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ARTICLE TYPE

Dinitrogen Supported Coordination Polymers

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One-pot solvothermal reactions of 3- and 4-(aminomethyl)pyridine with triethyl orthoformate and $\text{Cu}(\text{O}_2\text{CCH}_3)_2$ in methanol saturated with dinitrogen afforded the first examples of coordination polymer that are supported by dinitrogen, $[\text{Cu}_{2.5}(\text{3-mpyf})(\text{N}_2)_{1.5}]_n$ [3-Hmpyf = *N,N'*-bis(pyridine-3-ylmethyl)formamidine], **1**, and $\{[\text{Cu}_3(\text{4-Hmpyf})(\text{N}_2)_3] \cdot (\text{CH}_3\text{OH})\}_n$ [4-Hmpyf = *N,N'*-bis(pyridine-4-ylmethyl)formamidine], **2**. The dinitrogen anions of **1** adopt the end-on-dinuclear (μ - η^1 : η^1) bonding mode, resulting in a 4,4-connected binodal net with the new $(5^3 \cdot 7^3)_2(5^4 \cdot 8^2)$ topology, and those of **2** displays both end-on-dinuclear and end-on-trinuclear (μ - η^1 : η^1 : η^1) bonding modes, forming a 3,8-connected binodal net with the rare $(5^3)_4(5^8 \cdot 6^4 \cdot 7^8 \cdot 8^4 \cdot 9^4)_2$ -3,8T16 topology.

The chemistry of dinitrogen-coordinated metal complexes has been a topic of great interest¹ since 1965 when the first complex was reported by Allen and Senof.^{1(a)} In this regard, effort has been made to mimic some of the processes that are related to the conversion of N_2 to ammonia, which is an important precursor to prepare nitrogen-containing biomolecules.² Dinitrogen comprises the majority of the atmosphere and is a very weak base. Structural studies indicate that upon coordination to the metal ions, the bonding in M-N-N that contains σ and π components is similar to those of carbon monoxide and cyanide,³ which acts as both an electron donor and acceptor. Coordination modes involving end-on and side-on have been found for the dinitrogen molecules, as shown in Table S1. Mononuclear and polynuclear N_2 complexes are already known, but to our best knowledge, no coordination polymer supported by dinitrogen has been reported.

The coordination chemistry of metal complexes containing formamidate ligands has been investigated extensively.⁴⁻⁶ We have reported the one-pot solvothermal reactions of 4-aminopyridine and triethylorthoformate with divalent copper salt that afforded 2- and 3D coordination networks with distinct configurations.⁶ These findings have led us to investigate the reactions involving 3- and 4-(aminomethyl)pyridine in methanol saturated with N_2 , which resulted in the formation of two novel μ - N_2 coordination polymers, $[\text{Cu}_{2.5}(\text{3-mpyf})(\text{N}_2)_{1.5}]_n$ (3-Hmpyf = *N,N'*-bis(pyridine-3-ylmethyl)formamidine), **1**, and $\{[\text{Cu}_3(\text{4-Hmpyf})(\text{N}_2)_3] \cdot (\text{CH}_3\text{OH})\}_n$ (4-Hmpyf = *N,N'*-bis(pyridine-4-ylmethyl)formamidine), **2**, see experimental section in supporting information. Similar reaction with 2-(aminomethyl)pyridine gave the organic compound 2,3,5,6-tetrakis(2-pyridyl)pyrazine (**tppz**), which have been synthesized by aerial oxidation of a cobalt(II)-2-

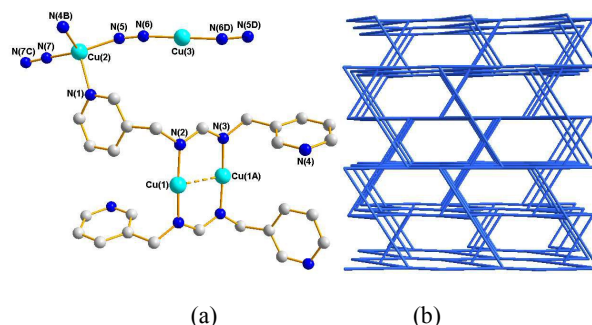


Fig. 1. (a) Coordination environment of **1**. Symmetry transformations used to generate equivalent atoms: (A) $-x + 2, -y + 2, -z + 1$. (B) $-x + 2, -y - 0.5, -z + 0.5$. (C) $-x + 1, -y + 1, -z + 1$. (D) $-x + 2, -y + 1, -z + 1$. (b) A simplified 3D structure of **1** with the $(5^3 \cdot 7^3)_2(5^4 \cdot 8^2)$ topology.

