Multiple Expression of Molecular Information: Enforced Generation of Different Supramolecular Inorganic Architectures by Processing of the Same Ligand Information through Specific Coordination Algorithms

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Dedicated to the memory of Professor John A. Osborn

Abstract: The multisubunit ligand **2** combines two complexation substructures known to undergo, with specific metal ions, distinct self-assembly processes to form a double-helical and a grid-type structure, respectively. The binding information contained in this molecular strand may be expected to generate, in a strictly predetermined and univocal fashion, two different, well-defined output inorganic architectures depending on the set of metal ions, that is, on the coordination algorithm used. Indeed, as predicted, the self-assembly of **2** with eight Cu^{II} and four Cu^{I} yields the intertwined structure **D1**. It results from a crossover of the two assembly subprograms and has been fully characterized by crystal structure determination. On the other hand, when the instructions of strand **2** are read out with a set of eight Cu^{I} and four M^{II} (M = Fe, Co, Ni, Cu) ions, the architectures **C1**–**C4**, resulting from a linear combination of the two subprograms, are obtained, as indicated by the available physico-chemical and spectral data. Redox interconversion of **D1** and **C4** has been achieved. These results indicate that the same molecular information may yield different output structures depending on how it is processed, that is, depending on the interactional (coordination) algorithm used to read it. They have wide implications for the design and implementation of programmed chemical systems, pointing towards multiprocessing capacity, in a one code/several outputs scheme, of potential significance for molecular computation processes and possibly even with respect to information processing in biology.

Keywords: bipyridines · metal complexes · self-assembly · supramolecular chemistry · terpyridines

Introduction

Self-assembly through metal-ion coordination has provided routes for the spontaneous but directed generation of highly complex molecular architectures, practically inaccessible by other means. A variety of discrete and highly organized species has been obtained by means of ligands designed to produce, with given metal ions, a well-defined architecture of a single type.[1–4]

We recently reported a “double subroutine self-assembly” process involving the coordination properties of a ligand (**1**) (Figure 1) that combines *two* complexation subunits known to yield specific and *different* structures of double-helical and of grid type, respectively, with tetrahedral metal ions[5]. This ligand complexes Cu^{I}, generating in almost quantitative yield a large highly intertwined architecture derived from four ligand molecules and twelve metal ions (Figure 1).

The reading of the binding instructions encoded in the structure of ligand **1**, through a tetrahedral coordination algorithm was expected to produce an inorganic architecture of either type **A** or **B**, depending on whether the processing of the two sets of instructions occurs in independent or in combined fashion, respectively. In fact, only structure **B** was obtained. Although this outcome made sense from a coordination point of view, the instructions in ligand **1** did not allow a univocal control of the self-assembly process at the outset.

It was therefore of much interest to try to design a ligand strand whose self-assembly with a given set of metal ions would lead to a *unique* output architecture. Furthermore, it was of even greater interest to demonstrate that the processing of the *same* structural and binding information through different coordination algorithms, that is, with different sets of metal ions, may allow the directed generation of *different*, specific and predictable self-organized architectures. This would also make possible a precise positioning within the same structure of two or several different metal cations in a well-defined manner, each of them displaying its own complexation features.

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We present here such a case: ligand **2** may be expected to generate architectures of either type **C** or type **D** (Figure 2) depending on the set of metal ions put into operation.

It has been established that ligands of type **3**, when treated with ions that display octahedral coordination (such as Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}), yield a square [2 × 2] grid-type complex, **4**.[7] On the other hand, ligand **5a** when treated with ions of tetrahedral coordination (such as Cu^{I} and Ag^{I}) forms a double-helical structure, the dihelicate **6**.[8]

Abstract in French: *Le ligand* **2** *contient plusieurs sites de complexation groupés en deux sous-unités connues pour donner lieu à deux processus d'autoassemblages distincts avec des ions métalliques spécifiques, résultant en une structure en double hélice ou en grille respectivement. L'information interactionnelle contenue dans ce brin moléculaire doit conduire de façon strictement prédéterminée et univoque à deux différentes architectures inorganiques dépendant de l'ensemble d'ions métalliques, c.à. d. de l'algorithme de coordination, mis en oeuvre. Effectivement, l'autoassemblage de* **2** *avec 8*Cu^{II} *et 4*Cu^{I} *fournit la structure entrelacée* ***D1****. Elle résulte de l'opération combinée des deux sous-programmes d'assemblage, et a été caractérisée en détail par détermination de sa structure cristalline. D'un autre côté, quand les instructions du ligand* **2** *sont lues par un ensemble de 8*Cu^{II} *et 4*M^{II} *(M = Fe, Co, Ni, Cu), les architectures* ***C1–C4****, résultant d'une combinaison linéaire des deux sous-programmes, sont obtenues, comme l'indiquent les données physico-chimiques et spectrales disponibles. L'interconversion électrochimique de* ***C4*** *et* ***D1*** *a été réalisée par oxydoréduction. Ces résultats indiquent que la même information moléculaire peut conduire à différentes structures finales dépendant de la façon dont elle est traitée, c.à. d. dépendant de l'algorithme d'interaction (coordination) utilisé pour la lire. Ils ont de vastes implications pour la mise en oeuvre de systèmes chimiques programmés, révélant des capacités de traitement multiple, en une correspondance un / plusieurs produits (sorties), potentiellement de grande portée dans le cadre de processus de calcul moléculaire et éventuellement même en rapport avec le traitement de l'information en biologie.*

