Controlling the formation of metallosupramolecular assemblies by metal ionic radii†

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The formation of either dinuclear double-stranded or pentanuclear circular helicates from a ligand containing two tridentate domains separated by a phenylene unit can be controlled by inter-ligand steric interactions which themselves are governed by the size of the metal ion.

Controlling the structure of multi-component assemblies is one of the leading challenges for the supramolecular chemist. One of the simplest assemblies is the dinuclear double-stranded helicate, and the rules that govern the formation of this species are largely established.1–3 The formation of the helicates’ higher nuclearity cousins, the cyclic helicate, is conversely less well understood. 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)8 or by intramolecular interactions which stabilise the formation of the cyclic species relative to its double-stranded alternative. As an example of the first of these approaches, in the work carried out by Ward et al., a ligand with two bidentate domains separated by a 1,8-naphthalenediyl spacer was reported to form a simple mononuclear species with Cu(CF3SO3)2, but in the presence of tetrafluoroborate, a tetranuclear cyclic helicate [Cu4L4](4+) was observed.9 Hannon et al., on the other hand, demonstrated that a metal ion’s preference for different coordination geometries could affect the self-assembly outcome. In this case a bis-bidentate ligand containing a 1,3-di(bromoacetyl)phenyl spacer formed linear dimers with tetrahedral metal ions and trinuclear circular helicates with octahedral metal ions.10 Other reports have cited inter-strand CH⋯π interactions as the principal driving force for the preferential formation of high complexity cyclic assemblies over their dimeric counterparts.11 There are also examples of intermediate systems where the self-assembly of ligands and metal ions results in a dynamic combinatorial library where a number of oligomers are formed in solution i.e. [MxLz]x+z where x = 2, 3, 4, 5, etc.12

In this communication we describe how the formation of either dinuclear double-stranded or pentanuclear circular helicates can be controlled by inter- ligand steric interactions which, in turn, are governed by the size of the metal ion. This approach allows for the specific formation of either of the two structures and gives valuable insight into some of the factors which control the formation of cyclic helicates.

The ligand L1, which was prepared by the reaction of 2,2′-bipyridine-6-thioamide with 1,3-di(α-bromoacetyl)benzene, contains two tridentate binding domains separated by a phenylene ring (Fig. 1). Reaction of this ligand with Cd(ClO4)2·6H2O in MeNO2 results in a colourless solution, from which crystals are formed upon slow diffusion of dichloromethane. In the ESI mass spectrum, peaks at m/z 1076 ([Cd2(L1)](ClO4)3)+ and 1629 ([Cd3(L1)2](ClO4)3)+, with the appropriate isotope pattern for their charged states, were present indicating the formation of the dinuclear double-stranded helicate. Formation of the complex [Cd3(L1)2](ClO4)4 was confirmed by a single crystal X-ray diffraction study (Fig. 2).† In the solid-state the ligand partitions into two tridentate domains, each comprising a thiazole-pyridyl-pyrydil

Fig. 1 Synthesis of L1.

Fig. 2 Ortep plot of the complex cation [Cd3(L1)2]4+ at 30% probability (hydrogens omitted for clarity).

† Electronic supplementary information (ESI) available: Ligand synthesis and characterisation; 1H and 13C NMR and NOESY spectra for [Cd2(L1)]3+ and [Zn2(L1)]3+; details of crystallographic refinements. CCDC 748335 and 748336. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b920840b

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The cadmium(II) centres have distorted octahedral geometries, imparted by coordination of one tridentate thiazole–pyridyl–pyridyl domain from each ligand (Cd–N: 2.282(4)–2.464(5) Å).

