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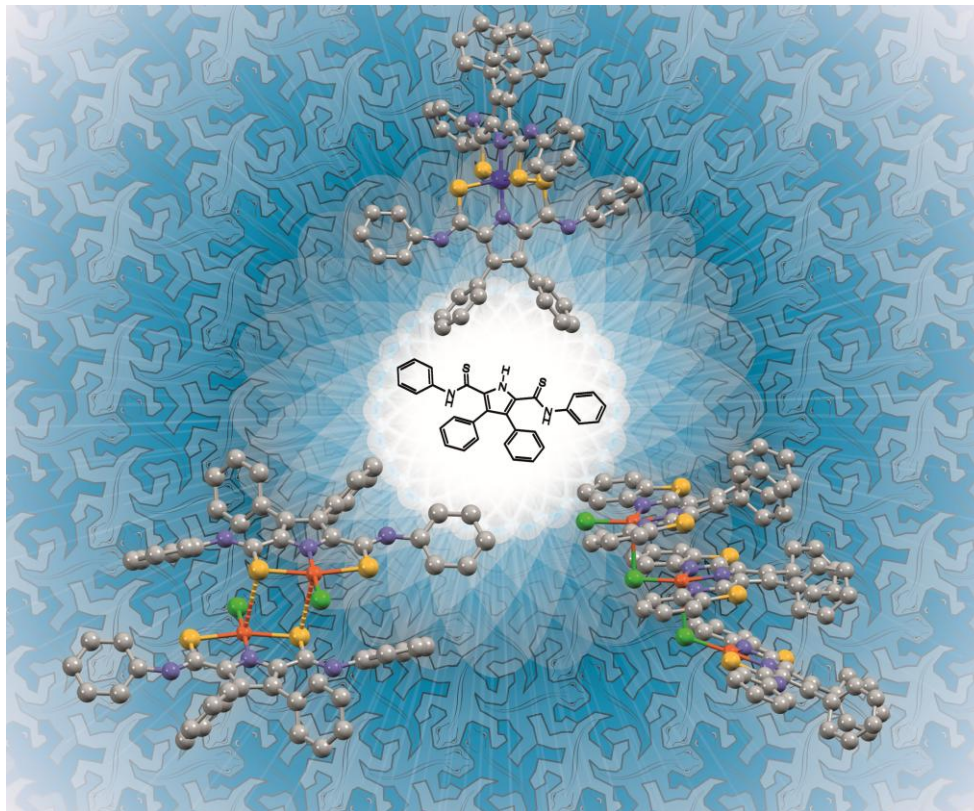


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PAPER

Nickel(II) and iron(II) triple helicates assembled from expanded quaterpyridines incorporating flexible linkages†

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In the present study the interaction of Fe(II) and Ni(II) with the related expanded quaterpyridines, 1,2-, 1,3- and 1,4-bis-(5'-methyl-[2,2']bipyridinyl-5-ylmethoxy)benzene ligands (**4–6** respectively), incorporating flexible, bis-aryl/methylene ether linkages in the bridges between the dipyrindyl domains, was shown to predominantly result in the assembly of $[M_2L_3]^{4+}$ complexes; although with **4** and **6** there was also evidence for the (minor) formation of the corresponding $[M_4L_6]^{8+}$ species. Overall, this result contrasts with the behaviour of the essentially rigid 'parent' quaterpyridine **1** for which only tetrahedral $[M_4L_6]^{8+}$ cage species were observed when reacted with various Fe(II) salts. It also contrasts with that observed for **2** and **3** incorporating essentially rigid substituted phenylene and biphenylene bridges between the dipyrindyl domains where reaction with Fe(II) and Ni(II) yielded both $[M_2L_3]^{4+}$ and $[M_4L_6]^{8+}$ complex types, but in this case it was the latter species that was assigned as the thermodynamically favoured product type. The X-ray structures of the triple helicate complexes $[H_2O \cdot Ni_2(\mathbf{4})_3](PF_6)_4 \cdot THF \cdot 2.2H_2O$, $[Ni_2(\mathbf{6})_3](PF_6)_4 \cdot 1.95MeCN \cdot 1.2THF \cdot 1.8H_2O$, and the very unusual triple helicate PF_6^- inclusion complex, $[(PF_6) \cdot Ni_2(\mathbf{5})_3](PF_6)_3 \cdot 1.75MeCN \cdot 5.25THF \cdot 0.25H_2O$ are reported.

Introduction

While considerable interest continues to be given to the metal-ion directed assembly of discrete metallosupramolecular systems that incorporate a central cavity,¹ the assembly of new systems of this type displaying predetermined properties continues to be a challenge.² This is due to the many influences that may affect the outcome of a given self-assembly experiment. In the first instance the choice of the metal ion and the other components (commonly an appropriately functionalised organic building block or blocks) are obviously of key importance. Metal ion properties such as its charge, radius, spin-state and the presence of any crystal field properties that may influence the coordination behaviour (including the degree of kinetic inertness of the resulting product) may all influence a given supramolecular assembly outcome. For

the organic component, careful design of both its structural and electronic properties are of course essential. Even factors such as its flexibility may influence a given supramolecular outcome. For example, a considerable number of polypyridyl ligands displaying different flexibilities have now been employed for the assembly of a wide variety of metallo-supramolecular structures whose architectures, at least in part, reflect the inherent flexibility of the particular ligand system used.³

Like many others, we have employed a metal-directed approach of the type mentioned above for synthesising a range of structures incorporating 2- and 3-dimensional voids, many of which include guest molecules or ions.^{4–7} For example, it has now been well demonstrated that when essentially linear bis-bidentate ligand systems react with octahedral metal ions, M_2L_3 helicates (or sometimes their corresponding *meso* isomers) or M_4L_6 tetrahedra are commonly formed; sometimes these occur in combination.^{8–10}

Although from entropic considerations alone the above reaction type might be expected to favour formation of a smaller M_2L_3 assembly, if the generation of such an assembly is sterically inhibited due to lack of flexibility in the organic component (L) then frequently the larger homologue, M_4L_6 , becomes the preferred thermodynamic product.^{8,11,12} Hence, in such a situation it is the balance between flexibility and rigidity of the ditopic ligand that may largely control which of the above assembly types predominates.

