Electrostatic control of the formation of heteroleptic transition metal helicates

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The synthesis of the potentially hexadentate ditopic ligand L^1, which contains both N-donor and crown ether binding units, is described. Reaction of L^1 with Zn(II) results in the formation of a dinuclear double helicate ($[Zn_2(L^1)_2](ClO_4)_4$), which has been structurally characterized. In the solid state, each ligand splits into two tridentate binding domains with two Zn(II) ions coordinated by two bridging ligands in a double helicate arrangement. This complex can further react with s-block metal ions *via* the crown ether unit resulting in the structurally characterized zinc-containing helicate $[Zn_2(L^1)_2Ba_2](ClO_4)_8$. Ligand recognition studies of this helicate with a ligand that does not contain the crown ether unit but does contain the same N-donor array (L^2) demonstrates, *via* both ^1H NMR and ESI-MS studies, that a ligand recognition process does occur and the major species observed are the homoleptic species ($[Zn_2(L^1)_2](ClO_4)_4$ and $[Zn_2(L^2)_2](ClO_4)_4$). Addition of barium ions to the mixture increases the amount of the heteroleptic species ($[Zn_2(L^1)(L^2)](ClO_4)_4$) present, resulting in an equal amount of homoleptic and heteroleptic species. This change in ligand recognition properties is attributed to electrostatic effects.

1 Introduction

To successfully assemble polynuclear transition metal helicates the ligands associated with these species must have information stored within them, so rather than forming a large number of different species only one metallosupramolecular structure results. The use of these "preprogrammed" ligands to form transition metal helicates is well documented. However, for most examples the information stored within the ligand strand is predetermined at the synthetic stage and cannot be subsequently altered.[1] The same type of preprogramming of ligand strands is observed with molecular recognition studies. For example, Lehn and co-workers demonstrated that reaction of Cu(I) with a mixture of oligo(2,2′-bipyridine) ligands of different lengths resulted only in formation of the homoleptic complexes, *i.e.* no mixed-ligand species were formed and ligand self-recognition played a crucial role in the assembly process.[2] In elegant contrast to this, a mixture of two different ligands containing all-bipyridyl or all-terpyridyl binding sites with Cu(II) resulted in formation of only the heteroleptic mixed-ligand double helicate, because of the preference of Cu(II) ions for a five-coordinate geometry—*i.e.* an electronic effect.[3] Although these systems elegantly demonstrate how ligand strands can be programmed to undergo molecular recognition, their ability is fixed and cannot be altered at a later stage.

Recently we have described a number of ditopic ligands that contain both pyridyl–thiazole N-donor and crown ether O-donor domains and we have demonstrated how the inherent information stored within these ligands can be changed or reprogrammed by a combination of both allosteric and electrostatic effects. For example, we have shown that a ditopic ligand which is preprogrammed to partition into two bidentate donor domains, forms a dinuclear double helicate with Hg(II). Addition of barium ions to the remote crown ether site changes the ligand programming so that it now acts as a tetradentate donor and forms a mononuclear complex with the same metal ion.[4] The ability to reprogramme this ligand strand also changes its metal specificity; thus the ligand's preference for Cu(I) ions can be changed to Zn(II) ions by addition of either Sr^{2+} or Ba^{2+}.[5] Other, more subtle effects have been reported such as the ability to modulate the pitch length of a Cu(II)-containing helicate by addition of various s-block metals ions to the crown ether unit.[6]

In this paper we report a potentially hexadentate ditopic ligand L^1 which forms a dinuclear double helicate with Zn(II) ($[Zn_2(L^1)_2](ClO_4)_4$) and demonstrate that the formation of heteroleptic transition metal helicates, with a ligand containing the same potentially hexadentate N-donor domain, can be controlled by addition of barium ions.

