

Stereoselective coordination chemistry of the tetradentate chelating ligand (2*R*,3*R*)-bis(2,2'-dipyridyl-5-methoxyl)butane †

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The enantiomerically pure ligand L^{3RR} (2*R*,3*R*)-bis(2,2'-dipyridyl-5-methoxyl)butane has been synthesised by linking two 2,2'-bipyridine units with (2*R*,3*R*)-butandiol. The reaction of L^{3RR} with Zn(II) afforded a mononuclear species and the ¹H NMR spectroscopy points to a C₁ symmetry, expected for a distorted trigonal bipyramidal coordination environment. These observations were confirmed by MM2 calculations and electrospray mass spectrometry. The reaction of L^{3RR} with iron(II) indicated the formation of a dinuclear species by mass spectrometry. Solution state CD spectroscopy indicates that both complexes adopt a Λ -configuration, implying a single stranded dinuclear iron(II) complex is present rather than the anticipated triple helical architecture.

Introduction

The self-assembled synthesis of oligonuclear coordination complexes using semi-rigid 2,2'-bipyridine complexes with labile metal ions has led to a wide variety of interesting structural motifs.¹⁻⁴ In particular, helicates composed of one or more organic ligands coordinating a series of metal ions have attracted much attention as they have enabled a critical understanding of synthetic self-assembly procedures to be developed.^{5,6} Careful consideration of the ligand's structure must be made to induce the desired molecular architecture. It must possess two (or more) distinct binding sites separated by a bridging or spacer unit. This linkage, in conjunction with the metal ion's coordination preference, plays a significant role in determining the resulting structure. If the spacer group is short and possesses a high degree of conformational rigidity, the metal binding sites will preferentially coordinate to two (or more) different metal ions.⁷⁻⁹ On the other hand, if a flexible ligand strand is used, the ligand will wrap around a single metal centre (Fig. 1).^{10,11} Recent reports have demonstrated that changing the metal oxidation state^{12,13} or even the phase from a solid to solution state¹⁴ can control these two coordination modes.

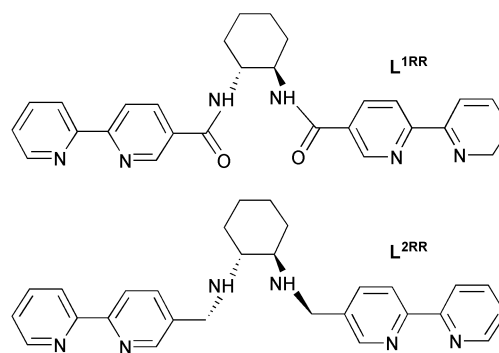


Fig. 1 Dinuclear helicate *versus* mononuclear complex formation.

As part of our ongoing research programme, we have been exploring the principles behind the control of metal centred chirality. Helicates with their sense of right (P) and left (M) handed orientations, offer exceptional opportunities to demonstrate stereoselective control. A number of related studies have demonstrated that the introduction of asymmetric carbon centres,^{5,7,15,16} or more recently controlled atropisomerism,⁸ into the ligand strand allows a preferential helicity to be imposed on the metal centres. To achieve a controllable induction of helicity three forms of chirality must be distinguished. Firstly, the ligands themselves must contain at least one optically active centre (typically denoted by *R/S* notation). Secondly, the coordination environment around the metal centres can adopt either a Δ or Λ orientation and finally, the sense of the helicity of the total structure is identified by M or P. In a recent study with ligand L¹ we reported that triple stranded dinuclear

complexes were observed with cobalt(III), iron(II), cadmium(II) and zinc(II) where in each case the *RR* isomer confirmed a preference for $\Delta\Delta$ metal centred chirality, and P helicity.¹⁷

To further explore the control of the helicity at the metal centre, the degree of flexibility required in the ligand strand to impose a rigorous helicity is being investigated. As a direct comparison to ligand L^{1RR}, ligand L^{2RR} was initially considered with two tetrahedral carbon atoms replacing the two trigonal planar centres adjacent to the bipyridine moieties (Scheme 1). Following a series of ambiguous results though, it was evident that coordination by the diamine spacer itself was playing a dominant role in complex formation leading to tri-, rather than dinuclear helicates.¹⁸ To overcome these difficulties and achieve the desired non-conjugated spacer, weakly coordinating ether linkages were introduced in place of the amine groups. And so we report here a chiral di-ether spacer L^{3RR} and compare the zinc(II) and iron(II) complexes with the related complexes of L^{1RR} (Scheme 2). Since the group priority assignment around the linkage is identical for both (1*R*,2*R*)-diaminocyclohexane and butan-(2*R*,3*R*)-diol, the helicity imposed by the spacer upon the metal coordination should have the same sense of handedness. It is recognised however that the diol is considerably more flexible due to the rotation along the central C–C bond than either ligand L^{1RR} or L^{2RR}.