Reaction of L\textsubscript{1} with Zn(ClO\textsubscript{4})\textsubscript{2}/C\textsubscript{1}\textsubscript{6}H\textsubscript{2}O in MeCN again results in a colourless solution and upon layering with Et\textsubscript{2}O micro-crystalline material appears. The ESI-MS shows a number of low nuclearity fragments (m/z: 980, 1269 and 1532 corresponding to [Zn\textsubscript{2}(L\textsubscript{1})\textsubscript{2}(ClO\textsubscript{4})\textsubscript{3}]\textsuperscript{+}, [Zn(L\textsubscript{1})\textsubscript{2}(ClO\textsubscript{4})]\textsuperscript{+} and [Zn\textsubscript{2}(L\textsubscript{1})\textsubscript{2}(ClO\textsubscript{4})\textsubscript{3}]\textsuperscript{+}, respectively), but also a peak at m/z 1942 corresponding to the pentanuclear species [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}(ClO\textsubscript{4})\textsubscript{8}]\textsuperscript{2+}. Crystals suitable for X-ray diffraction were grown by layering a solution of Zn(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} with L\textsubscript{1} in MeCN with Et\textsubscript{2}O, and structural analysis confirmed the formation of the pentanuclear cyclic helicate [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{10} (Fig. 3a and b). In the crystal, all five Zn\textsuperscript{2+} ions are six-coordinate, arising from the coordination of two tridentate thiazole–pyridyl–pyridyl domains (Zn–N: 2.072(8)–2.327(8) Å). The 1,3-phenylene spacers bridge each of the tridentate domains in an ‘over-and-under’ conformation, giving rise to a helical cyclic oligomer as opposed to a face-to-face array associated with more grid-like architectures.

Reaction of L\textsubscript{1} with Cd\textsuperscript{2+} or Zn\textsuperscript{2+} ions not only gives very different structures in the solid-state, \textsuperscript{1}H NMR (CD\textsubscript{3}NO\textsubscript{2}) studies also suggest that the respective structures are retained in solution. The one-dimensional \textsuperscript{1}H NMR spectra of solutions containing [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}(ClO\textsubscript{4})\textsubscript{4}] and [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}(OT\textsubscript{f})\textsubscript{10} in CD\textsubscript{3}NO\textsubscript{2} show the expected 11 aromatic resonances for complexes of D\textsubscript{2} and D\textsubscript{5} symmetry respectively (Fig. 4). For both species, protons on the tridentate chelate units appear between 7.0 and 8.4 ppm, consistent with the aromatic heterocycles on L\textsubscript{1} being coordinated to one of the two metal ions. For the pentanuclear species, however, the three protons on the bridging phenylene unit resonate at much lower frequency (6.5–5.9 ppm) than those in [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+}. In both structures this central phenylene ring is sandwiched between the internal pyridyl rings of the two thiazole–pyridine–pyridine tridentate domains, but in the pentanuclear helicate this packing motif is more compact, with an average centroid–centroid distance of 3.9(1) Å (cf. 4.2(1) Å for the dinuclear helicate). The phenylene protons in [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+} are thus more exposed to the shielding ring currents produced by the aromatic heterocycles on the two overlapping ligand strands, and hence the unusually low field chemical shifts. Additionally, \textsuperscript{1}H–\textsuperscript{1}H NOESY spectra evidence a complex network of inter-ligand through-space interactions for [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+}, where the cyclic arrangement brings up to seven pairs of protons into sufficiently close proximity for dipole–dipole induced relaxation effects to be observed (see ESI\textsuperscript{f}). None of these interactions occur for [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+}, however, in which the shortest corresponding non-bonded distances are up to ca. 2 Å longer in the solid-state structure. For [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+}, a diagnostic intra-ligand NOE effect also occurs between phenylene proton H\textsubscript{1} and thiazole proton H\textsubscript{4}, whose non-bonded distance is ca. 2.5 Å in the solid-state structure (cf. ca. 4.3 Å in [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+}).

Further evidence for the retention of the respective solid-state structures in solution was obtained by diffusion ordered NMR spectroscopy. Translational self-diffusion coefficients (in CD\textsubscript{3}NO\textsubscript{2}, 298 K) were determined to be 3.4(3) × 10\textsuperscript{–10} and 6.3(2) × 10\textsuperscript{–10} m\textsuperscript{2} s\textsuperscript{–1} for [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+} and [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+}, respectively. Conversion of these values into meaningful hydrodynamic radii is not trivial since microfrictional and shape effects can profoundly influence the apparent relationship between diffusion constant and molecular size.\textsuperscript{13} The significantly lower value obtained for [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+} is nonetheless consistent with it being the larger of the two diffusing species in solution.

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\textsuperscript{1}H NMR spectra (CD\textsubscript{3}NO\textsubscript{2}) of (a) [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+} and (b) [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+}.

Fig. 3 Two views of the complex cation [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+}: a conventional ortep view at 30% probability (top, hydrogens omitted for clarity) and a space-filling picture showing atoms with their van der Waals radii (bottom).

