Monitoring the Formation of Coordination Complexes Using Electrospray Mass Spectrometry

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Abstract: *cis,trans*-1,3,5-Triaminocyclohexane (*trans*-tach) has been shown to be an excellent ligand in the synthesis of discrete complexes, molecular clusters, and infinite architectures. Herein, we report the Schiff-base derivitization of *trans*-tach to form *cis,trans*-1,3,5-*tris* (pyridine-2-carboxaldimino) cyclohexane (ttop), and the complexation of this ligand with copper(II) salts. The complexation reaction leads to the crystallization of transition-metal complexes with nuclearities of 1, 2, and 4, and the formation of the complexes can be followed stepwise, in real time, using electrospray mass spectrometry.

Introduction

The control of transition-metal architectures is an area of great interest to chemists because of the vast potential for the design of functional compounds,[1–2] as well as expanding the understanding of the fundamental processes that underpin the formation of the complexes,[3–4] and large self-assembled structures based upon smaller building blocks.[5–6] Of course the development of optical,[7] porous,[8] catalytic,[9] and magnetic materials[10] based upon such complexes is of vital importance and interest, but understanding the assembly of larger cluster structures remains a great challenge, and arguably limits our ability to produce systems with radically new properties.[11] One route to address these problems has been to design ligands that will help create a new structure type with well-defined physical properties, and almost invariably the need to produce crystalline material for single crystal diffraction studies has been mandatory.[12] Indeed, much research has been focused on the use of ligand-design principles to develop polydentate ligands as building blocks
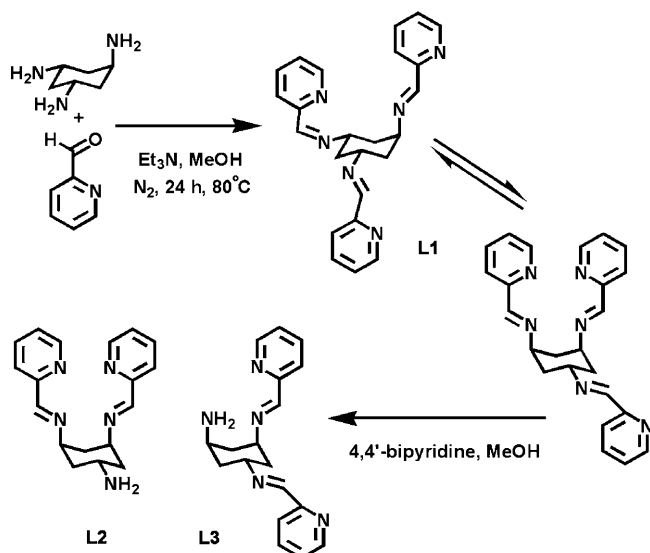
for supramolecular architectures[13] because of their ability to bind to multiple transition metals and to stabilize structures through noncoordinative interactions.[14] The design of a ligand, that is, the geometrical arrangement of the binding sites and the structural flexibility of the backbone, has great importance in the metal-binding ability of the ligand.[15–16]

Ideally, to engineer polynuclear coordination clusters, multiple discrete binding sites and a degree of structural rigidity is required. In this respect, the inclusion of a cyclohexane backbone in a ligand can satisfy both of these demands. For instance, in previous studies we have shown that the complexation of *cis,trans*-1,3,5-triaminocyclohexane (*trans*-tach) yielded a range of interesting complexes including polynuclear clusters,[17] coordination networks,[18] and one-dimensional chain complexes.[19] Herein, we not only report an extension to these studies, but also start to follow the complexation reactions using mass spectrometry. *cis,-trans*-1,3,5-Tris(pyridine-2-carboxaldimino) cyclohexane (ttop) was chosen for this work since we understand the complexation chemistry of this ligand system (see Scheme 1).

In this study, we have chosen to employ mass spectrometry to monitor the complexation process, in conjunction with a well-understood ligand system, to see if we can monitor the overall complexation process. Indeed, electrospray ionisation mass spectrometry (ESI-MS) has been shown to be a potent tool in the analysis of such labile coordination complexes.[20–23] Herein, we report our investigations into the coordination chemistry of the ligand ttop and its behavior when coordinated with copper(II) chloride. Using both stan-

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Scheme 1. Reaction scheme describing the formation of *cis,trans*-1,3,5-tris(pyridine-2-carboxaldimino) cyclohexane (ttop, **L1**) from *trans*-tach and pyridine2-carboxaldehyde in methanol, which yields a range of Schiff-base ligands.

dard crystallographic techniques and ESI-MS, the study aims to investigate the complex formation, and probe if we can control the assembly of the architecture with bulk reaction parameters (e.g., stoichiometry) with the particular aim of monitoring the assembly of multinuclear cluster species in solution.

