Self-Assembly of Tetra- and Hexanuclear Circular Helicates

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Abstract: The self-assembly of the tris-bipyridine ligands $\mathbf{B^I}$ and $\mathbf{B^{II}}$ with iron(II) salts yields polynuclear complexes displaying structures of cyclic double-helix type, termed circular helicates [*n*]**cH** (of order *n*). With $\mathbf{B^I}$ in which the bipyridine units in the ligand are connected by ethylene bridges, penta- or hexanuclear architectures [5]**cH** and [6]**cH** are obtained, depending on the anion present during the self-assembly process. The elongated tris-bipyridine ligand $\mathbf{B^{II}}$ with oxypropylene bridges forms a tetranuclear circular helicate [4]**cH**, whose structure has been confirmed by crystal structure determination. The possible oligomeric combinations of tris-bipy ligands and iron(II) ions may be considered to constitute the potential members of a virtual combinatorial library, generated via dynamic combinatorial chemistry, from which a specific real constituent of the virtual set of circular helicates is expressed in given conditions.

Introduction

The self-assembly of well-defined inorganic architectures may be considered to result from the operation of programmed supramolecular systems based on suitably designed ligands whose (steric and interactional) information is read out by given metal ions following their coordination algorithm.[1] A variety of inorganic entities have been obtained by processes following this general principle.[2] Among them, the helicates are polynuclear metal complexes of helical shape, in which two or three ligand strands wrap around a set of linearly disposed metal ions, thus forming inorganic double or triple helices, respectively.[1,2b,3−9] We recently reported the self-assembly of the first circular helicate, a pentanuclear double helicate closed into a ring.[10]

Although a number of transition metal complexes possessing cyclic structures have been described,[2c,11−14] circular helicates have specific features. Whereas in the former case the ligands usually bridge two neighboring metal centers, in circular helicates each ligand extends over three adjacent metal centers and, in addition, the ligand strands wrap around each other, thus generating a double-helical structure, bearing formal relation to circular double-stranded DNA.

The pentanuclear circular helicate [5]**cH**[15] has been obtained by the reaction of the tris-2,2′-bipyridine (bipy) ligand $\mathbf{B^I}$ and $FeCl_2$; it presents a pentagonal shape and encloses a strongly bound chloride anion that tightly fits into its central cavity (Figure 1). To build upon these results, it was of interest to investigate the features controlling the self-assembly of such circular double-helical architectures, in particular how variation in the features of the ligand or in the metal salt would affect the nature of the species generated. We report here that the use of a different Fe(II) salt or a slight modification of the structure of the ligand leads to the generation of a hexanuclear [6]**cH** (Figure 2) or a tetranuclear [4]**cH** circular double helicate, respectively.

Results and Discussion

1. Effect of the Iron(II) Salt on Self-Assembly. Generation of Hexanuclear Double Helicate [6]cH from Ligand $\mathbf{B^I}$ and $FeSO_4$. Since the pentanuclear complex [5]**cH** contained a tightly bound chloride ion, it was of primarily importance to ascertain to what extent the assembly of such a pentameric structure was directed by the presence of the enclosed anion

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(15) [*n*]^m**cH** is a general notation characterizing circular helicates (**cH**) with n = number of metal ions and m = helicity ($m = 2$ for a double helix); for simplicity the exponent $m = 2$ is omitted here because all complexes are double stranded.

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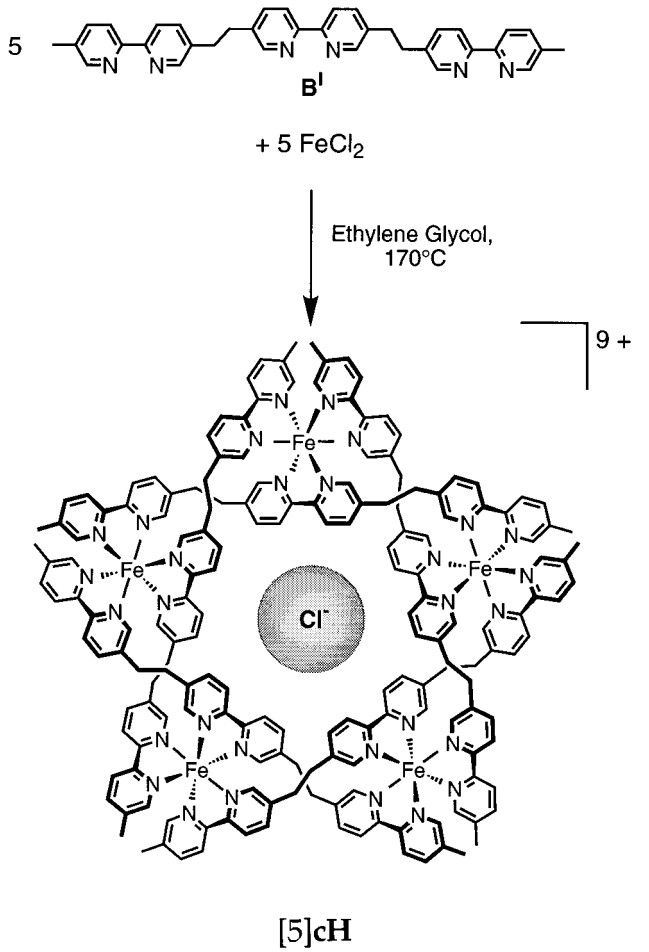

Figure 1. Self-assembly of the pentanuclear circular helicate [5]**cH** from five ligands $\mathbf{B^I}$ and five Fe(II) ions in the presence of chloride anions.