In our previous studies, it was shown that the near-rigid, linear ditopic ligand, 5,5'''-dimethyl-2,2':5',5''':2'',2'''-quaterpyridine **1**,

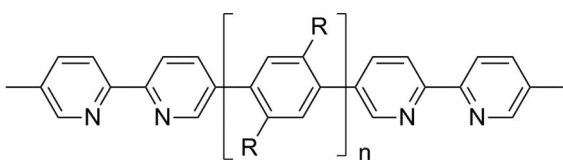
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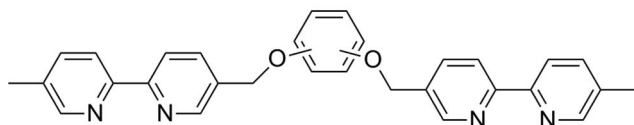
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† Electronic supplementary information (ESI) available: ESI-HRMS of $[Fe_2(\mathbf{4})_3](PF_6)_4$ and an additional X-ray structure figure for the $[Ni_2(\mathbf{6})_3]^{4+}$ cation. CCDC reference numbers [CCDC 824369–824371]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10820d



- 1; $n = 0$
 2; $n = 1$, R = OMe
 3; $n = 2$, R = OMe



- 4; 1,2-benzo bridged
 5; 1,3-benzo bridged
 6; 1,4-benzo bridged

yields solely $[\text{Fe}_4\text{L}_6]^{8+}$ tetrahedra when reacted with a range of Fe(II) salts (often spontaneously including an anion in the central cavity of the tetrahedral cage).^{4,6} However the slightly larger (and more kinetically inert) Ru(II) yielded a $[\text{Ru}_2\text{L}_3]^{4+}$ triple helicate under the conditions employed for the reaction.⁹ In a further study in our laboratories, the related expanded quaterpyridine derivatives **2** and **3** incorporating rigid dimethoxy-substituted 1,4-phenylene and tetramethoxy-substituted 4,4'-biphenylene bridges respectively between pairs of 2,2'-bipyridyl groups were prepared and in a comparative investigation their interaction with Fe(II) and Ni(II) was undertaken.¹³ In each case these fully conjugated ligand systems yielded a mixture of $[\text{M}_2\text{L}_3]^{4+}$ triple helicate and a $[\text{M}_4\text{L}_6]^{8+}$ tetrahedral species – behaviour that, at least in part, was attributed to the greater flexibility of these extended quaterpyridines allowing generation of both the above species type (although evidence suggested that the tetrahedral structures are of somewhat higher stability than the corresponding triple helicates in each case).

As an extension of the above studies, we now report the results of a further comparative investigation of the effect of extending the structure of quaterpyridine **1** to yield the flexibly-linked, bis-ether containing quaterpyridine ligands **4–6** on the nature of the metallosupramolecular assemblies formed with Ni(II) and Fe(II). In particular, it was of interest to observe what influence the increased flexibility of **4–6** would have on the nature of the corresponding metallosupramolecular systems generated relative to those formed by **1–3**.

Results and discussion

Expanded quaterpyridine ligand synthesis

The reaction of 5-chloromethyl-5'-methyl-2,2'-bipyridine with catechol, resorcinol and hydroquinone in the presence of K_2CO_3 in dimethylformamide afforded the flexibly bridged quaterpyridines **4–6** in 90, 93 and 58 percent yield, respectively. The ^1H and ^{13}C NMR of the respective products confirmed their expected C_2 -symmetries and in each case the spectra were in overall accord with the expected structures. In particular, for the ^1H NMR spectra NOEs were observed between methyl protons at ~ 2.4 ppm and protons in the 4'- and 6'-positions for each compound, allowing full assignment of the respective spectra.

$[\text{M}_2\text{L}_3]^{4+}$ complexes incorporating **4–6**

We now report the results of metal-directed assembly reactions involving the interaction of Fe(II) and Ni(II) with each of the new flexibly-bridged quaterpyridines **4–6**.

Fe(II) complexes. In an initial series of experiments, $\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$ or $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ were reacted with each of **4–6** in a 2:3 (M:L) ratio in a microwave reactor using methanol or acetonitrile as solvent. For the catechol-bridged species **4**, thin layer chromatography (TLC) of the crude product indicated the predominant formation of a single deep red product. This product was subjected to chromatography on silica gel and isolated as its PF_6^- salt. The deep red colouration is characteristic of the presence of a low-spin $[\text{Fe}(\text{bipyridine})_3]^{2+}$ chromophore.¹⁴

The ^1H NMR spectrum of this material indicated that the complexed ligand had retained its two-fold symmetry; there were eight aromatic resonances (Fig. 1a). However, despite the chromatographic purification step, there was evidence for the presence of a small amount ($\sim 10\%$) of a second product of high symmetry (see arrows in Fig. 1a).

The ESI-HRMS of the above product revealed +2 to +4 ions corresponding to successive losses of PF_6^- from the formula $[\text{Fe}_2(\mathbf{4})_3](\text{PF}_6)_4$ (see ESI†). There was also evidence of a second series of ions (much weaker peaks) corresponding to the successive losses of PF_6^- anions from the formula $[\text{Fe}_4(\mathbf{4})_6](\text{PF}_6)_8$. The presence of this latter series is exemplified by the theoretical and observed isotopic distributions for the +5 ion, $\{[\text{Fe}_4(\mathbf{4})_6](\text{PF}_6)_3\}^{5+}$ (see ESI†). Thus, the presence of a $[\text{Fe}_4\text{L}_6]^{8+}$ complex likely accounts for the symmetrical by-product observed in the ^1H NMR spectrum of this material. Based on the ^1H NMR spectrum and mass spectrum of the complex, $[\text{Fe}_2(\mathbf{4})_3](\text{PF}_6)_4$, it is assumed that the structure is either a true helicate (namely, metal centres: $\Delta\Delta$ or $\Lambda\Lambda$) or a *meso*-helicate (metal centres: $\Delta\Lambda$).

