DALTON
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Self-assembled triple helicates with preferential helicity †

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The enantiomerically pure ligands L^{RR} and L^{SS} (*N*,*N*′-bis(-2,2′-bipyridyl-5-yl)carbonyl-(1*S*/*R*,2*S*/*R*)-(+/−)-1,2-diaminocyclohexane) have been synthesised by linking two 2,2′-bipyridine units by (*R*,*R*)- and (*S*,*S*)-1,2-diaminocyclohexane respectively. The crystal structure confirmed that the ligand had a twisted orientation between the two chelating units. The reaction of L^{RR} and L^{SS} with Fe(II), Co(III), Cd(II) and Zn(II) afforded dinuclear complexes confirmed by electrospray mass spectroscopy. CD spectroscopy indicated that the chiral diaminocyclohexane conferred helicity to the metal centre giving a dominant triple helicate diastereoisomer, with the L^{RR} ligand giving a ΔΔ-configuration of each metal centre (P helicate) and the L^{SS} ligand a ΛΛ-configuration (M helicate). ^{1}H NMR spectroscopy confirmed a dominant major diastereoisomer with cadmium. The Zn(II) and Cd(II) complexes however were observed to undergo rapid ligand dissociation in solution.

Introduction

The synthesis of double and triple helicates is currently an intense area of research activity as such simple systems allow the development of a critical understanding of synthetic self-assembly procedures. In addition they possess considerable aesthetic appeal.[1–3] However, in only a handful of examples has the control of the inherent chirality been taken into consideration.[4–12] This is somewhat surprising considering the ultimate self-assembly helical structure; DNA, exists only in a right-handed form.

Helicates are composed of one or more organic ligands coordinating a series of metal ions to form a discrete linear polynuclear oligomer (Fig. 1). By far the most common examples are composed of two or three ligand strands able to bridge between a pair of metal centres, forming double or triple stranded dinuclear species respectively.[1–3] As a consequence of the ligand configuration at the metal centre, a chiral centre is generated. Two possible situations can exist; if the optical activity at the two metal centres is opposed, the *meso* (Δ/Λ) form (not a true helicate) arises. However, if the two metal centres are homochiral, a racemic (*rac*) mixture arises (the right-handed P or ΔΔ and left-handed M or ΛΛ forms).

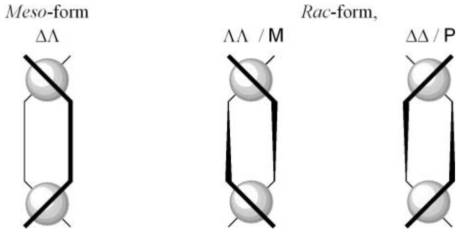

Fig. 1 Schematic illustration of helicate structure.

The majority of these supramolecular architectures described in the literature are composed of a racemic mixture. This can be rationalised by a lack of systematic methodology in the isolation of stereoisomers. The preparation of helicates, prepared *via* a self-assembly process relies on the formation of the most thermodynamically stable product. To achieve this kinetically labile reactants capable of undergoing suitable exchange reactions in solution are required but this allows rapid racemerization to occur. There are however several systems that serendipitously crystallise in a chiral space group with individual crystals containing only the left- or right-handed form (conglomeration), *e.g.* the tri-nuclear nickel(II) triple helix described by Lehn and co-workers.[4] An alternative strategy was described by Piguet where the oxidation of a dinuclear cobalt(II) triple helicate resulted in an inert cobalt(III) complex suitable for resolution by chromatography.[6]

To achieve a controllable induction of helicity chiral ligands have been considered. Three forms of chirality must be distinguished. First, the ligands themselves must contain at least one optically active carbon centre (denoted by *R*/*S* notation). Secondly, the coordination environment around the metal centres can adopt either a Δ or Λ orientation and finally, the overall sense of the helicity of the total structure denoted by M or P. Shanzer *et al.*[13] described the first triple-stranded helices where L-leucine groups introduce the chirality, forming stable dinuclear complexes with iron(III) with the configuration stabilised by hydrogen bonds. With a ligand containing three bipyridine units connected *via* an ethylene spacer containing a single chiral carbon atom between each chelating group (L^1), Lehn illustrated the formation of a single diastereoisomer of the tri-nuclear double helicate with silver(I) and copper(I).[7] The "*chiragen*" (chiral generator) ligand family described by von Zelewsky and Baret, containing two pinenyl groups placed either between (L^2)[14] or outside of (L^3)[15] two linked 2,2′-bipyridine units have demonstrated the predetermination of the stereochemistry of the overall molecular architecture in dinuclear triple helicates (see Scheme 1).

In order to address the control of the helicity we report here a new ligand system based on two chelating 2,2′-bipyridine moieties linked by (*R*,*R*)- or (*S*,*S*)-1,2-diaminocyclohexane. Several studies have considered the use of this optically active spacer group in the formation of double helicates (L^4), with the (*R*,*R*)-isomer adopting an M helicity.[10,16] By using labile metal centres such as Fe(II), Co(II/III), Zn(II) and Cd(II), an examination of the ligand configurational control of the helicity in the preparation of triple helicates is discussed.

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† Electronic supplementary information (ESI) available: plot of absorption *versus* metal-to-ligand ratio; rotatable 3-D diagrams for the structures shown in Fig. 6 in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b106479g/