Fig. 4 Aromatic regions in the \textsuperscript{1}H NMR spectra (CD\textsubscript{3}NO\textsubscript{2}) of (a) [Cd\textsubscript{2}(L\textsubscript{1})\textsubscript{2}]\textsuperscript{4+} and (b) [Zn\textsubscript{5}(L\textsubscript{1})\textsubscript{5}]\textsuperscript{10+}.

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It is worth noting that the dicadmium(II) helicate was obtained as the perchlorate salt whereas single crystals of the pentanuclear structure were only successfully obtained in the presence of the triflate anion. Indeed, in the latter structure, a disordered triflate anion resides within the central cavity of the circular complex cation. To investigate the potential role of counter anion in the two self-assembly reactions, therefore, solutions (CD$_3$NO$_2$) containing the two respective assemblies were monitored by $^1$H NMR as increasing amounts of the other’s anion were added (as the tetrabutylammonium salts). Even in the presence of 20 eq. of the corresponding anion, however, no changes were observed in either case and so the latter’s influence in directing the assembly is clearly minimal.

An alternative explanation for why L$^1$ gives such markedly different structures with the two spherical d$^{10}$ cations therefore requires consideration of the potential steric interactions occurring between the protons on the central phenylene units in the two respective structures. Although these units function well in partitioning the ligands into two tridentate domains—thus preventing the undesired mononuclear species—the formation of the dinuclear helicate structure brings them into relatively close proximity with one another (see Fig. 2). Indeed, the inter-strand C$^1$–C$^1’$ distance between these two rings is ca. 4.2 Å in [Cd$_2$(L$^1$)$_2$]$_4^+$, and examination of the van der Waals radii reveals marginal surplus space between these inward facing H$^1$ protons. Six coordinate zinc(II) is, needless to say, smaller than cadmium(II) (0.75 vs. 0.95 Å respectively). Due to correspondingly shorter Zn–N bonds, therefore, it is likely that any steric and/or electrostatic repulsion between these protons would be significantly emphasized in an isostuctural dizinc(II) helicate. The latter presumably being destabilized in this manner results in the formation of an alternative species which does not require that the two phenylene rings reside in such close proximity. In this case, the alternative is the observed pentanuclear cyclic helicate, whose apparent high relative stability ensures its quantitative formation and retention in the gas-, solution- and solid-states.

These results demonstrate how subtle changes in the metal/ligand bond distances can influence inter-ligand steric interactions and have a pronounced effect on the outcome of a self-assembly reaction.

Notes and references

† Crystal data for [Cd$_2$(C$_{32}$H$_{20}$N$_6$S$_2$)$_2$][ClO$_4$]$_2$, 2CH$_2$Cl$_2$: M = 1897.77, monoclinic C2/c, a = 24.3339(8), b = 12.1082(4), c = 28.2739(12) Å, $\beta$ = 112.7890(10)$^\circ$, V = 7680.3(5) Å$^3$, Z = 4; $\rho_{\text{calc}}$ = 1.641 Mg m$^{-3}$, $F(000)$ = 3792; crystal dimensions 0.10 × 0.07 × 0.07 mm; $\mu$(Mo K\textalpha) = 0.1073 mm$^{-1}$, T = 100 K. A total of 27 701 reflections were measured in the range 1.82 $^\circ$ $\leq \theta$ $\leq$ 25.68$^\circ$ (hkl range indices: $-$27 $\leq$ h $\leq$ 27, $-$29 $\leq$ k $\leq$ 30, $-$43 $\leq$ l $\leq$ 43), 18 926 unique reflections ($R_{\text{int}}$ = 0.0416). The structures were refined on $F^2$ to $R_w$ = 0.3224, $R = 0.1236$ (14 889 reflections with $I > 2\sigma(I)$ and GOOF was 1.49 for 1270 refined parameters). Largest peak and hole 1.862 and $-1.391$ e$^-3$. CCDC 748336. Scattering contributions from diffuse solvent were removed using the Squeeze routine in Platon. Crystals of both complexes grew as stacked platelets and the diffraction data were always to some extent contaminated with reflections from crystal sub-domains. The present data sets were the best of numerous trials, but the consequences of reflection overlap, in particular at low angle, can still be seen in the relatively high residuals, unusual weighting coefficients and the presence of some large (up to 3.6 e$^-3$) residual electron density peaks in chemically unusual weighting coefficients and the presence of large $R_{\text{int}}$ are largely sufficient to unambiguously determine atomic connectivity in the complex cations.