2 Results and discussion

2.1 Ligand synthesis

The ditopic potentially hexadentate ligand L^1 was synthesised as outlined in Scheme 1.[7]

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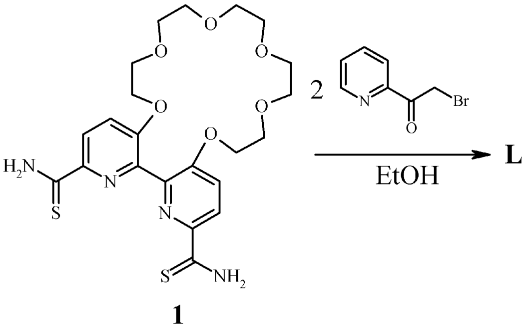

Scheme 1

2.2 Synthesis and structure of the dinuclear double helicates $[Zn_2(L^1)_2](ClO_4)_4$ and $[Zn_2(L^1)_2Ba_2](ClO_4)_8$

Reaction of L^1 with an equimolar amount of $[Zn(H_2O)_6]$-$(ClO_4)_2$ in MeCN gave a colourless solution and the ESI-MS showed an ion at *m*/*z* 1851 corresponding to the dinuclear double helicate $\{[Zn_2(L^1)_2](ClO_4)_3\}^+$. The formation of the complex $[Zn_2(L^1)_2](ClO_4)_4$ has been established by a single-crystal X-ray diffraction study (Fig. 1). In the solid state, each ligand splits into two tridentate binding domains with two Zn(II) ions coordinated by two bridging ligands in a double helicate arrangement with NCCN inter-domain torsion angles of 64.9(1) and 67.5(1)°. Each of the Zn(II) centres has a distorted octahedral geometry formed by the coordination of one tridentate pyridyl–thiazole–pyridyl N-donor unit from each ligand [Zn–N distances: 1.997(3)–2.413(3) Å].

The ^1H NMR spectrum of $[Zn_2(L^1)_2](ClO_4)_4$ in CD_3CN is consistent with the formation of the helicate with the 28 aromatic protons occurring in seven environments consistent with a D_2 symmetric helical structure in solution. As with similar systems the transition metal helicate can further co-ordinate s-block metals in the external crown ether units. Upon addition of excess $Ba(ClO_4)_2$ to $[Zn_2(L^1)_2](ClO_4)_4$ in MeCN a shift is observed in the ^1H NMR and ions at *m*/*z* 1213 and 2187 corresponding to $\{[Zn_2(L^1)_2Ba_2](ClO_4)_6\}^{2+}$ and $\{[Zn_2(L^1)_2Ba](ClO_4)_5\}^+$ are observed in the ESI-MS, indicative of coordination of the crown ether units. The formation of the complex $[Zn_2(L^1)_2Ba_2](ClO_4)_8$ has been established by a single-crystal X-ray diffraction study (Fig. 2). In the solid state, the ligand behaves in a similar manner to the parent complex with the two ligands acting as a bis-tridentate donors coordinating two Zn(II) ions. Again each of the Zn(II) centres has a distorted octahedral geometry formed by the coordination of one tridentate pyridyl–thiazole–pyridyl N-donor unit from each ligand [Zn–N distances: 1.985(5)–2.525(5) Å]. Both crown ethers coordinate barium ions. In one case the Ba^{2+} is nine coordinate and bonds to all six oxygen atoms of the crown ether unit. The remaining three coordination sites incorporate two perchlorate anions and a water molecule. The other Ba^{2+} ion is seven coordinate and is only coordinated by the four "outer" oxygen atoms of the crown ether ring. The Ba–O distances to the two oxygen atoms directly attached to the central 2,2′-bipyridine unit are too long (*ca.* 3.3 and 3.4 Å) to be considered bonding interactions. The remaining three coordination sites are occupied by perchlorate anions.

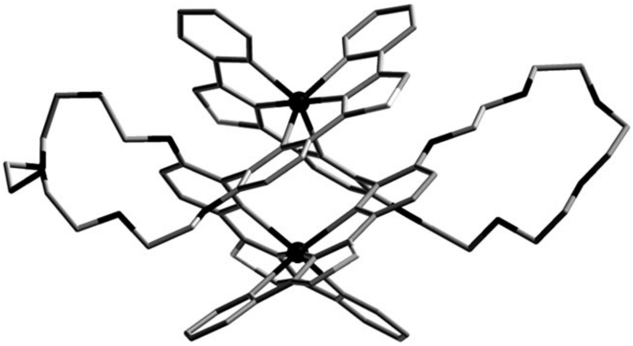

Fig. 1 Crystal structure of the helicate cation $[Zn_2(L^1)_2]^{4+}$. Anions and solvent molecules have been omitted for clarity.

