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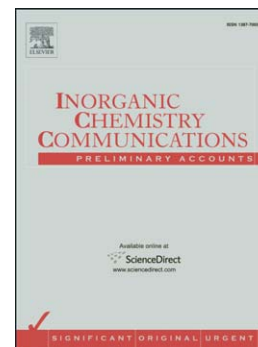
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**Two Novel Self-interpenetrating 3D Iron(II) Coordination Frameworks:
Synthesis, Spectroscopic and Structural Characterizations with Magnetic Properties**

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Abstract

Two novel self-interpenetrating 3D Fe(II) coordination frameworks namely {Fe(4,4'-bpy)[Ag₂(CN)₃]₂}_n (**I**) and {Fe(4,4'-bpy)[Ag(CN)₂]₂[AgCN]₂]_n (**II**) have been synthesized and fully characterized. The 3D architectures and degree of interpenetration of these coordination frameworks were significantly affected by silver(I) cyanide species. The crystal structure of **I** presents 4-fold interpenetrating 3D framework with 4,4'-bpy and [Ag₂(CN)₃]⁻ species. While, that of **II** constructed by 4,4'-bpy and two different silver(I) cyanide species, AgCN and [Ag(CN)₂]⁻ resulting to 2-fold interpenetrating 3D framework. The stability and rigidity of both coordination frameworks are mainly supported dominantly by Ag^I...Ag^I interactions. Their magnetic properties exhibit high spin behavior.

Keywords:

Fe(II) coordination frameworks; self-interpenetrate; Ag^I...Ag^I; magnetic properties

The studies on magnetic properties of molecular materials have been widely interested since the challenges of understanding on their magnetic behaviors for basic knowledge in magnetochemistry [1] and improving potential applications especially in the field of molecular memory devices and magnetic sensors/switches [2-3]. These molecular magnetic materials providing the spin-crossover (SCO) phenomenon which is the changing between high spin and low spin states of transition metal centres (d^4 - d^7 configurations) activated by external stimuli namely temperature, pressure and light irradiation [2-3] could be a good candidate to be carefully improved. Generally, two strategies to achieve this phenomenon which mediated by cooperativity between SCO centers such as “supramolecular approach” for discrete molecules and “coordination approach” for polynuclear complexes or multidimensional coordination frameworks have been considered [3]. For “coordination approach” strategy, the coordination iron(II) frameworks with pyridine derivatives and dicyanoargentate(I) or silver(I) cyanide bridging molecules that provide the SCO properties with interesting Hoffman-like structures or more complicated topologies such as self-interpenetrating frameworks have been investigated and continuously reported [4-18]. The advantages for using silver(I) cyanide in this system are variety of structural topologies, flexibility and also stabilization of the frameworks by $Ag^I \cdots Ag^I$ interactions for enhancing cooperativity.

In previous report, Real and coworkers (2002) reported SCO iron(II) coordination frameworks with doubly interpenetrating structures in general formula $\{Fe(L)_2[Ag(CN)_2]_2\} \cdot G$ when $L =$ pyrazine (pz), 4,4'-bipyridine (4,4'-bpy) and bispyridylethylene (bpe) [10]. Then, a number of this family is extended by using various pyridine or triazole derivatives namely 1,4-di(pyridin-4-yl)benzene (dpb) [6], 4,4'-bis(pyridyl)acetylene (bpac) [15], 1,4-bis(pyridin-4-ylmethyl)piperazine (bpmp) [16], pyridine (py) [17], 3-(3-methyl-2-pyridyl)-5-(2-pyridyl)-1,2,4-triazole (MebptH) [18] and 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (bpztH) [18]. With the aim to continue the design and synthesis of new SCO iron(II) coordination frameworks, rigid bipyridine derivative, 4,4'-bipyridine (4,4'-bpy) and flexible silver(I) cyanide anions were used. According to the solvothermal synthesis in the presence of $Fe(BF_4)_2$ salt, 4,4'-bpy, and $K[Ag(CN)_2]$ (see Supplementary Materials), two novel coordination frameworks were crystallized in the same batch namely $\{Fe(4,4'-bpy)[Ag_2(CN)_3]_2\}_n$ (**I**, orange crystals) and $\{Fe(4,4'-bpy)[Ag(CN)_2]_2[AgCN]_2\}_n$ (**II**, yellow crystals) in yields of ca. 30% and 20% respectively. The phase behavior of such a multi-component system may well be quite complex, but the concomitant formation in acceptable of two different complexes, albeit of

