**Synthesis and Characterization of Two Polydentate Pyridylamines,
Their Acidified Salts and Late First-Row Transition Metal Complexes**

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Abstract: Synthesis and characterization of a new tripodal polydentate pyridylamine ^C**L** and an improved synthesis of analogue ^N**L** were developed. Acidified salts of the two polyamines (^C**LH** and ^N**LH**), one trizinc (**1**), and two monometallic complexes (**2** and **3**) were synthesized and structurally characterized. Protonation of the polyamines occurred at the pyridine N atoms, strongly supported by the hydrogen bonds between the cations and anions in the extended network. Structural analysis of the three complexes supported by ^N**L** demonstrated its versatile coordination modes.

Graphic abstract:

Convenient synthesis of two tripodal polydentate pyridylamines was accomplished. Structural analysis of their acidified salts determined that protonation of the polyamines occurred at the pyridine N atoms. Versatile coordination modes of one pyridylamine with late first-row transition metal atoms were also revealed.

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Introduction

Ligand framework and design play a vital role in developing new transition-metal complexes and metal-containing catalysts.¹ Variations in ligand properties, including the nature, number and relative arrangement of the binding sites, as well as the geometric and electronic characteristics of the ligands, dictate the success of the synthesis, coordination modes and overall properties of the complex products.² Reactivities of these complexes are also dependent on these factors as a whole. In addition, catalyst design requires specific ligand scaffolds to accommodate special needs of the active centers. In general, catalysts demanding strong oxidizing powers require ligands that can resist oxidation,³ while catalysts of strong reducing abilities desire electron-rich ligands.⁴ Furthermore, remarkable catalytic reactivities have been revealed when a fine tune of the ligand scaffold was applied, which has led to widespread use of metal complexes as highly efficient catalysts.⁵

Polydentate ligand systems have exhibited extensive use in coordination chemistry due to the greater thermodynamic stability of the metal complexes when compared to those supported exclusively by monodentate ligands.⁶ During a catalytic

cycle, part of the ligand can fall off to free some coordination sites required for catalytic processes, while simultaneously maintaining the integrity of the metal catalysts.⁷ The ligand topology largely governs the properties and reactivities of the complex products. Ligand modification through derivatization and the choice of metal ions can further alter the properties of the complexes, thus allowing greater tunability in catalytic reactivity.⁸

One common design method of polydentate ligands is to install multiple groups of coordination sites onto a single- or multiple-atom core.⁹ Through this design, several classes of tripodal ligands containing three branches have been successfully developed.¹⁰ The lone pairs from the three branches together behave like a three-prong clamp and secure one or multiple metal centers in close proximity. This approach has led to the successful synthesis of single-metal compounds,¹¹ bimetallic complexes,¹² and polymetallic clusters,¹³ as well as remarkable reactivities of the complexes.¹⁴ When a N-containing hexadentate tripodal ligand *N,N,N*-tris[2-(2-pyridylamino)ethyl]amine (^N**L**, Scheme 1) was applied, both homobimetallic and heterobimetallic complexes with interesting interactive properties were obtained.¹⁵ Here, we developed a convenient methodology to synthesize the tripodal ligand ^N**L** and extend it to a new tripodal pyridylamine 1,1,1-tris[(2-pyridylamino)methyl]ethane (^C**L**).¹⁶ Acidification of both pyridylamines and metallation of ^N**L** with late first-row transition metal ions have been explored. Schematic diagrams of all five structurally characterized compounds are shown in Figure 1. Structural examination of their acidified salts (^C**LH** and ^N**LH**) may direct that the uncoordinated N sites in complexes **1**•2CH₃CN, **2**•CH₃CN and **3** could potentially work as bases to assist reactivities, mimicking the catalytic processes reported by the Borovik¹⁷ and DuBois¹⁸ groups.

