This article is published as part of the *Dalton Transactions* themed issue entitled:

Self-Assembly in Inorganic Chemistry

Guest Editors Paul Kruger and Thorri Gunnlaugsson

Published in issue 45, 2011 of *Dalton Transactions*

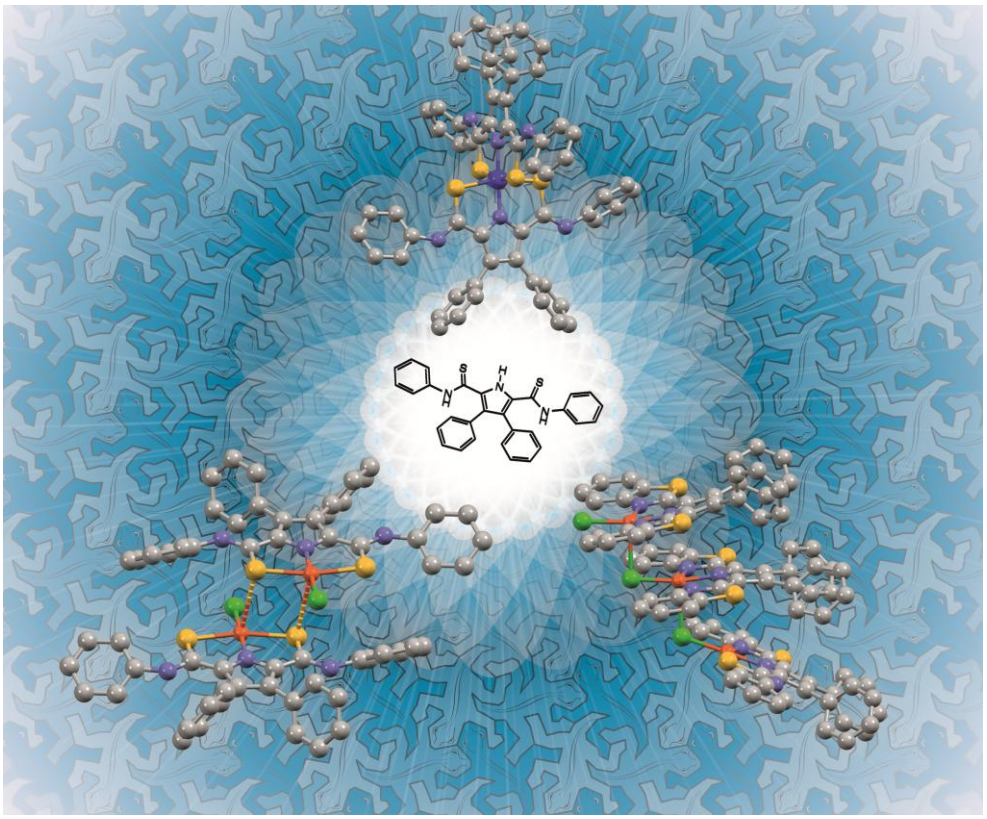


Image reproduced with permission of Mark Ogden

Articles in the issue include:

PERSPECTIVE:

ARTICLES:

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research
www.rsc.org/dalton

Dalton Transactions

Dynamic Article Links

Cite this: *Dalton Trans.*, 2011, **40**, 12381

www.rsc.org/dalton

PAPER

Diastereoselective assembly of pentanuclear circular helicates†

Oliver R. Clegg,[a] Rebecca V. Fennessy,[a] Lindsay P. Harding,[a] Craig. R. Rice,*[a] T. Riis-Johannessen[b] and Nicholas C. Fletcher[c]

Received 26th July 2011, Accepted 7th October 2011
DOI: 10.1039/c1dt11414j

Reaction of a ligand which contains two N-donor and O-donor tridentate domains separated by a 1,3-phenylene spacer unit with Zn^{2+} ions results in a pentanuclear circular helicate $[Zn_5(\mathbf{L})_5]^{10+}$ and this structure persists in both the solid and solution state. The formation of this high nuclearity species is governed by unfavourable steric interactions between the phenyl units which destabilize the simple linear helicate. Incorporation of enantiopure units within the ligand strand controls the diastereoselectivity with up to 80% d.e.

Introduction

Transition metal helicates arise from the reaction of a suitable ligand L with a transition metal ion M^{z+} giving, in the simplest case, the dinuclear species $[M_2(L)_2]^{2z+}$. This type of self-assembly is generally well understood and there are now numerous examples in the literature.[1–7] Circular helicates are cyclic oligomers of general formula $[M_n(L)_n]^{nz+}$ ($n > 2$) which retain the "over-and-under" ligand motif requisite of helical chirality. However, they are much less common and are more difficult to generate compared with the linear helicates. This is in part due to the fact that the requirements of the ligand strand are identical in both cases, *i.e.* the ligand must simply be able to partition into two different coordination domains each of which coordinates a different metal ion. For a cyclic helicate to result, therefore, the formation of the entropically favoured linear $[M_2(L)_2]^{2z+}$ helicate has to be prevented. This can be achieved by a number of methods. One mechanism is by anion templation, wherein intramolecular interactions between the metal complex and the anion result in a high nuclearity species.[8] For example, work reported by Ward *et al.* demonstrated that a ligand with two bidentate domains separated by a 1,8-naphthalenediyl spacer forms a simple mononuclear species with $Cu(CF_3SO_3)$, but in the presence of tetrafluoroborate, a tetranuclear cyclic helicate $[Cu_4L_4]^{4+}$ was observed.[9] Hannon, 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-bis(aminomethyl)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 $\cdots$ π interactions as the principal driving force for the preferential formation of high complexity cyclic assemblies over their dimeric counterparts.[11]

Destabilizing the linear helicate assembly can also result in the formation of a circular helicate. Recently we have shown that the ligand **L** (Fig. 1), which contains two tridentate binding domains separated by a 1,3-phenylene spacer unit, reacts with Cd^{2+} to give the simple linear helicate $[Cd_2(\mathbf{L})_2]^{4+}$ whilst Zn^{2+} gives a pentanuclear circular helicate $[Zn_5(\mathbf{L})_5]^{10+}$. This difference is attributed to steric interactions between the two spacer units. In the $[Cd_2(\mathbf{L})_2]^{4+}$ complex the distance between the two phenyl rings is *ca.* 4.2 Å and examination of the van der Waals radii reveals marginal surplus space between these inward facing protons. When smaller zinc ions are employed it is likely that any steric and/or electrostatic repulsion between these protons would be significantly emphasized in an isostructural di-zinc(II) helicate. As a result of this destabilization an alternative pentanuclear circular helicate $[Zn_5(\mathbf{L})_5]^{10+}$ is formed.[12]

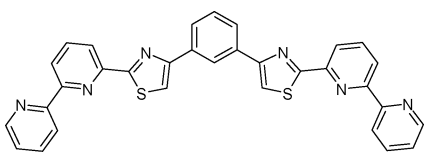


Fig. 1 Structure of the previously reported ligand **L**.

