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Metal-Mediated Controllable Creation of Secondary, Tertiary, and Quaternary Carbon Centers: A Powerful Strategy for the Synthesis of Iron, Cobalt, and Copper Complexes with in Situ Generated Substituted 1-Pyridineimidazo[1,5-*a*]pyridine Ligands

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Supporting Information

ABSTRACT: An efficient strategy for the synthesis of a wide variety of coordination complexes has been developed. The synthetic protocol involves a solvothermal in situ metal−ligand reaction of picolinaldehyde, ammonium acetate, and transition-metal ions, leading to the generation of 12 coordination complexes supported by a novel class of substituted 1-pyridineimidazo[1,5-*a*]pyridine ligands (**L1**−**L5**). The ligands **L1**−**L5** were afforded by metal-mediated controllable conversion of the aldehyde group of picolialdehyde into a ketone and secondary, tertiary, and quaternary carbon centers, respectively. Complexes of various nuclearities were obtained: from mono-, di-, and tetranuclear to 1D chain polymers. The structures of the in situ formed complexes could be controlled rationally via the choice of appropriate starting materials and tuning of the ratio of the starting materials. The plausible mechanisms for the formation of the ligands **L1**−**L5** were proposed.

INTRODUCTION

The synthesis of transition-metal complexes of imidazo[1,5-*a*]pyridine and its derivatives has attracted intense interest, especially for the following important reasons: (i) these complexes have been extensively studied for applications in OLEDs;[1] (ii) imidazo[1,5-*a*]pyridine and its derivatives have been employed as indispensable ligands in their N-heterocyclic carbene (NHC) forms to synthesize valuable transition-metal catalysts, which are useful for organic synthesis;[2] (iii) these compounds are also potential chemotherapeutic agents for DNA cleavage.[3] However, the coordination complexes of imidazo[1,5-*a*]pyridine and its derivatives are exceedingly rare, and only a handful of such complexes[1−4] were reported because of limited scope of the ligands and the strict reaction conditions required for the synthesis of the ligands. Hence, the development of a new strategy that provides access to these ligands in one step under mild conditions is in high demand and also poses an actual challenge.

The common access to imidazo[1,5-*a*]pyridine and its derivatives involves Vilsmeier-type cyclizations of *N*-2-pyridylmethylamides,[5] cyclizations of *N*-2-pyridylmethylthioamides,[6] and condensation of 2,2′-pyridil (or 2,2′-dipyridyl ketone), aldehydes, and ammonium acetate.[7] The coordination complexes of imidazo[1,5-*a*]pyridine and its derivatives are routinely generated via the traditional direct synthesis of metal ions and ligands. In the above-mentioned synthesis, researchers are guided by intuitive approaches. We envisioned that the combination of the condensation reaction[7] with the recently developed solvothermal in situ metal−ligand reaction[8,9] might be an overwhelming strategy for preparation of the targeted ligands as well as the expected complexes simultaneously.

To this end, we conducted a series of reactions of picolinaldehyde, ammonium acetate, and transition-metal ions under solvothermal conditions. Five new ligands, pyridin-2-yl(3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl) methanone (**L1**), 1,2-di(pyridin-2-yl)-1,2-bis[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl]ethane (**L2**), 1,1′,1″-(pyridin-2-ylmethanetriyl)-tris[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine] (**L3**), 1,1′-(pyridin-2-ylmethylene)bis[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine] (**L4**), and 3-(pyridine-2-yl)-1-(pyridin-2-ylmethyl)imidazo[1,5-*a*]pyridine (**L5**) (Scheme 1) and 12 novel coordination complexes, Fe(**L1**)Cl_2 (**L1-Fe**), Fe_2(**L2**)Cl_4 (**L2-Fe**), Fe_2(**L3**)-

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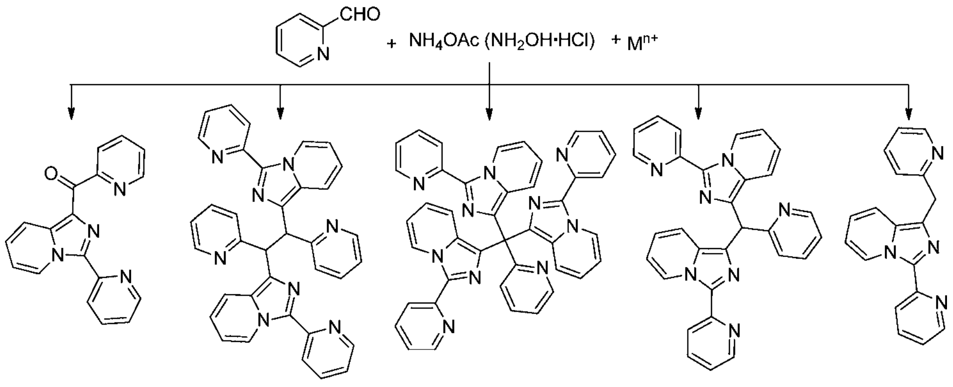
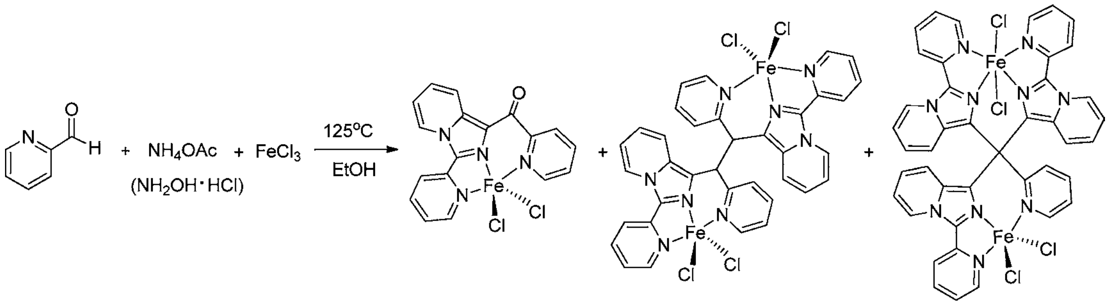
Scheme 1



L1 L2 L3 L4 L5

Table 1. Optimization of Conditions for the Controllable Synthesis of L1-Fe, L2-Fe, and L3-Fe·EtOH



L1-Fe L2-Fe L3-Fe

entry	picolinaldehyde (mmol)	NH_4OAc (mmol)	$NH_2OH·HCl$ (mmol)	$FeCl_3$ (mmol)	L1-Fe/L2-Fe/ L3-Fe·EtOH [a]
1	3	1	0	1	85:15:0
2	3	0	1	1	90:0:10
3	6	2	0	1	5:95:0
4	4	0	3	1	10:0:90
5	3	0	2	1	45:0:55
6	3	0	3	1	55:0:45
7	3	2	0	1	50:50:0
8	6	1	0	1	40:0:60

[a] Ratio of **L1-Fe**/**L2-Fe**/**L3-Fe·EtOH** in the products.