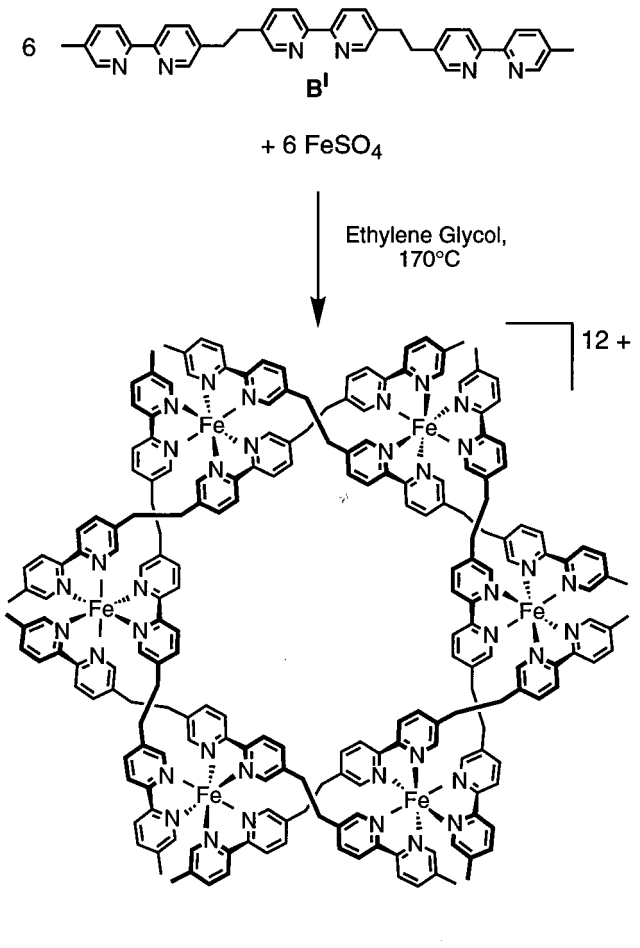

Figure 2. Self-assembly of the hexanuclear circular helicate [6]**cH** from six ligands $\mathbf{B^I}$ and six Fe(II) ions in the presence of sulfate anions. The same complex [6]**cH** is obtained with $FeSiF_6$, $Fe(BF_4)_2$, and $FeBr_2$.

and as a corollary, whether a change in anion might give access to other oligomeric circular entities [*n*]**cH**.

When a mixture of an equimolar amount of the tris-bipy ligand $\mathbf{B^I}$ [6] and $FeSO_4$ in ethylene glycol was heated to 170 °C for 22 h, a bright red solution was obtained, indicating the formation of a complex. The latter was precipitated by addition of NH_4PF_6 as a red powder in quantitative yield and characterized without further purification. Microanalysis showed that it contained equimolar amounts of $Fe(PF_6)_2$ and of ligand $\mathbf{B^I}$. Its absorption spectrum displays in the visible region a band at 519 nm typical of the charge transfer band (MLCT) of a $Fe(bipy)_3$ type center,[16] indicating that each Fe(II) ion was bound to three bipy groups. Due to the short linker between the bipy subunits within one ligand strand $\mathbf{B^I}$, the terminal and the central bipy cannot be arranged around the same metal ion. Furthermore, the binding of the same metal ion by the two terminal bipy units of a single strand would cause severe distortions of the central unit. Therefore, each Fe(II) ion should be complexed by three bipy units, one from each of three different ligand strands $\mathbf{B^I}$.

The ^{1}H-NMR spectrum of the complex indicates the presence of a single compound of high symmetry, all ligands being equivalent and symmetric about the C(2)−C(2′) bond of the central bipy unit. It exhibits a singlet at 2.20 ppm for the methyl protons and two multiplets between 2.7 and 3.0 ppm for the ethylene bridge, in agreement with a helical structure where the ethylene bridge forms an AA′BB′ system. Downfield, the spectrum shows three singlets and six doublets, each integrating for two protons corresponding to the aromatic protons. Hence the two halves of each ligand are equivalent. The signals of all the protons α to the nitrogens are shifted upfield, with respect to these of the free ligand, as expected for the formation of octahedral $Fe(bipy)_3$ type centers, where these protons come into close proximity of another bipy bound to the same metal. All the signals have been assigned unequivocally by means of the coupling constants and of NOEs. In particular, NOE interactions have been observed between all the protons α to the nitrogens, revealing the close proximity of these protons in space and implying as a consequence that a given Fe(II) ion is bound to both terminal and central bipy groups. Since, as already pointed out, these bipy subunits cannot belong to the same ligand strand, each Fe(II) ion should be surrounded by terminal and central bipy units belonging to three different ligands $\mathbf{B^I}$.

Similar features have been observed in the NMR spectra of the pentanuclear circular helicate [5]^2**cH**.[10] Both complexes are composed of "$Fe(bipy)_3$" type centers and share the 1:1 stoichiometry of Fe(II):$\mathbf{B^I}$, the occupation of all binding sites, the symmetry around the central C(2)−C(2′) bond, and the complexation of a given metal ion by two terminal bipys belonging to two different ligands and a central bipy of a third ligand strand. One may therefore conclude that the two complexes must possess closely related structures.

