Allosteric deprogramming of a trinuclear heterometallic helicate†

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Two multidentate ditopic ligands **L**^{1} and **L**^{2} which contain both N-donor and crown ether units have been synthesised. The potentially octadentate ligand **L**^{1} forms a trinuclear heterometallic double helicate with Cu(I) and Zn(II) ($[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$), whereas **L**^{2} forms a tetranuclear heterometallic double helicate with the same metal ions ($[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$). Both species have been characterised by ^{1}H NMR, ESI-MS and single crystal X-ray crystallography. Reaction of $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ with Ba^{2+} results in the coordination of the crown ether units giving the simple barium coordinated species $[Zn_2Cu_2(\mathbf{L}^2)_2Ba_2]^{10+}$. However, reaction of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ with Ba^{2+} deprograms the ligand and results in the formation of a mixture of species.

Introduction

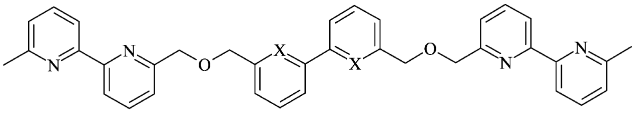
The formation of metallo-helicates from the self-assembly of organic donor ligand strands and transition metal ions has in recent years received a great deal of attention. However, for the successful generation of these helicates careful design of the ligand species is required to ensure that it has sufficient chemical *programming* to allow formation of the helicate assembly.[1]

For example work carried out by Lehn *et al.* has shown that a ligand strand comprising of two terminal 2,2′-bipyridine units and a central 2,2′:6′,2″-terpyridine unit forms a trinuclear double helicate with Cu(I) and Fe(II). Furthermore, the ligand strand is sufficiently instructed so that the Cu(I) metal ions are coordinated by the terminal bipyridine units and the Fe(II) coordinated by the central terpyridine domain.[2] Other examples of heterometallic helicates include the dinuclear double helicate $[CoML_2]^{3+}$ (where M = Ag(I) or Cu(I) and L = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine). In this complex the ligand strand is partitioned into both tridentate and bidentate domains which coordinate Co(II) and either Cu(I) or Ag(I), respectively.[3]

Examples by Cohen *et al.* show how the nature and disposition of binding sites within the ligand strand can greatly affect the formation of helicate species. For example, reaction of the oligo(2,2′-bipyridine) ligand **1** with Cu(I), Ag(I) and Zn(II) results in the formation of trinuclear double helicates ($[M_3(\mathbf{1})_2]^{n+}$), demonstrating that the ligand is sufficiently instructed, or programmed, to form helicate species with a variety of transition metal ions.[4] The ligand **2** contains the same terminal bipyridine binding domains, but in contrast to ligand **1** is separated not by a bipyridine binding domain but by a non-coordinating biphenyl unit. Reaction of this ligand with Cu(I) results in a number of species, only one of which is thought to be the helicate. This shows how a subtle change in the ligand strand can result in a species that is not sufficiently instructed to form metallo-helicate assemblies.[5]

Recently we have demonstrated that the information stored within a ligand strand can be changed or *reprogrammed* after the initial self-assembly event has occurred. For example, we developed a ditopic ligand that forms a dinuclear double-stranded helicate with Hg(II), but may be reprogrammed to form a mononuclear complex following binding of Ba^{2+} or Sr^{2+} ions to an external crown ether site.[6] This approach may also be employed to modify (i) a ligand's preference for different metal ions,[7] (ii) helical pitch-length[8] and (iii) gross molecular structure.[9] In the last case, ligand reprogramming causes a dicopper(I) double-stranded helicate to adopt a side-by-side configuration.

In this paper we report two novel ditopic ligands **L**^{1} and **L**^{2} which form heterometallic double stranded helicates with Zn(II) and Cu(I) giving the trinuclear species $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ and tetranuclear species $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$, respectively. These helicate assemblies also contain an exo-receptor crown ether unit. Reaction of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ with Ba^{2+} results in deprogramming of the ligand strand with the formation of $[Zn_n(\mathbf{L}^1)_n]^{2n+}$ polymers, whereas reaction of $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ with Ba^{2+} results in the barium-containing helicate species $[Zn_2Cu_2(\mathbf{L}^2)_2Ba_2]^{10+}$.



1 X = N
2 X = CH

Results and discussion

Synthesis

The synthesis of the ditopic ligand **L**^{1} was achieved by a 10 step convergent route starting from 6,6′-dimethyl-2,2′-bipyridine-3,3′-diol **3** (Scheme 1) and 2,2′-bipyridine-1-oxide **9** (Scheme 2).

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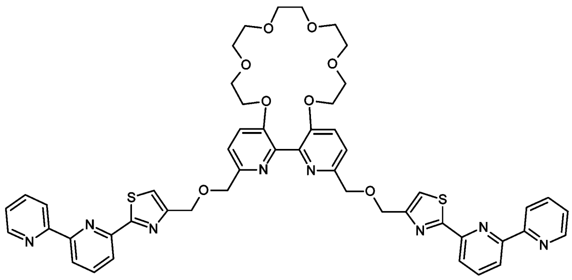
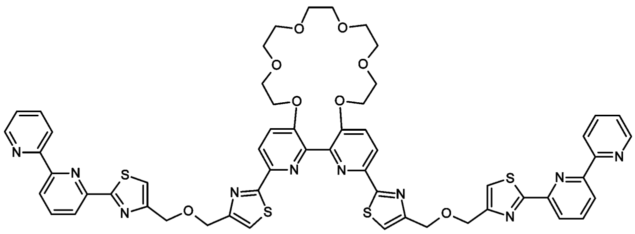
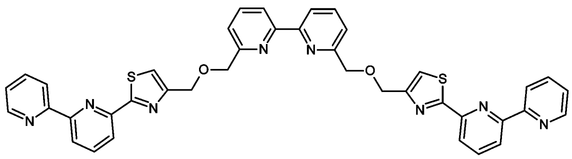
† Electronic supplementary information (ESI) available: Fig. 1: Mass spectrum of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ plus 20 equivalents of Ba(ClO$_4$)$_2$ and Fig. 2: The observed (top) and calculated (bottom) isotopic distribution pattern of $\{[ZnBa(\mathbf{L}^1)](ClO_4)_2\}^{2+}$. See DOI: 10.1039/b700539c