TLC of the product from an analogous metal-directed assembly experiment employing $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and the resorcinol-bridged **5** indicated the formation of a complex mixture of products. In this case, separation of these by chromatography on silica gel or by size exclusion chromatography was in each case unsuccessful leading to only a partially purified product whose ^1H NMR spectrum showed an underlying broadness and indicated the presence of impurities. However, the spectrum confirmed that in the major product the ligand maintains its two-fold symmetry. The ESI-HRMS of the above product showed the presence of +2 and +3 ions corresponding to the successive losses of BF_4^- from the formula $[\text{Fe}_2(\mathbf{5})_3](\text{BF}_4)_4$. No ions that could be assigned to arise from a $[\text{Fe}_4\text{L}_6](\text{BF}_4)_8$ species were observed.

The interaction of the hydroquinone-bridged quaterpyridine **6** with $\text{FeCl}_2 \cdot 5\text{H}_2\text{O}$ gave a deep red crude product that was isolated by addition of NH_4PF_6 . This was redissolved then passed down a silica gel column and was again isolated as its PF_6^- salt. Interestingly, in contrast to the ^1H NMR spectra of the respective products derived from **4** and **5**, the ^1H NMR spectrum of this material indicated that two different ligand environments were present. The most clearly seen proton resonances reflecting this are those corresponding to the hydroquinone-bridge protons, which in the free ligand are equivalent, but are now present as two singlets of relative intensities close to 1:1 (see peaks marked with asterisks in Fig. 1b). As well, there are two overlapping AB systems for the

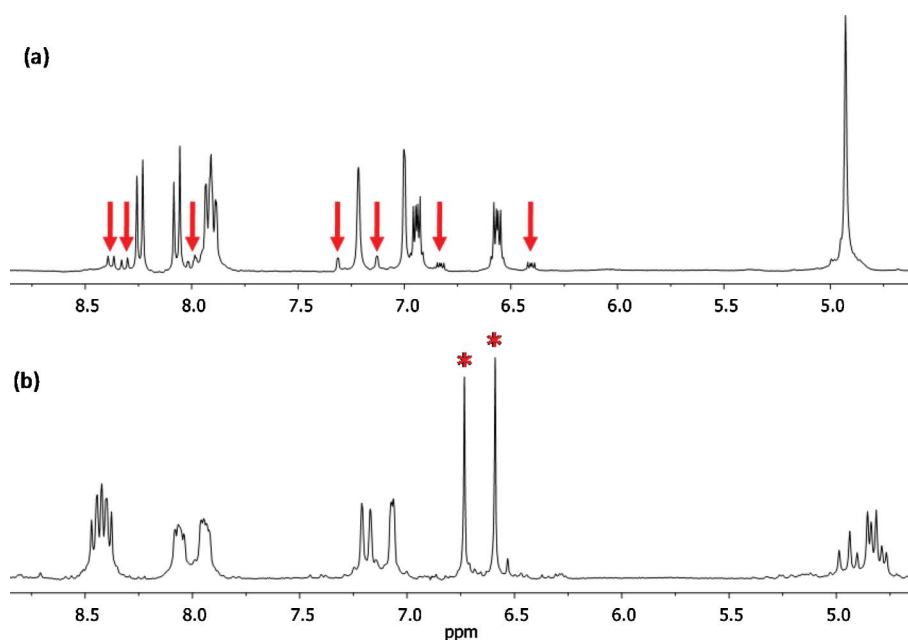


Fig. 1 ^1H NMR spectra in CD_3CN of (a) $[\text{Fe}_2(\mathbf{4})_3](\text{PF}_6)_4$ and (b) $[\text{Fe}_2(\mathbf{6})_3](\text{PF}_6)_4$. The two singlets arising from the hydroquinone-bridge proton in the latter spectrum are marked with asterisks (see discussion in main text).

phoxymethylene protons (see expanded peaks marked with red circle in Fig. 1b). The ESI-HRMS of this material revealed +2 and +3 ion species corresponding to successive losses of PF_6^- from the formula $[\text{Fe}_2(\mathbf{6})_3](\text{PF}_6)_4$ (while much less intense peaks were also present corresponding to the successive loss of PF_6^- ions from the formula $[\text{Fe}_4(\mathbf{6})_6](\text{PF}_6)_8$).

Based on the above evidence, the ~1:1 relative intensities for the ligand singlet peaks rule out possible simple $[\text{Fe}_2\text{L}_3]^{4+}$ helicate or *meso* structures (as well as a dinuclear structure of this stoichiometry incorporating two terminally coordinated **6** ligands and one bridging **6** ligand)¹⁵ in which two ligands are in one environment and one is in another. The most probable rationale for the observed NMR data appears to be that the product is a ~1:1 mixture of the corresponding (isomeric) triple helicate and *meso*-helicate. Although a single helicate or *meso*-helicate structure in which opposite ends are non-equivalent would also fit the data, we consider this unlikely since it is difficult to see what the driving force for the formation of such species would be.

Ni(II) complexes. In a subsequent set of experiments, a similar series of metal-directed assembly experiments to those just discussed for Fe(II) and **4–6** were undertaken in which $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was substituted for the iron salt. The ESI-HRMS of the resulting products indicated that the major species were the $[\text{M}_2\text{L}_3]^{4+}$ complexes, $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$, $[\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_4$, and $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4$ respectively; the spectrum of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$, which is representative of those for the other two products, is shown in Fig. 2a. In parallel to the corresponding Fe(II) systems of **4** and **6**, there was again mass spectral evidence for the additional formation of $[\text{Ni}_4\text{L}_6]^{8+}$ species for these two ligands. In each case, +3 ion species corresponding to the loss of three PF_6^- anions from the formulae $[\text{Ni}_4(\mathbf{4})_6](\text{PF}_6)_8$ and $[\text{Ni}_4(\mathbf{6})_6](\text{PF}_6)_8$ were observed. Good agreement between the theoretical and observed isotopic distributions leaves little doubt as to the identity of these species

(see, for example Fig. 2b). It is noted that the spectrum of $[\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_4$ only showed ions corresponding to the loss of PF_6^- anions from this formula; no evidence for formation of $[\text{Ni}_4(\mathbf{5})_6](\text{PF}_6)_8$ was observed in this case.

