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Perspective Article

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***mer* and *fac* isomerism in tris chelate diimine metal complexes**

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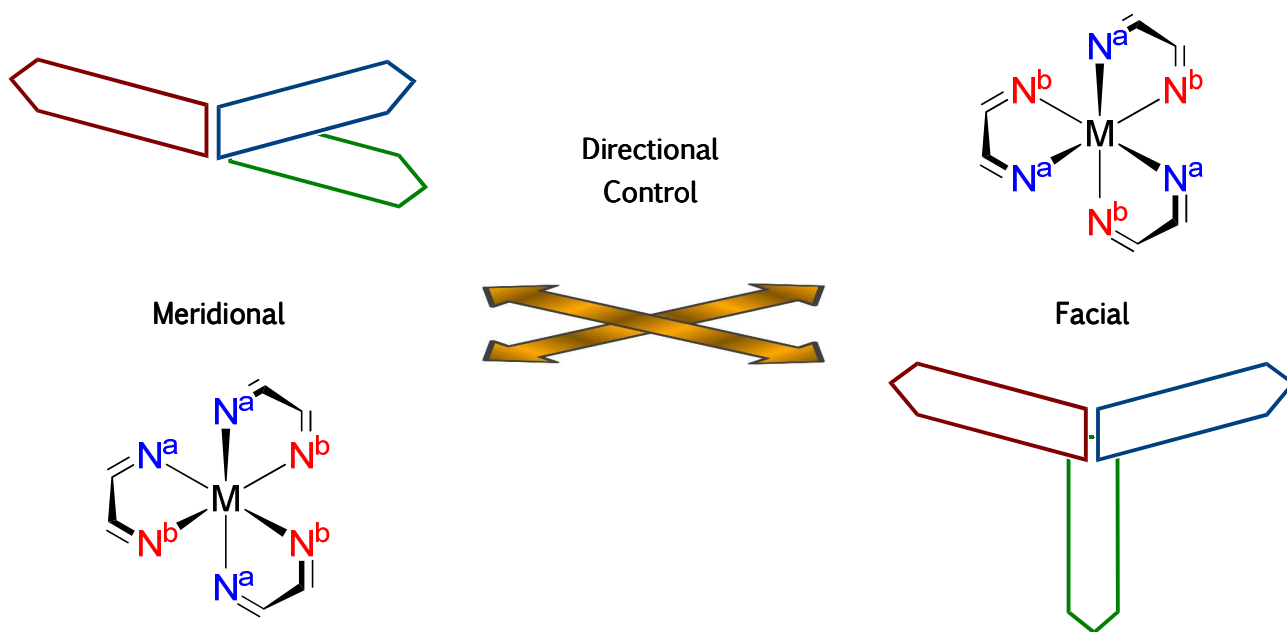
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ABSTRACT

In this perspective, we highlight the issue of meridional (*mer*) and facial (*fac*) orientation of asymmetrical diimines in tris-chelate transition metal complexes. Diimine ligands have long been the workhorse of coordination chemistry, and whilst there are now good strategies to isolate materials where the inherent metal centered chirality is under almost complete control, and systematic methodologies to isolate heteroleptic complexes, the conceptually simple geometrical isomerism has not been widely investigated. In systems where the two donor atoms are significantly different in terms of the σ -donor and π -accepting ability, the *fac* isomer is likely to be the thermodynamic product. For the diimine complexes with two trigonal planar nitrogen atoms there is much more subtlety to the system, and external factors such as the solvent, lattice packing and the various steric considerations play a delicate role in determining the observed and isolable product. In this article we discuss the possibilities to control the isomeric ratio in labile systems, consider the opportunities to separate inert complexes and discuss the observed differences in their spectroscopic properties. Finally we report on the ligand orientation in supramolecular systems where facial coordination leads to simple regular structures such as helicates and tetrahedra, but the ability of the ligand system to adopt a *mer* orientation enables self-assembled structures of considerable beauty and complexity.

SYNOPSIS



This overview analyzes the delicate interplay of the factors that control *mer* and *fac* isomerism in diimine tris-chelate complexes, giving consideration to the distribution of products in labile systems, the methods to isolate inert complexes and the implications to self-assembled coordination cages.

BIOGRAPHIES

Serin Dabb

Serin Dabb is currently an Executive Editor at the Royal Society of Chemistry, responsible for the database portfolio. She previously worked as a Post-Doctoral Research Associate with Nick Fletcher at Queen's University Belfast, studying ruthenium bipyridyl complexes and their potential biomimetic applications. She gained her Post-Graduate degree at the University of New South Wales in Sydney, Australia with Professor Barbara Messerle.

**Nick Fletcher**

Nick Fletcher graduated from Bristol University (1991) and completed his DPhil at the Oxford University under Prof. Paul Beer (1995). He then undertook postdoctoral research positions with Prof. A von Zelewsky (Fribourg, Switzerland), Prof Richard Keene (James Cook University, Townville, Australia) and Prof. Mike Ward (Bristol, UK) before being appointed as Lecturer, and then Senior Lecturer at Queen's University Belfast in 1999. Over this time he has developed a keen interest in the structural considerations in discrete transition metal complexes, with particular emphasis on their application in sensing within a biological environment. He will shortly be moving to take up a new post at the recently re-opened Chemistry department at Lancaster University.



1.0 INTRODUCTION

Chelating diimine ligands, including 2,2'-bipyridine, 1,10-phenanthroline and 2-iminopyridines have been in the vanguard of many areas of chemistry having found diverse applications ranging from material science and nanotechnology through to biological sensing and drug delivery.¹ In particular tris-chelate transition metal complexes have been studied to great effect given their relative stability and close to optimal metal centred “octahedral” coordination geometry. As highlighted in many undergraduate text books,^{2,3} these structures have an inherent chirality, resulting in a Δ and Λ helicity. This has been the focus of a number of studies dating back as far as 1949 when the complexes $[M(L)_3]^{2+}$ (where L = 2,2'-bipyridine (bpy) or phenanthroline (phen) and M = Fe, Ru and Os) were separated into the two enantiomers through the pioneering work of Dwyer⁴⁻⁶ by the co-crystallization with antimonyl-(+)-tartrate. Systematic control of the metal centred chirality has now become fairly routine though the seminal work reported by the research groups of von Zelewsky,⁷⁻⁹ Keene¹⁰⁻¹² and more recently by Meggers.^{13,14} Further to this, a number of different synthetic strategies have also been developed to isolate, and purify, a very wide variety of heteroleptic complexes¹⁵⁻¹⁹ providing routes to isolate a wonderful range of transition metal complexes with diverse and tuneable electronic and photophysical properties.

When attempting to prepare complexes with appropriate structural integrity to incorporate a “recognition” site adjacent to a rigid and well defined metal coordination site, we encountered a further problem with diimine tris-chelating complexes. In systems where the two donor sites within a bidentate ligand are dissimilar, the metal centred coordination can result in the formation of two geometric stereoisomers, namely the meridional (*mer*) and facial (*fac*) forms (Figure 1). In ligand systems where the two coordinating atoms are different, they can be readily separated, or selectively prepared. For example, both the *mer* and *fac* isomers of the cyclometallated iridium(III) complexes, bearing ligands derived from the parent 2-phenylpyridine are easily accessible.²⁰⁻²³ These are generally isolated initially as the kinetically favoured *mer* isomer, which can then be converted to the *fac* isomer on heating presumably as a result of an electronic *trans*-influence. Diimine tris-chelates complexes rarely show sufficient variance in the electronic behaviour between the two donor atoms to allow one of the isomers to be favoured over the other, although steric and secondary interactions can play a major role in determining the final ratio of the two forms as discussed below. Assuming that the two binding sites of the ligand do not differ significantly in their ability to act as both σ -donors and π -acceptors, and that there are no significant steric constraints, a 3 to 1 ratio of the *mer* isomer to the *fac* isomer would be anticipated on simple statistical arguments. This ratio between the two isomers can be readily determined by ¹H NMR spectroscopy, the *mer* isomer has no planes of symmetry, or axes of rotation, making the three ligands inequivalent. On the other hand, the *fac* isomer, has a C_3 axis of rotation giving full equivalence of all three ligands in a heteroleptic system.

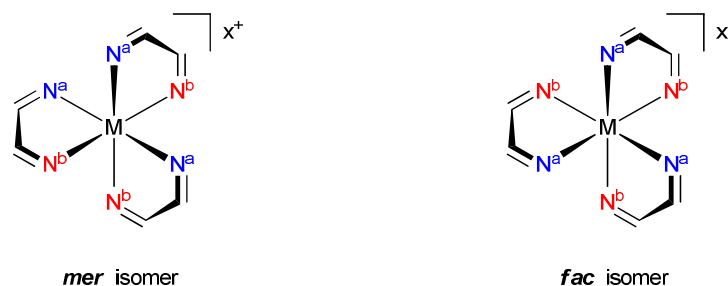


Figure 1. Schematic representation of *mer* and *fac* isomerism in diimine tris-chelate metal complexes.

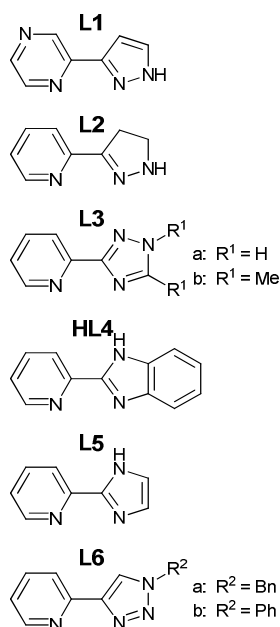
Despite the lack of general methodology to control and isolate diimine complexes of known and defined geometrical integrity, the possibility of *mer* / *fac* isomerism in such relatively simple systems has long been recognized. The kinetically inert systems such as the homoleptic pyridylpyrazole^{24,25} and pyridyloxazole and thiazole²⁶⁻²⁸ complexes of ruthenium(II) were identified and characterized using ¹H, ¹³C and even ⁹⁹Ru NMR studies over 30 years ago. Such species have very well defined photophysical characteristics,²⁹ including a long lived metal-to-ligand triplet states, but given the relatively small number of reported examples where they have been separated into the two isomeric forms, there is as yet, no clear indication as to what the effect the isomerism has on their behaviour, which will be addressed in the later sections of this article.

With more labile metal centres, such as iron(II), cobalt(II) and zinc(II), the matter has not perhaps been as readily accessible until recently where the aggregation of these simple units into large supramolecular assemblies such as helicates,³⁰⁻³³ tetrahedral capsules³⁴⁻³⁷ and even larger units³⁸ can require the selective organization of these units into the statistically less favoured *fac* isomer. Further, the packing and relative orientation of the *mer* and *fac* geometry in iron(II) complexes in the solid-state for application as spin-crossover species appears to be critical to the all important transition temperatures.³⁹ This article reviews the methodologies that can be adopted to control the geometrical isomerism in non-symmetric diimine systems, towards a perspective in the possible exploitation of these two structural configurations. As illustrated, these species offer a wide variety of opportunities in the isolation of rigid and well defined three dimensional structures and materials with tuneable function and behaviour.

