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ARTICLE

A Ligand Strand that Displays Anion-dependant Reactivity with Acetonitrile; Forming Either a Mononuclear Complex or Head-to-Tail Circular Helicate.

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The ligand $L^{2,2}$ contains two bidentate domains separated by a 3,3-diamino-2,2'-biphenyl spacer unit and with $Cu(ClO_4)_2$ a mononuclear species is formed (e.g. $[Cu(L^{2,2})]^{2+}$). Upon coordination with $Cu(triflate)_2$ the ligand undergoes reaction with an acetonitrile solvent, producing a different ligand with unsymmetrical bidentate and tridentate domain ($L^{2,3}$). This new ligand results in the formation of a tetranuclear head-to-tail circular helicate $[Cu_4(L^{2,3})_4]^{8+}$ showing that in the presence of the triflate anion the ligand denticity is changed.

Metallo-supramolecular chemistry is the construction of architecturally complex assemblies arising from coordination of metal ions to suitably instructed ligand strands. The formation of these assemblies is a result of the interplay between both the polydentate ligand strands and the coordination preference of metal ions. The successful formation of these architectures is often dependant on the number and arrangement of the binding domains contained within these ligand strands.[1]

One class of metallo-supramolecular self-assembly is the linear helicate which consist of two or more multi-dentate ligand strands helically wrapped about a central array of metal cations.[1] Not only can polynuclear double-, triple- and quadruple-stranded helicates now be made in a predictable fashion,[1f] they can also be programmed to express certain structural features of higher-order complexity. This may be achieved by elaborating on the basic design principles that govern helicate formation itself (i.e. careful consideration of ligand topology and metal stereoelectronic preference) and, amongst others, can entail; directional control over ligand alignment (termed *head-to-tail*),[2] selective incorporation of different metal cations (i.e. *heterometallic* helicates) and selective incorporation of different ligand strands within the helical array (i.e. *heteroleptic* helicates).[2]

Reaction of metal ions with a suitably partitioned ligand strand can also lead to the formation of the cyclic helicate which retain the 'over-and-under' ligand motif requisite of helical chirality but are cyclic oligomers of general formula $[M_n(\mathbf{L})_n]$ ($n > 2$). However, this assembly is less well understood than its linear counterpart and consequently formation of this species is more challenging. One of the major problems in the formation of these higher nuclearity assemblies is that the design principles that apply to helicate formation, *i.e.* using a ligand that contains two binding domains that coordinate *different* metal ions, equally apply to the formation of cyclic helicates. For the larger cyclic species to preside in solution, the formation of the entropically favoured dimer has to be prevented and this can be achieved by intermolecular interactions (*e.g.* templation by anions)[3] or by intramolecular interactions which stabilise the formation of the cyclic species relative to its double-stranded alternative.[4]

Consequently, the configuration of the binding domains within the ligand strand is crucial for the successful formation of linear and circular helicates as this arrangement imparts information which is expressed via the self-assembly process. As a result the ligands can be considered as pre-programmed as they contain the inherent geometric information required to form the self-assembled construct. However, apart from a few notable examples, the pre-programmed information held within the ligand chain is stored at the synthetic stage and cannot be changed.[5]

In this work, we describe a pyridyl-thiazole containing bis-bidentate ligand ($\mathbf{L}^{2,2}$) separated by a 3,3'-diamino-2,2'-biphenyl spacer unit which forms a simple mononuclear species with $Cu(ClO_4)_2$ e.g. $[Cu(\mathbf{L}^{2,2})](ClO_4)_2$. Reaction with $Cu(triflate)_2$ initially gives a similar species but the ligand undergoes reaction with the acetonitrile solvent and one of the amine units, producing a different ligand with unsymmetrical binding domains ($\mathbf{L}^{2,3}$). This new species contains both a bidentate and a tridentate binding domain and results in the formation of a tetranuclear head-to-tail circular helicate $(Cu_4(\mathbf{L}^{2,3})_4)^{8+}$ showing that in the presence of the triflate anion, the ligand undergoes a reaction with acetonitrile

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Electronic Supplementary Information (ESI) available: Full synthetic and crystallographic details. See DOI: 10.1039/x0xx00000x changing the denticity from bis-bidentate to a bidentate and tridentate donor unit (Fig. 1).