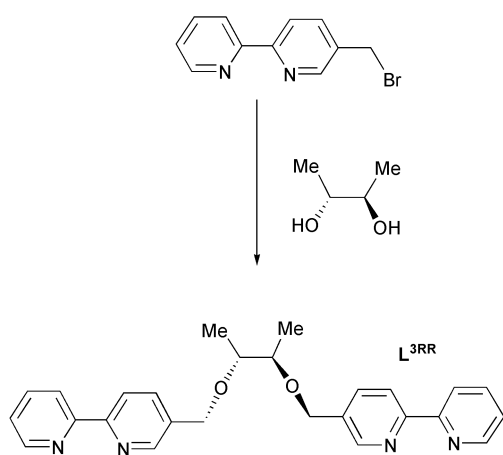
Scheme 1 Previously explored ligand systems.^{17,18}

Results and discussion

Synthesis and characterisation

(2*R*,3*R*)-Bis(2,2'-dipyridyl-5-methoxyl)butane (L^{3RR}) was prepared *via* a Williamson coupling of two equivalents of 5-bromo-methyl-2,2'-bipyridine with butan-(2*R*,3*R*)-diol.¹⁹ Following chromatography, the ligand was isolated in disappointing yield

† Electronic supplementary information (ESI) available: UV/vis absorption spectra of L^{3RR} with FeCl₃ and with Zn(OAc)₂. See <http://www.rsc.org/suppdata/dt/b3/b303803c>



Scheme 2 Synthesis of chiral ligand L^{3RR} .

(32%), although a significant quantity of the intermediate (2*R*)-[(2,2'-dipyridyl-5-methoxy)]-butan-(3*R*)-ol (24%) and the starting material 5-bromomethyl-2,2'-bipyridine (20%) were recovered. ^1H and ^{13}C NMR spectroscopy confirmed the expected structure and it is noteworthy that the ^1H NMR spectrum indicates that the methylene protons of ligand L^3 are prochiral, existing as a pair of well-separated doublets. This is consistent with the non-equivalent environment arising from the adjacent chiral spacer group. EI or CI mass spectrometry gave little indication of the desired ligand, however using softer electrospray ionisation techniques, the molecular ion was detected.

In the previous study, L^{1RR} demonstrated a significant Cotton effect in the circular dichroism (CD) spectrum of the bipyridine $\pi-\pi^*$ transitions.¹⁷ This arises from exciton coupling between the two chromophoric bipyridine groups which adopt a time averaged restricted skewed conformation relative to each other.²⁰ No Cotton effect was observed with ligand L^{3RR} when dissolved in a variety of solvents however. Thus it appears that the two bipyridine chromophores are not conformationally restrained in keeping with the increased rotational freedom along the spacer by moving to a fully nonconjugated linkage. It would therefore be reasonable to assume that the ligand is not adopting a preorganised helical conformation, such as that exhibited by L^{1RR} .

Metal complexes were prepared by the slow mixing of alcoholic solutions of the ligand with the appropriate hydrated iron(II) chloride and zinc(II) acetate salts as previously described.¹⁷ The complexes were isolated by precipitation with ammonium hexafluorophosphate. In common with similar complexes,^{7,17,21} the resulting iron(II) complex indicates a two metal to three ligand stoichiometry, confirmed by microanalysis and electrospray mass spectrometry, where the most intense signal (1825) was attributed to the molecular ion less one of the hexafluorophosphate counter anions. The stoichiometry was further confirmed by carrying out Job plot analysis (Supplementary Data †). UV/Vis absorption spectroscopy indicated complex formation by a red shift in the bipyridine ligand centred (LC) transitions and the appearance of characteristic metal-to-ligand charge transfer (MLCT) absorptions typical of the polypyridine complexes of iron(II) (which gives rise to the an intense pink colour). The complex demonstrated a low resolution ^1H NMR spectrum in both deuterated acetone and DMSO as has been previously observed with related systems and has been attributed to a relatively small ligand field giving rise to a spin crossover situation.^{7,17} However, examination of the protons attributed to the butyl linkage indicated the presence of more than the one set of signals expected for a triple helicate. The initial interpretation of the data indicated that both of the diastereomeric forms (*i.e.* the $\Delta\Delta$ and $\Lambda\Lambda$) were present in solution giving rise to this non-equivalence. However, this appears not to be the case upon subsequent evidence.