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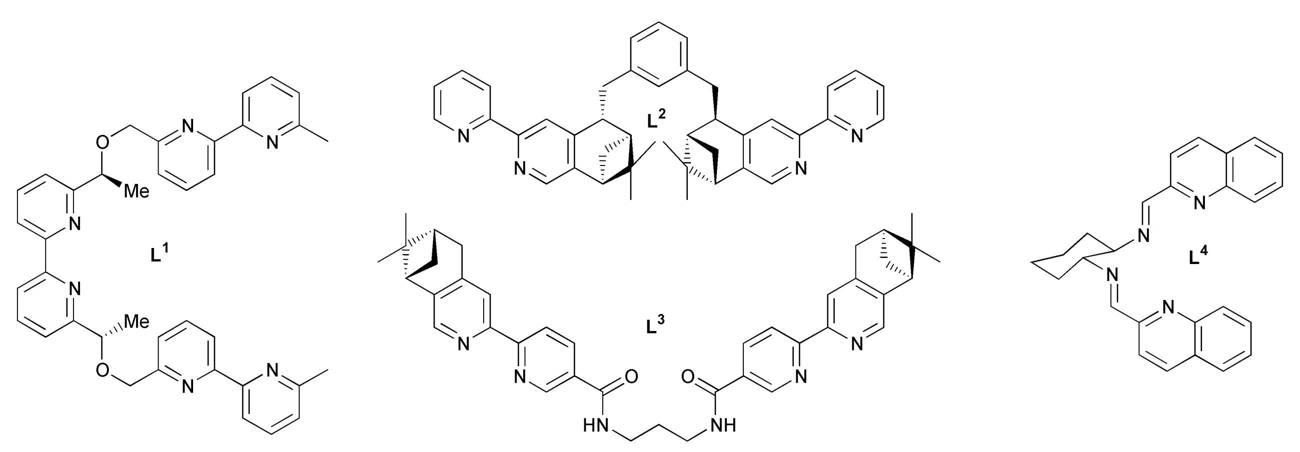
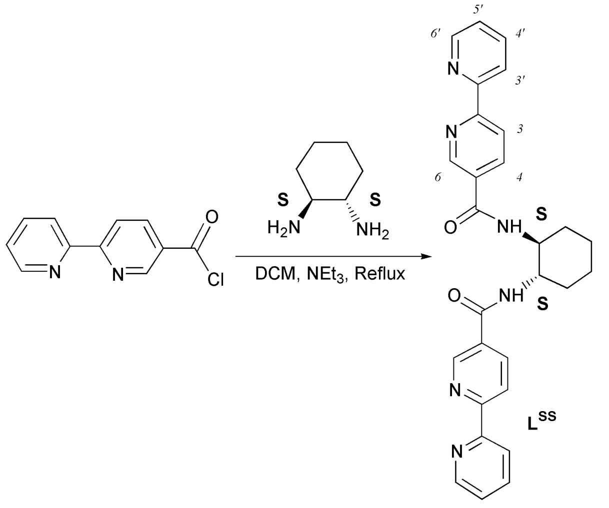


Scheme 1 Previously published ligand systems.

Results and discussion

Ligand synthesis and characterisation

Suitable ligands (L^{RR} and L^{SS}) with potentially the correct structural orientation for the formation of a complex possessing a helical architecture were synthesised in 74% yield by reacting two equivalents of 5-chlorocarbonyl-2,2′-bipyridine with either (*R*,*R*)- or (*S*,*S*)-1,2-diaminocyclohexane in dry dichloromethane (Scheme 2). L^{SS} and L^{RR} demonstrated extremely poor solubility in most common organic solvents, presumably because of its potential for intermolecular hydrogen bond formation *via* the amidic proton. However, due to the poor solubility purification was readily achieved by recrystallisation from methanol and the ligands were fully characterised by standard techniques.



Scheme 2 Synthesis of chiral ligand L^{SS}.

Crystals of the protonated form of L^{RR} ($[C_{28}H_{30}N_6O_2]^{4+}$-$[ClO_4]^-{}_4{\cdot}5H_2O$) were grown from an aqueous solution, by initially dissolving the material in perchloric acid, and slow solvent evaporation. (Note, perchlorate salts are potentially explosive and should be treated with extreme care). The crystals were poorly formed and consequently the diffraction was weak and thus the refinement is poor. However, despite this some general conclusions about the structure are still possible. The asymmetric unit contains one $[C_{28}H_{30}N_6O_2]^{4+}$ cation, four ClO_4^- anions and five water molecules. The ClO_4^- anions are disordered and have been modelled as having two sites. The structure determination was undertaken to confirm the atom connectivity and determine the conformation of the ligand in the solid state, Fig. 2. The conformation of the ligand is defined by torsion angle about N14a–C15a–C15b–N14b (61°) and the relative orientations of the mean planes N1a–C6a, N1b–C6b, C7a–N12a and N7b–N12b to the mean plane through the cyclohexyl bridge (C15a–C15b) of 85°, 46°, 94° and 131° respectively. The X-ray determination shows the $[C_{28}H_{30}N_6O_2]^{4+}$ cations form N–H ··· O hydrogen bonded layers in the *xy* plane. These layers are linked in the third dimension by a combination of N–H ··· O and O–H ··· O hydrogen bonds to and between the perchlorate anions and water molecules. This results in an extended three-dimensional hydrogen bonded structure.

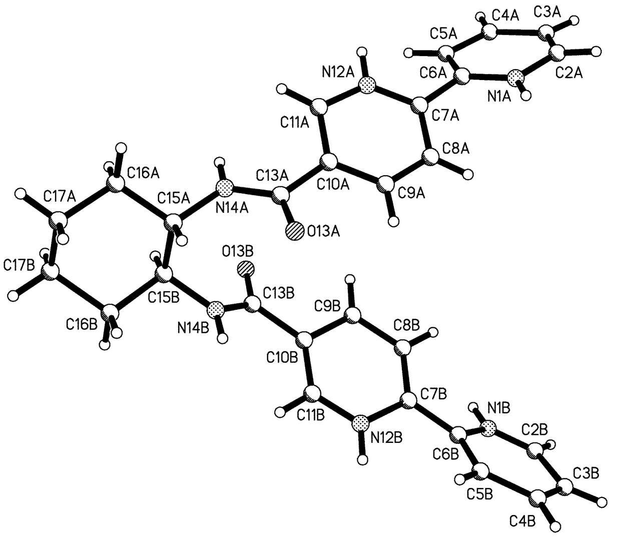


Fig. 2 A molecular connectivity and labelling scheme for the conformation of the cation of L^{RR}. Water molecules and anions have been removed for clarity.

The crystal structure confirmed that the ligand had a twisted orientation between the two chelating units, such that the two ends of the molecule could potentially form discrete dinuclear helical arrangements. The presence of a dominant enantiomer in solution was confirmed by polarimetry in both L^{RR} and L^{SS} ($[\alpha]_D$: −87.50 and +87.80 for L^{RR} and L^{SS} ligand respectively). More significantly, the circular dichroism spectra of the ligands demonstrated a small but significant Cotton effect in the π–π* ligand centred (LC) transition of the bipyridine functions (Fig. 3). Since the only source of the chirality in the molecule is derived from the aliphatic spacer group (which possesses no significant electronic absorption), there is a clear indication that the average solution conformation of the two chelating functions has the two units overlying each other in a twisted orientation as found in the solid state. Similar observations have been demonstrated by von Zelewsky in the "*chiragen*" ligand systems.[17]

Complex synthesis and characterisation

Metal complexes were prepared by the slow mixing of ethanolic ligand solutions of L^{RR} and L^{SS} with an aqueous solution of the