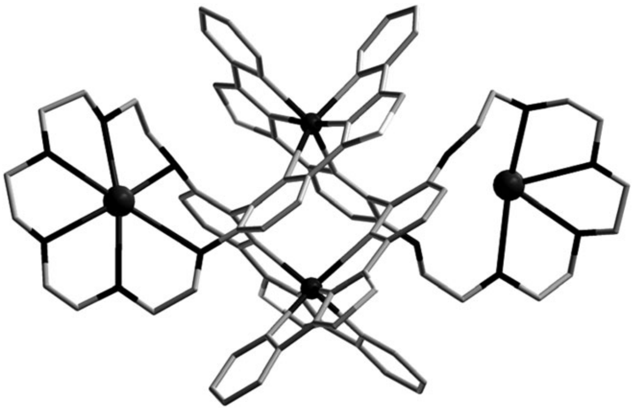

Fig. 2 Crystal structure of the helicate cation $[Zn_2(L^1)_2Ba_2]^{8+}$. Anions and solvent molecules have been omitted for clarity.

Apart from the coordination of the barium ions the only major difference between the two structures is the NCCN torsion angle formed between the two pyridyl–thiazole–pyridyl tridentate binding domains and the pitch length of the helicate (defined as the Zn···Zn distance). The inter-domain angle increases from 64.9(1) and 67.5(1)° for $[Zn_2(L^1)_2]^{4+}$ to 78.3(2) and 80.8(1)° for $[Zn_2(L^1)_2Ba_2]^{8+}$ and the pitch length also increases from 4.812(1) to 5.142(1) Å for $[Zn_2(L^1)_2]^{4+}$ and $[Zn_2(L^1)_2Ba_2]^{8+}$, respectively. This increase in torsion angle has been observed previously in similar systems and is as a consequence of the coordination of the crown ether by Ba^{2+}.[6] This coordination increases the torsion angle by a combination of both allosteric and electrostatic effects, as upon co-ordination of the crown ether unit the torsion angle must increase to facilitate better overlap between the aryl oxygen atoms and the barium ions, increasing the torsion angle by an allosteric effect. However, the change in structure could also have an electrostatic component. Thus upon coordination of the crown ether rings with barium metal ions the overall charge of the complex will substantially rise. An increase in the Zn···Zn distance might reduce the overall electrostatic repulsion, again increasing the torsion angle.

2.3 Ligand recognition studies

Since both the helicate systems $[Zn_2(L^1)_2]^{4+}$ and $[Zn_2(L^2)_2]^{4+}$ contain the same basic ligand chain we investigated their ability to form double stranded heteroleptic complexes. Reaction of L^1, L^2 and Zn(II) (1 : 1 : 2 molar ratio) in CD_3CN and monitoring by electrospray mass spectrometry and ^1H NMR revealed that a recognition process occurs. Thus in the ^1H NMR spectrum signals were observed for both homoleptic species $[Zn_2(L^1)_2]^{4+}$ and $[Zn_2(L^2)_2]^{4+}$ (Fig. 3(a)) which can be assigned by comparison with the ^1H NMR of the isolated complexes. The most diagnostic signals are the thiazolyl singlets (8.60 ppm for $[Zn_2(L^2)_2]^{4+}$ and 8.56 ppm for $[Zn_2(L^1)_2]^{4+}$). Also present is a subset of signals that correspond to the presence of a small amount (*ca.* 5%) of the mixed, heteroleptic species $[Zn_2(L^1)(L^2)]^{4+}$ (8.86 and 8.53 ppm for the corresponding two thiazolyl signals). This result was consistent with electrospray mass spectra studies as signals were observed for both homoleptic species $\{[Zn_2(L^2)_2](ClO_3)_3\}^+$ and $\{[Zn_2(L^1)_2](ClO_4)_3\}^+$ whilst a signal of only small intensity was observed for the heteroleptic complex $\{[Zn_2(L^1)(L^2)](ClO_4)_3\}^+$.