Cl_4·EtOH (**L3-Fe·EtOH**), Fe(**L4**)Cl_2 (**L4-Fe**), Co(**L1**)Cl_2·0.5EtOH (**L1-Co·0.5EtOH**), Co_2(**L2**)Cl_4 (**L2-Co**), Co_2(**L3**)Cl_4·EtOH (**L3-Co·EtOH**), Co(**L5**)Cl_2 (**L5-Co**), $\{Cu^{I}_{2}$(**L2**)$Cl_2\}_n$ (**L2-Cu**), [Cu^{II}(**L3**)Cl][$Cu^{I}Cl_2$]·2EtOH (**L3-CuA·2EtOH**), [Cu^{II}_{4}(**L3**)Cl_5][$Cu^{I}_{2}Cl_3$·2$Cu^{I}Cl_2$] (**L3-CuB**), and Cu(**L4**)Cl·EtOH (**L4-Cu·EtOH**), were generated via in situ metal−ligand reactions. The structures of the complexes could be controlled rationally via the choice of appropriate starting materials and tuning of the ratio of the starting materials. The most striking feature of the synthesis is that the controllable transformation of the aldehyde group of picolinaldehyde into ketone and secondary, tertiary, and quaternary carbon centers, respectively, has been realized. This is the first time that such conversions were achieved via a metal-mediated solvothermal in situ metal−ligand reaction.

We demonstrate in this paper this powerful strategy for the in situ generation of the 5 new ligands and 12 coordination complexes based on a solvothermal in situ metal−ligand reaction. A detailed description of the synthesis and the molecular structures of nine representative complexes are presented.

■ RESULTS AND DISCUSSION

Synthesis and Structures of Complexes L1-Fe, L2-Fe, and L3-Fe·EtOH. The initial experiment was conducted by heating a mixture of picolinaldehyde, ammonium acetate, and $FeCl_3$ (3:1:1) at 125 °C in EtOH under solvothermal conditions (Table 1). Two complexes, Fe(**L1**)Cl_2 (**L1-Fe**) and Fe_2(**L2**)Cl_4 (**L2-Fe**), with an approximate ratio of 85:15 were generated (Table 1, entry 1). Undoubtedly, the in situ metal−ligand reactions occurred and **L1-Fe** and **L2-Fe** were generated by self-assembly among picolinaldehyde, ammonium acetate, and $FeCl_3$ in ratios of 3:1:1 and 6:2:2, respectively.

Optimization of the reaction conditions was initiated upon the preparation of **L2-Fe**, motivated by the discovery that the aldehyde group of picolinaldehyde was converted into a tertiary carbon center in a one-pot reaction. Thus, the reaction aiming at improving the yield of **L2-Fe** was conducted by substituting hydroxylamine hydrochloride for ammonium acetate based on the fact that the acidic environment favors the alkylation of carbonyl[10] (Table 1, entry 2). To our delight, a new binuclear complex, Fe_2(**L3**)Cl_4·EtOH (**L3-Fe·EtOH**), was generated as a minor product, and complex **L2-Fe** was not afforded. This revealed that hydroxylamine hydrochloride and ammonium acetate played important and critical roles in controlling the chemoselectivity of the reaction. Several reactions aiming at the synthesis of **L2-Fe** using ammonium acetate as the reactant and the preparation of **L3-Fe·EtOH** employing hydroxylamine hydrochloride as the starting material were performed (Table 1, entries 3−8). It is found that the 3:1:1 reaction among picolinaldehyde, hydroxylamine hydrochloride, and $FeCl_3$, the 6:2:1 ratio of picolinaldehyde, ammonium acetate, and $FeCl_3$, and the 4:3:1 ratio of picolinaldehyde, hydroxylamine hydrochloride, and $FeCl_3$ is an optimal combination for **L1-Fe**, **L2-Fe**, and **L3-Fe·EtOH**, respectively.

The structure of **L1-Fe** was determined by X-ray diffraction (Figure 1). The central metal ion displays a 2+ valence state and is five-coordinated by two Cl^- ions and three nitrogen atoms originated from one **L1** ligand, exhibiting pseudo-trigonal-bipyramidal geometry.

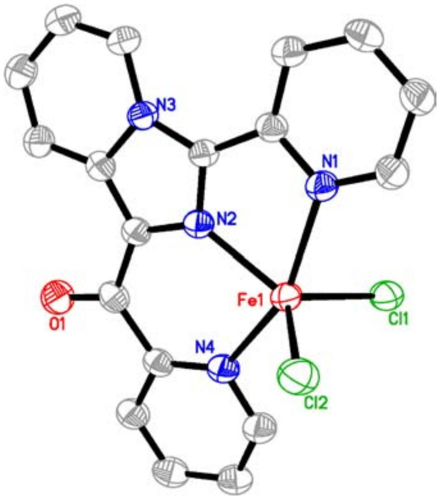


Figure 1. Labeled ORTEP plot at the 30% ellipsoid level of the molecule **L1-Fe**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

The most interesting feature regarding the synthesis of **1-Fe** is the direct coupling of picolinaldehyde and 3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine (HPIP). The latter was assumed to be preformed via the self-assembly of picolinaldehyde and ammonium acetate.[7]

The ligand **L1** was afforded from the reaction of **L1-Fe** with Na_2S.[11]

Single-crystal X-ray diffraction analysis reveals that **L2-Fe** crystallizes in the triclinic crystal system of the space group $P\bar{1}$. As shown in Figure 2, a molecule of **L2-Fe** possesses a crystallographically imposed inversion center. One ligand, **L2**, coordinates to 2 equiv of Fe^{2+} ions. Each metal ion is five-coordinated and structurally similar to that of **L1-Fe**.

The formation of **L2** in **L2-Fe** deserves some comments. Converting an aldehyde into a tertiary carbon center through nucleophilic attack of the aldehyde by 2 equiv of nucleophiles is one of the most important strategies for C−C bond making in organic synthesis, especially the preparation of porphyrin.[10] Different from the conventional reductive coupling reaction of ketones such as McMurry coupling[12] and a C−C bond-forming reaction mediated by a Grignard reagent,[13] the present method forms two tertiary carbon centers in one step. To the best of our knowledge, the simultaneous formation of two tertiary carbon centers by the self-arrangement of aldehydes and ammonium acetates via a solvothermal in situ metal−ligand reaction has never been reported.