The zinc(II) complex was initially synthesised using the anticipated two to three metal to ligand stoichiometry. The resulting complex did not give the expected elemental analysis or electrospray mass spectrum though. The UV/vis absorption spectrum indicated the formation of Zn(II) complexes by an intense absorption at 300 nm attributed to the ligand $\pi-\pi^*$ transitions, a 10 nm shift in absorption when compared to that of the free ligand (Table 1). In order to establish the metal to ligand stoichiometry, a Job plot analysis was carried out (Supplementary Data †). While the largest signal was obtained for a 2 : 3 stoichiometry, the intensity of the sign did not change significantly at low metal ion concentrations (as was observed with ligand L^{1RR})¹⁷ indicating the presence of other species in solution. A strong cluster of signals in the electrospray mass spectrum at 489 to 495 suggested the presence of a one to one ratio of the metal to the ligand with a good match for the theoretical isotopic configuration for $[\text{ZnL}^{3RR}]^+$. In addition, peaks were observed for $[\text{ZnL}^{3RR}]^{2+}$ at 245 and $[\text{ZnL}^{3RR} + \text{K}]^{2+}$ at 265 at lower cone voltages. While the presence of species of higher molecular mass can not be ruled out, the dominance of the 489 peak would indicate the stability of the $[\text{ZnL}^{3RR}]$ species and would be consistent with L^{3RR} acting as a tetradentate ligand to a single metal ion rather than a bridging ligand. Similarly, the elemental analysis indicated a much lower carbon and nitrogen content than anticipated for a triple helicate and was tentatively assigned to $[\text{Zn}(\text{OAc})(\text{L}^{3RR})](\text{PF}_6)\cdot\text{EtOH}$ with a 5-coordinate metal centred geometry in keeping with the ideas discussed subsequently.

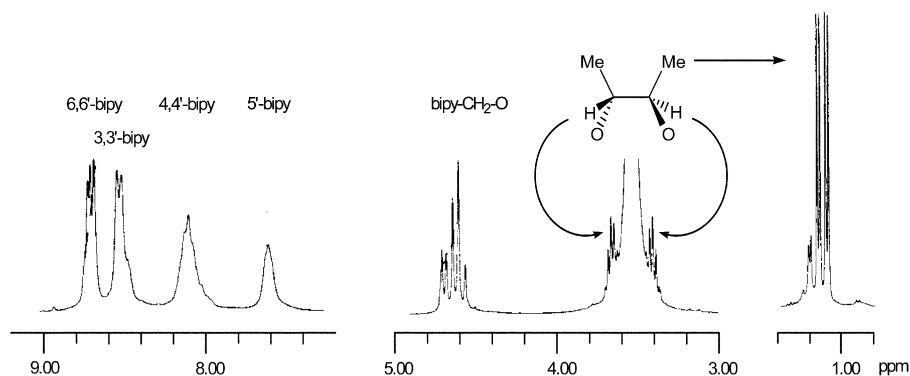
The ^1H NMR spectrum of the isolated zinc complex demonstrated significant broadening of the aromatic signals and two major sets of resonances for each of the aliphatic protons (Fig. 2). The identity of each of the major signals was confirmed by ^1H COSY spectroscopic techniques. The resonances pertaining to the methyl groups are dominated by a pair of doublets of equal intensity although other minor components (<10%) were also observed. A similar situation exists with the protons on the two chiral centres (the two peaks are sitting in the same spectral region as the water associated with the sample and deuterated DMSO making detailed analysis difficult) as well as the prochiral methylene protons where four doublets were identified. The formation of an enantiopure triple helical architecture would lead to a C_3 -axis, and one set of ligand signals reflecting the ligand's symmetry in the ^1H NMR spectrum. A possible interpretation of the observations could be that both diastereoisomers (with either $\Delta\Delta$ or $\Lambda\Lambda$ metal centres) are present. However, it is extremely unlikely that they would be present in equal proportions as the integration appears to suggest. To confirm this fact, variable temperature studies were attempted. On reduction in temperature (in a 50% D_6 -DMSO/ CD_3Cl mixture) the peaks were not observed to either sharpen or change their relative intensities (although the two signals of the protons on the chiral centre were observed to shift up field considerably as temperature is decreased). If two diastereoisomers were present, the relative ratios present should change with temperature with a labile metal such as zinc. An alternative explanation to account for the experimental evidence is that the two different ends of the ligand must be inequivalent in the dominant species present in solution. This can be achieved by having the ligand coordinating in a tetradentate fashion to a single metal centre, rather than the anticipated bridging architecture. This would then give the observed mass spec. peak relating to a $[\text{ZnL}^{3RR}]^{2+}$ ion and confirm the CHN elemental analytical assignment.

Numerous attempts to grow crystals suitable for X-ray structural analysis of both the zinc and iron(II) complexes failed despite changing both solvent and counter anions. Additionally, the iron(II) complex was noted to decompose upon prolonged standing in protic solution to $[\text{Fe}(\text{Mebipy})_3]^{2+}$ (where Mebipy is 5-methyl-2,2'-bipyridine) indicating that the complex is probably not stable in the presence of light over several weeks.