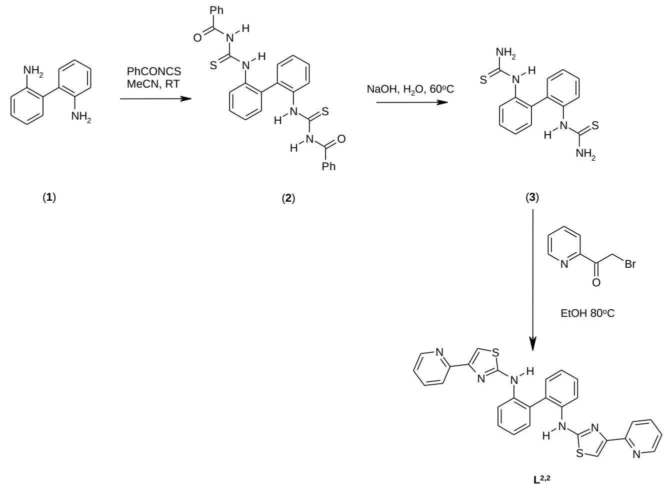

Figure 1. Synthesis of ligand $L^{2,2}$

Experimental

Synthesis of (2). To a solution of 1,1'-biphenyl-2,2'-diamine (**1**) (410 mg, 2.23 mmol) in acetonitrile (50 mL) was added benzoyl isothiocyanate (794 mg, 4.90 mmol) and the reaction stirred for 3 days at RT, during which time a colourless precipitate formed which was isolated by filtration, washed with MeCN (3 × 5 mL) and Et_2O (3 × 5 mL) giving (**2**) as a white solid. Yield = 743 mg (65 %). ^{1}H NMR (400 MHz, DMSO-*d*^{6}) δ (ppm) 12.2 (s, 2H, -NH), 11.4 (s, 2H, -NH), 7.86 (d, 4H, *J* = 7.52), 7.74 (d, 2H, *J* = 7.8), 7.63 (t, 2H, *J* = 7.4), 7.50 (t, 4H, *J* = 7.68), 7.43 (m, overlapping, 4H), 7.34 (t, 2H *J* = 7.38 Hz). ^{13}C NMR [100 MHz, DMSO-*d*^{6}]: *δ* (ppm) = 180.9 (C=S), 168.3 (C=O), 136.8 (Q), 135.0 (Q), 133.5 (CH), 132.5 (Q), 130.7 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 128.2 (CH), 127.3 (CH). ESI-MS *m/z* 511 (M + H$^+$), HR ESI-MS found 511.1251 $C_{28}H_{22}N_4O_2S_2$ requires 511.1257 (error 0.93 ppm).

Synthesis of (3). The diurea derivative (**2**) (400 mg, 0.784 mmol) was suspended in water (20 mL) and NaOH (191 mg, 4.78 mmol) added. The reaction was then heated to 60°C and MeOH slowly added drop wise until all the solid dissolved (1 ~ 2 mL). After 24 hrs the solution was allowed to cool to room temperature and then immersed in an ice bath, after which time a colourless solid precipitated. Isolation by filtration and washing with ice cold water (2 x 1 mL) gave the dithiourea (**3**) as a colourless solid. Yield = 140 mg (59 %). ^{1}H NMR (400 MHz, DMSO-*d*^{6}) δ (ppm) 8.81 (s, 2H, ArNH), 7.50 (m, 4H, Ar), 7.27 (m, 4H, Ar), 7.60 – 7.0 (s, broad, overlapping, 4H, $-CSNH_2$). ^{13}C NMR [100 MHz, DMSO-*d*^{6}]: *δ* (ppm) = 183.5 (C=S), 137.0 (Q), 135.4 (Q), 131.1 (CH), 129.4 (CH), 128.5 (CH), 126.6 (CH). ESI-MS *m/z* 303 (M + H$^+$), HR ESI-MS found 303.0732 $C_{14}H_{14}N_4S_2$ requires 303.0733 (error 0.41 ppm).