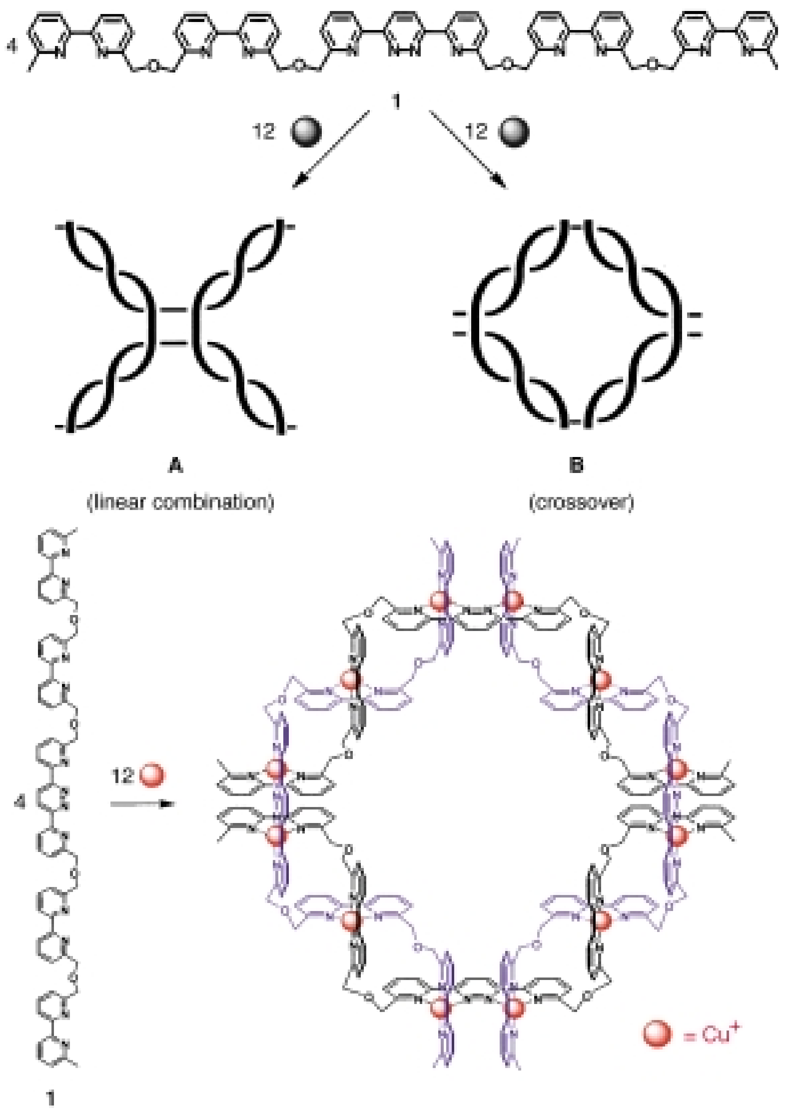
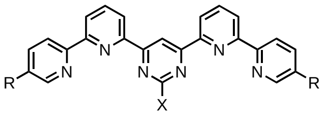
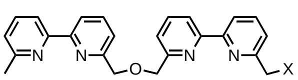


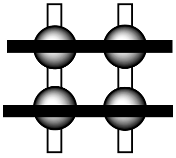
Figure 1. Self-assembly modes of ligand **1** (top) and formation reaction of the circular complex of type **B** (bottom).