Table 1 UV/Vis and CD spectral data and molar rotations of L^{1RR}, L^{3RR} and their zinc(II) and iron(II) complexes

Complexes	UV/Vis ^a λ_{\max} / nm ($\epsilon \times 10^3/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$)	CD ^a λ_{\max} / nm ($\Delta\epsilon/\text{dm}^{-3} \text{mol}^{-1} \text{cm}^{-1}$)	$[\alpha]_D^a$	Assigned metal centred helicity
L ^{1RR} 17	300 (23.9)	275 (+0.06) 303 (-0.23)	-87.5	—
L ^{3RR}	290 (21.4)	—	-10.7	—
[Zn ₂ (L ^{1RR}) ₃](PF ₆) ₄ 17	289 (85.4)	277 (+48) 303 (-254)	-323	Δ
[Zn(L ^{3RR})(OAc)](PF ₆) ^b	300 (23.4)	293 (-40.1) 316 (+69.6)	-173	Λ
[Fe ₂ (L ^{1RR}) ₃](PF ₆) ₄ 17	290 (108.6) 305 (93.4) 480 (9.8) 541 (10.7)	291 (+102.5) 309 (-252) 396 (+3.4) 486 (-9.1) 566 (+17.0)	-4670	Δ
[Fe ₂ (L ^{3RR}) ₃](PF ₆) ₄	300 (128) 465 (10.0) 522 (14.0)	289 (-417) 307 (+792) 515 (+27) 548 (-6.1)	-8140	Λ

^a All samples recorded in acetonitrile at room temperature (concentration typically $1-2 \times 10^{-5} \text{ mol dm}^{-3}$). ^b Assignment based upon the analytical data. It should be noted however that the likely cation in solution is $[\text{Zn}(\text{L}^{3RR})(\text{CH}_3\text{CN})_2]^{2+}$.

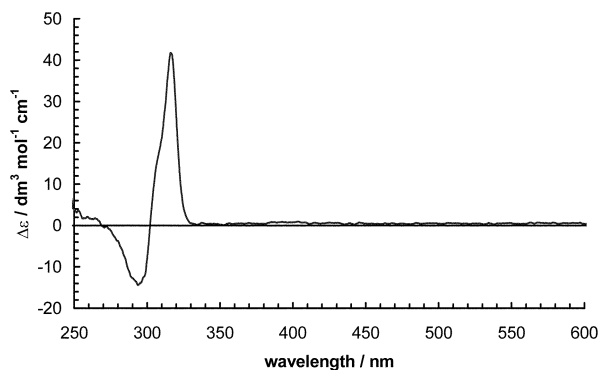
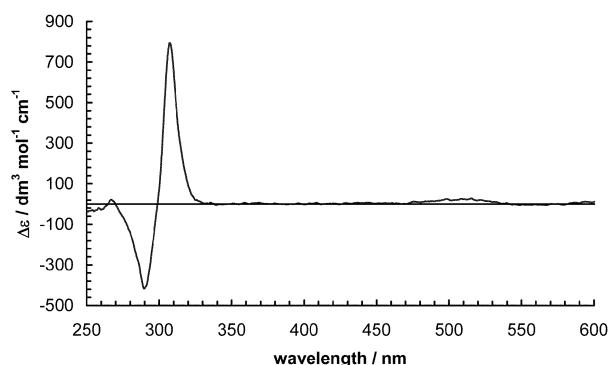
**Fig. 2** ¹H NMR spectrum of $[\text{Zn}(\text{L}^{3RR})(\text{D}_6\text{-DMSO})]^{2+}$ in $\text{D}_6\text{-DMSO}$.

Chiral induction. Since the ¹H NMR spectroscopic studies of both the iron(II) and zinc(II) complexes were ambiguous, the nature of the chiral induction was explored using polarimetry and CD spectroscopy. If two diastereoisomers were present in equal proportion, there would be little or no Cotton effect observed upon complexation, particularly in the iron(II) MLCT interactions (450–600 nm). Polarimetry studies indicate that in each case that a considerably larger value was observed for each complex when compared to the free ligand, as observed with ligand L^{1RR} (Table 1)¹⁷ and in all cases the RR isomer gave a negative rotation in the plane of polarised light as would be expected.

The polarimetry results were confirmed by solution circular dichroism (CD) spectroscopy. The complexes both gave considerable Cotton effects (Figs. 3 and 4) indicative of the two chromophoric bipyridyl groups being brought into a restrained

conformation,²² which has been observed in several similar studies.^{7,23} This orientation of the achiral bipyridine ligands into a helical arrangement is presumed to be due to association of the metal to the ligand. In addition to the enhancement of the ligand centred $\pi-\pi^*$ centred Cotton effects, the involvement of the metal coordination in the reorientation of the ligand is unambiguously confirmed by the appearance of Cotton effects in the Fe(II) MLCT absorptions.

