

Using Chiral Ligand Substituents To Promote the Formation of Dinuclear, Double-Stranded Iron, Manganese, and Zinc Mesocates

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Keywords: Ligand design / Helical structures / Ligand effects / Supramolecular chemistry / Chirality

The synthesis and structures of dinuclear manganese, iron, and zinc complexes of chiral di-iminodipyrromethane ligands (L) are reported. Schiff base condensation reactions between 5,5'-diformyl-2,2'-dipyrromethane and the chiral amines (–)-(R)-CH(Me)*t*Bu and (+)-(R)-CH(Me)Ph result in the straightforward synthesis of the new, chiral ligands H₂L² and H₂L³, respectively. Salt elimination reactions between K₂L and divalent Mn and Fe halides, and protonolysis reactions be-

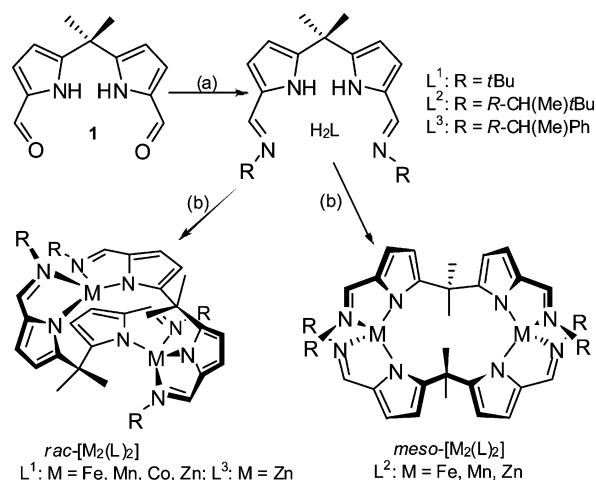
tween ZnMe₂ and H₂L result in the formation of the new dinuclear complexes [M₂(L)₂]. Investigation of the structures of these compounds in solution and in the solid state reveal that chiral mesocates are formed for L = L², whereas for L = L³, a racemic mixture of helicates is present.

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Introduction

Dinuclear metallohelicates are often viewed as the simplest and most fundamental of chiral supramolecular architectures.^[1] The clockwise (*P*) or counter-clockwise (*M*) helical rotation intrinsic to these compounds is inherited from the homochiral mechanical coupling of Δ or Λ chiral metal centres,^[2] i.e. ΔΔ or ΛΛ configurations, respectively, while heterochiral coupling (ΔΛ) results in the assembly of the achiral mesocate or box diastereomer. The significance of chirality throughout the natural and physical sciences has prompted increased efforts in supramolecular chemistry to develop simple methodologies that discriminate between the formation of helicate and mesocate diastereomers, and, ultimately, between (*M*) and (*P*) enantiomers of metallohelicates. Racemic mixtures of metallohelicates can be separated by fractional crystallisation or by chromatographic techniques,^[3] but a second chiral entity, such as a chiral anion or other templating agents,^[4] and/or chiral ligands,^[5–7] are necessary to direct the selective synthesis of single enantiomer helicates. The preferential, and diastereoselective, synthesis of mesocates instead of helicates appears controlled by a variety of factors, such as the modification (chiral or not) of the spacer unit between the two donor compartments,^[8–10] the variation of the metal,^[11–13] and the incorporation of a guest molecule.^[14]

We identified previously the donor-extended dipyrromethane H₂L¹ (Scheme 1) as a ligand that is suitable for use in the synthesis of neutral, dinuclear metallohelicates due to the rigidity of the iminopyrrole chelates, the preference of iminopyrrole to pyrrole–pyrrole chelation in the potassium salt of the *meso*-CPh₂ analogue, {K₂[*t*BuN=CH-(C₄H₂N)₂CPh₂]}^[15] and the presence of the sp³-hybridized hinge group between the two donor compartments. Indeed, divalent Mn, Fe, Co and Zn transition metal complexes of L¹ are isolated as the unusually volatile, double-stranded, dinuclear helicates [M₂(L¹)₂] which are isostructural and display distinctive cleft motifs as a result of offset face-to-face π-stacking interactions between iminopyrrole groups



Scheme 1. Synthesis of the dinuclear, double-stranded, helicates and mesocates, [M₂(L)₂]. Reagents and conditions: (a) L²: (R)-[*t*Bu(Me)HC]NH₂, K₂CO₃, EtOH; L³: (R)-[Ph(Me)HC]NH₂, *p*-C₆H₄MeSO₃H, MeOH, (b) M = Mn, Fe, Co: (i) KH, THF, (ii) MX₂, THF, M = Zn: ZnMe₂, toluene, Δ.

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of opposing ligand strands; this interaction is observed both in the solid state and in solution at low temperature.^[16,17] Herein, we demonstrate that the introduction of chiral imine substituents, derived from chiral primary amines, to these ligands can result in the diastereoselective formation of unusual chiral mesocates,^[10] and not the expected enantiopure helicates.

Results and Discussion

Synthesis of $[M_2(L)_2]$ Complexes

We have shown previously that the Schiff base condensation reaction between the dialdehyde **1** and *t*BuNH₂ in the presence of K₂CO₃ results in the formation of the imine-functionalised dipyrromethane ligand H₂L¹ in good yield.^[16] By using a similar synthetic protocol, the new, chiral ligand H₂L² [R = (*R*)-CH(Me)*t*Bu] was prepared in good yield (Scheme 1), and was isolated as a volatile, yellow oil that was best purified by vacuum sublimation at 130 °C/10^{−2} mbar. While the synthesis of H₂L³ [R = (*R*)-CH(Me)-Ph] according to this route proved problematic, Schiff base formation was found to be assisted by the addition of a catalytic amount of *p*-toluenesulfonic acid; H₂L³ was isolated as a very viscous orange oil from hot hexanes. The conversion of the dialdehyde **1** into the Schiff base ligands H₂L is supported by the appearance of characteristic imine resonances at δ = 7.76 and 7.78 ppm in the ¹H NMR spectra of H₂L² and H₂L³, respectively, coupled with the loss of the aldehyde proton resonance at δ = 9.29 ppm in **1**.