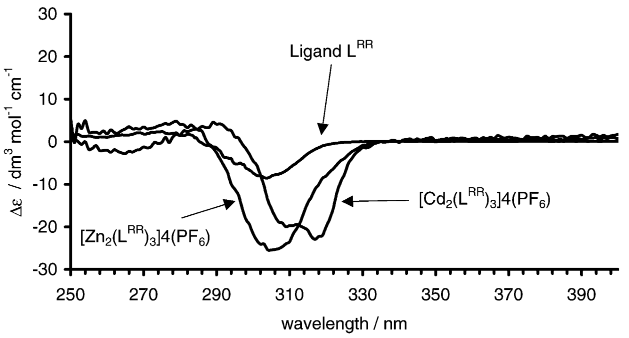


Fig. 3 CD spectra of L^{RR}, $[Zn_2(L^{RR})_3][PF_6]_4$ and $[Cd_2(L^{RR})_3][PF_6]_4$ (acetonitrile).

appropriate metal complex (hydrated iron(II) chloride, cobalt(II) chloride, zinc acetate and cadmium bromide). In order to ensure the thermodynamic product was isolated and to enhance the poor solubility, the reaction mixtures were refluxed for 4 h and the complexes isolated by precipitation with ammonium hexafluorophosphate. The identity of the products was confirmed by electrospray mass spectroscopy. Peaks corresponding to the molecular ion less one or more of the hexafluorophosphate counter anions were observed for all four metal complexes, indicating that a general 3 : 2 stoichiometry of ligand to metal was present. Microanalysis also confirmed the stoichiometry, although the complexes were observed to retain water despite prolonged drying *in vacuo* (particularly in the analysis of the iron(II) complex, a reasonable analysis of the chloride salt was however performed confirming the cation integrity).

In the case of the cobalt(II) complex, a colour change from yellow to brown was observed on standing in air, attributed to oxidation to cobalt(III). The same process could be achieved by adding a 30% hydrogen peroxide solution. The presence of six corresponding hexafluorophosphate anions was confirmed by both mass spectroscopy and elemental analysis.

UV/Vis absorption spectroscopy identified the complexes by a red shift in the bipyridine LC transitions when compared to the free ligand. The 3 : 2 stoichiometry was confirmed by carrying out Job plots (an example of which is included in the ESI). The iron(II) complex demonstrated the characteristic metal-to-ligand-charge-transfer (MLCT) typical of polypyridine complexes of iron(II) giving rise to an intense pink colour. Worthy of note is that this peak (541 nm) is red shifted compared to that of $[Fe(bipy)_3]^{2+}$ (500 nm)[18] because of the electron withdrawing carbonyl group, similar to an amide linked iron(II) helicate described by Baret and co-workers.[19] The cobalt(III) complex also demonstrated the characteristic weak absorptions, assigned as d–d transitions (380 and 465 nm).

Chiral induction

In order to indicate the presence of a preferred non-racemic chirality at the metal centre in solution, ^1H NMR spectroscopic studies were attempted. For all of the metal complexes there was significant broadening of the signals reducing resolution to only 0.05 ppm. In the case of the iron(II) complexes, the broadness of the signals prevented a detailed analysis of the spectra. Similar behaviour was observed by von Zelewsky[14] who indicated that this is possibly due to a near spin crossover situation. Similarly $[Co_2(L^{RR})_3](PF_6)_6$ demonstrated a very low resolution ^1H NMR spectrum, possibly due to contamination by cobalt(II). However in each case, the signal relating to the cyclohexane proton adjacent to the amide was observed to be composed of two signals, indicating the presence of two diastereoisomers, in approximately a 4 to 1 ratio. This particular proton, at the stereocentre of the spacer group will be extremely susceptible to the helicity of the resulting complex, and acts as a good indicator of the diastereomeric purity of the solution. By considering the simplicity of the spectra observed, a general C_3-symmetry appears to be adopted for each of the isomers present, indicating a triple helicate structure is observed.[14]

The ^1H NMR and ^{13}C NMR spectra of the cadmium complex $[Cd_2(L^{RR})_3][PF_6]_4$ indicated complex formation, by the shift in peak position of protons H^6 and $H^{5'}$ of L^{SS} and L^{RR} downfield relative to the free ligand by 0.3 and 0.2 ppm respectively (Fig. 4.) In order to rationalise the origin of the proton signals in the complex, a sequential addition of the metal cation to the ligand in DMSO was attempted and the change in peak position noted. Again the signals were significantly broader than those observed for the free ligand, indicating a fluctional behaviour but the titration clearly indicated a 2 : 3 metal to ligand stoichiometry as previously demonstrated by UV/vis spectroscopy. Due to the complex nature of the equilibria present in solution though it is apparent that obtaining quantitative thermodynamic data from the titrations is not possible. The presence of several diastereoisomers would be expected to be most pronounced on the cyclohexane proton adjacent to the amide group, however the peak remained as a single signal (albeit broad) during the titration indicating that either a single diastereoisomer exists, or more likely given the broadness of the signals that the two forms are interconverting on the ^1H NMR time scale. The same conclusion can be drawn from a titration

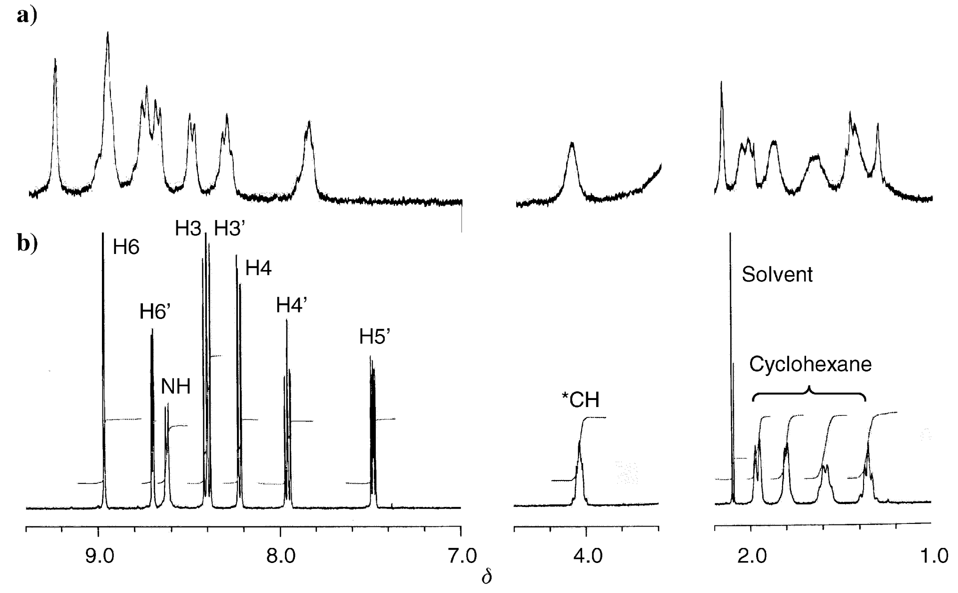


Fig. 4 ^1H NMR spectra (300 MHz) in DMSO-d_6 at room temperature of (a) Δ,Δ-$[Cd_2(L^{RR})_3][PF_6]_4$ (b) ligand L^{RR}.

