Monitoring the iron(II)-induced self-assembly of preorganized tritopic ligands by electrospray mass spectrometry: unique formation of metallomacrocycles

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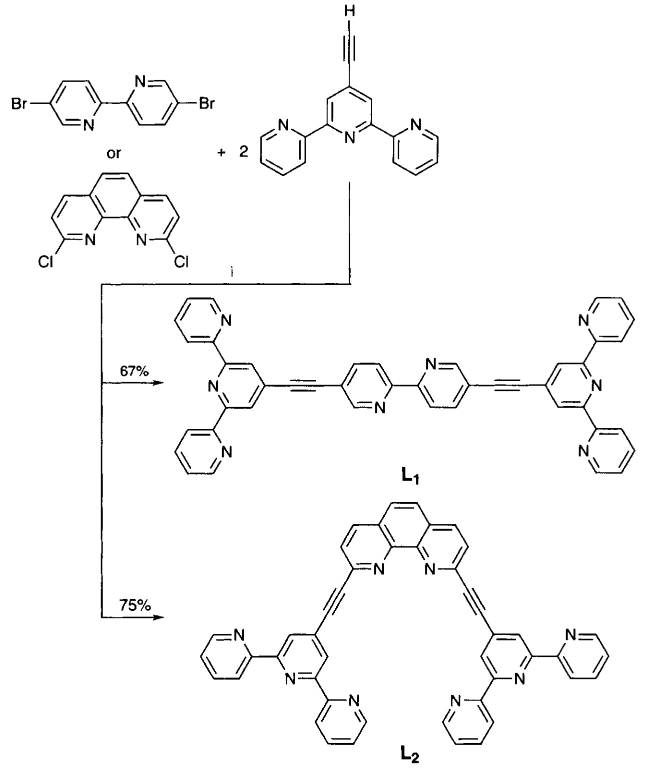
Complexation of preorganized octapyridino-alkyne-segmented ligand L$_2$ with Fe$^{\text{II}}$ salts afforded a trinuclear FeTr and a tetranuclear FeTe metallomacrocycle, the formation of which was followed by electrospray mass spectrometry.

There is much interest in the design and synthesis of polydentate ligands capable of self-assembly in the presence of appropriate cations. Thus, bidentate subunits complexed with tetrahedral cations, or tridentate subunits combined with octahedral or tricapped trigonal prismatic metal ions, give rise to helical structures.[1,2] Multidentate oligopyridine ligands (*i.e.* quinquepyridine, sexipyridine, septipyridine . . .) have also been used for the preparation of double-helical complexes. However, the lack of a spacer between the pyridine groups makes the synthesis of these ligands difficult and causes ambiguity about their binding.[3,4] It has further been demonstrated that the use of segmental ligands possessing different binding units along the strand allows self-assembly of heteropolynuclear helical complexes.[5] However, iron induced self-assembled systems have only rarely been studied[6] and there are only a few reports describing the different stages of formation of these polynuclear self-assembled structures.[7] Such novel structures have important topological interest, and may also have valuable electronic properties.

