A new Fe^{II} quaterpyridyl M_4L_6 tetrahedron exhibiting selective anion binding†

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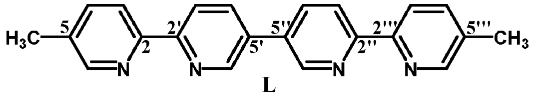
A rigid linear bis-bidentate quaterpyridine undergoes metal directed self-assembly with iron(II) salts yielding M_4L_6 host–guest complexes; selective anion binding for PF_6^- over BF_4^- is observed.

The design and synthesis of new molecular assemblies incorporating transition metal ions as structural elements has received very considerable attention over recent years.[1] Incorporation of transition metals in such systems yields the potential for generating additional functionality—including (unusual) optical, magnetic, photoactive, electrochemical and/or catalytic behaviour. The successful synthesis of a given system of this type normally depends on an appropriate match of the steric and electronic information inherent in both the chosen ligand system and metal ion; however, other considerations, including interligand stacking, templation and solvent effects, may also play a role.

Recently research within our group has focused on the assembly of cage-like systems that incorporate a central cavity and thus exhibit a potential for host–guest chemistry. A number of such structures have now been developed, including capsules,[2] cryptands[3] and tetrahedra.[4] In this context it has now been well documented that bis-bidentate ligand systems may interact with octahedral metal ions to yield triple helical species of type $[M_2L_3]^{n+}$ or larger species having stoichiometries that are a multiple of this ratio. Thus, amongst others, Saalfrank,[5] Raymond,[6] Ward[7] and Albrecht[8] have all described tetrahedral cage systems of M_4L_6 stoichiometry that exhibit interesting host–guest chemistry. Within this general area our group has employed 1,3- and 1,4-aryl linked bis-β-diketonato ligands[4,9] to generate uncharged $[M_3L_3]$ triangles, $[M_2L_3]$ triple helicates and $[M_4L_6]$ tetrahedral species. In the latter case, the metal ions occupy the vertices and aryl-linked bis-β-diketonato ligands define the edges; solvent molecules were included in the central cavities.

We now report the synthesis and characterisation of a new tetrahedral $[Fe_4\mathbf{L}_6]^{8+}$ host system incorporating the previously reported[10] 'bis-bidentate' ligand, 5,5‴-dimethyl-2,2′:5′,5″:2″,2‴-quaterpyridine (**L**).



L

Anion inclusion complexes of type $[Fe_4\mathbf{L}_6(\text{anion})]^{n+}$ (where anion = BF_4 or PF_6) have been synthesised. Thus, reaction of Fe^{II} tetrafluoroborate with **L** in acetonitrile in a 2 : 3 ratio generated a deep red colour, characteristic of a $[Fe(2,2'\text{-bipyridine})_3]^{2+}$ (low-spin) chromophore in the reaction solution and led to the isolation of a dark red product of stoichiometry $Fe_4\mathbf{L}_6(BF_4)_8{\cdot}4H_2O$. This product yielded a UV-Vis spectrum that exhibited a band at 529 nm (ε/dm^3 mol^{-1} cm^{-1} 21 800), similar to the MLCT band reported for $[Fe(2,2'\text{-bipyridine})_3]^{2+}$.[11] The ^1H NMR and ^{13}C NMR spectra of the product in CD_3CN were both in accord with the presence of a single compound of high symmetry in which all four ligands are in equivalent environments. ^1H–^1H COSY and NOESY experiments allowed the complete assignment of the ^1H NMR spectrum of the product (see ESI for NMR spectra†).

The high resolution electrospray ionisation mass spectrum (HR-ESI-MS) showed +2, +3, and +4 ions with masses corresponding to those calculated for successive losses of BF_4^- anions from the parent species of formula $Fe_4\mathbf{L}_6(BF_4)_8$ (Fig. 1); this result is thus in keeping with a structure incorporating a +8 charged M_4L_6 assembly.