The homoleptic complexes $[Zn_2(L^n)_2](ClO_3)_4$ (n = 1 or 2) show subtle structural differences because, whilst they have the same basic ligand chain, L^2 lacks the crown ether moiety on the central bipyridine unit. Although the unsubstituted ligand L^2 forms a dinuclear double helicate with Zn(II) ($[Zn_2(L^2)_2](ClO_4)_4$) in this complex each of the zinc ions is only four coordinate with the ligand partitioning into two bidentate binding domains with the central bipyridine group uncoordinated.[8] This bidentate coordination is associated with relatively small torsion angles within each non-coordinated bipyridyl unit (38 and 51°) indicating that the lone pairs of these pyridyl units are not directed at the metal centres. The presence of substituents on the 3,3′-positions of the central bipyridine core of L^1 evidently facilitates the ability of the ligand to partition into tridentate binding domains, as is observed in $[Zn_2(L^1)_2](ClO_4)_4$. It appears that unfavourable steric interactions imposed by the crown ether prevent the central bipyridine core from approaching planarity; resulting in the large torsion angle observed and necessitating the formation of two tridentate binding domains. Thus in the helicate species $[Zn_2(L^1)_2]^{4+}$ each of the metal centres adopts a pseudo-octahedral geometry which is in contrast to the complex $[Zn_2(L^2)_2]^{4+}$, in which the ligand coordinates in a bis-bidentate manner *via* the terminal thiazole-pyridyl sites, with the central bipyridine in each ligand uncoordinated giving rise to a four coordinate metal centre. Thus one possibility why mixing the ligands L^2 and L^1 with Zn(II) gives very little of the heteroleptic species is due to electronic effects, as formation of the mixed species would lead to a five-coordinate Zn(II) centre, formed from the pyridyl–thiazole–pyridyl domain from L^1 and the terminal pyridyl–thiazole from L^2. Although the formation of a five coordinate Zn(II) species with neutral N-donor ligands is entirely feasible, only four- and six-coordinate species have been observed with ligands containing pyridyl–thiazole *N*-donor domains.[8,9] However, other factors such as inter-ligand interactions cannot be ignored and may also be a factor in determining the recognition properties between ligand strands.

Addition of $Ba(ClO_4)_2$ to this system (20 equivalents) shows that, as well as a shift of the peaks due to coordination of the crown ethers, the peaks that correspond to the heteroleptic species increase in intensity to *ca.* 25% (Fig. 3(b)); on addition of an additional 20 equivalents a further increase is observed such that the ratio of the homoleptic and the heteroleptic species $[Zn_2(L^2)_2]^{4+}$, $[Zn_2(L^1)(L^2)]^{4+}$ and $[Zn_2(L^1)_2]^{4+}$ is now

