

# An inexpensive approach to supramolecular architecture

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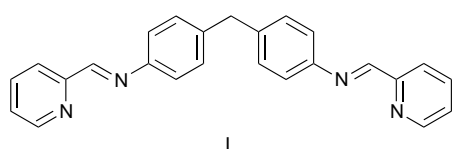
**A new approach to generating supramolecular architectures, based on inexpensive and easy-to-prepare imine ligands, is described together with its application to the self-assembly of supramolecular triple-helicates.**

There is considerable current interest in the supramolecular synthetic approach and its application to the quest to control molecular architecture.<sup>1</sup> The application of metal–ligand interactions has proved particularly fruitful and complex molecular architectures such as helicates,<sup>2–4</sup> knots,<sup>5</sup> grids,<sup>3</sup> catenanes,<sup>5</sup> cylinders<sup>3</sup> and boxes<sup>6</sup> have all been assembled. Indeed in a recent report, Lehn and co-workers have described a supramolecular system in which a number of different structural motifs are possible.<sup>7</sup>

A disadvantage to this metallo-supramolecular approach has been the almost exclusive use of ligand systems constructed from polypyridyl,<sup>2,3</sup> benzimidazole<sup>4</sup> and catechol binding sites.<sup>4</sup> These systems require time-consuming multi-step syntheses from relatively expensive starting materials. If supramolecular chemistry is to achieve its full potential then it is highly desirable that new, inexpensive and easy-to-prepare systems be developed. Not only should the development of an inexpensive system enable wider access to and application of this field, but creating systems which are easy to prepare and readily modified should enhance the rate at which novel molecular architectures are developed. For these reasons we are targeting inexpensive approaches to supramolecular architecture and communicate here both our approach and the preliminary results of our studies.

As an alternative donor set we have selected imine-based ligands. Imines are formed in high yield by simply mixing aldehydes and amines, a large number of which are available commercially at very competitive prices. Moreover multi-nucleating imine ligands may be prepared by simple iterative reactions.<sup>8</sup> The stability of the imine bond towards hydrolysis is greatly enhanced by conjugation with an aryl ring and the coordination chemistry of such donor units is well established. One of us has recently used copper(I) pyridylimine compounds to control atom transfer radical polymerisation processes.<sup>9</sup> An earlier report of an imine based double helix has appeared and recent work has identified double-helical twists in imine based macrocyclic complexes.<sup>10</sup>

To date, helices represent the best developed and most investigated supramolecular architectures.<sup>1–4</sup> To establish our approach we chose to address the challenge of creating the triple-helical architecture<sup>4</sup> using an inexpensive system. To achieve this we have prepared the ligand L. Our ligand design



incorporates two pyridylimine binding sites separated by a spacer. The chosen spacer incorporates phenylene groups that sterically prevent the two metal binding sites from coordinating to a single metal centre. The central methylene unit introduces

enhanced flexibility into the ligand backbone. This enhanced flexibility permits the ligand to support triple-helical ligand arrays. Importantly, the ligand is not sufficiently flexible to give the bridging non-helical arrangement observed by others.<sup>11</sup> Thus, octahedral metal ions, which require three didentate pyridylimine units to satisfy their coordination requirements, should induce the formation of the triple-helical architecture.

The ligand is prepared by simply mixing ethanolic solutions of pyridine-2-carbaldehyde and 4,4'-methylenedianiline. On stirring at room temperature, the ligand precipitates from the reaction mixture in high yield (80% after 8 h) and may be isolated by filtration. The ease of synthesis and the high yield in a single-step reaction from commercial, inexpensive reagents makes this an extremely attractive ligand system.

Warming methanol solutions containing 3 equiv. of ligand and 2 equiv. of nickel(II) salts at reflux for 4 h leads to the formation of red solutions from which salts of formulation  $[\text{Ni}_2\text{L}_3][\text{X}]_4$  are isolated in high (>80%) yield on addition of methanolic  $[\text{NH}_4][\text{X}]$  ( $\text{X} = \text{PF}_6$  or  $\text{BF}_4$ ). Mass spectrometric analysis (ESI) shows the presence of peaks corresponding to  $\{\text{M}_2\text{L}_3\text{X}_3\}^+$ ,  $\{\text{M}_2\text{L}_3\text{X}_2\}^{2+}$ ,  $\{\text{M}_2\text{L}_3\text{X}\}^{3+}$  and  $\{\text{M}_2\text{L}_3\}^{4+}$  consistent with this formulation. Modelling indicates that this formulation is consistent only with a triple-helical structure. Recrystallisation of the tetrafluoroborate complex salt from methanol afforded crystals suitable for X-ray analysis.<sup>†</sup> The structure of one of the two enantiomers of the cation is shown in Fig. 1 and confirms the formation of the triple-helical structure. Each nickel(II) centre is bound to three pyridylimine binding units to attain a pseudo-octahedral coordination geometry. Coordination to the metal centre forces interannular twisting between the phenylene ring and the pyridylimine unit and the logical consequence is the formation of a triple-helical array. The bond lengths and angles are unremarkable and the two nickel(II) centres are separated by 11.576(1) Å. The ligand twists through a half-turn around the metal–metal axis leading to a helical pitch of about 27 Å. This compares with pitches of around 18 Å for Williams' cobalt triple helicates<sup>4</sup> and 41 Å for Lehn's nickel triple helix.<sup>3</sup> The twisting of the phenylene units results in a chiral aryl-lined cavity at the centre of the helix with the shortest carbon–centroid distance *ca.* 2.8 Å, giving a 'hole' with the potential to trap small molecules. No face–face  $\pi$ -stacking interactions are observed.