Another important aspect of helicates is that they can be programmed to express certain structural features of higher-order complexity. This is 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 can entail: (i) directional control over ligand alignment, *i.e.* head-to-tail *vs.* head-to-head helicates, (ii) selective incorporation of different metal cations along the helical axis (*i.e.* heterometallic assemblies) and (iii) selective incorporation of different ligand

[a]*Department of Chemical and Biological Sciences University of Huddersfield, Huddersfield, HD1 3DH, UK. E-mail: c.r.rice@hud.ac.uk; Fax: (+44) 148-447-2182*
[b]*EPFL SB ISIC LCS BCH 3307 (Bâtiment de chimie UNIL), CH-1015, Lausanne, Switzerland*
[c]*School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, UK*

† CCDC reference number 836308. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11414j

strands within the helical array (*i.e.* heteroleptic assemblies). There are numerous examples of this type of control for the simple linear helicates[2–5] and the formation of head-to-tail and heteroleptic cyclic helicates has recently been reported.[13] Since helicates are intrinsically chiral, stereoselective control over their self-assembly can also been achieved, usually by incorporation of enantiopure units within the ligand framework (*i.e.* chiral auxiliaries). This type of control has already been implemented in the self assembly of both linear and circular helicates. However, although such elements of higher order complexity have often been incorporated into linear helicates, the analogous treatment of circular helicates has been studied to a much lesser degree.[14]

In the following we discuss the preparation of a ligand system that contains two tridentate binding domains comprised of two N-donors and one O-donor separated by a 1,3-phenylene unit. Reaction of this ligand strand with Zn^{2+} results in the formation of a pentanuclear circular helicate wherein the zinc ions are octahedrally coordinated by four N-donor and two O-donor atoms. Furthermore, incorporation of enantiopure amino acid esters on the amide functional groups results in diastereoselective assembly of a pentanuclear circular helicate with a d.e. of up to 80%.

Experimental

Crystallographic data

Single crystal X-ray diffraction data were collected at 150(2) K on a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(Kα) radiation source and a cold stream of N_2 gas. Crystal data for $[Zn_5(L^1)_5](CF_3SO_3)_{10}\cdot 10 \times$ EtOAc$\cdot 10 \times$ MeCN ($C_{170}H_{155}F_{30}N_{30}O_{40}\ S_{20}Zn_5\cdot 10 \times$ EtOAc$\cdot 10 \times$ MeCN): M = 6090, Triclinic, $P\bar{1}$, a = 20.3776(13), b = 21.5461(15), c = 28.7397(19) Å, α = 79.876(2), β = 85.013(2), γ = 77.697(2), V = 12120.6(1) Å^3, Z = 2; ρ_c = 1.668 Mg m^{-3}, $F(000)$ = 6290; dimensions 0.5 × 0.2 × 0.2 mm^{-3}; μ(Mo-Kα) = 0.71073 mm^{-1}, T = 150 K. A total of 131 442 reflections were measured in the range $1.44 \le \theta \le 23.37°$ (*hkl* range indices: $-22 \le h \le 22$, $-24 \le k \le 23$, $-31 \le l \le 32$), 35 025 unique reflections (R_{int} = 0.0667). The structure was refined on F^2 to R_w = 0.2819, R = 0.1032 (22 284 reflections with $I > 2\sigma(I)$) and GOF = 1.069 on F^2 for 2360 refined parameters, 369 restraints. Largest peak and hole 1.417 and –1.425 eÅ^{-3}. A number of triflate anions and terminal diethylamide fragments were refined with geometric similarity restraints (SAME and SIMU). A remaining four triflate anions were modelled using two-component disorder models. Each component was treated as a rigid body (AFIX 9) and population parameters for each component were refined against a free variable. The unit cell contained large amounts of diffuse electron density, presumably due to highly disordered interstitial solvent. However, attempts at modelling this were unsuccessful and the relevant scattering contributions were thus removed using the SQUEEZE routine in PLATON. We further note that of the ten expected triflate counter anions, only nine were resolved in the electron density map, the tenth presumably being likewise highly disordered. An estimated additional solvent/anion contents of 10 × EtOAc, 10 × MeCN and 1 × OTf has therefore been included in the moiety formula. CCDC 836308.†

General details

Chemicals were purchased and used without further purification. ^{1}H NMR spectra were recorded on a 400 MHz Bruker Avance DPX400. Mass spectra were obtained on a Bruker MicroTOF-q LC mass spectrometer. Circular Dichroism and UV vis spectra were recorded at a concentration of 2.5×10^{-5} mol dm^{-3} in acetonitrile at 298 K on a JASCO J-815. Extreme care should be taken when using NaCN and it should only be used in a well ventilated fume cupboard.

Synthesis of picolinamide derivative 1a. To a two necked round bottom flask charged with picolinic acid (1.5 g, 0.012 mol), anhydrous DCM was added and the reaction stirred under an atmosphere of nitrogen at 0 °C. To this was then added oxalyl chloride (2 M, 8.5 ml, 0.017 mol) and the solution left to stir for 10 min. After this time triethylamine (2.4 g, 0.024 mol) was slowly added and the reaction was left at room temperature for 3 h. The solvent was removed by rotary evaporation giving a black solid. This was re-dissolved in anhydrous DCM, stirred at 0 °C and triethylamine (1.9 g, 0.019 mol) and diethylamine (0.73 g, 0.010 mol) added and the reaction stirred at room temperature for 2 h. The solution was then poured into $NaHCO_3$ (aq) (30 ml) then extracted with DCM (3 × 50 ml), and the combined organic layers dried ($MgSO_4$) and evaporated. The crude product was dissolved in ether (100 ml) and de-colourising charcoal (0.1 g) added, filtration and removal of solvent gave the pure product as a dark yellow oil. Yield = 0.6 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.59 (ddd, J = 4.8, 1.6, 1.0, 1H, Py), 7.78 (dt, J = 7.7, 1.7, 1H, Py), 7.58 (dt, J = 7.8, 1.0, 1H, Py), 7.33 (ddd, J = 7.6, 4.9, 1.2, 1H, Py), 3.58 (q, J = 7.2, 2H, –C*H*$_2$CH$_3$), 3.39 (q, J = 7.1, 2H, –C*H*$_2$CH$_3$), 1.28 (t, J = 7.1, 3H, –CH$_2$C*H*$_3$), 1.16 (t, J = 7.1 Hz, 3H, –CH$_2$C*H*$_3$). ESI-MS m/z 201.1 (M + Na$^+$), HR ESI-MS found 201.1002 $C_{10}H_{14}N_2NaO$ requires 201.0998 (error 2.03 ppm).

Synthesis of picolinamide derivative 1b. This compound was prepared in an identical manner to **1a**, except glycine methyl ester was used in place of diethylamine and the resulting compound purified by column chromatography (Al_2O_3 5% MeOH in DCM). Yield = 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.60 (ddd, J = 4.8, 1.6, 0.9, 1H, Py), 8.49 (br s, 1H, –CON*H*), 8.19 (dt, J = 7.8, 1.0, 1H, Py), 7.86 (dt, J = 7.8, 1.7, 1H, Py), 7.46 (ddd, J = 7.6, 4.8, 1.2, 1H, Py), 4.29 (d, J = 5.7 Hz, 2H, –NHC*H*$_2$CO$_2$), 3.80 (s, 3H, –CO$_2$C*H*$_3$). ESI-MS m/z 217 (M + Na$^+$), HR ESI-MS found 217.0590 $C_9H_{10}N_2NaO_3$ requires 217.0584 (error = 3.11 ppm).