3a X=H, R=H
3b X=Me, R=H
3c X=R=Me



5a X=H
5b X=Br



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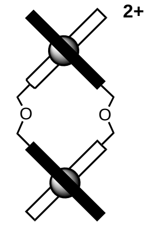

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One therefore predicts that the formation of the architecture **C** requires one equivalent of an octahedral coordination ion such as Fe^{II}, Co^{II}, Ni^{II} and two equivalents of Cu^{I} per ligand, whereas **D** requires two equivalents of a penta-

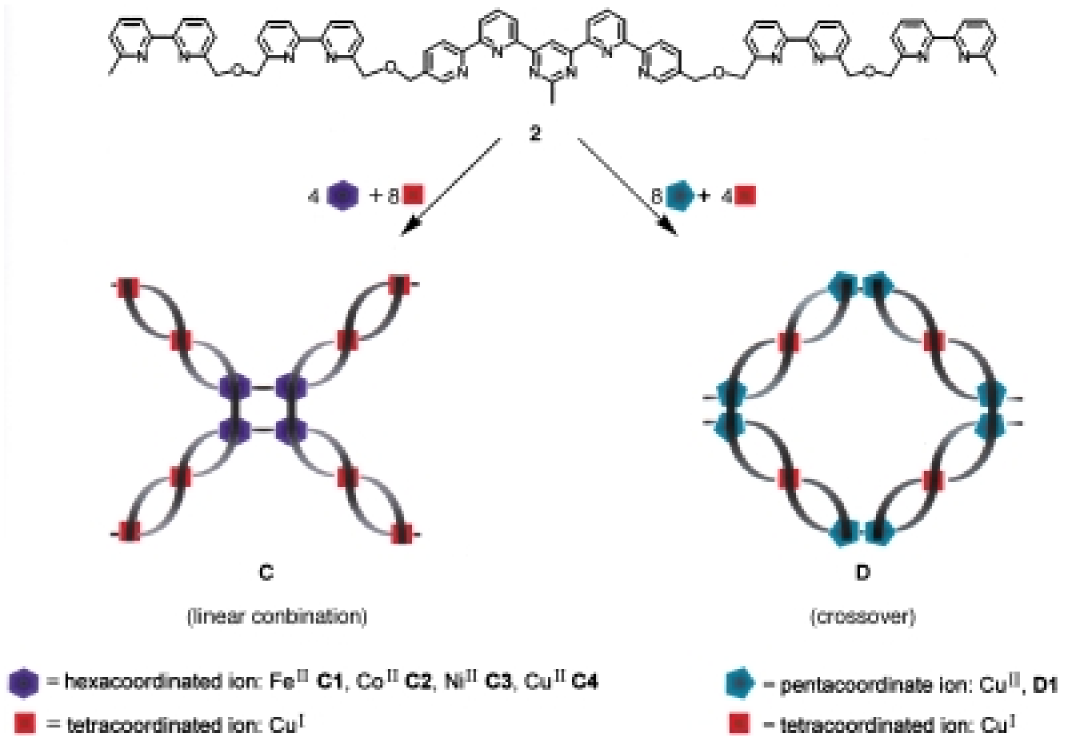


Figure 2. Self-assembly modes of ligand **2** and metal ions with different coordination geometries represented by a hexagon (octahedral hexacoordination), a pentagon (trigonal bipyramidal pentacoordination) and a square (tetrahedral tetracoordination). Left: linear combination architectures **C** with eight Cu^{I} and four Fe^{II} (**C1**) or four Co^{II} (**C2**) or four Ni^{II} (**C3**) or four Cu^{II} (**C4**) ions. Right: crossover architecture **D** with four Cu^{I} and eight Cu^{II} ions (**D1**).

coordinated ion, such as Cu^{II},[9] and one equivalent of Cu^{I} per ligand.

A related case is that of the formation of two different trinuclear helicates from the same ligand strand by using two different sets of metal ions.[6] As has been pointed out,[6b] such processes demonstrate that the operation of different reading/coordination algorithms on the same program/ligand allows the generation of different outputs/superstructures.

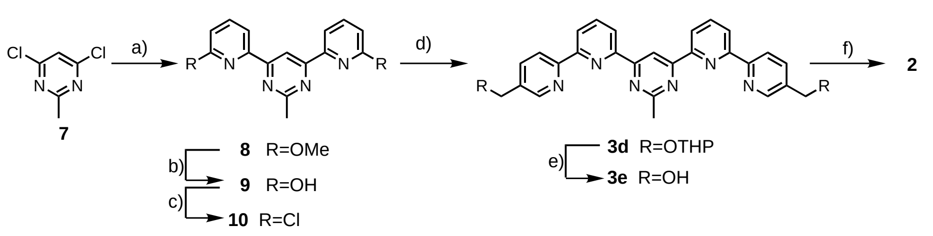
Results and Discussion

Ligand design: In the light of the above considerations we designed ligand **2**, which presents several special features:

1) it combines, within the same molecule, two ligand units that, independently taken, yield with two different types of cations two different inorganic architectures;
2) it possesses both bidentate and terdentate binding sites, which can be exploited for the complexation of hexacoordinate, tetracoordinate and/or pentacoordinate ions; this makes possible a more subtle control over the complexation event than in the case in which only one type of metal ion is complexed by the ligand, as was the case for ligand **1** previously investigated;
3) the oxomethylene bridge that connects the different binding groups of the ligand has proved to be a good compromise between rigidity (which is a crucial factor for preorganisation) and flexibility, such that the complexation units can wrap around each other in a helical fashion.[8]

Treatment of ligand **2** with a mixture of ions presenting octahedral and tetrahedral coordination in a 1:1:2 stoichiometry is expected to yield a linear combination of the structures **4** and **6**, namely structure **C** (Figure 2). A more complex situation holds when the same ligand **2** is treated in 1:2:1 ratio with ions displaying pentacoordinate and tetracoordinate geometries, such as Cu^{II}[9] and Cu^{I}, respectively. In this case, a crossover structure should be formed, resulting from a cross-operation of the two coordination routines. Species **D** (Figure 2) represents an entity of this type incorporating four ligands.

Synthesis of ligand 2: Ligand **2** was obtained by treating diol **3e** with NaH in excess followed by two equivalents of the bisbipyridine monobromide **5b**[10] in THF at reflux (72–75% yield). The diol **3e** itself was synthesized as shown in Scheme 1.



Scheme 1. Synthesis of ligand **2**. a) $[Pd(PPh_3)_4]$, toluene, 6-methoxy-2-(tributylstannyl)pyridine; b) HBr/AcOH; c) $POCl_3$, 73% (over two steps); d) $[Pd(PPH_3)_4]$, toluene, 2-[tri(*n*-butyl)stannyl]-5-hydroxymethyl-(2-tetrahydropyranyl)pyridine; e) HCl/MeOH, 55% (over two steps); f) **5b**, NaH, THF, 72%.

The dichloropyrimidine **7**[11] was coupled with 6-methoxy-2-(tributylstannyl)pyridine in toluene using [Pd(PPh$_3$)$_4$] as a catalyst to produce compound **8** in 87 % yield. Deprotection of **8** with HBr to **9**, followed by treatement with POCl$_3$ gave the dichloro compound **10** in 73 % overal yield. Coupling of **10** in toluene in the presence of [Pd(PPh$_3$)$_4$] with 2-[tri(*n*-butyl)stannyl]-5-hydroxymethyl-(2-tetrahydropyranyl)pyridine gave **3d**, which by deprotection with HCl/MeOH afforded the diol **3e** in 55 % yield. Experimental details about the synthesis of ligand **2** as well as of a series of other related ligands will be published elsewhere.

Complexation properties of ligand 2

*Formation and spectrometric properties of complex **D1***: The perchlorate salt of complex **D1** was obtained by treating a suspension of **2** in acetonitrile with one equivalent of [Cu(CH$_3$CN)$_4$]ClO$_4$ and two equivalents of Cu(ClO$_4$)$_2\cdot$ 6H$_2$O at reflux under Ar for 14 hours. The counteranion could be exchanged by adding dropwise the resulting brown solution to a concentrated aqueous solution of NH$_4$PF$_6$. The precipitate which formed was centrifuged, washed abundantly with water, followed by methanol and diethyl ether, and dried.

In order to characterize species containing paramagnetic ions that do not display an informative NMR spectrum, electrospray mass spectrometry (ESMS) is of particular interest. In the case of the ClO$_4^-$ salt of the complex **D1**, the ESM spectrum (Figure 3) displays a set of peaks that correspond to the successive loss of ClO$_4^-$ ions from a complex of composition [Cu$_{12}$(**2**)$_4$][(ClO$_4$)$_{20}$]. The signals obtained range from [Cu$_{12}$(**2**)$_4$][(ClO$_4$)$_{17}$]$^{3+}$ to [Cu$_{12}$(**2**)$_4$][(ClO$_4$)$_{12}$]$^{8+}$, thus indicating unambiguously that the composition of the complex corresponds to four ligands, four Cu$^{\text{I}}$ ions, and eight Cu$^{\text{II}}$ ions.

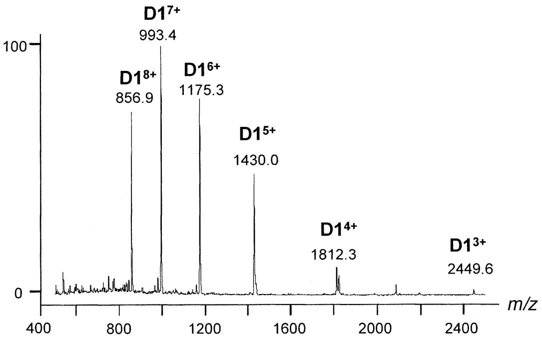


Figure 3. Electrospray mass spectrum of complex **D1**.