aminomethylpyridine complex,⁷ Fig. S1. The reactions thus show the isomeric effect exerted by the (aminomethyl)pyridine. The reduction of Cu(II) to Cu(I) has been observed in the hydro(solv)othermal reactions of Cu(II) salts with amine or pyridine containing ligands that may serve as effective reducing agent.^{6,8} Crystallographic data are shown in Table S2 and selected bond distances and angles are listed in Tables S3 and S(4).

The structure of **1** was solved in the space group $P2_1/c$ and Fig. 1(a) depicts a drawing showing the coordination environment about Cu(I) ions. The two Cu(I) ions that are

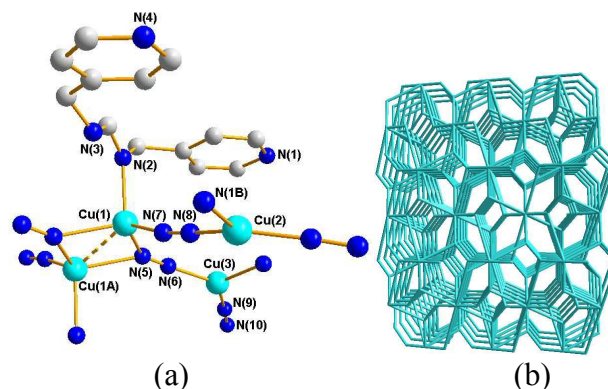


Fig. 2. (a) Coordination environment of **2**. Symmetry transformations used to generate equivalent atoms: (A) $-x + 1, -y, -z + 1$. (B) $x + 0.5, -y + 0.5, -z + 0.5$. (b) A simplified 3D structure of **2** with the $(5^3)_4(5^8 \cdot 6^4 \cdot 7^8 \cdot 8^4 \cdot 9^4)_2$ -3,8T16 topology.

bridged by two 3-mpyf ligands through two central amine nitrogen atoms show the Cu(I)---Cu(I) distance of 2.5605(8) Å, which is shorter than the sum of the van der Waals radii of Cu(I) centers (2.8 Å) and indicates the likely existence of cuprophilicity.⁹ The Cu-N distances to the inner nitrogen atoms are 1.877(3) and 1.884(3) Å, and are substantially shorter than those to the pyridyl nitrogen atoms, which are 2.128(3) and 2.160(3) Å. The Cu(2) ion that is coordinated by two pyridyl nitrogen atoms of two 3-mpyf ligands and two nitrogen atoms of two N₂⁻ anions displays the tetrahedral geometry with Cu-N distances of 1.911(3) - 2.160(3) and 2.128(3) Å, respectively. The Cu(3) ion is coordinated by two nitrogen atoms from two N₂⁻ anions with Cu-N distance of 1.849(4) Å, resulting in a linear