The salt elimination reactions between K₂L², prepared in situ by the reaction between H₂L² and KH in THF, and MnCl₂ and FeBr₂ were carried out, and resulted in the respective formation of yellow [Mn₂(L²)₂] and orange [Fe₂(L²)₂] as crystalline solids in moderate isolated yields.

The 1:1 metal/ligand ratios were supported by elemental analysis, and the formulation of these complexes as dinuclear by electron-impact mass spectrometry (EIMS), in which the molecular ion of [Mn₂(L²)₂] was observed at m/z (%) = 898 (14) [M⁺], and that for [Fe₂(L²)₂] at m/z (%) = 900 (21) [M⁺]. The solution magnetic susceptibilities were determined using Evans' method and found to be μ_{eff} = 8.06 and 7.28 μ_B for the Mn and Fe complexes, respectively. These data support the presence of two, spin-isolated tetrahedral Mn ($S = 5/2$, $\mu_{\text{calcd.}}$ = 8.37 μ_B) and Fe ($S = 2$, $\mu_{\text{calcd.}}$ = 6.93 μ_B) paramagnets; these magnetic moments are similar to those observed for the related helicate complexes [Mn₂(L¹)₂] and [Fe₂(L¹)₂], and suggest that neither direct M–M bonding nor magnetic superexchange pathways are present to enable spin coupling.^[16] The protonolysis reaction between ZnMe₂ and H₂L² in toluene formed the dinuclear zinc complex [Zn₂(L²)₂] in good yield. As with the Mn₂ and Fe₂ complexes above, the 1:1 metal/ligand ratio was supported by elemental analysis, although in this case the complex was found to be solvated by dichloromethane, and EIMS displayed a molecular ion at m/z (%) = 918 (8) [M⁺].

Solid-State Structures of $[M_2(L^2)_2]$

An X-ray crystallographic study on single crystals of the Mn, Fe, and Zn complexes was undertaken in order to determine their structures in the solid state. The [M₂(L²)₂] complexes were found to have similar structures, with the Mn and Fe compounds isomorphous, and, surprisingly, were not the expected helicates, but were instead dinuclear, double-stranded mesocates that result from opposing $\Delta\Lambda$ configurations at the metal atoms. The solid-state structure of *meso*-[Zn₂(L²)₂] is shown in Figure 1 as ORTEP and space-filled diagrams, with the space-filled structure of the

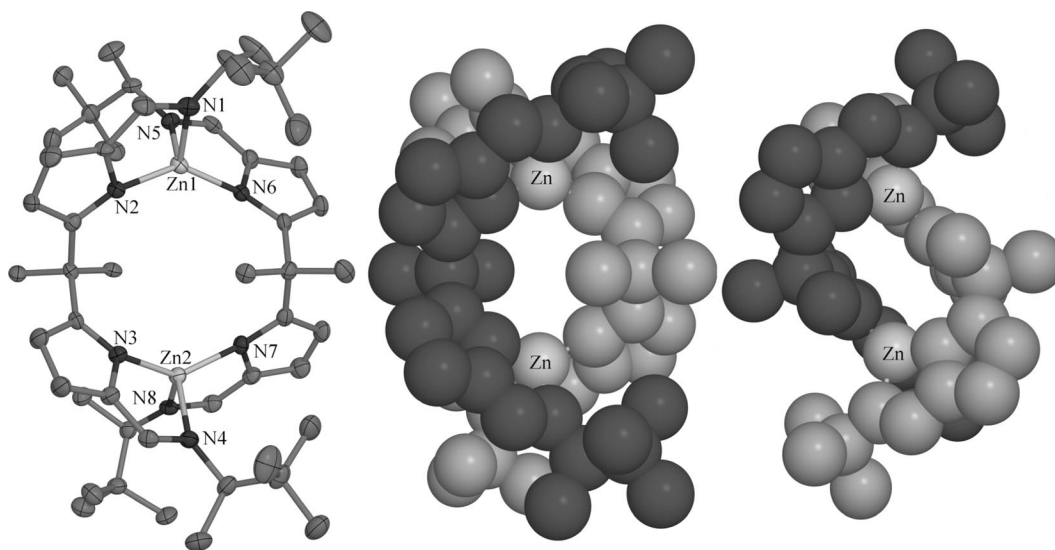


Figure 1. Solid-state structure of the mesocate [Zn₂(L²)₂] (left). For clarity, only one molecule from the asymmetric unit is shown, all hydrogen atoms are omitted, and thermal displacement ellipsoids are drawn at 50% probability; space-filled diagrams of *meso*-[Zn₂(L²)₂] (centre) and *rac*-[Zn₂(L¹)₂] (right) are included for comparison.

helicate analogue, *rac*-[Zn₂(L¹)₂], included for visual comparison; selected bond lengths and angles are described in Table 1 and crystal data in Table 2.

Table 1. Selected bond lengths [Å] and angles [°] of *meso*-[M₂(L²)₂] complexes, M = Mn, Fe, Zn.