The complex was further analyzed by electrospray mass spectrometry (ES-MS). This technique has been proven very

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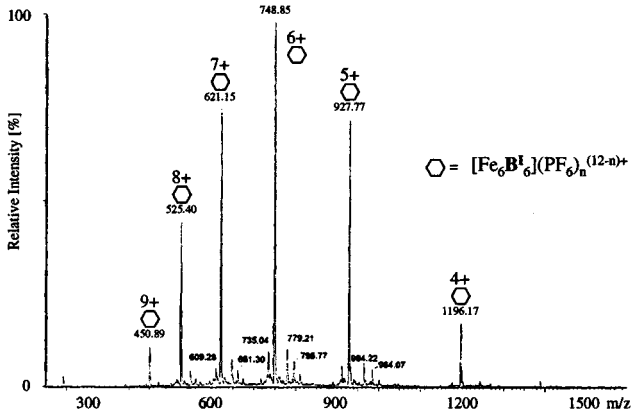

Figure 3. ES-mass spectrum of [6]**cH**. The complex cation is observed with different numbers of PF_6^- anions.

helpful for identifying polynuclear transition metal complexes with high molecular masses.[17] Usually the mass is calculated from a series of multiply charged ions obtained by the successive loss of counteranions. In case of ambiguity, the charge of the species corresponding to an observed ion can be deduced directly from the spacing of the isotopic peaks, provided that the instrument resolution is high enough.[18] In addition, the intensity of the signals for a given species corresponds to a good approximation to its abundance in the solution.[19] It has been shown that quantification based on ES-MS spectra is in good agreement with UV spectrophotometry studies.[20] Therefore ES-MS can provide an image of the composition of a solution.

Since the $Fe(bipy)_3$ complex remains intact at low potentials during the ES process,[21] polynuclear architectures containing this type of center are observed as one cation with different numbers of anions. Hence, a typical ES mass spectrum consists of a series of peaks corresponding to the polynuclear complex losing its anions successively.

The ES mass spectrum of the compound formed by the reaction of $FeSO_4$ with $\mathbf{B^I}$ followed by precipitation with NH_4PF_6 displays signals for the successive loss of PF_6^- anions from a $[Fe_6\mathbf{B^I}_6](PF_6)_8^{4+}$ species down to $[Fe_6\mathbf{B^I}_6](PF_6)_3^{9+}$ (Figure 3). No other complex or other anion is present in the acetonitrile solution of the material.

From all these spectral and analytical data one may conclude that the reaction of $FeSO_4$ with the tris-bipy ligand $\mathbf{B^I}$ yields quantitatively a hexanuclear complex $[Fe_6\mathbf{B^I}_6]^{12+}$ with a symmetrical arrangement of the ligands related to that of the pentanuclear circular helicate [5]**cH**. One may therefore assign to this complex a hexagonal double-helicate architecture [6]**cH**.

The helicates [5]**cH** and [6]**cH** were obtained under the exact same conditions, the only difference residing in the anion present during the helicate formation. Thus, whereas the pentanuclear circular helicate [5]**cH** forms in the presence of Cl^-, the hexanuclear circular helicate [6]**cH** is produced when SO_4^{2-} ions are present instead. The X-ray structure of [5]**cH**[10] showed that the chloride anion fits tightly into the central cavity of the torus formed by the circular helicate. In [6]**cH** the central cavity is widened enough for a SO_4^{2-} ion to fit inside. One may surmise that the formation of the hexameric structure [6]**cH** when iron(II) sulfate is used results from the fact that it contains a larger cavity capable of accommodating the SO_4^{2-} anion. Consequently, the size of the circular double helicate [*n*]**cH** obtained could be determined by the nature of the anion in the iron salt employed. This prompted us to investigate the reaction of ligand $\mathbf{B^I}$ with other iron(II) salts.

Table 1. Compounds Formed by Complexation of Ligand $\mathbf{B^I}$ with Different Iron(II) Salts

iron(II) salt	complex formed
FeF_2	insoluble
$FeCl_2$	[5]**cH**
$FeBr_2$	[5]**cH** + [6]**cH**
FeI_2	insoluble
$Fe(BF_4)_2$	[6]**cH**
$FeSO_4$	[6]**cH**
$FeSiF_6$	[6]**cH**

Self-Assembly with Other Iron(II) Salts. Ligand $\mathbf{B^I}$ was reacted with different iron(II) salts in the same conditions as those used with $FeSO_4$. When soluble complexes were formed, they were isolated by precipitation with PF_6^-. The results are summarized in Table 1.

The reactions with FeF_2 and FeI_2 yielded insoluble red powders, which could not be identified. In the case of FeF_2, about 30% of the ligand initially used was recovered. With $Fe(BF_4)_2$, a soluble red complex was obtained together with an insoluble red powder. Presumably the BF_4^- anions decompose partly under the harsh reaction conditions. The soluble complex was identified by ^{1}H-NMR and ES-MS as the hexamer [6]**cH**. $FeSiF_6$ yielded quantitatively [6]**cH**, identified by ^{1}H-NMR and ES-MS.

A more complicated situation was encountered with $FeBr_2$. The Br^- anion with a radius of 1.96 Å is slightly larger than Cl^- (1.80 Å radius). The reaction of $FeBr_2$ with $\mathbf{B^I}$ gave a nearly equimolar mixture of both circular helicates [5]**cH** and [6]**cH**. The pentanuclear circular helicate may be considered to include a Br^- ion in a fashion similar to Cl^- inclusion, as shown by the ^{1}H-NMR and ES-MS data. The protons at C(3) of the central bipy of [5]**cH**, which are pointing inside the cavity, are shifted downfield to 10 ppm, as in the case where Cl^- is bound. The ES mass spectrum displays the signals for the complex $[(Fe_5\mathbf{B^I}_5)Br](PF_6)_9$ for [5]**cH**. The ^{1}H-NMR and ES-MS data for the [6]**cH** compound are identical to those of the compound prepared with $FeSO_4$.

Circular Double Helicate Self-Assembly as a Selection from a Virtual Combinatorial Library. In the presence of the smallest anion, Cl^-, the self-assembly generates the pentanuclear circular helicate [5]**cH**. With the larger anions SO_4^{2-}, BF_4^-, and SiF_6^{2-}, the hexanuclear architecture is formed, while the Br^- anion of intermediate size yields a mixture of [5]**cH** and [6]**cH**. The charge of the anion has apparently little influence on the structure formed, as [6]**cH** is obtained with mono- and divalent anions. The structure depends rather on the size of the anion to be included in the circular helicates.