Results and Discussion

Synthesis. Both tripodal pyridylamines $^{\text{C}}\text{L}$ and $^{\text{N}}\text{L}$ were synthesized using one-step nucleophilic aromatic substitution reactions (Scheme 1), in which the primary amine groups on the precursors acted as the nucleophile and substituted the F atoms (the leaving group) on 2-fluoropyridine under basic conditions maintained by excess cesium carbonate. To avoid byproducts from incomplete substitutions, the reaction was kept under heat and was monitored by Mass Spectrometry until completion. Both cesium carbonate (Cs_2CO_3) and sodium carbonate (Na_2CO_3) were found to be capable of driving the reaction to completion when refluxed in DMSO, however the work-up procedure to eliminate the DMSO solvent proved to be time-consuming and resulted in low yields. The adapted reaction was completed in a sealed bomb to maintain a high temperature of 130 °C with CH_3CN as the solvent and Cs_2CO_3 as the base. Na_2CO_3 did not give comparable results under the same conditions. Reactions were kept at 130 °C for one week, giving pure products at relatively high yields (73% for $^{\text{C}}\text{L}$ and 72% for $^{\text{N}}\text{L}$). The synthesis is much more convenient than the recently published procedure for $^{\text{N}}\text{L}$ in which DMSO was used as the reaction solvent.¹⁵ Amine groups on the two tripodal pyridylamines are susceptible to oxidation by air, thus freshly synthesized products were quickly transferred into a glove box for storage.

Various first-row transition metal salts were chosen to react with the two polydentate pyridylamines at different ratios through direct metallation processes under regular wet-lab condition. Only a trizinc cluster $[(^{\text{N}}\text{L})_2\text{Zn}_3(\text{OH})_3](\text{triflate})_3$ (**1**, triflate is the anion of trifluoromethane sulfonic acid) was obtained, in which the hydroxide bridging ions were likely from the water content in the solvent. In addition, acidified

products of the two pyridylamines were generated from the reaction of the basic pyridylamines and the moisture content in the reaction solvent. Perchlorate salts of triprotonated 1,1,1-tris[(2-pyridylamino)methyl]ethane ($[\text{C}^+\text{LH}_3](\text{ClO}_4)_3$, C^+LH) and tetraprotonated *N,N,N*-tris[2-(2-pyridylamino)ethyl]amine ($[\text{N}^+\text{LH}_4](\text{ClO}_4)_4$, N^+LH) were then directly obtained from the amine solution upon addition of excess perchloric acid. Under anhydrous conditions, metallation reactions of the pyridylamines with late first-row transition metal salts nickel (II) bromide and cobalt (II) chloride in THF or CH_3CN at room temperature were explored. Vapor-diffusion crystallizations were setup after the removal of insoluble solid byproducts through filtration, resulting in the crystal formation of two complexes $[\text{N}^+\text{LNiBr}]\text{Br}$ (**2**) and N^+LCoCl_2 (**3**). Both products were air- and water-sensitive and rapidly decomposed after being taken out from the inert atmosphere.

Structural Analysis. Crystals of the acidified perchlorate salts of C^+L (C^+LH) were obtained from the vapor diffusion of ether into a methanol solution. The top diagram in Figure 2 illustrates the crystal structure of the triprotonated cation in C^+LH , in which each pyridine ring was scattered away from each other, possibly to minimize the steric repulsion among the three branches. Electron density analysis from X-ray diffraction during the structure solving process suggested the three new protons reside on the nitrogen atoms of the pyridine groups. The hydrogen bond interactions between the pyridinium and counter anions, shown as dashed lines in Figure 3, strongly supported the assignment of the new protons on the pyridine N atoms. In the crystal structure, five out of the six nitrogen-bound hydrogen atoms took part in the formation of the hydrogen bonds. Oxygen atoms of the perchlorate anions served as the acceptors for the hydrogen bonds originating from the protonated trication. Distances between the donor (D) and

acceptor (A) atoms in the hydrogen bonds slightly varied from 2.822 to 2.998 Å (Table 1), while the H $\cdots$ A distances were between 1.950 and 2.274 Å and the $\angle$ DHA angles ranged from 139.55 to 174.13°. All bonding parameters were in the normal ranges for characteristic hydrogen bonds.¹⁹

With the addition of a proton on the pyridine ring, a conjugated structure spread

over the amino group and pyridine ring

formed in each pedal

of the trication in ^C**LH**. Thus, the positive charge was best described as delocalized over the whole conjugated system. Bond matrices obtained from the X-ray structural analysis verified this assignment. In Table 2, the N_a–C_a, C_a–N_b and N_b–C_b bond lengths were very alike, in the range from 1.328(5) to 1.390(5) Å, whereas, the C_c–N_a bond lengths (1.453(5), 1.464(4) and 1.454(4) Å) were much longer.