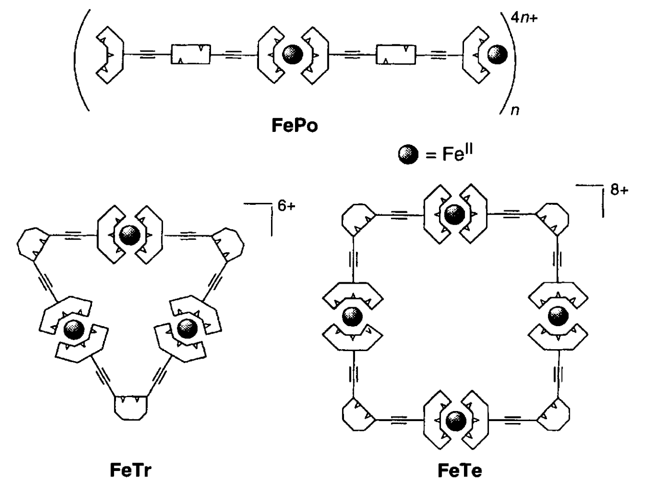
We have become interested in oligomultidentate ligands in which the spacer groups, used to orient the primary chelating functionalities, provide additional but disparate coordination sites, thus forming tetranuclear complexes with suitable cations by a self-assembling process.[8] We now describe the use of novel octapyridino segmented ligands possessing alkyne spacers between the coordinating subunits for the formation of iron(II) complexes with a defined nuclearity that may be controlled by the angle α between the alkyne bonds. The geometric constraints built into the preorganized tritopic ligands **L$_1$** bpy-5,5′-(C≡C-terpy)$_2$, with an angle α of 180°, and **L$_2$** phen-2,9-(C≡C-terpy)$_2$ with an angle α of 60° (bpy = 2,2′-bipyridine, terpy = 4′-substituted-2,2′ : 6′,2″-terpyridine, and phen = 1,10-phenanthroline) were initially designed to lead to the formation of a linear polymer **FePo** and a cyclic trimer **FeTr** upon complexation with iron(II), respectively. Ligands **L$_1$** and **L$_2$** were synthesized,[9] respectively, by Pd^0-catalysed cross-coupling reactions between 5,5′-dibromo-2,2′-bipyridine[10] or 2,9-dichloro-1,10-phenanthroline[11] with 4′-ethynyl-2,2′ : 6′,2″-terpyridine[12] (67% for **L$_1$**, 75% for **L$_2$**) (Scheme 1).†

Complexation of **L$_1$** with Fe$^{\text{II}}$ salts resulted in the immediate formation of a deep-blue insoluble compound, very likely a linear polymer **FePo**, whose physical properties are under investigation. On the other hand, **L$_2$** and Fe$^{\text{II}}$ in a 1 : 1 ratio, produced a soluble deep-violet solution,‡ which was submitted to electrospray mass spectrometry (ESMS) and NMR analysis.

ESMS, which has already been applied successfully to the characterization of various polynuclear complexes,[7] allowed the identification of two cationic polynuclear iron complexes present in solution: a trimeric complex **FeTr** (74%) and a tetrameric complex **FeTe** (26%) [Fig. 1(*c*)]. The spectra were clear and easy to interpret owing to the presence of several



Scheme 1 *Reagents and conditions*: i, [Pd^0(PPh$_3$)$_4$] 6 mol% in C$_6$H$_6$ + Pr$^i_2$NH, 80 °C



Scheme 2

pseudomolecular peaks corresponding to successive loss of PF_6^- counteranions. Moreover, an unambiguous determination of the charge states of the whole series of multiply-charged ions was obtained by a separate injection of the stoichiometric mixture of Fe^{II} with ligand $\mathbf{L_2}$ in the presence of methanol. Under these conditions, up to nine methanol adducts each separated by $32/z$ (z being the charge of the species), were observed (Fig. 2). The relative stability of **FeTr** and **FeTe** was investigated by increasing the extraction cone voltage (Vc)[13] in the ES source. At Vc = 50 V, intense fragmentation of **FeTe** was observed whereas **FeTr** remained stable. This higher stability of **FeTr** *vs.* **FeTe** might be due to higher rigidity of the molecular structure of the triangle. To minimize fragmentations, all the ESMS experiments were then performed at Vc = 20 V.