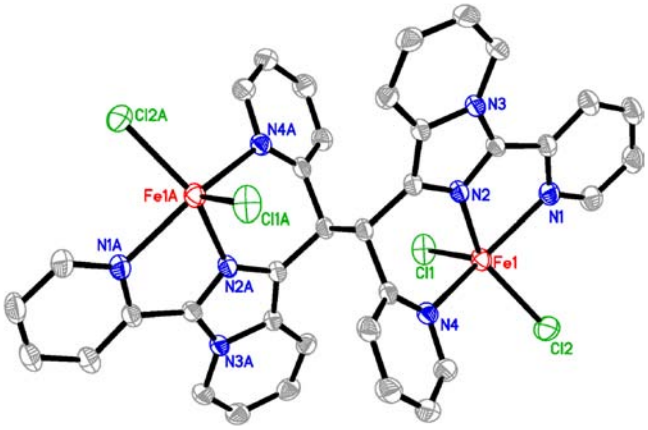


Figure 2. Labeled ORTEP plot at the 30% ellipsoid level of the molecule **L2-Fe**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

The crystal structure determination indicates that **L3-Fe·EtOH** crystallizes in the orthorhombic crystal system of the space group $Pna2_1$. A molecule of **L3-Fe·EtOH** (Figure 3) possesses one five-coordinated Fe^{2+} center and one six-coordinated Fe^{2+} ion. The six-coordinated center, Fe1, bears two Cl^- ions and four nitrogen atoms from two PIP^- ligands (the C1 position of HPIP was deprotonated), exhibiting octahedral geometry. The five-coordinated Fe2 center contains two Cl^- ions and three nitrogen atoms from one PIP^- ligand and one pyridine and is structurally similar to that of **L1-Fe**.

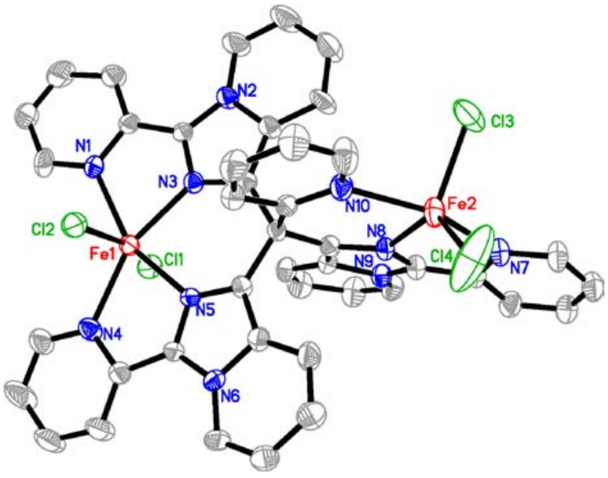
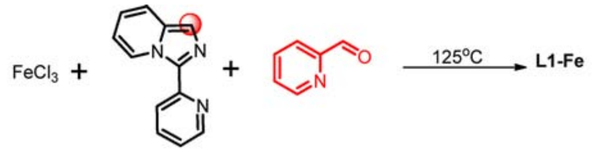


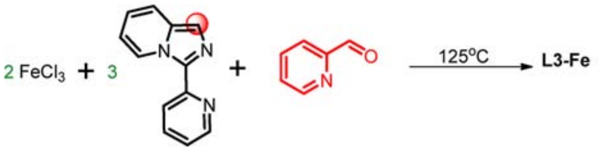
Figure 3. Labeled ORTEP plot at the 30% ellipsoid level of the molecule **L3-Fe·EtOH**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

A prominent structural feature in **L3-Fe·EtOH** is the presence of a quaternary carbon center derived from the triple additions of the aldehyde group of picolinaldehyde by 3 equiv of PIP^- ligands. The prevalence and importance of quaternary carbon scaffolds in naturally occurring biologically active molecules, pharmaceuticals, and advanced materials have made the preparation of quaternary carbon-containing compounds among the core interests of organic synthesis for over a century.[14] However, it is not easy for quaternary carbon construction.[15] This is the first time that the direct conversion of an aldehyde into a quaternary carbon center in a one-pot reaction was realized through a solvothermal in situ metal–ligand reaction.

Because the PIP$^-$ unit was consistently present in **L1-Fe**, **L2-Fe**, and **L3-Fe·EtOH**, we envisioned that these complexes may also be directly constructed via the reactions among $FeCl_3$, HPIP, and picolinaldehyde. Consequently, the reactions among these three reactants were conducted. The 1:1:1 reaction generated **L1-Fe** as a sole product (eq 1), and 2:3:1 reaction afforded **L3-Fe·EtOH** as a single product as well (eq 2). Thus, the employment of HPIP provides a perfect solution for the selective preparation of **L1-Fe** and **L3-Fe·EtOH**. The ligand **L3** was successfully isolated, and the structure was determined by X-ray diffraction.[11]

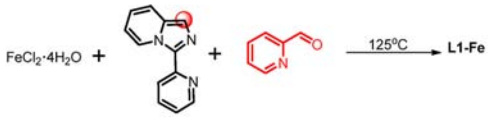


(1)

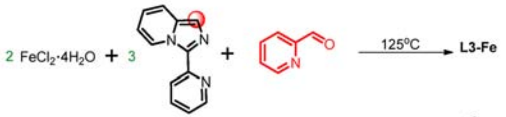


(2)

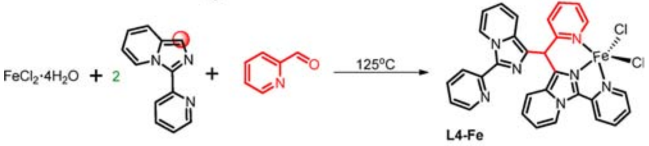
Synthesis and Structure of Complex L4-Fe. In light of the observations that the metal ions in complexes **L1-Fe**, **L2-Fe**, and **L3-Fe·EtOH** are all in 2+ valence states, we are curious whether the Fe^{2+} ion could also mediate the formations of **L1-Fe**, **L2-Fe**, and **L3-Fe·EtOH**. To this end, three reactions among $FeCl_2 \cdot 4H_2O$, HPIP, and picolinaldehyde were examined (eqs 3–5). The 1:1:1 reaction generated **L1-Fe** as a sole product in good yield, the 2:3:1 reaction afforded **L3-Fe·EtOH** in very low yield, and the 1:2:1 reaction provided a new complex, **L4-Fe**, as a sole product in moderate yield.