the same overall composition, implies that the thermodynamic stability of complexes **I** and **II** and the rates, both of their formation and their crystallization under the reaction conditions employed must be fairly similar. The role of silver(I) cyanide species in their crystal structures results different architectures of three-dimensional frameworks.

Complex **I** crystallized in orthorhombic, *Ccca* space group. The Fe(II) ions are crystallographically equivalent and lie on inversion center. The coordination environment of Fe(II) ion shows [FeN₆] type chromophore of distorted octahedral geometry as shown in Fig. 1a. The asymmetric unit with numbering atoms of **I** is shown in Fig. S1 in which C(12) and N(12) were assigned to be disordered atoms with occupancies of 0.5. Iron(II) ion is surrounded by two nitrogen atoms from 4,4'-bpy ligands in axial positions and four nitrogen atoms of cyanide donor groups in four tricyanidodiargentate(I), [Ag₂(CN)₃]⁻ units in equatorial positions with Fe-N distances in the range of 2.166(2)-2.196(2) Å. The Fe-N distances indicate the high-spin state of Fe(II) ion at 293 K [19-20]. The coordination framework of **I** exhibits 3D 4-fold self-interpenetrating framework as presented in Figs. 1b-c. Self-interpenetrating 3D coordination framework of **I** is performed by penetrating of flexible [Ag₂(CN)₃]⁻ linker in crystallographic *bc* plane and by rigid 4,4'-bpy linkers as pillars in crystallographic *a* axis, (Figs. 1c, S2). The Fe...Fe distances through those linkers, Fe-[Ag₂(CN)₃]-Fe and Fe-[4,4'-bpy]-Fe are 15.457(5) and 11.480(5) Å (Figs. S2-3), respectively. Consequently, the stability and rigidity of this 3D interpenetrating framework are supported by argentophilic interactions [Ag(1)⋯Ag(1)ⁱ] (symmetry code: *i* = 1-x,1/2-y,z) in which the flexible [Ag₂(CN)₃]⁻ units are linked together along crystallographic *b* axis with distance of 3.318(1) Å (Fig. 2). The argentophilic interaction is relatively short compared with the sum of van der Waals radii of Ag (3.60 Å) and longer than that of 2.89 Å in metallic silver [4]. The coordination of [Ag₂(CN)₃]⁻ at Ag(1) site deviates from linearity with C(11)-Ag(1)-C(12) angle of 169.8(1)°. According to structural feature of this framework above, the 3D framework presents no significant void space within the structure. Complex **II** crystallized in orthorhombic, *Cmca* space group. The Fe(II) ions are crystallographically equivalent and lie on inversion center. 3D framework of **II** consists of an organic ligand 4,4'-bpy, and two shorter and more rigid silver(I) cyanide species namely dicyanoargentate(I), [Ag(CN)₂]⁻ and unexpected silver(I) cyanide, [AgCN]. The asymmetric unit with numbering atoms of **II** is shown in Fig. S5. The geometry of Fe(II) center is distorted octahedron with [FeN₆] chromophore (Fig. 3a). Fe(II) ion is surrounded by four nitrogen atoms of cyanide donor groups of four [Ag(CN)₂]⁻ linkers in equatorial positions and