The electronic absorption spectrum (in acetonitrile) shows a metal-to-ligand charge transfer (MLCT) band in the visible region at $\lambda = 445$ nm ($\varepsilon = 21000\,\text{M}^{-1}\text{cm}^{-1}$) in line with what one may expect for a molecule containing four Cu$^{\text{I}}$ ions, each complexed to two bipyridines in a tetrahedral fashion. The corresponding data for a dihelicate containing two [Cu$^{\text{I}}$(bipy)$_2$] sites are 449 nm ($\varepsilon = 9800\,\text{M}^{-1}\text{cm}^{-1}$).[8] A weak band at 687 nm ($\varepsilon = 920\,\text{M}^{-1}\text{cm}^{-1}$) may be assigned to a d–d absorption, corresponding to the eight Cu$^{\text{II}}$ ions in a pentacoordinated (bipy, terpy) environment, to be compared with 636 nm ($\varepsilon = 91\,\text{M}^{-1}\text{cm}^{-1}$) for [Cu$^{\text{II}}$(bipy)(terpy)].[9a]

The data obtained in solution agree with the complex having structure **D1** in which the Cu$^{\text{II}}$ ions are pentacoordinated and the Cu$^{\text{I}}$ ions have tetrahedral coordination. In this way, following the principle of full site occupation,[12] all the coordination sites provided by the ligand are exploited by the Cu$^{\text{II}}$ and Cu$^{\text{I}}$ ions. The formation of **D1** corresponds therefore to the self-organization process shown in Figure 4. Its structure was confirmed by X-ray crystallography.

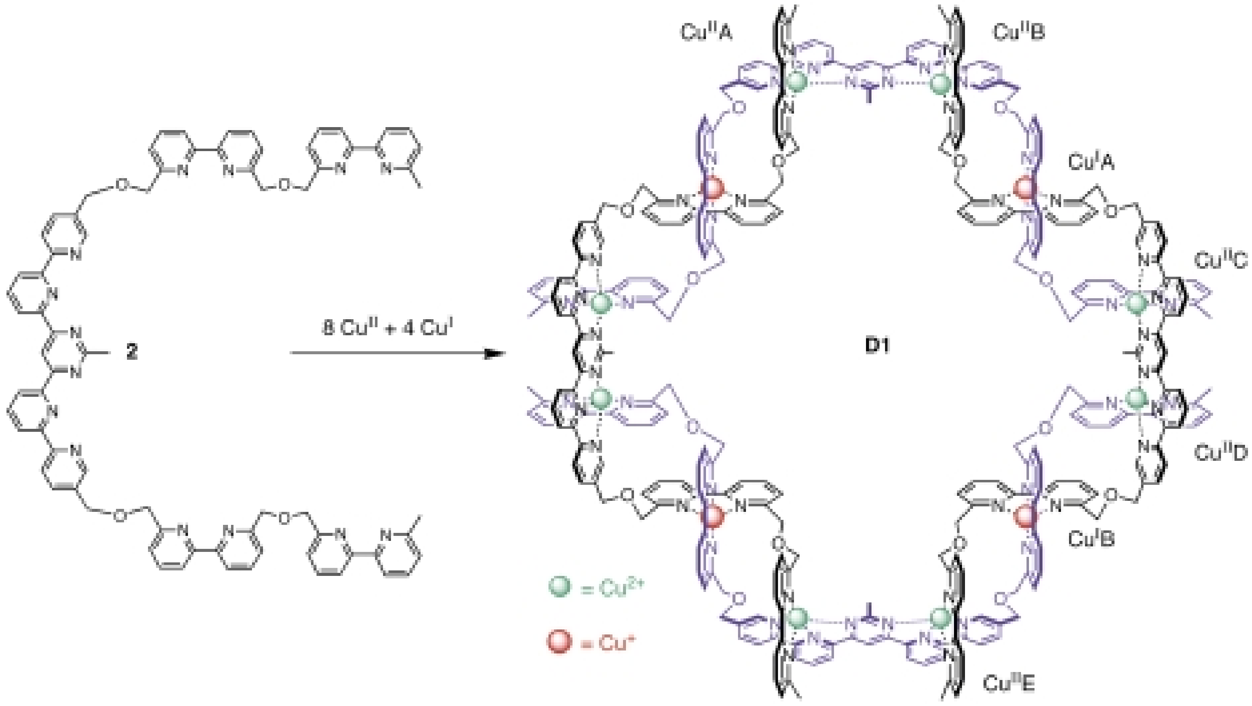


Figure 4. Self-organization of the inorganic architecture **D1** from ligand **2** and [8Cu$^{\text{II}}$ + 4Cu$^{\text{I}}$] metal cations.