The CD spectra for the complex $[\text{Fe}_2(\text{L}^{3RR})_3](\text{PF}_6)_4$ demonstrate a remarkably large Cotton effect in the ligand centred $\pi-\pi^*$ transitions (approx. 300 nm), while those in the MLCT region are similar to those described for the complex $[\text{Fe}_2(\text{L}^{1RR})_3](\text{PF}_6)_4$.¹⁷ By comparison of the signs of the $\pi-\pi^*$ ligand centred transitions to those of Δ - $[\text{Fe}(\text{bipy})_3]^{2+}$ ²⁴ and the application of exciton theory,²² it appears that the dominant metal centred diastereoisomer has the metal centres placed in a Λ configuration. This contradicts the results we previously

**Fig. 3** CD spectra of $[\text{Zn}(\text{L}^{3RR})(\text{DMSO})]^{2+}$ (DMSO).**Fig. 4** CD spectra of $[\text{Fe}_2(\text{L}^{3RR})_3][\text{PF}_6]_4$ (acetonitrile).

observed with the structurally similar ligand L^{1RR} , where the RR -chirality caused the ligand to twist in such a fashion that a Δ -metal centred helicity is adopted. While the sense of handedness along the axis of the ligand is the same in both cases, the induced complex helicity appears to be opposed. In addition, the strength in π - π^* transitions is much larger than anticipated and could potentially indicate a different type of binding mode. Again the CD spectrum of the Zn complex with L^{3RR} demonstrated much larger Cotton effects per metal centre than had been observed with the ligand L^{1RR} and again the two resulting complexes demonstrated opposing forms of helicity (Table 1). However, it was observed that upon changing solvent to DMSO (Fig. 3), the Cotton effect was substantially diminished, implying the solvent plays a considerable role in the nature of the complex, probably by occupying a free coordination site. Considering that the complexes of L^{1RR} and L^{3RR} all demonstrated the same sign in the polarimetry, but differing signs in the CD spectrum, it should be emphasised that assignment of absolute configuration on metal centred helicity using the former technique ought to be used with extreme care.

To rationalise this discrepancy with our previous results,¹⁷ a search of the Cambridge Crystallographic Structural Database indicated that the diimine complexes of zinc can adopt a wide variety of coordination environments including a number of examples of pseudo-octahedral tris(bipyridine) complexes.²⁵⁻²⁷ Another common arrangement has a penta-coordinate trigonal bipyramidal metal coordination geometry with the two diimines bound to an axial and an equatorial site, with a monodentate group such as the solvent or an appropriate anion assuming the final equatorial position.²⁸⁻³⁰ Ligands possessing two linked diimine ligands offer a wide range of structural motifs. Examples exist where the ligand acts in a tetradentate fashion leading to mononuclear complexes, a solvent or anion bringing the coordination number up to five in a distorted trigonal bipyramidal arrangement.^{11,31} A similar coordination environment has been observed by Harding and co-workers in a dinuclear double helicate with a rigid linkage between the two chelating groups.³² It should be noted though that pseudo-octahedral tris(bipyridine) coordination environments generally lead to triple helicates^{7,8,33} although tetra-nuclear cages have been described.³⁴

In the absence of crystals suitable for X-ray crystallographic analysis, simple molecular mechanics structural optimisations were carried out on the complex $[\text{Zn}L^{3RR}(\text{H}_2\text{O})]^{2+}$ to rationalise the possible identity of the species giving the intense CD activity.³⁵ The $[\text{Zn}(\text{bipy})_2]^{2+}$ unit was restrained to the conformation based on the published crystallographic data for $[\text{Zn}(\text{bipy})_2(\text{H}_2\text{O})]^{2+}$,²⁹ while the ethyl linkage between the two chelating groups was unconstrained. The first observation to be considered is the orientation of the spacer between the two chelating groups, relative to their coordination geometry. Since the preferred trigonal bipyramidal is adopted, the spacer can be connected at either equatorial/equatorial (Fig. 5a), equatorial/axial (Fig. 5b) or axial/axial locations (Fig. 5c). With the ligand L^{3RR} arranged in the former or latter case, the structure always minimised to the equatorial/axial arrangement (Fig. 5b). This structure possesses no axis of symmetry and so the two chelating moieties are inequivalent as observed by ^1H NMR spectroscopy. The other two disfavoured structures would possess a C_2 -axis giving rise to chemical equivalence of the two binding units, as would a dinuclear helical arrangement.

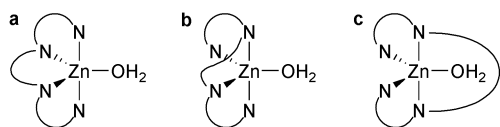


Fig. 5 Possible Δ -configurations of a tetradentate binding in a trigonal bipyramidal Zn(II) complex: (a) equatorial/equatorial, (b) equatorial/axial and (c) axial/axial.