Crystals of the above assembly suitable for X-ray diffraction were grown from THF–CH_3CN and the resulting structure‡

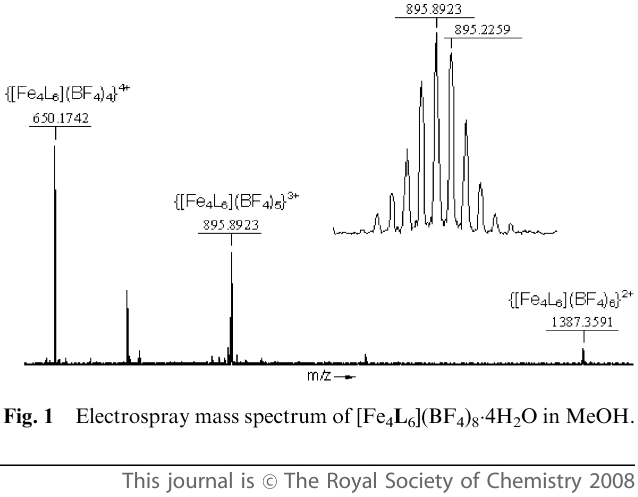


Fig. 1 Electrospray mass spectrum of $[Fe_4\mathbf{L}_6](BF_4)_8{\cdot}4H_2O$ in MeOH.

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† Electronic supplementary information (ESI) available: Experimental data for M_4L_6 complexes. See DOI: 10.1039/b717740b

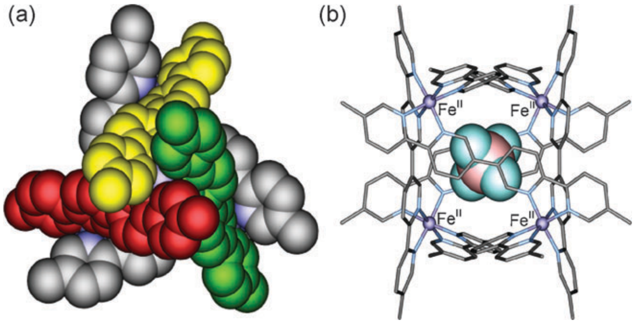

Fig. 2 X-Ray structure of the cation in the $[Fe_4\mathbf{L}_6(BF_4)]^{7+}$ assembly (*exo*-anions and solvents not shown); (a) space filling depiction viewed down the C_3 axis of the $\Delta\Delta\Delta\Delta$-$[Fe_4\mathbf{L}_6(BF_4)]^{7+}$ enantiomer; (b) schematic illustration of the host–guest complex.

showed a tetrahedral assembly of type $[Fe_4\mathbf{L}_6(BF_4)](BF_4)_7\cdot 3CH_3CN\cdot 6THF\cdot 3.6H_2O$ (Fig. 2) in which four octahedrally coordinated Fe^{II} centres occupy the vertices of the tetrahedron and six **L** ligands define the edges; a BF_4^- anion occupies the central cavity giving the overall cationic assembly a +7 charge. This latter charge is balanced by seven BF_4^- counterions that are arranged in the crystal lattice. The product crystallises in the cubic space group $P\bar{4}3n$ and individual Fe^{II} centres lie on 3-fold special positions and the ligands surround a 4-fold axis. Each of the two bipyridyl units of a given **L** is twisted by nearly 60° with respect to the other as the three-fold twist about the metal centres extends throughout the molecule. There is only one third of an Fe^{II} and half of one ligand in the asymmetric unit (one twelfth of the entire molecule). Individual tetrahedra contain homochiral metal centres; that is, each tetrahedron is either $\Lambda\Lambda\Lambda\Lambda$ or $\Delta\Delta\Delta\Delta$. As the space group contains *n*-glides, each crystal represents a racemic mixture. The chiral twist associated with a tetrahedron is evident when viewed down one of the C_3 axes (Fig. 2a). The distance between each of the Fe^{II} centres is 9.45 Å, which corresponds to an encapsulated volume of approximately 99 $Å^3$.

Despite the above solid-state structure showing an encapsulated BF_4^- guest, the ^{11}B and ^{19}F NMR spectra of this product in CD_3CN gave no evidence for the BF_4^- counterions existing in two environments over the temperature range 273.5–295 K. This is in accord with rapid *endo–exo* BF_4^- exchange of the central BF_4^- group occurring with respect to the NMR timescale under the conditions employed (see later).