two nitrogen atoms of 4,4'-bpy in axial positions. The Fe-N distances are in the range of 2.159(3)-2.251(3) Å, some are longer than that of complex **I**, corresponding to high spin state of Fe(II) ion at 153 K [19-20]. The existence of $[\text{Ag}(\text{CN})_2]^-$ and 4,4'-bpy rigid bridging ligands in **II** leads to two interpenetrating Hoffman-like structures as shown in Fig. 3b. Two interpenetrating frameworks in **II** are made up by 2D $\{\text{Fe}_4[\text{Ag}(\text{CN})_2]_4\}$ sheets displacement in crystallographic *bc* plane. While, the 4,4'-bpy bridging ligand that acts as the pillars threads the framework and links Fe(II) ions in crystallographic *a* axis (Figs. 3b, 4 and S6). The structural architectures of **II** exhibits 3D 2-fold self-interpenetrating framework. The Fe...Fe distances through both linkers, Fe- $[\text{Ag}(\text{CN})_2]$ -Fe and Fe-4,4'-bpy-Fe are 10.4011(3) and 11.6242(3) Å, respectively. Furthermore, the framework of **II** also composes of unexpected silver(I) cyanide, $[\text{AgCN}]$ units along crystallographic *b* axis (Fig. 4). This chain-like unit supports the stability of the framework through strong argentophilic interaction between Ag(2) of $[\text{Ag}(2)\text{CN}]$ chain and Ag(1) of $[\text{Ag}(\text{CN})_2]^-$ anionic linker at the shared edges in Hoffman-like structure with Ag(2)...Ag(1) distance of 2.992(1) Å, leading to the 1D chain-like structure in crystallographic *a* axis as shown in Fig. 4. According to structural feature above, the 3D interpenetrating framework of **II** also presents no significant void space within the structure.

The coordination polymers related to the novel complex **I** which contain tricyanodiargentate(I) anionic linker in $\{\text{M}(\text{L})[\text{Ag}_2(\text{CN})_3][\text{Ag}(\text{CN})_2]\}_n$ series have been reported, Table S4. The variety of their structural features depends on type of ligand L namely 3,5-dmpy [4], pmd [5], dpb [6], pyz [7], ampyz [8] and en [9] and also the incorporation of $[\text{Ag}(\text{CN})_2]^-$ to support the stability of frameworks by argentophilic interactions. For iron(II) complexes containing organic L ligand and two ionic $[\text{Ag}_2(\text{CN})_3]^-$ and $[\text{Ag}(\text{CN})_2]^-$ linkers [4-6] resulting the interpenetrating 3D coordination frameworks, these ionic linkers enhance high cooperativity, $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interaction and flexibility of the framework, resulting spin-crossover (SCO) behaviors. While, the rest reported complexes in this series which contain different types of metal ion and L, presented interesting 3D coordination frameworks [7] and 2D wavy sheet structures [8-9] and the stability of their frameworks were mainly supported by $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions. Clearly, the presence of the only $[\text{Ag}_2(\text{CN})_3]^-$ unit in coordination framework **I** does not support enough those of factors for the SCO occurrence. A number of 3D coordination frameworks related to complex **II** in $\{\text{Fe}(\text{L})_2[\text{Ag}(\text{CN})_2]_2\}_n$ series (L are various types of organic ligands) have been reported, Table S4 [6,7,10-18]. The structural features of these complexes exhibit Hoffman-like

framework. The magnetic properties for most of iron(II) complexes in this series present the SCO behaviors. If without [AgCN] unit, the composition of complex **II** shall be closely related to that of previously reported by Niel et al. for $\{\text{Fe}(4,4'\text{-bpy})_2[\text{Ag}(\text{CN})_2]_2\}_n$ [10] which presented interpenetrated 3D framework and 1-step SCO property. However, the topologies of both framework are different and the interpenetrating Hoffman-like 3D framework for complex **II** is more rigid than that of this previously reported complex, by the connection between $[\text{Ag}(\text{CN})_2]^-$ and [AgCN] units via strong $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interaction (Fig. 3b) resulting to the linear coordination of silver atoms in $[\text{Ag}(\text{CN})_2]^-$ with the C-Ag-C angle in $[\text{Ag}(\text{CN})_2]^-$ of $176.38(1)^\circ$. While, $\{\text{Fe}(4,4'\text{-bpy})_2[\text{Ag}(\text{CN})_2]_2\}_n$ [10] which lacked of argentophilic interaction, presented $[\text{Ag}(\text{CN})_2]^-$ with the C-Ag-C angle in of $159.24(1)^\circ$. Obviously, the existence of [AgCN] within complex **II** could be the main cause to enhance rigidity of the framework, thus quenching cooperativity and resulting stuck in high-spin state for Fe(II) ion.