Table 1 UV/Vis spectra, CD spectra and molar rotations of dinuclear and mononuclear metal complexes

Complexes	UV/Vis λ_{max}/nm ($\varepsilon \times 10^3$/dm^3 mol^{-1}cm^{-1})	CD λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1}cm^{-1})	Transitions	$[\alpha]_D$	Ref.
Δ,Δ-[Fe$_2$(L^{RR})$_3$]$^{4+}$	290 (108.6)	291 (102.5)	LC	−4672	
	305 (93.4)	309 (−252)			
	480 (9.8)	396 (3.4)	MLCT		
	541 (10.7)	486 (−9.1)	MLCT		
		566 (17.0)	MLCT/d–d		
Λ,Λ-[Fe$_2$ (L^{SS})$_3$]$^{4+}$	290 (108.0)	291 (−93.8)	LC	+4696	
	305 (102.0)	309 (299)			
	480 (10.5)	396 (−3.6)	MLCT		
	541 (10.8)	486 (12.2)	MLCT		
		566 (22.3)	MLCT/d–d		
Δ,Δ-[Fe$_2$(L^2)$_3$]$^{4+}$	290 (81)	295 (242)	LC		14
	305 (37)	315 (−529)			
	361 (17)	395 (13.6)	MLCT		
	485 (17)	477 (12.0)	MLCT		
	531 (23)	526 (−7.5)	MLCT/d–d		
Δ,Δ-[Fe$_2$(L^3)$_3$]$^{4+}$	Unavailable	302 (249)	LC		15
		322 (−445)			
		512 (−6.7)	MLCT		
		573 (18.4)	MLCT/d–d		
Δ-[Fe(bipy)$_3$]$^{2+}$	293 (36.3)	284 (+50.0)	LC	−4600	21
	354 (60)	300 (−500)			
	415 (6.3)	385 (+3.2)	MLCT		
	621 (8.7)	476 (−12)	MLCT		
		545 (+19)	MLCT/d–d		
Δ,Δ-[Co$_2$(L^{RR})$_3$]$^{6+}$	290 (101.3)	286 (77.7)	LC	−2700	
	300 (105.1)	317 (−269)			
	380 (9.2)	427 (0.9)	d–d		
	465 (5.3)	479 (0.5)	d–d		
	540 (3.4)	543 (0.8)	d–d		
Λ,Λ-[Co$_2$(L^{SS})$_3$]$^{6+}$	290 (84.2)	292 (58.4)	LC	+2722	
	300 (110.5)	317 (−233)			
	380 (8.4)	[a]	d–d		
	465 (4.8)		d–d		
	540 (4.1)		d–d		
Δ-[Co(bipy)$_3$]$^{3+}$	316 (35)	298 (+62.1)	LC	−263	20
	450 (0.72)	318 (−111)			
		502 (−0.30)	d–d		
Δ,Δ-[Zn$_2$(L^{RR})$_3$]$^{4+}$	289 (85.4)	277 (+4.8)	LC	−322.6	
		303 (−25.4)			
Δ,Δ-[Cd$_2$(L^{RR})$_3$]$^{4+}$	289 (82.6)	265 (−2.8)	LC	−467.2	
		291 (4.2)			
		309 (−20.0)			
		317 (−22.9)			

[a] Base line of the spectrum too noisy to allow $\Delta\varepsilon$ to be obtained for this complex in the visible range.

with zinc, although extremely broad signals resulted for the zinc complex at room temperature, potentially indicating rapid ligand dissociation. In both the zinc and the cadmium complexes no resolution of the peaks was observed upon either cooling or heating.

In order to assess whether there is a transference of the chirality from the enantiomerically pure chiral spacer group to the metal centres and consequently to the helicity of the oligomeric structure the optical rotations of each of the complexes were recorded. In each case considerably larger values than those for the free ligand were observed, being approximately equal and opposite for each pair of enantiomers (Table 1). (It is assumed that the small discrepancies in the values, with the L^{RR} isomer being lower by typically by 1–2% than L^{SS}, can be accounted for by the purity of the commercial enantiomers used in the ligand synthesis).

The polarimetry results were confirmed by solution circular dichroism (CD) spectroscopy. The complexes all demonstrated an enhanced Cotton effect by comparison to the free ligand (Fig. 3 and Fig. 5) indicative of enhanced polarisation of the LC bipyridine transitions in keeping with the results described for ligands L^2 and L^3.[14,15] This orientation of the non-chiral bipyridine ligands into a helical arrangement is most probably associated with complex formation. In addition to the enhancement of the Cotton effect, the peaks for the iron(II),

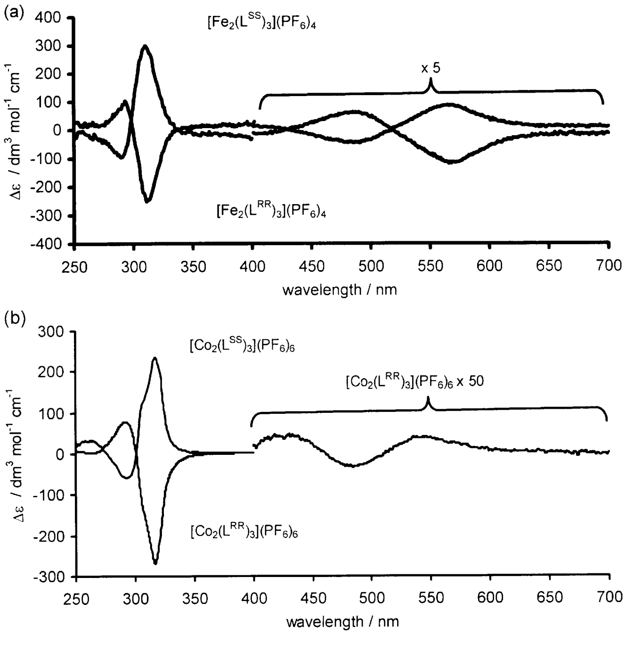


Fig. 5 CD spectra of (a) [Fe$_2$(L^{RR})$_3$][PF$_6$]$_4$ and [Fe$_2$(L^{SS})$_3$][PF$_6$]$_4$, (b) [Co$_2$(L^{RR})$_3$][PF$_6$]$_6$ and [Co$_2$(L^{SS})$_3$][PF$_6$]$_6$.