Solid-state structure of tetraprotonated ^N**LH** (bottom of Figure 2) was also obtained from the acidification reaction of ^N**L** in a polar solvent. Interaction between two pyridine rings in ^N**LH** gave rise to a π -stacking interaction with their centroids separated by roughly 3.661 Å. Hydrogen bonds between the NH groups on the pyridinium rings and perchlorates in ^N**LH** (Figure 4) demonstrated the location of the protonation on the pyridine N atoms, consistent with the observation in ^C**LH**. The fourth extra proton resided on the center N1 atom, supported by the hydrogen bond between the N1 atom and O14 atom from a perchlorate. Six out of the seven nitrogen-bound hydrogen atoms participated in the hydrogen bond formation. Bond parameters of the hydrogen bonding interactions in ^N**LH** were comparable with those in ^C**LH** (Tables 1 and 2).

A trizinc cluster $[\text{N}^{\text{L}}_2\text{Zn}_3(\text{OH})_3](\text{triflate})_3$ (**1**) were obtained when N^{L} reacted with Zinc triflate. The three Zn ions in **1**•**2**CH₃CN as shown in Figure 5 were brought together by three hydroxyl groups, resulting in a Zn₃(OH)₃ core sandwiched by two N^{L} ligands. All six N atoms from the amine groups were free from coordination. Each Zn₃ cluster carried a 3+ charge, counter balanced by three triflate anions floating in the crystal lattice (top diagram in Figure 6). Calculation of the total charge of the complex reinforced the presence of bridging hydroxides in **1**•**2**CH₃CN. Additional support for the assignment of an OH versus an O bridge came from the hydrogen bonds between the OH groups and the counter triflate anions (Figure 6). It was clear that the hydrogen bond interaction would not be viable if the bridging groups were described as oxo groups. The absence of a signal for the OH groups in the ¹H NMR spectrum of **1** cannot be used as definitive evidence that the bridging groups are oxygen atoms because such signal may be obscured by other signals corresponding to a large number of hydrogen atoms in the tripodal ligands. In addition, the signal of the OH groups in ¹H NMR may overlap with the signal due to the water content in the deuterated solvent. Similar to the large number of polymetallic Zn-OH clusters that have been structurally characterized,²⁰ the hydroxide ions in **1**•**2**CH₃CN were most likely from the moisture content in the solvent. Zn-O bond lengths in the range of 1.923(4) to 1.959(4) Å in Table 3 were comparable to those in the hydroxide-bridged clusters in the literature.²⁰

Two monometallic complexes $[\text{N}^{\text{L}}\text{NiBr}]\text{Br}$ (**2**) and $\text{N}^{\text{L}}\text{CoCl}_2$ (**3**) from reactions of the N^{L} ligand and corresponding salts were obtained and structurally characterized. Selected bond lengths of both complexes were listed in Table 4. As shown in Figure 5, the Ni ion in **2**•CH₃CN was held in a pseudo-octahedral ligand environment comprised

of a bromide and five binding sites from a neutral ^NL ligand. The Ni ion carried a 2+ charge, counter balanced by two bromide anions with one directly binding to the metal while the other connected to the ligand through a hydrogen bond (Figure S1). Two of the seven N donor sites on the ligand are left vacant, which could be used for additional metal incorporation. Because of its low solubility in common solvents and paramagnetic property, a ¹H NMR spectrum of high quality could not be obtained.

The Co ion in complex **3** was held in a pseudo-tetrahedral coordination environment accommodated by two N donor sites from the pyridine rings of a neutral ^NL ligand and two chloride anions. There were five additional N donor sites on the supporting ligand that could be used for further coordination. The chloride anion pointing toward the center of the tripodal ligands interacted with one of the amine N-H group through a hydrogen bond (Figure S2). Similar to the complex **2**, a ¹H NMR spectrum of publishable quality could not be obtained for **3** because of its paramagnetism and low solubility in common solvents.

