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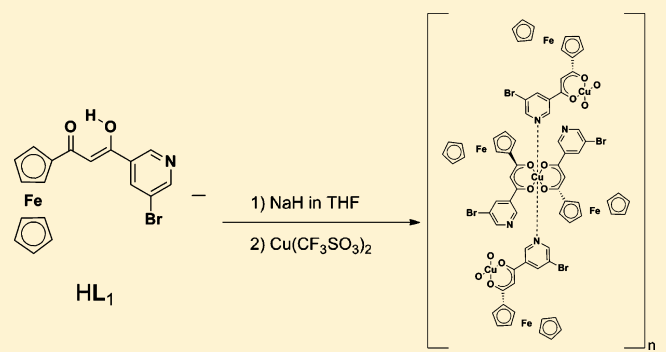
# Rational Design and Synthesis of a New Organometallic Ligand, 1-Ferrocenyl-3-(5-bromopyridyl)-prop-3-enol-1-one and Its Heteronuclear Coordination Polymer, $\{Cu[1\text{-ferrocenyl-3-(5-bromopyridyl)prop-1,3-dionate}]_2\}_n$

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## S Supporting Information

**ABSTRACT:** A new bifunctional organometallic ligand was synthesized, by reacting ferroceneacyl anion with ethyl-5-bromonicotinic acid, isolated, and characterized as 1-ferrocenyl-3-(5-bromopyridyl)-prop-3-enol-1-one ( $HL_1$ ). This new ligand reacts with Cu(II) salt to yield a new two-dimensional (2D) heteronuclear (Fe–Cu) coordination polymer of type  $[Cu(L_1)_2]_n$ . Single crystal X-ray diffraction analysis of both the ligand and the coordination polymer is provided in this report.



## INTRODUCTION

Crystal engineering of porous materials such as zeolites, coordination polymers, and metal–organic frameworks (MOFs) is a contemporary area of research<sup>1</sup> with potential uses in areas such as gas storage,<sup>2</sup> ion exchange,<sup>3</sup> catalysis,<sup>4</sup> conductivity,<sup>5</sup> drug delivery,<sup>6</sup> magnetism,<sup>7</sup> spin-transition, and nonlinear optics.<sup>8</sup> Since the early 1990s, research interest in this field is driven not only by the desire to synthesize aesthetically attractive and functionally accessible molecular helicates, strings, rings, boxes, and grids<sup>9–17</sup> but also to establish structurally complex coordination polymers similar to that of biopolymers such as proteins.<sup>18</sup>

In most of the coordination network polymers, ions of a single metal, usually labeled as nodes, are bonded to two or more multidentate organic ligands that also serve as spacers.<sup>19</sup> Coordination polymers with one type of metal center are relatively abundant, as evident from the number of reports in the literature. Recent emphasis on coordination polymers has been to introduce a second or even a third metal center in order to produce multifunctional materials.<sup>20–23</sup> While most of the heterometallic coordination polymers consist of naked metal ions bridged by organic ligands,<sup>24–28</sup> structures in which a metal is part of the linker, as an organometallic ligand, are much rarer.<sup>29–38</sup> Incorporating organometallic ligands in the design and synthesis of coordination polymers is still at a very early stage. For example, Sweigart and co-workers have used an “organometallogand”,  $[(\eta^6\text{-benzoquinone})Mn(CO)_3]^-$ , to synthesize various bimetallic coordination polymers and coined the term “metal–organometallic frameworks (MOMFs)” to identify them.<sup>39,40</sup> An organometallic sandwich complex of iron,  $[(\eta^5\text{-Cp})Fe(\eta^6\text{-1,4-benzenedicarboxylate})]^-$ , has been used to synthesize a series of 3D MOMFs containing Co(II) and Ni(II) ion.<sup>41</sup> Apart from these examples,

most of the organometallic ligands used in coordination polymer synthesis are based on commercially available ferrocenecarboxylic acid.<sup>33,34,42,43</sup> Integrating organometallic moieties as parts of multidentate ligands will be useful not only in constructing ligands with specific shapes but also in designing coordination polymers with interesting optical and electrochemical properties.<sup>44,45</sup>

Ligands such as acetylacetonate anion, pyridine, bipyridine, and their functionalized analogues are used extensively in the preparation of both classical coordination complexes and coordination polymers.<sup>24,46</sup> Similarly, ferrocene, other metallocenes, and their derivatives are generally viewed as cornerstones of contemporary organometallic chemistry.<sup>47</sup> With these basic facts in mind, we initiated a study to synthesize simple ligands<sup>48–50</sup> comprising a pyridine ring with a labile group, a metallocene, and a  $\beta$ -diketonate moiety and explore their reaction chemistry in the design and synthesis of heteronuclear coordination polymers and metal organometallic networks.