X-ray structures

Crystals of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$, $[\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_4$ and $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4$ suitable for X-ray diffraction were grown from a tetrahydrofuran/acetonitrile solvent mixture in each case. The structure of $[\text{H}_2\text{O} \cdot \text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4 \cdot \text{THF} \cdot 2.2\text{H}_2\text{O}$ (Fig. 3) confirmed the $[\text{M}_2\text{L}_3]^{4+}$ formulation of the complex cation. The product crystallised in the centrosymmetric monoclinic space group $C 2/c$ with $Z = 4$; thus the molecule has a two-fold axis. The two octahedral Ni(II) centres are separated by 10.8 Å and bridged by three quaterpyridine ligands such that the stereochemistry of the metal centres of each discrete unit are either $\Delta\Delta$ (*P*) or $\Delta\Delta$ (*M*). Thus, the solid state structure of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$ is a true helicate. There is a guest water molecule encapsulated in the centre of the helix.

$[(\text{PF}_6) \cdot \text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_3 \cdot 1.75\text{MeCN} \cdot 5.25\text{THF} \cdot 0.25\text{H}_2\text{O}$ crystallised in the centrosymmetric monoclinic space group $P 2_1/c$. The two octahedral Ni(II) centres are separated by 12.8 Å and bridged by three quaterpyridine ligands such that the stereochemistry of the metal centres of each discrete unit is again either $\Delta\Delta$ (*P*) or $\Delta\Delta$ (*M*). The structure reveals that a PF_6^- anion is encapsulated in the central cavity of the helicate such that in the solid state the structure corresponds to $[(\text{PF}_6) \cdot \text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_3$ (Fig. 4).

Finally the crystal structure of $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4 \cdot 1.95\text{MeCN} \cdot 1.2\text{THF} \cdot 1.8\text{H}_2\text{O}$ confirmed its formulation as $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4$ (Fig. 5). This product crystallised in the centrosymmetric triclinic space group $P\bar{1}$. The two octahedral Ni(II) centres are separated by 14.1 Å and bridged by three quaterpyridine ligands such that the stereochemistry of the metal centres of each discrete unit are once again either $\Delta\Delta$ (*P*) or $\Delta\Delta$ (*M*). Interestingly, in this product the

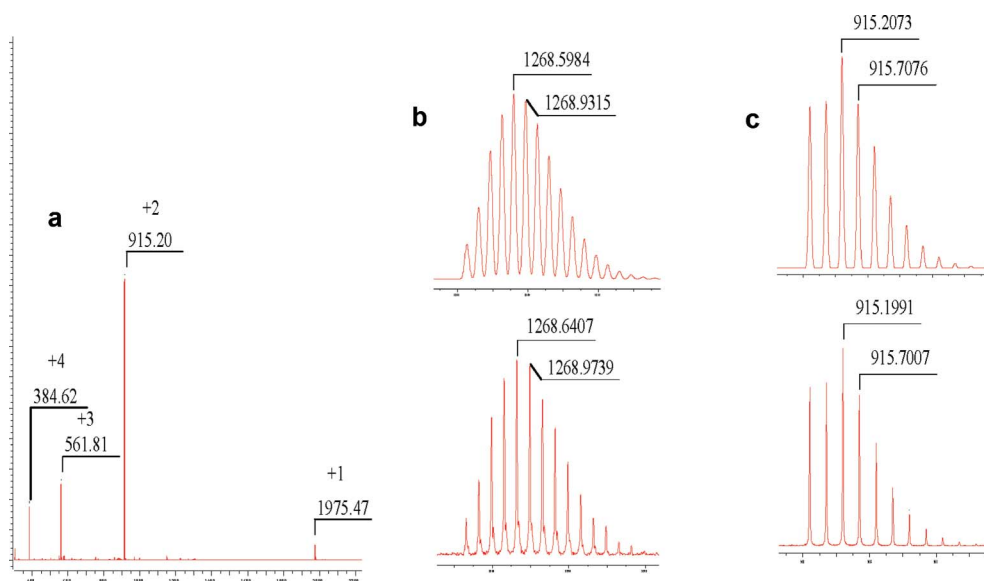


Fig. 2 (a) The mass spectrum of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$ and the theoretical (top) and observed (bottom) isotopic distributions for (b) $\{[\text{Ni}_4(\mathbf{4})_6](\text{PF}_6)_5\}^{3+}$ and (c) $\{[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_2\}^{2+}$.

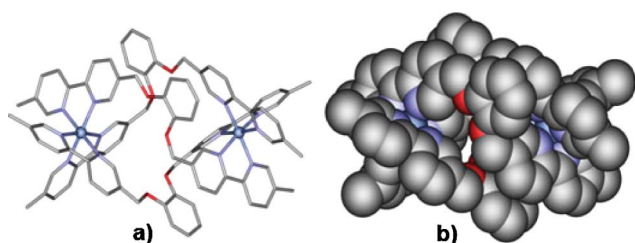


Fig. 3 (a) Stick representation of the crystal structure of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4 \cdot \text{THF} \cdot 2.2\text{H}_2\text{O}$ and (b) space filling representation (hydrogens, counterions and solvents removed for clarity).

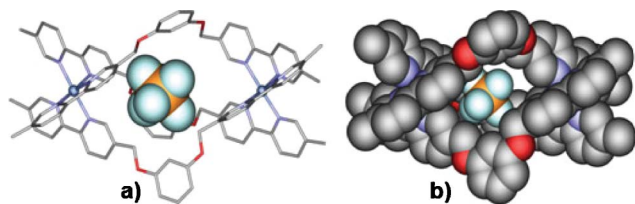


Fig. 4 (a) Stick representation of the crystal structure of $[(\text{PF}_6)\text{C}-\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_3 \cdot 1.75\text{MeCN} \cdot 5.25\text{THF} \cdot 0.25\text{H}_2\text{O}$ and (b) space filling representation both views showing the encapsulated PF_6^- anion (hydrogens, counterions and solvents are removed for clarity).