L^1



L^2

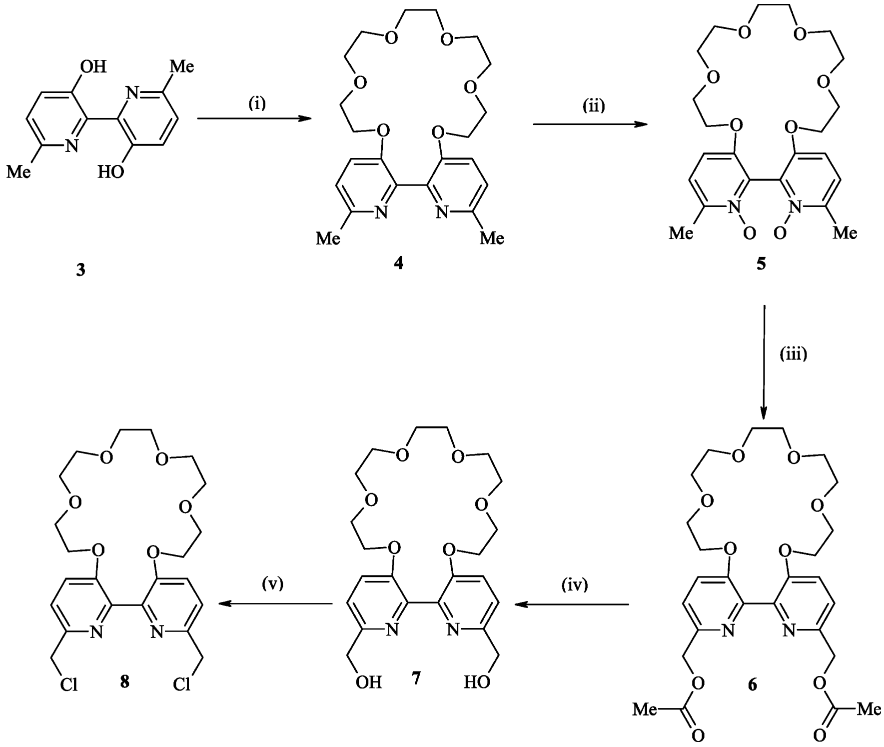


L^3

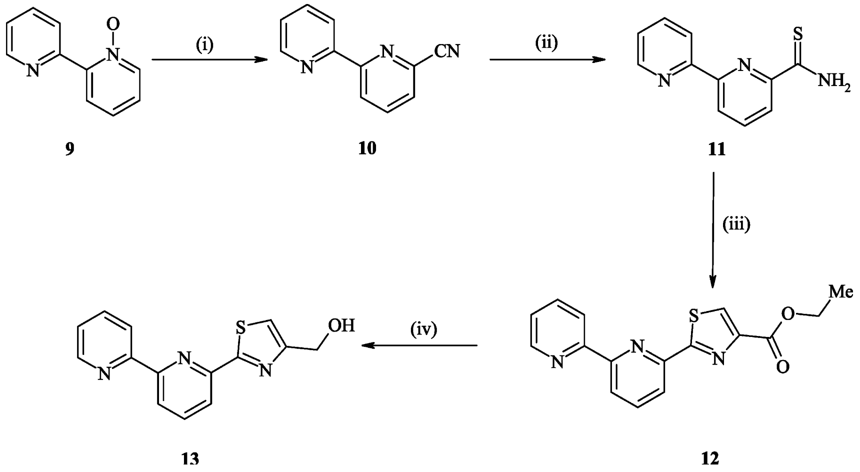
Reaction of 6,6′-dimethyl-2,2′-bipyridine-3,3′-diol **3** with penta-(ethylene glycol)-di-*p*-tosylate in the presence of excess NaH in anhydrous DMF gave the 2,2′-bipyridine 20-crown-6 derivative **4** in moderately high yield. Reaction of **4** with excess *m*CPBA gave the bis-*N*-oxide **5** in almost quantitative yield. The bis-*N*-oxide **5** was then converted to the diacetate **6** by reaction with acetic anhydride. Hydrolysis of **6** afforded the diol **7** which on reaction with thionyl chloride gave the 6,6′-di(choloromethyl) derivative **8**. The synthesis of the terminal terdentate units was achieved in four steps starting from 2,2′-bipyridine-1-oxide. Reaction of the mono-*N*-oxide **9** with trimethylsilylcyanide in the presence of benzoyl chloride gave 6-carbonitrile-2,2′-bipyridine **10** which was converted to the thioamide **11** by reaction with H_2S gas. Reaction of **11** with ethyl 3-bromopyruvate gave the thiazole-containing species **12**, which was reduced by $LiAlH_4$ to give the alcohol derivative **13**. Formation of **L**^{1} was achieved by reaction of the 6,6′-di(choloromethyl) derivative **8** with excess alcohol **13** and NaH in THF, giving the desired ligand in moderate yield.

The synthesis of the ditopic ligand **L**^{2} was achieved by an 11 step convergent route starting from 2,2′-bipyridine-3,3′-diol **14** and 2,2′-bipyridine-1-oxide **9** (Scheme 3).

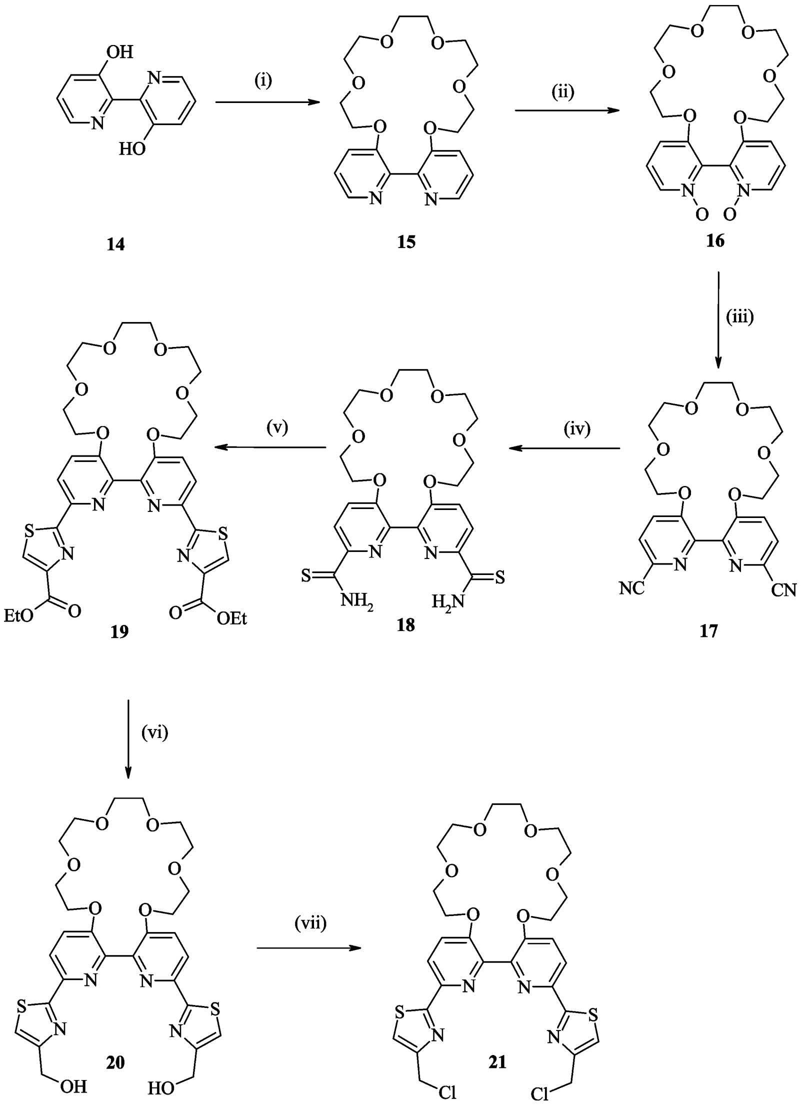
In a similar fashion to the preparation of **4**, 2,2′-bipyridine-3,3′-diol was reacted with penta-(ethylene glycol)-di-*p*-tosylate and NaH in DMF giving the crown ether derivative **15**. N-oxidation with *m*CPBA and reaction with trimethylsilylcyanide in the presence of benzoyl chloride gave the 6,6′-dicyano derivative **17**. This was then converted to the thioamide **18** by reaction with H_2S and subsequent reaction with ethyl 3-bromopyruvate gave the thiazole-containing diester **19**. Reduction of this ester with $LiAlH_4$ and chlorination with thionyl chloride gave the di(chloromethyl)



Scheme 1 Synthesis of compound **8** from 6,6′-dimethyl-2,2′-bipyridine-3,3′-diol (**3**). Reagents and conditions: (i) NaH, penta-(ethylene glycol)-di-*p*-tosylate, anhydrous DMF, N_2, 60 °C, (ii) *m*CPBA, DCM, RT, (iii) acetic anhydride, N_2, 120 °C, (iv) K_2CO_3, anhydrous methanol, RT, (v) thionyl chloride, DCM, reflux.



Scheme 2 Synthesis of compound **13** from 2,2′-bipyridine-1-oxide (**9**). Reagents and conditions: (i) benzoyl chloride and TMSCN, reflux, DCM (ii) H_2S(g), Et_3N, ethanol, (iii) ethyl 3-bromopyruvate, reflux, ethanol, (iv) $LiAlH_4$, 0 °C, N_2, anhydrous THF.



Scheme 3 Synthesis of compound **21** from 2,2′-bipyridine-3,3′-diol (**14**). Reagents and conditions: (i) NaH, penta-(ethylene glycol)-di-*p*-tosylate, anhydrous DMF, N_2, 60 °C, (ii) *m*CPBA, DCM, RT, (iii) benzoyl chloride, TMSCN, reflux DCM, (iv) H_2S(g), Et_3N, ethanol, (v) ethyl 3-bromopyruvate, reflux, ethanol (vi) $LiAlH_4$, THF, 0 °C (vii) $SOCl_2$, reflux, DCM.

derivative **21**. Formation of $\mathbf{L}^2$ was achieved by reaction of **21** with excess alcohol **13** and NaH in THF, giving the desired product in moderate yield.