2.0 CONTROL WITH LABILE METAL IONS

Until relatively recently, the art of specifically isolating either the *mer* or the *fac* isomer of the first row transition metal tris(diimines) has relied upon either selective crystallization or differential solubility with the isomer isolated and characterized in the solid-state. For example, the complexes [Fe(L1-L3)₃] were found to crystallize in the *mer* isomeric form,⁴⁰⁻⁴⁴ as does the complex [Co(L4)₃].⁴⁵ In keeping with this, the paramagnetic “spin-crossover” complex [Fe(HL4)₃](ClO₄)₂ has also been tentatively assigned as the *mer* isomer based on the results from magnetic-perturbation Mössbauer spectroscopy.⁴⁶ But changing the anion and solvent permitted selective isolation of the *fac* isomer as an open hexagonal network.⁴⁰ Generally however, these will re-isomerise upon solvation to form the statistically favoured 3 *mer* to 1 *fac* ratio, making it an unfavourable ‘permanent’ separation technique. Gaining a significant dominance of a single species

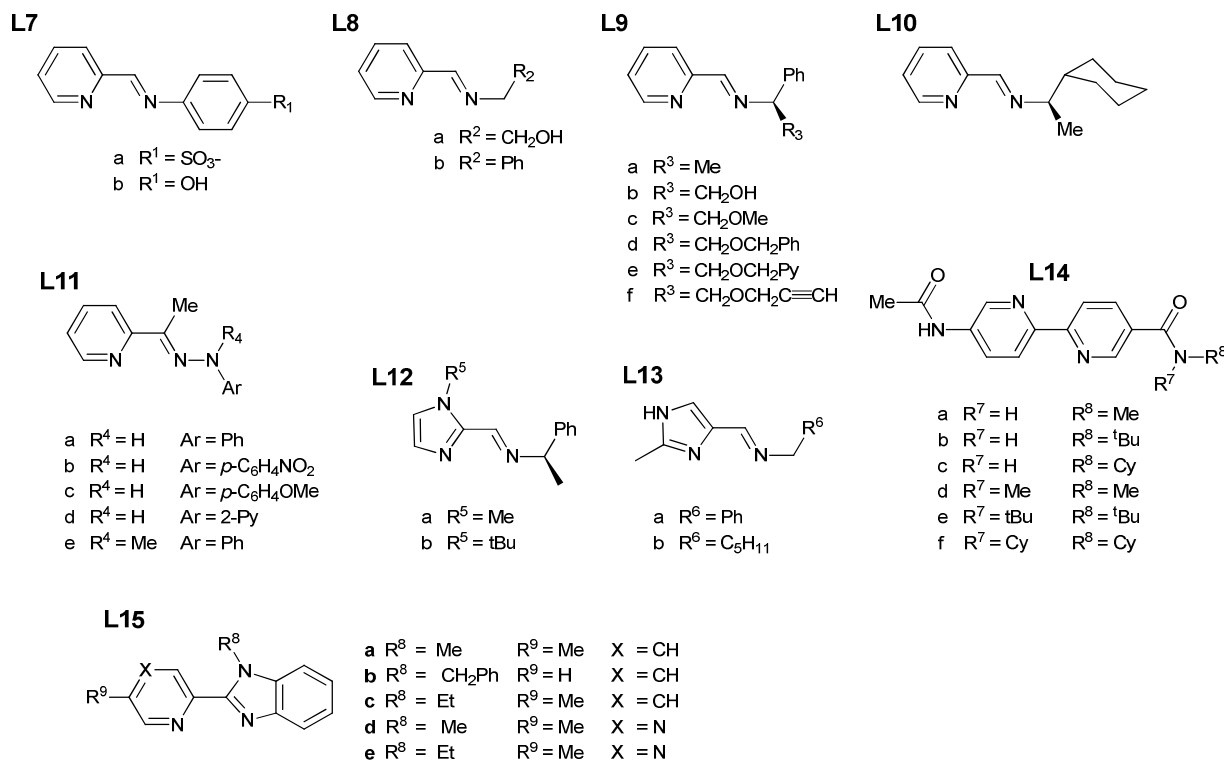
in solution remains problematic; in the case of $[M(L5)_3]^{x+}$ (where $M = Ni^{II}$, Co^{II} and Fe^{II}) the solution was shown to have both isomers present, although with the oxidized Co^{III} complex there is a surprisingly high 15 to 1 ratio in favour of the *mer* isomer.⁴⁷ A dynamic mixture of the two isomers of the Fe^{II} complex of the “click” pyridyl-triazol ligand was similarly observed, but on crystallization $[Fe(L6a)_3](BF_4)_2$ forms exclusively the *fac* isomer, although $[Fe(L6b)_3](BF_4)_2$ forms the *mer* isomer, presumably due to favourable intermolecular packing interactions in the solid-state.⁴⁸



Scheme 1. The identity of ligands L1 to L6.

Nitschke and co-workers noted that the complexes $[Fe(L7a)_3]^-$ and $[Fe(L8a)_3]^{2+}$ gave the anticipated 3 *mer* to 1 *fac* ratio of isomers,⁴⁹ but significantly the selective isolation of the *fac* isomers of a number of first row transition metal complexes was achieved by Howson and Scott with simple derivization. They showed that the *in situ* formation of $[Fe(L7b)_3](ClO_4)_2$ resulted in a 15 *mer* to 1 *fac* ratio,^{50,51} presumably as a result of strong steric interactions, while N-benzyl-1-(pyridin-2-yl)methanimine (L8b) with Fe^{II} resulted in a tris-chelate with a 2 to 1 ratio for the *mer* and *fac* isomers. With the addition of a methyl group to form a range of N-benzyl-1-(pyridin-2-yl)ethanimine derivatives (L9), the resulting additional steric and inter-ligand π -stacking constraints cause an almost complete (> 200 to 1) formation of the *fac* form of the complex $[M(L9)_3]^{2+}$ (where $M = Fe^{II}$, Mn^{II} , Ni^{II} , Co^{II} and Co^{III}).^{50,51} It was also found that this ligand could induced good control over the chirality at the metal centre. The importance of internal π -stacking interactions are clearly evident given that changing the phenyl group to cyclohexyl ring reduces the selectivity for the *fac* isomer to a 2.6 to 1 ratio (complex $[Fe(L10)_3](ClO_4)_2$), as does changing the metal ion to Zn^{2+} . Interestingly the Cu^{II} complex $[Cu(L9a)_3](ClO_4)_2$ crystallizes exclusively as the *mer* isomer where it appears that Jahn-Teller distortions can also perturb the π -stacking interactions necessary for the dominance of the *fac* form, although the metal centred chirality is unaffected.⁵² The structurally similar keto-hydrazone ligands L11 have also been observed to form exclusively *fac*- $[Fe(L11)_3](ClO_4)_2$, and in the case of ligand L11a the formation of optically pure conglomerates from a racemic solution.⁵³ *Fac* geometries were also observed in changing the pyridyl function for an imidazole group in the complex $[Fe(L12)_3](ClO_4)_2$, although these proved to be paramagnetic.⁵⁰

In a related spin-crossover system reported by Matsumoto and co-workers, $[\text{Fe}(\text{L13a})_3]^{2+}$ can be isolated as a “cubane” cluster of the *fac* isomer from ethanol and as the *mer* isomer from methanol, with each material displaying switchable paramagnetic behaviour.^{54,55} The complex $[\text{Fe}(\text{L13b})_3]^{2+}$ was also isolated as the *fac* isomer⁵⁶ with a similar structure to that of $[\text{Fe}(\text{L13a})_3]^{2+}$ suggesting that there may be rules governing the selective crystallization and possibilities to tune procedures to isolate materials with precisely controlled geometries in the solid-state.



Scheme 2. The identity of ligands L7 to L15.

With labile tris-chelate complexes comprising non-symmetric 2,2'-bipyridine ligands there have been relatively few attempts to rationalize and control the relative stereochemical ratio of the two isomers. To highlight one significant example, the group of Ishida demonstrated that with a series of unnatural amino acids (L14) in the presence of Fe^{II} , that a degree of control over the dominant isomer could be introduced. By studying $[\text{Fe}(\text{L14})_3](\text{SO}_4)$ in methanol and water, the primary amides (L14a-c) showed a *mer* to *fac* ratio of close to the statistical 3 to 1 ratio, but in moving to the bulky secondary amides (L14d-f) the ratio moved to 13 *mer* to 1 *fac* in the case of L14f, suggesting that the *mer* isomer is the more favourable form in sterically demanding situations.⁵⁷

The nature of the lability in such systems was first systematically studied by Williams and co-workers⁵⁸ whilst looking at the preparation of helicates as discussed in a subsequent section. The complex $[\text{Co}(\text{L15a})_3]^{2+}$ showed that the rate of the interconversion of the *mer* and *fac* isomers was of the order of 1.6 s^{-1} in acetonitrile, with pressure dependence suggestive of a dissociatively activated process, and that the *mer* and *fac* complexes of the inert Co^{III} complexes $[\text{Co}(\text{L15a})_3]^{3+}$ (following oxidation from the labile Co^{II} precursor) could be separated on a Dowex 50WX2 cation-exchange resin, with an X-ray structure determination of the *fac*-isomer.⁵⁹ L15a also reacts with

[Ru(DMSO)₄Cl₂] in ethanol to give statistical 3 to 1 mixtures of the *mer* and *fac* isomers, but it was noted that in more polar solvents the system shows a degree of lability and that the free energy favours the *mer* isomer, which is the only form observed in acetonitrile or methanol.⁶⁰ For the complex [Ru(L15a)₃]²⁺, the *mer* / *fac* conversion takes several days (and could be separated by cation-exchange chromatography using Sephadex SP C-25, eluted with antinomyl sodium tartrate), but the related complex [Ru(L15b)₃]²⁺ only provides the *mer* form after chromatography. The Os^{II} complex [Os(L15a)₃]²⁺ has also been prepared and separated into Δ -*mer*, Λ -*mer*, and *rac-fac* isomers using the same procedure, and slight differences were observed in the photophysical and electrochemical properties of the respective compounds.⁶¹