Substitution of Fe^{II} tetrafluoroborate by Fe^{II} bromide in the above synthetic procedure followed by treatment with potassium hexafluorophosphate and subsequent column purification again produced a deep red crystalline solid whose HR-ESI-MS was related to that just discussed. This showed the presence of +2 to +7 charged ions, consistent with the sequential loss of up to seven PF_6^- anions from a parent species of type $Fe_4\mathbf{L}_6(PF_6)_8$. The ^{19}F NMR spectrum (Fig. 3a) of the product in CD_3CN clearly showed that the PF_6^- counterions are in two environments in a 7 : 1 ratio. This result is in keeping with the product being formulated as $[Fe_4\mathbf{L}_6(PF_6)](PF_6)_7$ with PF_6^- exchange between the *endo–exo* environments being slow (or absent) on the NMR timescale; furthermore over a temperature range of 273–350 K the ^{19}F NMR spectra revealed no significant change in peak widths. Clearly these results are in accord with the PF_6^- guest species being strongly held within the cage. As discussed above, this contrasts with the fast exchange behaviour on the NMR timescale of the cage derived from Fe^{II} tetrafluoroborate. The crystal structure‡ of $[Fe_4\mathbf{L}_6(PF_6)](PF_6)_7\cdot 9CH_3OH\cdot 6H_2O$ (Fig. 3b) (crystallised from CH_3OH–CH_3CN) using synchrotron radiation once again confirmed the production of a symmetric $M_4\mathbf{L}_6$ tetrahedron which encapsulates a PF_6^- anion. The latter is disordered over two positions, both located on a 12-fold special position.

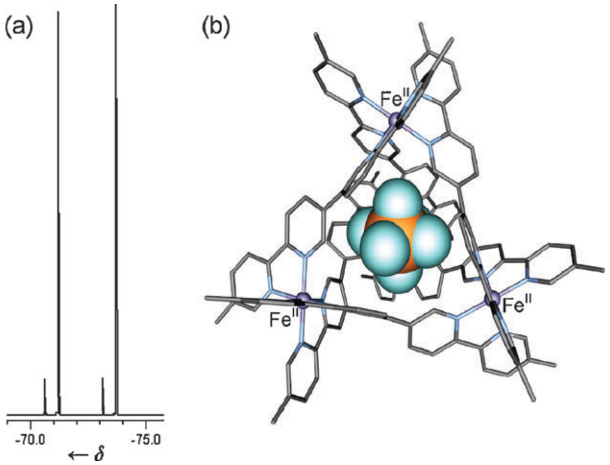

Fig. 3 (a) ^{19}F NMR spectrum of $[Fe_4\mathbf{L}_6(PF_6)](PF_6)_7\cdot 2H_2O$ in acetonitrile-d_3 at 300 K; (b) X-ray structure of the hexafluorophosphate-containing cation $[Fe_4\mathbf{L}_6(PF_6)]^{7+}$.

The different anion exchange inclusion behaviour for BF_4^- *versus* PF_6^-, as revealed by the ^{19}F NMR results, raises the question of whether the BF_4^- exchange in the case of $[Fe_4\mathbf{L}_6(BF_4)](BF_4)_7\cdot 4H_2O$ occurs *via* this anion passing through a side of the tetrahedron or whether Fe–pyridyl N bond breaking is involved—both mechanisms have been considered for guest exchange in related tetrahedral species.[12] In the present case, the apparent fast exchange seems unlikely to involve bond breaking given that the postulated exchange is fast on the NMR timescale and also that the low-spin Fe^{II} (d^6 configuration) is a moderately kinetically inert metal ion. In support of this, inspection of a space filling molecular model suggests that BF_4^- anion exchange without bond-breaking appears feasible provided moderate flexing/twisting of the bound ligands is able to occur. From size considerations, such a mechanism appears less likely for the larger PF_6^- ion (but it cannot be ruled out).

Intriguingly, in a further ^{19}F NMR experiment, slow replacement of encapsulated BF_4^- was observed to occur in the presence of a moderate excess of PF_6^- at 300 K over 80 min (with no further change in the spectrum occurring after 24 h). This result is perhaps best interpreted as involving 'fast' through-side exchange of encapsulated BF_4^- while entry into the 'empty' cage by PF_6^- occurs either *via* a slow (minutes) bond breaking mechanism or *via* a size-inhibited, through-side process. In any case, both interpretations imply a degree of anion selectivity by the cage, with PF_6^- being bound more strongly than BF_4^- within the cavity. In keeping with this, an attempt to induce the reverse exchange process (taking

$[Fe_4\mathbf{L}_6(PF_6)](PF_6)_7 \cdot 2H_2O$ in CD_3CN and adding BF_4^- under similar conditions) yielded no change in the initial spectrum after 24 h.