Synthesis of picolinamide derivative 1c. This compound was prepared in an identical manner to **1a**, except L-valine methyl ester was used in place of diethylamine. Yield = 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.61 (ddd, J = 4.8, 1.6, 0.9, 1H, Py), 8.53 (br d, J = 8.9, 1H, –CON*H*), 8.19 (dt, J = 7.8, 1.0, 1H, Py), 7.86 (dt, J = 7.7, 1.7, 1H, Py), 7.45 (ddd, J = 7.6, 4.8, 1.2, 1H, Py), 4.75 (dd, J = 9.3, 5.2, 1H, –NHC*H*), 3.78 (s, 3H, –CO$_2$C*H*$_3$), 2.33 (m, 1H, –C*H*(CH$_3$)$_2$), 1.03 (d, J = 6.9, 3H, –CH(C*H*$_3$)$_2$), 1.02 (d, J = 6.9 Hz, 3H, –CH(C*H*$_3$)$_2$). ESI-MS m/z 259 (M + Na$^+$), HR ESI-MS found 259.1051 $C_{12}H_{16}N_2NaO_3$ requires 259.1053 (error = 0.98 ppm).

Synthesis of picolinamide derivative 1d. This compound was prepared in an identical manner to **1a**, except L-phenylalanine methyl ester was used in place of diethylamine. Yield = 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.56 (ddd, J = 4.8, 1.6, 0.9, 1H, Py), 8.50 (br d, J = 8.2, 1H, –CON*H*), 8.17 (dt, J = 7.8, 1.0, 1H, Py), 7.85 (dt, J = 7.7, 1.7, 1H, Py), 7.44 (ddd, J = 7.6, 4.8, 1.2, 1H, Py), 7.31–7.20 (m, overlapping, 5H, Ph), 5.08 (dt, J = 8.4, 6.1,

1H,–C*H*CH_2Ph), 3.74 (s, 3H, –CO_2C*H_3), 3.28 (dd, *J* = 13.8, 6.0, 1H, –C*H*$_2$Ph), 3.23 (dd, *J* = 13.8, 6.2 Hz, 1H, –C*H*$_2$Ph). ESI-MS *m/z* 307 (M + Na^+), HR ESI-MS found 307.1047 $C_{16}H_{16}N_2NaO_3$ requires 307.1053 (error = 1.95 ppm).

Synthesis of picolinamide-*N*-oxide derivative 2a. To a solution of **1a** (0.3 g, 1.7 mmol) in DCM (25 ml) was added *m*CPBA (70%, 0.89 g. 3.7 mmol) and the solution stirred at room temperature. The reaction was monitored by TLC and upon completion (~8 h) the reaction was carefully evaporated (Caution: *N*-oxides are potentially explosive). Purification by column chromatography (2% methanol in DCM, Al_2O_3) gave the *N*-oxide **2a** as a white solid (0.3 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = ^{1}H NMR (400 MHz, CD_3Cl_3): δ_H = 8.32 (d, *J* = 6.2, 1H, Py), 7.35–7.28 (m overlapping, 3H, Py), 3.65 (m, 1H, –C*H*$_2$$CH_3$), 3.54 (m, 1H, –C*H*$_2$$CH_3$), 3.20 (m, 2H, –C*H*$_2$$CH_3$), 1.29 (t, *J* = 7.2, 3H, –CH_2C*H*$_3$), 1.13 (t, *J* = 7.2 Hz, 3H, –CH_2C*H*$_3$). ESI-MS *m/z* 217 (M + Na^+), HR ESI-MS found 217.0958 $C_{10}H_{14}N_2NaO_2$ requires 217.0947 (error = 4.91 ppm).

Synthesis of picolinamide-*N*-oxide derivative 2b. This compound was prepared in an identical manner to **2a**, except **1b** was used instead of **1a**. Yield = 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 11.72 (br s, 1H, –CON*H*), 8.43 (dd, *J* = 7.8, 2.3, 1H, Py), 8.29 (dd, *J* = 6.4, 1.2, 1H, Py), 7.47 (dt, *J* = 7.7, 1.3, 1H, Py), 7.42 (dt, *J* = 6.4, 2.3, 1H, Py), 4.29 (d, *J* = 5.6 Hz, 2H, –NHC*H*$_2$$CO_2$), 3.80 (s, 3H, –$CO_2C*H_3$). ESI-MS *m/z* 233 (M + Na^+), HR ESI-MS found 233.0538 $C_9H_{10}N_2NaO_4$ requires 233.0533 (error = 2.25 ppm).

Synthesis of picolinamide-*N*-oxide derivative 2c. This compound was prepared in an identical manner to **2a**, except **1c** was used instead of **1a**. Yield = 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 11.82 (br d, *J* = 7.9, 1H, –CON*H*), 8.42 (dd, *J* = 7.9, 2.2, 1H, Py), 8.28 (dd, *J* = 6.3, 0.9, 1H, Py), 7.47 (dt, *J* = 7.8, 1.0, 1H, Py), 7.42 (dt, *J* = 6.4, 2.3, 1H, Py), 4.70 (dd, *J* = 8.0, 4.9, 1H, –NHC*H*), 3.77 (s, 3H, –CO_2C*H_3), 2.36 (m, 1H, –C*H*$(CH_3)_2$), 1.05 (d, *J* = 6.8, 3H, –CH(C*H*$_3$)$_2$), 1.04 (d, *J* = 6.9 Hz, 3H, –CH(C*H*$_3$)$_2$). ESI-MS *m/z* 275 (M + Na^+), HR ESI-MS found 275.1008 $C_{12}H_{16}N_2NaO_4$ requires 275.1002 (error = 2.24 ppm).

Synthesis of picolinamide-*N*-oxide derivative 2d. This compound was prepared in an identical manner to **2a**, except **1d** was used instead of **1a**. Yield = 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 11.75 (br d, *J* = 5.5, 1H, –CON*H*), 8.38 (dd, *J* = 7.9, 2.3, 1H, Py), 8.25 (dd, *J* = 6.3, 1.2 1H, Py), 7.44 (dt, *J* = 7.6, 1.4, 1H, Py), 7.39 (dt, *J* = 6.3, 2.4, 1H, Py), 7.34–7.23 (m, overlapping, 5H, Ph), 5.00 (dt, *J* = 7.5, 5.5, 1H,–C*H*CH_2Ph), 3.74 (s, 3H, –CO_2C*H_3), 3.28 (dd, *J* = 13.9, 5.5, 1H, –C*H*$_2$Ph), 3.19 (dd, *J* = 13.9, 7.6 Hz, 1H, –C*H*$_2$Ph). ESI-MS *m/z* 323 (M + Na^+), HR ESI-MS found 323.1013 $C_{16}H_{16}N_2NaO_4$ requires 323.1002 (error = 3.32 ppm).