Synthesis and crystal structure of $[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2](\mathrm{ClO_4})_5$

Reaction of $\mathbf{L}^1$ with $\mathrm{Zn(CF_3SO_3)_2}$ and $\mathrm{[Cu(NCMe)_4]PF_6}$ in MeCN (in a ratio 2 : 2 : 1) produced an orange solution from which a good yield of crystalline material was produced by slow diffusion of diethyl ether vapour into the solution. ESI-MS indicated formation of the heterometallic trinuclear double helicate $[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2]^{5+}$ with ions present at *m*/*z* 1272, 798 and 562 whose charge states correspond to $\{[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2](\mathrm{CF_3SO_3})_3\}^{2+}$, $\{[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2](\mathrm{CF_3SO_3})_2\}^{3+}$ and $\{[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2](\mathrm{CF_3SO_3})\}^{4+}$, respectively. Formation of the helicate species was confirmed by single crystal X-ray crystallography. In the crystal structure the ligand partitions into three binding domains each separated by the $–\mathrm{CH_2OCH_2}–$ ether linking units (Fig. 1). The helicate comprises of two Zn(II) ions and a Cu(I) ion coordinated by two $\mathbf{L}^1$ bridging ligands in a double helicate arrangement. Each of the Zn centres has a pseudo-octahedral coordination geometry formed by coordination of two thiazole-bipyridyl tridentate N-donor units [2.066(7)–2.228(7) Å]. The Cu(I) ion has a distorted tetrahedral coordination geometry formed by coordination of the bidentate N-donor units of the central bipyridine ditopic units [2.020(7)–2.043(6) Å]. This metal ion has a distorted geometry due to the inability of the central bipyridine units to adopt planar bidentate chelate arrangements, which arises due to the oxygen atoms present in the 3,3′-positions which due to unfavourable steric interactions prevent the unit from approaching planarity (NCCN torsion angle of the central bipyridine unit 30.56 and 33.41°). It is worth noting that due to the isoelectronic nature of the Cu(I) and Zn(II) metal ions they may not be easily distinguished by X-ray diffraction studies. Thus it is possible that formulations such as $[\mathrm{Zn_3}(\mathbf{L}^1)_2]^{6+}$ or $[\mathrm{ZnCu_2}(\mathbf{L}^1)_2]^{4+}$ are present in the solid state. However, the formation of homometallic zinc species can be ruled out as *five* perchlorate counter anions are present within the crystal structure. This fact, coupled with the evidence given by the ESI-MS, strongly supports the formation of $[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2]^{5+}$.

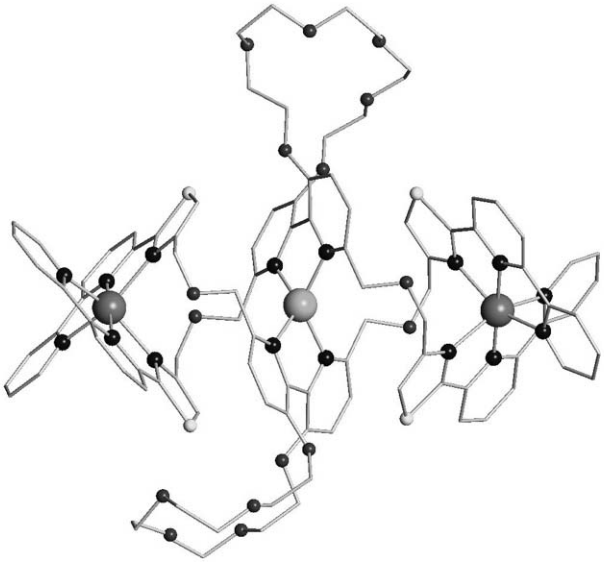


Fig. 1 X-Ray single crystal structure of the complex cation $[\mathrm{Zn_2Cu}(\mathbf{L}^1)_2]^{5+}$.

The ^{1}H NMR in $\mathrm{CD_3CN}$ is as expected for a D_{2d}-symmetric helicate species with a total of forty aromatic protons occurring in ten environments between 6.5 and 8.75 ppm. Furthermore, four doublets are observed between 3.6 and 2.9 ppm corresponding to the diastereotopic methylene protons present on the ether linking units. Also present between 4.6 and 3.6 ppm are highly coupled signals corresponding to the 20-crown-6 unit (Fig. 2a).

Synthesis and crystal structure of $[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2](\mathrm{ClO_4})_6$

Reaction of $\mathbf{L}^2$ with $\mathrm{Zn(CF_3SO_3)_2}$ and $\mathrm{[Cu(NCMe)_4]PF_6}$ in MeCN (in a ratio 1 : 1 : 1) produced a dark orange solution from which crystalline material was produced by slow diffusion of diethyl ether vapour into the solution. ESI-MS indicated formation of the heterometallic tetranuclear double helicate $[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2]^{6+}$ with ions present at *m*/*z* 1545, 980 and 698 whose charge states correspond to $\{[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2](\mathrm{CF_3SO_3})_4\}^{2+}$, $\{[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2](\mathrm{CF_3SO_3})_3\}^{3+}$ and $\{[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2](\mathrm{CF_3SO_3})_2\}^{4+}$, respectively. Formation of this helicate species was confirmed by single crystal X-ray crystallography. In the crystal structure the ligand partitions into four binding domains (Fig. 3) comprising two Zn(II) and two Cu(I) ions coordinated by two $\mathbf{L}^2$ bridging ligands producing a heterometallic tetranuclear double helicate. In an analogous fashion to that seen in the complex formed with $\mathbf{L}^1$ both of the Zn(II) ions are pseudo-octahedrally coordinated by the two terminal thiazole-bipyridyl tridentate N-donor domains [2.038(6)–2.348(6) Å]. However, the central ditopic unit, although potentially tetradentate, partitions into two bidentate pyridyl-thiazole N-donor units each of which coordinates a Cu(I) centre. Each of the copper ions are coordinated by two of these bidentate domains, one from each ligand resulting in a pseudo-tetrahedral coordination geometry [1.982(5)–2.097(5) Å]. Although the central domain could partition into a variety of different binding domains (*e.g.* tetradentate or tridentate units) it is pre-programmed to act as a bis-bidentate. This partitioning is a consequence of the oxygen atoms present on the 3,3′- positions on the bipyridyl central unit, which separates the central core into two bidentate domains to minimise unfavourable steric interactions between the two oxygen atoms (NCCN torsion angle of the central bipyridine unit 57.86 and 58.62°). The Cu $\cdots$ Cu distance is 3.608 Å and is quite large compared to other Cu(I)-containing dinuclear double helicates.[10] Due to the length of this distance any Cu–Cu interaction can be disregarded.

The ^{1}H NMR in $\mathrm{CD_3CN}$ is as expected for this helicate species with a total of forty four aromatic protons occurring in eleven environments between 6.70 and 8.80 ppm. The crown ether protons occur as their usual multiplets between 3.45 and 4.30 ppm. Also four doublets are observed between 3.11 and 3.60 ppm corresponding to the diastereotopic methylene protons present on the $–\mathrm{CH_2OCH_2}–$ spacer unit (Fig. 4a).

As with the trinuclear helicate it is worth noting that the Cu(I) and Zn(II) metal ions may not be easily distinguished by X-ray diffraction studies. The crystal structure does show one complex cation $[\mathrm{Zn_2Cu_2}(\mathbf{L}^2)_2]^{6+}$ and six interstitial $\mathrm{ClO_4}^-$ anions. However these anions are heavily disordered and several residual peaks in the electron density map were assigned and satisfactorily refined as an additional *ca.* 0.5 site-occupancy perchlorate moiety. The