Variable-temperature magnetic susceptibilities of the two complexes have been measured and the $\chi_{\text{M}}T$ versus T plots are shown in Fig. 5. Magnetic studies reveal that the both complexes show very similar magnetic properties. At room temperature, the $\chi_{\text{M}}T$ values for **I** and **II** are 3.78 and $3.70 \text{ cm}^3 \text{ K mol}^{-1}$, respectively, which are larger than the theoretical one for one high-spin Fe(II) ion ($S = 2$ and $g = 2.0$), suggesting significant contribution from the orbital angular moment. The $\chi_{\text{M}}T$ values remain almost constant upon temperature decreasing, and rapidly decrease from about 40 K. These behaviors indicate that the two complexes are paramagnetic with negligible inter-metal magnetic interactions, and the rapid decreases of $\chi_{\text{M}}T$ values at low temperature can be assigned to the spin-orbital coupling effects of the high-spin Fe(II) ions. Though a few relevant complexes show interesting spin-crossover behaviors (Table S4), our complexes are unexpected high spin in whole temperature range. The reason may arise from different architectures of both frameworks due to different silver cyanide species as compared to those of the relevant SCO complexes. For example, **I** is a 4-fold self-interpenetrated structure with $[\text{Ag}_2(\text{CN})_3]^-$ species and **II** is a 2-fold interpenetrated structure with $[\text{Ag}(\text{CN})_2]^-$ and encapsulated 1D $\{\text{AgCN}\}_n$ chains. Consequently, both complexes are highly dense and rigid thus, preventing the structural changes upon external stimuli (“breath” of Fe-N bonds during spin crossover).

In summary, two novel iron(II) complexes which present self-interpenetrating 3D coordination frameworks namely $\{\text{Fe}(4,4'\text{-bpy})[\text{Ag}_2(\text{CN})_3]_2\}_n$ (**I**) and $\{\text{Fe}(4,4'\text{-bpy})-[\text{Ag}(\text{CN})_2]_2[\text{AgCN}]_2\}_n$ (**II**) have been synthesized regarding to high temperature reaction and fully characterized. Degree of interpenetration and rigidity of the coordination frameworks

for both polymorphs are affected by an existence of silver(I) cyanide species and $\text{Ag}^{\text{I}}\cdots\text{Ag}^{\text{I}}$ interactions, respectively. Clearly, these polymorphs provide an understanding in the role of silver(I) cyanide species on the cooperativity and magnetic properties which will be useful to improve the desired magnetic properties of the SCO systems.

Acknowledgement

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Appendix A. Supplementary materials

Supplementary material associated with this article: Firstly, the experimental section which contains the synthetic method of complexes **I** and **II**, crystallographic data section, details of crystallographic data (Table S1), selected bond lengths and angles of the complexes **I** and **II** (Tables S2-3), and the last section of additional figures (Figs. S1-6) and Table S4 of physical properties for relevant complexes. X-ray crystallographic files in CIF format for complexes **I** and **II** (CCDC No. 1445356 and 1445357)). These data can be obtained free of charge by <http://www.ccdc.com.ac.uk/conts/retrieving.html>, or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB22, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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Figure Captions

Fig. 1. Views of (a) coordination environment of Fe(II) ion in **I** and views of four-fold interpenetrating 3D framework of **I** in (b) top and (c) side views. Hydrogen atoms are omitted for clarity.

Fig. 2. Views of (a) the existence of argentophilic interaction in interpenetrating 3D framework of **I** and (b) 1D chain along *b* axis showing the $\text{Ag}^{\text{I}} \cdots \text{Ag}^{\text{I}}$ interactions between $[\text{Ag}_2(\text{CN})_3]^-$ linkers. (atomic color: red = Fe; pink = Ag; light blue = N; grey = C and symmetry codes: $i = 1-x, 1/2-y, z$).