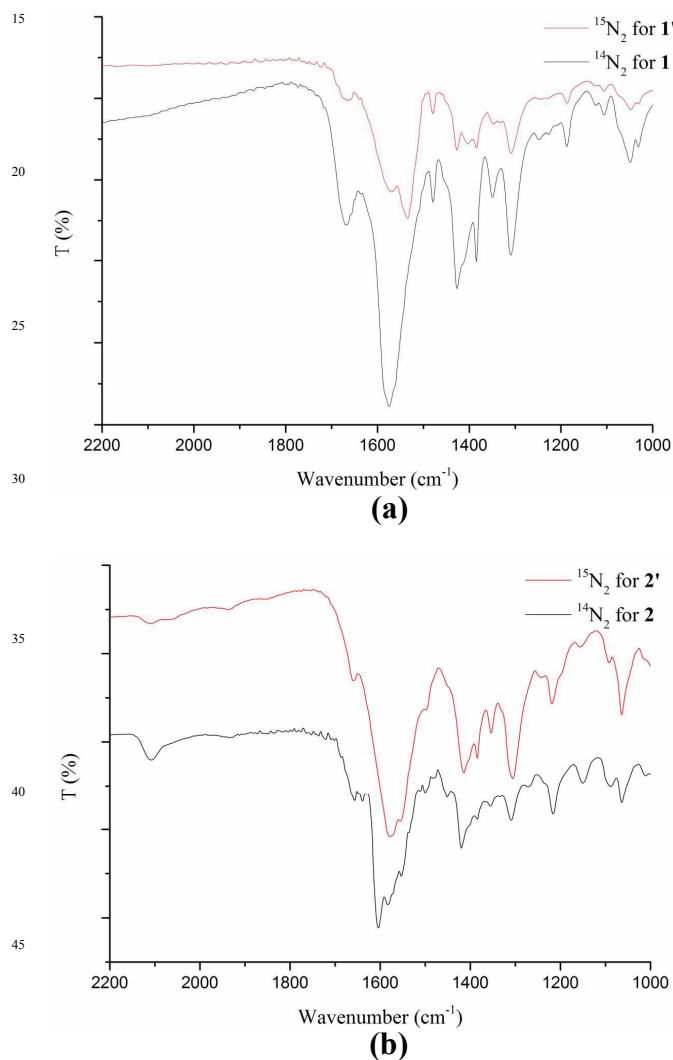


Fig. 3. IR spectroscopy for (a) **1** and **1'** on ¹⁵N labeling and (b) **2** and **2'** on ¹⁵N labeling.

geometry. The N₂⁻ anions adopt the end-on dinuclear modes with N-N distances of 1.168(4) and 1.178(6) Å that are between 1.10 and 1.25 Å found for neutral N₂ and anionic N₂²⁻, respectively.^{2h} The anionic 3-mpyf ligand coordinates to the Cu(I) ions in a tetradentate fashion through all the four nitrogen atoms. If both the Cu₂(3-mpyf)₂ unit involving the Cu(I) atoms and the Cu(2) atoms are considered as 4-connected nodes, Fig. S2(a), the 3D

structure of **1** can be regarded as a 4,4-connected binodal net with the new (5³·7³)₂(5⁴·8²) topology, Fig. 1(b), determined using TOPOS.¹⁰ Interestingly, the N₂⁻ anions and Cu(2) and Cu(3) atoms form 1D linear chains as shown in Fig. S2(b).

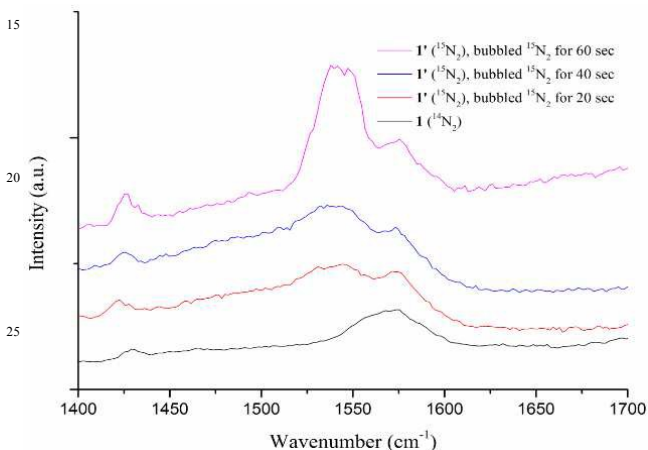
The structure of **2** was solved in the space group *P2₁/c* and Fig. 2(a) depicts a drawing showing the coordination environment about the Cu(I) ions. The Cu(1) atom is coordinated by one amine nitrogen atom of 4-Hmpyf ligand [Cu-N = 2.048(5) Å] and three N₂⁻ ligands [Cu-N = 1.924(4) - 2.174(5) Å], resulting in a tetrahedral geometry, Fig. S3(a). The two Cu(1) atoms that are bridged by two N₂⁻ anions show the Cu---Cu distance of 2.4460(13) Å, indicating the possible formation of cuprophilicity. Both of the Cu(2) and Cu(3) ions adopt the trigonal planar geometries, and each of which is coordinated by one pyridyl nitrogen atom of 4-Hmpyf ligand [Cu-N = 2.063(4) and 2.037(4) Å] and two N₂⁻ anions [Cu-N = 1.856(5) - 1.931(5) Å]. Two Cu(I) ions and two nitrogen atoms form a four-membered ring with a Cu-N-Cu angle of 71.41(16)°. The N₂⁻ anions of **2** adopt both the end-on dinuclear and the end-on trinuclear coordination modes with N-N distances of 1.152(6) - 1.168(6) Å. The rare end-on trinuclear coordination mode has been found in the heteronuclear complexes [WCl(Py)(PMe₂Ph)₃(μ₃-N₂)₂](AlCl₂)₂·C₆H₆, [WCl(PMe₂Ph)₄(μ₃-N₂)₂](GaCl₂)₂ and [(Me₃P)₃Co(μ₃-N₂)AlMe₂]₂.¹¹ The neutral 4-Hmpyf ligand coordinates to the Cu(I) ions in a tridentate fashion through the two pyridyl nitrogen atoms and one of the two central nitrogen atoms. If the center of the Cu₂(N₂)₂ unit is considered as a 8-connected node, Fig. S3(b), and the Cu(2) and Cu(3) atoms as 3-connected nodes, the 3D structure of **2** can be simplified as a 3,8-connected net with the rare (5³)₄(5⁸·6⁴·7⁸·8⁴·9⁴)₂-3,8T16 topology, Fig. 2(b), determined using TOPOS.