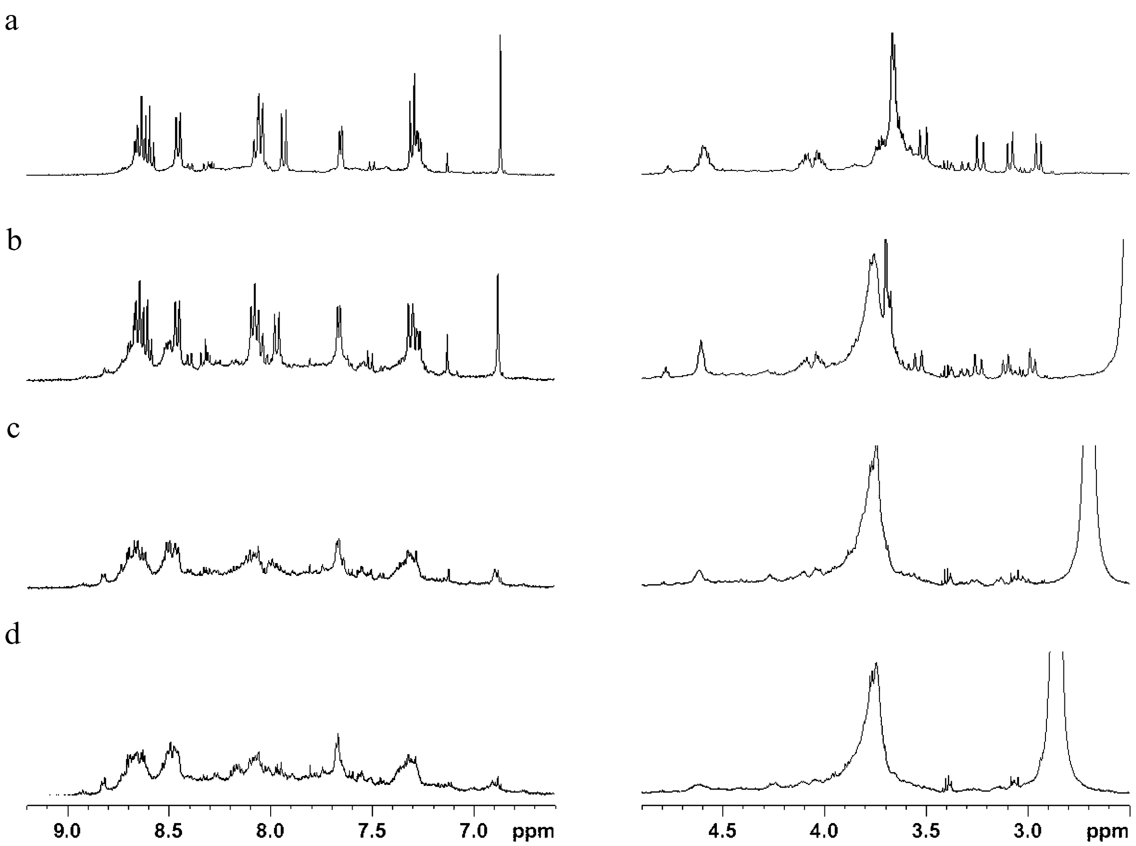


Fig. 2 Selected aromatic and aliphatic regions of the ^{1}H NMR spectrum, recorded in CD_3CN, of (a) $[CuZn_2(\mathbf{L}^1)_2]^{5+}$, (b) $[CuZn_2(\mathbf{L}^1)_2]^{5+}$ + 4 equivalents $Ba(ClO_4)_2$, (c) $[CuZn_2(\mathbf{L}^1)_2]^{5+}$ + 10 equivalents $Ba(ClO_4)_2$, (d) $[CuZn_2(\mathbf{L}^1)_2]^{5+}$ + 20 equivalents $Ba(ClO_4)_2$.

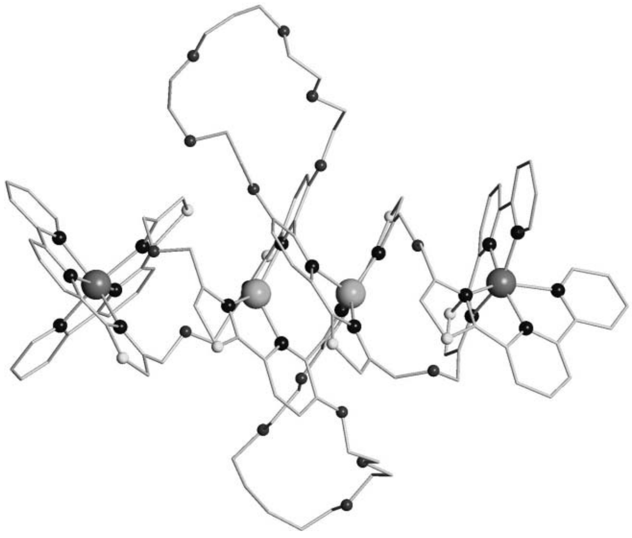


Fig. 3 X-Ray single crystal structure of the complex cation $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$.

presence of the latter may be due to a small amount of $HClO_4$ co-crystallate, but it is also a possible indication that the Cu(I) sites in the helicate are occasionally occupied by a Zn(II) dication. Regardless of this, no Zn(II) rich species is observed in the ESI-MS and the ^{1}H NMR spectra shows one major species, indicating that at least in solution the major component is $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$.

Reaction of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ and $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ with Ba^{2+} and Na^+

As $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ and $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ both contain crown ether units various s-block metal ions were added to a solution of the complexes in CD_3CN and the reactions monitored by ^{1}H NMR. Upon addition of 2 equivalents of $Ba(ClO_4)_2$ to the trinuclear helicate $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ the ^{1}H NMR spectrum does not change greatly. However, addition of further equivalents of Ba^{2+} results in the signals becoming broader and upon addition of 20 equivalents a very different spectrum results (Fig. 2). Comparison of this spectrum with that of the starting complex shows that none of the original peaks are present and the spectrum now has a large number of peaks, many of which are overlapping. The resultant ^{1}H NMR is a highly complex spectrum from which no one compound is identifiable. Conversely reaction of $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ only results in a change in the chemical shift of both aromatic and aliphatic signals which is most pronounced for both the crown ether and $–CH_2OCH_2–$ ether linkers (Fig. 4)

Thus for the complex $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ addition of Ba^{2+} results in a complicated ^{1}H NMR spectrum indicating that a large number of species is present. Previously we have shown that to facilitate better overlap between the crown aryl oxygen atoms and the barium ions the torsion angle of the central bipyridine unit must increase.[8] Such an increase in the torsion angle of this unit present in $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ would result in the bipyridine unit no longer being able to act as a bidentate unit. We have previously demonstrated that upon addition of barium ions to this ditopic unit the bipyridine unit is prevented from acting as a bidentate chelate.[9]

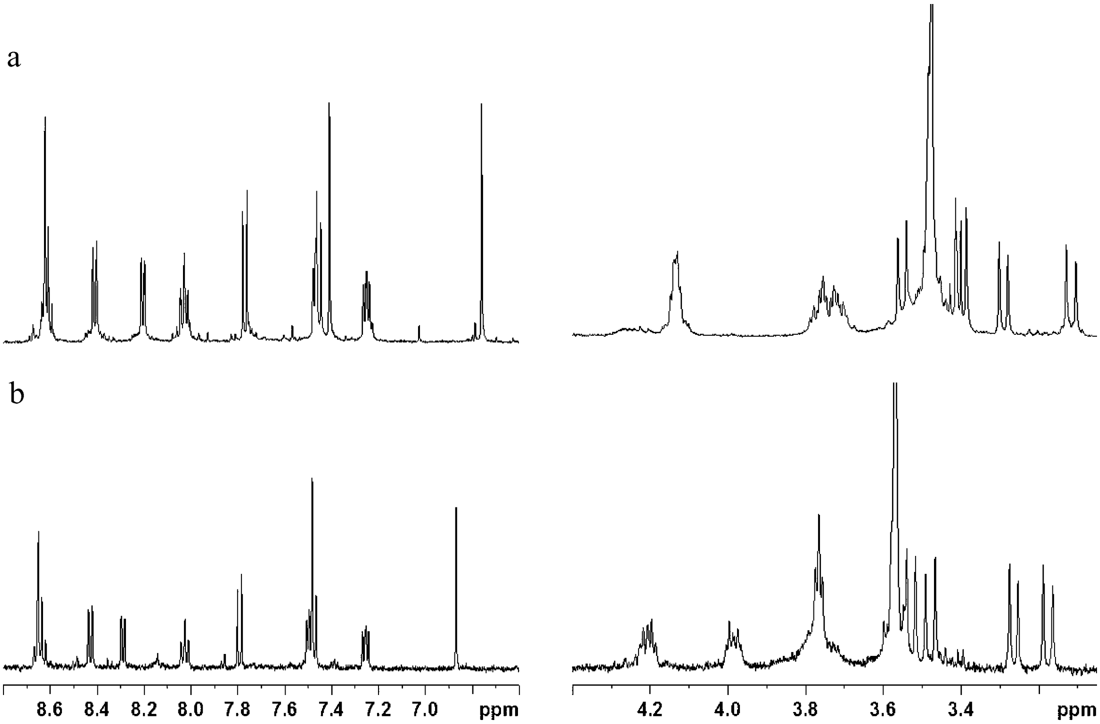


Fig. 4 Selected aromatic and aliphatic regions of the ^1H NMR spectra recorded in CD_3CN of (a) $[Cu_2Zn_2(\mathbf{L}^2)_2]^{6+}$ and (b) $[Cu_2Zn_2(\mathbf{L}^2)_2]^{6+}$ + 20 equivalents of Ba^{2+} ions.