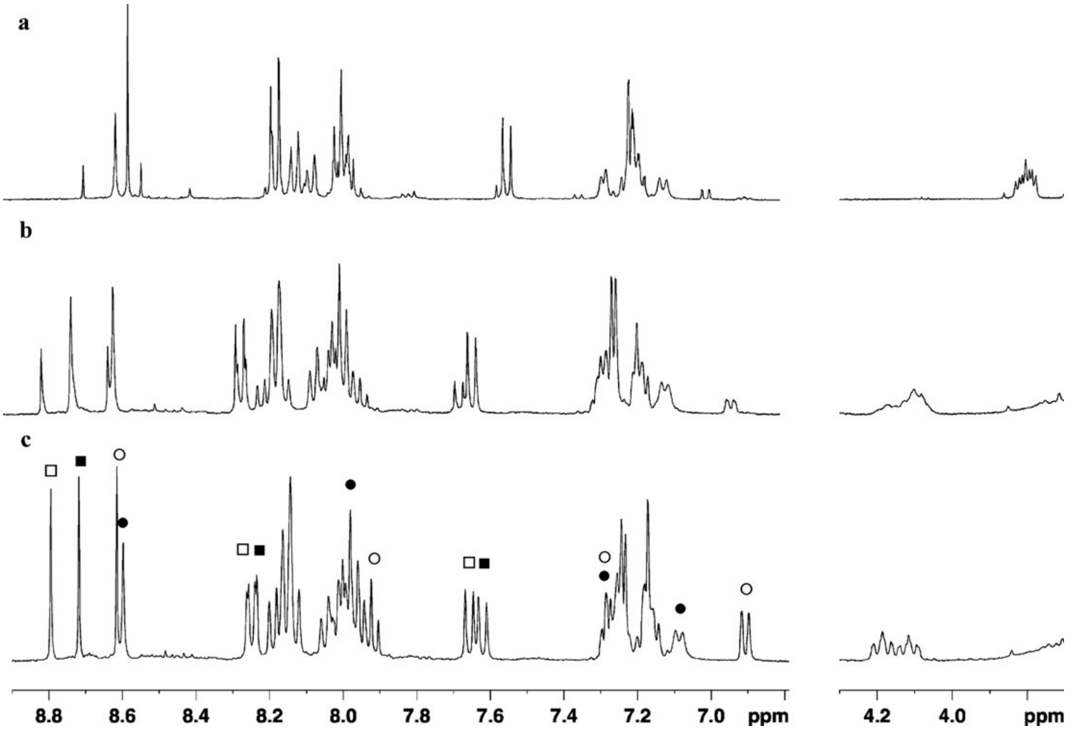

Fig. 3 Aromatic region and selected methylene signals of the ^1H NMR spectrum of a mixture of $[Zn_2(L^1)(L^2)]^{4+}$, $[Zn_2(L^2)_2]^{4+}$ and $[Zn_2(L^1)_2]^{4+}$: (a) 0, (b) 20 and (c) 40 equivalents of Ba^{2+}: (□) $[Zn_2(\mathbf{L^1})(L^2)]^{4+}$, (●) $[Zn_2(\mathbf{L^2})_2]^{4+}$, (■) $[Zn_2(\mathbf{L^1})_2]^{4+}$, (○) $[Zn_2(L^1)(\mathbf{L^2})]^{4+}$.

1 : 2 : 1 (Fig. 3(c)). A further change in the distribution of products is not observed upon addition of more Ba^{2+}. Here, two regions of the ^1H NMR are useful in determining the distribution of species. The signals due to the thiazolyl groups are all of similar intensity, as would be expected if a 1 : 2 : 1 mixture is formed (8.60 $[Zn_2(L^2)_2]^{4+}$ and 8.72 $[Zn_2(L^1)_2]^{4+}$; 8.62 and 8.80 ppm $[Zn_2(L^2)(L^1)]^{4+}$). Furthermore, a "doubling-up" of the methylene signals at 4.12 and 4.19 ppm is also observed, indicating two environments for the crown ether region in the ligand L^1; this is not observed upon addition of Ba^{2+} to just $[Zn_2(L^1)_2]^{4+}$. Unfortunately, due to the amount of Ba^{2+} required to form the mixture of helicates ESI-MS was uninformative as any ions of interest are suppressed by the barium.

Generation of such a distribution indicates that there is now a statistical mixture of species present, with both homo- and heteroleptic species present, and that all self-recognition between the ligand strands is lost. There are two possible reasons for the formation of a mixture of species. First an allosteric affect, where upon coordination of the barium ions to the crown ether unit the ligand partitioning is altered and consequently the ligand acts as a bis-bidentate donor unit in a similar fashion to L^2. This would create a helicate with two four-coordinate Zn(II) ions allowing formation of the heteroleptic species. To form a "matching" set of two bidentate coordination domains found in the unsubstituted ligand L^2, a decrease in the torsion angle would be required. However, as can be seen in the solid-state structure of $[Zn_2(L^1)_2Ba_2]^{8+}$ this does not occur and the inter-domain torsion angle increases and correspondingly the ligand still acts as a bis-terdentate donor. Nor is it an effect of the change in pitch length of the helicate, as to match the pitch length of the complex formed by the unsubstituted ligand (L^2: 4.609 Å) the pitch length observed in the zinc complex of L^1 (4.812(1) Å) would have to decrease upon addition of Ba^{2+}. However, the opposite effect was observed and the pitch length increases to 5.142(1) Å.

The second possibility is an electrostatic effect, where in the presence of excess Ba^{2+} the $[Zn_2(L^1)_2]^{4+}$ complex will form a highly charged 8+ ion. The high charge on this helicate species destabilises the complex favouring formation of the lower charged mixed ligand system $[Zn_2(L^1)(L^2)Ba]^{6+}$. Thus the previously unfavourable heteroleptic species $[Zn_2(L^1)(L^2)Ba]^{6+}$ would be stabilised with respect to the highly charged homoleptic species $[Zn_2(L^1)_2Ba_2]^{8+}$. The ability of electrostatic factors to control the ligand recognition properties is also supported by studies with other s-block metal ions. Upon addition of K^+, which is virtually identical in size to the barium ion but is only monocationic, to the homoleptic system no change in the proportion of the heteroleptic species is observed. Although other factors cannot be ignored, it would seem that the electrostatic effects would be the basic driving force in the formation of a statistical mixture of species.