In order to get more insight into the charges of Cu atoms and dinitrogen, Natural Population Analysis (NPA), Natural Bond Orbital (NBO)^{12a} and Natural Localized Molecular Orbitals (NLMO)^{12b} bond order analysis were performed on the proposed complex [Cu₆(NH₃)(μ₂-N₂)₂(μ₃-N₂)₂]²⁺ assuming a *Ci* symmetry. The calculation was proceeded at the HF/6-311++G(d,p) level,¹³ which is implemented by the Gaussian 09W software package and NBO 5.0.¹⁴ The coordinates of the Cu atoms and N₂ molecules were obtained from single crystal X-ray crystallography data, whereas the 4-Hmpyf ligand is reduced as NH₃. Based on the calculations, the bond orders for μ₂-N₂⁻ and μ₃-N₂⁻ anions are 2.18 and 2.52, respectively, and the natural charges are between -0.82 and -0.83 for dinitrogen and 0.77 and 0.94 for copper atoms, respectively, which verify the formation of N₂⁻ and Cu(I) ions, Table S5 and Table S6.

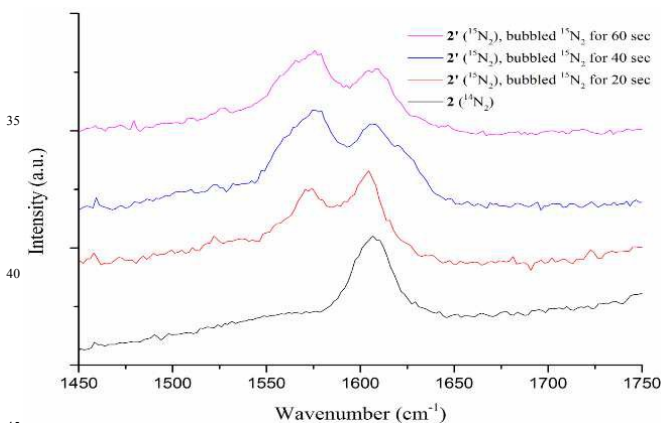
The IR spectra of **1** and **2**, Fig. 3(a) and Fig. 3(b), show strong bands at 1574 cm⁻¹ for **1** and 1603 cm⁻¹ for **2**, respectively, which shift to lower frequencies of 1534 and 1578 cm⁻¹ on ¹⁵N labeling and are thus associated with the N₂ stretching frequencies. In the resonance Raman spectra (λ_{ex} = 514 nm) measured in the solid-state, the strong bands appear at 1576 and 1607 cm⁻¹ for **1** and **2**, respectively, Fig. 4, which shift to lower frequencies of 1537 and 1575 cm⁻¹ on ¹⁵N labeling. To further confirm ν(N₂), the reaction mixtures were bubbled with different amounts of ¹⁵N₂. As shown in Fig. 4, the intensities of the bands assigned for ¹⁵N₂⁻ increase as the time of bubbling for ¹⁵N₂ increase, indicating the

correct assignment for $\nu(\text{N}_2)$. Some of inorganic complexes containing dinitrogen show bands below 1600 cm^{-1} that shift $30\text{--}50\text{ cm}^{-1}$ to lower frequencies in resonance Raman spectra on ^{15}N labeling.¹⁵