Synthesis of $\mathbf{L^{2,2}}$. The dithiourea containing compound (**3**) (141 mg, 0.47 mmol) was suspend in EtOH (20 mL) and to this, α-bromoacetylpyridine hydrobromide (393 mg, 1.40 mmol) was added and the reaction heated at 80°C overnight. During this time a yellow precipitate had formed which was isolated by filtration and washed with EtOH (2 x 1 mL) and Et_2O (2 x 1 mL). This yellow solid was suspended in ammonia (sp. gr 0.88, 10 mL) and stirred for 24 hrs. The solid was then filtered, washed with H_2O (2 x 1 mL), EtOH (2 x 1 mL) and Et_2O (2 x 1 mL) to give $\mathbf{L^{2,2}}$ as a cream solid. Yield = 120 mg (51 %). ^{1}H NMR (400 MHz, DMSO-*d*^{6}) δ (ppm) 8.56 (d, 2H, *J* = 4.32), 8.20 (d, 2H, *J* = 8.16), 7.89 (d, 2H, *J* = 7.92), 7.69 (td, 2H, *J* = 7.72, 1.6), 7.53 (td, 2H, *J* = 7.81, 1.4), 7.33 (m, overlapping, 4H), 7.23 (t, 2H, *J* = 7.44), 7.18 (dd, 2H, *J* = 7.02, 4.96 Hz), 6.96 (2H, br s, -NH). ^{13}C NMR (500 MHz, DMSO-*d*^{6}) δ (ppm) = 165.6 (Q), 151.7 (Q), 149.6 (CH), 139.2 (Q), 137.6 (CH), 131.9 (CH), 130.8 (Q), 129.5 (Q), 129.0 (CH), 123.9 (CH), 122.9 (CH), 122.0 (CH), 120.8 (CH), 107.2 (CH). ESI-MS *m/z* 505 (M + H$^+$), HR ESI-MS found 505.1256 $C_{28}H_{20}N_6S_2$ requires 505.1264 (error 1.24 ppm).

Synthesis of $\mathbf{[Cu(L^{2,2})](ClO_4)_2}$. To a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (10 mg. 0.027 mmol) in MeCN (1 ml) was added a suspension of ligand $\mathbf{L^{2,2}}$ (13 mg, 0.026 mmol) in MeCN and the reaction warmed and sonicated until a clear light blue solution had formed. Diisopropyl ether was slowly allowed to diffuse into the solution resulting in blue plate-like crystals after several days. Filtration and washing with diisopropyl ether (1 mL) and diethyl ether (1 mL) gave blue crystals which lost solvent rapidly (yield = 52%). ESI-MS *m/z* 669 corresponding to $\{Cu(\mathbf{L^{2,2}})(ClO_4)\}^+$ along with higher molecular species. Crystallisation of this material produced a minor amount of a decomposition product precluding elemental analysis.

Synthesis of $\mathbf{[Cu_4(L^{2,3})_4](trif)_8}$. To a solution of $Cu(triflate)_2$ (10 mg. 0.028 mmol) in MeCN (1 mL) was added a suspension of ligand $\mathbf{L^{2,2}}$ (14 mg, 0.026 mmol) in MeCN and the reaction warmed and sonicated until a clear light blue solution had formed. Diisopropyl ether was slowly allowed to diffuse into the solution resulting in pale blue block crystals after several days. Filtration and washing with diisopropyl ether (1 ml) and diethyl ether (1 ml) gave blue crystals which lost solvent rapidly (yield = 68%). ESI-MS *m/z* 3479 corresponding to $\{[Cu_4(\mathbf{L^{2,3}})_4](trif)_7\}^+$), along with a ion at *m/z* 1665 corresponding to both the singly charged dinuclear assembly $\{[Cu_2(\mathbf{L^{2,3}})_2](trif)_3\}^+$ and the doubly charged tetranuclear assembly (e.g. $\{[Cu_4(\mathbf{L^{2,3}})_4](trif)_6\}^{2+}$). Found: C, 41.4; H, 2.6; N, 10.0%; $C_{128}H_{92}N_{28}S_{16}Cu_4F_{24}O_{24}\cdot 2H_2O$ requires C, 41.9; H, 2.6; N, 10.7%.

Results and Discussion

Ligand $\mathbf{L^{2,2}}$ was synthesised from reaction of 2,2'-diaminobiphenyl with benzoyl isothiocyanate, hydrolysis to form the diurea-containing precursor and subsequent reaction with 2-(bromoacetyl)pyridine to give the bis-bidentate ligand. Reaction of $\mathbf{L^{2,2}}$ with one equivalent of $Cu(ClO_4)_2$ in MeCN gave a pale blue solution from which was deposited a blue crystalline material upon slow diffusion of diisopropyl ether.