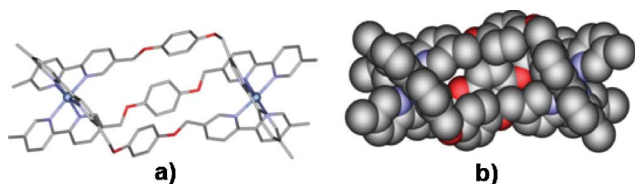


Fig. 5 (a) Stick representation of the crystal structure of $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4 \cdot 1.95\text{MeCN} \cdot 1.2\text{THF} \cdot 1.8\text{H}_2\text{O}$ illustrating the two bound ligand conformations present in this helicate and (b) a space filling representation (hydrogens, counterions and solvents removed for clarity).

three ligands exist in two different conformations. For two ligands one of the bipyridyl groups is orientated at approximately 80° to

the plane of the hydroquinone bridge which is coplanar to the other bipyridyl group. The other ligand is in a near planar conformation throughout, with each coordination domain orientated $\sim 180^\circ$ to the other. The latter is related to the S-shaped conformation that Albrecht described as being beneficial for helicate formation.¹²

Conclusions

In this report we have demonstrated that the interaction of Fe(II) and Ni(II) with the expanded flexible quaterpyridines **4–6** predominantly results in the formation of $[\text{M}_2\text{L}_3]^{4+}$ complexes although with **4** and **6** there was also evidence for the (minor) formation of the corresponding $[\text{M}_4\text{L}_6]^{8+}$ species under the conditions employed. This result contrasts with the behaviour of the quite rigid ‘parent’ quaterpyridine **1** for which only $[\text{M}_4\text{L}_6]^{8+}$ species were observed. To a lesser degree the present results for **4–6** also contrast with those obtained for the expanded quaterpyridines of intermediate flexibility, **3** and **4**, for which both $[\text{M}_2\text{L}_3]^{4+}$ and $[\text{M}_4\text{L}_6]^{8+}$ species were seen to occur but in these cases the $[\text{M}_4\text{L}_6]^{8+}$ appears to be the favoured (thermodynamic) product. Finally, it is noted that the structure of the complex cation $[(\text{PF}_6)\text{C}-\text{Ni}_2(\mathbf{5})_3]^{3+}$ is quite unusual in that it provides a rare example of the inclusion of a large polyatomic anion in a dinuclear triple helicate complex.

Experimental

All reagents were of analytical grade unless otherwise indicated. 5-Trimethylsilylmethyl-5'-methyl-2,2'-bipyridine and 5-chloromethyl-5'-methyl-2,2'-bipyridine were prepared using a combination of literature methods.^{16,17} Chromatography grade solvents were distilled through a fractionation column packed with glass helices. NMR spectra were recorded on a Bruker AM-300 or a Varian Mercury 300 MHz spectrometer (300.133 MHz) at 298 K. Electrospray (ES) high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) measurements were obtained on a Bruker BioAPEX 47e mass spectrometer

equipped with an Analytica of Branford electrospray ionisation (ESI) source.

1,2-Bis-(5'-methyl-[2,2']bipyridinyl-5-ylmethoxy)benzene (4). 5-Chloromethyl-5'-methyl-2,2'-bipyridine (241 mg, 1.1 mmol), catechol (55 mg, 0.5 mmol) and K_2CO_3 (415 mg, 3.0 mmol) in dimethylformamide (10 mL) was stirred at room temperature over 12 h. H_2O (20 mL) was then added to the reaction mixture, and the resulting precipitate filtered off and washed with water followed by a minimum volume of chilled methanol. The crude product was purified by chromatography on silica gel with dichloromethane (98.75%), methanol (1%) and saturated NH_3 (0.25%) as eluent to afford **4** (215 mg, 90%) as a white powder. 1H -NMR δ ($CDCl_3$, 300 MHz) 2.40 (s, 6 H, CH_3), 5.22 (s, 4 H, OCH_2Ar), 6.96 (m, 4 H, Ar-H), 7.63 (dd, $^3J = 8.1$, $^4J = 1.8$ Hz, 2 H, H-4'), 7.90 (dd, $^3J = 8.1$, $^4J = 2.1$ Hz, 2 H, H-4), 8.29 (d, $^3J = 8.1$ Hz, 2 H, H-3'), 8.38 (d, $^3J = 8.1$ Hz, 2 H, H-3), 8.50 (d, $^4J = 1.8$ Hz, 2 H, H-6'), 8.72 (d, $^4J = 2.1$ Hz, 2 H, H-6); ^{13}C -NMR δ (75 MHz, $CDCl_3$) 18.61, 69.17, 115.70, 120.97, 121.07, 122.43, 132.73, 133.86, 136.57, 137.97, 148.45, 148.87, 149.61, 153.26, 155.88; positive ion ESI-HRMS: m/z ($M = C_{30}H_{26}N_4O_2$ in dichloromethane/methanol): calc for $[M + Na]^+$: 497.1948, found 497.1948.

1,3-Bis-(5'-methyl-[2,2']bipyridinyl-5-ylmethoxy)-benzene (5). The procedure was similar to that employed for the synthesis of **4**. 5-Chloromethyl-5'-methyl-2,2'-bipyridine (241 mg, 1.1 mmol), resorcinol (55 mg, 0.5 mmol) and K_2CO_3 (415 mg, 3.0 mmol) were reacted in DMF (10 cm^3) for 12 h. Standard workup yielded **5** (220 mg, 93%) as a white powder. 1H NMR δ ($CDCl_3$, 300 MHz) 2.41 (s, 6 H, CH_3), 5.12 (s, 4 H, OCH_2Ar), 6.64 (dd, $^3J = 8.1$, $^4J = 2.3$ Hz, 2 H, H-b), 6.65 (d, $^4J = 2.3$ Hz, 1 H, H-a), 7.23 (t, $^3J = 8.1$ Hz, 1 H, H-c), 7.65 (dd, $^3J = 8.1$, $^4J = 2.1$ Hz, 2 H, H-4'), 7.89 (dd, $^3J = 8.1$, $^4J = 2.1$ Hz, 2 H, H-4), 8.30 (d, $^3J = 8.1$ Hz, 2 H, H-3'), 8.41 (d, $^3J = 8.1$ Hz, 2 H, H-3), 8.52 (d, $^4J = 2.1$ Hz, 2 H, H-6'), 8.72 (d, $^4J = 2.1$ Hz, 2 H, H-6); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.61, 67.75, 102.60, 107.89, 120.99, 121.07, 130.41, 132.43, 133.96, 136.61, 138.05, 148.50, 149.60, 153.21, 155.93, 159.88$; positive ion ESI-HRMS: m/z ($M = C_{30}H_{26}N_4O_2$ in dichloromethane/methanol): calc. for $[M + H]^+$: 475.2129, found 475.2200; calc. for $[M + Na]^+$: 497.1948, found 497.1945.