Synthesis of 6-cyanopicolinamide derivative 3a. To a 50 ml round bottom flask containing **2a** (0.2 g, 1.00 mmol) was added dimethyl sulfate (3 ml) and the reaction was placed under nitrogen and heated at 60 °C for 24 h with stirring. The reaction was allowed to cool to room temperature then ether (25 ml) was added and left to stir for 1 h. The reaction was allowed to settle for 12 h. The ether was decanted off and the remaining oil was washed with ether and decanted again and any remaining solvent removed by rotary evaporation. Distilled water was added (10 ml) and the solution neutralised with $NaHCO_3$, to this was then added NaCN (0.1 g, 2.00 mmol) and the reaction stirred for 5 mins, during which time a yellow oil was produced. Extraction into DCM (3 × 30 ml), followed by drying ($MgSO_4$) and evaporation produced the nitrile derivate **3a** as a light purple solid (0.16 g, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 7.96 (t, *J* = 7.9, 1H, Py), 7.90 (dd, *J* = 8.0, 1.3, 1H, Py), 7.75 (dd, *J* = 7.9, 1.3, 1H, Py), 3.58 (q, *J* = 7.1, 2H, –C*H*$_2$$CH_3$), 3.40 (q, *J* = 7.1, 2H, –C*H*$_2$$CH_3$), 1.29 (t, *J* = 7.1, 6H, –CH_2C*H*$_3$), 1.32 (t, *J* = 7.1 Hz, 6H, –CH_2C*H*$_3$). ESI-MS *m/z* 226 (M + Na^+), HR ESI-MS found 226.0951 $C_{11}H_{13}NaN_3O$ requires 226.0951 (error = 0.06 ppm).

Synthesis of 6-cyanopicolinamide derivative 3b. This compound was prepared in an identical manner to **3a**, except **2b** was used instead of **2a**. Yield = 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.43 (dd, *J* = 8.9, 1.0, 1H, Py), 8.28 (br s, 1H, –CON*H*), 8.06 (t, *J* = 7.9, 1H, Py), 7.87 (dd, *J* = 7.9, 1.0, 1H, Py), 4.30 (d, *J* = 5.8, 2H, –NHC*H*$_2$$CO_2$), 3.82 (s, 3H, –$CO_2C*H_3$). ESI-MS *m/z* 242 (M + Na^+), HR ESI-MS found 242.0529 $C_{10}H_9N_3NaO_3$ requires 242.0536 (error = 2.80 ppm).

Synthesis of 6-cyanopicolinamide derivative 3c. This compound was prepared in an identical manner to **3a**, except **2c** was used instead of **2a**. Yield = 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.42 (dd, *J* = 8.0, 1.1, 1H, Py), 8.25 (br d, *J* = 8.9, 1H, –CON*H*), 8.05 (t, *J* = 7.9, 1H, Py), 7.87 (dd, *J* = 7.7, 1.1, 1H, Py), 4.73 (dd, *J* = 9.2, 5.1, 1H, –NHC*H*), 3.97 (s, 3H, –CO_2C*H_3), 2.34 (m, 1H, –C*H*$(CH_3)_2$), 1.04 (d, *J* = 1.7, 3H, –CH(C*H*$_3$)$_2$), 1.03 (d, *J* = 1.7 Hz, 3H, –CH(C*H*$_3$)$_2$). ESI-MS *m/z* 284 (M + Na^+), HR ESI-MS found 284.1017 $C_{13}H_{15}N_3NaO_3$ requires 284.1006 (error = 3.96 ppm).

Synthesis of 6-cyanopicolinamide derivative 3d. This compound was prepared in an identical manner to **3a**, except **2d** was used instead of **2a**. Yield = 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.38 (dd, *J* = 8.0, 1.1, 1H, Py), 8.22 (br d, *J* = 8.2, 1H, –CON*H*), 8.03 (t, *J* = 7.9, 1H, Py), 7.84 (dd, *J* = 7.8, 1.1, 1H, Py), 7.35–7.19 (m, overlapping, 5H, Ph), 5.05 (dt, *J* = 8.3, 5.9, 1H, –C*H*CH_2Ph), 3.77 (s, 3H, –CO_2C*H_3), 3.29 (dd, *J* = 13.9, 5.9, 1H, –C*H*$_2$Ph), 3.23 (dd, *J* = 13.9, 5.8 Hz, 1H, –C*H*$_2$Ph). ESI-MS *m/z* 332 (M + Na^+), HR ESI-MS found 332.0991 $C_{17}H_{15}N_3NaO_3$ requires 332.1006 (error = 4.35 ppm).

Synthesis of picolinamide-6-thioamide derivative 4a. To a solution of the nitrile derivative **3a** (0.1 g, 0.49 mmol) in ethanol (20 ml), triethylamine (1.0 g, 9.9 mmol) was added and H_2S was slowly bubbled through the solution which turned yellow after a few minutes, the solution was then left to stand at room temperature for 48 h during which a precipitate was produced. Filtration gave the thioamide **4a** as a light yellow powder (0.9 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 9.31 (br s, 1H, –N*H*$_2$), 8.76 (dd, *J* = 7.8, 1.0, 1H, Py), 7.96 (t, *J* = 7.8, 1H, Py), 7.71 (dd, *J* = 7.8, 1.0, 1H, Py), 7.67 (br s, 1H, –N*H*$_2$), 3.60 (q, *J* = 7.1, 2H, –C*H*$_2$$CH_3$), 3.30 (q, *J* = 7.1, 2H, –C*H*$_2$$CH_3$), 1.30 (t, *J* = 7.1, 3H, –CH_2C*H*$_3$), 1.18 (t, *J* = 7.1 Hz, 3H, –CH_2C*H*$_3$). ESI-MS *m/z* 260.1 (M + Na^+), HR ESI-MS found 260.0820 $C_{11}H_{15}N_3NaOS$ requires 260.0828 (error = 2.92 ppm).

Synthesis of picolinamide-6-thioamide derivative 4b. This compound was prepared in an identical manner to **4a**, except **3b** was used instead of **3a**. Yield = 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 9.08 (br s, 1H, –N*H*$_2$), 8.89 (dd, *J* = 7.9, 1.0, 1H, Py), 8.39 (dd,

J = 7.9, 1.0, 1H, Py), 8.12 (br s, 1H, –CONH), 8.04 (t, J = 7.9, 1H, Py), 7.71 (brs, 1H, –NH_2), 4.31 (d, J = 5.4 Hz, 2H, –NHC$H_2$$CO_2$), 3.84 (s, 3H, –$CO_2CH_3$). ESI-MS m/z 253 (M + H^+), HR ESI-MS found 253.0510 $C_{10}H_{11}N_3O_3S$ requires 253.0516 (error = 2.37 ppm).

Synthesis of picolinamide-6-thioamide derivative 4c. This compound was prepared in an identical manner to **4a**, except **3c** was used instead of **3a**. Yield = 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 9.06 (br s, 1H, –NH_2), 8.88 (dd, J = 7.9, 1.1, 1H, Py), 8.38 (dd, J = 7.8, 1.1, 1H, Py), 8.16 (br d, J = 8.8, 1H, –CONH), 8.04 (t, J = 7.8, 1H, Py), 7.76 (br s, 1H, –NH_2), 4.77 (dd, J = 8.8, 5.0, 1H, –NHCH), 3.81 (s, 3H, –CO_2CH_3), 2.34 (m, 1H, –CH$(CH_3)_2$), 1.03 (d, J = 7.0 Hz, 3H, –CH(CH_3)$_2$), 1.02 (d, J = 7.0 Hz, 3H, –CH(CH_3)$_2$). ESI-MS m/z 318 (M + Na^+), HR ESI-MS found 318.0893 $C_{13}H_{17}N_3NaO_3S$ requires 318.0883 (error = 3.21 ppm).