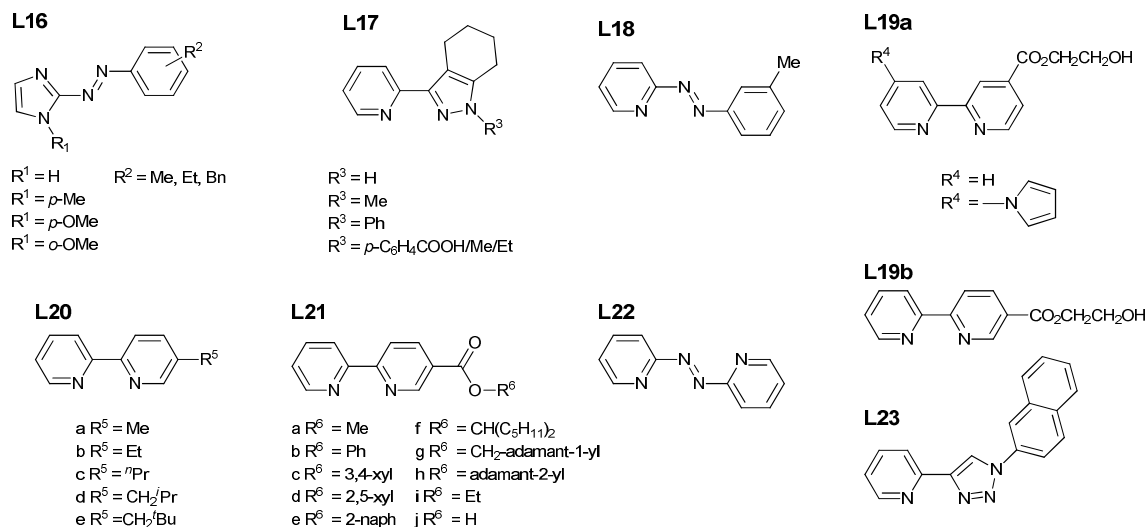
On balance labile diimine systems do generally support the statistically preferable 3 to 1 ratio in favour of the *mer* form, although steric interactions can drive the system to demonstrate higher proportions of the *mer* isomer. As Piguet and co-workers have recently reported,⁶² the possibilities to observe a thermodynamic *trans*-influence remains slight, although it should theoretically favour the *fac* isomer. Certainly given the evidence with 2,2'-bipyridine type systems, this effect is so weak as to be regarded as being negligible. Yet in providing sufficiently dissimilar imines within the chelate, such as with the L15 family, Piguet's group have illustrated a simple approach for potentially quantifying this effect in the complexes [Zn(L)₃]²⁺ (where L is L15a, c, d and e). In line with statistics, the triply degenerated *mer* isomers are stabilized by between 0.8 and 4.2 kJ/mol for the *mer* to *fac* exchange over their non-degenerate *fac* analogues, and so show no apparent *trans*-influence at room temperature. But the dissection of the free energy terms into the *fac* favouring enthalpic, and the *mer* favouring entropic contributions reveals a weak *trans* influence assigned to solvation processes in polar solvents, although for [Zn(L15c/d)₃]²⁺ it is over an order of magnitude smaller than the chelate effect. But a weak templating effect provided by additional inter-ligand cooperativity, such as π -stacking as in the case of Scott's complexes, or the inclusion of a weakly coordinating lanthanide template ion as in the cases subsequently discussed from the Piguet group, can be used to produce the wanted *fac* isomer at room temperature.

3.0 SEPARATION OF KINETICALLY INERT MATERIALS

Given the inertness of the *mer* and *fac* isomers of the late transition metal diimine complexes, separation can theoretically be achieved, and consequently the differences in their physical properties investigated. The complexes of Ru^{II} in particular have found widespread application as photosensitizers, photocatalyst, sensors and molecular probes. And yet a detailed and systematic understanding of how their properties vary with the geometrical arrangement has surprisingly not been undertaken, probably due to the intrinsic difficulty in isolating isomerically pure materials.

There are a few cases where only one geometrical form is recovered following the synthesis in keeping with labile species discussed above, but in general the diimine complexes of the second and third row transition metals are isolated as a mixture of the two forms, typically in the 3 *mer* to 1 *fac* ratio, such as for example with [Ru(L5)₃]²⁺.⁴⁷ There are a couple of exceptions to this however worth commenting upon. In the case [Ru(L16)₃]Cl₂ only the *mer* isomers were identified in 55 to 70% yield,⁶³ and similarly with [Ru(L17)₃](PF₆)₂,⁶⁴ presumably because of unfavourable steric interactions in the *fac* configuration. In an interesting example from 40 years ago, Chakravorty and co-workers report that for [Ru(L18)₃], if produced in a stepwise procedure from *trans*-Py-*Cis* _{α} -[Ru(L18)₂(OH₂)₂]²⁺, only the *mer* isomer was obtained, while if the *cis* _{β} -[Ru(L18)₂(OH₂)₂]²⁺

starting material was used, in theory a 50% mixture of the *mer* and *fac* isomers should be observed, although in this case, this also favoured the *mer* isomer, again presumably due to steric constraints.⁶⁵



Scheme 3. The identity of ligands L16 to L23.

Somewhat surprisingly Grabulosa *et al.* found in the 4-functionalized 2,2'-bipyridine ligand L19 that only the *fac*-isomer was present in the tris-chelate system $[\text{Ru}(\text{L19})_3]^{2+}$ following preparation from RuCl_3 under microwave irradiation (250W at 200 °C). This implies that under these conditions that a *trans* influence is present that makes the *fac* isomer the more thermodynamically stable product.⁶⁶ This has not been the case in our own studies where we found that a systematic increase in the size of the appended substituents at the 5-position of 2,2'-bipyridine resulted in considerable discrepancies in the *mer* to *fac* ratio following a traditional overnight reflux in ethanol, ethylene glycol or DMF resulting in the stable complexes $[\text{Ru}(\text{L20})_3]^{2+}$. It became apparent that the size of the appended substituent has a direct influence on the ratio of the two isomers; complexes $[\text{Ru}(\text{L20a/b})_3]^{2+}$ gave the anticipated 3 *mer* to 1 *fac* ratio in the ^1H NMR spectra, whilst this ratio moved in favour of the *mer* isomer for the complexes comprised of L20c and L20d, whilst for the complex $[\text{Ru}(\text{L20e})_3]^{2+}$ only the *mer* isomer was observed.⁶⁷ For complex $[\text{Ru}(\text{L20a})_3](\text{PF}_6)_2$, the two forms were both present in the crystal lattice, with the appropriate methyl group disordered over two positions. The ^1H -NMR spectra of these species were remarkably similar, and in this case, only careful examination of the H6' proton resonance permitted determination of the relative abundance of the two geometrical isomers.

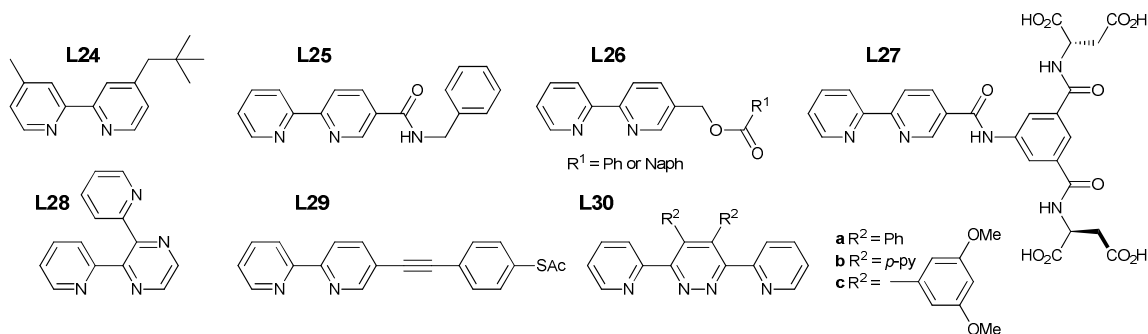
We also found that with ligands L21 their reaction with $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ gives rise to tris-chelate Ru^{II} complexes which show an unusually high proportion of the *fac*-isomer judged by ^1H NMR spectroscopy following conversion to the methyl ester complex $[\text{Ru}(\text{L21a})_3]^{2+}$.⁶⁸ The initial reaction appears to have a degree of thermodynamic control with the steric bulk of the ligands causing the third ligand to be sufficiently labile under the reaction conditions to give disappointing yields, and to permit rearrangement to the stable facial form, resulting in up to a 50% distribution of the two isomers in line with the earlier observations from Chakravorty.⁶⁵ DFT studies indicated that

this does not appear to be as a result of a metal centred electronic effect suggesting that the ratio can be controlled by the steric preference of the precursor dichelate complex in the reaction.

To consider the difference between the *mer* and *fac* structural forms, separation strategies have had to be developed to isolate the two isomers in good purity. In an early study by Krejčík *et al.* using 2,2'-azobis(pyridine) in the complex $[\text{Ru}(\text{L22})_3]^{2+}$,³⁶ they found that the two forms could be separated using a preparative HPLC on "Separon SGX", and that the IR vibrational intensity was more intense for the more polar *fac* isomer, whilst there were slight differences in the respective cyclic voltammograms and the UV / vis spectra. Similarly, Happ *et al.* prepared a series of functionalized pyridine triazol ligands, but only in the naphthyl derivatized example (L23) were they able to separate the *mer* and *fac* isomers of $[\text{Ru}(\text{L23})_3]^{2+}$ using silica chromatography eluted with a DMF / ethanol / ammonium chloride mixture⁶⁹ in a similar procedure to the one developed by ourselves. Interestingly they showed a considerable spectral difference in the metal-to-ligand-charge-transfer (MLCT) absorptions between the two isomers, with the *mer* isomer blue shifted relative to the *fac* isomer by 14 nm.