	M = Mn	M = Fe	M = Zn
M–M	5.32	5.29	5.39
M1–N1	2.199(4)	2.096(6)	2.090(4)
M1–N2	2.067(4)	2.024(6)	1.984(4)
M1–N5	2.167(4)	2.134(6)	2.080(4)
M1–N6	2.082(4)	2.005(6)	1.973(4)
N1–M1–N2	82.79(15)	84.8(3)	85.02(16)
N1–M1–N5	102.78(16)	102.1(2)	103.05(15)
N1–M1–N6	119.81(14)	117.9(3)	120.64(16)
N2–M1–N5	120.20(16)	117.8(2)	119.53(16)
N2–M1–N6	145.31(14)	144.6(2)	140.38(16)
N5–M1–N6	82.50(15)	85.4(2)	85.84(16)

In each structure, the metal atoms adopt distorted tetrahedral geometries with exceptionally obtuse angles (>140°) towards the intrametallic cavity of the mesocate, as defined by N2–M1–N6. These angles contrast to those observed for other dinuclear mesocates which are generally more acute, for example, the (diphenylmethane-linked iminopyridyl)dicopper complex, [Cu₂{CH₂(*p*-C₆H₄N=CH-*o*-C₅H₄N)₂}₂], displays an N–Cu–N angle of 134.65(16)°,^[13] and similarly, the internal N–Zn–N angle in the dizinc mesocate [Zn₂{(-CH₂N=CH-*o*-C₆H₄NSO₂C₆H₄Me-*p*)₂}₂] measures 110.0(5)°; in this latter complex, however, there does exist a larger angle *exo* to the molecular cleft of 134.2(4)°.^[12] The internal angles in the *meso*-[M₂(L²)₂] complexes are also significantly more obtuse than those of the corresponding helicates, *rac*-[M₂(L¹)₂]: 136.59(9)° (M = Mn), 137.35(9)° (Fe), 132.08(11)° (Zn). The M–N(pyrrole) and M–N(imine) bond lengths in the *meso*-[M₂(L²)₂] complexes are similar to those in *rac*-[M₂(L¹)₂], and are consistent with the transition metals in their divalent oxidation states. The intrametallic M···M separations in *meso*-[M₂(L²)₂] (5.3–5.4 Å) are

significantly longer than those observed for the *rac*-[M₂(L¹)₂] complexes: 4.75 Å (M = Mn), 4.69 Å (Fe), 4.69 Å (Zn), and this lack of metal–metal bonding supports the above magnetochemical analysis.

Solution Structures

The possible presence of both helicate and mesocate diastereomers in solution was assessed using ¹H NMR spectroscopy. It was reasoned that the addition of chiral imine substituents located at the termini of the ligand would have no effect on the *D*₂ symmetry of the helicate, whereas that of the mesocate diastereomer would reduce from *C*_{2h} to *C*₂ (Figure 2).

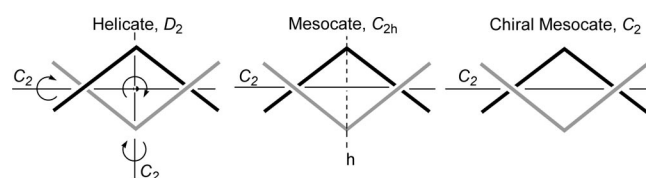


Figure 2. Effect of chiral ligand substituents on the symmetries of *rac*- and *meso*-[M₂(L²)₂].

The ¹H NMR spectrum of [Fe₂(L²)₂] showed clean, paramagnetically shifted resonances that could be tentatively assigned by integration to the majority of the ligand protons, and was possibly indicative of a reduction in symmetry. However, the ¹H NMR spectrum of [Zn₂(L²)₂], recorded in C₆D₆ (Figure 3), was more informative, and can be assigned to either a 50:50 mixture of diastereomers of the *rac*-helicate, i.e. (*R**,*R**)-(*M*)-[Zn₂(L²)₂] and (*R**,*R**)-(*P*)-[Zn₂(L²)₂], or the chiral mesocate (*R**,*R**)-*meso*-[Zn₂(L²)₂] as two sets of resonances are observed for each ligand proton environment. To differentiate between these two possibilities, ¹H NMR NOE spectra were recorded (Figure 3), and show that irradiation of the single *meso*-methyl resonance at δ =

Table 2. Crystallographic data for the complexes *meso*-[M₂(L²)₂] (M = Mn, Fe, Zn).

	[Mn ₂ (L ²) ₂]·0.75(hexane)	[Fe ₂ (L ²) ₂]·0.5(hexane)	[Zn ₂ (L ²) ₂]
Empirical formula	C _{54.5} H _{86.5} Mn ₂ N ₈	C ₅₃ H ₈₃ Fe ₂ N ₈	C ₅₀ H ₇₆ N ₈ Zn ₂
<i>M_r</i>	963.70	943.97	919.42
Cell setting, space group	monoclinic, <i>P</i> ₂ ₁	monoclinic, <i>P</i> ₂ ₁	monoclinic, <i>P</i> ₂ ₁
<i>a</i> [Å]	12.651(2)	12.6987(15)	13.9099(21)
<i>b</i> [Å]	18.971(3)	18.764(2)	20.317(3)
<i>c</i> [Å]	13.773(2)	13.680(2)	18.746(3)
β [°]	107.297(3)	106.080(2)	111.249(2)
<i>V</i> [Å ³]	3156(2)	3132.1(11)	4937.5(7)
<i>Z</i>	2	2	4
<i>D_x</i> [Mg m ⁻³]	1.014	1.001	1.237
μ [mm ⁻¹]	0.436	0.498	1.013
<i>T</i> _{min} , <i>T</i> _{max}	0.552, 1.000	0.787, 1.00	0.82, 1.000
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0702	0.0819	0.0529
<i>wR</i> (<i>F</i> ²)	0.1968	0.2310	0.1283
<i>S</i>	1.028	1.056	0.990
Δρ _{max} , Δρ _{min} [e Å ⁻³]	0.665, −0.404	1.037, −0.408	1.235, −0.538
Flack parameter	−0.03(2)	0.04(3)	0.010(9)
CCDC-	651323	651322	651321