Synthesis of picolinamide-6-thioamide derivative 4d. This compound was prepared in an identical manner to **4a**, except **3d** was used instead of **3a**. Yield = 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.86 (dd, J = 7.8, 1.1, 1H, Py), 8.75 (br s, 1H, –NH_2), 8.36 (dd, J = 7.8, 1.1, 1H, Py), 8.03 (t, J = 7.8, 1H, Py), 7.99 (br d, J = 8.2, 1H, –CONH), 7.53 (br s, 1H, –NH_2), 7.26–7.10 (m, overlapping, 5H, Ph), 5.10 (dt, J = 8.1, 5.2, 1H, –CHCH$_2$Ph), 3.80 (s, 3H, –CO_2CH_3), 3.34 (dd, J = 13.8, 5.2, 1H, –CH_2Ph), 3.27 (dd, J = 13.8, 5.2 Hz, 1H, –CH_2Ph). ESI-MS m/z 366 (M + Na^+), HR ESI-MS found 366.0870 $C_{17}H_{17}N_3NaO_3S$ requires 366.0883 (error = 3.41 ppm).

Synthesis of L^1. To a solution of 1,3-(α-dibromoacetyl) benzene (0.05 g, 0.16 mmol) in ethanol (25 ml) was added the thioamide **4a** (0.08 g, 0.34 mmol) and the reaction refluxed for 3 h. On cooling a white precipitate formed, which was isolated by filtration, followed by washing with EtOH (2 × 2 ml) and Et_2O (2 × 2 ml). (0.064 g, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.60 (t, J = 1.6, 1H, Ph), 8.42 (dd, J = 7.8, 1.0, 2H, Py), 8.02 (dd, J = 7.7, 1.6, 2H, Ph), 7.95 (t, J = 7.8, 2H, Py), 7.75 (dd, J = 7.8, 1.0, 2H, Py), 7.74 (s, 2H, tz), 7.58 (t, J = 7.7, 1H, Ph), 3.63 (q, J = 7.1, 4H, –CH_2CH$_3$), 3.51 (q, J = 7.0, 4H, –CH_2CH$_3$), 1.38 (t, J = 7.0, 6H, –CH$_2$CH_3), 1.32 (t, J = 7.0 Hz, 6H, –CH$_2$CH_3). ESI-MS m/z 619 (M + Na^+), HR ESI-MS found 619.1932 $C_{32}H_{32}N_6NaO_2S_2$ requires 619.1920 (error = 1.88 ppm).

Synthesis of L^2. This compound was prepared in an identical manner to **L^1**, except **4b** was used instead of **4a**. Yield = 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.62 (t, J = 1.6, 1H, Ph), 8.55 (dd, J = 7.7, 1.0, 2H, Py), 8.51 (br t, J = 5.4, 2H, –CONH), 8.26 (dd, J = 7.7, 1.0, 2H, Py), 8.05 (m, *overlapping*, 4H, Py/Ph), 7.79 (s, 2H, tz), 7.59 (t, J = 7.8, 1H, Ph), 4.36 (d, J = 5.4 Hz, 4H, –CH_2–), 3.86 (s, 6H, –CO_2CH_3). ESI-MS m/z 629 (M + H^+), HR ESI-MS found 629.1282 $C_{30}H_{25}N_6O_6S_2$ requires 629.1272 (error = 1.74 ppm).

Synthesis of L^3. This compound was prepared in an identical manner to **L^1**, except **4c** was used instead of **4a** and the resulting ligand purified by column chromatography (Al_2O_3 1% MeOH in DCM). Yield = 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.63 (t, J = 1.0, 1H, Ph), 8.59 (br d, J = 8.9, 2H, –CONH), 8.54 (dd, J = 7.8, 1.0, 2H, Ph), 8.24 (dd, J = 7.6, 1.0, 2H, Py), 8.05 (t, J = 7.6, 2H, Py), 8.04 (dd, J = 7.6, 1.0, 2H, Py), 7.78 (s, 2H, tz), 7.60 (t, J = 7.8, 1H, Ph), 4.78 (dd, J = 8.9, 4.7, 2H, –NHCH), 3.83 (s, 6H, –CO_2CH_3), 2.41 (m, 2H, –CH$(CH_3)_2$), 1.11 (d, J = 1.6, 6H, –CH(CH_3)$_2$), 1.09 (d, J = 1.5 Hz, 6H, –CH(CH_3)$_2$). ESI-MS m/z 735 (M + Na^+), HR ESI-MS found 735.2027 $C_{36}H_{36}N_6NaO_6S_2$ requires 735.2030 (error = 0.39 ppm).

Synthesis of L^4. This compound was prepared in an identical manner to **L^1**, except **4d** was used instead of **4a**. Yield = 67%. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.62 (t, J = 1.6, 1H, Ph), 8.53 (dd, J = 7.8, 1.0, 2H, Py), 8.47 (br d, J = 8.0, 2H, –CONH), 8.23 (dd, J = 7.8, 1.0, 2H, Py), 8.05 (t, J = 7.8, 2H, Py), 8.04 (dd, J = 7.7, 1.6, 2H, Ph), 7.78 (s, 2H, tz), 7.59 (t, J = 7.7, 1H, Ph), 7.38–7.29 (m, overlapping, 10H, Ph), 5.09 (dt, J = 8.0, 5.9, 2H, –CHCH$_2$Ph), 3.80 (s, 6H, –CO_2CH_3), 3.32 (d, J = 5.9 Hz, 4H, –CH_2Ph). ESI-MS m/z 831 (M + Na^+), HR ESI-MS found 831.2029 $C_{44}H_{36}N_6NaO_6S_2$ requires 831.2030 (error = 0.10 ppm).

Synthesis of [Zn$_5$(L^1)$_5$](CF$_3$SO$_3$)$_{10}$. To a suspension of **L^1** (0.05 g, 0.08 mmol) in MeCN (1 ml) was added Zn(CF_3SO_3)$_2$ (0.03 g, 0.08 mmol) and the suspension sonicated until all the ligand had dissolved. Ethyl acetate was then slowly allowed to diffuse into the solution giving colourless crystals, which were filtered and dried under vacuum (0.04 g, 50%). NMR and mass spectroscopy data are discussed in the text. Found: C, 42.9; H, 3.7; N, 12.2%. Calculated for $C_{170}H_{160}N_{30}F_{30}O_{40}S_{20}Zn_5$: C, 42.5; H, 3.4; N, 11.9%. All the other circular helicates using ligands **L^2–L^4** were synthesised in an identical manner. [Zn$_5$(L^2)$_5$](CF$_3$SO$_3$)$_{10}$ (yield = 45%) Found: C, 39.3; H, 2.7; N, 11.9%. Calculated for $C_{160}H_{120}N_{30}O_{60}S_{20}F_{30}Zn_5$: C, 38.7; H, 2.4; N, 11.5%. [Zn$_5$(L^3)$_5$](CF$_3$SO$_3$)$_{10}$ (yield = 50%) Found: C, 42.6; H, 3.8; N, 7.4%. Calculated for $C_{190}H_{180}N_{30}O_{60}S_{20}F_{30}Zn_5$: C, 42.4; H, 3.4; N, 7.8%. [Zn$_5$(L^4)$_5$](CF$_3$SO$_3$)$_{10}$ (yield = 55%) Found: C, 47.5; H, 3.2; N, 10.1%. Calculated for $C_{230}H_{180}N_{30}O_{60}S_{20}F_{30}Zn_5$: C, 47.1; H, 3.1; N, 9.7%.