Systems derived from 2,2'-bipyridine derivatives have perhaps been more of a challenge; for example, the Ru^{II} complexes, *mer* and *fac*- $[\text{Ru}(\text{L14})]^{2+}$ (where L = 14b, c and f) have been separated using HPLC techniques obtaining approximately 60 mg of the *mer*, and 20 mg of the *fac* isomer.⁷⁰ A study of the photophysical/electrochemical properties reveal that there is a small solvent effect on the photophysical properties between *mer* and *fac*- $[\text{Ru}(\text{L14b})_3]^{2+}$. The excitation polarization spectra have been measured showing almost no difference in the excitation polarization spectra between the two complexes. Rutherford *et al.* also showed that preparative cation-exchange chromatography can be applied to the separation of systems with large bulky functional groups, and also reported the isolation and characterization of *mer* and *fac*- $[\text{Ru}(\text{L24})_3]^{2+}$, although in this case there is no evidence of any spectroscopic difference between the species other than the ¹H NMR spectra reflecting the different symmetries inherent to the two isomers.⁷¹

From our own studies, we initially had difficulty separating the two forms of a number of ruthenium tris-chelate 2,2'-dipyridine complexes such as the relatively simple methyl ester L21a using cation-exchange chromatography, and our silica chromatographic studies did not provide significantly different R_f values for the two isomeric forms to permit separation.⁶⁷ We noted similar problems with complexes of the simple alcohol 5-hydroxymethyl-2,2'-bipyridine. However on increasing the steric bulk, and presumably extending the electronic dipole of the complexes with ligand systems L21b,⁶⁸ L25⁷², and L26,⁷³ there was a clear and definite separation in the two forms on silica, and these could be readily separated using preparative plate chromatography eluted with a DMF / ethanol / saturated NH₄Cl mixture. With all these complexes there was no significant difference in the photophysical characteristics between the *mer* and *fac* isomers, although for the complex $[\text{Ru}(\text{L25})_3]^{2+}$ the *fac*-isomer appears to show enhanced binding interactions with dihydrogenphosphate salts, even though the difference is much less marked with spherical chloride ions, suggesting that the specific orientation of the secondary functions does matter when identifying materials for consideration as molecular sensors.⁷² In a related study, Wilson and co-workers separated the four stereoisomers of $[\text{Ru}(\text{L27})_3]^{2+}$ using silica column chromatography (5% increasing to 10% methanol in dichloromethane) giving several distinctive red coloured bands subsequently identified as the Λ -*mer*, Δ -*mer*, Δ -*fac* and Λ -*fac* isomers in yields of 34, 39, 11, 12 % respectively. Given the relative special arrangement of the functional groups, there is a significant enhancement in the surface binding of cytochrome *c* shown by the *mer* isomer.⁷⁴



Scheme 4. The identity of ligands L24 to L30.

Since our initial studies, similar techniques have now been applied to separate a range of different materials presumably as a direct result of the considerable difference in the dipole moment of the two isomers. For example the inert dpq rhodium(III) complex $[\text{Rh}(\text{L28})_3]^{3+}$ has been separated by column chromatography into the two geometrical components,⁷⁵ and the complex $[\text{Ru}(\text{L29})_3]^{2+}$ has been separated using flash silica column chromatography, eluted by an aqueous potassium nitrate solution. In the latter case, as with many other cited examples, again it does not show any significant variation in the photophysical behaviour between the two isomers.⁷⁶ Silica preparative plate chromatography (eluted with acetone / water / saturated KNO_3) has also been used to separate the *mer* and *fac* isomers of both the Fe^{II} and Ru^{II} complexes of ligand L30, and in this case the *mer* isomer is bathochromically shifted relative to the *fac* isomer in both the UV / vis absorption and the emission spectra, with a peak difference of up to 27 nm in the emission of the two forms of $[\text{Ru}(\text{L30a})_3]^{2+}$.

In review there are evidently a number of chromatographic techniques that are generally applicable to separate the geometric isomers of inert transition metal diimine complexes on a preparative scale. In particular silica, in the presence of either potassium nitrate or ammonium chloride, is widely applicable relying on the considerable difference in the dipole moments between the two forms, and as highlighted above, can give rise to a notable difference in the IR absorption intensities.³⁶ Sephadex cation-exchange techniques are also valid in many cases, although in our experience the chiral nature of the support can result in competing separation of the enantiomer pairs.

With the dominance of the *mer* isomer, in a number of cases only this one form is obtained, but in a select number of examples where the two separated forms can be isolated, the difference in the physical properties, in particular the photochemical behaviour has been considered. With 2,2'-bipyridine and 1,10-phenanthroline systems such as those studied in our own laboratory, there does not appear to be a significant difference in the absorption, emission or lifetimes of the isolated species. However where the two imine systems are significantly different such as in the case of the triazole $[\text{Ru}(\text{L23})_3]^{2+}$ and the pyridazine $[\text{Ru}(\text{L30a})_3]^{2+}$, differences in the metal-to-ligand-charge-transfer absorption is observed, presumably resulting from small differences in a weak *trans*-influence effecting the metal centred ground state. Given the considerable difference in the dipole of the two structural isomers, and the evidence of a weak solvent induced *trans*-influence in a

related zinc system,⁶² these differences probably arise from subtle solvent and anion interactions, especially given that similar effects have been demonstrated in *meso/rac* dinuclear systems by D'Alessandro and Keene.⁷⁷⁻⁷⁹

4.0 STRUCTURAL CONTROL USING CAPS, CHAINS and TAILS

Over and above the simple use of steric or electronic considerations to influence the preference for the *mer* isomeric form, there have been a number of interesting strategies to influence the ratio of the two geometric isomers which can theoretically preclude the use of protracted chromatographic procedures, or serendipitous crystallization of one of the isomers, as discussed up to this point.

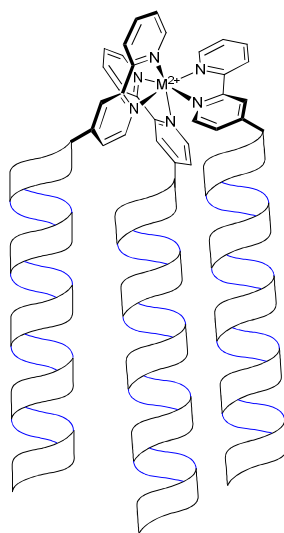


Figure 2. Representation of A tris-chelate complex with appended protein “tails”.

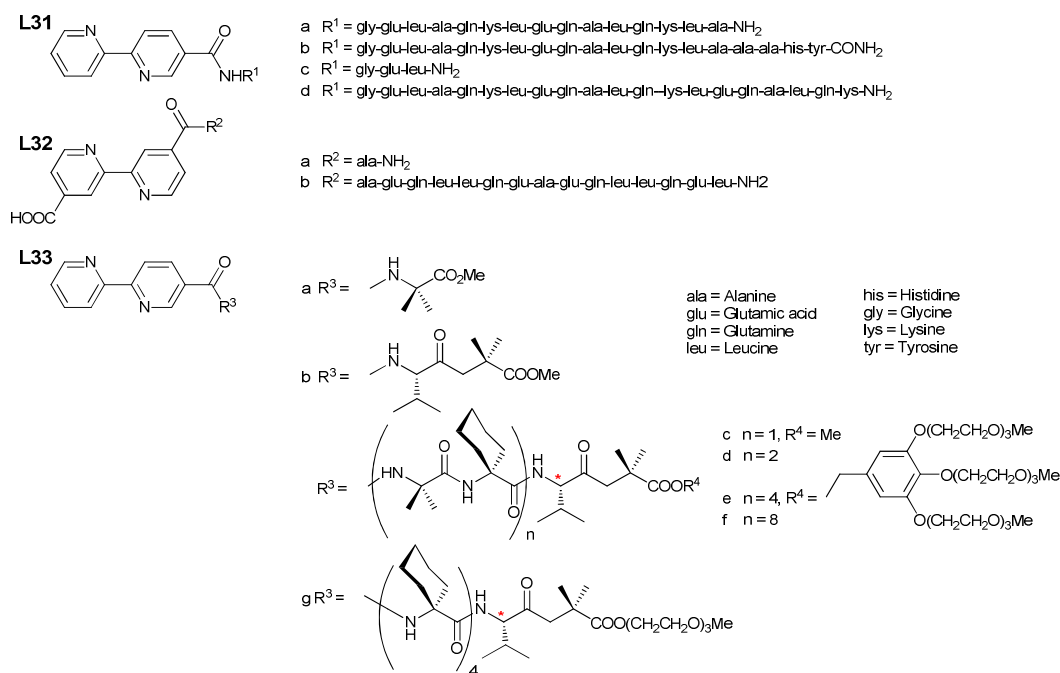
One interesting approach has been the inclusion of peptide chains, with the aim of the metal ion inducing the formation of α -helical bundles.⁸⁰ The initial studies illustrated that a degree of chiral induction was observed, but there was no direct method to determine the ratio of the *mer* and *fac* isomers (Figure 2).^{81,82} This is highlighted by the initial studies by Ghadiri,^{83,84} where peptide chains were attached to 2,2'-bipyridine (L31a and b), and when complexed they permit close contact to enable the formation of α -helices in the peptide tails, and induce a non-racemic coordination around Ni^{II}. This strategy also permits a degree of control over the inclusion of additional groups at a precise distance from the primary metal centre, and has for example permitted studies into the electron and energy transfer from a Ru^{II} centre to secondary functions at a known distance. However the precise coordination environment at the metal centre remains ambiguous.⁸⁵ Significant progress was made by Sasaki and co workers with the amidic bipyridine ligands L32 where separation and the relative isomeric distribution could be observed for the various isomers using reverse phase HPLC.⁸⁶ Unsurprisingly, the complexes [Fe(L32a)₃]²⁺ and [Fe(L32b)₃]²⁺ showed a strong preference for the *mer* isomer in a 76 to 24%, and 71 to 29% ratios respectively, and little stereochemical determination either, although the complex *A-mer*-[Fe(L32b)₃]²⁺ induced up to 92% helicity in the peptide tail. In a related study, Case *et al.* demonstrated that when

functionalized at the 5-position of 2,2'-bipyridine, a much greater helicity in the protein could be induced. The three chain peptide L31c gave the expected 3 *mer* to 1 *fac* ratio with $[\text{Fe}(\text{L31c})_3]^{2+}$ and little diastereotopic control,⁸⁷ however the 20 long peptide chain in the complex $[\text{Fe}(\text{L31d})_3]^{2+}$ (and the analogous Ni^{II} and Co^{II} complexes^{88,89}) were suggested to be predominantly the *fac* form with the diastereomeric excess of 40% in favour of the Δ diastereoisomer.

In a recent development, Yashima and co-workers have demonstrated that 2,2'-bipyridine ligands substituted at the 5 position with differing lengths of peptide chains can have a very marked effect on the isomeric distribution with a high dependency on the counter anion.⁹⁰ For the simplest complex $[\text{Fe}(\text{L33a})_3](\text{BF}_4)_2$ a 69% *mer* to 31% *fac* ratio was detected by integration of the terminal methoxy ^1H NMR resonances, however on the introduction of chloride anions the ratio dramatically changed to favour the *fac* isomer by 9 to 1 which was accompanied by a significant enhancement of the Δ diastereoisomer. Similar results are seen with L33b to d, with the increasing size of the ligand favouring the *mer* isomer (Table 1), but by changing the anion to one which readily associates with the valine amidic protons, in this case chloride, the structure adjusts to favour the *fac* isomer. For ligands L33e and f, the ^1H NMR spectra were too complicated to deconvolute, but a similar behaviour is anticipated based on the circular dichroism (CD) spectroscopic evidence. The peptide chain in L33g suggests that it assembles α -helical coils which initially favour the *fac* isomer, but this is further enhanced with chloride ions.