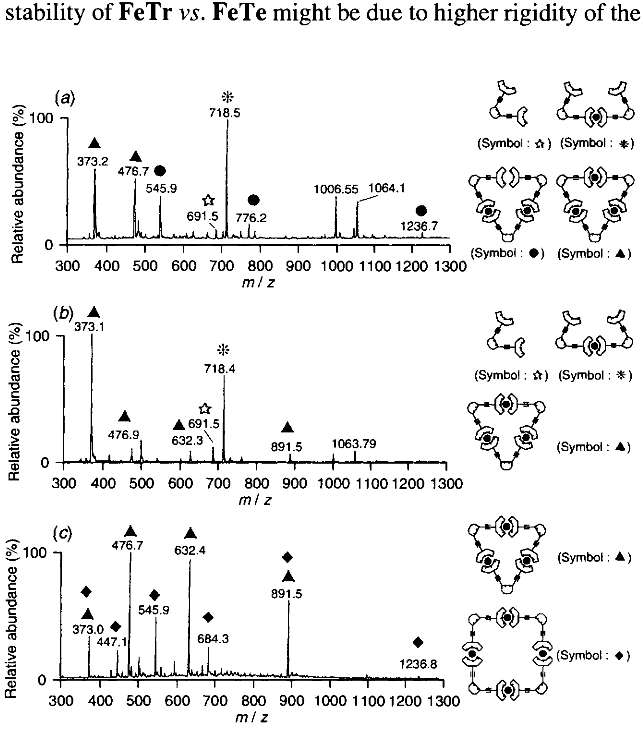


Fig. 1 ESMS spectra of four titration solutions, in acetonitrile, containing $\mathbf{L_2}$ (10^{-4} mol dm^{-3}) and either (*a*) 0.25 equiv., (*b*) 0.5 equiv. or (*c*) 1 equiv. of Fe^{II} salt. The 0.75 equiv. spectrum is similar to spectrum (*c*), the ratio of **FeTe** *vs.* **FeTr** being *ca.* 30%. The extraction cone voltage (Vc) was set at 20 V. Calculated *m/z* for **FeTr**: 373.3 (M – $6PF_6$); 477.0 (M – $5PF_6$); 632.4 (M – $4PF_6$); 891.6 (M – $3PF_6$); for **FeTe** 373.3 (M – $8PF_6$); 447.4 (M – $7PF_6$); 546.1 (M – $6PF_6$); 684.3 (M – $5PF_6$); (M – $5PF_6$); 891.6 (M – PF_6); 1237.0 (M – $3PF_6$); for $[(L_2)_2Fe](PF_6)_2$ 718.7 (M – $2PF_6$); for $[(L_2)_3Fe_2](PF_6)_4$ 546.0 (M – $4PF_6$), 776.3 (M – $3PF_6$), 1237.0 (M – $2PF_6$); for L_2 691.8 (M + H).

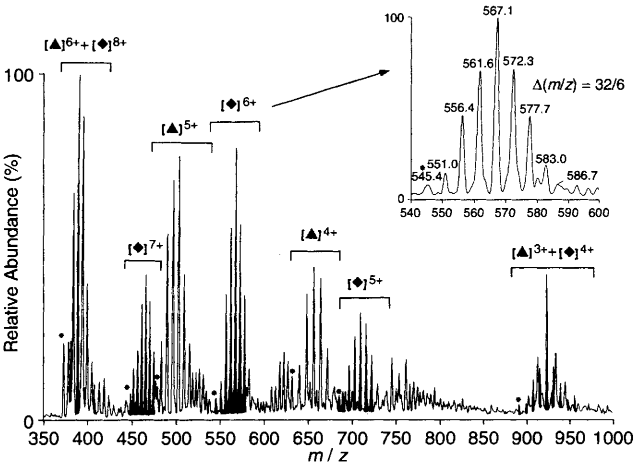


Fig. 2 ESMS at Vc = 20 V for the stoichiometric mixture of Fe^{II} and ligand $\mathbf{L_2}$ in MeOH. Peaks represented by * correspond to the pseudo-molecular peaks of each pattern: ▲ for **FeTr** and ◆ for **FeTe**.

ESMS was then used to monitor the formation intermediates of **FeTr** and **FeTe**. A titration of $\mathbf{L_2}$ with Fe^{II} was performed (Fig. 1). Increasing the amount of Fe^{II} relative to ligand (in increments of 0.25 equiv.) showed progressive depletion of the $[(\mathbf{L_2})_2Fe]$ and $[(\mathbf{L_2})_3Fe_2]$ complexes. A concomitant increase in the **FeTr** species was observed. Interestingly, at 0.5 equiv. Fe^{II} the $[(\mathbf{L_2})_3Fe_2]$ complex had almost totally disappeared, while the $[(\mathbf{L_2})_2Fe_2]$ intermediate was still evident in the spectrum [Fig. 1(*b*)]. Indeed, the higher degree of preorganization in $[(\mathbf{L_2})_3Fe_2]$ favours faster complexation of Fe^{II}, leading to **FeTr** rather than Fe^{II} complexation of $[(\mathbf{L_2})_2Fe]$, which leads to $[(\mathbf{L_2})_3Fe_2]$. As expected, some free ligand could also be detected in its protonated form for 0.25 and 0.5 equiv. Fe^{II}. Formation of the higher oligomer **FeTe** could also be detected at 0.75 equiv. Fe^{II} while stoichiometric mixing of Fe^{II} and ligand $\mathbf{L_2}$ resulted in the formation of **FeTr** and **FeTe** [Fig. 1(*c*)]. It is noteworthy that no other complexes have been observed by ESMS during the complexation of $\mathbf{L_2}$ with Fe^{II}.