Fig. 3. View of (a) coordination environment of Fe(II) ion in **II** and (b) two interpenetrating frameworks, supported by argentophilic interactions (pink color), $\text{Ag}(2) \cdots \text{Ag}(1)$ at the shared edges in Hoffman-like structure (atomic color: red = Fe; pink = Ag; light blue = N; grey = C and Symmetry codes: $v = 1-x, 1-y, 1-z$). Hydrogen atoms are omitted for clarity.

Fig. 4. View of (a) the arrangement of $[\text{Ag}(2)\text{CN}]$ units (spacefill plot) and (b) the $\text{Ag}(1) \cdots \text{Ag}(2)$ interactions of $[\text{Ag}(1)(\text{CN})_2]$ and $[\text{Ag}(2)\text{CN}]$ units in interpenetrating 3D framework of **II** (atomic color: pink = Ag; light blue = N; grey = C).

Fig. 5. The χ_{MT} versus *T* plots for complexes **I** (□) and **II** (○).

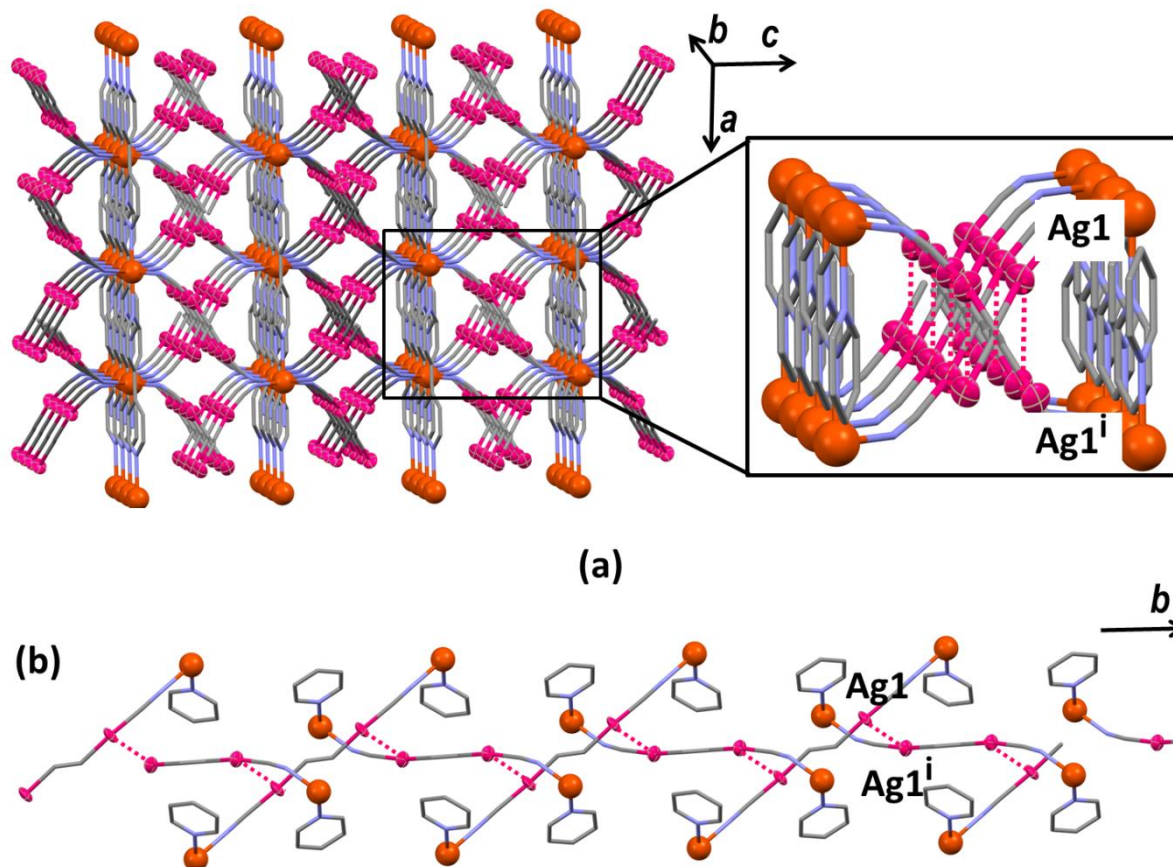


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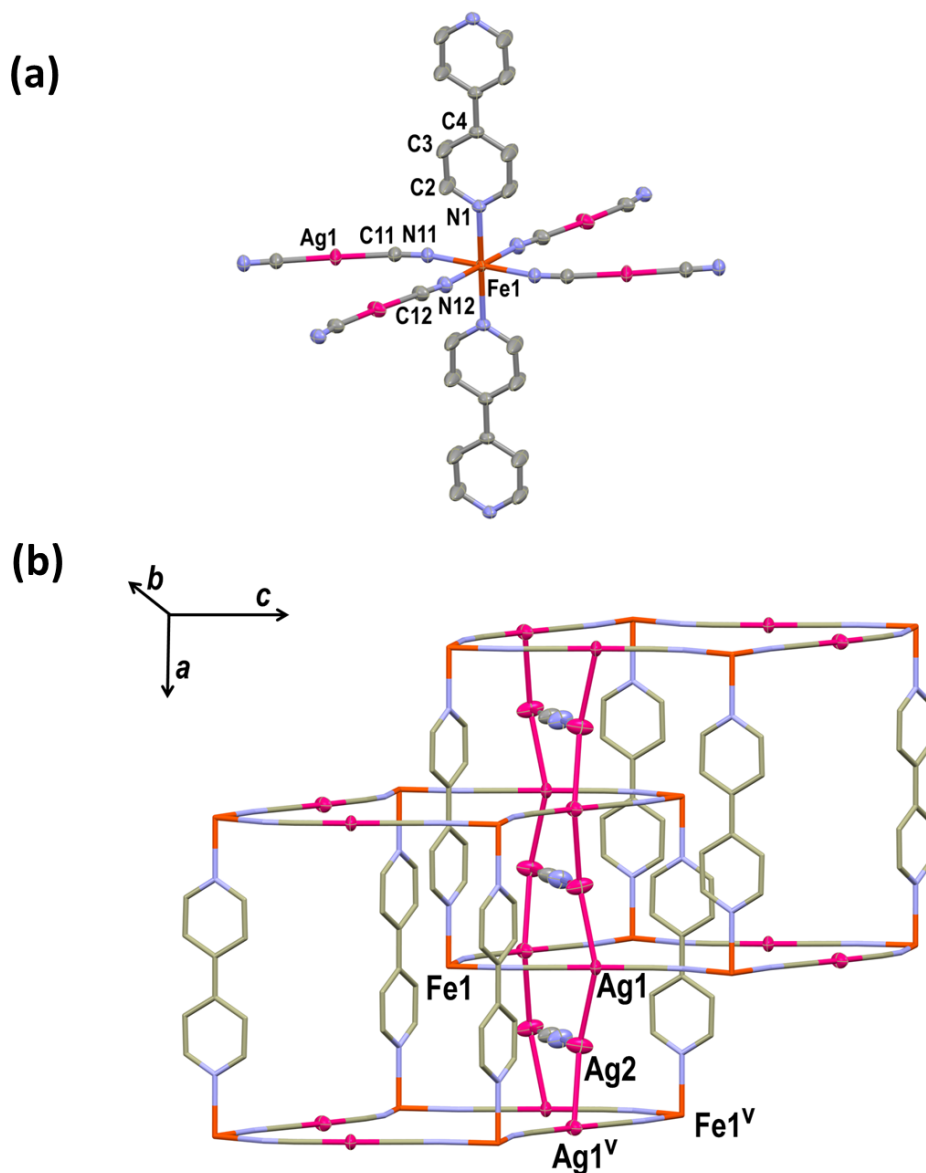