These differences in the products formed might be considered as resulting from a templating effect of the anion during the formation of the circular helicate. Yet, the process can also be seen as the self-assembly of a receptor as a function of its substrate, a given circular helicate acting as specific receptor for anions having the proper size. Thus, the pentanuclear torus [5]**cH** binds a Cl^- anion, and the larger hexanuclear torus [6]-

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cH accommodates, for example, a SO_4^{2-} ion in its central cavity. The self-assembly process toward one or the other structure from the same components is determined by the substrate to be bound. It can thus be considered to represent a procedure of selection from a virtual combinatorial library (VCL)[10,22] consisting of all the possible complexes that can be generated from the available components, here, the ligand $\mathbf{B^I}$ and the Fe(II) ions. In principle, oligomeric circular structures of all sizes with the stoichiometry $[Fe_n\mathbf{B^I}_n]^{2n+}$ ($n \geq 3$) can be formed. The anions may screen this virtual collection of potential complexes for a suitable receptor. The pentanuclear helicate [5]**cH** is selected by Cl^- ions, [6]**cH** is formed with SO_4^{2-}, BF_4^-, and SiF_6^{2-}, and two entities of this virtual combinatorial library are expressed while in presence of Br^- ions. As the self-assembly forming the constituents of the VCL is reversible, nonusable members are dissociated, so that finally the whole VCL is converted into the selected structure.

Such behavior implies that each member of the VCL represents the whole library, since it can be disassembled and reassembled into every other member in a dynamic combinatorial chemistry (DCC) process. Thus, if a species that was selected once is screened again by a different kind of screen, a new member should be selected as if a whole library were reconstituted out of the components.

To verify this corollary, we first prepared the hexanuclear circular helicate [6]**cH** in the presence of SO_4^{2-}. The anion was then exchanged against Cl^-, and the complex was heated again to the initial temperature in the same conditions. ^{1}H-NMR and ES-MS analysis indicated the quantitative transformation of the compound into the pentanuclear circular helicate [5]**cH**, containing a Cl^- in its central cavity, i.e., [6]**cH** → [5]-**cH**. The same supramolecular architecture [5]**cH** was thus formed from one element of the VCL, [6]**cH**, as was generated from the components, $\mathbf{B^I}$ and $FeCl_2$ themselves.

From the point of view of the VCL concept,[10,22] the chloride anion may be considered to play a role beyond templating, that of selecting a given structure out of all the potential combinations. The formation of [6]**cH** in the case of SO_4^{2-}, BF_4^-, and SiF_6^{2-} does not imply that this structure is templated by the anions (although it may be so) but simply that it is expressed. The case of Br^- is intermediate.

2. Effect of the Ligand on the Self-assembly. Generation of Tetranuclear Double Helicate [4]cH from Ligand $\mathbf{B^{II}}$. The replacement of the CH_2CH_2 groups of ligand $\mathbf{B^I}$ by CH_2OCH_2 should yield a somewhat longer ligand $\mathbf{B^{II}}$ (Figure 4) of appreciably higher flexibility than $\mathbf{B^I}$. The effect of such a rather minor change on the outcome of the self-assembly may be quite instructive for analyzing the structure/assembly relationship. Ligand $\mathbf{B^{II}}$ has been synthesized following a procedure developed previously for related oligobipyridines.[23] The reaction with $FeCl_2$ under the conditions described above gave a red complex which was isolated as the PF_6^- salt in 90% yield after one recrystallization. Elemental analysis indicated that this product had a composition equimolar in $Fe(PF_6)_2$ and in ligand $\mathbf{B^{II}}$. Its absorption maximum at 516 nm identified a complex of "Fe(bipy)$_3$" type.[16]

The ^{1}H-NMR data show that there is only one type of ligand in the complex and that it is symmetric around the central C(2)−C(2′) bond. The CH_2 protons next to the terminal bipys give an AB system in agreement with a helical structure. Three singlets and six doublets are observed for the aromatic protons, displaying the expected chemical shifts for "Fe(bipy)$_3$" type complexes. Furthermore, NOE interactions are observed between all protons α to the nitrogens.

These features are similar to those presented by both circular helicates [5]**cH** and [6]**cH** so that an analogous structure can be inferred for the compound formed by $\mathbf{B^{II}}$.

When the complex was precipitated once with a small excess of PF_6^- ions, the ES-MS spectra indicated that it was a tetranuclear species $[(Fe_4\mathbf{B^{II}}_4)Cl](PF_6)_7$ (Figure 5). Two series of peaks were observed for the $(Fe_4\mathbf{B^{II}}_4)^{8+}$ cation, the first with only PF_6^- counteranions and the second with one Cl^- and several PF_6^- anions. No fragment containing more than one