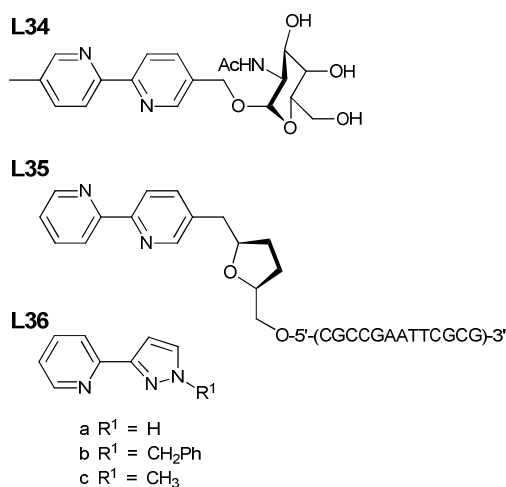
Table 1. The isomer distribution for complexes $[\text{Fe}(\text{L33})_3]^{2+}$ with and without chloride.⁹⁰

Ligand	<i>fac</i> to <i>mer</i> ratio [%]	de [%]
33b	25 / 75	3 (Δ)
33b + Cl^-	70 / 30	63 (Δ)
33c	17 / 18	16 (Δ)
33c + Cl^-	86 / 14	18 (Δ)
33d	15 / 85	39 (Δ)
33d + Cl^-	87 / 13	48 (Δ)
33e	n/a	35 (Δ)
32e + Cl^-	n/a	31 (Δ)
33f	n/a	28 (Δ)
33f + Cl^-	n/a	24 (Δ)
33g	66 / 34	60 (Δ)
33g + Cl^-	80 / 20	>98 (Δ)



Scheme 5. The identity of ligands L31 to L33.

While helical peptide tails have now shown a significant role in determining the *mer* to *fac* dynamic equilibria in solution, Sakai *et al.* has also demonstrated that the N-acetylgalactosamine modified 2,2'-bipyridine ligand L34 can readily form a tris-chelate complex with Fe^{II} which then can bind to *Vicia villosa* B₄ and *Glycin Max* lectins, and the relative ratio of the four diastereoisomers determined by reverse phase HPLC. In the absence of the proteins, the Δ -*mer* isomer was present in the largest ratio, but on incubation with *Vicia villosa* B₄ lectins, the *A*-*mer* isomer was dramatically enriched to 85%. Whilst with *Glycin Max* lectin the association with the metal complex was much lower, with a similar preference for the Δ -*fac* and Δ -*mer* forms.^{91,92} Attention is also drawn to the work of Muller and co-workers who have prepared an oligonucleotide appended to a 2,2'-bipyridine function (L35). These self associating short strands of DNA combine to form a network. AFM studies indicated that two different topologies were observed with these systems, which are tentatively attributed to the formation of networks (Figure 3) derived from the two different metal centred geometries, although definitive evidence is not yet available.^{93,94}



Scheme 6. The identity of ligands L34 to L36.

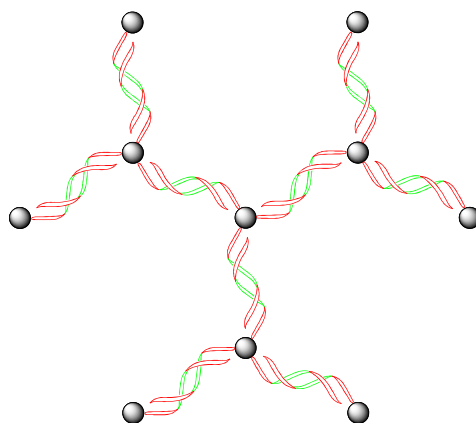
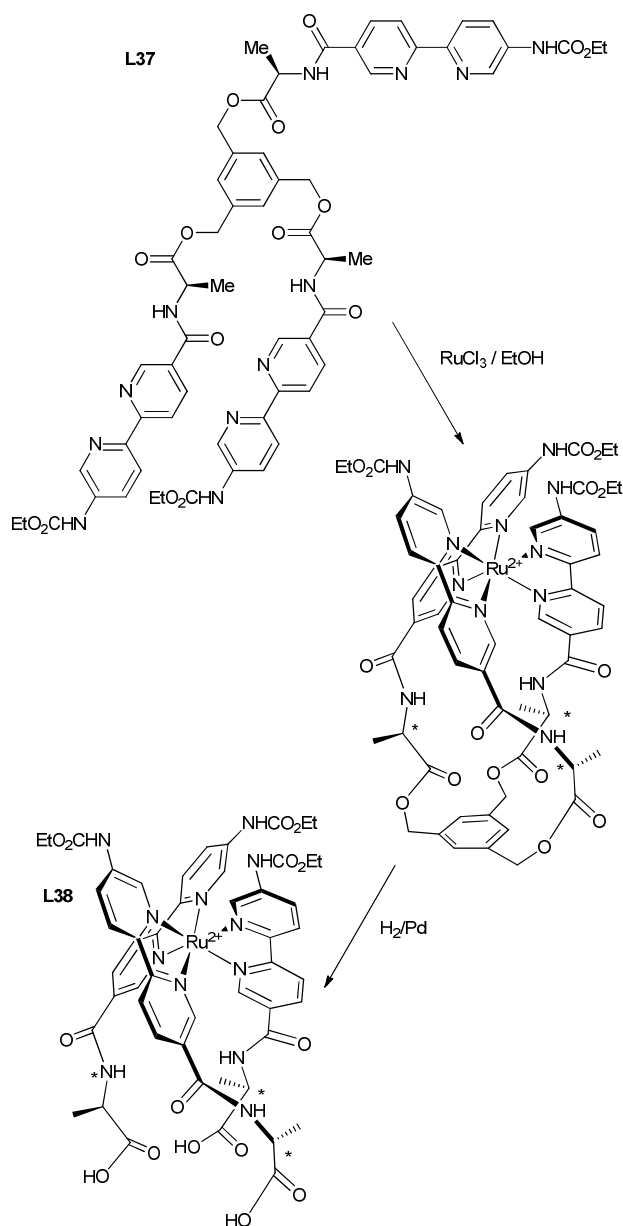


Figure 3. Proposed network composed of $[\text{Fe}(\text{L35})_3]^{2+}$.^{93,94}

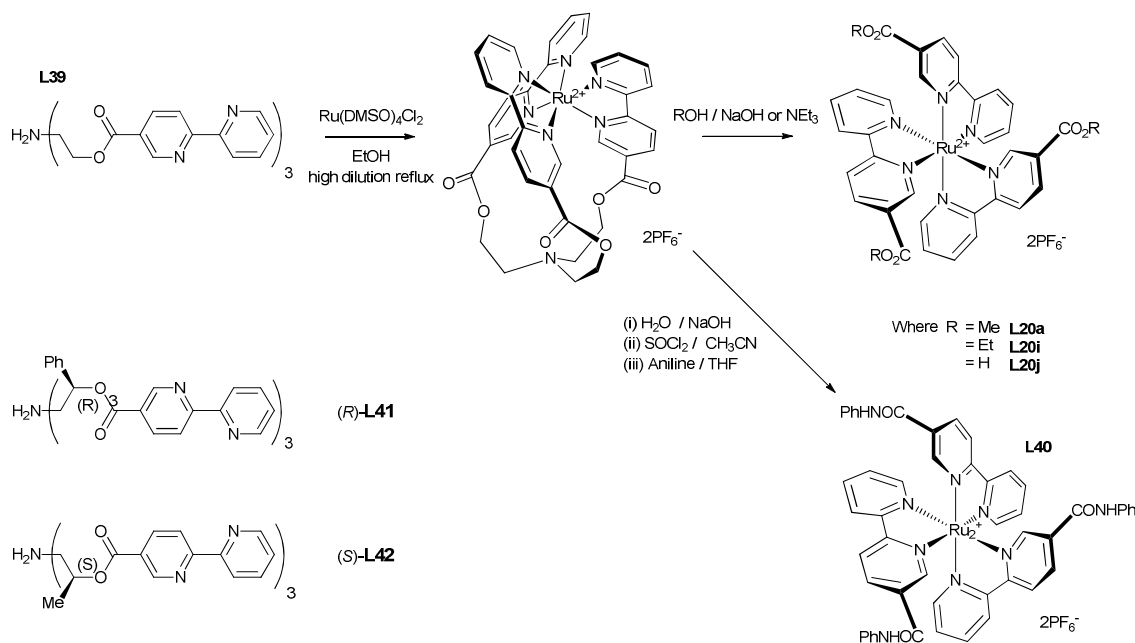
In moving to a more demanding synthetic strategy, the selective isolation of the *fac* isomer has been realized by “capping” the three ligands using a precursor complex. One of the earliest examples reported by Lam *et al.* showed that ligand L36a could be selectively crystallized as the *fac* isomer bridged by three Cu^I ions in a “helicite” type $[\text{Ru}(\text{L36a-H})_3\}_2\text{Cu}_3](\text{ClO}_4)$ arrangement.⁹⁵ Similarly, Metherell *et al.* very recently demonstrated that both the *fac* and *mer* isomers of $[\text{Ru}(\text{L36a})_3]^{2+}$ could be isolated using this chelating pyrazolyl-pyridine ligand by virtue of the selective formation of a Cu^I adduct with the *fac* isomer.⁹⁶ They then show that the isomeric integrity is then preserved following alkylation of the pyrazolyl NH group with methyl iodide or benzyl bromide. In the case of the *fac* isomers, a weak one to one binding was observed with isoquinoline N-oxide that was absent with the *mer* isomer.