Results and Discussion

Ligand Design

The ligand designed for this investigation was produced by the reaction of *trans*-tach with pyridine-2-carboxaldehyde to give the ligand, ttop ($C_{24}H_{24}N_6$) (**L1**), the *trans* hydrolyzed ttop ($C_{18}H_{21}N_5$) (**L2**), and the mono *cis* hydrolyzed ttop (**L3**) (see Scheme 1). These ligands are highly labile and can flip from a bisequatorial monoaxial to a bisaxial monoequatorial conformation arising from the ring-flip ability of the cyclohexane backbone. The energetically favored conformer, in which the ligand takes on the ring-flipped 'closed' conformation, is maintained in each of the presented complexes **2**–**6**: [Cu(**L1**)Cl]Cl(CH$_3$OH)$_2$ (**2**), [Cu$_2$(**L1**)Cl$_4$]CH$_3$OH (**3**), [Cu(**L2**)Cl(H$_2$O)]Cl$_2$ (**4**), [Cu$_2$(**L3**)$_2$(NO$_3$)](NO$_3$)$_3$ (**5**), and {[Cu$_2$(**L1**)Cl$_3$]Cl}$_2$ (**6**). As such, this favored conformation of **L1** gives rise to two coordination sites, an axial tetradentate site, constructed from the nitrogen atoms on both the pyridine groups and the associated imine groups, and an equatorial bidentate coordination site, formed from the two nitrogen atoms from the *trans* arm of ttop. As expected, the axial tetradentate coordination site is the most favored site for metal ion coordination, and is filled first.

Structural Analysis

In total, in this paper we present five new crystal structures (**2**–**6**) (see Figure 1), and the structural data is summarized in Table 1. For complex **2**, a stoichiometry of 1:2 Cu^{II}Cl$_2$/ttop

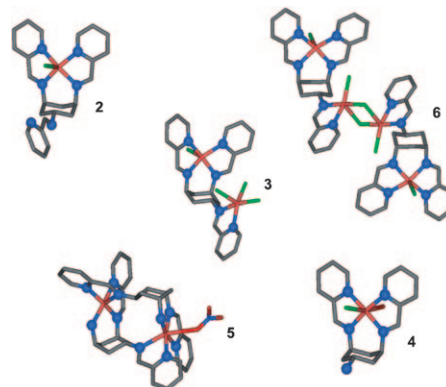Figure 1. Crystal structure of [Cu(**L1**)Cl]Cl(CH$_3$OH)$_2$ **2** showing only the tetradentate coordination site being filled; Crystal structure of [Cu$_2$(**L1**)Cl$_4$]CH$_3$OH **3** showing both the tetradentate and bidentate coordination sites being filled; Crystal structure of [Cu(**L2**)Cl(H$_2$O)]Cl$_2$ **4** showing the hydrolyzed ligand, in which the *trans*-pyridyl arm has been cleaved; Crystal structure of [Cu$_2$(**L3**)$_2$(NO$_3$)$_2$](NO$_3$) **5** showing two hydrolyzed ligands complexed with two metals. The two axial pyridine groups are twisted in relation to each other and the equatorial *trans* pyridine arm has been cleaved off to allow the nitrogen from the *trans* arm to coordinate to the adjacent copper(II) center; Crystal structure of {[Cu$_2$(**L1**)Cl$_3$]Cl}$_2$ **6** showing the two ligand-four metal center complex. The two ligands are held together by two bridging chlorides coordinating to the bidentate copper(II) centers. (Grey corresponds to carbon atoms; dark blue to nitrogen atoms; light blue to copper; green to chloride) (hydrogen atoms, counterions, and noncoordinated solvent molecules are excluded for clarity).

yields the mononuclear complex [Cu(L**1**)Cl]Cl(CH$_3$OH)$_2$ (**2**) (see Figure 2), with the imine double bonds substituted in the sterically favored *E*-conformation. The copper(II) ion is coordinated within the tetradentate binding site in a distorted square-pyramidal geometry by basal coordination to each of the four nitrogen atoms of the *cis*-imidyl pyridyl moieties. The Cu1−N bond lengths for the imine groups are 1.997(2) and 2.019(2) Å, with the bond lengths for the pyridyl Cu1−N being 2.099(2) and 2.035(2) Å, which lie within expected ranges,[24–26] and an apical coordination of one chloride ion with a bond length of 2.4198(7) Å. The chloride ligand is oriented above the cyclohexane ring with the copper(II) ion also oriented towards the center of the molecule at an angle of 166.5(8)°, placing the copper(II) over the cyclohexane ring. The bidentate binding site is not involved in the coordination of a metal center. The nitrogen atoms of the imine group and pyridyl group are oriented *anti* with respect to each other to minimise electronic repulsion between the lone pair on each nitrogen. The *trans*-imidyl pyridine arm is twisted with respect to the cyclohexane ring at an angle of 60.0(1)°.

Table 1. Crystal structure data for compounds **2**–**6**.