Solutions obtained during the titration experiments were again analysed one week later, and showed that the $[(\mathbf{L_2})_2Fe]$ complex obtained with 0.25 and 0.5 equiv. Fe^{II}, had almost totally disappeared in favour of **FeTr**. For 1 equiv. Fe^{II}, the spectrum remained after several months identical to that obtained just after mixing the species, showing that the thermodynamic equilibrium is reached immediately in the case of both **FeTr** and **FeTe**.

The $^{13}C\{^1H\}$ NMR spectrum of the product‡ shows the presence of 22 signals (14 in the aromatic region and 8 for the ethynyl carbons, Fig. 3).§ It is noteworthy that the **FeTr** and **FeTe** complexes exhibit no marked differences in the aromatic region and that the metal-induced self-assembled process gave, under stoichiometric conditions, only two complexes with a high degree of symmetry. However, the ethynyl part of the carbon spectrum (inset, Fig. 3) shows four close sets of alkyne C atoms. The more intense peaks (97.38, 97.57 and 87.12, 86.89) correspond to **FeTr** and show that the two triple bonds in a single ligand, are chemically inequivalent. From space filling (CPK) models, we conclude that one set of terpyridines lies in the phenanthroline plane while the second set is close to orthogonal. This situation is imposed by the octahedral arrangement around Fe^{II} and by the cyclic nature of the species. A ratio of 27% of tetramer **FeTe** *vs.* trimer **FeTr** has been obtained by NMR integration of the ethynyl signals, in good agreement with that found by ESMS.

Both complexes exhibit a strong m.l.c.t. absorption band at λ/nm (MeCN) 575 with ε/dm^3 mol^{-1} cm^{-1} 33600 per '$Fe(terpy)_2$' subunit. The significant bathochromic shift (*ca.* 25 nm) and hyperchromic effect (*ca.* 9000 dm^3 mol^{-1} cm^{-1}) observed compared to $[Fe(terpy)_2]^{2+}$ are due to a π-electronic

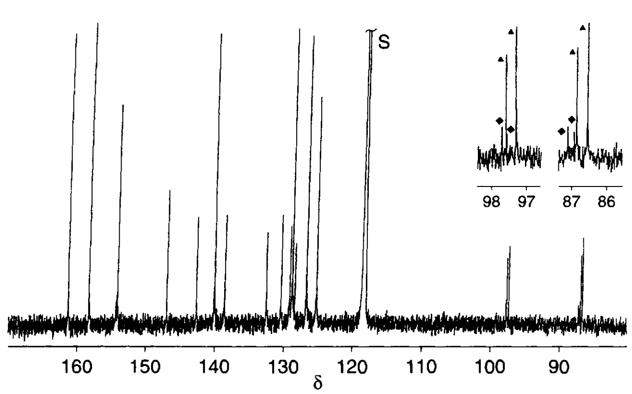


Fig. 3 $^{13}C\{^1H\}$ NMR (CD_3CN) from 180 to 70 ppm measured at 125.8 MHz on the crude Fe^{II}–PF_6 complex. The inset shows the 98 to 97 and 87 to 86 ppm regions of the spectrum: ▲ for **FeTr** and ◆ for **FeTe**.