Previous reports[13] have concluded that the formation of related tetrahedral M_4L_6 host–guest species of type M_4L_6(guest) involves a guest template process. At this stage, it seemed that an anion templating mechanism might also apply for the present systems. Evidence bearing on this was obtained in a further synthetic study in which Fe^{II} chloride was employed as the metal salt and, as before, reacted with **L** in a 2 : 3 stoichiometric ratio. In this case the synthesis was performed in a microwave reactor at 393 K with water (rather than acetonitrile) as solvent.[14] On completion of this reaction, excess Zn^{II} chloride was added to the reaction solution in order to precipitate the product as its $[ZnCl_4]^{2-}$ salt. 'Instant' precipitation of a deep red solid occurred on addition of the latter ion. The ^1H NMR spectrum of this crude material indicated the presence of a product of high symmetry. Crystals suitable for X-ray diffraction were grown from THF–CH_3CN and the resulting structure‡ confirmed the presence of the usual tetrahedral $[Fe_4\mathbf{L}_6]^{8+}$ cage structure but in this case there was *no anion* included in its cavity (Fig. 4). Instead, the latter is occupied by disordered acetonitrile molecules.[15] The cage is again chiral although two-fold symmetric and crystallising in monoclinic *P*2/*n*. It appears that the absence of a polyatomic anion during the main reaction sequence coupled with the relative insolubility of the $[Fe_4\mathbf{L}_6][ZnCl_4]_4$ species may be important contributions to the isolation of the anion-free cage in this case. While this result does not *preclude* a templating role for the anions encapsulated in the structures discussed previously, it does suggest that such a polyatomic anion is *not essential* for assembly of the present $[Fe_4\mathbf{L}_6]^{8+}$ cage structure.

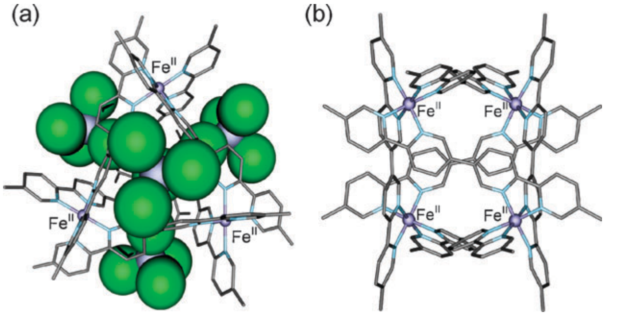

Fig. 4 (a) The '*empty*' cage in $[Fe_4\mathbf{L}_6]([ZnCl_4])_4 \cdot CH_3CN \cdot 5.5THF \cdot 2.5H_2O$ illustrating the locations of the four *exo* $[ZnCl_4]^{2-}$ counterions (solvent molecules removed); (b) $[Fe_4\mathbf{L}_6]^{8+}$ cation with $[ZnCl_4]^{2-}$ counterions and solvent molecules removed.

In conclusion, the present communication describes the synthesis and characterisation of a new class of anion binding tetrahedra capable of encapsulating PF_6^- over BF_4^- in its central cavity. While examples of such anions being encapsulated in tetrahedral structures have been reported previously,[7] we have been able to clearly demonstrate that the present cage system exhibits unusual anion selectivity for PF_6^- over BF_4^-. Finally, a successful synthetic procedure for isolating the cage free of an encapsulated anion is also reported—a result with implications for the role of anion templation (or otherwise) in the formation of tetrahedral structures of the present type.

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‡ CCDC 668029–668031. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b717740b

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14 A negligible concentration of $[FeCl_4]^{2-}$ will be present in water under the conditions employed.
15 When PF_6^- or BF_4^- was substituted for $[ZnCl_4]^{2-}$ in the isolation procedure and the resulting product recrystallised from acetonitrile, the inclusion species $[Fe_4L_6(PF_6)](PF_6)_7$ (characterised by NMR and HRMS) or $[Fe_4L_6(BF_4)](BF_4)_7$ (characterised by NMR, HRMS and a second X-ray structure determination) was isolated.