cobalt(III) and cadmium(II) complexes were observed to be red shifted when compared to those of the free ligand, in a similar fashion to that observed in the electronic spectra described above further confirming that the observed spectra are as a consequence of complex formation. However, the involvement of the metal in the reorientation of the ligand is unambiguously confirmed by the appearance of Cotton effects in the Fe(II) MLCT absorptions and the Co(III) d–d transitions. It is worth noting that the Co(III) d–d transitions both in the absorption and CD spectra are extremely weak as they arise from spin forbidden transitions. However, the Cotton effects observed for $[Co_2(L^{RR})_3]^{6+}$ are comparable, if not larger than that observed for the isomerically pure Δ-$[Co(bipy)_3]^{3+}$.[20]

The zinc complexes did not give the red shift in peak position observed for the other metal complexes, although titration studies clearly indicated that a dominant complex was formed upon the addition of a small quantity of the metal salt to the ligand. Being the smallest cation, it would be expected to bring the 2,2′-bipyridine groups into the closest arrangement and consequently give the largest observed interaction. Hence it is postulated that in solution, the zinc complex is undergoing rapid ligand dissociation from the metal centre, which was previously indicated by ^{1}H NMR studies.

The CD spectra for the iron(II) complexes of L^{SS} and L^{RR} are similar to those described for the dinuclear helicates prepared form ligands L^2 and L^3 (Table 1).[14,15] As expected they are equal and opposite in appearance with absorptions attributed to the LC transition at 291 nm and 309 nm. By comparison of the signs of the signals to those of Δ-$[Fe(bipy)_3]^{2+}$,[21] it appears that the dominant diastereoisomer has the metal centres placed in a Δ configuration, indicating a P helicity is adopted. Similar results were observed with the analogous cobalt, zinc and cadmium complexes indicating that in each case L^{RR} gives a preference to a P helicity upon complexation. Interestingly though, the Cotton effects arising from the MLCT absorptions are similar to those of the complex $[Fe_2(L^3)_3]^{4+}$,[15] but differ significantly from those observed for $[[Fe_2(L^2)_3]^{4+}$ where the maxima and minima are apparently inverted.[14]

The helicity derived from (*R*,*R*)-1,2-diaminocyclohexane in previous studies has given rise to an M helicity, for example Amendola *et al.* described the preparation of a dicopper(I) double helicate from ligand L^4, with the metal centres adopting a Λ configuration.[16] In order to rationalise this discrepancy with the observations made in this publication, simple molecular mechanics structural optimisation studies were performed on the complex $[Fe_2(L^{RR})_3]^{4+}$,[22] optimising the two $Fe(bipy)_3$ units into a rigid conformation based on published average crystallographic data.[23] The two possible chair configurations of the cyclohexane moiety were considered with the amide groups positioned either axially or equatorially for each of the two metal stereochemistries. This gives rise to the structures illustrated in Fig. 6 (PDB files available as ESI). The ΔΔ configuration appears to be the most stable (refining to a minimum total steric energy of 40 kJ mol^{-1} for both the axial and equatorial cyclohexyl configurations). Energetically though, the diastereomeric ΛΛ form is not too dissimilar (60 kJ mol^{-1} for the axial and 46 kJ mol^{-1} for the equatorial configuration) indicating that both forms of helicity are possible. With the functionality of the cyclohexane moiety being equatorial, the two metal centres are brought closer together than for the equivalent axial configuration, while the latter structure points the three cyclohexane units further away from the intermolecular space creating a very polar cavity. These preliminary studies indicate that there is potentially a structural change due to the polarity of the solvent and will be the subject of future research. The modelling studies indicate that the P- or ΔΔ-complex configuration is preferred for ligand L^{RR} confirming the CD studies. The discrepancy between this result and previous studies can be rationalised by examining the two 2,2′-bipyridine orientations relative to the cyclohexyl ring. To form a triple helicate with a six-coordinate metal centre, the two chelating groups must be positioned in a different configuration than that required for a pseudo-tetrahedral metal centre examined in previous studies.

The results from the spectroscopic studies indicate a diastereomeric preference assigned by comparison to similar

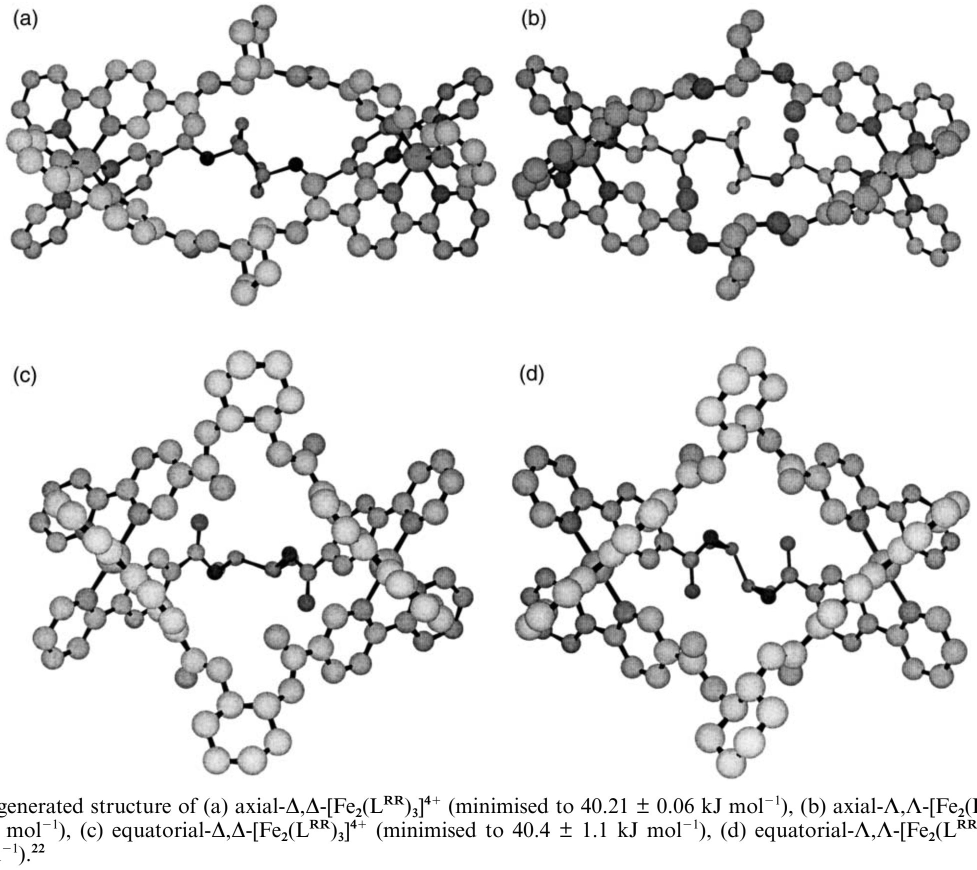


Fig. 6 Computer generated structure of (a) axial-Δ,Δ-$[Fe_2(L^{RR})_3]^{4+}$ (minimised to 40.21 ± 0.06 kJ mol^{-1}), (b) axial-Λ,Λ-$[Fe_2(L^{RR})_3]^{4+}$ (minimised to 60.82 ± 0.05 kJ mol^{-1}), (c) equatorial-Δ,Δ-$[Fe_2(L^{RR})_3]^{4+}$ (minimised to 40.4 ± 1.1 kJ mol^{-1}), (d) equatorial-Λ,Λ-$[Fe_2(L^{RR})_3]^{4+}$ (minimised to 46.31 ± 0.10 kJ mol^{-1}).[22]