Thus addition of barium ions to the crown ether unit of this trimetallic helicate results in the central bipyridine unit no longer being able to coordinate the Cu(I) ions. Consequently, with this central unit no longer coordinating, the ligand now effectively only contains two tridentate units separated by a spacer unit. This allosteric effect results in a ligand strand which is not sufficiently programmed to form a helicate, or indeed any single species. However the terminal tridentate domains will be unaffected by this coordination of the crown ether and are still able to coordinate metal ions. Thus it seems highly likely that the species now present in solution are zinc-containing oligomers and polymers of $\mathbf{L}^1$ *i.e.* $[Zn_n(\mathbf{L}^1)_n]^{2n+}$. The ESI-MS does support this, but due to the large amount of Ba^{2+} added to the sample analyte ions of interest are somewhat suppressed. Nonetheless, the main ion observed is at *m/z* 677 which corresponds to the monomeric unit $\{[Zn(\mathbf{L}^1)Ba](ClO_4)_2\}^{2+}$. Ions in the ESI-MS at higher *m/z* are also observed but none of these ions can be attributed to complexes of the ligand. However, these are highly charged (3+) and would appear to be adducts of $Ba(ClO_4)_2$. ^1H NMR studies of the addition of $NaClO_4$ to $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ result in only a slight change in chemical shift of both the aromatic and aliphatic regions, indicating that the crown ether unit is coordinating the Na^+ but no disassembly of the helicate is occurring. This cation, due to its smaller ionic radius and reduced charge, does not have such a great effect on the torsion angle of the crown ether unit and consequently the central bipyridine unit can still act as a bidentate binding domain.

The ligand $\mathbf{L}^3$ which contains the same N-donor binding domains as $\mathbf{L}^1$ also forms a trinuclear double helicate with Zn(II) and Cu(I) (ESI-MS for $[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)_5$; *m/z* 964 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)_3\}^{2+}$, *m/z* 610 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)_2\}^{3+}$ and *m/z* 432 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)\}^{4+}$). However, upon addition of an excess of barium ions to this system no observable change is seen in the ^1H NMR. This indicates that coordination of the crown ether unit is instrumental in the change observed upon addition of Ba^{2+} to $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$.

The change observed in the ^1H NMR spectrum upon addition of Ba^{2+} to $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ is indicative of coordination of the crown ether by this ion and results in the barium-containing helicate $[Zn_2Cu_2(\mathbf{L}^2)_2Ba_2]^{10+}$. The relatively small change in chemical shift of the aromatic signals indicates that addition of Ba^{2+} has no effect on the overall structure and the tetranuclear structure still remains. In contrast to the central bipyridine unit of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ where coordination results in the disassembly of the helicate, coordination of ions to the crown ether unit in $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ has no effect on the gross molecular structure. This "innocent" coordination of the crown ether unit is due to the partitioning of the central unit. In the tetrametallic helicate the central bis-bidentate domain has a large torsion angle between the central bipyridine (approaching 90°). Coordination of this crown ether will thus have no effect on its ability to coordinate Cu(I) ions, as the torsion angle is already large, and the helicate species remains intact.[8]

The ligand $\mathbf{L}^1$, due to the design of both the binding domains and linkers, is programmed to form a trinuclear heterometallic double helicate with Zn(II) and Cu(I) metal ions. However, addition of barium ions to the crown ether unit present on the central bipyridine core effectively stops the central unit acting as a bidentate donor. This allosteric effect results in the formation of a large number of different metal-containing complexes of $\mathbf{L}^1$. As no single $\mathbf{L}^1$ containing complex results the ligand has now no inherent programming and the action of addition of barium ions to the remote crown ether site effectively *deprogrammes* the ligand strand. This behaviour is not observed in complexes of $\mathbf{L}^2$ which although similar to $\mathbf{L}^1$ differs in the partitioning of the binding domains.

Conclusion

Two multidentate ditopic ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ have been synthesised which upon reaction with Cu(I) and Zn(II) form the heterometallic double helicates $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ and $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$. Reaction of $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$ with Ba^{2+} results in the coordination of the crown ether units giving the simple barium coordinated species $[Zn_2Cu_2(\mathbf{L}^2)_2Ba_2]^{10+}$. However, reaction of $[Zn_2Cu(\mathbf{L}^1)_2]^{5+}$ with Ba^{2+} *deprogrammes* the ligand and results in the formation of a mixture of species. This different behaviour is due to the differing nature of the binding domains.

Experimental

Chemicals were purchased and used without further purification. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance DPX400 for the organic species and the ^{1}H NMR for the complexes was recorded on a 500 MHz Bruker Avance 500. Mass spectra were obtained on a Bruker MicroTOF LC.

Synthesis of 4

To a two necked round bottom flask charged with 6,6′-dimethyl-2,2′-bipyridine-3,3′-diol[8] (**3**) (1.0 g, 4.62 mmol) and sodium hydride (60% dispersion in oil) (0.74 g, 18.5 mmol), anhydrous DMF (50 ml) was added and the reaction heated under an atmosphere of nitrogen at 60 °C for 1 h. After this time penta-(ethylene glycol)-di-*p*-tosylate (2.53 g, 4.62 mmol) was added to the reaction mixture and the heating continued for a further 24 h. The reaction was allowed to cool and methanol (5 ml) added. Removal of the solvents gave a brown oil to which $NaHCO_3$(aq) (40 ml) was added and extracted with DCM (3 × 50 ml). Evaporation of the combined organic layers gave a brown oil which was purified *via* column chromatography (10% MeOH in DCM, SiO_2) giving **4** as a viscous amber oil.[11] This solidified on standing to give a pale brown waxy solid (1.1 g, 57% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 7.15 (d, $J = 8.0$, 2 H), 7.04 (d, $J = 8.0$ Hz, 2 H), 4.10–3.40 (m, 20 H), 2.48 (s, 6 H). ESI-MS m/z 441 (M + Na$^+$).

Synthesis of the bis-*N*, *N*′-oxide 5

A solution of **4** (1.0 g, 2.39 mmol) and *m*CPBA (77%, 1.18 g, 5.26 mmol) in DCM (40 ml) was stirred at room temperature for 6 h. The reaction was followed by TLC and upon completion the solvent was reduced to half its volume and purified by column chromatography (1% MeOH in DCM, Al_2O_3) giving **5** as a white solid (0.9 g, 85% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 7.27 (d, $J = 10.0$, 2 H), 6.95 (d, $J = 10.0$ Hz, 2 H), 4.21–3.56 (m, 20 H), 2.53 (s, 6 H). ESI-MS m/z 473 (M + Na$^+$).

Synthesis of the acetylated 2,2′-bipyridine 6

To a 50 ml round bottom flask containing the bis-*N*,*N*′-oxide **5** (0.4 g, 0.89 mmol) was added acetic anhydride (10 ml). The reaction vessel was then placed under an atmosphere of nitrogen and heated to 120 °C for 4 h with stirring. Upon completion, toluene (20 ml) was added and all the solvent removed by rotary evaporation. The resulting brown oil was immediately purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving **6** as a colourless oil (0.39 g, 82% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 7.29 (d, $J = 8.0$, 2 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 5.13 (s, 4 H), 4.12–3.42 (m, 20 H), 2.03 (s, 6 H). ESI-MS m/z 557 (M + Na$^+$).

Synthesis of 2,2′-bipyridine-6,6′-dimethanol derivative 7

The acetylated 2,2′-bipyridine derivative **6** (0.4 g, 0.75 mmol) was completely dissolved in anhydrous methanol (20 ml) and to this an excess of potassium carbonate (0.38 g, 3.00 mmol) was added and the reaction stirred for 4 h. Upon completion the solvent was removed by rotary evaporation then distilled water (20 ml) was added and extracted with DCM (3 × 50 ml). Evaporation of the combined organic extracts gave **7** as an off-white solid (0.3 g, 89% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 7.27 (d, $J = 8.0$, 2 H), 7.24 (d, $J = 8.0$ Hz, 2 H), 4.68 (s, 4 H), 4.20-3.40 (m, 20 H), 3.50 (overlapping, 2 H, –OH). ESI-MS m/z 472 (M + Na$^+$).

Synthesis of 2,2′-bipyridine-6,6′-dimethylchloride derivative 8

A solution of 2,2′-bipyridine alcohol (**7**) (0.35 g, 0.78 mmol) and thionyl chloride (2 ml) in DCM (50 ml) was refluxed for 4 h. Upon completion the solution was allowed to cool before slowly pouring into $NaHCO_3$(aq) (40 ml). The organic phase was separated, washed with $NaHCO_3$(aq) (20 ml) and evaporated to dryness. The resulting brown oil was immediately purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving **8** as a white solid (0.3 g, 79% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 7.53 (d, $J = 8.0$, 2 H), 7.38 (d, $J = 8.0$ Hz, 2 H), 4.72 (s, 4 H), 4.24–3.57 (m, 20 H). ESI-MS m/z 487 (M$^+$).