1,4-Bis-(5'-methyl-[2,2']bipyridinyl-5-ylmethoxy)-benzene (6). The procedure was similar to that employed for the synthesis of **4**. 5-Chloromethyl-5'-methyl-2,2'-bipyridine (241 mg, 1.1 mmol), hydroquinone (55 mg, 0.5 mmol) and K_2CO_3 (415 mg, 3.0 mmol) were reacted in DMF (10 cm^3) for 12 h. Standard workup yielded **6** (138 mg, 58%) as a sparingly soluble white powder. This material was used without further purification. 1H NMR δ ($CDCl_3$, 300 MHz) 2.41 (s, 6 H, CH_3), 5.09 (s, 4 H, OCH_2Ar), 7.65 (dd, $^3J = 8.1$, $^4J = 1.8$ Hz, 2 H, H-4'), 7.89 (dd, $^3J = 8.4$, $^4J = 2.1$ Hz, 2 H, H-4), 8.31 (d, $^3J = 8.1$ Hz, 2 H, H-3'), 8.41 (d, $^3J = 8.4$ Hz, 2 H, H-3), 8.52 (d, $^4J = 1.8$ Hz, 2 H, H-6'), 8.71 (d, $^4J = 2.1$ Hz, 2 H, H-6); positive ion ESI-HRMS: m/z ($M = C_{30}H_{26}N_4O_2$ in dichloromethane/methanol): calc. for $[M + Na]^+$: 497.1948, found 497.1956.

$[Fe_2(4)_3](PF_6)_4$. A mixture of $FeCl_2 \cdot 5H_2O$ (30 mg, 0.14 mmol) and **4** (110 mg, 0.232 mmol) in methanol (10 mL) was heated with microwave energy in a sealed pressurised microwave vessel with temperature and pressure sensors (Step 1 – ramped to 130 °C over

2 min using 100% of 400 W; Step 2 – held at 130 °C for 20 min using 25% of 400 W). The reaction mixture was filtered and the crude product precipitated by the addition of an excess of aqueous NH_4PF_6 . This deep red material was purified by chromatography on silica gel with a mixture of acetonitrile, H_2O and saturated KNO_3 (7 : 1 : 0.5) as eluent. The resulting product was isolated by precipitation with excess aqueous NH_4PF_6 in H_2O (20 mL) and removed by filtration to afford crude $[Fe_2(4)_3](PF_6)_4$ (132 mg, 90%) as a red solid. 1H -NMR (see Fig. 1a) δ (300 MHz, CD_3CN) 2.16 (s, 18 H, CH_3), 4.93 (s, 12 H, OCH_2Ar), 6.56 (dd, $^3J = 6.0$ Hz, $^4J = 3.6$ Hz, 6 H, Ar-H), 6.94 (dd, $^3J = 6.0$ Hz, $^4J = 3.6$ Hz, 6 H, Ar-H), 7.00 (br s, 6 H), 7.22 (br s, 6 H), 7.91 (br m, 12 H), 8.07 (d, $^3J = 8.4$ Hz, 6 H), 8.24 (d, $^3J = 8.3$ Hz, 6 H; positive ion ESI-HRMS: m/z ($M = C_{90}H_{78}P_4F_{24}Fe_2N_{12}O_6$ in acetonitrile/methanol): calc for $[M - 2PF_6]^{2+}$: 912.2073, found 912.2130; calc for $[M - 3PF_6]^{3+}$: 559.8166, found 559.8168; calc for $[M - 4PF_6]^{4+}$: 383.6213, found 383.6210.

$[Fe_2(5)_3](BF_4)_4$. A mixture of $Fe(BF_4)_2 \cdot 6H_2O$ (47 mg, 0.14 mmol) and quaterpyridine **5** (110 mg, 0.232 mmol) in acetonitrile (10 mL) was heated with microwave energy in a sealed pressurised microwave vessel with temperature and pressure sensors (Step 1 – ramped to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 20 min using 25% of 400 W). The solvent was evaporated and the crude deep red material was purified by chromatography on Sephadex LH-20 with acetonitrile as eluent. This allowed the isolation of $[Fe_2(5)_3](BF_4)_4$ (109 mg, 83%) as a deep red solid. 1H -NMR δ (300 MHz, CD_3CN) 2.21 (s, 18 H, CH_3), 4.94 (d, $^2J = 14.8$ Hz, 6 H, OCH_2Ar), 5.04 (d, $^2J = 14.8$ Hz, 6 H, OCH_2Ar), 6.35, 6.38, 7.15, 7.93, 8.04, 8.39; positive ion ESI-HRMS: m/z ($M = C_{90}H_{78}B_4F_{16}Fe_2N_{12}O_6$ in acetonitrile/methanol): calc for $[M - 2BF_4]^{2+}$: 854.2472, found 854.2486; calc for $[M - 3BF_4]^{3+}$: 540.4966, found 540.4973.