(3)



(4)



(5)

The solid-state structure of **L4-Fe** determined by X-ray diffraction is shown in Figure 4. The complex consists of the ligand **L4**, which bears a tertiary carbon center assumed to be derived from the double additions[16] of the aldehyde group by 2 equiv of HPIP molecules, two Cl^- ions, and one Fe^{2+} ion. Two nitrogen atoms of one PIP$^-$ unit are involved in the coordination, and the coordination geometry of the Fe^{2+} ion is analogous to that of **L1-Fe**.

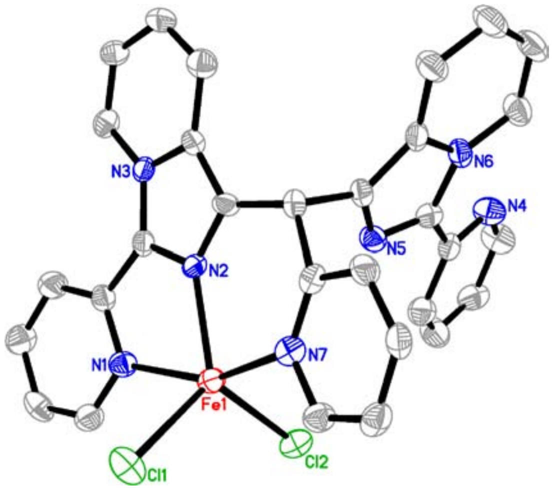


Figure 4. Labeled ORTEP plot at the 30% ellipsoid level of the molecule **L4-Fe**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

The ligand **L4** was also successfully isolated from the reaction of **L4-Fe** with Na_2S.[11]

Synthesis and Structures of Complexes L1-Co·0.5EtOH, L2-Co, L3-Co·EtOH, and L5-Co. Intrigued by the unexpected synthesis of **L4-Fe** via the employment of the Fe^{2+} ion as the metal source, we next turned our attention to Co^{2+}. Accordingly, a series of reactions targeted for generation of the ketone (**L1**), with the molecules bearing tertiary and quaternary carbon centers employing optimized reaction conditions, were conducted. The results are collected in Table 2.

As can be seen from Table 2, four complexes, **L1-Co·0.5EtOH**, **L2-Co**, **L3-Co·EtOH**, and **L5-Co**, were synthesized. The structures of these complexes were all determined by X-ray diffraction.[11] The structures of **L1-Co·0.5EtOH**, **L2-Co**, and **L3-Co·EtOH** are isomorphous and isostructural with **L1-Fe**, **L2-Fe**, and **L3-Fe·EtOH**, respectively.

To our delight, the 4:1:1 reaction among picolinaldehyde, ammonium acetate, and $CoCl_2 \cdot 6H_2O$ provided a mononuclear complex, **L5-Co**. The solid-state structure of **L5-Co** determined by X-ray diffraction is shown in Figure 5. The metal center of **L5-Co** was supported by the in situ formed ligand **L5**. The coordination environment around the Co^{2+} ion is analogous to that of **L1-Fe**.

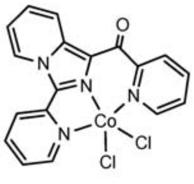
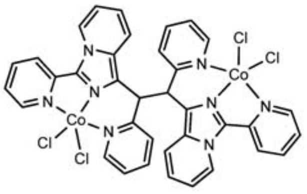
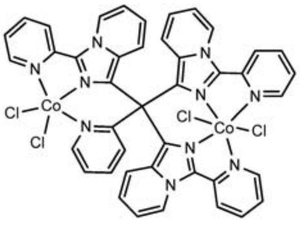
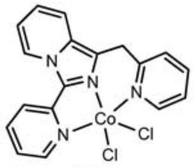
An intriguing feature regarding the synthesis of **L5-Co** is the direct conversion of the aldehyde group of picolinaldehyde into a secondary carbon center. The successful preparation of **L5-Co** perfects our attempts for stepwisely transforming the aldehyde group of picolinaldehyde into a ketone and secondary, tertiary, and quaternary carbon centers, respectively.

Synthesis and Structures of Complexes L2-Cu, L3-CuA·2EtOH, L3-CuB, and L4-Cu·EtOH. The solvothermal in situ metal–ligand reactions among $CuCl_2 \cdot 2H_2O$, HPIP, picolinaldehyde, and ammonium acetate were also explored. The results are summarized in Table 3.

As can be seen from Table 3, four complexes, **L2-Cu**, **L3-CuA·2EtOH**, **L3-CuB**, and **L4-Cu·EtOH**, were generated.

The 6:1:1 reaction among picolinaldehyde, ammonium acetate, and $CuCl_2 \cdot 2H_2O$ provides **L2-Cu** as a coordination polymer. The X-ray diffraction analysis reveals that **L2-Cu** exhibits a 1D polymeric chain structure (Figure 6). The asymmetric unit of **L2-Cu** involves one Cu^+ ion, one in situ

Table 2. Complexes Produced by the Reactions among HPIP, Picolinaldehyde, NH_4OAc, and $CoCl_2·6H_2O$

HPIP:Picolialdehyde:NH_4OAc:$CoCl_2·6H_2O$	Complex
1:1:0:1[a]	 **L1-Co**
0:6:2:1	 **L2-Co**
3:1:0:2[a]	 **L3-Co**
0:4:1:1	 **L5-Co**

[a] The solvate molecule was omitted for clarity.

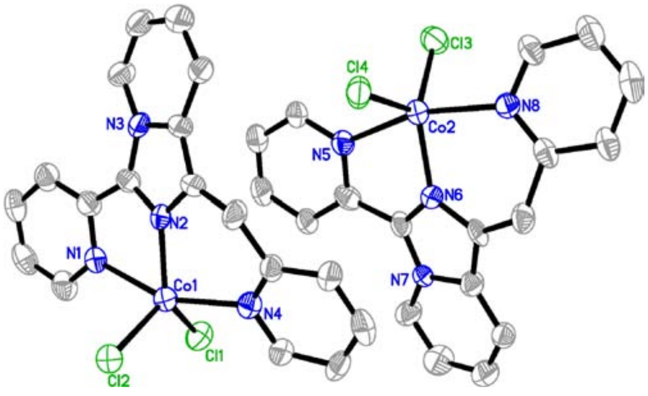
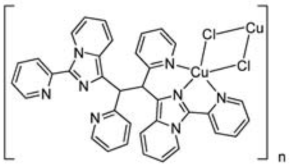
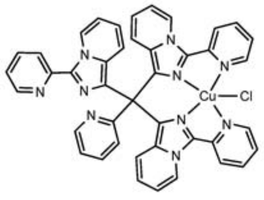
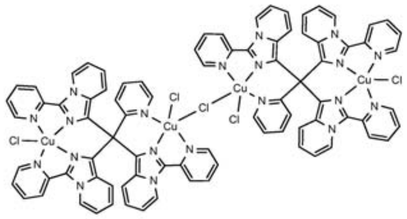
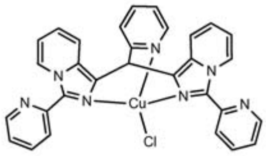