Due to the chiral nature of the bridge (possessing two R -stereotopic carbon atoms), four diastereoisomers are possible. The metal centres can adopt either a Δ or Λ configuration (Fig. 6), while the ligand can twist with either a δ or λ arrangement (Fig. 7). The modelling studies indicated that each of these four configurations gave rise to localised minima at 10.2 ± 0.4 kcal mol⁻¹ for the $\Delta\delta$ diastereoisomer, 12.3 ± 0.5 kcal mol⁻¹ for the $\Lambda\delta$ diastereoisomer, 10.2 ± 0.4 kcal mol⁻¹ for the $\Delta\lambda$ diastereoisomer and 8.6 ± 0.30 kcal mol⁻¹ for the $\Lambda\lambda$ diastereoisomer. Comparison of the relative energies leads to the conclusion that the λ ligand arrangement is lower in energy by approximately 2 kcal mol⁻¹. This would be expected as the *gauche* arrangement of the two methyl groups (as observed in the λ configuration) would be sterically less demanding than when placed *anti* to each other. Secondly, it would appear the two bipyridine ligands adopt a Λ configuration, as observed by CD spectroscopy.

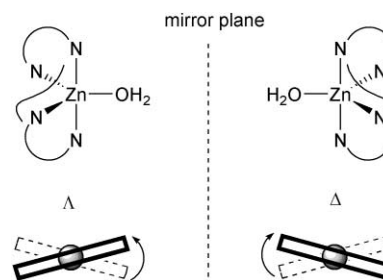


Fig. 6 Skew line system for the chirality descriptors Λ - and Δ - for tetradentate binding in a trigonal bipyramidal Zn(II) complex.

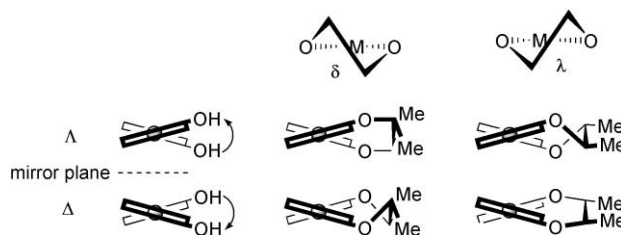


Fig. 7 Schematic illustration of the local minimised configurations of $[\text{Zn}(L^{3RR})(\text{H}_2\text{O})]^{2+}$.³⁵

Attempts to model the zinc complex $[\text{Zn}(L^{1RR})(\text{H}_2\text{O})]^{2+}$ did not result in a low energy form. Considerable strain was evident along the $\text{bipy}-\text{C}=\text{O}-\text{NH}$ groups, with the carbonyl being forced out of planarity with the bipyridine moiety. Hence it can be predicted that ligand L^{1RR} will act as a bridging ligand while L^{3RR} is more likely to act as a tetradentate ligand, forming discrete mononuclear zinc complexes. Since tetradentate systems are going to be less prone to ligand dissociation (chelate effect), it is anticipated that larger Cotton effects will be observed with labile metal ions, in keeping with experimental observations.

The iron(II) complex $[\text{Fe}_2(L^{3RR})_3]^{4+}$ gave very similar Cotton effects to those observed for the zinc complex, with extremely large π - π^* transitions. The two metals possess very similar ionic radii (low spin Fe^{2+} : 0.75 Å and Zn^{2+} : 0.74 to 0.88 Å)³⁶ and so it would be reasonable to assume that the ligand L^{3RR} can bind the iron(II) centre in a tetradentate fashion imposing the same Λ helicity observed with the zinc complex. This would be confirmed by the appearance of the unexpected signals observed in the ^1H NMR spectrum for the complex. Iron(II) differs from zinc(II) though in its preference for a pseudo-octahedral coordination sphere with diimine ligands. To compensate, a second ligand must then bridge between the two metal centres forming a single stranded structure as illustrated in Fig. 8b. Due to the number of degrees of freedom associated with the complex $[\text{Fe}_2(L^{3RR})_3]^{4+}$, it has been impossible to perform molecular mechanic calculations on either the single stranded or the triple stranded architectures. However, the previous

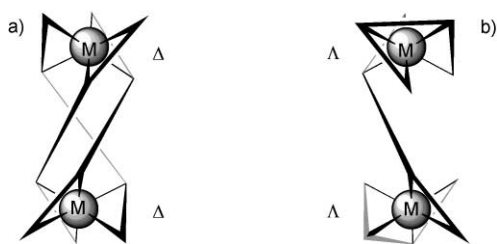


Fig. 8 Illustration of the assumed different binding modes for the complex (a) $\Delta\Delta$ - $[\text{Fe}_2(\text{L}^{3RR})_3]^{4+}$ and (b) $\Lambda\Lambda$ - $[\text{Fe}_2(\text{L}^{1RR})_3]^{4+}$.

studies with ligand L^{1RR} implies that RR -chirality in the ligand strand imposes a Δ (or P) helicity in a triple stranded architecture, confirmed by CD spectroscopy. It would be reasonable to assume that the ligand L^{3RR} (with the same sense of twisting down the ligand length) would impose the same chirality in a triple stranded structure. However, when wrapped around a single metal centre it appears to predetermine a Λ (or M) form. Amendola *et al.* observed that the RR -diaminocyclohexyl spacer did in fact impose a Λ (M) helicity in a dinuclear double helicate.¹⁶