$[Fe_2(6)_3](PF_6)_4$. The procedure was similar to that employed for the synthesis of $[Fe_2(4)_3](PF_6)_4$. $FeCl_2 \cdot 5H_2O$ (30 mg, 0.14 mmol) and quaterpyridine **6** (110 mg, 0.232 mmol) afforded $[Fe_2(6)_3](PF_6)_4$ (125 mg, 85%) as a red solid. 1H -NMR (see Fig. 1b) δ (300 MHz, CD_3CN) 2.21 (s, CH_3), 2.22 (s, CH_3), 4.79 (d, $^2J = 14.5$ Hz, OCH_2Ar), 4.81 (d, $^2J = 14.9$ Hz, OCH_2Ar), 4.88 (d, $^2J = 14.5$ Hz, OCH_2Ar), 4.96 (d, $^2J = 14.9$ Hz, OCH_2Ar), 6.59 (s, 6 H, Ar-H), 6.73 (s, 6 H, Ar-H), 7.06 (s, 3 H), 7.07 (s, 3 H), 7.17 (s, 3 H), 7.21 (s, 3 H), 7.94 (m, 6 H), 8.06 (m, 6 H), 8.42 (m, 12 H); positive ion ESI-HRMS: m/z ($M = C_{90}H_{78}P_4F_{24}Fe_2N_{12}O_6$ in acetonitrile/methanol): calc for $[M - 2PF_6]^{2+}$: 912.2073, found 912.2130; calc for $[M - 3PF_6]^{3+}$: 559.8166, found 559.8179.

$[Ni_2(4)_3](PF_6)_4$. A stirred solution of $NiCl_2 \cdot 6H_2O$ (17 mg, 0.07 mmol) and **4** (50 mg, 0.105 mmol) in methanol (10 mL) was heated with microwave energy in a sealed pressurised microwave vessel with temperature and pressure sensors (Step 1 – ramped to 130 °C over 2 min using 100% of 400 W; Step 2 – held at 130 °C for 20 min using 25% of 400 W). The product was isolated by precipitation with excess aqueous NH_4PF_6 in H_2O (20 mL) followed by filtration affording $[Ni_2(4)_3](PF_6)_4$ quantitatively as a yellow solid. Positive ion ESI-HRMS: m/z ($M = C_{90}H_{78}P_4F_{24}Ni_2N_{12}O_6$ in acetonitrile/methanol): calc for $[M - 2PF_6]^{2+}$: 915.2073, found 915.1991; calc for $[M - 3PF_6]^{3+}$: 561.8166, found 561.8224; calc for $[M - 4PF_6]^{4+}$: 385.1213, found 385.1229. Found: C, 49.15; H, 3.75; N, 7.55%. Calc. for $C_{90}H_{78}P_4F_{24}Ni_2N_{12}O_6 \cdot 4H_2O$: C 49.31, H

3.96, N 7.67%. X-ray quality crystals were obtained by diffusion of tetrahydrofuran into an acetonitrile solution of the product.

The crude product before recrystallisation also showed evidence for the presence of the corresponding M_4L_6 complex, $[\text{Ni}_4(\mathbf{4})_6](\text{PF}_6)_8$. Positive ion ESI-HRMS: m/z ($M = \text{C}_{180}\text{H}_{156}\text{P}_8\text{F}_{48}\text{Ni}_4\text{N}_{24}\text{O}_{12}$ in acetonitrile/methanol): calc for $[M - 3\text{PF}_6]^{3+}$: 1268.5984, found 1268.6407.

$[\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_4$. The procedure was similar to that employed for the synthesis of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (17 mg, 0.07 mmol) and quaterpyridine **5** (50 mg, 0.105 mmol) yielded $[\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_4$ quantitatively as a yellow solid. Positive ion ESI-HRMS: m/z ($M = \text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}\text{O}_6$ in acetonitrile/methanol): calc for $[M - 2\text{PF}_6]^{2+}$: 915.2073, found 915.1989; calc for $[M - 3\text{PF}_6]^{3+}$: 561.8130, found 561.8224; calc for $[M - 4\text{PF}_6]^{4+}$: 385.1213, found 385.1192. Found: C 49.31, H 3.72, N 7.66%. Calc. for $\text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}\text{O}_6 \cdot 4\text{H}_2\text{O}$: C 49.31, H 3.96, N 7.67%. X-ray quality crystals were obtained by diffusion of tetrahydrofuran into an acetonitrile solution of the product.

$[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4$. The procedure was similar to that employed for the synthesis of $[\text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4$. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (17 mg, 0.07 mmol) and quaterpyridine **6** (50 mg, 0.105 mmol) yield $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4$ quantitatively as a yellow solid. Positive ion ESI-HRMS: m/z ($M = \text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}\text{O}_6$ in acetonitrile/methanol): calc for $[M - 2\text{PF}_6]^{2+}$: 915.2073, found 915.1974; calc for $[M - 3\text{PF}_6]^{3+}$: 561.8130, found 561.8131; calc for $[M - 4\text{PF}_6]^{4+}$: 385.1213, found 385.1235. Found: C, 49.43; H, 3.80; N, 7.75%. Calc. for $\text{C}_{90}\text{H}_{78}\text{P}_4\text{F}_{24}\text{Ni}_2\text{N}_{12}\text{O}_6 \cdot 4\text{H}_2\text{O}$: C, 49.31; H, 3.96; N, 7.67%. X-ray quality crystals were obtained by diffusion of tetrahydrofuran into an acetonitrile solution of the product.

The crude product before recrystallisation also showed evidence for the presence of the corresponding M_4L_6 complex, $[\text{Ni}_4(\mathbf{6})_6](\text{PF}_6)_8$. Positive ion ESI-HRMS: m/z ($M = \text{C}_{180}\text{H}_{156}\text{P}_8\text{F}_{48}\text{Ni}_4\text{N}_{24}\text{O}_{12}$ in acetonitrile/methanol): calc for $[M - 3\text{PF}_6]^{3+}$: 1268.5984, found 1268.6423.

X-ray studies

Data for $[\text{H}_2\text{O} \cdot \text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4 \cdot \text{THF} \cdot 2.2\text{H}_2\text{O}$ and $[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4 \cdot 1.95\text{MeCN} \cdot 1.2\text{THF} \cdot 1.8\text{H}_2\text{O}$ were collected on a Bruker-Nonius APEX2-X8-FR591 diffractometer employing graphite-monochromated $\text{Mo-K}\alpha$ radiation generated from a rotating anode (0.71073 Å) with ω and ψ scans to approximately 56° 2θ at 150(2) K.¹⁸ Data for $[(\text{PF}_6)_3\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_3 \cdot 1.75\text{MeCN} \cdot 5.25\text{THF} \cdot 0.25\text{H}_2\text{O}$ were collected at approximately 100 K using double diamond monochromated synchrotron radiation (0.48595 Å) and ω and ψ scans at the ChemMatCARS beamline at the Advanced Photon Source. Data integration and reduction were undertaken with SAINT and XPREP.¹⁹ Subsequent computations were carried out using the WinGX-32 graphical user interface.²⁰ Structures were solved by direct methods using SIR97.²¹ Multi-scan empirical absorption corrections, when applied, were applied to the data set using the program SADABS.²² Data were refined and extended with SHELXL-97 and SHELXH-97.²³ In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. As oxygen bound hydrogen atoms could not be located in the difference Fourier map they were not modelled. In

all cases the crystals employed were extremely solvent sensitive and required rapid handling (~ 30 s) at low temperatures in order to facilitate data collection. Crystallographic data and specific details pertaining to structural refinements is summarised below.