Synthesis of 2,2′-bipyridine-6-carbonitrile 10[12]

A solution of 2,2′-bipyridine-1-oxide (**9**) (0.8 g, 4.65 mmol) and benzoyl chloride (0.71 g, 5.11 mmol) in DCM (50 ml) was refluxed, and trimethylsilyl cyanide (0.51 g, 5.11 mmol) was added slowly over a period of 30 min. The reaction was monitored by TLC and upon completion the solution was cooled and washed with $NaHCO_3$(aq) (20 ml). Removal of the solvent by rotary evaporation gave the crude product as a brown oil, purification *via* column chromatography (1% MeOH in DCM, Al_2O_3) afforded 2,2′-bipyridine-6-carbonitrile (**10**) as a white solid (0.52 g, 62% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 8.72 (m, 2 H), 8.50 (d, $J = 9.9$, 1 H), 7.97 (t, $J = 9.8$, 1 H), 7.88 (dt, $J = 9.7$, 2.2, 1 H), 7.72 (dd, $J = 9.5$, 1.2, 1 H), 7.40 (ddd, $J = 9.4$, 5.9, 1.4 Hz, 1 H). ESI-MS m/z 181 (M$^+$).

Synthesis of 2,2′-bipyridine-6-thioamide 11[12]

To a solution of 2,2′-bipyridine-6-carbonitrile (**10**) (0.7 g, 3.84 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol) was added and H_2S was slowly bubbled through the solution for 15 min, during which time the solution turned yellow. The yellow solution was allowed to stand for 48 h during which time a yellow solid slowly precipitated. Collection *via* filtration gave pure 2,2′-bipyridine-6-thioamide (**11**) as a yellow solid (0.7 g, 85% yield).

^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 9.61 (broad s, 1 H), 8.78 (d, $J = 7.8$, 1 H), 8.73 (d, $J = 4.7$, 1 H), 8.64 (d, $J = 7.9$, 1 H), 8.38 (d, $J = 7.95$, 1 H), 8.01 (t, $J = 7.8$, 1 H), 7.88 (dt, $J = 7.8$, 1.5, 1 H), 7.73 (br s, 1 H), 7.39 (dd, $J = 7.4$, 4.8 Hz, 1 H). ESI-MS m/z 215 (M^+).

Synthesis of tridentate ester 12

A solution of 2,2′-bipyridine-6-thioamide (**11**) (0.6 g, 2.79 mmol) and ethyl 3-bromopyruvate (0.60 g, 3.07 mmol) in ethanol (50 ml) was refluxed for 6 h. On cooling large brown crystals of **12** slowly formed which were filtered and washed with ethanol (2 × 2 ml) and diethyl ether (2 × 2 ml) (0.5 g, 58% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 9.19 (d, $J = 5.5$ Hz, 1 H), 9.12 (d, $J = 8.0$ Hz, 1 H), 8.85 (d, $J = 8.0$ Hz, 1 H), 8.56 (d, $J = 8.0$ Hz, 1 H), 8.54 (m, 1 H), 8.33 (s, 1 H), 8.18 (t, $J = 8.0$ Hz, 1 H), 7.98 (t, $J = 6.5$ Hz, 1 H), 4.45 (q, $J = 7.0$ Hz, 2 H), 1.44 (t, $J = 7.0$ Hz, 3 H). ESI-MS m/z 312 ($M + H^+$).

Synthesis of tridentate alcohol 13

The tridentate ester (**12**) (0.2 g, 0.64 mmol) was added to a dry 100 ml two necked round bottom flask, under an atmosphere of nitrogen. Anhydrous THF (30 ml) was added to the flask and the resulting solution stirred in an ice bath at 0 °C for 15 min. To this lithium aluminium hydride, (1.0 M solution in diethyl ether, 1.28 ml, 1.28 mmol) was slowly added over the course of 20 min. Stirring was continued for 2 h at 0 °C before removing the ice bath and allowing the reaction to gradually warm up to room temperature. Any remaining lithium aluminium hydride was quenched by slow addition of THF (2 ml), methanol (2 ml) and finally water (2 ml). The solvents were removed by rotary evaporation to leave a viscous yellow emulsion to which distilled water (20 ml) was added and extracted into DCM (4 × 50 ml). Evaporation of the organic solvent gave a yellow solid that was purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving the tridentate alcohol (**13**) as a pale yellow solid (0.1 g, 58% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 8.71 (d, $J = 5.0$ Hz, 1 H), 8.57 (d, $J = 8.0$ Hz, 1 H), 8.48 (d, $J = 8.0$ Hz, 1 H), 8.19 (d, $J = 7.0$ Hz, 1 H), 7.95 (t, $J = 8.0$ Hz, 1 H), 7.9 (dt, $J = 7.5$, 1.5 Hz, 1 H), 7.37 (ddd, $J = 7.5$, 5.0, 1.0 Hz, 1 H), 7.34 (s, 1 H), 4.89 (s, 2 H), 2.45 (br s, 1 H, –OH). ESI-MS m/z 292 ($M + Na^+$).

Synthesis of L^1

To a dry 100 ml two necked round bottom flask the tridentate unit (**13**) (0.050 g, 0.19 mmol), sodium hydride (60% dispersion in oil, 0.029 g, 0.74 mmol) and tetra-*n*-butylammonium bromide (5 mg, 0.015 mmol) was added. The flask was immediately fitted with a dry reflux condenser and placed under an atmosphere of nitrogen. To this anhydrous THF (40 ml) was added and the mixture heated under reflux for 1 h. After this time the 2,2′-bipyridine-6,6′-dimethyl chloride derivative (**8**) (0.045 g, 0.093 mmol) was added and the reaction was heated under reflux for a further 36 h, monitoring the progress by TLC. Upon completion methanol (5 ml) was added and the solvent removed by rotary evaporation. To the residual yellow oil distilled water (10 ml) was added and extracted with DCM (3 × 50 ml). Evaporation of the combined organic layers gave a crude product that was purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving the ligand L^1 as an off-white solid (0.04 g, 45% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 8.67 (dd, $J = 4.0$, 0.5 Hz, 2 H), 8.54 (d, $J = 7.5$ Hz, 2 H), 8.43 (d, $J = 7.5$ Hz, 2 H), 8.18 (d, $J = 8.0$ Hz, 2 H), 7.89 (t, $J = 8.0$ Hz, 2 H), 7.84 (dt, $J = 7.5$, 3.0 Hz, 2 H), 7.54 (d, $J = 8.5$ Hz, 2 H), 7.41 (s, 2 H), 7.34 (m, 2 H), 7.33 (m, 2 H), 4.84 (s, 4 H), 4.82 (s, 4 H), 4.18-3.50 (m, 20 H). ESI-MS m/z 953 (M^+). Found C: 62.8, H: 4.9, N: 11.5% $C_{50}H_{48}N_8O_8S_2$. Requires: C: 63.0, H: 5.1, N: 11.8%.

Synthesis of 2,2′-bipyridine-crown ether 15

Under an atmosphere of nitrogen a two necked round bottom flask was charged with 3,3-dihydroxy-2,2-bipyridine[13] (**14**) (1.0 g, 5.3 mmol) and sodium hydride (60% dispersion in oil, 0.85 g, 22.2 mmol). To this anhydrous DMF (50 ml) was added and the reaction heated to 60 °C with stirring for 1 h. After this time penta-(ethylene glycol)-di-*p*-tosylate (2.9 g, 5.3 mmol) was added to the reaction mixture and heating continued for a further 24 h. Methanol (5 ml) was then added and the solvents removed by rotary evaporation. To the resulting brown oil, $NaHCO_3$(aq) (40 ml) was then added and extracted with DCM (4 × 50 ml). Evaporation of the combined organic layers gave a brown oil that was purified *via* column chromatography (10% MeOH in DCM, SiO_2) giving **15** as a viscous amber oil.[8] This solidified on standing to give a pale brown waxy solid (1.3 g, 63% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.35 (d, $J = 4.2$ Hz, 2 H), 7.35 (m, 2 H), 7.30 (m, 2 H), 4.20-3.40 (m, 20 H). ESI-MS m/z 391 ($M + H^+$).

Synthesis of bis-*N*,*N*′-oxide 16

A solution of 2,2′-bipyridine-crown ether (**15**) (1.0 g, 2.56 mmol) and *m*CPBA (77%, 1.26 g, 5.63 mmol) in DCM (40 ml) was stirred at room temperature for 6 h. The reaction was followed by TLC and upon completion the solvent was reduced to half its volume by rotary evaporation. Purification of the crude product *via* column chromatography (1% MeOH in DCM, Al_2O_3) gave the bis-*N*,*N*′-oxide (**16**) as a white solid (0.9 g, 83% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.05 (d, $J = 6.5$, 2 H), 7.25 (m, 2 H), 7.0 (d, $J = 8.6$ Hz, 2 H), 4.30-3.45 (m, 20 H). ESI-MS m/z 422 (M^+).