Figure 5. Labeled ORTEP plot at the 30% ellipsoid level of the molecule **L5-Co**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

formed **L2** ligand, and two Cl^- ions. The central Cu^+ ion was coordinated by two bridging Cl^- ions, two nitrogen atoms from one PIP^- unit, and one nitrogen atom from pyridine, displaying distorted tetrahedral geometry. The two adjacent Cu^+ ions were doubly bridged by two Cl^- ions, leading to a 1D infinite chain structure (Figure 7).

Table 3. Complexes Produced by the Reactions among HPIP, Picolinaldehyde, NH_4OAc, and $CuCl_2·2H_2O$

HPIP:Picolialdehyde:NH_4OAc:$CuCl_2·2H_2O$	Complex
0:6:1:1[a]	 **L2-Cu**
3:1:0:2[b,d]	 **L3-CuA**
2:1:0:4[c]	 **L3-CuB**
2:1:0:1[d]	 **L4-Cu**

[a] $NH_2OH·HCl$ was employed for the synthesis of **L2-Cu**. [b] Counterion $[CuCl_2]^-$ was omitted for clarity. [c] Counterion $[Cu_2Cl_3][CuCl_2]_2{}^{3-}$ was omitted for clarity. [d] The solvate molecule was omitted for clarity.

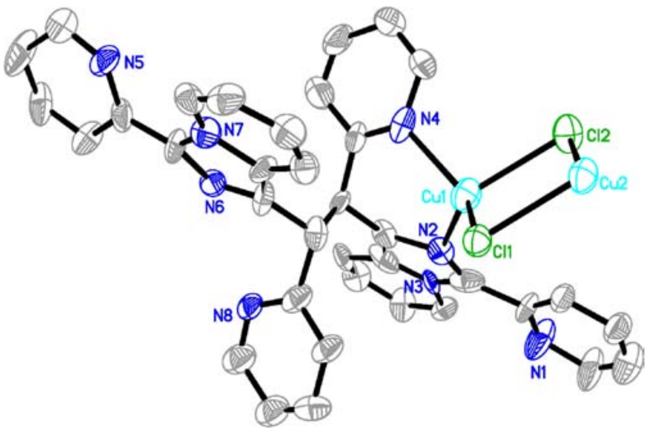


Figure 6. Asymmetric unit of **L2-Cu** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

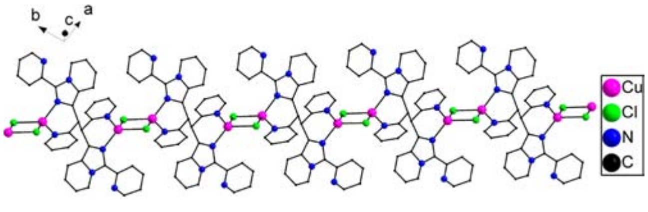


Figure 7. 1D polymeric chain of **L2-Cu** with alternating **L2** ligand and Cu_2Cl_2 unit.

Complex **L2-Cu** features intramolecular C−H···N hydrogen contacts between the CH group of the imidazo[1,5-*a*]pyridine ring as the hydrogen-atom donor and the nitrogen atom from a pyridine molecule as the acceptor. In addition, noticeable intermolecular C−H···Cl contacts from the CH group of the imidazo[1,5-*a*]pyridine (donor) to the coordinated chloride ion (acceptor) are determined. A 3D network is formed in the crystal packing through intermolecular C−H···Cl hydrogen bonds (Figure 8).

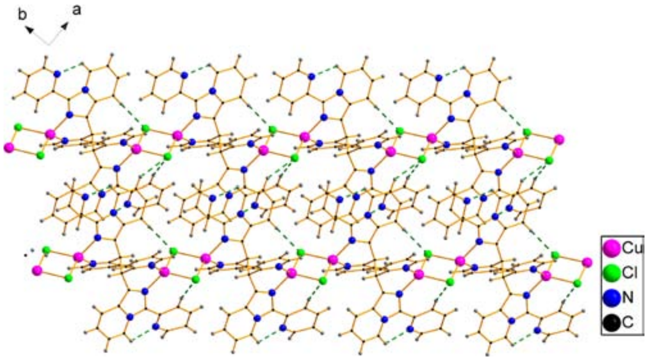


Figure 8. Crystal-packing diagram of **L2-Cu** formed by intermolecular C−H···Cl hydrogen bonds. Hydrogen contacts are represented by the dotted lines.

The syntheses of **L3-CuA·2EtOH** and **L3-CuB** are also intriguing. Instead of giving a **L3**-supported binuclear complex, the 3:1:2 reaction among HPIP, picolinaldehyde, and $CuCl_2·2H_2O$ provided a mononuclear complex, **L3-CuA·2EtOH**. The crystal structure determination reveals that **L3-CuA·2EtOH** (Figure 9) is a mixed-valent Cu^{2+}/Cu^{+} complex. The Cu^{2+} ion was coordinated by four nitrogen atoms from two PIP^- units and one Cl^- ion, leaving two nitrogen atoms of the third PIP^- moiety and one nitrogen atom of the pyridine uncoordinated. The positive charge of the central metal was balanced by $[CuCl_2]^-$. We envisioned that these three metal-free nitrogen atoms would further coordinate to the copper ion to yield a polynuclear Cu^{2+} complex.

Along this line, we carried out the 2:1:4 reaction among HPIP, picolinaldehyde, and $CuCl_2·2H_2O$. Gratifyingly, a tetranuclear complex, **L3-CuB**, was afforded.

X-ray analysis reveals that **L3-CuB** is a tetranuclear mixed-valent Cu^{2+}/Cu^{+} complex (Figure 10). The coordination modes of the two terminal Cu^{2+} ions are analogous to that of the copper ion in **L3-CuA·2EtOH**. The two central Cu^{2+} ions are bridged by one Cl^- ion, with the coordination environment of each Cu^{2+} ion being similar to that of **L1-Fe**. The positive charge of the coordination unit $[Cu_4(L3)_2Cl_5]^{3+}$ was compensated for by a $[Cu_2Cl_3][CuCl_2]_2^{3-}$ ion.