In the solid-state a simple mono-nuclear complex is formed (i.e. $[Cu(\mathbf{L^{2,2}})]^{2+}$) with the ligand acting as a simple tetradentate donor coordinating the Cu^{2+} ion via four nitrogen donor atoms from the two bidentate pyridyl-thiazole domains (fig. 2). In the ligand strand there is a substantial twist about the biphenyl unit allowing the ligand to act as a donor to a single metal ion (Fig 2a and 2b). The Cu^{2+} metal ion adopts a distorted tetrahedral geometry with the Cu – N bonds ranging from 1.974(4) - 1.988(4) Å. The two amine units both point away from the complex and form hydrogen bonding interactions with perchlorate anions (fig. 3). This type of behaviour is to be expected as ligands containing this type of amine unit have been shown to interact with both perchlorate and tetrafluoroborate anions.[4e]

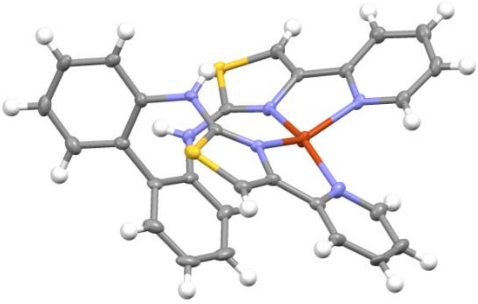

Figure 2. X-ray structure of $[Cu(\mathbf{L^{2,2}})]^{2+}$. Thermal ellipsoids shown at the 50% probability level. Colour code: orange, Cu(II); blue, N; yellow, S; grey, C.

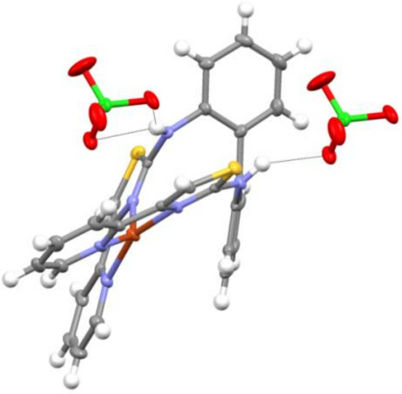

Figure 3. X-ray structure of $[Cu(\mathbf{L^{2,2}})](ClO_4)_2$ showing the hydrogen bonding interaction between the cation and anions. Thermal ellipsoids shown at the 50% probability level. Colour code: orange, Cu(II); blue, N; yellow, S; grey, C; red O; green, Cl.

Reaction of ligand $\mathbf{L^{2,2}}$ with $Cu(trif)_2$ initially gives a similar blue colour to the perchlorate derivative but this significantly lightens over a period of 48 hrs. Slow diffusion of disopropyl ether deposited a homogenous mass of light blue crystals which were examined by single crystal X-ray diffraction. In the solid-state the structure contains four ligand strands and four Cu^{2+} metal ions with the ligand partitioning into two donor domains each of which coordinates a different metal ion producing a tetranuclear circular helicate (Fig 4). The most interesting feature of this structure is that *one* of the amine units present on the ligand strand has reacted with a molecule of acetonitrile solvent giving a new amidine-containing R_2N-$C{=}NH(CH)_3$ unit (Fig. 5). This amidine unit is incorporated within the ligand chain producing an unsymmetrical strand containing both a bidentate pyridyl-thiazole and a tridentate amidine-pyridyl-thiazole binding domains (*i.e.* $\mathbf{L^{2,3}}$). In the crystal the copper ions are coordinated by a tridentate domain from one ligand and a bidentate domain for a different ligand giving a 5-coordinate metal centre which is a common coordination geometry for this metal ion (with the Cu – N bond lengths ranging from 1.926(3) - 2.249(4) Å). Due to the unsymmetrical nature of the ligand chain it can be considered to contain both a head and a tail due to the copper ions preference for five coordinate geometry. Directional control over ligand alignment is achieved and a *head-to-tail* tetranuclear circular helicate is formed.