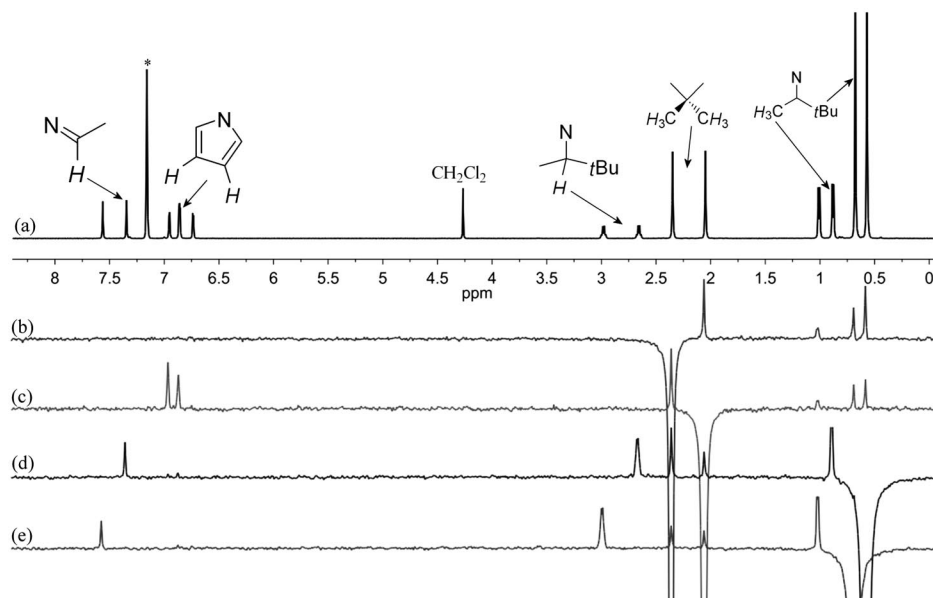


Figure 3. ^1H NMR NOE experiments for $[\text{Zn}_2(\text{L}^2)_2]$ in C_6D_6 (*) at 298 K: (a) full ^1H NMR spectrum; (b)/(c) irradiation of *meso*- CH_3 groups; (d)/(e) irradiation of terminal *t*Bu groups.

2.34 ppm results in positive NOE with the other *meso*-methyl resonance at $\delta = 2.04$ ppm, and vice versa. In the helicate, the *meso*-methyl protons are identical by symmetry, and no NOE would be expected between the two (R^*, R^*) -(*M*) and (R^*, R^*) -(*P*) diastereomers as they are magnetically and chemically different; hence, it is clear that the complex $[\text{Zn}_2(\text{L}^2)_2]$ is a mesocate in solution. This is further corroborated by the observation of positive NOEs for both *meso*-methyl protons on the irradiation of separate *tert*-butyl protons. In the solid state, the *meso*-methyl groups of $[\text{Zn}_2(\text{L}^2)_2]$ occupy non-equivalent positions inside (*endo*) and outside (*exo*) the intrametallic cleft. It is evident that this structure is also adopted in solution, as positive NOEs between the *meso*-methyl protons at $\delta = 2.04$ ppm and the pyrrolic protons at $\delta = 6.95$ and 6.86 ppm are observed, while no NOE between the other *meso*-methyl and the pyrrolic protons is seen, i.e. only the *meso*-methyl protons with resonance at $\delta = 2.04$ ppm have through-space proximity to the pyrrolic protons and so can be assigned as the *exo*-Me group.

Helicate Formation

The reaction between H_2L^3 and ZnMe_2 was carried out to further assess the effect of chiral imine substituents on mesocate and helicate formation, and resulted in the formation of the dinuclear complex $[\text{Zn}_2(\text{L}^3)_2]$ in good yield; ligand H_2L^3 incorporates (R) -CH(Me)Ph imine substituents that have the same absolute configuration as those in H_2L^2 . While we have been unable to determine the solid-state structure of $[\text{Zn}_2(\text{L}^3)_2]$ by single-crystal X-ray diffraction, the ^1H NMR spectrum of the crude material in C_6D_6 (Figure 4a) was recorded, and was found to be similar to that

of *meso*- $[\text{Zn}_2(\text{L}^2)_2]$ in which two pairs of resonances are observed for each ligand proton environment. However, it was noticed that the crude solid $[\text{Zn}_2(\text{L}^3)_2]$ was only partially soluble in Et_2O , and that after extraction with Et_2O , the ^1H NMR spectrum of the residual solids had changed (Figure 4b) to one in which the two sets of proton resonances were now of unequal intensity (5:1 integral ratio); elemental analysis of these solids supported the 1:1 metal/ligand ratio expected for a dinuclear complex. As such, and in contrast to the complexes of L^2 , it is clear that a racemic mixture of the two helical diastereomers, (R^*, R^*) -(*M*)- $[\text{Zn}_2(\text{L}^3)_2]$ and (R^*, R^*) -(*P*)- $[\text{Zn}_2(\text{L}^3)_2]$, has been formed, and that the two diastereomers can be partially separated by solvent extraction.

It is evident that upon elaboration of the ligand terminus, i.e. changing the imine substituent from *t*Bu to (R) -CH(Me)Ph to (R) -CH(Me)*t*Bu, there is a change in the gross structures of the dinuclear complexes, from double-stranded metallohelicates to mesocates, and that the effect of ligand variation is extremely subtle. Modifications to ligands that are capable of supporting helical structures have been shown previously to result in changes to the gross molecular structure. For example, variation of the stereocontrolling units between dicatecholates groups can result in the formation of triple-stranded mesocates in preference to helicates.^[7,8] In these systems, however, it is likely that host-guest solvate interactions are the primary factor in favouring helicate or mesocate structures.^[14] It has also been found that increasing the steric bulk from H to Et at the *ortho* positions of the phenyl spacers in double-stranded dicopper iminopyridine complexes promotes a helical twist at the methylene position, and so results in a change from a mixture of *meso* and *rac* diastereomers to purely *rac*-helicates. In the case of the above $[\text{M}_2(\text{L})_2]$ complexes, it is

