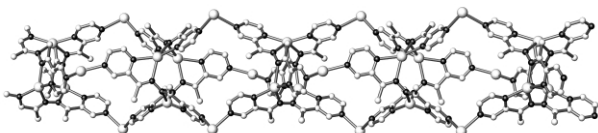


Fig. 1 1-D metal–organic tube (side view) in **1**. CHCl₃ guest molecules are omitted for clarity.

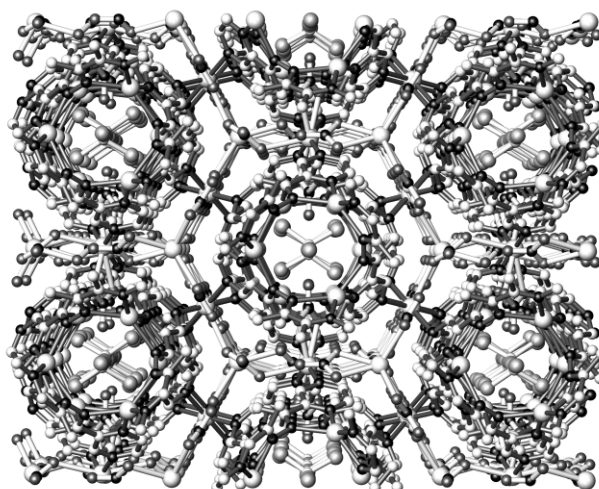


Fig. 3 3-D network in **1**.

† Electronic supplementary information (ESI) available: experimental conditions. See <http://www.rsc.org/suppdata/cc/b3/b311510k/>

assembly of molecular and ionic components offers a viable route for preparing designed crystalline hybrid compounds.⁶ So far, a number of inorganic–organic hybrid materials have been generated based on it. To the best of our knowledge, compound **1** reported herein represents the first example of an extended non-interpenetrating 3-D network containing several different chemical species, *i.e.* organic, organic/inorganic hybrid and inorganic components.⁷

As shown in Fig. 4, there are two types of Ag(I) centers and two types of ligands L1 in **2**. L1 uses only five of six N-donors to bind Ag(I) centers and one terminal N_{pyrazinyl} is free, which is distinctly different from the coordination behavior of L1 in **1**. The four N-donors (N(9), N(10), N(3) and N(4)) on –C(CH₃)=N–N=(CH₃)C–spacers incorporate with four pyrazinyl N-donors to chelate Ag(1) and Ag(2) into a distorted tetrahedral building block. The disordered CH₂Cl₂ solvent molecules are located between two adjacent Ag(1) and Ag(2) centers. In the solid state, these building blocks are linked together *via* one coordinated N-donor into novel infinite 1-D metal–organic tubes along the crystallographic *c* axis (Fig. 5). The tubes are square in shape (viewed down *a* axis) with crystallographic dimensions of 7.6 × 7.6 Å,⁴ in which the SbF₆[−] counter ions are located and hydrogen bonded to the framework through weak C–H⋯F bonds.⁸ In contrast to the well developed molecular square chemistry,⁹ efforts on polymeric organic–inorganic coordination square 1-D tubes are still unusual, although some inorganic 1-D tubes based on inorganic counter ions such as CN[−] and N(CN)₂[−] have been reported.¹⁰

It is well known that the syntheses of coordination polymers by the judicious choice of organic spacers and metal centers can be an efficient method for obtaining new types of luminescent materi-

als.¹¹ The luminescent properties of L1 and **1–2** were investigated in the solid state. For L1, no significant emissions were found in the range of 400–800 nm. The fluorescence spectrum of **1** exhibits two emission maxima at 460 and 483 nm, while the emission spectrum of **2** exhibits three maxima at 422, 447 and 487 nm. The luminescent property of the free L1 was significantly affected by its incorporation into the Ag-containing polymeric compounds **1–2**, as evidenced by the large enhancement of the fluorescence intensity in the emission.

This study demonstrates that the specific geometry of bipyrazine-type Schiff-base ligand L1 yielded a series of coordination polymers with novel network patterns not achievable by linear rigid linking ligands, such as bipy, bpe and bpethy. We anticipate this approach will continue to be viable for the construction of many more new and interesting coordination polymers and, consequently, current efforts toward the preparation of new coordination polymers containing other transition metals are underway.

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Notes and references

‡ Crystal data for **1**: yellow plate crystal, 0.32 × 0.07 × 0.06 mm³. Orthorhombic, space group *Pnna*, *a* = 21.5758(10), *b* = 25.1163(11), *c* = 11.9420(5) Å, *V* = 6471.4(5) Å³, *Z* = 4, ρ_{calc} = 2.154 Mg m^{−3}. Of 59190 measured reflections, 7153 independent reflections with *I* > 2σ(*I*) were used in the refinement; R1 (*F*) = 0.0476, wR2 (*F*²) = 0.0983 for all data; max./min. residual electron density, 1.159/−1.008 e Å^{−3}. Crystal data for **2**: yellow needle crystal, 0.46 × 0.20 × 0.06 mm³. Orthorhombic, space group *Pccn*, *a* = 15.9230(7), *b* = 32.0114(15), *c* = 15.5787(7) Å, *V* = 7431.0(6) Å³, *Z* = 8, ρ_{calc} = 2.239 Mg m^{−3}. Of 58821 measured reflections, 7641 independent reflections with *I* > 2σ(*I*) were used in the refinement; R1 (*F*) = 0.0506, wR2 (*F*²) = 0.1323 for all data; max./min. residual electron density, 1.157/−2.223 e Å^{−3}. The structures were solved and refined by a combination of direct methods and difference Fourier syntheses, using SHELXTL. CCDC 210243 and 210244. See <http://www.rsc.org/suppdata/cc/b3/b311510k/> for crystallographic data in .cif or other electronic format.

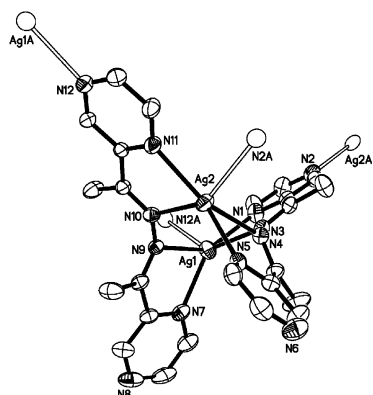


Fig. 4 Ag(I) coordination environment in **2**.

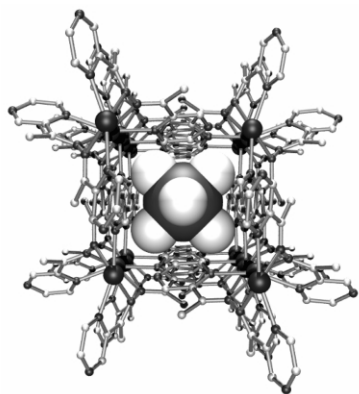


Fig. 5 1-D metal–organic tube in **2**.

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