Scheme 7. The synthetic procedure to the isolation of $\text{fac-}[\text{Ru}(\text{L38})]^{2+}$.⁹⁷

In 1998 Weizman, Libman and Shanzer reported a templated strategy for aligning non-symmetric ligands around an inert metal centre, by tethering the three ligands together using esters linkages so that there is tripodal cage $[\text{Ru}(\text{L37})]^{2+}$ (Scheme 7). Upon hydrolysis of the ester bonds, the tris-bidentate chelate is forced to adopt the facial orientation in the hexadentate ligand in complex $[\text{Ru}(\text{L38})]^{2+}$. In this example, the inclusion of alanine groups in the system also predetermines the metal centred stereochemistry.⁹⁷ We have followed a similar strategy to isolate the targeted facial isomers of 5-carboxy-2,2'-bipyridine, using a hexadentate ligand (L39),⁹⁸ which upon transesterification can be used to selectively form $\text{fac-}[\text{Ru}(\text{L21})]^{2+}$ which could then be separated into the two enantiomers by cation-exchange chromatography (Scheme 8). Further hydrolysis followed by formation of the acylchloride, and reaction with aniline permitted conversion to $\text{fac-}[\text{Ru}(\text{L40})]^{2+}$ without loss of the predetermined fac isomerism. In an adaptation of this, the inclusion of three chiral centres in the templating tether, with ligands L41 and L42

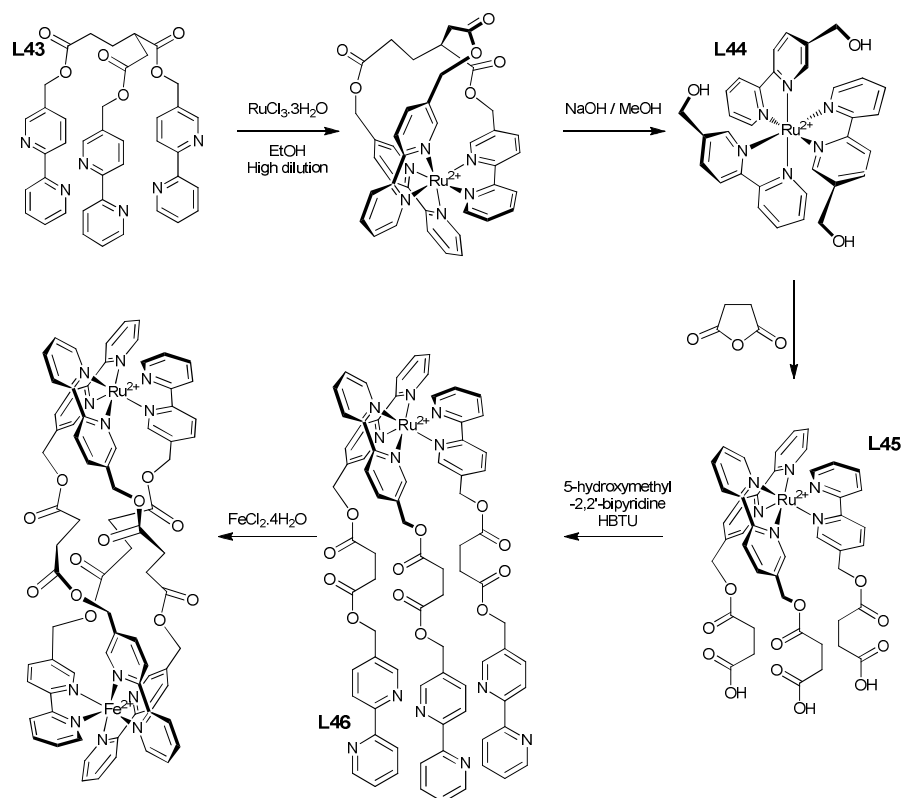
permitted control of the metal centred chirality.⁹⁹ Liu *et al.* subsequently demonstrated that these procedures could also be replicated with the analogous Co^{III} complexes.¹⁰⁰



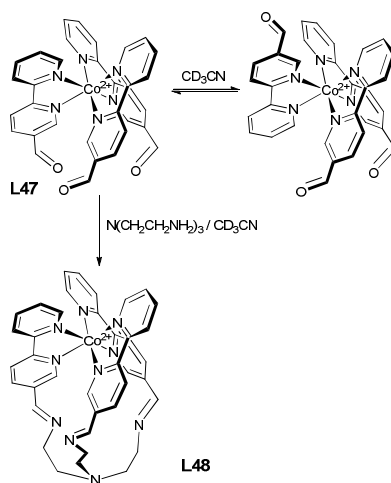
Scheme 8. The synthetic procedure to the isolation of *fac*-[Ru(L21)₃]²⁺ and subsequent conversion to the triamide *fac*-[Ru(L40)₃]⁴⁺.^{98,99}

To demonstrate the versatility of this procedure, we have also shown that, the triol *fac*-[Ru(L44)₃]²⁺ can be synthesized as a single geometric isomer via a non-symmetric tripodal hexadentate triester L43 (Scheme 9). The isolated *fac* isomer can then be used as the starting point in a “complex as ligand” synthetic strategy by reaction with succinic anhydride to give L45, which can then be subsequently functionalized with additional 2,2'-bipyridine chelating groups with retention of the facial orientated geometry to give *fac*-[Ru(L46)₃]²⁺. This synthetic strategy has permitted isolation of the only example of a kinetically inert heterometallic helicate with two identical metal binding sites.¹⁰¹

Constable and co-workers have also adopted a capping strategy; the labile complex *mer* and *fac*-[Co(L47)₃]²⁺ can react with tren giving a *fac* orientated hexadentate complex (Scheme 10).¹⁰² Our own investigations with this ligand (L48) on Ru^{II} has however been unsuccessful in forming a *fac* orientated trialdehyde system encountering problems of the ligand decomposing during complexation leading to contamination of the *mer* isomer in the isolated final products.



Scheme 9. The synthetic procedure to the isolation of $\text{fac-}[\text{Ru}(\text{L44})_3]^{2+}$ and subsequent conversion to the heterometallic helicate $[\text{RuFe}(\text{L46})_3]^{4+}$.¹⁰¹

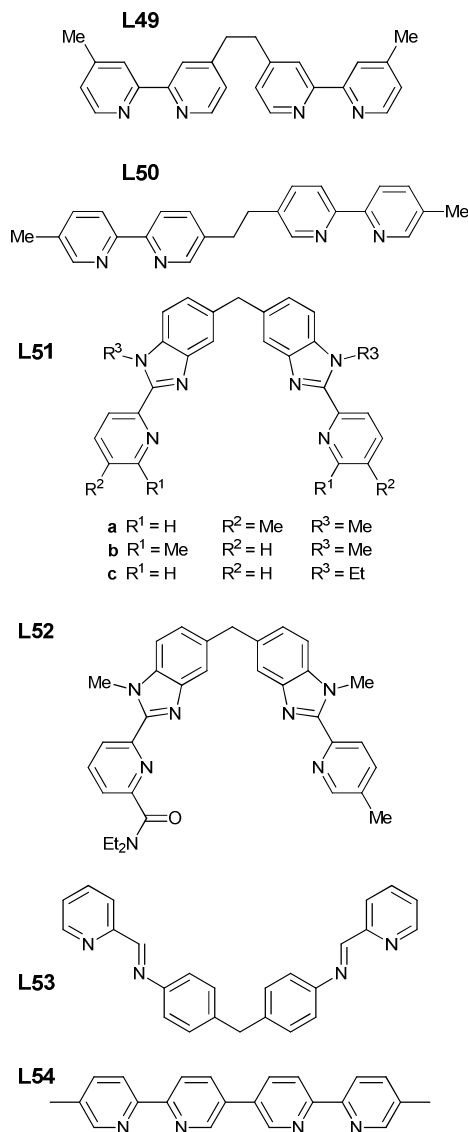


Scheme 10. The synthetic procedure to the isolation of $\text{fac-}[\text{Co}(\text{L47})_3]^{3+}$.¹⁰²

5.0 POLYNUCLEAR ASSEMBLIES

In moving from single metal complexes to polynuclear assemblies, the meridional and facial orientations potentially become more important in determining the final outcome of a “self-assembly” synthetic procedure. The formation of larger nano-scaled structures is reliant on the

versatility of the ligand to be able to adopt the “correct” geometry, which can often be determined by a delicate balance in the ligand structure as highlighted in the labile mono-nuclear systems discussed in Section 2. Slight changes in the rigidity, the ability to form additional supramolecular interactions (such as π -stacking and hydrogen bonds), and the inclusion of “coordinated” ionic species can dramatically change the resulting structure.



Scheme 11. The identity of ligands L49 to L54.

The isolation of dinuclear triple “helicates” using diimine chemistry has played a considerable role in the fundamental understanding of supramolecular “self-assembly”, and includes some of the earliest examples.³⁰⁻³³ In a linear triple stranded helicate, the terminal metals must adopt the less favourable facial arrangement while the ligand must be sufficiently flexible to “twist” between the metal centres, and yet be sufficiently short or rigid so as not to wrap around a single metal centre and in the case of ditopic ligand strands form the so called “single-stranded” helicites (Figure 4). Two early examples of such systems includes the bridging of 2,2'-bipyridine

ligands linked by ethylene groups, namely ligands L49¹⁰³ and L50¹⁰⁴ which readily form dinuclear homochiral helicates with Fe^{II}.

In a pioneering study by Williams and co-workers,⁵⁸ the lability of the ditopic ligand L51 in the Co^{II} dinuclear complex [Co₂(L51)₃]⁴⁺ established that the formation mechanism of the larger triple helix required the initial formation of the mononuclear [Co(L51)₃]²⁺, presumably in a *fac* orientation. This then captures a second Co^{II} ion, and similar behaviour is observed with the analogous Fe^{II} complexes with the formal identification of mononuclear [Fe(L51)₃]²⁺ as part of the stepwise establishment of the dinuclear triple helicate [Fe₂(L51)₃]⁴⁺, a material that showed spin-crossover behaviour.⁵⁹ Piguet and co-workers have continued this with the consideration of appropriate strategies to prepare helicates where the geometry around individual metal centres can be locked in place in a *fac* orientated geometry as discussed at the close of Section 2. For example, the formation of heterometallic helicates such as [MLn(L52)₃]⁵⁺ can be readily achieved using labile ions such as cobalt(II)^{105,106} or chromium(II)¹⁰⁷⁻¹¹⁰ encouraged by templation with a lanthanide ion, orientating the transition metal tris-chelate complexes in a *fac* orientation. Conversion to the corresponding inert 3+ oxidation states (Co^{III} or the Cr^{III}) permits removal of the labile lanthanide ions and results in a stable *fac*-orientated product.