The thermogravimetric analysis (TGA) of **1**, Fig. S4 and Table S7, shows the gradual weight loss of N_2 molecules (calculated 9.86 %; observed 9.17 %) in $140\text{--}200\text{ }^\circ\text{C}$ and the weight loss in $255\text{--}450\text{ }^\circ\text{C}$ corresponds to the decomposition of 3-mpyf ligand (calculated 52.86 %; observed 53.60 %). TGA curve of **2** shows the gradual weight loss of methanol (calculated 6.01 %; observed 5.86 %) in $30\text{--}200\text{ }^\circ\text{C}$ and the removal of N_2 (calculated 15.77 %; observed 14.58 %) occurs in $200\text{--}270\text{ }^\circ\text{C}$. The weight loss of 43.17 % between $315\text{--}500\text{ }^\circ\text{C}$ corresponds to



(a)



(b)

Fig. 4. Resonance Raman spectroscopy for (a) **1** and **1'** on ^{15}N labeling and (b) **2** and **2'** on ^{15}N labeling.

the decomposition of 4-Hmpyf ligand. From the weight losses, the formation of dinitrogen in **1** and **2** can be shown. The PXRD patterns of **1** and **2** heated at $200\text{ }^\circ\text{C}$ for 3 hours, Fig. S5 and Fig. S6, reveal that their structures are not stable upon the removal of N_2 and CH_3OH . When the de-solvated samples were exposed to CH_3OH vapor and N_2 atmosphere, further changes were observed, indicating that the transformations are irreversible. Fig. S7 depicts the solid-state emission spectra of the **1** and **2** and their ^{15}N labeling complexes at room temperature. Each complex

displays two emission bands in $417\text{--}466\text{ nm}$, Table S8, which can most probably be ascribed to the metal-metal to ligand charge transfer (MMLCT) and/or ligand to ligand charge transfer (LLCT).⁶

In summary, we have successfully accomplished the first coordination polymers supported by dinitrogen. The dinitrogen anions of **1** adopt the end-on-dinuclear bonding mode, resulting in a novel 4,4-connected binodal net with the new $(5^3\cdot 7^3)_2(5^4\cdot 8^2)$ topology, whereas those of **2** display both end-on-dinuclear and end-on-trinuclear bonding modes, resulting in a rare 3,8-connected binodal net with the $(5^3)_4(5^8\cdot 6^4\cdot 7^8\cdot 8^4\cdot 9^4)_2\text{-}3,8\text{T}16$ topology. These results demonstrate that the coordination of dinitrogen is feasible through the one-pot synthesis of the Cu(I)-formamidinate and Cu(I)-formamidine coordination polymers and the structural diversity of the coordination polymers thus prepared is dependent on the donor atom position of the starting isomeric (aminomethyl)pyridine.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental Section. General bonding modes of N_2 in metal complexes (Table S1). Crystallographic data for **tpbz**, **1** and **2** (Table S2). Selected bond lengths for **1** and **2** (Table S3 and S4). Summary of natural population analysis for $[\text{Cu}_6(\text{NH}_3)(\mu_2\text{-N}_2)_2(\mu_3\text{-N}_2)_2]^{2+}$ (Table S5). Atom-atom net linear NLMO/NPA bond orders (Table S6). TGA analyses for **1** and **2** (Table S7). Luminescence data for crystalline **1** and **2** (Table S8). An ORTEP diagram for **tpbz** (Fig. S1). Connection node and packing diagram for **1** (Fig. S2). Coordination environment and connection node for **2** (Fig. S3). TGA curves for **1** and **2** (Fig. S4). Powder XRD patterns for **1** and **2** (Fig. S5 and S6). Emission and excitation spectra for **1**, **1'**, **2**, and **2'** (Fig. S7). CCDC 1056081-1056082. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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Two novel three-dimensional dinitrogen-supported coordination polymers adopting the $(5^3 \cdot 7^3)_2(5^4 \cdot 8^2)$ and $(5^3)_4(5^8 \cdot 6^4 \cdot 7^8 \cdot 8^4 \cdot 9^4)_2$ -3,8T16 topologies are reported.