Herein, we report the synthesis of a new organometallic ligand, 1-ferrocenyl-3-(5-bromopyridyl)-prop-3-enol-1-one,  $HL_1$ , and its reaction with Cu(II) salt to form a new heteronuclear coordination polymer with  $Fe^0$ – $Cu^{II}$  ions. The coordination chemistry of this new organometallic ligand, with both transition and lanthanide metals, will enable us to design and synthesize various heteronuclear coordination polymers. Postsynthetic modification of metal organic frameworks is an emerging branch in the study of MOFs.<sup>51</sup> The “C–Br” in our new class of ligands

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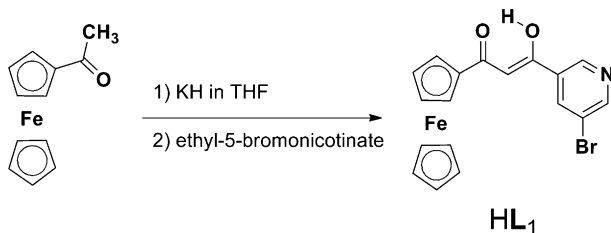


could be either converted to nonlinear ligand derivatives with more coordination sites or used for postsynthetic modification reactions of resulting coordination polymers.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Ligand.** A new organometallic ligand 1-ferrocenyl-3-(5-bromopyridyl)-prop-3-enol-1-one,  $HL_1$ , was synthesized, as shown in Scheme 1, from

Scheme 1. Synthesis of  $HL_1$



readily available acetylferrocene and ethyl-5-bromonicotinate in moderate yield (60%).

The structure of ligand  $HL_1$  was fully characterized by NMR, IR, MS, elemental analysis, and single crystal X-ray diffraction.<sup>52</sup> Even though the  $\beta$ -diketonate fragment is known to be in equilibrium between keto and enol forms, the X-ray structure of ligand  $HL_1$  clearly illustrates, as shown in Figure 1a, it to be in the enol form. The packing diagram of ligand  $HL_1$  is shown Figure 1b.

The enolic  $[=C(OH)-]$  carbon is bonded to the pyridine ring, and the carbonyl ( $>C=O$ ) carbon is connected to the ferrocene moiety. The observed bond length for the C–O single bond of the enolic moiety is 1.31 Å, and the observed bond length for the C–O double bond of the carbonyl moiety is 1.27 Å. These values are in agreement with the reported values for similar bonds.<sup>53</sup> Additional support for the enolic structure is offered by both  $^1H$  NMR and  $^{13}C$  NMR. The enolic proton  $[=C(OH)-]$  is observed at 16.64 ppm as a broad peak ( $^1H$ -MNR) and the ene carbon with a proton ( $=CH-$ ) is observed at 96.1 ppm.

**Synthesis and Characterization of a New  $Fe^0$ – $Cu^{II}$  Coordination Polymer.** The reaction chemistry of ligand  $HL_1$  was investigated. Slightly more than 2 equiv of ligand  $HL_1$  in THF reacts with NaH to generate its sodium salt, which reacts with 1 equiv of  $Cu(II)$  trifluoromethane sulfonate as shown in Scheme 2.