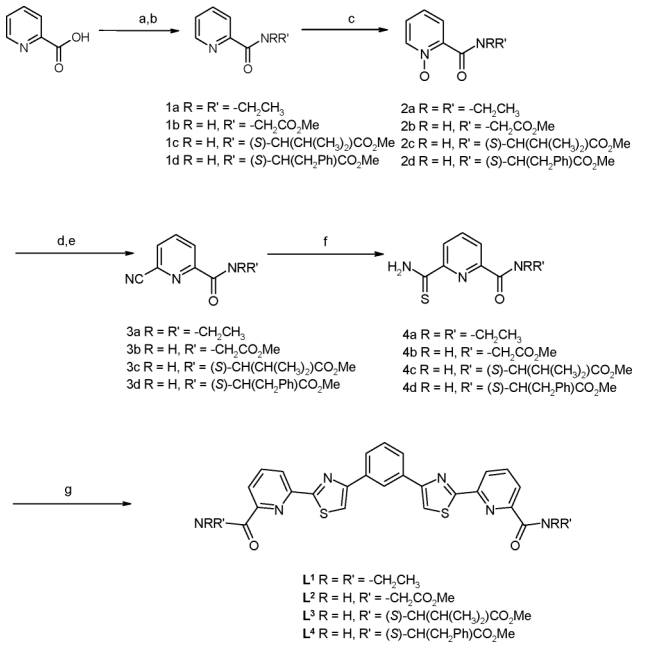
Results and discussion

Ligand synthesis

Ligands **L^1–L^4** were all synthesised in an analogous fashion as outlined in Scheme 1. Activation of picolinic acid with oxalyl chloride and reaction with either diethylamine or an amino acid ester gave the amides **1a–d** and reaction with mCPBA gave the corresponding N-oxides **2a–d**. Methylation with dimethyl sulphate and reaction with sodium cyanide gave the 6-cyanopicolinamide species **3a–d**. Reaction with hydrogen sulphide then gave the thioamides **4a–d** which after reaction with 1,3-di(α-bromoacetyl)benzene gave the potentially hexadentate ligands **L^1–L^4**. In all cases the ligands and their precursors were characterized by ^{1}H NMR, ESI-MS and HR ESI-MS.

Coordination chemistry

Reaction of **L^1** with Zn(CF_3SO_3)$_2$ in MeCN gave a colourless solution from which were deposited colourless crystals upon slow diffusion of ethyl acetate. Analysis by ESI-MS gave an ion at m/z 2251 corresponding to $\{[Zn_5(L^1)_5](CF_3SO_3)_8\}^{2+}$, also present were ions at m/z 2731 and 1771 corresponding to $\{[Zn_3(L^1)_3](CF_3SO_3)_5\}^+$ and $\{[Zn_4(L^1)_4](CF_3SO_3)_6\}^{2+}$ respectively. Peaks corresponding to smaller di-/mononuclear species were also present but these are likely due to fragmentation of the parent pentanuclear species, as has been reported previously.[13] Conformation of the formation of the $[Zn_5(L^1)_5]^{10+}$ pentanuclear species was obtained by X-ray analysis (Fig. 2). In the solid state



Scheme 1 Synthesis of ligands $\mathbf{L^1}$–$\mathbf{L^4}$. Reagents and conditions a) $C_2O_2Cl_2$, Et_3N, DCM 0 °C; b) RR′NH, Et_3N, DCM, RT; c) *m*CPBA, DCM, RT; d) $(MeO)_2SO_2$, 60 °C; e) $NaHCO_3$, NaCN, H_2O RT; f) H_2S, Et_3N, EtOH, RT; g) 3-di(α-bromoacetyl)benzene, EtOH, reflux.

the ligand partitions into two tridentate donor units separated by the 1,3-phenylene unit. All five Zn^{2+} ions are six-coordinate, arising from the coordination of two tridentate *N*,*N*,*O*-donor units (Zn–N: 2.028(7)–2.262(7) Å; Zn–O 2.105(6)–2.203(6) 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.

The one-dimensional ^{1}H NMR spectrum of a CD_3NO_2 solution of $[Zn_5(\mathbf{L^1})_5](CF_3SO_3)_{10}$ shows the expected 9 resonances for a complex of D_5 symmetry (Fig. 3a). Of the seven aromatic signals, four corresponding to the pyridyl and thiazole protons are present between 7.0 and 8.4 ppm. The three protons on the bridging phenylene unit, however, resonate at much lower frequency (7.0–5.8 ppm). This has been observed previously in related circular helicates and it is attributed to the close proximity of the central phenylene rings to the pyridyl-thiazole domains (average centroid $\cdots$ centroid distance of 3.87 Å). The phenylene protons in $[Zn_5(\mathbf{L^1})_5]^{10+}$ are thus exposed to the shielding ring currents produced by the aromatic heterocycles on adjacent ligand strands, hence the unusually low chemical shifts. Indeed, this phenomenon is a useful diagnostic tool for the confirmation of helical wrapping in both linear and circular helicates.

Having established that the $\mathbf{L^1}$ ligand system gives rise to circular helicates, we decided to incorporate peripheral amino acid esters in attempt to control the *enantio*-selectivity of the chiral helicate assembly. Reaction of the glycine-containing ligand $\mathbf{L^2}$ with $Zn(CF_3SO_3)_2$ in CD_3NO_2 gave a colourless solution for which the ESI-MS showed a signal at *m*/*z* 2330 corresponding to $\{[Zn_5(\mathbf{L^1})_5](CF_3SO_3)_8\}^{2+}$. The ^{1}H NMR spectrum showed a total of seven aromatic signals, two aliphatic signals and a signal corresponding to the amide –NH (Fig. 3b). Again, the most informative signals are those due to the central phenylene spacer,