3 Experimental

3.1 General methods

All reagents were used as supplied. The NMR spectra were recorded on either a Bruker Avance DPX400 or Bruker Avance 500 spectrometer. ESI-MS were obtained on either a Bruker MicroTOF or Micromass Quattro II mass spectrometer.

3.6 Synthesis of L^1

The 6,6′-dithioamide derivative[10] (**1**) (0.25 g, 0.49 mmol) and 2-(α-bromoacetyl)pyridine (0.55 g, 1.96 mmol) were dissolved in ethanol (25 cm^3) and heated at reflux for 8 h. After this time the solvent was removed and the resulting residue was dissolved in water, neutralised with $NaHCO_3$(aq) and extracted into CH_2Cl_2. The organic solvent was evaporated giving crude L^1 as a pale oil. The oil was then twice triturated with diethyl ether (5 cm^3), giving L^1 as a tan solid (0.2 g, 0.28 mmol, 57%). Further purification can be achieved by column chromatography (1% MeOH in CH_2Cl_2, Al_2O_3). ^1H NMR [400 MHz, ($CDCl_3$)]: δ (ppm) 8.65 (2H, d, J = 4.50; py), 8.37 (2H, d, J = 8.52; py), 8.26 (2H, d, J = 7.81; py), 8.13 (2H, s, th), 7.81 (2H, dd, J = 1.33, 7.77 py), 7.48 (2H, m, py), 7.25 (2H, m, py), 4.25 (4H, m, py), 3.76 (4H, m, py), 3.70–3.20 (12H, m, cr). ^{13}C NMR [400 MHz, ($CDCl_3$)]: δ (ppm) 169.1, 155.9, 154.8, 152.8, 149.4, 146.0, 143.7, 136.9, 122.6, 121.1, 120.7, 120.1, 118.7, 70.6, 70.5, 70.3, 70.1 and 69.9. ESI-MS: m/z 711.3 ($M + H^+$). Found: C, 61.1; H, 5.0; N, 11.4. $C_{36}H_{34}N_6O_6S_2$ requires: C, 60.8; H, 4.8; N, 11.8%.

3.7 $[Zn_2(L^1)_2](ClO_4)_4$

Reaction of $[Zn(H_2O)_6](ClO_4)_2$ (0.008 g, 0.021 mmol) and L^1 (0.015 g, 0.021 mmol) in MeCN (2 cm^3) resulted in a colourless solution. Filtration followed by layering with diethyl ether (10 cm^3) afforded small colourless crystals (11 mg, 54%). ^1H NMR [400 MHz, ($CDCl_3$)]: δ (ppm) 8.58 (s, 2H, th), 8.19 (d, J = 8.89, 2H), 8.13 (d, J = 7.89, 2H), 8.01 (m, 2H), 7.56 (d, J = 8.78 Hz, 2H), 7.22 (m overlapping, 4H), 3.79 (m, 2H), 3.64 (m, 2H), 3.48 (m, 2H), 3.40 (m, 8H), 3.23 (m, 2H), 3.75 (m, m, 2H), 2.96 (m, 2H). ESI-MS m/z 1851 $\{[Zn_2(L^1)_2(ClO_4)_3]\}^+$. Found: C, 44.1; H, 3.8; N, 8.8. $C_{72}H_{68}Cl_4Zn_2N_{12}O_{28}S_4 \cdot MeCN$ requires: C, 44.6; H, 3.6; N: 9.1%.