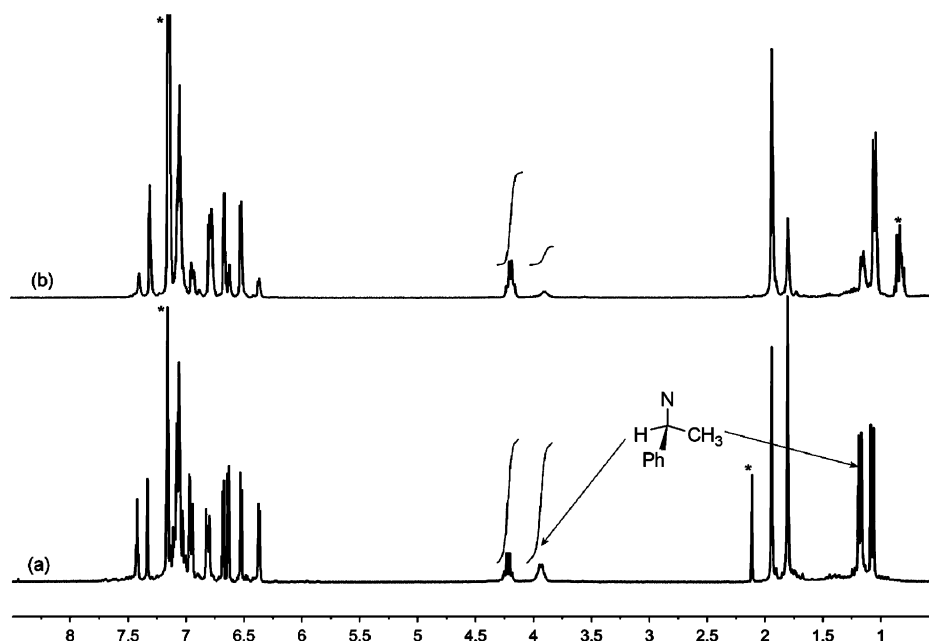


Figure 4. ^1H NMR spectra of (a) crude $[\text{Zn}_2(\text{L}^3)_2]$, and (b) Et_2O -washed $[\text{Zn}_2(\text{L}^3)_2]$, in C_6D_6 (* C_6D_6 , toluene and hexanes impurities).

unusual that the use of the chiral ligand substituent $\text{CH}(\text{Me})t\text{Bu}$ at the ligand terminus has resulted in a helicate to mesocate interconversion, as the addition of chiral terminal groups to the ligand usually results in the preferential formation of one helical enantiomer.^[5] Furthermore, to the best of our knowledge, there is only a single reported example of a chiral dinuclear mesocate, formed as a result of reaction between an enantiopure tetradentate binaphthoxy-diimine ligand and $\text{Cu}(\text{OAc})_2$.^[10] In this latter case, however, the formation of the chiral mesocate was found to depend on the length of the alkyl chain between the two N-O donor sets, with a shorter alkyl chain length resulting in the preferential formation of an enantiopure trinuclear circular helicate.

It is difficult to account for the favoured formation of the mesocate complexes over the helicates on addition of the bulky chiral imine substituent $\text{CH}(\text{Me})t\text{Bu}$. However, it is clear that this preference is metal-independent, as Mn, Fe, and Zn helicates are formed using L^1 , while only mesocates are formed with L^2 for the same metals. While it is possible that the salt elimination synthetic methodology could impart diastereoselectivity through host-guest or solvate interactions,^[14] this appears unlikely as helicates of L^1 are also formed using transamination routes in nonpolar solvents.^[16] To try to gain a better understanding of the factors behind the formation of helicates vs. mesocates, molecular-mechanics-based conformational analysis and geometry optimisations were carried out to determine the difference in energy between the helicate and mesocate structures of each of the three Fe complexes $[\text{Fe}_2(\text{L})_2]$, where $\text{L} = \text{L}^1, \text{L}^2$ and L^3 . The Fe complexes were chosen because of the availability of crystallographically determined helicate and mesocate Fe complex structures.^[16]

Molecular Mechanics Calculations

Energy differences between the helicate and mesocate structures for each of the Fe complexes were calculated using the Extensible and Systematic Force Field (ESFF) molecular mechanics method, which has been parameterized for all elements up to radon in the Periodic Table.^[18] The conformational space of the substituents was explored using dihedral angle driving calculations where rotation around the substituent(C)–imine(N) bond was carried out in 60° increments, followed by energy minimisation of all resulting conformations. The crystallographic structures of the helicate $[\text{Fe}_2(\text{L}^1)_2]$ and the mesocate $[\text{Fe}_2(\text{L}^2)_2]$ were used as templates for generating the required pairs of structures. Inspection of the crystal structures of the helicate $[\text{Fe}_2(\text{L}^1)_2]$ and the mesocate $[\text{Fe}_2(\text{L}^2)_2]$ indicated that the bond lengths in the pyrrole rings corresponded, as expected, to partial double bonds. The bond lengths of the imine moieties, and the adjoining bond to the pyrrole ring, were more akin to double and single bonds, respectively. These bond types were therefore used in the ESFF calculations, and atom types were assigned accordingly.

The lowest energy structures arising from the dihedral angle driving calculations were identified, and the energy differences between the mesocate and helicate structures determined. While the differences in global minimum energy obtained were small ($<10 \text{ kcal mol}^{-1}$) and insufficient to account for the observed differences in product distributions, it is notable that for L^1 ($\Delta E = 6.51 \text{ kcal mol}^{-1}$) and L^3 ($\Delta E = 4.75 \text{ kcal mol}^{-1}$), the helicate structure is of lower energy, whilst in the case of L^2 ($\Delta E = -1.26 \text{ kcal mol}^{-1}$) the mesocate structure is of lower energy; as such, these calculated energies correlate to the products observed experimentally.

Although only weak effects, it is therefore likely that the steric demand and relative conformation of the imine substituents are contributory factors towards the preferential formation of the helicate or mesocate structures.