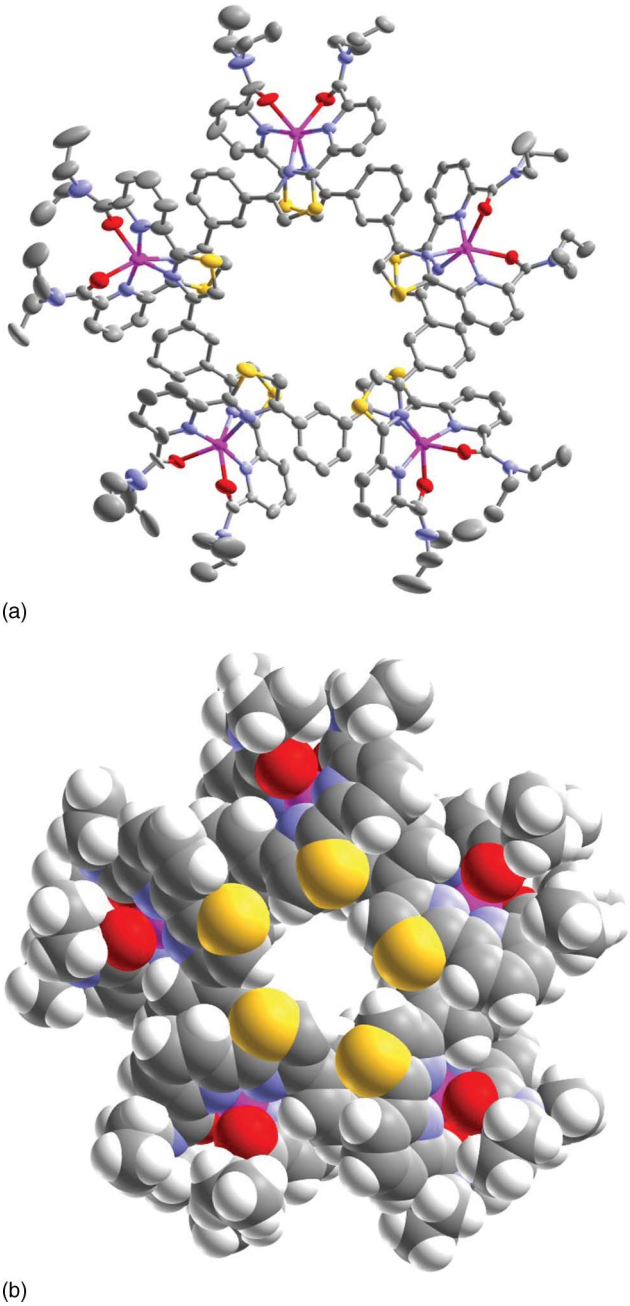


Fig. 2 (a) X-ray crystal structure of the complex cation $[Zn_5(\mathbf{L^1})_5]^{10+}$. Ellipsoids are shown at a 30% probability level. (b) Space-filling picture of $[Zn_5(\mathbf{L^1})_5]^{10+}$ showing atoms with their van der Waals radii.

which are between 7.0–6.0 ppm, confirming the formation of a helical structure. Indeed, the spectrum is remarkably similar to $[Zn_5(\mathbf{L^1})_5](CF_3SO_3)_{10}$ and this, coupled with the ESI-MS results, indicates that the glycine derivative forms an analogous pentanuclear species $[Zn_5(\mathbf{L^2})_5](CF_3SO_3)_{10}$. The presence of the broad triplet at 9.4 ppm corresponding to the amide –NH suggests that the ligand has not deprotonated, as is sometimes observed with coordination of primary amides to metal ions.

Ligands $\mathbf{L^3}$ and $\mathbf{L^4}$ feature the same ligand scaffold of $\mathbf{L^1}$, but the terminal amide groups have been functionalized with enantiopure valine and phenylalanine units, respectively. Reaction with $Zn(CF_3SO_3)_2$ in MeCN gives, in each case, a

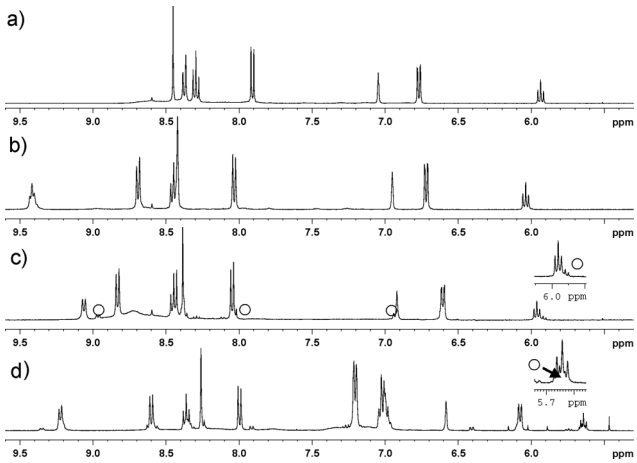


Fig. 3 Aromatic region of the ^{1}H-NMR spectra of a) $[Zn_5(\mathbf{L}^1)_5]^{10+}$ (CD_3NO_2), b) $Zn_5(\mathbf{L}^2)_5]^{10+}$($CD_3NO_2$), c) $Zn_5(\mathbf{L}^3)_5]^{10+}$($CD_3NO_2$), and d) $Zn_5(\mathbf{L}^4)_5]^{10+}$ (CD_3CN): ○ = selected peaks corresponding to the minor diastereoisomer.

colourless solution for which ESI-MS shows peaks for the usual adducts of the corresponding pentanuclear complex cations (*e.g.* *m/z* 2541 for $\{[Zn_5(\mathbf{L}^3)_5](CF_3SO_3)_8\}^{2+}$ and *m/z* 2781 for $\{[Zn_5(\mathbf{L}^4)_5](CF_3SO_3)_8\}^{2+}$). The main features in the ^{1}H NMR spectra (Fig. 3c,d) are likewise consistent with the formation of pentanuclear circular helicates, with the characteristic phenylene protons appearing at significantly lower frequency than the other aromatic protons. In both cases, however, a subset of low-intensity peaks is also observed. It is unlikely that these signals correspond to different nuclearity species, *e.g.* $[M_6L_6]^{12+}$ or $[M_4L_4]^{8+}$, as signals for these generally appear at substantially different frequencies ($\Delta\delta > 0.2$ ppm). They can therefore be assigned with confidence to the corresponding minor diastereoisomers.[15] Integration of the two sets of peaks for $[Zn_5(\mathbf{L}^3)_5]^{10+}$ suggests that the two diastereoisomers are present in a *ca.* 9 : 1 ratio. This demonstrates that the optically pure unit controls the self-assembly process and that one isomer is formed in *ca.* 80% d.e. For $[Zn_5(\mathbf{L}^4)_5]^{10+}$ the process is less selective with d.e. of ~ 70%.

The CD spectra of ligands $\mathbf{L}^3$ and the opposite diasteroisomer derived from D-valine $\mathbf{L}^5$ (Fig. 4a)[16] shows a very weak, equal and opposite bi-signate Cotton effect relating to the higher energy π–π* transitions. These probably arise from a degree of exciton coupling between the two halves of the ligand. On the introduction of Zn^{2+} to the solution, there is a considerable change to the observed CD spectrum (Fig. 4b), with the growth of a second signal around 355 nm, although the intensity of the signals does not dramatically increase, as had initially been anticipated. Similarly, the UV/vis absorption spectrum also shows a considerable change with the large absorption at 264 nm reducing in intensity and significantly broadening. This is an indication of a strong exciton coupling assuming the complex is adopting a similar configuration to that demonstrated in the solid-state structure of $[Zn_5(\mathbf{L}^1)_5]^{10+}$.[16]

In principle it should be possible to tentatively assign an overall sense of handedness to the dominant isomer using an exciton theoretical analysis.[17] The 330 nm absorption is assumed to relate to the π–π* transitions of the pyridyl-thiazole group. The complex derived from $\mathbf{L}^3$ demonstrates a negative signal at the lowest energy transitions in the CD spectrum in this region. Assuming a similar structure is adopted to that of ligand $\mathbf{L}^1$,