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{26}H_{32}N_6O_2CuCl_2$	$C_{25}H_{28}N_6OCu_2Cl_4$	$CuC_{18}H_{28}N_5O_3Cl_3$	$C_{36}H_{42}N_{14}Cu_2O_{12}$	$C_{26}H_{32}N_6Cu_2Cl_4O_2$
F_w	595.02	697.41	532.34	1086.04	729.46
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
a [Å]	7.5983(2)	9.1119(4)	7.4342(5)	11.8957(3)	9.7929(3)
b [Å]	11.5797(5)	8.8875(8)	11.5628(6)	26.6195(8)	12.8175(5)
c [Å]	16.5969(7)	17.8313(7)	14.1665(8)	15.8896(3)	13.9117(7)
α [°]	73.601(4)	90	95.409(3)	90	88.942(2)
β [°]	89.339(3)	98.715(8)	94.561(3)	110.442(1)	78.430(2)
γ [°]	84.940(3)	90	106.415(3)	90	69.323(2)
Space group	$P\text{-}1$	Pc	$P\text{-}1$	$P2_1/n$	$P\text{-}1$
V [Å³]	1395.3(1)	1412.2(2)	1155.7(2)	4714.7(2)	1597.9(1)
Z value	2	2	2	4	2
ρ_{calcd} [g cm⁻³]	1.416	1.624	1.530	1.530	1.516
μ [mm⁻¹]	1.002	1.915	1.321	0.985	1.699
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)
No. of Reflections Collected	9129	6892	14110	30755	21121
No. of Unique Reflections	4474	4393	4218	8258	5623
No. parameters	338	345	289	645	370
$R_1(I>2\sigma(I))$	0.0275	0.0288	0.0490	0.0751	0.0659
wR_2 (all data)	0.0611	0.0474	0.0914	0.1770	0.1666

If the stoichiometry is changed to 1:1 $Cu^{II}Cl_2$/ttop, then the complex $[Cu_2(\mathbf{L1})Cl_4]CH_3OH$ **3** (see Figure 2) can be formed. From **3**, it can be seen that both binding sites have been filled by copper(II) centers. One copper(II) ion is coordinated in the tetradentate binding site in a distorted square-pyramidal geometry by a basal coordination to each of the four nitrogen donors, with a chloride ligand occupying the apical binding site oriented away from the cyclohexane ring. The Cu1−N bond lengths for the imine groups of the *cis* arms are 1.998(2) and 1.980(2) Å, and 2.081(2) and 2.026(2) Å for the pyridyl nitrogen to copper(II) bond lengths. The apical coordination of one chloride ligand (Cu1−Cl bond length = 2.429(8) Å) completes the square-pyramidal coordination sphere. The bidentate site of the *trans* arm binds a second copper(II) ion, which is coordinated, in square-pyramidal geometry, by the imidyl and pyridyl nitrogen atoms, with bond lengths of Cu−N$_{imidyl}$ = 2.026(2) Å and Cu−N$_{pyridyl}$ = 2.074(2) Å. The final three coordination sites are occupied by chloride anions, with binding distances of 2.282(8), 2.273(8), and 2.562(8) Å. The *trans*-imidyl pyridyl arm is oriented perpendicular to the two axial pyridine rings, as with the mononuclear complex **2**, and is twisted with respect to the cyclohexane ring at an angle of 66.1(2)°.

Complex **2** reacted with 4,4′-bipyridine resulting in the formation of a monoligand complex $[Cu(\mathbf{L2})Cl(H_2O)]Cl_2$ **4** (see Figure 2). The *trans* arm is hydrolyzed and protonated preventing coordination, but increasing the donor ability of the amino group to form hydrogen-bonded interactions with the chloride counterions. The tetradentate pocket, formed by the *cis* arms of the ring-flipped cyclohexane backbone, coordinates to one copper(II) ion with the octahedral geometry being completed by one chloride ion and one water molecule. The Cu−N bond lengths for the imine groups are 1.9991(3) Å and 2.022(3) Å, and 2.066(3) Å and 2.030(3) Å for the pyridyl nitrogens. The Cu−Cl bond length is

2.6590(11) Å with the Cu−OH$_2$ bond length being 2.407(3) Å.

If the stoichiometry and counterion are changed to 1:1 $Cu^{II}(NO_3)_2$/ttop, a dinuclear, diligand complex $[Cu_2(\mathbf{L3})_2(NO_3)](NO_3)_3$ **5** (see Figure 2) is formed. The copper(II) is coordinated at the hydrolyzed *cis* amine and the *cis* imidyl pyridyl arm of the first ligand, and the *trans* imidyl pyridyl arm from the second ligand. The octahedral coordination sphere is completed by an axial nitrate group. The Cu1−N bond distances are 1.999(5) Å and 2.279(5) Å for the imine groups, 2.023(5) Å and 2.045(5) Å for the pyridyl nitrogens, and 2.035(5) Å for the amine group. Cu2 has a distorted octahedral coordination geometry with the Cu2−N bond distances for the imine groups being 2.333(5) Å, 2.010(5) Å, 2.054(5) Å, and 2.034(5) Å for the pyridyl nitrogens, 2.014(5) Å for the amine group, and 2.827(5) Å for the nitrate ion. Cu2 also exhibits long range axial coordination to the neighboring nitrate of the nearest ligand, forming a chain-like structure. The Cu2−ONO$_2$ bond length is 2.635(5) Å, this bond length lying within the range previously reported for highly distorted octahedrons.[27]