$[\text{H}_2\text{O} \cdot \text{Ni}_2(\mathbf{4})_3](\text{PF}_6)_4 \cdot \text{THF} \cdot 2.2\text{H}_2\text{O}$

Formula $\text{C}_{94}\text{H}_{86.4}\text{F}_{24}\text{N}_{12}\text{Ni}_2\text{O}_{10.20}\text{P}_4$, M 2244.61, Monoclinic, space group $C2/c(\#15)$, a 23.0800(16), b 15.0530(11), c 32.656(3) Å, β 105.778(4), V 10918.0(15) Å³, D_c 1.362 g cm⁻³, Z 4, crystal size 0.300 × 0.250 × 0.100 mm, colour yellow, habit needle, temperature 150(2) K, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 0.502 mm⁻¹, $T(\text{SADABS})_{\text{min,max}}$ 0.813, 0.951, $2\theta_{\text{max}}$ 50.00, hkl range -21 27, -17 17, -38 38, N 111989, N_{ind} 9594 (R_{merge} 0.0267), N_{obs} 8211 ($I > 2\sigma(I)$), N_{var} 798, residuals $R_1(F)$ 0.0735, $wR_2(F^2)$ 0.2345, GoF(all) 1.094, $\Delta\rho_{\text{min,max}}$ -0.568, 1.084 e⁻ Å⁻³.

Specific details. The O(3)-containing ligand is disordered over two equal occupancy positions and the P(2)-containing PF₆ is disordered over two positions with occupancies of 0.7 and 0.3. The THF molecule is also disordered over two unequal positions (0.35 and 0.15) and the remaining disordered water molecules were modelled over 10 positions with a total occupancy of 1.2. Some bond length and angle restraints were required to facilitate realistic models.

$[(\text{PF}_6)_3\text{Ni}_2(\mathbf{5})_3](\text{PF}_6)_3 \cdot 1.75\text{MeCN} \cdot 5.25\text{THF} \cdot 0.25\text{H}_2\text{O}$

Formula $\text{C}_{114.50}\text{H}_{125.75}\text{F}_{24}\text{N}_{13.75}\text{Ni}_2\text{O}_{11.50}\text{P}_4$, M 2575.83, monoclinic, space group $P21/c(\#14)$, a 26.028(2), b 22.7450(17), c 21.4660(16) Å, β 113.663(2), V 11639.6(16) Å³, D_c 1.470 g cm⁻³, Z 4, crystal size 0.100 × 0.050 × 0.050 mm, colour yellow, habit needle, temperature 100(2) K, $\lambda(\text{synchrotron})$ 0.49594 Å, $\mu(\text{synchrotron})$ 0.259 mm⁻¹, $T(\text{SADABS})_{\text{min,max}}$ 0.5994, 0.7444, $2\theta_{\text{max}}$ 38.62, hkl range -33 33, -30 26, -27 28, N 99393, N_{ind} 27767 (R_{merge} 0.0847), N_{obs} 16878 ($I > 2\sigma(I)$), N_{var} 1577, residuals $R_1(F)$ 0.0624, $wR_2(F^2)$ 0.1880, GoF(all) 1.010, $\Delta\rho_{\text{min,max}}$ -0.858, 1.628 e⁻ Å⁻³.

Specific details. The O(3T)-containing THF is modelled as disordered over 3 positions with a total occupancy of 1 and the O(5T)-containing THF is modelled over two equal occupancy positions. The O(6T)-containing THF is 0.75 occupancy and is superimposed with a 0.25 occupancy MeCN. A number of bond length and angle constraints were required to facilitate realistic modelling.

$[\text{Ni}_2(\mathbf{6})_3](\text{PF}_6)_4 \cdot 1.95\text{MeCN} \cdot 1.2\text{THF} \cdot 1.8\text{H}_2\text{O}$

Formula $\text{C}_{98.70}\text{H}_{97.05}\text{F}_{24}\text{N}_{13.95}\text{Ni}_2\text{O}_9\text{P}_4$, M 2317.49, triclinic, space group $P \bar{1}(\#2)$, a 14.9978(6), b 15.0666(6), c 25.7786(11) Å, α 91.398(2), β 104.152(2), γ 99.563(2)°, V 5556.9(4) Å³, D_c 1.385 g cm⁻³, Z 2, crystal size 0.300 × 0.100 × 0.100 mm, colour yellow, habit needle, temperature 150(2) K, $\lambda(\text{MoK}\alpha)$ 0.71073 Å, $\mu(\text{MoK}\alpha)$ 0.496 mm⁻¹, $T(\text{SADABS})_{\text{min,max}}$ 0.799, 0.952, $2\theta_{\text{max}}$ 50.00, hkl range -17 17, -17 17, -30 30, N 107006, N_{ind} 19484 (R_{merge} 0.0534), N_{obs} 13655 ($I > 2\sigma(I)$), N_{var} 1534, residuals $R_1(F^2)$ 0.0734, $wR_2(F^2)$ 0.2194, GoF(all) 1.072, $\Delta\rho_{\text{min,max}}$ -0.552, 0.993 e⁻ Å⁻³.

Specific details. Each of the anions is disordered over two positions as is the O(1T) and O(2T)-containing THFs. The N(4S)-containing MeCN and O(3T)-containing THF have occupancies

of less than 1 and have disordered water molecules superimposed on their positions. A number of bond length constraints were required to produce realistic models.

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