UV-Vis Spectroscopy. Crystalline sample of **2**•CH₃CN in CH₃CN at various concentrations produced light green solutions for UV-Vis analysis. A strong absorption peak centred at 351 nm with a molar absorptivity ε value of 666 M⁻¹cm⁻¹ was observed. Based on the *d* orbital splitting pattern and electronic configuration of the metal centre, a preliminary molecular orbital diagram of the frontier orbitals for **2** was predicted (**I** in Figure 7). The *d* orbitals of the Ni²⁺ ion (*d*⁸ electron configuration) in an octahedral ligand field were split into two energy levels (*t*_{2g} and *e*_g), filled with eight valence electrons. Low-lying unoccupied orbitals could be the π* orbitals from the pyridine rings on the pyridylamine ^NL ligand. Therefore, the peak at 351 nm with a large ε value could

tentatively be assigned as a metal-ligand charge transfer (MLCT). Extremely low ϵ values (around $10 \text{ M}^{-1}\text{cm}^{-1}$) were obtained for the two bands at longer wavelength. The peak at 621 nm, accounting for the green colour of the Ni complex, could be assigned as the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ transition. The energy of this transition (2.00 eV) is exactly the Δ_o value in the Ni complex.²¹ The peak at 1017 nm could be assigned as the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ transition. Low ϵ values for both $d-d$ transitions were in the normal range for complexes in an octahedral geometry where the $d-d$ transition is against Laporte selection rule.^{21,22}

THF solutions of intense blue crystals of **3** at different concentrations were prepared for UV-Vis analysis. Two absorption peaks, one at 316 nm with an ϵ value of $8.18 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ and the other one at 639 nm with an ϵ value of $6.81 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$ were observed. In a pseudo-tetrahedral environment, the d orbitals of the Co^{2+} ion filled with seven valence electrons were split into two energy levels, with d_{xy} , d_{xz} , d_{yz} at a high energy level (the t_2 set) and d_z^2 , $d_{x^2-y^2}$ at a lower energy level (the e set) shown as **II** in Figure 7. Similar to those of complex **2**, Low-lying unoccupied orbitals of **3** could also be the π^* orbitals from the pyridine rings on the ^NL ligand. Tentatively, a MLCT from an occupied d orbital to an unoccupied empty ligand orbital could account for the absorption at 316 nm, while the absorption at 639 nm was possibly resulted from the $d-d$ transition $^4\text{A}_2 \rightarrow ^4\text{T}_2$. Δ_t value in the Co complex (1.94 eV) was directly converted from the wavelength of this $d-d$ transition.²¹ Peaks of $d-d$ transitions are usually observed at high intensity for complexes in a tetrahedral geometry because orbital mixing between the p orbitals and the t_2 set of d orbitals broke the central symmetry of the t_2 set. Therefore, the transition between the e set to the t_2 set could obey the Laporte selection rule.²²

Conclusions. A convenient synthesis method for a tripodal polydentate pyridylamine ^NL and a new analogue ^CL was developed from direct one-step nucleophilic aromatic substitution. Their acidified salts (^NLH and ^CLH) were obtained accidentally and then synthesized on purpose. Hydrogen bond interactions between the cations and anions confirmed the location of the protons at the N atoms on the pyridine rings. Structural analysis of the metallation products of the ^NL ligand demonstrated its versatile coordination modes with late first-row transition metal ions. A trizinc cluster (**1**) contained a hexagonal $\text{Zn}_3(\text{OH})_3$ core sandwiched by the six pyridine rings from two ^NL ligands, leaving all six amines unbound. Uncoordinated N donor sites were also observed in the two monometallic complexes (**2**• CH_3CN and **3**), where one metal core was buried in the tripodal centre of the ligand and the other metal atom was only supported by two side arms of the ligand.

Experimental Sections

General procedures. Syntheses of ^CL , ^NL , ^CLH , ^NLH and **1** were conducted in a regular wet-lab condition, using chemicals and solvents directly from commercial vendors and glassware dried at 100 °C overnight. Manipulations involving metal complexes **2** and **3** were carried out using glove-box techniques in a nitrogen atmosphere. All glassware was oven-dried at 150 °C for a minimum of 10 h and cooled in an evacuated antechamber prior to use in the glove box. Ether, acetonitrile, hexanes and THF were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in THF in order to confirm

effective oxygen and moisture removal. The tris-amine 1,1,1-tris(aminomethyl)ethane hydrochloric acid (tame·3HCl) was synthesized by following the literature.²³ Chloroform-*d*₁ and CD₃OH were purchased from Cambridge Isotope Labs. All other reagents were purchased from commercial vendors and used without further purification unless explicitly stated.