Conclusions

In this work we have shown that the incorporation of the bulky chiral imine substituent (*R*)-CH(Me)*t*Bu at the termini of the tetradentate ligand H₂L² disrupts the expected formation of the dinuclear, double-stranded helicates [M₂(L)₂] to form preferentially the *meso* diastereomers [M₂(L²)₂]; use of the sterically less demanding (*R*)-CH(Me)-Ph substituent results in racemic mixtures of the diastereotopic helicates, [Zn₂(L³)₂]. The solid-state structures of the mesocates are retained in solution and can be differentiated from the helicates using ¹H NMR NOE spectroscopy. In the solid state, the M...M separations are considerably longer in the mesocate structures than those of the helicate analogues, and a more obtuse N–M–N angle is subtended towards the intrametallic cleft. This transformation from helicate to mesocate is independent of the metals employed, and provides straightforward methodology to charge-neutral, chiral mesocates. However, the fundamental reasons behind preferential mesocate formation remain unclear, as, while molecular mechanics calculations suggest that the steric influence of the imine-substituent is influential, there remains insufficient thermodynamic distinction between helicate and mesocate structures.

Experimental Section

General Remarks: Unless otherwise stated, all reactions were carried out using standard Schlenk techniques under nitrogen or argon or in a nitrogen-filled Vacuum Atmospheres OmniLab glovebox. Solvents were dried (hexanes, pentane, Et₂O and THF were passed through activated alumina towers;^[19] dichloromethane was distilled from CaH₂) and stored over molecular sieves (4 Å); all other solvents were used as purchased. Deuterated benzene was refluxed in the presence of K, vacuum-distilled, and freeze-pump-thaw-degassed three times. The dipyrromethane Me₂C(C₄H₄N)₂,^[20] and the dialdehyde synthon 5,5'-CHO-Me₂C(C₄H₄N)₂ (**1**)^[15] were prepared according to literature procedures. MnCl₂·4H₂O was dried according to literature methods.^[21] The ¹H NMR and ¹³C{H} NMR spectra were recorded with a Bruker DPX-300 spectrometer operating at 300.13 and 75.47 MHz, respectively; residual protiosolvent served as an internal reference for the former. Combustion analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University and EIMS by Dr. Ali Abdul-Sada of the University of Sussex.

Crystallography. General Methods and Solution and Refinement Details: Single-crystal diffraction data were collected using graphite-monochromated Mo-*K*_α X-radiation with either a Bruker SMART1000 {[Fe₂(L²)₂] or SMART APEX {[Mn₂(L²)₂], [Zn₂(L²)₂] CCD area detector diffractometer equipped with an Oxford Cryostream cooling device. All data were collected at 150 K. Details of the individual data collections and refinements are given in Table 2. Structures were solved with SHELXS-97 using heavy-atom methods for [Mn₂(L²)₂] and direct methods for [Fe₂(L²)₂] and

[Zn₂(L²)₂]. All structures were refined by least-squares full-matrix refinement against *F*² using SHELXL-97,^[22] and all fully occupied non-H atoms refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed and refined as part of a riding model. [Mn₂(L²)₂] showed disorder in the two chiral C(Me)*t*Bu groups C20 and C26 which were modelled over two sites with occupancies 0.60 and 0.40 in both cases. C45 was modelled over two sites with occupancies 0.60 and 0.40. Geometric and rigid-bond restraints were applied in all cases, and partially occupied atom sites were refined with isotropic adps. The chiral C(Me)*t*Bu groups C1 and C45 showed large adps with no disorder model, so were refined with isotropic adps. The poorly defined solvent was accounted for by SQUEEZE and found to be 73 electrons/cell and was assigned as 1.5 molecules of hexane. [Fe₂(L²)₂] showed disorder in the two chiral C(Me)*t*Bu groups C20 and C45 which were modelled over two sites with occupancies 0.60 and 0.40, and 0.50 and 0.50, respectively. Geometric and rigid-bond restraints were applied in all cases, and partially occupied atom sites were refined with isotropic adps. The poorly defined solvent was accounted for by SQUEEZE and found to be 57 electrons/cell and was assigned as one molecule of hexane. [Zn₂(L²)₂] contained two molecules per asymmetric unit, and showed disorder in carbon C96 which was modelled over two sites with occupancies 0.45 and 0.55. CCDC-651321 to -651323 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Molecular Modeling Calculations: Molecular mechanics energy calculations were carried out using the Extensible and Systematic Force Field (ESFF), as implemented within the Discover programme.^[23] Modification, visualisation and analysis of molecular structures were carried out using the Insight II molecular graphics software.^[23] Low-energy structures were obtained by conformational analysis and energy minimisation of the helicate and mesocate geometries of all three Fe complexes [Fe₂(L)₂], where L = L¹, L² and L³. The starting geometries for these complexes were obtained by either using or modifying the crystallographically determined Fe complex structures. For the helicate geometries, the crystal structure of [Fe₂(L¹)₂] was used as a backbone structure, and the substituent altered using the Builder module within Insight II. For the mesocate geometries, the crystal structure of [Fe₂(L²)₂] was used as a backbone structure, and the CH(Me)*t*Bu substituents altered. In all cases the stereochemistry of the substituents were confirmed as (*R*). Conformational analysis was carried out by rotating around the C(substituent)–N(imine) bond, as defined in Figure 5, and subsequent geometry optimisation of the resulting conformations. The dihedral drive calculation involved rotation of the C1–N2–C3–C4 dihedral angle in each of the four substituents, from –180° to +180° in 60° increments, followed by unrestrained energy

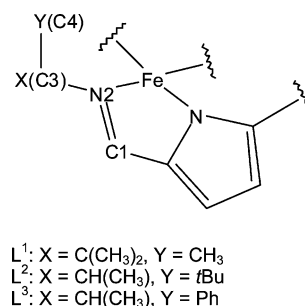


Figure 5. Dihedral angle (C1–N2–C3–C4) rotated during conformational analysis calculations.

minimisation of each of the 2401 conformations arising. ESFF partial atomic charges and atom types were assigned; in particular the NH atom type was assigned for the pyrrole nitrogen atom. Minimisations were carried out using steepest descents, followed by conjugate gradient and Newton–Raphson methods, until the convergence criterion (maximum derivative = 0.001) was reached.