Reaction of methanol solutions of 3 equiv. of the ligand with 2 equiv. of iron(II) salts leads to the instantaneous formation of

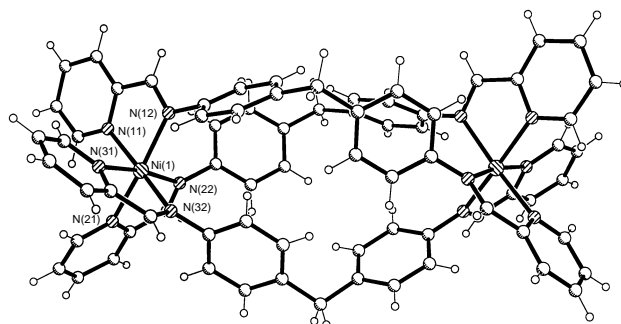


Fig. 1 Crystal and molecular structure of the cation  $[\text{Ni}_2\text{L}_3]^{4+}$

purple solutions. Heating at reflux for 3 h followed by treatment with  $[\text{NH}_4][\text{X}]$  gives similar  $[\text{Fe}_2\text{L}_3][\text{X}]_4$  salts. The purple colour ( $\lambda_{\text{max}} = 572 \text{ nm}$ ,  $\epsilon = 15000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) is characteristic of iron(II) trispyridylimine compounds. Mass spectrometric analysis (ESI) is consistent with this formulation and a preliminary crystallographic study has confirmed the triple-helical nature of the cation. The 250 MHz  $^1\text{H}$  NMR spectrum of this diamagnetic compound in  $\text{CD}_3\text{CN}$  reveals, as anticipated, the presence of one aliphatic and seven aromatic proton resonances. The phenylene rings in the spacer rotate freely at room temperature and the four protons give rise to two resonances. As the temperature is decreased to 243 K, the rate of rotation decreases and the peaks split to give four resonances.

Reacting the ligand with tetrahedral metal ions such as copper(I) and silver(I) gives rise to dimeric  $[\text{M}_2\text{L}_2]^{2+}$  cations. Whilst modelling indicates a unique triple-helical structure when the ligand complexes to octahedral metal ions, the flexibility of the ligand is such that for the dimeric  $[\text{M}_2\text{L}_2]^{2+}$  species two conformations are possible: a double-helical structure or a non-helical bridging cage-like structure. At low temperature, the  $^1\text{H}$  NMR spectra of  $\text{CD}_3\text{CN}$  solutions of the salts show the presence of two species, one of which is present only in small amounts. Similar behaviour in potentially double-helical systems has been reported by Harding and Sauvage.<sup>12</sup> This is the subject of further investigation.

We have established a novel ligand system which is prepared simply by mixing inexpensive commercial reagents and which allows us to generate a complex triple-helical molecular architecture. This inexpensive system makes the triple-helical architecture readily accessible for the first time. We are currently investigating the possibility of binding small molecules in the chiral helical cavity and we are also developing our approach further to create related ligands with which we will address a variety of alternative architectures.

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## Footnotes and References

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† Crystal data for  $[\text{Ni}_2\text{L}_3][\text{BF}_4]_4 \cdot 2\text{MeOH}$ ;  $\text{C}_{77}\text{H}_{67}\text{O}_2\text{N}_{12}\text{B}_4\text{F}_{16}\text{Ni}_2$ ,  $M = 1657.09$ , monoclinic, space group  $C2/c$ ,  $a = 29.037(2)$ ,  $b = 10.4395(10)$ ,  $c = 24.446(3) \text{ \AA}$ ,  $\beta = 93.025(3)^\circ$ ,  $U = 7400.1(11) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 180(2) \text{ K}$ ,  $\mu = 0.606 \text{ mm}^{-1}$ . Goodness-of-fit on  $F^2$  was 1.008,  $R1$  [for  $I > 2\sigma(I)$ ] = 0.056,  $wR2 = 0.142$  for 551 parameters. Largest diff. peak and hole 0.715 and  $-0.367 \text{ e \AA}^{-3}$ . Data were collected using a Siemens SMART CCD area-detector diffractometer; a multiscan absorption correction was applied using SADABS<sup>14</sup> and gave  $T_{\text{max,min}} = 0.94, 0.79$ .

The structure was solved by direct methods using SHELXTL-PC<sup>15</sup> and refined by full matrix least-squares on  $F^2$  for all data using SHELXL-96.<sup>13</sup> CCDC 182/570.

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