If the stoichiometry is changed to 2:1 $Cu^{II}Cl_2$/ttop, a two ligand-four metal center complex $\{[Cu_2(\mathbf{L1})Cl_3]Cl\}_2$ **6** (see Figure 2) is formed. Both coordination sites on each ligand are complexed to copper(II) ions in a square-pyramidal geometry. As with the mononuclear and dinuclear complexes **2** and **3**, respectively, the tetradentate binding site coordinates Cu1 by its four nitrogen atoms available upon ring-flip of the cyclohexane ring (Cu1−N imine groups = 1.996(2) and 2.004(6) Å, Cu1−N pyridyl = 2.036(6) and 2.069(5) Å). The coordination sphere of Cu1 is completed by one chloride ligand, which like **3**, is pointing away from the cyclohexane ring (Cu1−Cl = 2.427(2) Å). The bidentate binding site coordinates a second copper(II) with its two nitrogen atoms (Cu2−N$_{imine}$ = 2.046(6) Å, Cu2−N$_{pyridyl}$ = 2.045(6) Å), along
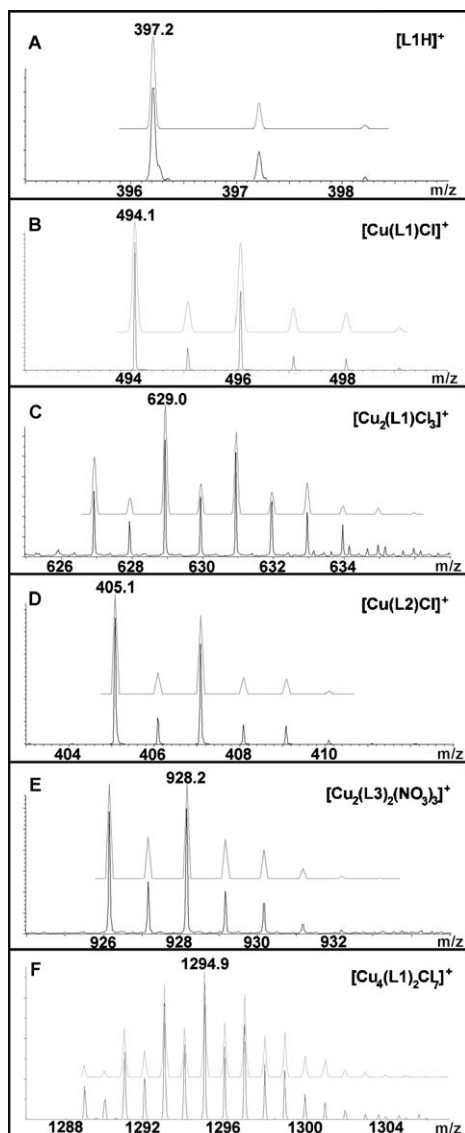
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Figure 2. A) ESI-MS measurement of [**L1**H]$^+$ (**1**); B) ESI-MS measurement of [Cu(**L1**)Cl]$^+$ **2**; C) ESI-MS measurement of [Cu$_2$(**L1**)Cl$_3$]$^+$ **3**; D) ESI-MS measurement of [Cu(**L2**)Cl]$^+$ **4**; E) ESI-MS measurement of [Cu$_2$(**L3**)$_2$(NO$_3$)$_3$]$^+$ **5**; F) ESI-MS measurement of [Cu$_4$(**L1**)$_2$Cl$_7$]$^+$ **6**. (Black spectrum = experimental measurement; grey spectrum = predicted measurement).