There have also been successful attempts to form inert helicates, trapping the *fac*-orientated tris-chelate metal complexes directly with inert metals such as Ru^{II} and Os^{II}, which as discussed above, have been traditionally considered to be unreactive. In 2004 Torelli *et al.* reported the first example with the isolation of [RuLu(L52)₃]⁵⁺, where the lanthanide ion can selectively assist in the template formation of the *fac* isomer, with the ruthenium ion labilized by the use of polar solvents.^{60,110} The Lu^{III} ion can be removed to obtain *fac*-[Ru(L52)₃]²⁺ and Ca²⁺ added to give a remarkable Ru-Ca helicate which could not be obtained directly using a standard self-assembly synthetic procedure.¹¹¹ It is recognized though that the obtained yield of [RuLu(L52)₃]⁵⁺ was only 25 %, with presumably *mer*-[Ru(L52)₃]²⁺ not being isolated. The inert metal ion Os^{II} behaves in an analogous fashion as exemplified in the complex [OsLu(L52)₃]⁵⁺ in 6 to 10% overall yield.⁶¹ Without a templating ion, the formation of triple helicates with Ru^{II} and Os^{II} has proved to be much less successful; Hannon and co-workers reported the first example [Ru₂(L53)₃](PF₆)₄ isolated in just 1% yield.¹¹² However in extremely forcing conditions such ethylene glycol at 225 °C for 4.5 hrs under microwave irradiation a dinuclear triple stranded helicate [Ru₂(L54)₃](PF₆)₄ was obtained by Glasson *et al.* in 36% yield.¹¹³

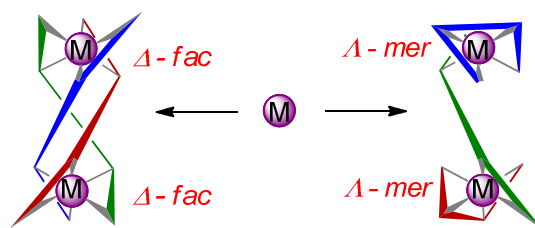
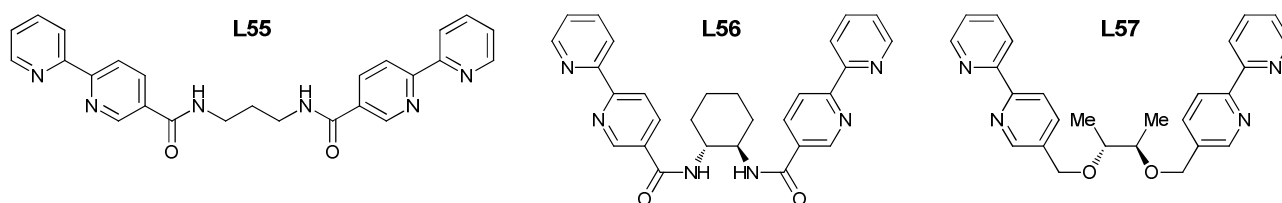


Figure 4. Schematic representation of *mer* and *fac* orientation in flexible ligand “helicates”.



Scheme 12. The identity of ligands L55 to L57.

With the semi-flexible ligand L55 reported by Fatin-Rouge *et al.*, a detailed study of the kinetics and thermodynamics of dissociation of the triple helicate $[\text{Fe}_2(\text{L55})_3]^{4+}$ revealed that it also goes through a mononuclear $[\text{Fe}(\text{L55})_2]^{2+}$ intermediate that presumably needs to be orientated into a *fac* geometry to coordinate the second metal. Interestingly though $[\text{Fe}(\text{L55})_2]^{2+}$ and an $[\text{Fe}_2(\text{L55})_2]^{2+}$ species were also identified in this study, presumably with one ligand wrapping round a single metal centre, although the detail of the orientation of the metal coordination has not been determined; it is likely that these “side reactions” involve the formation of a *mer* isomer.¹¹⁴ In our own work with ligand L56 containing “enantiopure” diaminocyclohexane, we found that triple helicates could be obtained with good stereochemical control over the metal centred helicity with a range of divalent metal ions including Fe^{II} , Zn^{II} and Cd^{II} however in permitting a greater flexibility in the ligand system, such as with ligand L57, we observed that single stranded systems could be obtained (Figure 4). Our initial observations suggested that due to the symmetry around the metal centre in the ^1H NMR spectra, that these were probably adopting a favourable *mer*-configuration rather than the sterically demanding *fac*-configuration, and at the same time, there appears to be a concomitant change in the metal centred helicity.^{115,116}

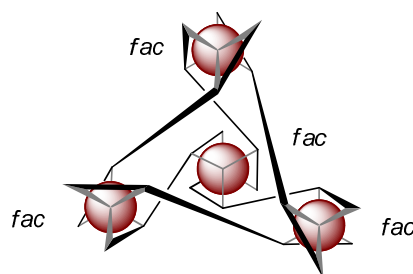
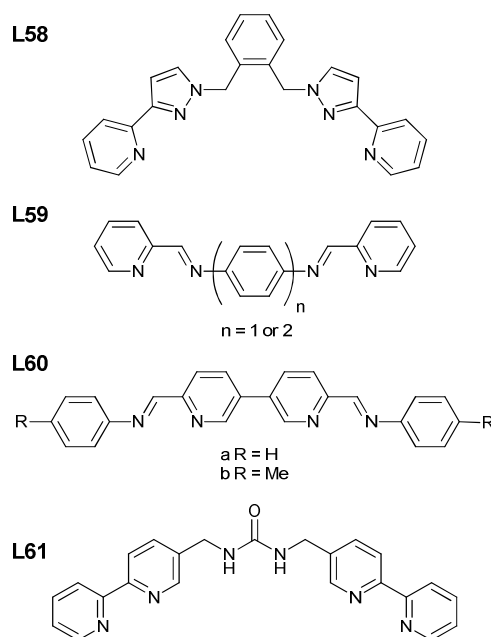


Figure 5. Schematic representation of a 4 metal to 6 ligand tetrahedron with *fac* metal centred geometry.



Scheme 13. The identity of ligands L58 and L61.

Moving beyond two metal systems to encapsulating three dimensional coordination assemblies, a large number of coordination architectures have been realized using ditopic bridging tris-chelating diimine ligands, with a 2 metal to 3 ligand stoichiometry. In such cases, again the delicate interplay of the ligand structure (such as rigidity, length, and the ability to form inter-ligand π -stacking interactions), the solvent, the counter ion, and the size and relative stability of the labile metal ion has produced a range of remarkable nano-scaled structures. The simplest form is based on a $[M_4L_6]$ tetrahedron (Figure 5).³⁴⁻³⁷ In most cases these appear to be composed of four self selecting *fac* orientated metal centres, either templated around an appropriate counter ion, or through favourable π -stacking interactions.

Attention is drawn to the initial examples of such systems published by Ward and co-workers with the tris-pyrazolyl-pyridine unit such as (L58) which formed a tetrahedron such as $[Co_4(L58)_6](BF_4)_8$ templated around a BF_4 anion,¹¹⁷ although the same ligand with Ni^{II} was observed to adopt a *mer* geometry and the formation of a single stranded helicate (Figure 4). Similarly Nitschke and co-workers have also demonstrated that (pyridin-2-yl)methanimine complexes readily form *fac* orientated metal complexes in tetrahedra such as the $[Fe_4(L59/60)_6]^{8+}$ systems, where detailed studies of the relative metal centred chirality have also been completed.^{118,119} Tetrahedral capsules of 2,2'-bipyridine complexes are far less common, although attention is drawn to Custelcean's *de-novo* computer aided complex $[Ni_4(L61)_6]^{8+}$ designed as a selective sulfate receptor,¹²⁰ and the remarkable $[Fe_4(L54)_6]^{2+}$ reported by Glasson *et al.* templated around a PF_6^- ion.¹²¹ Interestingly, Nitschke and co-workers have also extended the *in situ* formation of (pyridin-2-yl)methanimine motifs using the "planar" ligands L62 and L63 as the six faces of a cube with eight Fe^{II} centres forming the vertices, each in a *fac* orientation (Figure 6).^{122,123}

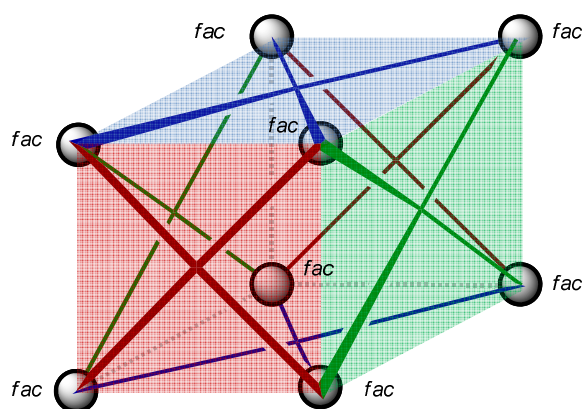
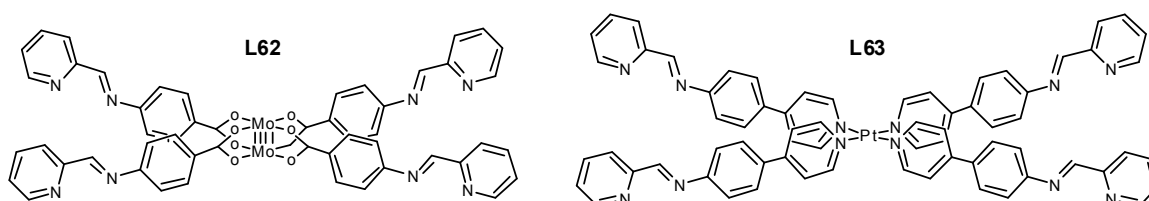
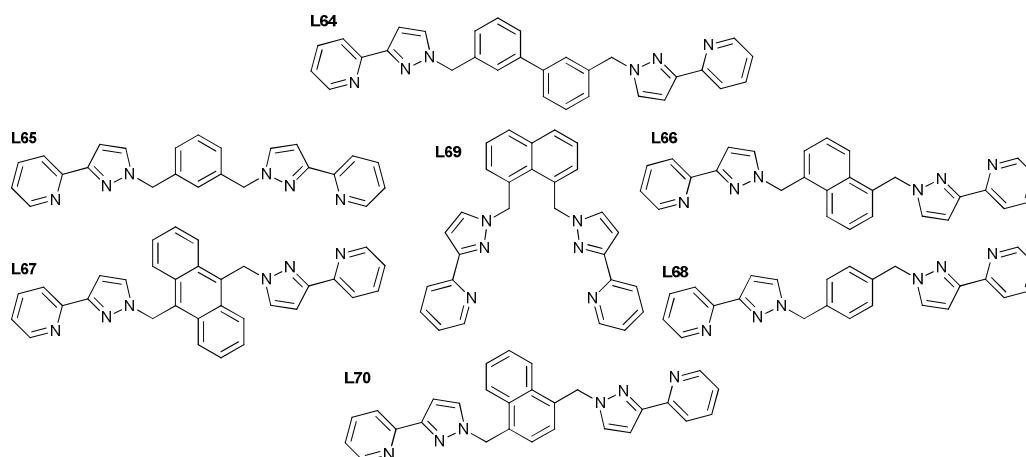


Figure 6. Schematic representation of a 6 sided cube with *fac* metal centred geometry formed from ligands L62 and L63 (the six crosses representing the ligand orientations).^{122,123}



Scheme 14. The identity of ligands L62 and L63.



Scheme 15. The identity of ligands L64 to L70.