Synthesis of 1,1,1-tris[(2-pyridylamino)methyl]ethane (^CL). 10.00 g tame·3HCl (0.0440 mol), 21.56 g 2-fluoropyridine (0.222 mol), 90.63 g cesium carbonate (0.267 mol) and 150. mL acetonitrile were added together into a sealed bomb. The bomb was then charged with partial vacuum (72.8 mm Hg) and heated at 120-130 °C for 7 days. The reaction progress was monitored by Mass Spectrometry, verifying that all three amine groups were successfully connected to pyridyl groups. The resulting orange mixture was filtered through a frit with a plug of aluminum oxide, eluting with 1000. mL ethyl acetate. The yellow/orange filtrate was then dried, producing a yellow, oily product. Yield: 11.23 g, 73%. Further purification was completed by evaporation crystallization of a product solution in CH₂Cl₂. Yellow crystals were obtained after a few days. ¹H NMR (600 MHz, CDCl₃): 8.05-8.04 (d, 3H, aromatic *H*, *J* = 5.10 Hz), 7.32-7.29 (t, 3H, aromatic *H*, *J* = 7.02 Hz), 6.47-6.44 (t, 3H, aromatic *H*, *J* = 5.10 Hz), 6.42-6.40 (d, 3H, aromatic *H*, *J* = 8.40 Hz), 6.02 (br, 3H, CH₂NHAr), 3.31 (d, 6H, CCH₂NH, *J* = 5.16 Hz), 0.95 (s, 3H, CCH₃). ¹³C NMR (600 MHz, CDCl₃): 159.4, 147.5, 137.2, 112.0, 109.2, 44.8, 41.5, 19.8. HRMS (*m/z*): C₂₀H₂₅N₆⁺, 349.2191 (calcd 349.2141).

Synthesis of *N,N,N*-tris[2-(2-pyridylamino)ethyl]amine (^NL). Synthesis of ^NL is similar to the synthesis of ^CL. 10.00 g (0.0680 mol) of tris(2-aminoethyl)amine (tren), 26.56 g (0.274 mol) of 2-fluoropyridine, and 89.13 g (0.273 mol) of cesium carbonate

were added into a sealed bomb with 150 mL acetonitrile. The bomb was charged with partial vacuum (72.8 mm Hg) and then heated at 120 °C for 8 days. The reaction completion was monitored by Mass Spectrometry, verifying that all three primary amine groups were successfully connected to pyridyl groups. The reaction mixture was filtered through a plug of aluminum oxide, eluting with 1000 mL ethyl acetate. The resulting filtrate was dried to produce a yellow, oily product. Further purification was completed by leaving a product solution in CH₂Cl₂ for slow evaporation crystallization. All spectroscopic analysis data, close to what was in the literature, confirmed the purity of the desired product.¹⁵ Yield: 23.87 g, 72%.

Synthesis of the perchlorate salt of protonated 1,1,1-tris[(2-pyridylamino)methyl]ethane [^CLH₃](ClO₄)₃ (^CLH). ^CLH with three tetrafluoroborate counter anions was obtained first accidentally as a byproduct during the metallation of ^CL with Cu(BF₄)₂•6H₂O in THF. Its structure was verified by X-ray crystallography. ^CLH with three perchlorate counter anions was later synthesized on purpose from direct acidification of ^CL using excess perchloric acid. 0.10 g ^CL (0.29 mmol) and 0.247 g 70% perchloric acid (1.76 mmol) were dissolved in 10 mL methanol. After the resulting yellow solution was stirred at room temperature for 24 h, the mixture was filtered through Célite and vapor diffusion crystallization with diethyl ether diffusing into the ^CLH solution afforded a small amount of light yellow crystals.

Synthesis of the perchlorate salt of protonated N,N,N-tris[2-(2-pyridylamino)ethyl]amine [^NLH₄](ClO₄)₄ (^NLH). 0.20 g ^NL (0.53 mmol) and 0.247 g 70% perchloric acid (3.26 mmol) were dissolved in 10 mL methanol. The resulting cloudy solution mixed with yellow oil was stirred at room temperature for 24 h. 3.0 mL

of dichloromethane was then added to the mixture to dissolve the oil. The suspension was filtered through Célite to remove any insoluble byproducts. Vapor-diffusion crystallization with diethyl ether diffusing into a ^NLH filtrate produced a small amount of light yellow crystals for X-ray studies.