with one terminal chloride ligand (Cu2−Cl = 2.256(2) Å) and two bridging chloride ligands (Cu2−Cl = 2.284(18) and 2.651(2) Å). The Cu2−Cu2* distance of 3.497 Å lies within the reported range of μ_2-chloride bridged copper(II) dimers.[28–30] A number of different divalent 1st row transition metals can also be coordinated to the **L1**, **L2**, and **L3** ligands. Cobalt(II) and zinc(II) can be coordinated (with both chloride and nitrate counter ions as with copper(II)) to give the isostructural complexes of those found in copper(II) systems.[31]
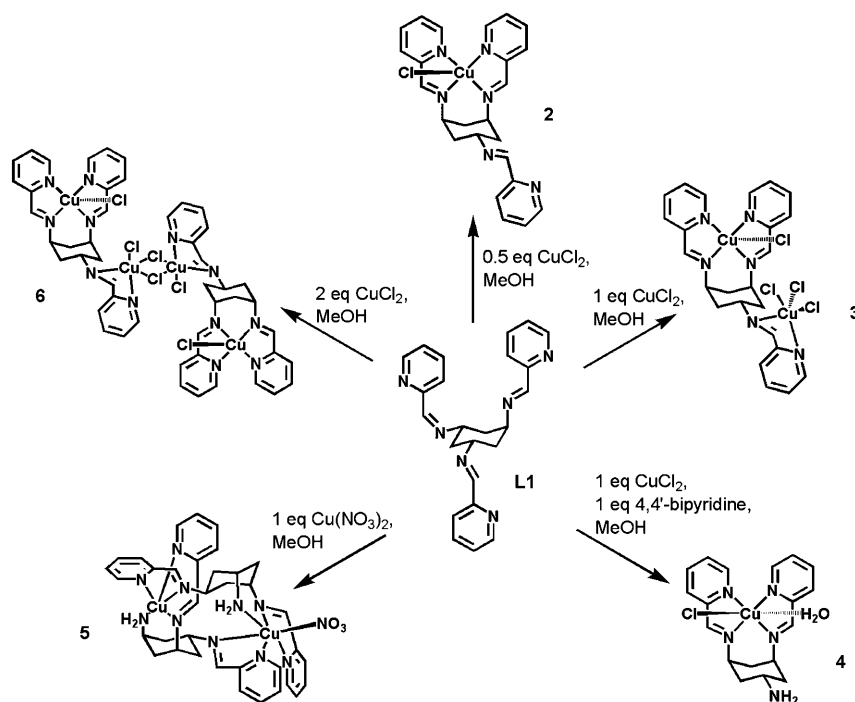
Mass Spectrometry

ESI-MS studies were used to observe the stepwise construction of **2**–**6** (see Figure 2). From the electrospray measurements, it can be seen that the labile ttop ligand can complex with the copper(II) chloride firstly to form the mononuclear complex [Cu(**L1**)Cl]$^+$, while the change of the stoichiometry gives the higher nuclearity complexes. The ability to observe the formation of the complexes from low to higher nuclearity probably arises from the most favorable site (the tetradentate binding site) being filled first, and therefore allowing control over the nuclearity of the complex. Ttop in methanol (10^{-5} M) gave the ESI-MS spectrum **A** (ESI-MS of [**L1**H]$^+$, $m/z = 397.2$); half an equivalent of copper(II) chloride to one equivalent of **L1** produced spectrum **B** (ESI-MS of [Cu(**L1**)Cl]$^+$, $m/z = 494.1$); one equivalent of copper(II) chloride reacted with one equivalent of **L1** produced spectrum **C** (ESI-MS of [Cu$_2$(**L1**)Cl$_3$]$^+$, $m/z = 629.0$); one equivalent of 4,4'-bipyridine reacted with one equivalent of complex **2** and gave spectrum **D** (ESI-MS of [Cu(**L2**)Cl]$^+$, $m/z = 405.1$); one equivalent of copper(II) nitrate reacted with one equivalent of **L1** producing complex **5** and gave spectrum **E** (ESI-MS of [Cu$_2$(**L3**)$_2$(NO$_3$)$_3$]$^+$, $m/z = 928.2$); two equivalents of copper(II) chloride with one equivalent of **L1** produced spectrum **F** (ESI-MS of [Cu$_4$(**L1**)$_2$Cl$_7$]$^+$, $m/z = 1294.9$).

From the spectra produced, it can be seen that the stoichiometry of the reactant used in the reaction is the predominant factor in the formation of the complex. The copper(II) chloride salt reacts to give complexes **2**–**4** and **6** with the nitrate salt producing the hydrolyzed dimer **5** (Scheme 2).

In-situ Mass Spectrometry

The combination of pre-diluted reactants in-situ was investigated using ESI-MS to allow the kinetically favored product to be observed and analysed. To create such experimental conditions, a tee-piece was used to enable the input and subsequent mixing of the reactants (see Figure 3). Initially, input A was **L1** in methanol (10^{-5} M) and input B was a blank control containing only methanol. This reaction mixture resulted in a spectrum with a predominant peak at 397 m/z being **L1**. Replacing the blank with 0.5 equivalents, 1 equivalent, and 2 equivalents of copper(II) chloride produced spectra b) to d), respectively. The spectra produced show the kinetic product formed with each equivalent (Figure 4): 0.5 equivalents of copper(II) chloride gave the species [Cu(**L2**)(H$_2$O)$_4$(OH)]$^+$; the predominant species with 1 equivalent of copper(II) chloride being [Cu(**L1**)Cl]$^+$; 2 equivalents of copper(II) chloride produces a spectrum showing the species [Cu$_2$(**L1**)Cl$_3$]$^+$.