Synthesis of H_2L^2 : (–)-(R)-3,3-Dimethyl-2-butylamine (4.83 g, 47.7 mmol) and K_2CO_3 (5.00 g) were added to a stirred solution of **1** (5.00 g, 21.7 mmol) in EtOH (100 mL). The resulting slurry was stirred for 24 h, after which the mixture was filtered and the precipitate washed once with EtOH (10 mL). The combined filtrate and washings were dried at reduced pressure, the resulting viscous red oil extracted with CH_2Cl_2 (10 mL) and transferred to a sublimation tube. The oil was sublimed twice at $130^\circ\text{C}/10^{-2}$ mbar to yield H_2L^2 as a pale yellow oil, 6.46 g, 75%. ^1H NMR (C_6D_6 , 298 K): δ = 9.81 (br. s, 2 H, NH), 7.76 (s, 2 H, CH=N), 6.31 (d, J = 3.6 Hz, 2 H, pyrrole H), 5.95 (d, J = 3.6 Hz, 2 H, pyrrole H), 2.75 (q, J = 6.5 Hz, 2 H, chiral CH), 1.08 (s, 6 H, *meso* CH_3), 1.04 (d, J = 7.7 Hz, 6 H, chiral CH_3), 0.92 (s, 18 H, chiral CMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 149.7 (s, CH=N), 142.5 (s, C_q), 130.6 (s, C_q), 114.1 (s, CH), 106.8 (s, CH), 75.7 (s, chiral CH), 36.1 (s, C_q), 34.7 (s, C_q), 28.8 (s, *meso* CH_3), 27.2 (s, chiral CMe_3), 18.2 (s, chiral CH_3) ppm. EIMS: m/z (%) = 397 (100) [M^+].

Synthesis of H_2L^3 : (+)-(R)-Phenylethylamine (5.06 mL, 39.6 mmol) and *p*-toluenesulfonic acid (342 mg, 1.80 mmol) were added to a stirred solution of **1** (4.15 g, 18.0 mmol) in MeOH (100 mL). The resulting orange solution was stirred for 1 h and then concentrated to dryness at reduced pressure. The orange residues were extracted with hot hexanes (15 mL), filtered through a plug of Celite and the volatiles removed at low pressure for 24 h to yield H_2L^3 as a viscous orange oil, 5.02 g, 64%. $\text{C}_{29}\text{H}_{32}\text{N}_4$ (436.59): calcd. C 79.76, H 7.40, N 12.83; found C 79.68, H 7.87, N 12.57. ^1H NMR (C_6D_6 , 298 K): δ = 8.87 (br. s, 2 H, NH), 7.78 (s, 2 H, CH=N), 7.38 (d, J = 7.1 Hz, 4 H, phenyl H), 7.10 (m, 6 H, phenyl H), 6.27 (s, J = 3.6 Hz, 2 H, pyrrole H), 5.91 (s, J = 3.6 Hz, 2 H, pyrrole H), 4.23 (q, J = 6.6 Hz, 2 H, chiral CH), 1.49 (d, J = 6.6 Hz, 6 H, chiral CH_3), 1.07 (s, 6 H, *meso* CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 150.0 (s, CH=N), 145.9 (s, C_q), 142.6 (s, C_q), 130.2 (s, C_q), 128.6 (s, CH), 127.1 (s, CH), 127.0 (s, CH), 114.6 (s, CH), 106.6 (s, CH), 69.5 (s, chiral CH), 35.7 (s, C_q), 28.2 (s, *meso* CH_3), 24.9 (s, chiral CH_3) ppm.

Synthesis of $[\text{Mn}_2(\text{L}^2)_2]$: A solution of H_2L^2 (586 mg, 1.48 mmol) in THF (10 mL) was added to a stirred slurry of KH (178 mg, 4.43 mmol) in THF (10 mL). Effervescence occurred immediately and the resulting slurry was stirred for 1 h, after which the ligand salt was added dropwise to a slurry of MnCl_2 (186 mg, 1.48 mmol) in THF (10 mL). The resultant yellow slurry was heated at 80°C for 24 h, after which the mixture was filtered through Celite, and the yellow filtrate concentrated to dryness under reduced pressure. The yellow solid was extracted into hexanes (5 mL) and cooled to deposit 109 mg, 16% of $[\text{Mn}_2(\text{L}^2)_2]$ as a yellow crystalline solid. Crystals suitable for X-ray diffraction were grown by slow cooling a hexane solution to -30°C . $\text{C}_{50}\text{H}_{76}\text{Mn}_2\text{N}_8$ (899.08): calcd. C 67.31, H 8.54, N 12.46; found C 67.39, H 8.42, N 12.45. EIMS: m/z (%) = 898 (14) [M^+], 841 (53) [$\text{M}^+ - t\text{Bu}$], 450 (43) [MnL^2], 43 (100) [$t\text{Bu} - \text{Me}$]. μ_{eff} (C_6D_6) = 8.06 μ_{B} .