complexes previously reported. A tentative 4 : 1 ratio of the diastereoisomers appears to be present in the ^{1}H NMR spectra of $[FeL_3]^{2+}$ and $[CoL_3]^{3+}$ but definitive calculations of the excess have not been possible due to the broadness of the peaks. All attempts to crystallise the material and confirm the solution assignment by X-ray structural analysis have been unsuccessful. Due to the small energy differences between the various structural forms, it is entirely feasible though that the solid-state structure is not representative of the solution phase due to the packing interactions.

Conclusions

The new ligand system described has the potential to form triple helical architectures with labile transition metals as determined in solution *via* ^{1}H NMR and CD spectroscopic studies. Due to the steric restraints, L^{RR} has the potential to favour a ΔΔ configuration at the metal centres, and consequently gives rise to the preference of a P helicity in the structure (with L^{SS} a preference for M). However, it appears that at least two diastereoisomeric forms exist at room temperature. Modelling studies indicate that the energy difference between the M and P forms is extremely small. While there is an imposition on the helicity, it would appear not to be as strong as using the bulky pinenyl groups described by von Zelewsky and Baret.[14,15] The implication is that the control of the diastereoisomeric excess in a self-assembled system containing a fluctional cyclohexane space possesses too many degrees of freedom. To achieve well-behaved structural control, spacer groups with restricted motion either through steric interactions or conjugation are required. As a consequence, new ligand systems are currently being explored in an attempt to create a library of chiral metal complexes with defined helical architectures.

Experimental

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Brüker DPX 300 and DRX500 using the solvent as an internal reference, electronic spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer (concentration approximately 7×10^{-6} mol dm^{-3} for the iron(II) complexes and $1–2 \times 10^{-5}$ mol dm^{-3} for all other samples). Circular dichroism (CD) spectra were recorded on a Jasco J-720 spectropolarimeter (concentration approximately 7×10^{-6} mol dm^{-3} for the iron(II) complexes and $1–2 \times 10^{-4}$ mol dm^{-3} for all other samples). Optical rotations were recorded on a Perkin Elmer 241 polarimeter (concentration approximately 7×10^{-6} mol dm^{-3} for the iron(II) complexes and $1–2 \times 10^{-5}$ mol dm^{-3} for all other samples). Microanalyses were performed by ASEP, the School of Chemistry, Queen's University of Belfast. The LSIMS (FAB) and electrospray mass spectroscopy was performed by the EPSRC mass spectroscopy service, the University of Wales, Swansea.

Materials

(1*S*,2*S*)-(+)−1,2-Diaminocyclohexane (99%) and (1*R*,2*R*)-(−)-1,2-diaminocyclohexane (99%), were purchased from Aldrich. Dichloromethane was dried by distillation from anhydrous calcium chloride. 5-Methyl-2,2′-bipyridine[24] was prepared *via* a Kröhnke synthesis from 2-acetylpyridine (99%; Aldrich) and methacrolein (Aldrich) and oxidised to 5-carbonyl-2,2′-bipyridine with potassium manganate(VII).[25]

Ligand synthesis

***N*,*N*′-Bis(-2,2′-bipyridyl-5-yl)carbonyl-(1*S*,2*S*)-(+/−)-1,2-diaminocyclohexane (L^{SS}).** 5-Chlorocarbonyl-2,2′-bipyridine was prepared from 5-carbonyl-2,2′-bipyridine (0.20 g, 1.00 mmol) in thionyl chloride (15 ml) and reacted *in situ* following distillation. The yellow solid was dissolved in dry dichloromethane (30 ml) to which (*R*,*R*)- or (*S*,*S*)-1,2-diaminocyclohexane (51.3 mg, 0.45 mmol) and triethylamine (1.37 ml, 10.0 mmol) in dry dichloromethane (30 ml) was added dropwise over 15 min at room temperature under nitrogen. The reaction mixture was refluxed for 15 h after which the solid was removed by filtration through Celite®, and the filtrate washed with water (7 × 100 ml) and dried with anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave a white solid. Recrystallisation from methanol gave a colourless crystalline solid. Yield 0.160 g, 74%. Melting point >300 °C, Found C: 69.51, H: 5.30, N: 17.49%; Analysis calculated for $C_{28}H_{26}O_2N_6$: C: 69.28, H: 5.36, N: 17.32%. ^{1}H NMR (500MHz, DMSO-d$_6$) δ 1.34 (2H, m, cycloH), 1.58 (2H, m, cycloH), 1.79 (2H, m, cycloH), 1.95 (2H, m, cycloH), 4.02 (2H, m, C*H*–N), 7.48 (2H, dd, $J = 4.7$ and 7.5 Hz, bipyH$^{5'}$), 7.95 (2H, dd, $J = 7.5$ and 8.0 Hz, bipyH$^{4'}$), 8.21 (2H, d, $J = 8.3$ Hz, bipyH^4), 8.38 (2H, d, $J = 8.0$ Hz, bipyH$^{3'}$), 8.40 (2H, d, $J = 8.3$ Hz, bipyH^3), 8.62 (2H, d, $J = 7.6$ Hz, N*H*), 8.69 (2H, d, $J = 4.7$ Hz, bipyH$^{6'}$), 8.96 (2H, s, bipyH^6), ^{13}C NMR (300 MHz, DMSO-d$_6$) δ 24.13, 30.0, 52.4, 120.0, 122.0, 124.1, 130.3, 135.9, 137.2, 147.6, 148.9, 153.8, 156.6, 165.0. ESMS: *m*/*z* 479 (100%, MH$^+$). IR (KBr disc) λ_{max} (cm^{-1}) 3287 (br, N–H), 1720 and 1628 (C=O stretch). $[\alpha]_D$: −87.50 and +87.80 (CH_2Cl_2) L^{RR} and L^{SS} respectively.