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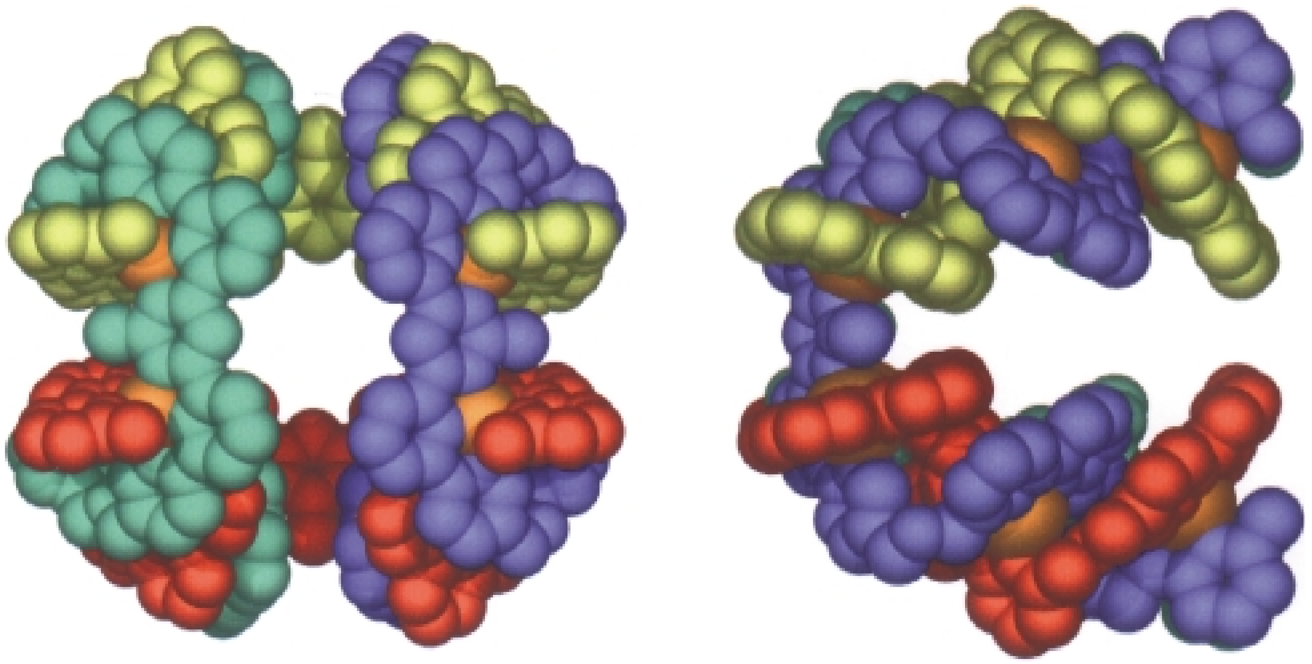

Figure 5. Front view (left) and side-view (right) of the crystal structure of complex cation $[Cu_{12}(\mathbf{2})_4]^{20+}$ of **D 1** in a space-filling representation. The four ligand molecules are represented in four different colors (yellow, green, red, and blue); the copper atoms are in orange.

*Crystal structure of complex **D 1***: Single crystals of compound **D 1** as the PF_6^- salt were grown by diffusion of benzene into a 3 $mg\,mL^{-1}$ solution of the complex in CH_3NO_2/CH_3CN 1:1; the crystal structure was determined. The compound consists of a large complex ion $[Cu_{12}(\mathbf{2})_4]^{20+}$ (Figure 5) of saddle shape, with an overall diameter of 31 Å (including the Van der Waals radii).

The structure of this cation is strongly curved, probably because of the fact that the distance between the two bipyridine sites (within the same ligand) is shorter than the distance between the terdentate unit and the neighboring bipyridine site. This forces the molecule to bend in order for the terminal bipyridine unit of one ligand to match the "complementary" (with respect to Cu^{II}) coordination site defined by one of the terpyridine-like subunits placed in the central part of the second ligand. This bending can be seen (in relation to the structure of proteins) as a tertiary structure, resulting from factors expressed in the primary (subunits of the ligands) and secondary (helical arrangement of the ligands) structures.

The ligand strands are wrapped around each other as schematically represented by structure **D**, forming four linked double-helical sections and with twelve crossing points. There are two types of duplexes in **D** of opposite (+) and (−) helicity and these are arranged alternately around the ring so that the structure is an achiral, *meso* form with two planes of symmetry through the middle of the pyrimidine ring of the central components **3e**. As in the previously reported nanocycle,[5] this structure of D_{2d} symmetry presents the unusual feature of combining four chiral double-helical elements into an achiral object. Structure **D** also corresponds to the intertwining of two pairs of strings into a "perpendicular braid".