The use of a tee-piece allows a combination of dilute reactants to be observed directly after mixing. By using the most simple of building blocks, clusters were formed almost instantaneously, providing further evidence of the coordination self-assembly processes occuring in ttop Cu^{II} systems. It is interesting to note that the stoichiometry used to produce the thermodynamic products is different to that used to pro-

Scheme 2. Summary of complexes (**2**–**6**) obtained from ttop (**L1**) under different stoichiometries and reaction conditions.
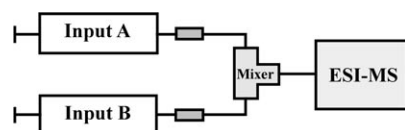

Figure 3. Schematic of tee-piece (mixer) combining two inputs to ESI-MS. The distance *d* is variable, but for these experiments was set at 5 cm. The mixer had no dead volume and the tubing had a diameter, *d*, of 0.9 mm. Inputs were set to a rate of approximately $100\ \mu L\,h^{-1}$, and thus, a combined input of approximately $200\ \mu L\,h^{-1}$ was obtained.
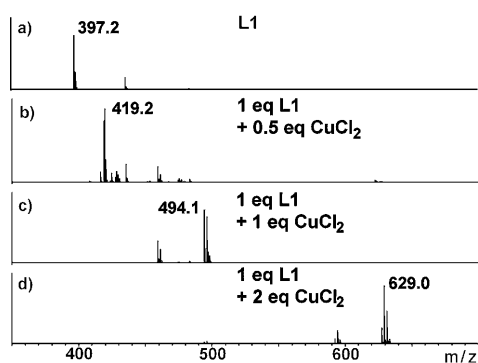

Figure 4. ESI-MS measurement of a) Input A: **L1** in methanol (10^{-5} M), Input B: methanol, predominant species $[\mathbf{L1H}]^{+}$, $m/z = 397$; b) Input A: **L1** in methanol (10^{-5} M), Input B: 0.5 equivalents copper(II) chloride, predominant species $[Cu(\mathbf{L2})(H_2O)_4(OH)]^{+}$, $m/z = 419$; c) Input A: **L1** in methanol (10^{-5} M), Input B: 1 equivalent copper(II) chloride, predominant species $[Cu(\mathbf{L1})Cl]^{+}$, $m/z = 494$; d) Input A: **L1** in methanol (10^{-5} M), Input B: 2 equivalents copper(II) chloride, predominant species $[Cu_2(\mathbf{L1})Cl_3]^{+}$, $m/z = 629$.

duce the same complex when using in-situ mass spectrometry.

Conclusions

The labile ligand ttop has the ability to form a range of coordination complexes when combined with copper(II) salts. This coordination reaction can be followed in real time using ESI-MS.[34] Control over the stoichiometry and reaction conditions allows the formation of complexes with different metal to ligand ratios. As both cobalt(II) and zinc(II) can be coordinated to the ttop ligand, it is hoped to continue the work to include cobalt(III), nickel(II), and iron(II) using both the chloride and nitrate salts. Further, by using metals that can be 'switched' between relatively labile and inert kinetic forms (e.g., cobalt II/III), the use of in-situ mass spectrometry to monitor the assembly of very large systems using a variety of control parameters (stoichiometry, REDOX reagent, concentration, range, and rigidity of ligands) will become possible.

Experimental Section

All reagents were used as received from commercial sources, without further purification. The ligand *cis,trans*-1,3,5-triaminocyclohexane was synthesized according to literature methods.[32] ^{1}H and ^{13}C NMR spectra were recorded at room temperature (RT) unless otherwise stated, on a Bruker DRX-500 and DPX-400 spectrometer in CH_3Cl. Infra-red spectral analyses were performed on a JASCO 410 spectrophotometer, using a KBr disc and a Shimadzu FTIR 8400S; peaks are quoted in wavenumbers (cm^{-1}) and their relative intensity are reported as follows: s = strong, m = medium, w = weak. UV/Vis spectroscopy was performed on Shimadzu UV-310PC UV/Vis/NIR scanning spectrophotometer. Microanalyses were performed on a CE-440 elemental analyzer. Mass spectra were obtained using a Bruker MicrOTOF-Q in ESI positive ion mode. X-ray diffraction was performed using an Oxford Diffraction Gemini Ultra with a CrysAlis CCD detector [λ Mo$_{K\alpha}$ = 0.71073 Å]. Crystal data for compounds **2**–**6** is presented in Table 1. Structure refinements were performed using the SHELXS-97[33] by WinGX[35] software package. CCDC 714504, CCDC 714505, CCDC 714506, CCDC 714507, CCDC 714508 contain the supplementary crystallographic data for this paper for compounds **2**–**6** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at www.ccdc.cam.ac.uk/data_request/cif.