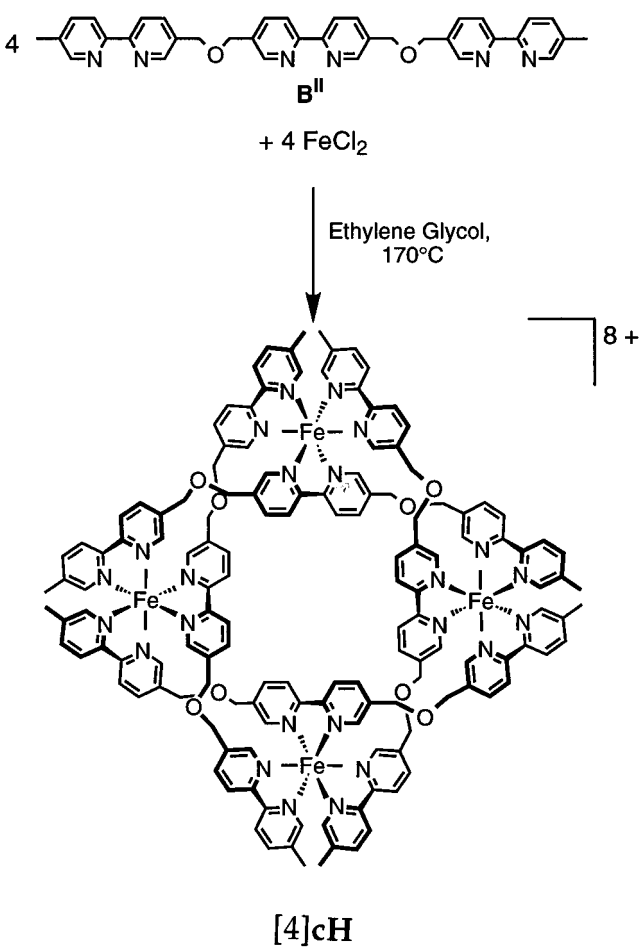

Figure 4. Self-assembly of the tetranuclear circular helicate [4]**cH** from four ligands $\mathbf{B^{II}}$ and four Fe(II) ions in the presence of chloride anions. The same complex [4]**cH** is obtained with $FeSO_4$, $FeSiF_6$, and $FeBr_2$.

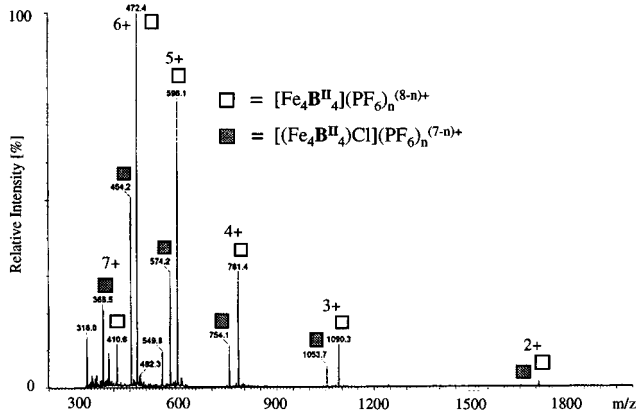

Figure 5. ES-mass spectrum of [4]**cH**. The complex cation is observed with one Cl^- and different numbers of PF_6^- anions (filled squares) or with only different numbers of PF_6^- anions (empty squares).

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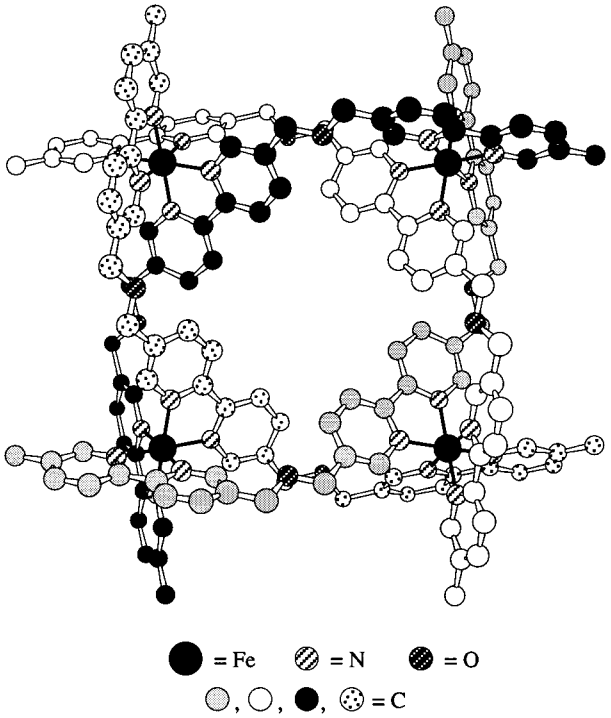

Figure 6. Ball-and-stick representation of the X-ray structure of [4]-**cH**.

Cl^- was seen, excluding a statistical distribution of the anions. The chloride ion thus appeared to be associated weakly but specifically with the $(Fe_4\mathbf{B^{II}}_4)^{8+}$ cation. A second precipitation in the presence of an excess of PF_6^- eliminated all mass peaks corresponding to species with Cl^-.

All these data agreed with the formation in solution of a tetranuclear complex with an arrangement of four ligands $\mathbf{B^{II}}$ similar to that in the circular helicates [5]**cH** and [6]**cH**. In addition weak binding of a chloride ion was indicated. It was therefore possible to conclude that the product of ($\mathbf{B^{II}}$ + $FeCl_2$) self-assembly was a tetranuclear circular helicate [4]**cH**. This structure was confirmed in the solid state by X-ray diffraction analysis.

Single crystals of the complex $[Fe_4\mathbf{B^{II}}_4](PF_6)_8$ were obtained by diffusion of diethyl ether into an acetonitrile solution. They belong to the space group *P*4/*n*, containing two cations $(Fe_4\mathbf{B^{II}}_4)^{8+}$ per unit cell which correspond to the two enantiomers of the circular helicate [4]**cH**.

The cation $(Fe_4\mathbf{B^{II}}_4)^{8+}$ presents D_4 symmetry with the Fe(II) ions located at the corners of a square (Figures 6 and 7). Thus, two C_2 axes pass through opposite metal centers, and two C_2 axes bisect the square. The Fe−Fe distance is 10.62 Å, 2.2 Å longer than in [5]**cH**.[10] As expected, the elongation of the bridging ligand moves the metal ions apart from each other.

Each Fe(II) ion is coordinated to three bipy subunits, one central and two terminal ones, belonging to three different ligands. The coordination environment is pseudo-octahedral, very similar to that of the mononuclear compound $[Fe(bipy)_3]^{2+}$.[24] The bond angles (N−Fe−N) within each bipy unit are ≈81°. The Fe−N distances are 1.98 Å for all bipys, which is slightly longer than the distance of 1.96 Å in $[Fe(bipy)_3]^{2+}$.[24]

Each ligand $\mathbf{B^{II}}$ binds three Fe(II) ions by adopting a bent, L shape. The CH_2OCH_2 bridge presents antiperiplanar conformations of both C−O bonds with dihedral angles of 179.0 and 175.9°.