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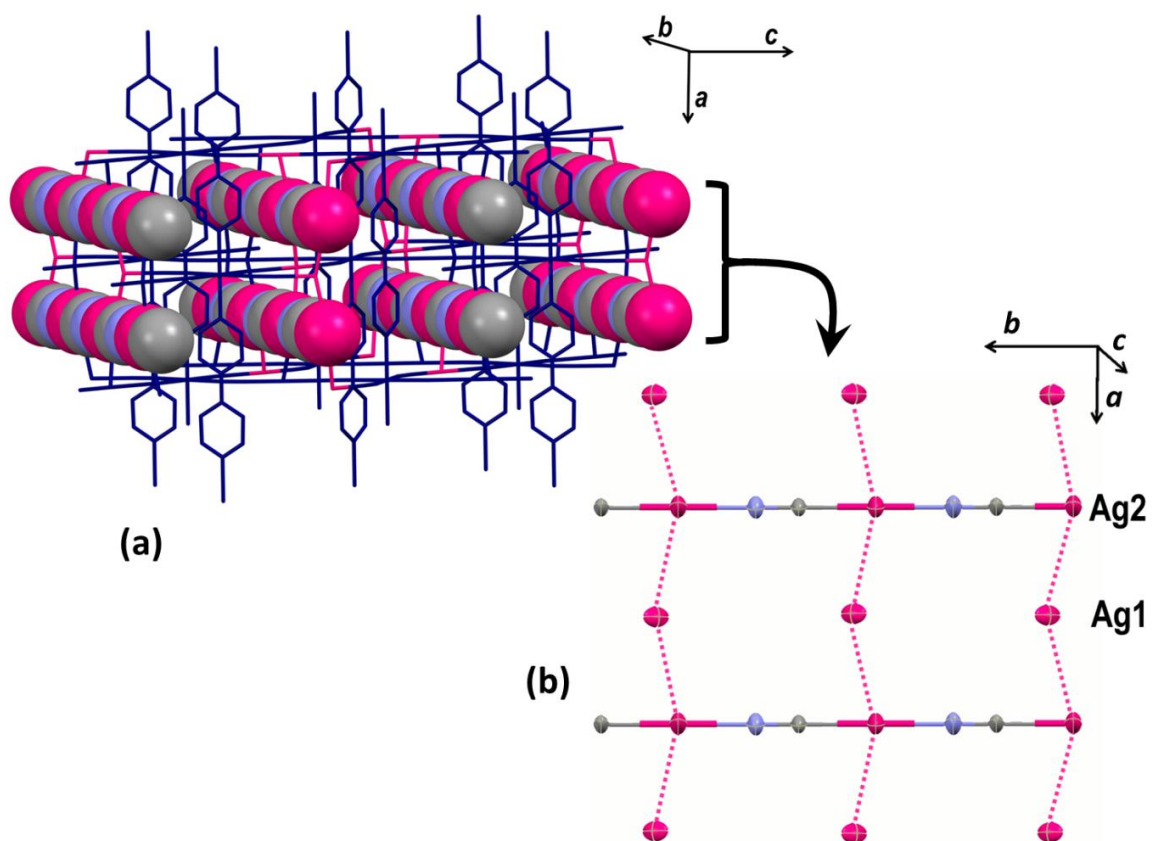