3.8 $[Zn_2(L^1)_2Ba_2](ClO_4)_8$

Reaction of $[Zn(H_2O)_6](ClO_4)_2$ (0.008 g, 0.021 mmol) and L^1 (0.015 g, 0.021 mmol) in MeCN (2 cm^3) resulted in a colourless solution, to which was added $Ba(ClO_4)_2$ (0.071 g, 0.21 mmol). Filtration followed by layering with diethyl ether (10 cm^3) afforded small colourless crystals (17 mg, 62%). ^1H NMR [400 MHz, ($CDCl_3$)]: δ (ppm) 8.69 (s, 2H, th), 8.26 (d, J = 8.90, 2H), 8.17 (d, J = 7.90, 2H), 8.03 (m, 2H), 7.63 (d, J = 8.87 Hz, 2H), 7.26 (m overlapping, 4H), 4.10 (m, 2H), 3.62–3.33 (m, 14H), 3.19 (m, 2H), 2.93 (m, 2H). ESI-MS m/z 1213 $\{[Zn_2(L^1)_2Ba_2](ClO_4)_6\}^{2+}$ and 2187 $\{[Zn_2(L^1)_2Ba](ClO_4)_5\}^+$. Found: C, 32.8; H, 2.9; N, 6.4. $C_{72}H_{68}Ba_2Cl_8Zn_2N_{12}O_{44}S_4 \cdot 2H_2O \cdot MeCN$ requires: C: 33.0, H: 2.8, N: 6.7%.

3.9 Crystallography

$[Zn_2(L^1)_2](ClO_4)_4$. X-Ray single-crystal diffraction data were collected on a Bruker APEX CCD area-detector diffractometer under a stream of cold nitrogen.

Crystal data: $[Zn_2(L^1)_2](ClO_4)_4 \cdot 3MeCN \cdot H_2O$; M = 2082.33, triclinic, $P\bar{1}$, a = 13.641(3), b = 17.738(4), c =

18.898(4) Å, $\alpha = 75.86(3)$, $\beta = 82.89(3)$, $\gamma = 84.78(3)°$, $V = 4391.0(15)$ Å^3, $Z = 2$, $D_c = 1.575$ Mg m^{-3}, $F(000) = 2142$, μ(Mo-Kα) = 0.853 mm^{-1}, $T = 100$ K. A total of 49 434 reflections were measured in the range $1.51 \le \theta \le 27.48°$ (*hkl* range indices $-17 \le h \le 17$, $-23 \le k \le 23$, $-24 \le l \le 24$), 20 080 independent reflections ($R_{int} = 0.0621$). The structure was refined on F^2 to $R_w = 0.1368$, $R = 0.0560$ (12 221 reflections with $I > 2\sigma(I)$) and GOF = 1.024 on F^2 for 1190 refined parameters, largest difference peak and hole 1.329 and −0.594 e Å^{-3}.

CCDC reference number 637341.

$[Zn_2(L^1)_2Ba_2](ClO_4)_8$. X-Ray single-crystal diffraction data were collected on a PROTEUM CCD area-detector diffractometer under a stream of cold nitrogen.

Crystal data: $[Zn_2L_2Ba_2(ClO_4)_5(H_2O)][ClO_4]_3 \cdot 3.5MeCN$; $M = 2784.35$, triclinic, $P\bar{1}$, $a = 16.9511(3)$, $b = 18.4571(3)$, $c = 20.1644(4)$ Å, $\alpha = 108.4580(10)$, $\beta = 103.3020(10)$, $\gamma = 110.4970(10)°$, $V = 5176.026(16)$ Å^3, $Z = 2$, $D_c = 1.786$ Mg m^{-3}, $F(000) = 2790$, μ(Mo-Kα) = 9.887 mm^{-1}, $T = 100$ K. A total of 41 199 reflections were measured in the range $2.50 \le \theta \le 70.12°$ (*hkl* range indices $-20 \le h \le 19$, $-21 \le k \le 22$, $-24 \le l \le 23$), 17 747 independent reflections ($R_{int} = 0.0638$). The structure was refined on F^2 to $R_w = 0.1281$, $R = 0.0525$ (17 747 reflections with $I > 2\sigma(I)$) and GOF = 0.996 on F^2 for 1388 refined parameters, largest difference peak and hole 2.031 and −1.851 e Å^{-3}.

CCDC reference number 637342.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702608k

4 Conclusion

We have demonstrated how a potentially hexadentate ditopic ligand reacts with Zn(II) to form a dinuclear double helicate $[Zn_2(L^1)_2]^{6+}$, this complex can further coordinate barium ions in the remote crown ether sites giving $[Zn_2(L^1)_2Ba_2]^{8+}$. Upon mixing with a similar hexadentate ligand, ligand recognition occurs and none of the heteroleptic species is formed. However, upon coordination of Ba^{2+} in the crown ether unit all ligand recognition is lost and a mixture results.

Acknowledgements

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