Synthesis of 2,2′-bipyridine-crown ether 6,6′-dicarbonitrile 17

A solution of bis-*N*,*N*′-oxide (**16**) (0.8 g, 1.9 mmol) and benzoyl chloride (0.59 g, 4.16 mmol) in DCM (50 ml) was refluxed, and trimethylsilyl cyanide (0.41 g, 4.17 mmol) added slowly over a period of 30 min. Upon completion the solution was cooled and washed with $NaHCO_3$(aq) (50 ml). Removal of the solvent by rotary evaporation give the crude product as a brown oil, purification *via* column chromatography (1% MeOH in DCM, Al_2O_3) afforded the 6,6′-dicarbonitrile derivative (**17**) as a white solid (0.6 g, 72% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 7.75 (d, $J = 8.7$, 2 H), 7.45 (d, $J = 8.6$ Hz, 2 H), 4.35–3.55 (m, 20 H). ESI-MS m/z 441 ($M + H^+$).

Synthesis of 2,2′-bipyridine-crown ether 6,6′-dithioamide 18

To a solution of 6,6′-dicarbonitrile derivative (**17**) (0.7 g, 1.59 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol) was added and H_2S was slowly bubbled through the solution for

15 min, during which time the solution turned yellow. The yellow solution was allowed to stand for 48 h during which time a yellow solid slowly precipitated. Filtration gave pure 6,6′-dithioamide derivative (**18**) as a yellow solid (0.68 g, 84% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 9.40 (s, 2 H), 8.50 (d, $J = 9.2$, 2 H), 7.60 (s, 2 H), 7.4 (d, $J = 9.2$ Hz, 2 H) 4.50-3.50 (m, 20 H). ESI-MS *m/z* 509 (M + H$^+$).

Synthesis of 19

A solution of 6,6′-dithioamide derivative (**18**) (0.6 g, 1.18 mmol) and ethyl 3-bromopyruvate (0.51 g, 2.60 mmol) in ethanol (50 ml) was refluxed for 6 h. On cooling large brown crystals of **19** slowly formed. The crystalline material was then filtered and washed with ethanol (2 × 1 ml) and diethyl ether (2 × 1 ml) (0.62 g, 75% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.38 (d, $J = 8.7$, 2 H), 8.19 (s, 2 H), 7.45 (d, $J = 8.7$, 2 H), 4.47 (q, $J = 7.1$ Hz, 4 H), 4.26–3.58 (m, 20 H), 1.45 (t, $J = 7.1$ Hz, 6 H). ESI-MS *m/z* 700 (M$^+$).

Synthesis of 20

A dry 100 ml two necked round bottom flask, under an atmosphere of nitrogen, was charged with **19** (0.2 g, 0.29 mmol) and to this anhydrous THF (30 ml) was added to the flask and the resulting solution stirred in an ice bath at 0 °C for 15 min. To this lithium aluminium hydride, (1.0 M solution in diethyl ether, 1.14 ml, 1.14 mmol) was slowly added over the course of 20 min. Stirring was continued for 2 h at 0 °C before removing the ice bath and allowing the reaction to gradually warm up to room temperature. Any remaining lithium aluminium hydride was quenched by slow addition of THF (2 ml), methanol (2 ml) and finally water (2 ml). The solvents were removed by rotary evaporation to leave a viscous yellow emulsion to which distilled water was added (50 ml) and extracted into DCM (4 × 50 ml). Evaporation of the organic solvent gave a yellow solid that was purified *via* column chromatography (3% MeOH in DCM, Al_2O_3) giving **20** as a pale yellow solid (0.09 g, 50% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.20 (d, $J = 8.7$, 2 H), 7.45 (d, $J = 8.7$ Hz, 2 H), 7.22 (s, 2 H), 4.84 (s, 4 H), 4.31-3.57 (m, 20 H), 2.49 (br s, 2 H, –OH). ESI-MS *m/z* 639 (M + Na$^+$).

Synthesis of 21

A solution of **20** (0.15 g, 0.24 mmol) and thionyl chloride (2 ml) in DCM (50 ml) was refluxed for 4 h. Upon completion the solution was allowed to cool before slowly pouring into $NaHCO_3$(aq) (20 ml). The organic phase was separated, washed with $NaHCO_3$(aq) (20 ml) and evaporated to dryness. The resulting brown oil was immediately purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving **21** as a white solid (0.13 g, 83% yield). ^{1}H NMR [400 MHz, $CDCl_3$]: δ (ppm) 8.15 (d, $J = 8.7$, 2 H), 7.35 (d, $J = 8.7$ Hz, 2 H), 7.24 (s, 2 H), 4.68 (s, 4 H), 4.16-3.49 (m, 20 H). ESI-MS *m/z* 653 (M$^+$).

Synthesis of L^2

To a dry 100 ml two necked round bottom flask containing **13** (0.050 g, 0.19 mmol), sodium hydride (60% dispersion in oil) (0.029 g, 0.74 mmol) and tetra-*n*-butylammonium bromide (5 mg, 0.015 mmol) was added. The flask was immediately fitted with a dry reflux condenser and placed under an atmosphere of nitrogen. To this anhydrous THF (40 ml) was added and the mixture heated under reflux for 1 h. To this was then added a solution of the dichloride **21** (0.046 g, 0.07 mmol) in anhydrous THF (5 ml). The reaction was heated under reflux for a further 36 h, monitoring the progress by TLC. Upon completion methanol (5 ml) was added and the solvent removed by rotary evaporation giving a yellow oil. Distilled water (10 ml) was then added and extracted with DCM (4 × 50 ml). Evaporation of the combined organic layers gave a crude product that was purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving the final ligand **L**^{2} as a white solid (0.04 g, 51% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 8.70 (d, $J = 5.0$, 2 H), 8.57 (d, $J = 5.0$, 2 H), 8.46 (d, $J = 5.0$, 2 H), 8.22 (t, $J = 5.0$, 4 H), 7.93 (t, $J = 7.85$, 2 H), 7.87 (dt, $J = 6.3$, 1.4 2 H), 7.46 (s, 2 H), 7.43 (d, $J = 8.7$ Hz, 2 H), 7.35 (m, 2 H), 7.34 (s, 2 H), 4.89 (s, 4 H), 4.87 (s, 4 H), 4.34–3.56 (m, 20 H). ESI-MS *m/z* 1119 (M$^+$). Found C: 59.8, H: 4.1, N: 12.1% $C_{56}H_{50}N_{10}O_8S_4$ Requires: C: 60.1, H: 4.5, N: 12.5%.

Synthesis of L^3

To a dry 100 ml two necked round bottom flask containing **13** (0.050 g, 0.19 mmol), sodium hydride (60% dispersion in oil) (0.029 g, 0.74 mmol) and tetra-*n*-butylammonium bromide (5 mg, 0.015 mmol) was added. The flask was immediately fitted with a dry reflux condenser and placed under an atmosphere of nitrogen. To this anhydrous THF (40 ml) was added and the mixture heated under reflux for 1 h. To this was then added a solution of 6,6′-bis(chloromethyl)-2,2′-bipyridine[14] (0.018 g, 0.07 mmol) in anhydrous THF (5 ml). The reaction was heated under reflux for a further 36 h, monitoring the progress by TLC. Upon completion methanol (5 ml) was added and the solvent removed by rotary evaporation giving a yellow solid. Distilled water (10 ml) was then added and extracted with DCM (4 × 50 ml). Evaporation of the combined organic layers gave a crude product that was purified *via* column chromatography (1% MeOH in DCM, Al_2O_3) giving the final ligand **L**^{3} as a white solid (0.013 g, 26% yield). ^{1}H NMR [500 MHz, $CDCl_3$]: δ (ppm) 8.70 (d, $J = 4.7$, 2 H), 8.57 (d, $J = 8.0$, 2 H), 8.47 (d, $J = 7.85$, 2 H), 8.32 (d, $J = 7.85$, 2 H), 8.21 (d, $J = 7.75$, 2 H), 7.92 (t, $J = 7.8$, 2 H), 7.85 (m, 2 H), 7.84 (m, 2 H), 7.58 (d, $J = 7.75$, 2 H), 7.45 (s, 2 H), 7.34 (dd, $J = 7.3$, 5.2, 2 H), 4.91 (d, $J = 6.85$ Hz, 8 H). ESI-MS *m/z* 719 (M$^+$). Found C: 66.2, H: 3.9, N: 11.5% $C_{40}H_{30}N_8O_2S_2$. Requires: C: 66.8, H: 4.2, N: 15.6%.