The structure of complex **L4-Cu·EtOH** is interesting as well (Figure 11). The central copper ion of **L4-Cu·EtOH** exhibits a

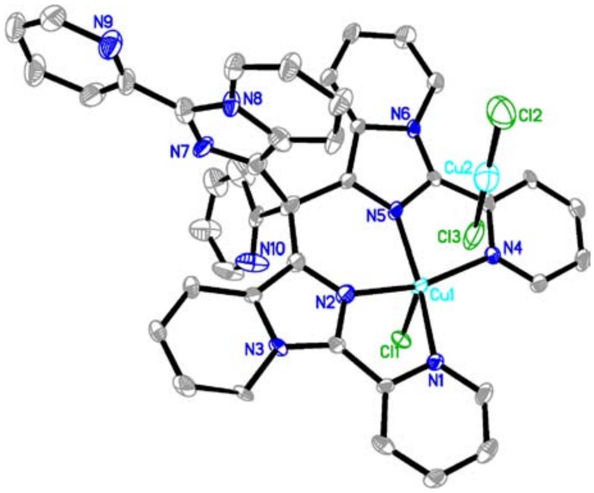


Figure 9. Labeled ORTEP plot at the 30% ellipsoid level of **L3-CuA·2EtOH**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

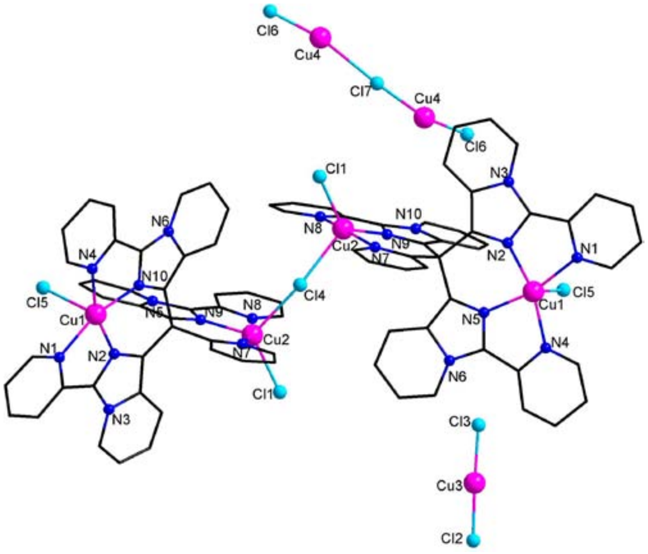


Figure 10. Molecular structure of **L3-CuB**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

1+ valence state and is four-coordinated by two nitrogen atoms from two PIP^- units, one nitrogen atom from one pyridine atom, and one Cl^- ion. The geometry of the central Cu^+ ion is best described as tetrahedron. The coordination mode of the **L4** ligand of **L4-Cu** is totally different from that of **L4-Fe**.

Mechanisms for the in Situ Generation of the L1−L5 Ligands. Naturally, we were interested in the mechanisms for the formation of the **L1**−**L5** ligands, i.e., the plausible pathways for converting the aldehyde group of picolinaldehyde into the ketone and secondary, tertiary, and quaternary carbon centers, respectively.

The proposed mechanisms for the construction of **L1**−**L5** are outlined in Scheme 2. Initially, coordination of the oxygen atom of picolinaldehyde to M^{n+} or H^+ enhances the electrophilicity of the carbon atom of the aldehyde, triggering the formation of an alcoholic intermediate, **IN1**, via the nucleophilic attack of HPIP to the carbonyl electrophile. Next,

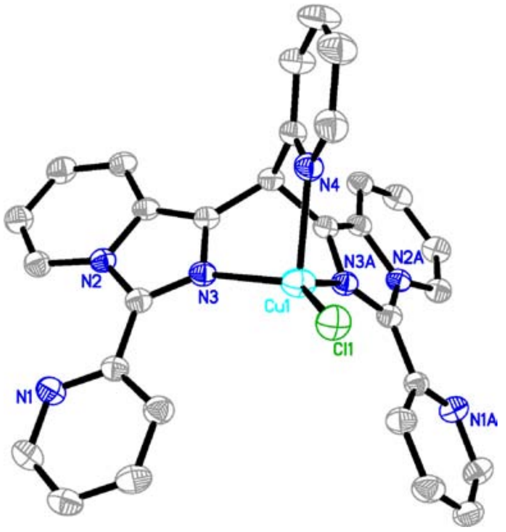


Figure 11. Labeled ORTEP plot at the 30% ellipsoid level of **L4-Cu**. Hydrogen atoms have been omitted for clarity. Crystallographic data and selected bond lengths and angles are given in the Supporting Information.

three competitive reactions may occur for **IN1**: (1) Formation of **L1** upon oxidation of the O_2 molecule (**L1** can also be generated from 2,2′-pyridil).[7b] (2) Cleavage of the C−O bond gives a radical intermediate, **IN2**, which subsequently either undergoes dimerization to afford **L2** or attacks electron-rich HPIP to furnish the formation of **L5**. (3) The Friedel−Craft reaction of **IN1** with another 1 equiv of HPIP affords **L4** because HPIP is a nitrogen-containing 10π-electron aromatic moiety and easily undergoes alkylation reaction in the presence of a Lewis acid. Two tentative pathways are proposed for the generation of **L3**. The double additions of the carbonyl of the aldehyde accompanying dehydration result in a quaternary carbon moiety (**L3**). Alternatively, **L1** reacts with HPIP through the addition of a ketone to give a tertiary alcohol intermediate, **IN3**, which subsequently is subjected to C−O cleavage, affording a radical intermediate, **IN4**. The attack of **IN4** on HPIP either provides **L3** or affords **L4**.