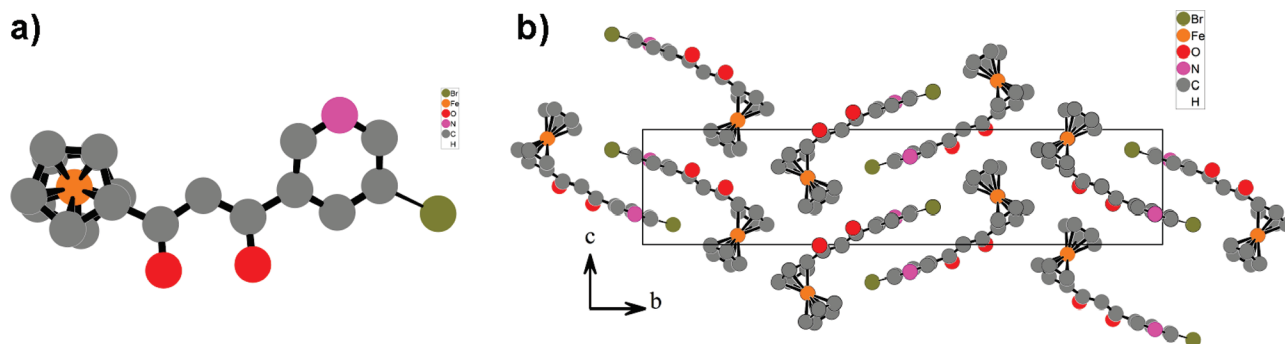
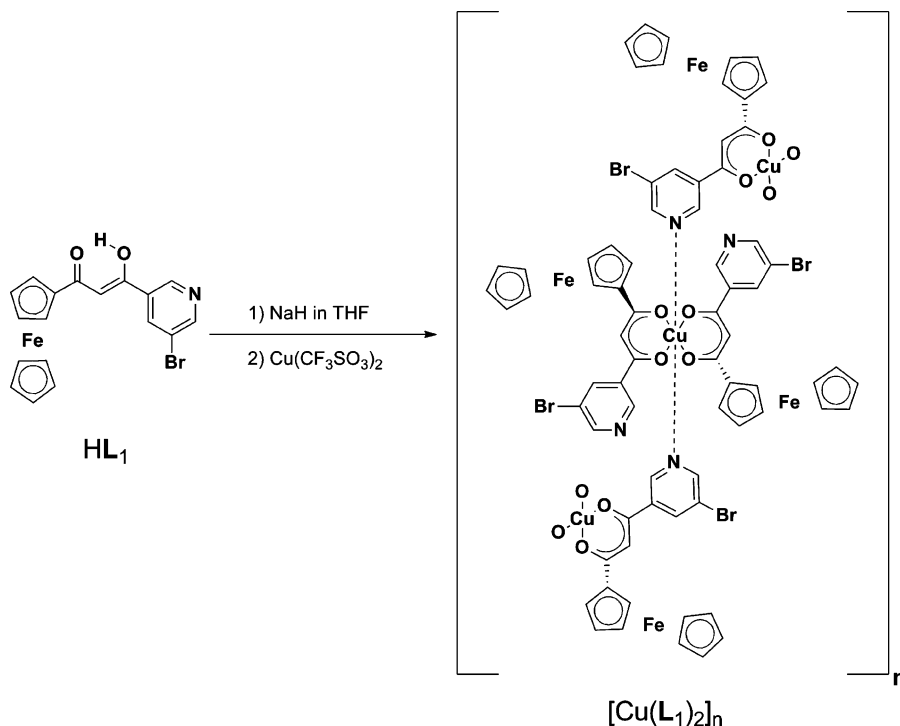
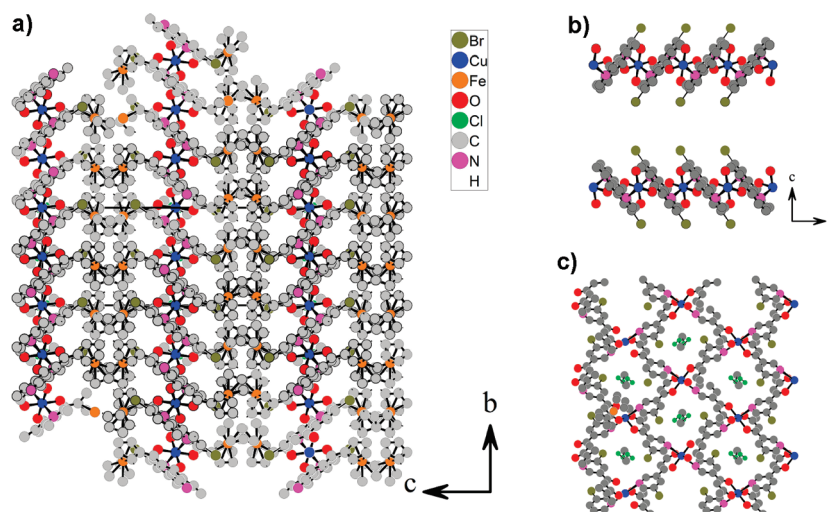


Figure 1. (a) Single molecule of the ligand,  $HL_1$ . (b) Molecular packing diagram of the ligand as seen down the  $a$ -axis.

Scheme 2. Synthesis of  $[Cu(L_1)_2]_n$  Coordination Polymer





**Figure 2.** (a) Structure of the 2D coordination polymer,  $\text{Cu}(\text{C}_{37}\text{H}_{28}\text{Fe}_2\text{N}_2\text{O}_4)_n$ , looking down the *a*-axis. Ferrocene units occupy the interlayer space. H atoms have been removed for clarity. (b) Removal of ferrocene moieties clearly shows the 2D nature of the structure. (c) Looking down a single layer of the polymer shows disordered solvent molecules occupying the voids within the layers.