Whilst the intricate structures discussed so far rely on the formation of the *fac* isomer, the versatility of the diimine ligands to permit both thermodynamically stable *fac* and *mer* complexes provides opportunities to introduce far greater complexity through the delicate interplay between these two accessible geometries. For example, if a bridging ligand with greater separation between the chelating sites is used, along with further opportunities to form π -stacking interactions, as in the case with ligand L64, greater complexity is introduced. Whilst it maintains a tetrahedral arrangement, the symmetry is considerably reduced in the isolated $[\text{Co}_4(\text{L64})_6]^{8+}$ and $[\text{Cd}_4(\text{L64})_6]^{8+}$ cages;¹²⁴⁻¹²⁶ the metal centred orientation changes to give a *mer* configured triangular ring of metal

ions, capped with a *fac* configured metal which appears to be closely associated with one of the anions. Ward and co-workers have also shown that subtle variations in the bridging unit can elicit systems with much higher complexity, for example they have recently shown that the reaction of L65 and L66 with Co^{II} or Zn^{II} results in distorted cubic $[\text{M}_8\text{L}_{12}]^{16+}$ cages with two opposing metal centres adopting a facial orientation, and six meridional configurations on the other vertices (Figure 7).¹²⁷⁻¹³⁰ L66 was also shown to behave similarly using an inert Ru^{II} centre, where the anticipated 3 *mer* to 1 *fac* ratio potentially assisted in the formation of a Ru_4Cd_4 coordination cage.¹³¹ However increasing the aromatic bridging function with ligand L67 results in a distorted parallelepiped cage with a *mer* configuration at each metal vertex which can be viewed as two bridge circular tetranuclear helicates.¹²⁸

A similar *mer* orientated bridged circular helicate structure is also adopted in the Cu^{II} complex formed from ligand L68 which provides a trigonal prismatic cage $[\text{Cu}_6(\text{L68})_9]^{12+}$ with two bridged “*mer*” circular trinuclear motifs.¹³² This circular trinuclear helicate motif has also been identified in a number of truncated tetrahedra such as $[\text{M}_{16}(\text{L69})_{24}]^{32+}$ where M is Zn^{II} and Cd^{II} . A simpler, yet structurally similar, architecture based on this trinuclear circular helicate is also seen with L69 and Co^{II} , Cu^{II} and Cd^{II} ,^{133,134} and in the “cuneane” cage $[\text{Ni}_8(\text{L70})_{12}]^{16+}$,¹³⁵ an interesting topological isomer of a cube. This behaviour can also be seen with ligand L60b which depending on the anion, and the metal ion involved, will form tetrahedra with labile divalent ions Co^{II} and Fe^{II} with a *fac* metal centred geometry. But both of these convert to a pentagonal prismatic cage $[\text{M}_{10}(\text{L60b})_{15}]^{20+}$ on the addition of perchlorate ions composed of two staggered pentagonal circular helicates, with each metal centre adopting a *mer* geometry. This larger structure is also formed with the larger Ni^{II} and Zn^{II} cations.^{136,137} Interestingly a cuboid cage $[\text{M}_8(\text{L60b})_{12}]^{20+}$ was also observed with nitrate and either Co^{II} and Ni^{II} presenting alternating *mer* and *fac* configurations.

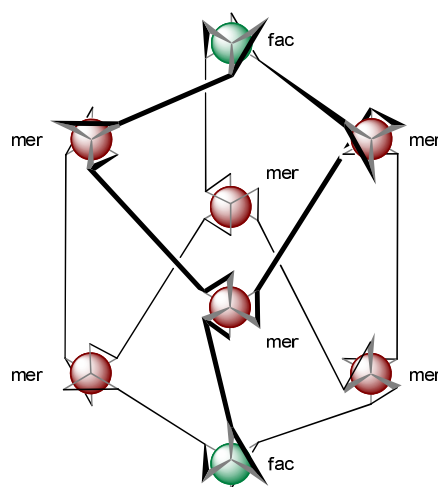


Figure 7. Schematic representation of a 6 cube containing both *mer* and *fac* metal centred geometry formed from ligands L65 and L66.¹²⁷⁻¹³⁰

In the earlier section examining the formation of discrete mononuclear complexes, there is a statistical preference for the *mer* isomer, which can be enhanced by unfavourable steric interactions. In the majority of supramolecular structures however, the *fac* isomer appears to be dominant. As the studies of Piguet have shown,⁶² the ability to interconvert between the two forms therefore become very significant in driving forward the assembly of a polynuclear system which will be less entropically favoured. This is likely to arise from additional enthalpic contributions such as π -

stacking, hydrogen bonding, Coulombic, or other secondary interactions within the assembly. The inclusion of *mer* orientated units within these larger assemblies and the resultant formation of “cyclic helicate” units can evidently give rise to structures of far greater complexity. This could potentially assist in developing the range of known structures, and remove the serendipity in isolating these larger discrete cages and clusters.

6.0 CONCLUDING REMARKS

On the surface, geometrical isomerism appears to be a relatively simple problem, but we hope we have highlighted that the selective isolation and general control over the *mer* and *fac* forms with non-symmetric diimine ligands remains a significant challenge. In the absence of steric constraints that typically favour the *mer* isomer, the statistical 3 *mer* to 1 *fac* ratio is normally observed. While the initial studies were in the main serendipitous, it is evident that the underlying principles are sufficiently well understood now that labile systems can potentially be “guided” towards a dominant structural form by consideration of the secondary functions. Most of these systems rapidly equilibrate in solution, although either form can be trapped through inter-ligand co-operativity, which could be built in through π -stacking, or templation around a secondary metal ion or counter anion. Even the solvent itself appears to offer opportunities to provide a solvent induced *trans*-influence, although these effects remain subtle at best.

For inert systems, guiding the synthesis towards a particular target is not as readily available, but thankfully there are now chromatographic separation techniques that can be employed, either using simple silica chromatography, or cation-exchange techniques. However given that the *fac* isomers is typically only obtained in 25% yield, alternative strategies such as a templated hexadentate ligand systems and appropriate disconnection does offer a viable route to stereochemically pure materials, even though synthetically it is more demanding. But the question remains, is there a necessity to do so? Certainly there are only subtle intensity differences in the IR spectra of the two isomers due to the higher dipole moment in the *fac* isomer, a fact which in itself can be readily exploited in chromatographic separation of the two species. With regard to the electronic spectra of the complexes discussed, the differences remain small and are in the main inconsequential unless there is a considerable dissimilarity of the two imine donors. In such cases, the spatial interaction of the two forms with the surrounding environment, the counter anions and the solvent probably plays a more significant role in expressing the observed differences.

Moving away from the simple measurement of physical properties of molecules in isolation, the spatial orientation of the various ligand components around the metal centre are of more significance when attempting to orientate these species to form supramolecular assemblies. This becomes particularly important when considering using the functional groups to attach these species to a surface; the tripodal facial geometry offers a much better way to pack together and the functional groups could assist in orientating the complexes on a plane. Likewise, the *fac* isomer could be envisioned to provide a good C_3 cavity for the inclusion of guest species as we have demonstrated in our own anion binding studies with dihydrogen phosphate. However the more extended shape presented by the *mer* form has potentially better interactions with protein surfaces and DNA, an area of study we are currently pursuing. In extending these ideas to the formation of larger nano-scaled self-assembled structures, the aesthetically pleasing *fac* geometry has perhaps

limited our expectation to just helicates and tetrahedra, but from the recent studies by Ward and Nitschke, the versatility to introduce a *mer* orientated geometry into the structure guides the formation towards circular rings which have been shown to be the basis of much larger assemblies with surprising complexity. These ideas could potentially be extended to the formation of lattices where the relative orientation and packing could be critical in the fine tuning of spin-cross over properties in the complexes of Fe^{II} for example.

So where are the current and future challenges in this area? As we have alluded to, the “ground rules” are now in place using the simple homoleptic systems discussed in this report in tandem with the methodologies to ensure the enantiopurity of the resulting materials. We are now in a position to exploit these interesting and versatile transition metal complexes in a wide variety of applications. And yet there are new challenges; in particular the development of heteroleptic systems where the number of available structural isomers is even greater, but the reward in terms of enhanced functionality of the isolated materials could be of benefit towards a wide range of applications.

ACKNOWLEDGEMENTS

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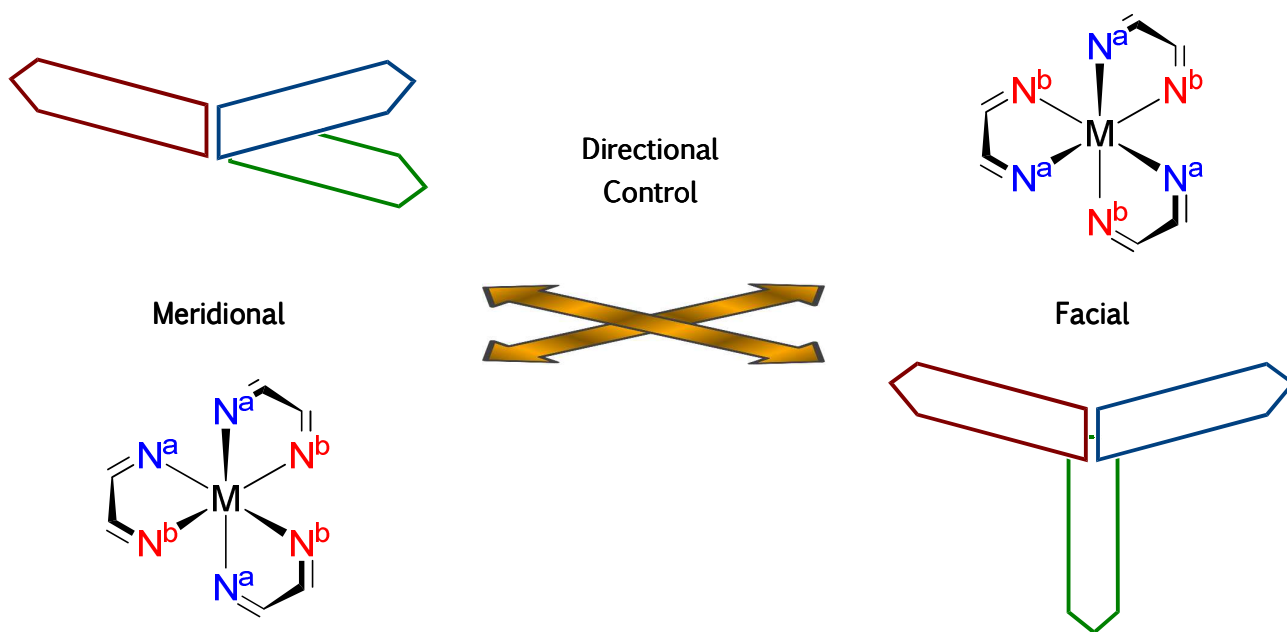
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SYNOPSIS



This overview analyzes the delicate interplay of the factors that control *mer* and *fac* isomerism in diimine tris-chelate complexes, giving consideration to the distribution of products in labile systems, the methods to isolate inert complexes and the implications to self-assembled coordination cages.