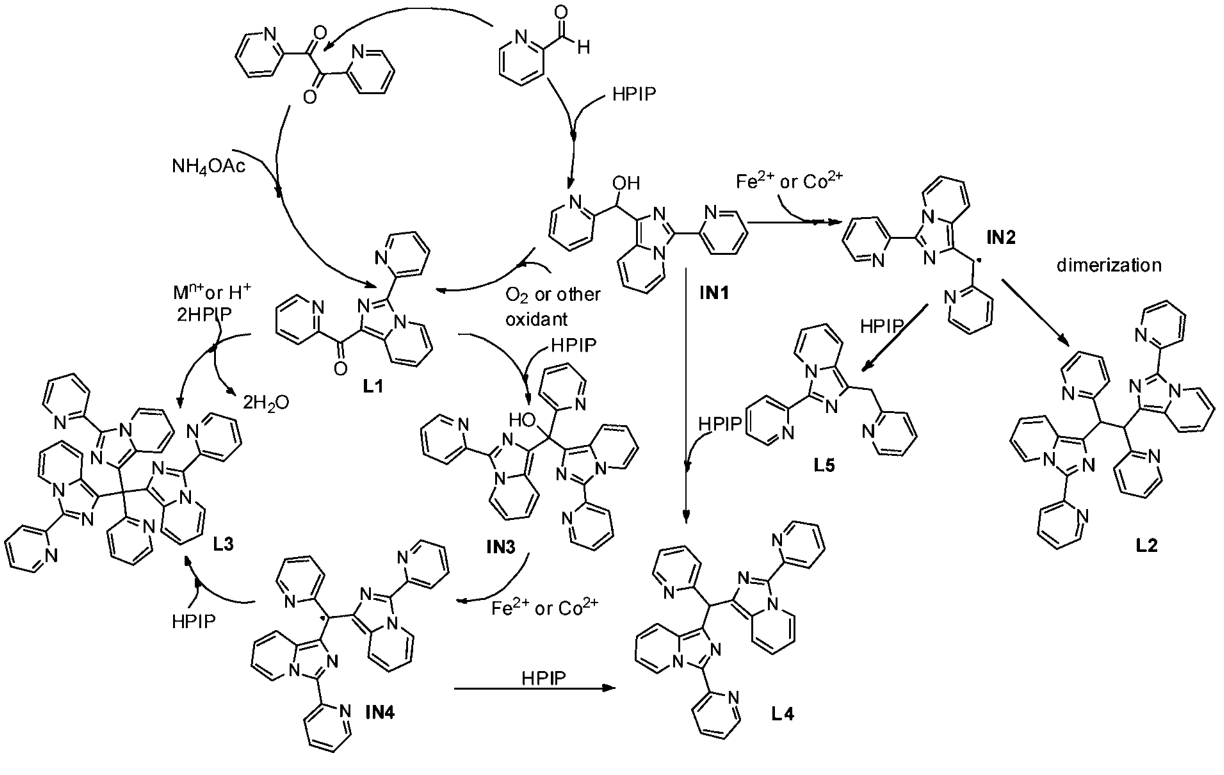
The radical mechanism and the involvement of O_2 in the reactions were furthur confirmed by a series of experiments. Adding the radical scavenger 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl to the 3:1:2 reaction among HPIP, picolinaldehyde, and $FeCl_3$ (or $CoCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$) did not result in the formation of **L3-Fe** (or **L3-Co** and **L3-CuA**). The 3:1:2 reaction among HPIP, picolinaldehyde, and $FeCl_2{\cdot}4H_2O$ (or $CoCl_2{\cdot}6H_2O$) was performed in a drybox (exclusive inert atmosphere), and **L3-Fe** (or **L3-Co**) was not afforded, indicating that O_2 serves as the oxidant in some reactions.

The functions of the metals in the reaction system were investigated by conducting blank experiments without the aid of metal ions. The ligands **L2**, **L3**, and **L5** could not be afforded in the blank experiments. The ligand **L1** can be synthesized from the reaction of picolinaldehyde and NH_4OAc in acetic acid,[7a] and the structure was determined by X-ray diffraction;[11] ligand **L4** could be generated by the 2:1 reaction of HPIP and picolinaldehyde.[11] However, the yields of **L1** and **L4** in the above-mentioned blank experiments are low, indicating that the metals serve as either oxidants or templates in the syntheses of the complexes reported in this paper.

■ CONCLUSION AND PERSPECTIVE

In summary, the metal-mediated controllable and stepwise conversion of the aldehyde group of picolinaldehyde into a ketone and secondary, tertiary, and quaternary carbon centers, respectively, was realized for the first time, leading to the in situ

Scheme 2. Proposed Mechanisms for the Synthesis of L1−L5



generation of 12 novel coordination complexes. The 3:1:1 reaction of picolinaldehyde, NH_4OAc, and $FeCl_3$ gave two products, **L1-Fe** and **L3-Fe·EtOH**. The strategy of employing HPIP as the reactant provided a perfect and convenient solution for the selective preparation of **L1-Fe** and **L3-Fe·EtOH**. Substituting hydroxylamine hydrochloride for ammonium acetate in the 3:1:1 reaction afforded **L2-Fe** in good yield. The introduction of the Fe^{2+} ion as the reactant provided **L4-Fe**, and the involvement of the Co^{2+} ion in the reaction generated **L5-Co**. Moreover, two mixed-valent Cu^{2+}/Cu^+ complexes, **L3-CuA·2EtOH** and **L3-CuB**, and two Cu^+ complexes, **L2-Cu** and **L4-Cu·EtOH**, were synthesized. As polydentate nitrogen-fused heterocycles, the **L1−L5** ligands have potential utility in supramolecular structures (network, helical, box, etc.) The dichloro-coordinated complexes are potential catalysts for the olefin polymerization reaction. An in-depth research to produce more interesting products by the addition of alternative aldehydes (furan-2-carbaldehyde and thiophene-2-carbaldehyde) and the catalytic properties of these complexes are under investigation in our laboratory. Our studies, already well advanced, will be reported in due course.

■ EXPERIMENTAL SECTION

All manipulations were performed under aerobic (unless otherwise stated) and solvothermal conditions using reagents and solvents as received.

{Pyridin-2-yl[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl]methanone}$FeCl_2$ (L1-Fe). A mixture of picolinaldehyde (0.0321 g, 0.3 mmol), ammonium acetate (0.0077 g, 0.1 mmol), $FeCl_3$ (0.0161 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave brown crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 40% (based on $FeCl_3$). Elem anal. Calcd for $C_{18}H_{12}Cl_2FeN_4O$: C, 66.66; H, 4.48; N, 15.55. Found: C, 65.98; H, 4.34; N, 15.48.

{1,2-Di(pyridin-2-yl)-1,2-bis[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl]ethane}Fe_2Cl_4 (L2-Fe). A mixture of picolinaldehyde (0.0642 g, 0.6 mmol), ammonium acetate (0.0154 g, 0.2 mmol), $FeCl_3$ (0.0161 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave orange crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 53% (based on $FeCl_3$). Elem anal. Calcd for $C_{36}H_{26}Cl_4Fe_2N_8$: C, 52.46; H, 3.18; N, 13.60. Found: C, 51.61; H, 2.96; N, 14.25.