Table 1. Distances [Å] between the copper ions in complex **D 1**.[a]

	$Cu^{II}A$	$Cu^{II}B$	$Cu^{II}C$	$Cu^{II}D$	$Cu^{II}E$	$Cu^{I}B$	$Cu^{I}C$
$Cu^{II}A$	–	6.33	16.16	18.44	14.89	17.47	15.22
$Cu^{II}B$	6.33	–	13.12	15.85	13.29	14.64	17.50
$Cu^{I}A$	11.50	7.06	6.88	11.43	15.22	13.13	18.55

The distances between the copper ions are listed in Table 1. The Cu^I and Cu^{II} ions have tetra- and pentacoordination, respectively. The bite angles of the bipyridine units complexing Cu^I are 81.8(3)° on average, whereas the interbipyridine angles vary between 121.9(4)° and 128.4(5)°, leading to a distorted tetrahedral coordination sphere. The average bite angles of the bipyridine ligands at the pentacoordinated Cu^{II} ions are 83.5(3)°, while those of the terpyridine-type units are smaller, about 79.5(3)°. The N-Cu-N angles between the bipyridine and terpyridine groups vary from 100.0(2)° to 128.4(5)°, yielding a severely distorted trigonal bipyramidal coordination geometry for the Cu^{II} ions, with the bipyridine nitrogens and the central nitrogen of the terpyridine-like unit in equatorial location and the two outer N atoms of the latter in axial position, with an average N-Cu-N angle of 155°. The Cu^I–N distances lie in the 2.018(8) Å to 2.033(9) Å range, while those for Cu^{II}–N vary between 1.918(6) Å and 2.142(4) Å. A related pentacoordination geometry is found for the central Cu^{II} site in a tris-Cu^{II} double helicate.[9a]

The previously reported nanocycle **B** (Figure 1)[5] was found to contain four PF_6^- anions that tightly filled up its central cavity (Figure 6). In contrast, complex **D 1** does not appear to include any counterion or solvent molecule within the central cavity, as a result of the bending previously discussed, which leaves virtually no empty space within the structure. However, four PF_6^- ions are "pinched" between two pyridines of two opposite bis-terdentate sites as shown in Figure 7. The remaining PF_6^- anions are found in between the cationic units, together with the solvent molecules.

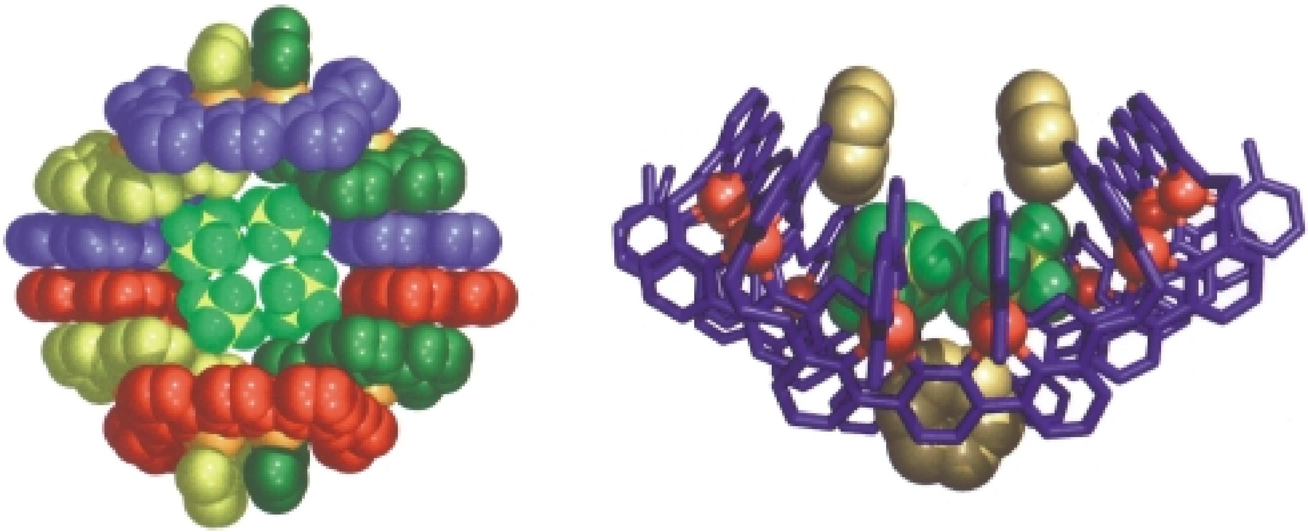

Figure 6. Front view (space-filling representation, left) and side-view (stick representation, right) of the crystal structure of complex **B** containing $4\,PF_6^-$ anions and $4\,C_6H_6$ molecules; the latter are omitted on the left for clarity. The four ligand molecules are represented in four different colors (left: yellow, green, red, and blue) or in the same color (right, blue).