Complex synthesis

Ethanolic solutions of ligand L^{SS} and L^{RR} were treated with an aqueous solution of iron(II) chloride dihydrate, anhydrous cobalt(II) chloride, zinc(II) acetate tetrahydrate and cadmium(II) bromide in a 3 : 2 stoichiometry. The resulting solutions were heated at reflux for 4 h and the solvent was removed *in vacuo*. The solid residues were dissolved in a small amount of water (15 ml) and precipitated by addition of saturated aqueous NH_4PF_6.

$[Fe_2(L^{RR})_3][PF_6]_4$ and $[Fe_2(L^{SS})_3][PF_6]_4$. Yield: 65% and 60% for the *R*,*R* and *S*,*S* enantiomers respectively. Found: C: 41.98, H: 4.50, N: 8.90%, Analysis calculated for $C_{84}H_{78}O_6N_{18}Fe_2P_4F_{12}\cdot 15H_2O$; C: 42.00, H: 4.50, N: 10.50%. ^{1}H NMR (300MHz, DMSO-d$_6$, RT) δ 1.25 (2H, m, H^{C4}), 1.50 (2H, m, H^{C2}), 1.70 (2H, m, H^{C3}), 1.90 (2H, m, H^{C1}), 3.95 (2H, br, C*H*–N), 7.40 (2H, m, bipyH$^{5'}$), 7.90 (2H, dd, $J = 8.0$ Hz, bipyH$^{4'}$), 8.10 (2H, d, $J = 8.0$ Hz, bipyH^4), 8.30 (2H, d, $J = 7.0$ Hz, bipyH$^{3'}$), 8.55 (2H, d, $J = 8.0$ Hz, bipyH^3), 8.60 (2H, d, $J = 8.0$ Hz, N*H*) 8.65 (2H, d, $J = 4.0$ Hz, bipyH$^{6'}$), 8.90 (2H, s, bipyH^6). ESMS: *m*/*z* 1690 (75%, $[H_2M - 3PF_6]^+$). IR (KBr disc) λ_{max} (cm^{-1}): 3410 (br, N–H), 1606 (C=O stretch).

[Analysis of the chloride salt prior to precipitation by removal of the solvent: Found: C: 57.68, H: 5.11, N: 14.43%, Analysis calculated for $C_{84}H_{78}O_6N_{18}Fe_2Cl_4\cdot 3.5H_2O$: C: 57.63, H: 4.86, N: 14.40%].

$[Co_2(L^{RR})_3][PF_6]_6$ and $[Co_2(L^{SS})_3][PF_6]_6$. During the isolation of the hexafluorophosphate salt, the solution was allowed to stand in air for 16 h, during which time a colour change from yellow to brown was observed. (The same result was achieved by the addition of 2 ml of a 30% solution of hydrogen peroxide) Yield: 76% and 67% for the *R*,*R* and *S*,*S* enantiomers respectively. Found: C: 41.40, H: 3.92, N: 9.53%, Analysis calculated for $C_{84}H_{78}O_6N_{18}Co_2P_6F_{36}\cdot 2EtOH\cdot H_2O$: C: 41.60, H: 3.63, N: 9.92%. ^{1}H NMR (300 MHz, DMSO-d$_6$, RT) δ 1.40 (2H, m, H^{C4}), 1.67 (2H, m, H^{C2}), 1.90 (2H, m, H^{C3}), 2.09 (2H, m, H^{C1}), 3.90 (2H, br, C*H*–N), 6.80 (2H, m, bipyH$^{5'}$), 7.30 (2H, m, bipyH$^{4'}$), 7.85 (2H, d, $J = 8.0$ Hz, bipyH^4), 8.15 (2H, d, $J = 8.0$ Hz, bipyH$^{3'}$), 8.30 (2H, d, $J = 8.0$ Hz, bipyH^3), 8.55 (2H, d, $J = 7.0$ Hz, N*H*), 8.60 (2H, d, $J = 4.0$ Hz, bipyH$^{6'}$), 8.85 (2H, s, bipyH^6). ESMS: *m*/*z* 2136 (85%, $[HM - 2PF_6]^+$). IR (KBr disc) λ_{max} (cm^{-1}): 3414 (br, N–H), 1610 (C=O stretch).

$[Zn_2(L^{RR})_3][PF_6]_4$ and $[Zn_2(L^{SS})_3][PF_6]_4$. Yield: 76% and 65% for the *R*,*R* and *S*,*S* enantiomers respectively. Found: C: 47.52, H: 4.26, N: 10.99%, Analysis calculated for $C_{84}H_{78}O_6N_{18}Zn_2P_4F_{24}$·2EtOH: C: 47.14, H: 4.01, N: 11.25%. ^{1}H NMR (300 MHz, DMSO-d$_6$, RT) δ 1.20 (2H, m, H^{C4}), 1.40(2H, m, H^{C2}), 1.80 (2H, m, H^{C3}), 2.25 (2H, m, H^{C1}), 3.80 (2H, br, C*H*–N), 7.80 (2H, m, bipyH$^{5'}$), 8.20 (2H, m, bipyH$^{4'}$), 8.30 (2H, d, J = 8.0 Hz, bipyH^4), 8.55 (2H, d, J = 8.0 Hz, bipyH$^{3'}$), 8.75 (2H, d, J = 8.0 Hz, bipyH^3), 9.00 (4H, m, N*H* and bipyH$^{6'}$), 9.15 (2H, s, bipyH^6). ESMS: *m*/*z* 2002 (30%, [M − PF$_6$]$^+$), 1856 (40%, [HM − 2PF$_6$]$^+$), 1710 (100%, [2HM − 3PF$_6$]$^+$). IR (KBr disc) λ_{max} (cm^{-1}): 3414 (br, N–H), 1607 (C=O stretch).

[Cd$_2$(L^{RR})$_3$][PF$_6$]$_4$ and [Cd$_2$(L^{SS})$_3$][PF$_6$]$_4$. Yield: 74% and 78% for the *R*,*R* and *S*,*S* enantiomers respectively. Found: C: 43.92, H: 4.23, N: 10.13%, Analysis calculated for $C_{84}H_{78}O_6N_{18}Cd_2P_4F_{24}$·4H$_2$O·EtOH. C: 43.17, H: 3.90, N: 10.67%. ^{1}H NMR (300 MHz, DMSO-d$_6$, RT) δ 1.40 (2H, m, H^{C4}), 1.60 (2H, m, H^{C2}), 1.85 (2H, m, H^{C3}), 2.0 (2H, m, H^{C1}), 4.10 (2H, br, C*H*–N), 7.90 (2H, m, bipyH$^{5'}$), 8.30 (2H, dd, J = 8.0 Hz bipyH$^{4'}$), 8.40 (2H, d, J = 8.0 Hz, bipyH^4), 8.70 (2H, d, J = 7.4 Hz, bipyH$^{3'}$), 8.90 (2H, d, J = 8.0 Hz, bipyH^3), 8.95 (2H, d, J = 10.0 Hz, N*H*), 9.00 (2H, d, J = 4.0 Hz bipyH$^{6'}$), 9.30 (2H, s, bipyH^6), ^{13}C NMR (300 MHz, DMSO-d$_6$) δ 15.0, 25.0, 32.50, 60.0, 122.0, 123.5, 124.30 125.0, 127.5, 128.0, 137.50, 140.0, 149.0 150.0. ESMS: *m*/*z* = 2096 (100%, [M − PF$_6$]$^+$), 1807 (55%, [H$_2$M − 3PF$_6$]$^+$). IR (KBr disc), λ_{max} (cm^{-1}): 3421 (br, N–H), 1603 (C=O stretch).