{1,1′,1″-(Pyridin-2-ylmethanetriyl)tris[3-(pyridine-2-yl)imidazo[1,5-*a*]pyridine]}Fe_2Cl_4·EtOH (L3-Fe·EtOH). A mixture of picolinaldehyde (0.0428 g, 0.4 mmol), hydroxylamine hydrochloride (0.0207 g, 0.3 mmol), $FeCl_3$ (0.0161 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave red crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 54% (based on $FeCl_3$). Elem anal. Calcd for $C_{44}H_{34}Cl_4Fe_2N_{10}O$: C, 54.35; H, 3.52; N, 14.41. Found: C, 54.47; H, 3.14; N, 14.37.

{1,1′-(Pyridin-2-ylmethylene)bis[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridine]}$FeCl_2$ (L4-Fe). A mixture of HPIP (0.0195 g, 0.1 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $FeCl_2·4H_2O$ (0.0199 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave light-green crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 19% (based on $FeCl_2·4H_2O$). Elem anal. Calcd for $C_{30}H_{21}Cl_2FeN_7$: C, 59.43; H, 3.49; N, 16.17. Found: C, 59.59; H, 3.26; N, 16.06.

{Pyridin-2-yl[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl]methanone}$CoCl_2$·0.5EtOH (L1-Co·0.5EtOH). A mixture of HPIP (0.0195 g, 0.1 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $CoCl_2·6H_2O$ (0.0237 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave brown crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 16% (based on $CoCl_2·6H_2O$). Elem anal. Calcd for $C_{38}H_{30}Cl_4Co_2N_8O_3$: C, 50.36; H, 3.34; N, 12.36. Found: C, 50.28; H, 3.52; N, 12.65.

{1,2-Di(pyridin-2-yl)-1,2-bis[3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-1-yl]ethane}Co_2Cl_4 (L2-Co). A mixture of picolinaldehyde (0.0642 g, 0.6 mmol), ammonium acetate (0.0154 g, 0.2 mmol), $CoCl_2·6H_2O$ (0.0237 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave purple crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 55% (based on $CoCl_2·6H_2O$). Elem anal. Calcd for $C_{36}H_{26}Cl_4Co_2N_8$: C, 52.07; H, 3.16; N, 13.50. Found: C, 51.97; H, 3.17; N, 12.88.

{1,1′,1″-(Pyridin-2-ylmethanetriyl)tris[3-(pyridin-2-yl)-imidazo[1,5-*a*]pyridine]}Co_2Cl_4·EtOH (L3-Co·EtOH). A mixture of HPIP (0.0585 g, 0.3 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $CoCl_2·6H_2O$ (0.0237 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave light-brown crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 19% (based on $CoCl_2·6H_2O$). Elem anal. Calcd for $C_{44}H_{34}Cl_4Co_2N_{10}O$: C, 54.01; H, 3.50; N, 14.31. Found: C, 53.36; H, 3.25; N, 14.17.

{3-(Pyridin-2-yl)-1-(pyridin-2-ylmethyl)imidazo[1,5-*a*]-pyridine}$CoCl_2$ (L5-Co). A mixture of picolinaldehyde (0.0428 g, 0.4 mmol), ammonium acetate (0.0077 g, 0.1 mmol), $CoCl_2·6H_2O$ (0.0237 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave purple crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 10% (based on $CoCl_2·6H_2O$). Elem anal. Calcd for $C_{18}H_{14}Cl_2CoN_4$: C, 51.95; H, 3.39; N, 13.46. Found: C, 51.38; H, 3.19; N, 13.05.

{{1,2-Di(pyridin-2-yl)-1,2-bis[3-(pyridin-2-yl)imidazo-[1,5-*a*]pyridin-1-yl]ethane}$Cu^{I}_2Cl_2$}$_n$ (L2-Cu). A mixture of picolinaldehyde (0.0647 g, 0.6 mmol), hydroxylamine hydrochloride (0.0070 g, 0.1 mmol), $CuCl_2·2H_2O$ (0.0169 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 135 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave green crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 20% (based on $CuCl_2\cdot 2H_2O$). Elem anal. Calcd for $[C_{36}H_{26}Cl_2Cu_2N_8]_n$: C, 56.25; H, 3.41; N, 14.58. Found: C, 56.05; H, 3.34; N, 14.43.

{1,1′,1″-(Pyridin-2-ylmethanetriyl)tris[3-(pyridin-2-yl)-imidazo[1,5-*a*]pyridine]}$Cu^{I}Cu^{II}Cl_3\cdot 2EtOH$ (L3-CuA·2EtOH). A mixture of HPIP (0.0585 g, 0.3 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.0338 g, 0.2 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave green crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 38% (based on picolinaldehyde). Elem anal. Calcd for $C_{46}H_{40}Cl_3Cu_2N_{10}O_2$: C, 55.34; H, 4.04; N, 14.03. Found: C, 54.47; H, 4.22; N, 14.74.

{1,1′,1″-(Pyridin-2-ylmethanetriyl)tris[3-(pyridin-2-yl)-imidazo[1,5-*a*]pyridine]}$Cu^{II}_4Cl_5\cdot Cu^{I}_2Cl_3\cdot 2Cu^{I}Cl_2$ (L3-CuB). A mixture of HPIP (0.0390 g, 0.2 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.0676 g, 0.4 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave green crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 20% (based on picolinaldehyde). Elem anal. Calcd for $C_{84}H_{56}Cl_{12}Cu_8N_{20}$: C, 44.26; H, 2.48; N, 12.29. Found: C, 44.09; H, 2.56; N, 11.44.

{1,1′-(Pyridin-2-ylmethylene)bis[3-(pyridin-2-yl)-imidazo[1,5-*a*]pyridine]}$CuCl\cdot EtOH$ (L4-Cu·EtOH). A mixture of HPIP (0.0390 g, 0.2 mmol), picolinaldehyde (0.0107 g, 0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.0169 g, 0.1 mmol), and EtOH (3 mL) was sealed in a 8 mL Pyrex tube. The tube was heated for 3 days at 125 °C under autogenous pressure. Slow cooling of the resultant solution to room temperature over 24 h gave yellow crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 3 mL), and dried in air. Yield: 60% (based on $CuCl_2\cdot 2H_2O$). Elem anal. Calcd for $C_{32}H_{27}ClCuN_7O$: C, 61.53; H, 4.36; N, 15.70. Found: C, 61.89; H, 4.35; N, 16.20.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, details of the synthesis of the complexes, and additional X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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