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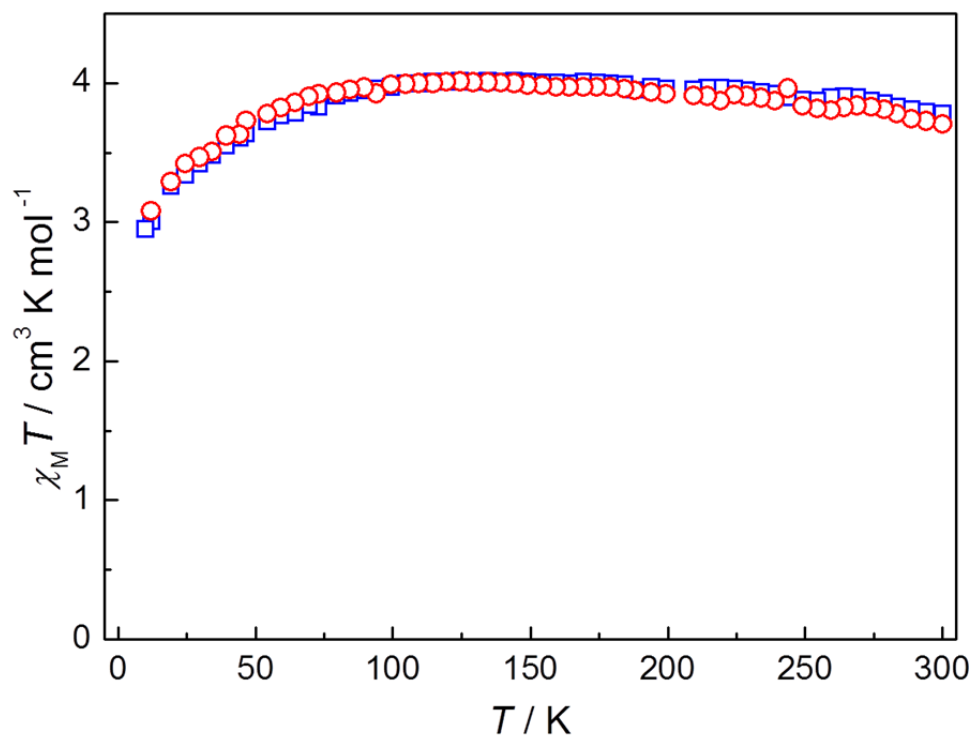
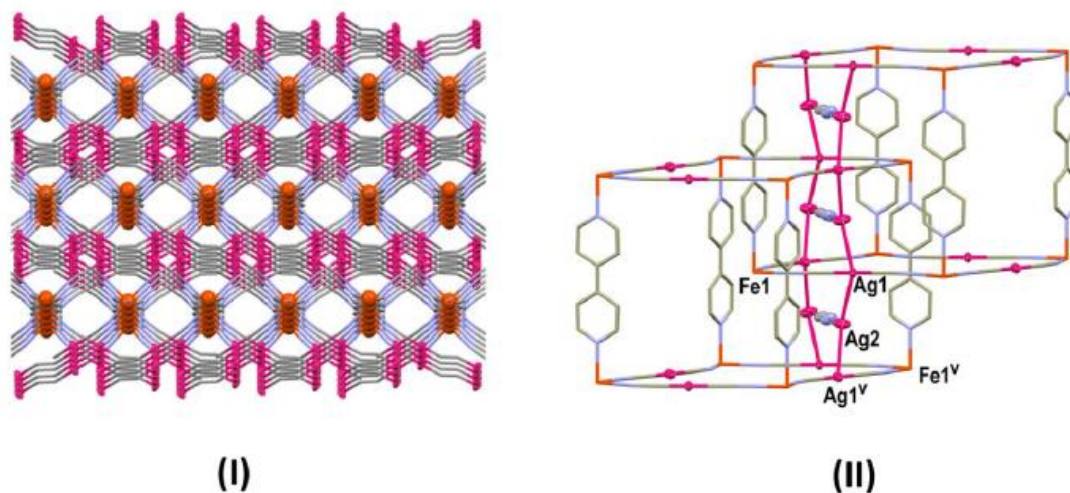


Fig. 5. The $\chi_M T$ versus T plots for complexes **I** (\square) and **II** (\circ).

Graphical abstract



Two novel self-interpenetrating 3D Fe(II) coordination frameworks namely $\{\text{Fe}(4,4'\text{-bpy})[\text{Ag}_2(\text{CN})_3]_2\}_n$ (**I**) and $\{\text{Fe}(4,4'\text{-bpy})[\text{Ag}(\text{CN})_2]_2[\text{AgCN}]_2\}_n$ (**II**) have been synthesized and fully characterized. The 3D architectures and degree of interpenetration of these coordination frameworks were significantly affected by silver(I) cyanide species. Their magnetic properties exhibit high spin behavior.