Polymeric  $[\text{Cu}(\text{L}_1)_2]_n$  was isolated as a red powder in 61% yield. Single crystals suitable for X-ray analysis were obtained by dissolving  $[\text{Cu}(\text{L}_1)_2]_n$  in dichloromethane and then layering the solution with diethyl ether. The single crystal analysis revealed, as shown in Figure 2, that we have a new heteronuclear (Fe–Cu) coordination polymer of type  $[\text{Cu}(\text{L}_1)_2]_n$ .<sup>54</sup>

The oligomer in this new coordination polymer is a slightly distorted square planar  $\text{Cu}(\text{L}_1)_2$  molecule, and the Cu(II) is coordinated to two deprotonated ligands  $\text{HL}_1$  in a trans planar fashion, with two Cu–O bond lengths at 1.9279 Å and the other two at 1.9422 Å. The Cu ion is ligated to the N-terminals of two other ligands along the *z*-axis to form a distorted octahedral around the Cu. The Cu–N distance is elongated at 2.480 Å, indicative of a typical Jahn–Teller effect in Cu(II) compounds.<sup>46a</sup> Each ligand thus coordinates to two Cu ions, and each Cu is connected to four ligands to form the two-dimensional network parallel to the *bc*-plane. Figure 2a shows that the ferrocene and bromine occupy the interlayer space. Disordered methylene chloride solvent molecules are found within the voids of the layers (Figure 2c). Another interesting structural feature is the orientation of the ferrocenyl moiety and the 5-bromopyridine moiety on each ligand bonded to Cu. The ferrocenyl units are on opposite sides of “Cu–O<sub>4</sub>” square plane, the 5-bromopyridine rings are slightly twisted from the “Cu–O<sub>4</sub>”, and as a result of this, two Br atoms in each oligomer are also on opposite sides of “Cu–O<sub>4</sub>” square plane.

## CONCLUSION

In this report, we have presented the rational synthesis and structural characterization of a new organometallic ligand and a new heterometallic coordination polymer derived from it. Investigations of the reactions of this new ligand with other metal ions and the chemistry of the resulting coordination polymers are currently underway. We expect this area of investigation to be very productive on the basis of the number of permutations possible for the positions of the Br atom and the carbonyl group connected to the pyridine group. Further structural derivations can be visualized by functionalizing the ferrocenyl-end of the ligand. Hence, this new ligand may be the first in a class of new organometallic ligands with enormous

potential. We are actively exploring the possibilities and will share our results as soon as possible.

## ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures, X-ray crystallography data, ESI-MS, IR spectra, and elemental analysis results of ligand and coordination polymer; copies of NMR of ligand; and TGA curve of the coordination polymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (52) Crystal structure data for ligand: A clear, red rod of dimensions 0.5 mm × 0.08 mm × 0.03 mm was used to collect X-ray diffraction intensity data at room temperature using Mo K $\alpha$  radiation on a Bruker APEX-Kappa Duo diffractometer. A total of 7141 reflections were collected, of which 1919 reflections were independent, giving an average redundancy of 3.721 and 100% completeness to 0.95 Å resolution and a maximum  $\theta$  angle of 22.08°. Integration of the data

was done with the Bruker SAINT software package, and absorption correction was done using SADABS. The structure was solved and refined in the space group  $P2_1/n$  with  $a = 6.1383(8)$  Å,  $b = 33.808(4)$  Å,  $c = 7.5866(9)$  Å,  $b = 99.557(8)$ , and volume =  $1552.5(3)$  Å<sup>3</sup>. The data refinement converged at  $R1/wR2 = 3.96\%/9.51\%$ . GOF = 1.012. The CIF file was deposited at the Cambridge Crystallographic Data Center (CCDC 850746).

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(54) Crystal structure data for coordination polymer: A clear red platelike specimen of  $C_{37}H_{38}Br_2CuFe_2N_2O_4$ , approximate dimensions  $0.21\text{ mm} \times 0.33\text{ mm} \times 0.62\text{ mm}$ , was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at room temperature using Mo  $K\alpha$  radiation on a Bruker APEX-Kappa Duo diffractometer. A total of 13924 reflections were measured, of which 3198 were independent, giving an average redundancy of 4.35 and a completeness of 99.7% to  $0.84$  Å resolution, a maximum  $\theta$  angle of  $25.06^\circ$ , and  $R_{\text{int}} = 3.93\%$ . The frames were integrated with the Bruker SAINT software package, and absorption correction was performed using SADABS. The structure was solved and refined in the orthorhombic space group  $Pbca$  with cell constants of  $a = 14.3396(7)$  Å,  $b = 9.6045(5)$  Å,  $c = 26.1938(13)$  Å, and volume =  $3607.5(3)$  Å<sup>3</sup>. The final anisotropic full-matrix least-squares refinement on  $F^2$  with 231 variables converged at  $R1 = 3.63\%$  for the observed data and  $wR2 = 11.06\%$  for all data. The goodness-of-fit was 0.783. The largest peak in the final difference electron density synthesis was  $1.015\text{ e}^-/\text{\AA}^3$ , and the largest hole was  $-1.076\text{ e}^-/\text{\AA}^3$  with an rms deviation of  $0.104\text{ e}^-/\text{\AA}^3$ . The CIF file was deposited at the Cambridge Crystallographic Data Center (CCDC 850748).