The ligands constitute a double helix wrapped around the square formed by the four Fe(II) ions. The complex $(Fe_4\mathbf{B^{II}}_4)^{8+}$ is thus a circular double helicate [4]**cH**. The overall architecture is similar to that of [5]**cH** in agreement with the spectrometric data.

The torus described by [4]**cH** has an outer diameter between opposite H atoms of ≈24 Å and a height of ≈10 Å. The inner cavity has a radius of 1.85 Å, which is slightly larger than that of [5]**cH** (1.75 Å). In addition to the smaller charge of [4]**cH** as compared to [5]**cH**, the increase in the size of the cavity can explain the weaker binding of Cl^- indicated by ES-MS.

The PF_6^- ions are too large to be placed at the center of the cavity. In the crystal, two PF_6^- anions are located 1.0 Å above and below the plane of the metal ions, while the other anions fill the space between the tori.

The self-assembly reaction was repeated with the ligand $\mathbf{B^{II}}$ and $FeBr_2$, $FeSiF_6$, and $FeSO_4$. In all cases, [4]**cH** is formed exclusively without any complex of higher nuclearity. Thus, even in the presence of larger anions, the size of the circular helicate is not increased. This might be explained by the possible binding of large anions slightly outside the center of the cavity, as it is observed in the crystal structure.

The self-assembly of ligand $\mathbf{B^{II}}$ and Fe(II) ions into the tetrameric circular architecture [4]**cH** can be related to both the increased length of the ligand, leading to a larger cavity, and its higher flexibility, allowing the larger bending required for the formation of a square.

Conclusion

We have shown that the tris-bipy ligand $\mathbf{B^{I}}$ or $\mathbf{B^{II}}$ and iron(II) salts undergo self-assembly into a family of circular double helicates [4]**cH**, [5]**cH**,[10] and [6]**cH**. The assembly into a given architecture results from both the ligand structural features (such as subunit separation and flexibility) and substrate binding effects (interactions with the anions). It may also be considered as the selection of a given member of the collection of oligomeric [*n*]**cH** species forming a virtual combinatorial library. It involves a process in which each iron(II) ion binds to three bipy units from three different ligand strands to complete its octahedral coordination geometry. The ligand strands wrap into a helical arrangement as in linear double helicates.[2−5] The "$Fe(bipy)_3$" centers then organize themselves into a torus, due to interaction with the anions. Hence, two levels of self-assembly can be distinguished. First, the organization of the ligands around the metal ions, which results in a helical architecture. Second, the ring closure into a torus of defined size.[25] A parallel with the self-organization of biological structures can be drawn. The circular helicates correspond to a tertiary structure. Each circular helicate is unique, but all of them share the same secondary structure, i.e., the double helical arrangement of the ligands. The present work thus extends further the combination of biological-type complexity with chemical diversity.

Experimental Section

All commercial chemicals were of best available grade and used without further purification. Ligands $\mathbf{B^{I}}$ and $\mathbf{B^{II}}$ were prepared according to published procedures.[6,23]

NMR spectra were recorded on Bruker AM300 and AM400 spectrometers in acetonitrile-d_3 with residual solvent peak as standard.

ES-MS was performed on a Quattro triple-quadrupole mass spectrometer with a mass to charge (*m/z*) range of 4000 (Micromass, Manchester, UK) using a standard electrospray ion source. The

(24) Garcia Posse, M. E.; Juri, M. A.; Aymonino, P. J.; Piro, O. E.; Negri, H. A.; Castellano, E. E. *Inorg. Chem.* **1984**, *23*, 948−952.

(25) For a recent report on the assembly of DNA cycles see Shi, J.; Bergstrom, D. E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 111−113.

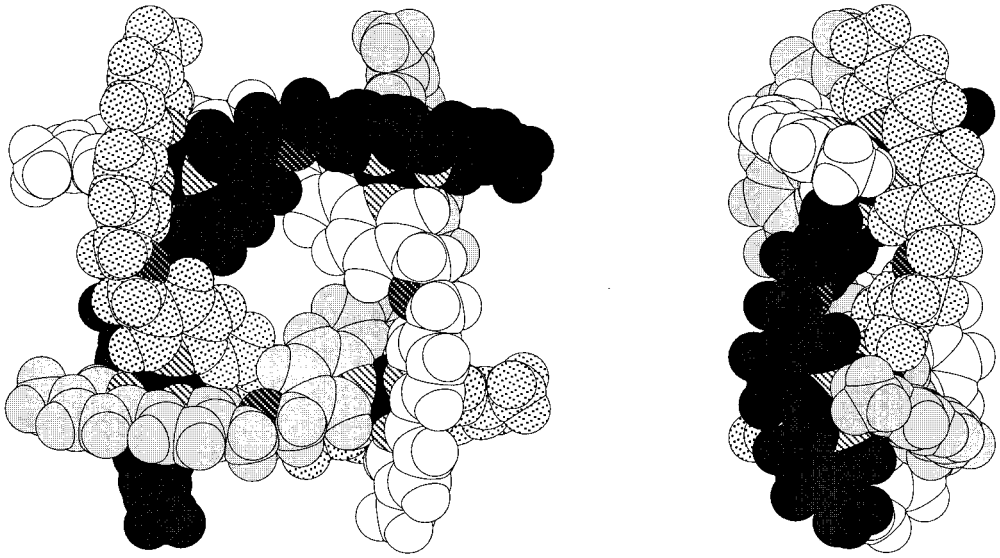

Figure 7. Space-filling representation of the X-ray structure of [4]**cH**. Left, top view; right, side view. The ligands $\mathbf{B^{II}}$ are shown in different patterns.

accelerating cone voltage (V_c) was set to 20 volts to minimize fragmentation processes. Resolution was usually set about 1000 at *m/z* 1000. Solutions ($10^{-4}-10^{-5}$ M) were infused in the ion source in a continuous flow at about 5 μL/min with a syringe pump. The source temperature was 60 °C.