Syntheses

cis,trans-1,3,5-Tris(pyridine-2-carboxaldimino) cyclohexane (**L1**) **1**: Pyridine-2-carboxaldehyde (2.38 g, 23.18 mmol) was added to a methanolic solution (100 mL) of *cis,trans*-1,3,5-triaminocyclohexane (1 g, 7.85 mmol)

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and triethylamine (2.38 g, 23.55 mmol) and refluxed for 24 h under nitrogen. The solvent was removed under vacuum, the resulting brown product (2.24 g, 5.64 mmol, 72%) being taken off in dichloromethane (150 mL), and washed with water (3×50 mL). The organic layer was dried over magnesium sulfate and the dichloromethane removed in vacuo. M.p.: 75°C; IR (Golden Gate): $\tilde{v}$ = 3059 (w), 2928 (m), 2858 (m), 1643 (s), 1585 (s), 1566 (s), 1466 (s), 1435 (s), 1373 (m), 1319 (w), 1288 (w), 1227 (w), 1134 (m), 1080 (m), 1042 (m), 1018 (w), 991 (s), 972 (s), 860 (s), 772 (s), 741 (s), 664 (m), 650 (m), 617 (s), 562 (m), 517 (s) cm^{-1}; ^{1}H NMR (400 MHz, CDCl3): δ = 8.56 (d, 1H, J 4.9 Hz), 8.55 (d, 2H, J 5.0 Hz), 8.40 (s, 2H), 8.38 (s, 1H), 8.02 (d, 1H, J 8.0 Hz), 7.90 (d, 2H, J 8.0 Hz), 7.68 (d, 1H, J 8.0, 7.5 Hz), 7.62 (td, 2H, J 8.0, 7.5 Hz), 7.23 (ddd, 1H, J 6.5, 6.0 Hz), 7.12 (ddd, 2H, J 6.5, 6.0 Hz), 4.11 (pt, 2H, J 11.3 Hz), 3.97 (br s, 1H), 2.07 (m, 3H), 1.95 (br d, 1H, J 12.5 Hz), 1.80 ppm (br d, 2H, J 12.5 Hz); ^{13}C NMR (75 MHz, CDCl3): δ = 159.16 (CH$_2$), 158.83 (CH), 153.38 (C), 153.33 (C), 147.95 (CH), 147.84 (CH), 135.00 (CH), 123.20 (CH), 123.10 (CH), 119.99 (CH), 119.75 (CH) 63.48 (CH), 61.68 (CH), 39.90 (CH$_2$), 38.68 ppm (CH$_2$); MS (ESI): m/z (%): 419 [M+Na]$^+$; elemental analysis: calcd (%) for C$_{24}$H$_{24}$N$_6$: C 72.70, H 6.10, N 21.20; found: C 72.53, H 6.31, N 20.90.

[Cu(**L1**)Cl]Cl(CH$_3$OH)$_2$ **2**: A methanolic solution (20 mL) of **L1** (100 mg, 0.25 mmol) was added to a solution of copper(II) chloride (30 mg, 0.23 mmol) in methanol (5 mL). The solution changed from a pale yellow color to dark green. The solution was stirred for 30 min and reduced in volume to approximately 5 mL. Crystallization by diffusion of ether resulted in dark green crystals (20 mg, 0.034 mmol, 13%). IR (KBr): $\tilde{v}$ = 3433 (s), 2928 (w), 2356 (w), 1644 (m), 1602 (m), 1385 (s), 1309 (m), 1242 (s), 1135 (m), 978 (w), 867 (w) cm^{-1}; elemental analysis: calcd (%) for C$_{24}$H$_{24}$Cl$_2$CuN$_6$: C 54.29, H 4.56, N 15.83; found: C 53.18, H 4.63, N 15.54.

[Cu$_2$(**L1**)Cl$_4$] **3**: A methanolic solution (20 mL) of **L1** (100 mg, 0.25 mmol) was added to a solution of copper(II) chloride (34 mg, 0.25 mmol) in methanol (5 mL). The solution changed from a pale yellow color to dark green. The solution was stirred for 30 min and reduced in volume to approximately 5 mL. Crystallization by diffusion of ether resulted in dark green crystals (133.9 mg, 0.192 mmol, 76%). IR (KBr): $\tilde{v}$ = 3430 (s), 2926 (w), 2065 (w), 1638 (s), 1598 (s), 1478 (m), 1446 (m), 1384 (m), 1305 (m), 1271 (w), 1226 (m), 1158 (w), 1132 (m),1048 (w), 1019 (w), 992 (w),926 (w), 874 (w), 775 (m) cm^{-1}; elemental analysis: calcd (%) for Cu$_2$C$_{24}$H$_{24}$N$_6$Cl$_4$: C 43.32, H 3.64, N 12.63; found: C 40.78, H 3.98, N 11.19.