delocalization in the ground-state and to geometrical considerations,[14] as previously observed in rigid rod-like multinuclear complexes.[12] Both **FeTr** and **FeTe** complexes possess a reversible redox couple in the positive potential range $E_{1/2}$ = +1.23 V, ΔE_p = 60 mV [in anhydrous MeCN, 0.1 mol dm^{-3} TBAP, *vs.* Ag^0, using Fc/Fc^+ (Fc = ferrocene) as internal reference $E_{1/2}$ = +0.43 V, ΔE_p = 72 mV], a value close to the one found for the parent $[Fe(terpy)_2]^{2+}$ complex.[15]

To summarize, the novel segmented octapyridine ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ permitted to generate three discrete structures: namely, a linear polymer and two macrocycles of various size and shape. It is clear that the dihedral angle present between the external complexation subunits in such tritopic ligands (180° in $\mathbf{L_1}$ and 60° in $\mathbf{L_2}$) plays a major role in the degree of selectivity of subsequent complexation. Confirmation of the importance of the angle between the terpy subunits is apparent from the properties of bpy-6,6'-(C≡C-terpy)$_2$ which is the analogue of $\mathbf{L_2}$ and the isomer of ligand $\mathbf{L_1}$, but in which the lack of rigidity and the transoid conformation of the central bpy subunit in solution resulted, after complexation with Fe^{II}, in a mixture of insoluble polymeric complexes.

Footnotes

† *Selected data* for $\mathbf{L_2}$: ^1H NMR (CD_2Cl_2, 200.1 MHz) δ 7.38 (ddd, $^3J_{HH}$ 7.5 Hz, $^3J_{HH}$ 4.8 Hz, $^4J_{HH}$ 1.2 Hz, 2 H), 7.91 (td, $^3J_{HH}$ 7.2 Hz, $^4J_{HH}$ 1.8 Hz, 6 H), 7.96 (t, $^3J_{HH}$ 8.4 Hz, 2 H), 8.35 (d, $^3J_{HH}$ 8.3 Hz, 2 H), 8.66 (d, $^3J_{HH}$ 8.0 Hz, 4 H), 8.71 (dd, $^3J_{HH}$ 4.8 Hz, $^4J_{HH}$ 1.8 Hz, 4 H) and 8.79 (s, 4 H); $^{13}C\{H\}$ NMR (CD_2Cl_2, 50.3 MHz) δ 156.31(C_q), 155.94(C_q), 149.77(CH), 143.13(C_q), 137.28(CH), 136.79(CH), 128.87(C_q), 127.60(CH), 127.30(CH), 124.92(C_q), 124.51(CH), 123.82(C_q), 123.60(CH), 121.43(CH) and 93.34(C≡C); FAB^+ (NBA): 691 ($[M + H]^+$, 100%); FTIR (KBr)/cm^{-1} 3054, 3000, 1581, 1565, 1538, 1490, 1466, 1389, 1268 and 1150.

‡ Complexes were prepared by mixing a 1.2×10^{-3} mol dm^{-3} solution of ligand $\mathbf{L_2}$ in CH_2Cl_2 with an equal volume of a 1.2×10^{-3} mol dm^{-3} solution of $FeSO_4.7H_2O$ in EtOH. The solution turned deep violet instantaneously showing very fast complexation. Addition of excess NH_4PF_6 and slow evaporation of the solvent resulted in the precipitation of the complex, which was isolated by centrifugation and redissolved in MeCN for ESMS analysis and titration experiments (2×10^{-4} mol dm^{-3}). This experimental procedure has also been used for the preparation of the iron(II) complexes in 100 mg scale. The crude product was then recrystallized twice by slow diffusion of Et_2O into a DMF solution.

§ $^{13}C\{^1H\}$ NMR (CD_3CN, 125.8 MHz) δ 162.28(CH), 158.23(CH), 154.11(CH), 146.92(CH), 142.61(C_q), 140.02(CH), 138.49(C_q), 132.49(C_q), 130.28(C_q), 129.00(C_q), 128.68(CH), 128.26(CH), 126.60(CH), 125.17(CH), 97.71*(C≡C), 97.59(C≡C), 97.57*(C≡C), 97.29(C≡C), 87.20*(C≡C), 86.98*(C≡C), 86.87(C≡C) and 86.57(C≡C). * = minor peaks.

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