Preparation of the Circular Helicates [4]cH and [6]cH. Equimolar amounts of the iron(II) salt and of ligand $\mathbf{B^{I}}$ or $\mathbf{B^{II}}$ were mixed in ethylene glycol under argon. The concentration of both components was about 10^{-2} mol L^{-1}. On heating to 170 °C, the ligand slowly dissolved. Heating was continued overnight. After cooling to room temperature, the same volume of an aqueous solution of NH_4PF_6 (ca. 0.15 mol L^{-1}) was added. The red precipitate was isolated by centrifugation from the colorless solution and washed several times with ether/methanol 2:1 and dried under vacuum. [6]**cH** was obtained in quantitative yield as a red powder. [4]**cH** was recrystallized once by vapor diffusion of ether into an acetonitrile solution of the complex to give red microcrystals in 90% yield.

Hexakis{5,5′-bis[2-(5′-methyl-2,2′-bipyridin-5-yl)ethyl]-2,2′-bipyridine}hexairon(II) Hexafluorophosphate [6]cH. TLC: R_f (SiO_2, CH_3CN:H_2O:KNO_3 aq. sat. 5:4:1) 0.3. ^{1}H-NMR (400 MHz): δ 2.20 (*s*, 6H, CH_3), 2.70−2.77 (*m*, 4H, CH_2), 2.87−3.02 (*m*, 4H, CH_2), 6.30 (*s*, 2H, H-C(6_A)), 6.40 (*s*, 2H, H-C(6_B)), 6.86 (*s*, 2H, H-C($6'_A$)), 7.30 (*d*, J = 8.2, 2H, H-C(4_A)), 7.66 (*d*, J = 8.0, 2H, H-C(4_B)), 8.05 (*d*, J = 8.2, 2H, H-C($4'_A$)), 8.22 (*d*, J = 8.3, 2H, H-C(3_A)), 8.49 (*d*, J = 8.3, 2H, H-C($3'_A$)), 8.69 (*d*, J = 8.2, 2H, H-C(3_B)); A = terminal bipys, B = central bipy. ^{13}C-NMR (50 MHz): δ 18.8 (CH_3), 29.5, 29.9 (CH_2), 123.4, 123.9, 139.1, 139.2, 139.6, 139.8, 140.0, 140.9, 153.4, 154.4, 155.3, 156.2, 156.7, 157.7 (C_{arom}). ES-MS: *m/z* 1196.17 (15, $[Fe_6\mathbf{B^{I}}_6](PF_6)_8^{4+}$), 927.77 (75, $[Fe_6\mathbf{B^{I}}_6](PF_6)_7^{5+}$), 748.85 (100, $[Fe_6\mathbf{B^{I}}_6](PF_6)_6^{6+}$), 621.15 (80, $[Fe_6\mathbf{B^{I}}_6](PF_6)_5^{7+}$), 525.40 (45, $[Fe_6\mathbf{B^{I}}_6](PF_6)_4^{8+}$), 450.89 (12, $[Fe_6\mathbf{B^{I}}_6](PF_6)_3^{9+}$). FT-IR (KBr): 3423 brs, 1636 w, 1478 s, 1400 w, 1247 w, 840 vs, 558 s cm^{-1}. UV−vis (CH_3CN): $\lambda(\epsilon)$ 519 (5.2×10^4), 361 (3.8×10^4), 315 (3.1×10^5), 294 (2.6×10^5), 263 nm (1.9×10^5 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{216}H_{192}F_{72}Fe_6N_{36}P_{12}$ (5367.24) + $4H_2O$: C, 47.70; H, 3.71; N, 9.27. Found: C, 47.65; H, 3.79; N, 9.02.