[Cu(**L2**)(H$_2$O)Cl]Cl$_2$ **4**: A methanolic solution (20 mL) of **2** (55 mg, 0.041 mmol) was added to a solution of 4,4'-bipyridine (6 mg, 0.041 mmol) in methanol (5 mL). A green-brown precipitation was formed immediately. Methanol was added until the volume was 75 mL and the solution was refluxed for 30 min. After evaporation of methanol to a volume of approximately 5 mL, filtration through cotton wool afforded a clear brown solution. Crystallization by diffusion with ether resulted in brown-green crystals (5.1 mg, 0.0095 mmol, 23%). IR (KBr): $\tilde{v}$ = 3424 (s), 2857 (w), 2057 (w), 1639 (s), 1598 (s), 1479 (w), 1444 (w), 1383 (m), 1303 (w), 1269 (w), 1227 (w), 1157 (m), 1132 (w), 1101 (w), 1047 (w), 1019 (w), 882 (m), 776 (m) cm^{-1}; elemental analysis: calcd (%) for CuC$_{18}$H$_{28}$N$_5$O$_3$Cl$_3$: C 40.611, H 5.301, N 13.156; found: C 40.61, H 4.46, N 12.33.

[Cu$_2$(**L3**)$_2$(NO$_3$)$_2$](NO$_3$)$_2$ **5**: A methanolic solution (20 mL) of **L3** (80 mg, 0.20 mmol) was added to a solution of copper(II) nitrate (48.32 mg, 0.20 mmol) in methanol. The color changed from colorless to dark green. The solution was stirred for one hour and reduced in volume to approximately 5 mL. Crystallization by diffusion of ether resulted in green crystals (169.4 mg, 0.156 mmol, 78%). λ_{max} (Abs) = 602.5 nm (0.0565); IR (KBr): $\tilde{v}$ = 3444 (s), 3203(w), 3104 (w), 2906 (w), 2426 (w), 1763 (w), 1639 (m), 1600 (m), 1482 (w), 1383 (s), 1225 (w), 1159 (w), 1133 (w), 1108 (w), 1075 (w), 1042 (w), 1023 (w), 959 (w), 910 (w), 887 (w), 826 (w), 781 (s) cm^{-1}; elemental analysis: calcd (%) for Cu$_2$C$_{39}$H$_{54}$O$_{15}$N$_{14}$: C 43.13, H 5.01, N 18.06; found: C 43.55, H 4.39, N 18.38.

{[Cu$_2$(**L1**)Cl$_3$]Cl}$_2$ **6**: A methanolic solution (20 mL) of **L1** (100 mg, 0.25 mmol) was added to a solution of copper(II) chloride (68 mg, 0.50 mmol) in methanol (5 mL). The solution changed from a pale yellow color to dark green. The solution was stirred for 30 min and reduced in

volume to approximately 5 mL. Crystallization by diffusion of ether resulted in dark green crystals (278.1 mg, 0.209 mmol, 83%). IR (Golden Gate): $\tilde{v}$ = 3435 (m), 2037 (m), 2951 (m), 2925 (m), 1643 (s), 1597 (s), 1567 (m), 1479 (m), 1444 (s), 1398 (w), 1381 (w), 1323 (w), 1302 (s), 1269 (w), 1227 (s), 1159 (w), 1132 (s), 1105 (m), 1049 (m), 1014 (m), 980 (s), 935 (w), 881 (m), 768 (s), 742(m), 696 (w), 642 (s) cm^{-1}; elemental analysis: calcd (%) for Cu$_2$C$_{24}$H$_{24}$N$_6$Cl$_4$: C 43.32, H 3.64, N 12.63; found: C 42.33, H 3.48, N 12.17.

ESI-MS Experimental and Analyses

All MS data were collected using a Q-trap, time-of-flight MS (MicrO-TOF-Q MS) instrument supplied by Bruker Daltonics Ltd. A cryospray source, also supplied by Bruker Ltd., was used to collect data under the conditions specified below. The detector was a time-of-flight, microchannelplate detector, and all data were processed using the Bruker Daltonics Data Analysis 3.4 software, while simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. The following parameters were consistent for all CSI-MS scans given below. The calibration solution used was Agilent ES tuning mix solution, Recorder No. G2421A, enabling calibration between −100 m/z and 3000 m/z. This solution was diluted 60:1 with acetonitrile. Samples were introduced into the MS by direct injection at 180 μL h^{-1} having been diluted to 10^{-5} M in methanol. The drying nitrogen gas temperature was at 180°C. The ion polarity for all MS scans recorded was positive, with the voltage of the capillary tip set at 4500 V, end plate offset at −500 V, funnel 1 RF at 300 Vpp, and funnel 2 RF at 400 Vpp.

All theoretical peak assignments were determined by comparison of the experimentally determined isotopic patterns for each peak, with simulated isotopic patterns. For relatively small complexes, such as the ttop complexes, the isotopic pattern is quite distinct, and comparison between experimental and simulated patterns is more meaningful (see Figure 2) than in the case of larger fragments, in which the isotopic pattern takes on a Gaussian shape, and it cannot be said with certainty that the suggested peak is unequivocally correct.

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