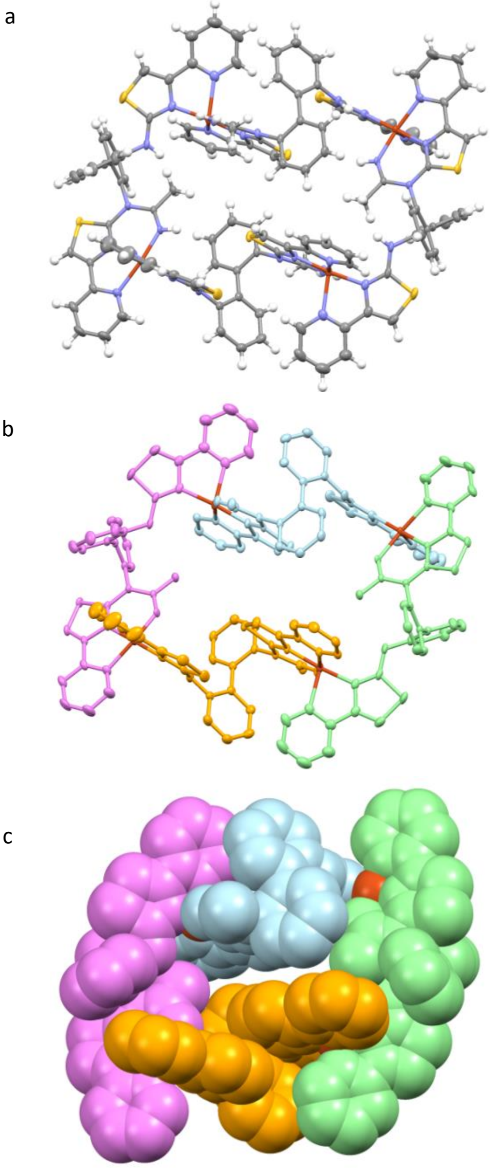

Figure 4. (a) – (c) Single-crystal X-ray structure of $[Cu_4(\mathbf{L^{2,3}})_4]^{8+}$. Anions, some of which hydrogen bond to the –NH donors, omitted for clarity and thermal ellipsoids shown at the 50% probability level. Colour code: orange, Cu(II); blue, N; yellow, S; grey, C (apart from 4b and 4c where the ligands have been coloured for clarity).

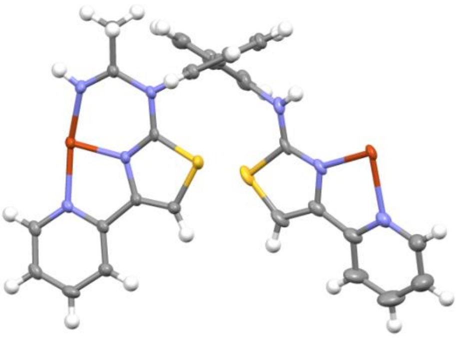

Figure 5. Partial view of $[Cu_4(\mathbf{L^{2,3}})_4]^{8+}$ showing the bidentate and tridentate domains. Anions, some of which hydrogen bond to the –NH donors, omitted for clarity and thermal ellipsoids shown at the 50% probability level. Colour code: orange, Cu(II); blue, N; yellow, S; grey, C.

Examination of the ESI-MS of the reaction of $Cu(ClO_4)_2$ with $\mathbf{L^{2,2}}$ shows an ion at *m/z* = 669 corresponding to the mononuclear complex $\{[Cu(\mathbf{L^{2,2}})](ClO_4)\}^+$ consistent with the solid-state observations. However, also present in the ESI-MS are ions at *m/z* 1433 and 2201 which correspond to $\{[Cu_2(\mathbf{L^{2,2}})_2](ClO_4)_3\}^+$, and $\{[Cu_3(\mathbf{L^{2,2}})_3](ClO_4)_5\}^+$. This indicates that the ligand is sufficiently flexible to adopt a number of conformations allowing a variety of polynuclear species to be accessible and in the gas phase, with the double helicate and the tri-nuclear circular helicate observed. However, as would be expected due to entropic reasons, only the mononuclear species is observed in the solid-state.

Reaction of $Cu(trif)_2$ with $\mathbf{L^{2,2}}$ initially shows an ion at *m/z* 716 corresponding to $\{[Cu(\mathbf{L^{2,2}})](trif)\}^+$ as well as ions corresponding to the higher oligomer $\{[Cu_2(\mathbf{L^{2,2}})_2](trif)_3\}^+$, in a similar fashion to the perchlorate derivative. However, over the period of 48 hrs a new set of peaks, 41 mass units higher for each ligand strand, are observed in the ESI-MS indicating that the ligand has reacted with the acetonitrile solvent producing $\mathbf{L^{2,3}}$ (e.g. *m/z* 1665 corresponding to $\{[Cu_4(\mathbf{L^{2,3}})_4](trif)_6\}^{2+}$). Monitoring the perchlorate derivative over a similar period of time shows no such change with all the ions corresponding to complexes containing $\mathbf{L^{2,2}}$, indicating that no reaction with acetonitrile is observed. The same lack of reactivity is also observed with the tetrafluoroborate derivative which gives an ESI-MS essentially identical to $[Cu_2(\mathbf{L^{2,2}})_2](ClO_4)_4$.