Synthesis of $[\text{Fe}_2(\text{L}^2)_2]$: To a stirred slurry of KH (154 mg, 3.83 mmol) in THF (10 mL) was added a solution of H_2L^2 (507 mg, 1.28 mmol) in THF (10 mL). Effervescence occurred immediately and the resulting slurry was stirred for 1 h, after which the ligand salt was added dropwise to a stirred slurry of FeBr_2 (291 mg, 1.35 mmol) in THF (10 mL). The resultant red-brown slurry was

heated at 80°C for 24 h, after which the mixture was filtered, and the red filtrate concentrated to dryness under reduced pressure. The resultant orange solid was extracted into Et_2O (5 mL) and cooled to -20°C to deposit 276 mg, 48% of $[\text{Fe}_2(\text{L}^2)_2]$ as an orange crystalline solid. Crystals suitable for X-ray diffraction were grown by slow cooling a hexane solution to -30°C . $\text{C}_{50}\text{H}_{76}\text{Fe}_2\text{N}_8$ (900.90): calcd. C 66.65, H 8.52, N 12.44, found C 66.46, H 8.52, N 12.29. ^1H NMR (C_6D_6 , 298 K): δ = 58.7 (s, 2 H) = 48.2 (s, 2 H), 8.6 (s, 2 H), 6.5 (br. s, 6 H), 4.8 (s, 6 H), -0.9 (s, 2 H), -2.4 (s, 18 H), -3.8 (s, 18 H) ppm. EIMS: m/z (%) = 900 (21) [M^+], 843 (11) [$\text{M}^+ - t\text{Bu}$], 396 (48) [L^2], 339 (100) [$\text{L}^2 - t\text{Bu}$]. μ_{eff} (C_6D_6) = 7.28 μ_{B} .

Synthesis of $[\text{Zn}_2(\text{L}^2)_2](\text{CH}_2\text{Cl}_2)$: A solution of ZnMe_2 (2.0 M) in toluene (1 mL) was added to a stirred solution of H_2L^2 (574 mg, 1.45 mmol) in toluene (15 mL). Effervescence occurred immediately and the solution turned pale orange. The reaction mixture was heated at 80°C under reduced pressure for 24 h, after which the solvents were evaporated under reduced pressure and the residues extracted with CH_2Cl_2 (2 mL). Pentane (10 mL) was then added until cloud point, and the solution was cooled, resulting in the deposition of 352 mg, 53% of $[\text{Zn}_2(\text{L}^2)_2](\text{CH}_2\text{Cl}_2)$ as a pale yellow, crystalline solid. Crystals suitable for X-ray diffraction were grown by diffusion of pentane into a CH_2Cl_2 solution. $\text{C}_{50}\text{H}_{76}\text{N}_8\text{Zn}_2\cdot\text{CH}_2\text{Cl}_2$ (1004.9): calcd. C 60.96, H 7.82, N 11.15; found C 61.19, H 8.09, N 11.04. ^1H NMR (C_6D_6 , 298 K): δ = 7.55 (s, 1 H, CH=N), 7.33 (s, 1 H, CH=N), 6.95 (d, J = 3.6 Hz, 1 H, pyrrole H), 6.86 (d, J = 3.8 Hz, 2 H, pyrrole H), 6.73 (d, J = 3.7 Hz, 1 H, pyrrole H), 4.24 (s, 1 H, CH_2Cl_2), 2.97 (q, J = 6.8 Hz, 1 H, CH), 2.64 (q, J = 6.6 Hz, 1 H, CH), 2.34 (s, 3 H, *meso* CH_3), 2.04 (s, 3 H, *meso* CH_3), 1.00 (d, J = 6.8 Hz, 3 H, CH_3), 0.87 (d, J = 6.6 Hz, 3 H, CH_3), 0.67 (s, 9 H, CMe_3), 0.56 (s, 9 H, CMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K): δ = 159.5 (s, CH) = 158.3 (s, C_q), 158.2 (s, C_q), 158.0 (s, CH), 134.2 (s, C_q), 120.4 (s, CH), 120.1 (s, CH), 113.1 (s, CH), 112.5 (s, CH), 72.8 (s, CH), 68.3 (s, CH), 53.1 (s, CH_2Cl_2), 39.1 (s, C_q), 34.8 (s, C_q) ppm. 34.7 (s, C_q), 31.9 (s, *meso* CH_3), 26.8 (s, CMe_3), 26.7 (s, CMe_3), 23.3 (s, *meso* CH_3), 16.6 (s, CH_3), 15.8 (s, CH_3). EIMS: m/z (%) = 918 (8) [M^+], 863 (26) [$\text{M}^+ - t\text{Bu}$], 49 (100) [$t\text{Bu} - 8\text{H}$].

Synthesis of $[\text{Zn}_2(\text{L}^3)_2]$: A solution of ZnMe_2 (2.0 M) in toluene (0.5 mL) was added dropwise to a stirred solution of H_2L^3 (393 mg, 0.9 mmol) in toluene (10 mL). Gas evolved immediately and the resulting yellow-brown solution was heated at 80°C for 24 h, after which the orange-yellow solution was dried at reduced pressure and the pale yellow solids inspected by ^1H NMR spectroscopy. ^1H NMR (C_6D_6 , 298 K): δ = 7.60 (s, 2 H, CH=N), 7.34 (s, 2 H, CH=N), 7.3–6.7 (m, 20 H, phenyl H), 6.68 (d, J = 3.5 Hz, 2 H, pyrrole H), 6.63 (d, J = 3.5 Hz, 2 H, pyrrole H), 6.51 (d, J = 3.5 Hz, 2 H, pyrrole H), 6.36 (d, J = 3.5 Hz, 2 H, pyrrole H), 4.22 (q, J = 7.1 Hz, 2 H, chiral CH), 3.92 (q, J = 6.2 Hz, 2 H, chiral CH), 1.93 (s, 6 H, *meso* CH_3), 1.80 (s, 6 H, *meso* CH_3), 1.19 (d, J = 7.0 Hz, 6 H, chiral CH_3), 1.08 (d, J = 7.0 Hz, 6 H, chiral CH_3) ppm. The yellow solids were then extracted into Et_2O (5 mL) and cooled. The resulting slurry was filtered and the liquors concentrated to dryness to yield 112 mg, 25%, of $[\text{Zn}_2(\text{L}^3)_2]$ as yellow solids. $\text{C}_{58}\text{H}_{60}\text{N}_8\text{Zn}_2$ (999.93): calcd. C 69.67, H 6.05, N 11.21; found C 69.54, H 6.15, N 11.15.

Acknowledgments

The authors thank the EPSRC (UK), The Royal Society, and the Universities of Nottingham and Edinburgh for their support.

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Received: June 21, 2007

Published Online: September 24, 2007