Examination of the results indicates that there does not appear to be a general rule to predict the helicity by simply using the chirality of the ligand strands. The “chiragen” type ligands prepared by von Zelewsky’s group have been observed to impose the same sense of metal centred helicity in a tetradentate binding fashion¹⁰ as well as in the formation of a dinuclear triple helicate.⁷

Conclusions

The new ligand system described has the potential in solution to wrap around a single metal giving either mononuclear architectures as observed in the presence of zinc(II) or dinuclear complexes with iron(II). Due to the similarity and strength of the Cotton effect observed in the CD spectra it would be appropriate to assume that the ligand binds to the iron(II) centre in a tetradentate fashion forming a single stranded complex rather than the anticipated triple helicate. However, given the considerable strength of the Cotton effect related to the π - π^* ligand centred transitions it would appear there is virtually complete control of the diastereoisomerism. The precise nature of the zinc complexes has not been fully ascertained in the study as in the solution phase the fifth coordination site appears to be extremely labile, with rapid substitution with either anions, or coordinating solvent depending on the conditions. Also it is noted that the species present in solution would probably not be representative of the crystalline material.

With the ligand systems L^{1RR} and L^{3RR} explored in this study and a number of related but as yet unpublished ligands, a pattern is beginning to emerge. Hindered rotation along the six atom linkage between the two chelating sites leads to the formation of a triple helicate, and the RR -ligand centred chirality leading to the Δ (or P) handedness (all examples studied have the same group priority in the assignment of the carbon centred chirality). With an increase in the degrees of freedom between the two chelating groups, structurally similar ligands act as tetradentate ligands to a single metal centre, the RR -isomer leading to a Λ form. In the current study, it appears that this apparent inversion of chirality is consistent with moving from dinuclear triple helical architecture to a tetradentate binding mode.

Experimental

Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker 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 – 2×10^{-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 – 2×10^{-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 – 2×10^{-5} mol dm^{-3} for all other samples). Microanalyses were performed by ASEP, the School of Chemistry, the Queen’s University of Belfast. The electrospray mass spectroscopy was performed by the EPSRC mass spectroscopy service, the University of Wales, Swansea.

Materials

(–)-Butane-(2*R*,3*R*)-diol (Aldrich 98%), hydrated iron(II) chloride (Aldrich) and zinc acetate (Aldrich) were used as received. Tetrahydrofuran (thf) was distilled under N_2 from potassium. 5-Methyl-2,2′-bipyridine³⁷ and 5-bromomethyl-2,2′-bipyridine³⁸ were prepared according to published procedures.

(2*R*,3*R*)-Bis(2,2′-dipyridyl-5-methoxy)butane (L^{3RR})

Butane-(2*R*,3*R*)-diol (0.11 g, 1.26 mmol) was mixed in dry thf with NaH 60% dispersion in mineral oil (0.40 g, 10.0 mmol) and stirred at room temperature for 40 min under nitrogen. When effervescence ceased, 5-bromomethyl-2,2′-bipyridine (1.09 g, 4.23 mmol) was added and the mixture subsequently refluxed for 24 h. After cooling to room temperature, the solid was removed by filtration through Celite®. The solvent was removed *in vacuo* and the brown residue was taken up in water (50 ml), extracted into dcm (3×50 ml), dried over MgSO_4 and the solvent removed. The crude product was chromatographed on silica eluting with 2% methanol in dcm and the third fraction collected. Removal of the solvent under reduced pressure gave a brown solid. Recrystallization from methanol gave colourless fine needle like crystals. Yield: 180 mg, 32%. Melting point: 60–64 °C, Found C 63.44, H 4.68, N 11.39%; analysis calculated for $\text{C}_{26}\text{H}_{26}\text{O}_2\text{N}_4 \cdot 3.5\text{H}_2\text{O}$: C 63.80, H 6.74, N 11.45%. ^1H NMR (300 MHz, CDCl_3) δ 1.23 (6H, d, $J = 6.6$ Hz, $-\text{CH}_3$), 3.63 (2H, m, $-\text{CH}-$), 4.69 (2H, m, $-\text{CH}_2-$), 7.30 (2H, d/d, $J = 4.8$ and 7.5 Hz, bipyH^5), 7.76 (2H, d/d, $J = 2.0$ and 7.9 Hz, bipyH^4), 7.80 (2H, d, $J = 7.7$ Hz, bipyH^4), 8.33 (2H, d, $J = 7.9$ Hz, bipyH^3), 8.40 (2H, d, $J = 8.6$ Hz, bipyH^3), 8.63 (2H, d, $J = 4.7$ Hz, bipyH^6), 8.69 (2H, s, bipyH^6). ^{13}C NMR (300 MHz, CDCl_3) δ 15.7, 30.72, 68.6, 121.4, 122.1, 123.6, 134.3, 136.4, 137.14, 148.6, 150.0, 157.1. ES-MS: m/z 427 (100%, MH^+).