Thus in the reaction of $\mathbf{L^{2,2}}$ with $Cu(ClO_4)_2$ the ligand acts as a simple tetradentate donor and produces a mononuclear species $[Cu(\mathbf{L^{2,2}})](ClO_4)_2$. However, upon coordination with $Cu(trif)_2$ the amine nitrogen atom present within the ligand strand undergoes nucleophilic reaction with the acetonitrile solvent producing a ligand that contains a new donor set which comprises of both a bidentate and tridentate domain e.g. $\mathbf{L^{2,3}}$. This ligand cannot now act as a simple pentadentate donor and form a mononuclear complex as, due to steric constraints, all five *N*-donor units cannot coordinate the same metal ion; instead a tetranuclear *head-to-tail* circular helicate is produced. Effectively the ligand chain changes denticity by reaction with the solvent changing it from a tetradentate donor to one that contains both a bidentate and tridentate donor set. The reactivity is confined to only one of the amine functional groups as a consequence of the preference of the Cu(II) for a 5-coordinate geometry as reaction of both amine units would lead to a bis-tridentate ligand giving a 6-coordinate metal centre.[6] We have shown that certainly with ligands of this type Cu(II) does show a preference for this geometry.[5]

Why the reactivity is dependent on the anion present isn't immediately obvious. However, we have shown that metallo-supramolecular complexes that contain similar amine units strongly interact with both perchlorate and tetrafluoroborate anions[4e,5g] and it is possible that, in forming hydrogen bonding interactions, the *sp²* hybridized nitrogen atom is stabilised thereby reducing its nucleophilicity. Indeed, the use of $Cu(BF_4)_2$ in the coordination of $\mathbf{L^{2,2}}$ resulted in a ion in the ESI-MS at *m/z* 1394 corresponding to both the dinuclear species $\{[Cu_2(\mathbf{L^{2,2}})_2](BF_4)_3\}^+$ and the doubly charged tetranuclear species $\{[Cu_4(\mathbf{L^{2,2}})_4](BF_4)_7\}^{2+}$ indicating the lack of reactivity to MeCN in a similar fashion to the perchlorate salt.

To probe this further a series of reactions were carried out in MeCN containing MeOH (9:1), as the inclusion of this protic solvent should disrupt amine···anion hydrogen-bonding interactions and better solvate counter anions. As would be expected the reaction of $Cu(triflate)_2$ with $\mathbf{L^{2,2}}$ showed little difference and the ESI-MS gave ions attributable to $\mathbf{L^{2,3}}$ which grew in intensity over time. However, reaction of $\mathbf{L^{2,2}}$ with $Cu(ClO_4)_2$ in the solvent containing 10% MeOH does show ions in the ESI-MS corresponding to reaction with MeCN (e.g *m/z* 707 $\{[Cu(\mathbf{L^{2,3}})](ClO_4)\}^+$ and *m/z* 1517 $\{[Cu_4(\mathbf{L^{2,3}})_4](ClO_4)_6\}^{2+}$), ions which are not observed when pure MeCN is used. The difference observed upon addition of MeOH to the reaction solvent does support the hydrogen-bonding deactivation of the –NH unit, as the methanol present will disrupt amine···anion hydrogen-bonding and solvate the perchlorate counter anion, allowing the amine unit to react with the solvent.

We have shown that the incorporation of –NH hydrogen-bonding units can govern the reactivity of a ligand dependent upon which anion is used. Strongly interacting anions prevent the ligands from reacting while weaker interacting anions allow reaction with acetonitrile. In this case this induces a change in the denticity of the ligand strand and results in either a simple mononuclear species with $Cu(ClO_4)_2$ e.g. $[Cu(\mathbf{L^{2,2}})](ClO_4)_2$ but reaction with MeCN in the presence of $Cu(triflate)_2$ gives a tetranuclear head-to-tail circular helicate $[Cu_4(\mathbf{L^{2,3}})_4](trif)_8$.

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