Synthesis of [(^NL)₂Zn₃(OH)₃](triflate)₃ (1). 0.400 g ^NL (1.06 mmol) and 0.386 g Zn(triflate)₂ (1.06 mmol) were mixed in 10 mL of acetonitrile and stirred at room temperature for 24 hours. The resulting suspension, a light yellow mixture with small amount of white solids, was filtered through Célite and flushed with 10 mL acetonitrile. The filtrate was then left at room temperature with ether diffusing into the filtrate for vapor-diffusion crystallization. After a few days, light yellow crystals with yellow oil on the surface were obtained for structural analysis. Crystals were then collected and dried completely under vacuum after washing with 3 × 5 mL ether three times. Yield: 0.343 g, 67%. ¹H NMR (600 MHz, CD₃OH): 7.82 (d, 3H, aromatic *H*), 7.36 (t, 3H, aromatic *H*), 6.51 (t, 3H, aromatic *H*), 6.45 (d, 3H, aromatic *H*), 3.61 (br, 3H, CH₂NHAr), 3.41 (q, 6H, CH₂CH₂NH), 3.19 (t, 6H, NCH₂CH₂). Anal. Calcd. for C₄₅H₅₇F₉N₁₄O₁₂S₃Zn₃ (1): C, 37.29; H, 3.96; N, 13.53%. Found: C, 37.16; H, 3.93; N, 13.51%.

Synthesis of [^NLNiBr]Br (2). 0.500 g ^NL (1.33 mmol), 0.290 g NiBr₂ (1.33 mmol) and 20 mL of acetonitrile were mixed together and stirred at room temperature for 24 hours in a glove box. The mixture turned green over time, which was then filtered through célite. The green residue resulted from the filtrate after solvent removal under vacuum was washed with 10 mL ether three times. Isolated yield: 0.535 g, 68%. Green needle-shaped crystals were obtained from vapor diffusion with ether diffusing into a product solution in acetonitrile. UV-Vis spectroscopy (CH₃CN): 351 nm (ε = 666 M⁻¹

1 cm^{-1}), 621 nm ($\epsilon = 12\text{ M}^{-1}\text{cm}^{-1}$), 1017 nm ($\epsilon = 9.5\text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{Br}_2\text{N}_7\text{Ni}$ (**2**): C, 42.32; H, 4.57; N, 16.45 %. Found: C, 42.24; H, 4.49; N, 16.36 %.

Synthesis of $^{\text{N}}\text{LCoCl}_2$ (3**).** 0.500 g $^{\text{N}}\text{L}$ (1.33 mmol), 0.172 g CoCl_2 (1.33 mmol) and 20 mL THF were mixed and stirred at room temperature for 24 hours. The mixture turned intense blue over time. The green residue resulted from the filtrate after drying under vacuum was washed with hexanes ($3 \times 10\text{ mL}$) and then dried under vacuum. Isolated yield: 0.429 g, 64%. Blue crystals for X-ray analysis were obtained by vapor diffusion with hexanes diffusing into a product solution in THF. UV-Vis spectroscopy (THF): 316 nm ($\epsilon = 8.18 \times 10^3\text{ M}^{-1}\text{cm}^{-1}$), 639 nm ($\epsilon = 6.81 \times 10^2\text{ M}^{-1}\text{cm}^{-1}$). Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{Cl}_2\text{CoN}_7$ (**3**): C, 49.72; H, 5.36; N, 19.33 %. Found: C, 49.76; H, 5.42; N, 19.26 %.

Determination of X-ray Structures. Crystals of air-sensitive samples **2**• CH_3CN and **3** were carefully sealed with Teflon- and Para-film in a capped vial and stored in a N_2 filled zip-lock bag before transportation. Single crystals for all samples were coated with deoxygenated Paratone-N oil and mounted on Kaptan loops. Crystallographic data for compound **1**• $2\text{CH}_3\text{CN}$ was collected at 100(2) K on a Siemens (Bruker) SMART CCD area detector instrument with Mo $K\alpha$ radiation. Crystallographic data for compound $^{\text{C}}\text{LH}$, $^{\text{N}}\text{LH}$, **2**• CH_3CN , and **3** were collected on Beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Lab using monochromatic radiation ($\lambda = 0.7749\text{ \AA}$) at 150(2) K. Raw data was integrated and corrected for Lorentz and polarization effects using Bruker APEX2 v. 2009.1.²⁴ Absorption corrections were applied using SADABS.²⁵ Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. The program PLATON²⁶ was