$[Zn_2Cu(\mathbf{L}^1)_2](ClO_4)_5$

To a solution of **L**^{1} (10 m g, 0.01 mmol) in MeCN (1 ml) was added a solution of $[Cu(NCMe)_4]PF_6$ (1.9 mg, 0.005 mmol) and $Zn(ClO_4)_2 \cdot 6\ H_2O$ (3.8 mg, 0.01 mmol) in MeCN (1 ml). To the orange solution was added an excess of Et_4NClO_4 and it was then layered with diethyl ether. After a period of several days, orange crystals were formed which were collected by filtration (6.7 mg, 46% yield). ESI-MS *m/z* 1198 $\{[Zn_2Cu(\mathbf{L}^1)_2](ClO_4)_3\}^{2+}$, 765 $\{[Zn_2Cu(\mathbf{L}^1)_2](ClO_4)_2\}^{3+}$ and 549 $\{[Zn_2Cu(\mathbf{L}^1)_2](ClO_4)\}^{4+}$. Found C: 46.1, H: 4.1, N: 8.8% $C_{100}H_{96}N_{16}Cl_5CuO_{36}S_4\ Zn_2 \cdot 2MeCN \cdot H_2O$. Requires: C: 46.3, H: 3.9, N: 9.3%.

$[Zn_2Cu_2(L^2)_2](ClO_4)_6$

To a solution of **L**^{2} (10 mg, 0.009 mmol) in MeCN (1 ml) was added a solution of $[Cu(NCMe)_4]PF_6$ (3.3 mg, 0.009 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (3.3 mg, 0.01 mmol) in MeCN (1 ml). To the orange solution was added an excess of Et_4NClO_4 and it was then layered with diethyl ether. After a period of several days, dark orange crystals were formed which were collected by filtration (7.1 mg, 48% yield). ESI-MS *m*/*z* 1446 $\{[Zn_2Cu_2(\mathbf{L}^2)_2](ClO_4)_4\}^{2+}$, 931 $\{[Zn_2Cu_2(\mathbf{L}^2)_2](ClO_4)_3\}^{3+}$ and 673 $\{[Zn_2Cu_2(\mathbf{L}^2)_2](ClO_4)_2\}^{4+}$. Found C: 42.8, H: 3.8, N: 9.1% $C_{112}H_{100}N_{20}Cl_6Cu_2O_{40}S_8Zn_2{\cdot}2MeCN{\cdot}2H_2O$. Requires: C: 43.0, H: 3.4, N: 9.5%.

$[Zn_2Cu(L^3)_2](ClO_4)_5$

To a solution of **L**^{3} (10 mg, 0.014 mmol) in MeCN (1 ml) was added a solution of $[Cu(NCMe)_4]PF_6$ (2.59 mg, 0.007 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (5.2 mg, 0.014 mmol) in MeCN (1 ml). To the orange solution was added an excess of Et_4NClO_4 and it was then layered with diethyl ether. After a period of several days, orange crystals were formed which were collected by filtration (5.2 mg, 35% yield). ESI-MS *m*/*z* 964 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)_3\}^{2+}$, 610 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)_2\}^{3+}$ and 432 $\{[Zn_2Cu(\mathbf{L}^3)_2](ClO_4)\}^{4+}$. Found C: 44.5, H: 3.6, N: 10.3% $C_{80}H_{60}N_{16}Cl_5CuO_{24}S_4Zn_2{\cdot}MeCN{\cdot}H_2O$. Requires: C: 45.0, H: 3.0, N: 10.9%.

Crystallography

Crystals were visually inspected for defects and singularity under a binocular microscope fitted with a polarising attachment. Suitable crystals were then coated with epoxy resin, mounted on a glass fibre and quickly transferred to a Bruker-AXS APEX (CCD area-detector) diffractometer under a stream of cold N_2 gas. Preliminary scans were employed to assess crystal quality, lattice symmetry, ideal exposure time *etc.* prior to collecting a sphere or hemisphere (for low- and high-symmetry crystal systems, respectively) of diffraction intensity data using SMART operating software.[15] Intensities were then integrated from several series of exposures (each exposure covering 0.3° in ω), merged and corrected for Lorentz and polarisation effects using SAINT software.[16] Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix non-linear least squares on all F^2 data, using SHELXS-97 and SHELXL software, respectively (as implemented in the SHELXTL suite of programs).[17] Empirical absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS[18] and, where stated, the scattering contributions from diffuse solvent moieties were removed using the SQUEEZE function in PLATON.[19] All structures were refined until convergence (max. shift/esd < 0.01) and in each case, the final Fourier difference map showed no chemically sensible features.

$[Zn_2Cu(L^1)_2](ClO_4)_5$

Crystal data for $C_{116}H_{128}Cl_5CuN_{20}O_{38}S_4Zn_2$: M = 2910.15, monoclinic, space group $P2(1)/n$, $a = 20.516(4)$, $b = 26.356(5)$, $c = 23.514(5)$ Å, $\beta = 93.22(3)°$, $V = 12694(4)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.523$ Mg m^{-3}, $F(000) = 6024$; crystal dimensions 0.35 × 0.3 × 0.1 mm, μ(Mo-Kα) = 0.802 mm^{-1}, $T = 100$ K. A total of 46 057 reflections were measured in the range to $1.16 \le \theta \le 22.50°$ (*hkl* range indices: $-21 <= h <= 22$, $-21 <= k <= 28$, $-25 <= l <= 24$), 16 586 unique reflections (R(int) = 0.0670). The structure was refined on F^2 to $R_w = 0.2023$, $R = 0.0714$ (10 207 reflections with $I > 2\sigma(I)$) and GOF = 0.797 on F^2 for 1595 refined parameters, largest difference peak and hole 1.098 and −0.624 e Å^{-3}.

$[Zn_2Cu_2(L^2)_2](ClO_4)_6$

Crystal data for $C_{122}H_{119}Cl_{6.50}Cu_2N_{23}O_{43}S_8Zn_2$: $M = 3340.13$, triclinic, space group $\bar{P}$, $a = 19.657(4)$, $b = 19.758(4)$, $c = 23.241(5)$ Å, $\alpha = 94.39(3)$, $\beta = 108.43(3)$, $\gamma = 119.51(3)°$, $V = 7152(2)$ Å^3, $Z = 2$; $\rho_{calcd} = 1.551$ Mg m^{-3}, $F(000) = 3425$; crystal dimensions 0.2 × 0.15 × 0.1 mm, μ(Mo-Kα) = 0.953 mm^{-1}, $T = 100$ K. A total of 67 789 reflections were measured in the range to $0.96 \le \theta \le 25.00°$ (*hkl* range indices: $-23 <= h <= 23$, $-23 <= k <= 23$, $-27 <= l <= 27$), 25187 unique reflections ($R_{(int)} = 0.0489$). The structure was refined on F^2 to $R_w = 0.2458$, $R = 0.0877$ (15 881 reflections with $I > 2\sigma(I)$) and GOF = 1.125 on F^2 for 1676 refined parameters, largest difference peak and hole 1.373 and −1.272 e Å^{-3}.

CCDC reference numbers 633279 and 633280 for $[Zn_2Cu_2(L^2)_2](ClO_4)_6$ and $[Zn_2Cu(L^1)_2](ClO_4)_5$, respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700539c

The asymmetric unit contains one complex cation $[Zn_2Cu_2(\mathbf{L}^2)_2]^{6+}$, six interstitial perchlorate counter ions, one diethyl ether molecule and three acetonitrile molecules. Residual peaks in the electron density map were assigned and refined as a *ca.* half-site occupancy perchlorate moiety [ClO_4(**7**)]. The latter may simply be due to a small quantity of perchloric acid co-crystallate. However, it may also be a possible indication that the Cu(I) sites are partially substituted/doped by additional Zn(II) dications. Given that both Cu(I) and Zn(II) have similar electronic configurations and that the usual problems associated with supramolecular crystallography (weak high angle data *etc.*) were encountered it is not possible to confirm which of these scenarios is most applicable based solely on the present X-ray diffraction studies. Solution and gas-phase studies (discussed in the results and discussion) do however suggest the formation of only one species with the expected ZnCuCuZn distribution of metals.

Regions of extensive disorder are present in both the complex cation and many of the interstitial ClO_4^- anions. In the complex cation, both crown ethers have been resolved into two positions with *ca.* 60 : 40 population parameters.

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