$[\text{Fe}_2(\text{L}^{3RR})_3][\text{PF}_6]_4$

A solution of $\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$ (30.4 mg, 0.14 mmol) in ethanol was added into a solution of L^{3RR} (90.0 mg, 0.21 mmol) in ethanol giving a dark red solution. The mixture was heated at reflux under nitrogen for 6 h. After cooling the solvent was removed *in vacuo*. The solid residue was dissolved in a small amount of water (15 ml) and the complex precipitated by the addition of excess NH_4PF_6 and collected on Celite® by filtration and washed with diethyl ether (15 ml). It was redissolved in acetone and precipitated with diethyl ether three times to obtain a red powder. Yield: 120 mg, 86%. Found C 44.32, H 4.32, N 7.77%; analysis calculated for $\text{C}_{78}\text{H}_{78}\text{N}_{12}\text{O}_6\text{Fe}_2\text{P}_4\text{F}_{24} \cdot 8\text{H}_2\text{O}$: C 44.29, H 4.48, N 7.95%. ^1H NMR (300 MHz, Acetone- D_6) δ 0.66 (d, $J = 5.1$ Hz, CH_3), 0.99 (d, $J = 5.4$ Hz, $-\text{CH}_3$), 3.29 (m, $-\text{CH}-$), 3.48 (m, $-\text{CH}-$), 4.46 (2H, br, $-\text{CH}_2-$), 7.29 (1H, br, bipyH^5), 7.40 (2H, br, $\text{bipyH}^{4,4'}$), 8.00 (2H, br, $\text{bipyH}^{3,3'}$), 8.09 (1H, br, bipyH^6), 8.49 (1H, br, bipyH^6). ES-MS: m/z 1826 (100%, $[\text{M} - \text{PF}_6]^+$), 1681 (50%, $[\text{M} - 2\text{PF}_6]^+$), 1533 (15%, $(\text{M} - 3\text{PF}_6)^+$).

[Zn(OAc)(L^{3RR})](PF₆)

A solution of Zn(OAc)₂·2H₂O (22.0 mg, 0.10 mmol) in methanol (10 ml) was added into a solution of L^{3RR} (41 mg, 96 μmol) in methanol (5 ml) and the mixture stirred for 16 h. The solvent was removed *in vacuo* and the solid residue was dissolved in a small amount of water (10 ml) and the complex precipitated by the addition of a saturated aqueous solution of ammonium hexafluorophosphate. The precipitate was collected by filtration and recrystallised from ethanol. After drying *in vacuo* a white powder was obtained. Yield: 46 mg, 62%. Found C 48.70, H 4.84, N 7.36%; analysis calculated for C₂₈H₂₉N₄O₄Zn·EtOH: C 48.56, H 4.75, N 7.55%. ¹H NMR (300 MHz, DMSO-D₆, RT) δ 1.03 (3H, d, *J* = 6.3 Hz –CH₃), 1.17 (3H, d, *J* = 6.3 Hz –CH–), 3.40 (1H, m, –CH–), 3.66 (1H, m, –CH–), 4.66 (2H, m, –CH₂–), 7.63 (2H, br, bipyH⁵), 8.09 (4H, br, bipyH^{4,4'}), 8.46 (4H, m, bipyH^{3,3'}), 8.75 (4H, m, bipyH^{6,6'}). ES-MS: *m/z* 489 (100%, [ZnL^{3SS}]⁺).

Molecular mechanics modelling studies were carried out using standard MM2 organic parameters provided by Chem3D.³⁵ The bond lengths and angles for the complex [Zn(L^{3RR})(H₂O)]²⁺ complex were constrained using data from the crystal structure of [Zn(bipy)₂(H₂O)]²⁺.²⁹ (Bond lengths Zn–O: 2.06, Zn–N (axial): 2.11, Zn–N (equatorial): 2.08, bipyridyl C–N: 1.36, C–C: 1.40, 1.41 and 1.465 Å; bond angles O–Zn–N: 90 and 123°, N–Zn–N: 79 and 180°.) The target configuration was arranged roughly by eye, and the energy minimized at an RMS gradient of 0.010 kcal mol⁻¹. The procedure was repeated on five independent arrangements ensuring that in each case the desired target configuration was obtained for each of the four structural configurations considered. Four local minima were identified, (a) (Δδ) minimised to 10.2 ± 0.4 kcal mol⁻¹, (b) (Λδ) minimised to 12.3 ± 0.5 kcal mol⁻¹, (c) (Δλ) minimised to 10.2 ± 0.4 kcal mol⁻¹, (d) (Λλ) minimised to 8.6 ± 0.30 kcal mol⁻¹.

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