employed to confirm the absence of higher symmetry for any of the crystals. The program CELL_NOW²⁷ was employed to check and solve twining problems of the crystals. The position of the heavy atoms was determined using direct methods in the program SHELXTL.²⁸ Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were added in idealized positions. Crystallographic data is shown in Table S1. Selected bond lengths and parameters of hydrogen bonding interactions are shown in Tables 1-4. Figures of X-ray crystal structures of **C₁LH**, **N₁LH**, and complexes **1•2CH₃CN**, **2•CH₃CN** and **3** (Figures 2 and 5) were generated from Ortep-3 for Windows²⁹ and rendered using POV-Ray v3.6 for Windows.³⁰ X-ray structures showing hydrogen bonds (Figures 3, 4, 6, S1 and S2) were generated from Mercury 3.3.³¹

Other Physical Measurements. Elemental analysis was performed by Complete Analysis Laboratories, Inc., Parsippany, New Jersey. ¹H NMR and ¹³C NMR spectra were acquired on a JEOL ECA-600 NMR-spectrometer (600 MHz for ¹H and 150 MHz for ¹³C) with spinning at r.t. UV/Visible spectra were recorded on a Perkin Elmer Lambda 25 Spectrometer using quartz cuvettes. HRMS spectrum of **C₁L** was obtained from a JEOL DART AccuTOF instrument. Samples of air-sensitive compounds **2•CH₃CN** and **3** were carefully sealed under a nitrogen environment before being sent for measurements.

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Appendix A. Supplementary data

Crystallographic data, X-ray structures showing hydrogen bonds in complexes **2•CH₃CN** and **3**, and NMR spectra of **^CL** were provided as supplementary data associated with this article, which can be found in the online version, at link xxxx. CCDC 1060981 (**^CLH**), 1060982 (**^NLH**), 1060978 (**1•2CH₃CN**), 1060979 (**2•CH₃CN**), and 1060980 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Scheme 1. Synthesis of cL and nL .

Table 1. Bonding Parameters of Selected Hydrogen Bonding Interactions in the Structures of ^C**LH**, ^N**LH**, **1•2CH₃CN**, **2•CH₃CN** and **3**.

Compound	H-bond	D···A (Å)	H···A (Å)	∠DHA (°)
^C LH	N1–H1A···O2	2.977	2.143	157.75
	N2–H2A···O12	2.969	2.150	154.51
	N3–H3A···O11	2.901	2.023	174.13
	N4–H4A···O6	2.998	2.274	139.55
	N6–H6A···O9	2.822	1.950	170.64
	N1–H1A···O14	2.760	1.990	138.99
^N LH	N2–H2A···O15	2.950	2.168	147.59
	N3–H3A···O16	2.811	2.115	135.41
	N4–H4B···O5	3.024	2.333	135.45
	N6–H6A···O12	2.870	2.140	140.00
	N7–H7A···O11	2.887	2.027	165.34
	N1–H1A···O14	2.760	1.990	138.99
1•2CH₃CN	O1–H1···O7	2.570	1.620	177.97
	O2–H2···O12	2.796	2.039	135.34
	O3–H3···N15	3.064	2.321	134.71
	N4–H4A···O1	3.065	2.368	136.37
	N11–H11A···O2	3.012	2.263	142.81
2•CH₃CN	N2–H2A···O15	3.354	2.357	174.54
3	N4–H4A···Cl1	3.246	2.389	164.36

Table 2. Selected Bond Lengths (Å) in ^C**LH** and ^N**LH**.

^C LH		^N LH	
N1–C3	1.453(5)	N2–C2	1.450(4)
N1–C6	1.339(5)	N2–C3	1.353(4)
N2–C4	1.464(4)	N3–C3	1.347(4)
N2–C11	1.328(4)	N3–C7	1.362(4)
N3–C5	1.454(4)	N4–C9	1.455(4)
N3–C16	1.328(5)	N4–C10	1.347(4)
N4–C6	1.359(5)	N5–C10	1.368(4)
N4–C10	1.361(5)	N5–C14	1.369(4)
N5–C11	1.390(5)	N6–C16	1.459(3)
N5–C15	1.416(7)	N6–C17	1.335(3)
N6–C16	1.351(4)	N7–C17	1.345(3)
N6–C20	1.351(5)	N7–C21	1.366(4)

Table 3. Selected Bond Lengths (Å) in **1•2CH₃CN**.