Tetrakis{5,5″-[(2,2′-bipyridine-5,5′-diyl)bis(methyleneoxymethylene)]-5′,5‴-dimethylbis[2,2′-bipyridine]}tetrairon(II) Hexafluorophosphate [4]cH. TLC: R_f (SiO_2, CH_3CN:H_2O:KNO_3 aq. sat. 5:4:1) 0.4. ^{1}H-NMR (300 MHz): δ 2.18 (*s*, 6H; CH_3), 4.36 (*s*, 4H, CH_2(B)); 4.66 (*d*, J = 14.2, 2H, C*H*H(A)); 4.76 (*d*, J = 14.2, 2H, CH*H*(A)); 7.06 (*s*, 2H, H-C($6'_A$)), 7.16 (*s*, 2H, H-C(6_B)), 7.46 (*s*, 2H, H-C(6_A)), 7.73 (*d*, J = 8.0, 2H, H-C(4_B)), 7.91 (*d*, J = 8.2, 4H, H-C(4_A) and H-C($4'_A$)), 8.37 (*d*, J = 8.3, 2H, H-C($3'_A$)), 8.41 (*d*, J = 8.4, 2H, H-C(3_A)), 9.30 (*d*, J = 7.3, 2H, H-C(3_B)) A = terminal bipys, B = central bipy. ^{13}C-NMR (50 MHz): δ 18.7 (CH_3); 69.4, 70.0 (CH_2); 123.8, 124.3, 125.3, 136.6, 138.6, 138.9, 139.2, 139.5, 140.1, 150.8, 152.6, 154.5, 157.4, 158.7, 159.6 (C_{arom}). ES-MS: *m/z* 1709.3 (5, $[Fe_4\mathbf{B^{II}}_4](PF_6)_6^{2+}$), 1090.3 (25, $[Fe_4\mathbf{B^{II}}_4](PF_6)_5^{3+}$), 1053.7 (18, $[Fe_4\mathbf{B^{II}}_4]Cl(PF_6)_4^{3+}$), 780.8 (45, $[Fe_4\mathbf{B^{II}}_4](PF_6)_4^{4+}$), 753.5 (20, $[Fe_4\mathbf{B^{II}}_4]Cl(PF_6)_3^{4+}$), 595.3 (80, $[Fe_4\mathbf{B^{II}}_4](PF_6)_3^{5+}$), 573.2 (35, $[Fe_4\mathbf{B^{II}}_4]Cl(PF_6)_2^{5+}$), 471.4 (100, $[Fe_4\mathbf{B^{II}}_4](PF_6)_2^{6+}$), 453.2 (45, $[Fe_4\mathbf{B^{II}}_4]Cl(PF_6)^{6+}$), 384.3 (15, $[Fe_4\mathbf{B^{II}}_4](PF_6)^{7+}$), 367.3 (35, $[Fe_4\mathbf{B^{II}}_4]Cl^{7+}$). FT-IR (KBr): 3423 brs, 1609 w, 1477 s, 1383 w, 1247 w, 1121 m, 841 vs, 558 s cm^{-1}. UV−vis (CH_3CN): $\lambda(\epsilon)$ 516 (3.5×10^4), 354 (2.6×10^4), 306 (3.2×10^4), 257 nm (1.5×10^5 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{144}H_{128}F_{48}Fe_4N_{24}O_8P_8$ (3706.16) + $5H_2O$: C, 45.56; H, 3.66; N 8.86. Found: C, 45.48; H, 3.62; N, 8.80.

Crystal Structure Determination. Crystal Data for {$[Fe_4\mathbf{B^{II}}_4]_{0.25}(PF_6)_2$·1.5$Et_2O$·1EtOH·0.5MeCN}. Crystal description: red blocks (grown by Et_2O diffusion into MeCN solution of [4]**cH**), 0.3 × 0.3 × 0.4 mm^3.

Diffractometer and data collection: STOE · IPDS (−80 °C), graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), tetragonal, space group $P4/n$, $a = b$ = 27.978(4), c = 14.567(3) Å, V = 11403(3) $Å^3$, Z = 8, μ = 0.402 mm^{-1}, $F(000)$ = 4460, D_c = 1.258 Mg/m^3, M = 1079.72, $2\theta_{max} = 52°$.

Structure solution and refinement: Primary structure solution by direct methods (SHELXS-92).[26a] Anisotropic refinement for all non-hydrogen atoms (SHELXL-93).[26b] A riding model starting from calculated positions was employed for the hydrogen atoms, and due to disorder no hydrogen positions were calculated for solvent molecules. 36 168 measured reflections, 10 487 independent [R(int) = 0.0763], of which 9530 within a resolution shell of 15.00 ≥ d ≥ 0.84 Å were employed in the refinement of 1085 parameters using 11 182 appropriate restraints, as follows.

Ligand B^{II}: Planarity restraints for pyridyl rings, combined 1,2-/1,3-distance restraints for chemically equivalent distances, rigid-bond, and similarity restraints for anisotropic displacement parameters.

PF_6^- Ions: Combined 1,2-/1,3-distance restraints for chemically equivalent distances, restraints on distances for P−F (1.60 Å) and F···F (2.24 Å) contacts. Rigid-bond and isotropical restraints for the anisotropic displacement parameters. Displacement parameters of opposite fluorine positions were equated by means of constraint in order to save parameters since the anions show up to 3-fold positional/rotational disorder.

Solvent: Combined 1,2-/1,3-distance restraints for chemically equivalent distances, restraints on distances for C−N (1.15 Å), C−O (1.45 Å), and C−C (1.54 Å) contacts. Antibumping restraints were used to prevent close contacts between nonbonded atoms within the solvent molecules (C···O ≥ 2.40 Å, C···N ≥ 2.60 Å). Rigid-bond,

(26) (a) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467−473. (b) Sheldrick, G. M. SHELXL-93. Program for crystal structure refinement; University of Göttingen, Germany, 1993.

similarity, and isotropical restraints for the anisotropic displacement parameters. Solvent molecules show heavy positional disorder, which could be partially resolved. "Babinet's principle"[27] was employed to model diffuse water (convergence of the parameters at g = 6.375, U = 2.000).

The structure was refined against F^2 (full-matrix least-squares). The weighting scheme converged at $w^{-1} = \sigma 2(F_o^2) + (0.1946P)^2 + 2.8761P$, with $P = (F_o^2 + 2F_c^2)/3$, $R1 = 0.0786$ ($F > 4\sigma F$) [$R1 = 0.1178$ (all data)] and wR2 = 0.3051 (all data), GooF on F^2 = S = 1.038, max/min residual density: +0.956/−0.423 e Å^{-3}, ($R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n = number of reflections and p = number of parameters).

(27) (a) Langridge, R.; Marvin, D. A.; Seeds, W. E.; Wilson, H. R.; Hooper, C. P.; Wilkins, M. H. F.; Hamilton, L. D. *J. Mol. Biol.* **1960**, *2*, 38−64. (b) Driessen, H.; Haneef, M. I. J.; Harris, G. W.; Howlin, B.; Khan, D.; Moss, C. *J. Appl. Cryst.* **1989**, *22*, 510−516.

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Supporting Information Available: ROESY-^{1}H-NMR spectrum and tables of X-ray diffraction data (positional and anisotropic thermal parameters and full intramolecular distances and angles) for [4]**cH** (18 pages). See any current masthead page for ordering and Internet access instructions.

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