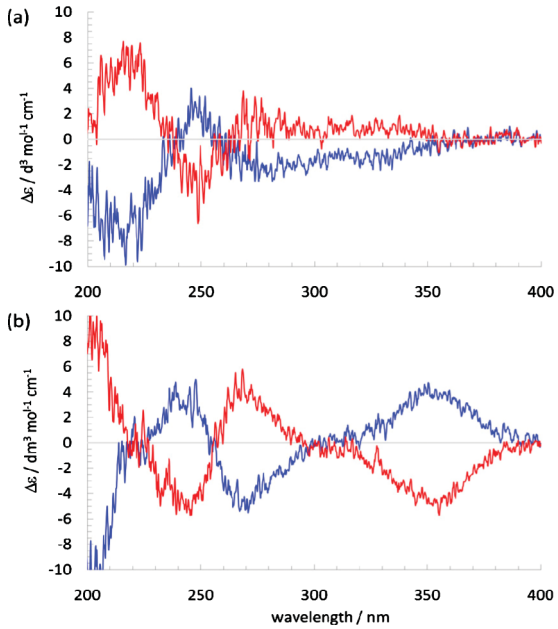


Fig. 4 The CD spectra of (a) ligands $\mathbf{L}^3$ (red) and $\mathbf{L}^5$ (blue) and (b) the resulting complexes on the addition of one equivalent of Zn^{2+} in acetonitrile at 298 K at a concentration of 2.5×10^{-5} mol dm^{-3}.

with a dihedral angle between the two chromophores of 70.8°, and the two chromophores at an angle of 59.8° relative to the perpendicular between them, then the resulting dominant complex can tentatively be assigned as having a Δ metal centred configuration, and an overall M helicity as shown in Fig. 2b. However extreme caution should be placed on this assignment given that the metal centred exciton couplings will invariably be cancelled out by additional couplings in the structure as previously reported by Telfer and co-workers.[18] In this particular case, it is observed in the structural analysis of $[Zn_5\mathbf{L}^1{}_5]^{10+}$ that inter-ligand phenyl-thiazole contacts possess the opposite sense of handedness with a separation of only 4.0 to 5.0 Å, whilst the metal centred chromophores are longer (4.5–5.5 Å). Given that the strength of the observed exciton coupling being related by an inverse r^3 relationship these interactions can not be ignored,[16] with the possibility that these conflicting bis-ignate interactions could account for the surprisingly low observed Cotton effect, and could even lead to the mis-assignment of the overall helicity.

Conclusion

We have shown that a ligand which contains both N-donor and O-donor domains and a 1,3-phenylene spacer unit forms pentanuclear circular helicates upon reaction with Zn^{2+} ions and this structure persists in both the solid and solution state. The formation of this high nuclearity species is governed by unfavourable steric interactions between the phenyl units which destabilize the similar linear helicate. Incorporation of enantiopure units within the ligand strand controls the diastereoselectivity with up to 80% d.e.

Notes and references

1 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, John Wiley and Sons, Chichester, 2000.

2 M. J. Hannon and L. J. Childs, *Supramol. Chem.*, 2004, 167.
3 M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; M. Albrecht, *Chem. Soc. Rev.*, 1998, **27**, 281.
4 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
5 E. C. Constable, in *Comprehensive Supramolecular Chemistry*, vol. 9; Polynuclear Transition Metal Helicates, ed J.-P. Sauvage, Elsevier, Oxford, 1996, pp. 213.
6 For examples of metallo-helicates see: S. P. Argent, H. Adams, L. P. Harding, T. Riis-Johannessen, J. C. Jeffery and M. D. Ward, *New J. Chem.*, 2005, 904; Q. Z. Sun, Y. Bai, G. J. He, C. Y. Duan, Z. H. Lin and Q. J. Meng, *Chem. Commun.*, 2006, 2777; M. Cantuel, F. Gumy, J. C. G. Bunzli and C. Piguet, *Dalton Trans.*, 2006, 2647; M. Hutin, R. Frantz and J. R. Nitschke, *Chem.–Eur. J.*, 2006, 4077.
7 C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *Chem. Commun.*, 2000, 1529; C. R. Rice, S. Wörl, J. C. Jeffery, R. L. Paul and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2001, 550; C. R. Rice, C. J. Baylies, J. C. Jeffery, R. L. Paul and M. D. Ward, *Inorg. Chim. Acta*, 2001, **324**, 331.
8 B. Hasenknopf, J-M. Lehn, N. Boumediene, E. Leize and A. Van Dorsselaer, *Angew. Chem., Int. Ed.*, 1998, **37**, 3265; B. Hasenknopf, J-M. Lehn, N. Boumediene, A. Dupont-Gervais, A. Van Dorsselaer, B. Kneisel and D. Fenske, *J. Am. Chem. Soc.*, 1997, **119**, 10956.
9 S. P. Argent, H. Adams, T. Riis-Johannessen, J. C. Jeffery, L. P. Harding, O. Mamula and M. D. Ward, *Inorg. Chem.*, 2006, **45**, 3905.
10 J. Hamblin, F. Tuna, S. Bunce, L. J. Childs, A. Jackson, W. Errington, N. W. Alcock, H. Nierengarten, A. V. Dorsselaer, E. Leize-Wagner and M. J. Hannon, *Chem.–Eur. J.*, 2007, **13**, 9286; Y. Pang, S. Cui, B. Li, J. Zhang, Y. Wang and H. Zhang, *Inorg. Chem.*, 2008, **47**, 10317.
11 L. J. Childs, M. Pascu, A. J. Clarke, N. W. Alcock and M. J. Hannon, *Chem.–Eur. J.*, 2004, **10**, 4291; L. J. Childs, N. W. Alcock and M. J. Hannon, *Angew. Chem., Int. Ed.*, 2002, **41**, 4244.
12 L. Bain, S. Bullock, L. P. Harding, T. Riis-Johannessen, G. Midgley, C. R. Rice and M. Whitehead, *Chem. Commun.*, 2010, **46**, 3496.
13 K. E. Allen, R. A. Faulkner, L. P. Harding, C. R. Rice, T. Riis-Johannessen, M. L. Voss and M. Whitehead, *Angew. Chem., Int. Ed.*, 2010, 6655.
14 O. Mamula, A. von Zelewsky and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1998, 289; O. Mamula, F. J. Monlien, A. Porquet, G. Hopfgartner, A. E. Merbach and A von Zelewsky, *Chem.–Eur. J.*, 2001, **7**, 533; O. Mamula, A. von Zelewsky, P. Brodard, C. W. Schlapfer, G. Bernardinelli and H. Stoeckli-Evans, *Chem.–Eur. J.*, 2005, **11**, 3049.
15 We have found that the chemical shift of the central phenylene unit is very susceptible to a change in the nuclearity of the circular helicate and lower nuclearity species (*e.g.* $[M_4L_4]^{8+}$ compared with $[M_5L_5]^{10+}$) tend to have a higher chemical shift compared to the pentanuclear species; the difference in chemical shift is also quite pronounced (>0.3 ppm), C.R. Rice, *unpublished results*.
16 The (*R*,*R*)-enantiomer of $\mathbf{L^3}$ (giving $\mathbf{L^5}$) was prepared in an identical manner to the (*S*,*S*)-enantiomer of $\mathbf{L^3}$ apart from D-valine was used in the initial synthetic procedure. To all intents and purposes the NMR, ESI-MS data and yields of $\mathbf{L^5}$ were identical to that of $\mathbf{L^3}$.
17 M. Ziegler and A. von Zelewsky, *Coord. Chem. Rev.*, 1998, **177**, 257–300; S. G. Telfer, T. M. McLean and M. R. Waterland, *Dalton Trans.*, 2011, **40**, 3097.
18 S. G. Telfer, N. Tajima and R. R. Kuroda, *J. Am. Chem. Soc.*, 2004, **126**, 1408–1418.