Zn1–O1	1.933(4)	C12–N6	1.350(8)
Zn1–O3	1.923(4)	N6–C16	1.354(8)
Zn2–O1	1.940(4)	C6–N4	1.461(7)
Zn2–O2	1.946(4)	N4–C17	1.353(7)
Zn3–O3	1.937(4)	C17–N7	1.351(7)
Zn3–O2	1.959(4)	N7–C21	1.354(8)
Zn1–N5	2.011(5)	C23–N9	1.450(8)
Zn1–N6	2.019(5)	N9–C28	1.364(8)
Zn2–N7	2.025(5)	C28–N12	1.352(8)
Zn2–N14	2.021(4)	N12–C32	1.364(8)
Zn3–N12	2.019 (5)	C25–N10	1.458(8)
Zn3–N13	2.032 (6)	N10–C33	1.338(8)
C2–N2	1.447(8)	C33–N13	1.345(8)
N2–C7	1.352(7)	N13–C37	1.363(9)
C7–N5	1.346(7)	C27–N11	1.458(7)
N5–C11	1.349(7)	N11–C38	1.346(8)
C4–N3	1.451(7)	C38–N14	1.370(7)
N3–C12	1.346(7)	N14–C42	1.350(8)

Table 4. Selected Bond Lengths (Å) in Complexes **2•CH₃CN** and **3**.

2•CH₃CN		3	
Ni1–Br1	2.4774(3)	Co1–Cl1	2.2486(7)
Ni1–N1	2.0958(15)	Co1–Cl2	2.2579(7)
Ni1–N2	2.1398(17)	Co1–N3	2.052(2)
Ni1–N3	2.2060(15)	Co1–N5	2.042(2)
Ni1–N4	2.1518(15)	N2–C9	1.449(3)
Ni1–N7	2.1830(17)	N2–C10	1.348(3)
N2–C2	1.491(2)	C10–N3	1.356(3)
N2–C10	1.434(2)	N3–C14	1.360(3)
C10–N5	1.329(2)	C2–N4	1.453(3)
N5–C14	1.343(3)	N4–C3	1.343(3)
N3–C4	1.490(2)	C3–N5	1.358(3)
N3–C20	1.416(2)	N5–C7	1.362(3)
C20–N6	1.332(2)	C16–N6	1.456(4)
N6–C24	1.347(3)	N6–C17	1.379(4)
N4–C30	1.430(3)	C17–N7	1.325(4)
C30–N7	1.342(2)	N7–C21	1.352(5)
N7–C34	1.334(3)

Figure 1. Schematic drawing of structurally characterized compounds.

Figure 2. X-ray crystal structures of C^+LH and $N^{4+}LH$. Anions are omitted for clarity.

Ellipsoids are shown at the 50% probability level.

Figure 3. Hydrogen bonds in $^{\text{C}}\text{1H}$. Intramolecular hydrogen bonds are shown in sky blue, while intermolecular hydrogen bonds are in red. The two oxygen atoms (O2, O12) represent the neighboring molecules in the extended network. Color code: H (white), N (purplish blue), C (gray), O (red), Cl (green).

Figure 4. Hydrogen bonds in N^LH . Intramolecular hydrogen bonds are shown in sky blue, while intermolecular hydrogen bonds are displayed in red. The three oxygen atoms (O5, O11, O16) represent the neighboring molecules in the extended network. Color code: H (white), N (purplish blue), C (gray), O (red), Cl (green).

Figure 5. X-ray crystal structures of compounds **1**•2CH₃CN, **2**•CH₃CN and **3**. Hydrogen atoms, anions and solvent molecules are omitted for clarity. Ellipsoids are shown at the 50% probability level.

Figure 6. Hydrogen bonds in $1 \cdot 2\text{CH}_3\text{CN}$. Intramolecular hydrogen bonds are shown in sky blue, while intermolecular hydrogen bonds are displayed in red. Top: solvent molecules and the second part of the disordered triflate anions were omitted for clarity. Bottom: Further simplified drawing of the top figure. N15 atom at the right bottom corner

is from the neighboring trizinc cluster in the extended network. Color code: H (white), N (purplish blue), C (gray), O (red), S (yellow), F (green), Zn (purplish gray).

Figure 7. Preliminary molecular orbital diagrams of complexes $2 \cdot \text{CH}_3\text{CN}$ (I, left) and 3 (II, right)

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