X-Ray structural analysis

Data were collected on a Bruker-AXS SMART diffractometer using the SAINT-NT[26] software with graphite-monochromated Mo-K$_\alpha$ radiation. A crystal was mounted onto the diffractometer at low temperature under nitrogen at *ca.* 120 K. Crystal stability was monitored and there were no significant variations (< ± 2%). Cell parameters were obtained from 250 accurately centred reflections. ω/θ scans were employed for data collection and Lorentz, polarisation and empirical absorption corrections were applied.

The structure was solved using direct methods and refined with the SHELXTL version 5.0 and SHELXL-98 program packages[27] and the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen-atom positions were added at idealised positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded), was used for subsequent refinements. The absolute configuration is assigned based on the fact that pure (*S*,*S*)-1,2-diaminocyclohexane was used in the ligand synthesis. The function minimised was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g_1P)^2 + (g_2P)]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$.

Crystal data for $C_{28}H_{30}N_6O_2(ClO_4)_4$·5H$_2$O. M = 970.46, tetragonal, space group $P4_3$, a = 8.671(5), b = 8.671(5), c = 54.06(4), U = 4064(5) Å^{-3}, Z = 4, μ = 0.386 mm^{-1}, R_{int} = 0.1142, transmission range(max,min) = 0.9698, 0.9096. A total of 11993 reflections were measured for the angle range 3 < 2θ < 40 and 3802 independent reflections were used in the refinement. The final parameters were $wR2$ = 0.3011 and $R1$ = 0.1044 [$I > 2\sigma I$], Flack x = 0.2(2).

CCDC reference number 168683.

See http://www.rsc.org/suppdata/dt/b1/b106479g/ for crystallographic data in CIF or other electronic format.

Molecular mechanics modelling studies

These were carried out using standard MM2 organic parameters provided by Chem3D.[22] The two Fe(bipy)$_3$ were constrained by optimising the bond lengths to Fe–N: 1.965, C–N: 1.354, C–C: 1.379 (ar) and 1.456.[23] The target configuration was arranged roughly by eye, and the energy minimized at an RMS gradient of 0.010. The procedure was repeated on five independant arrangements to ensure that in each case the desired target configuration was obtained for each of the four structural configurations considered. Results: (a) axial-Δ,Δ-[Fe$_2$(L^{RR})$_3$]$^{4+}$ minimised to 40.21 ± 0.06 kJ mol^{-1}, (b) axial-Λ,Λ-[Fe$_2$(L^{RR})$_3$]$^{4+}$ minimised to 60.82 ± 0.05 kJ mol^{-1}, (c) equatorial-Δ,Δ-[Fe$_2$(L^{RR})$_3$]$^{4+}$ minimised to 40.4 ± 1.1 kJ mol^{-1}, (d) equatorial-Λ,Λ-[Fe$_2$(L^{RR})$_3$]$^{4+}$ minimised to 46.31 ± 0.10 kJ mol^{-1}.

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References

1 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
2 D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185.
3 U. Knof and A. von Zelewsky, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 302.
4 R. Kramer, J.-M. Lehn, A. De Cian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 703.
5 B. Hasenknopf and J.-M. Lehn, *Helv. Chim. Acta*, 1996, **79**, 1643.
6 L. J. Charbonniere, G. Bernardinelli, C. Piguet, A. M. Sargeson and A. F. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1419.
7 W. Zarges, J. Hall, J.-M. Lehn and C. Bolm, *Helv. Chim. Acta*, 1991, **74**, 1843.
8 E. J. Enemark and T. D. P. Stack, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 996.
9 M. G. Cory and M. C. Zerner, *J. Am. Chem. Soc.*, 1996, **118**, 4148.
10 G. C. van Stein, G. van Koten, K. Vrieze, C. Brevard and A. L. Spek, *J. Am. Chem. Soc.*, 1984, **106**, 4486.
11 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1999, 195.
12 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Eur. J.*, 1999, **5**, 1862.
13 J. Libman, Y. Tor and A. Shanzer, *J. Am. Chem. Soc.*, 1987, **109**, 5880.
14 H. Mürner, A. von Zelewsky and G. Hopfgartner, *Inorg. Chim. Acta*, 1998, **271**, 36.
15 P. Baret, D. Gaude, G. Gellon and J. L. Pierre, *New J. Chem.*, 1997, **21**, 1255.
16 V. Amendola, L. Fabbrizzi, C. Mangano, P. Palavicini, E. Roboli and M. Zema, *Inorg. Chem.*, 2000, **39**, 5803.
17 N. C. Fletcher, F. R. Keene, M. Ziegler, H. Stoeckli-Evans, H. Viebrock and A. von Zelewsky, *Helv. Chim. Acta.*, 1996, **79**, 1192.
18 G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, 1971, **24**, 275.
19 D. Zurita, P. Baret and J.-L. Pierre, *New J. Chem.*, 1994, **18**, 1143.
20 B. J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire and H. Lip, *Inorg. Chem.*, 1969, **8**, 771.
21 S. F. Mason and B. J. Peart, *J. Chem. Soc., Dalton Trans.*, 1973, 949.
22 CS Chem3D Pro, CambridgeSoft Corporation, Cambridge, MA, 1999.
23 V. Shklover, R. Nesper, S. M. Zakeeruddin, D. M. Fraser and M. Gratzel, *Inorg. Chim. Acta*, 1996, **247**, 237.
24 T. L. J. Huang and D. G. Brewer, *Can. J. Chem.*, 1981, **59**, 1689.
25 N. Fletcher, M. Nieuwenhuyzen and S. Rainey, *J. Chem. Soc., Dalton Trans.*, 2001, 2641.
26 SAINT-NT, Bruker, Madison, WI, 1998.
27 G. M. Sheldrick, in SHELXTL Version 5.0, Madison, WI, 1998.