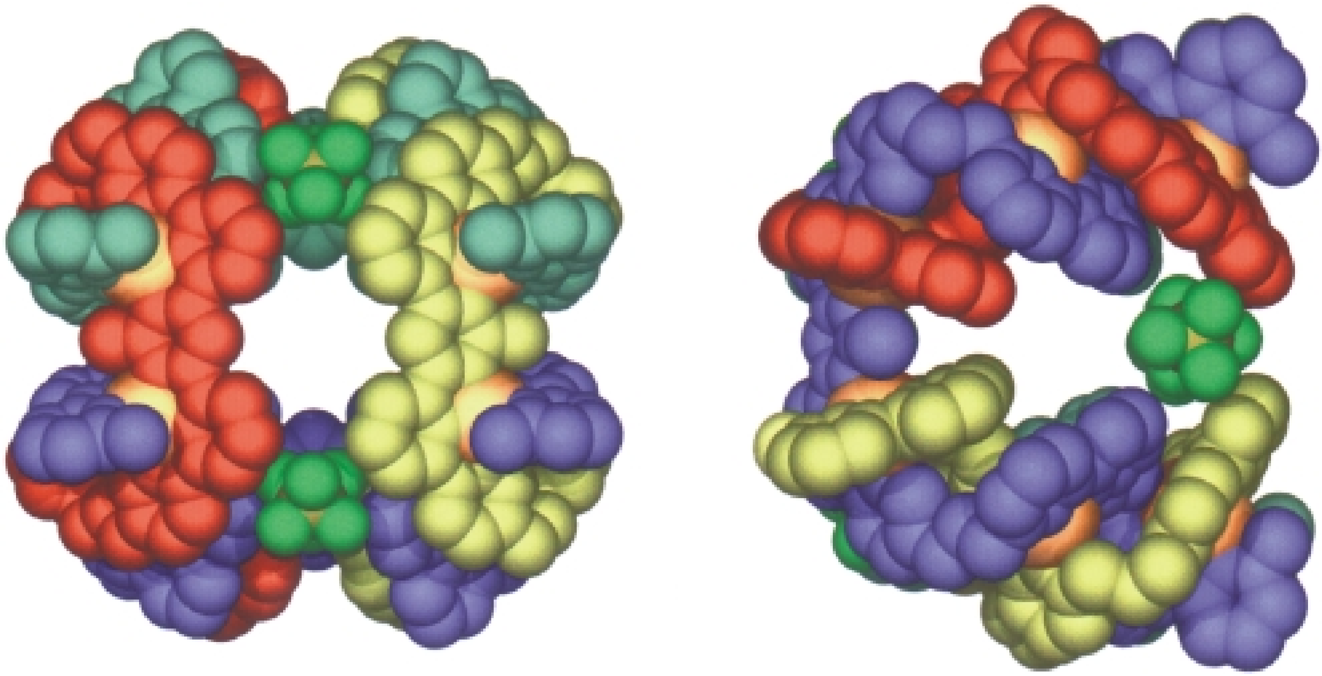

Figure 7. Front view (left) and side-view (right) of the crystal structure of complex cation of **D1** with $4\,PF_6^-$ (light green) anions, in space-filling representation. The four ligand molecules are represented in four different colors (yellow, green, red, and blue); the copper atoms are in orange.

In the lattice, the complexes are positionned with respect to each other as shown in Figure 8.

Formation and characterization of complexes ***C1–C4***: When the ligand **2** was refluxed in CH_3CN for 14 hours with a mixture of ClO_4^- salts of Cu^I and M^{II} (M = Fe, Co, Ni, Cu) in a ratio $\mathbf{2}/Cu^I/M^{II} = 1{:}2{:}1$, in each case a complex was yielded possessing the composition $[M_4Cu_8(\mathbf{2})_4](ClO_4)_{16}$ as indicated by ESMS. Indeed, the mass spectra contain a clear pattern of peaks corresponding to the successive loss of four to nine perchlorate anions from the parent entity (see Figure 9 for $M = Fe^{II}$, Co^{II}, and Cu^{II}).

Only highly shifted broad resonances were observed by proton NMR spectroscopy owing to the magnetic properties of the complexes,[13] so that no structural information could be obtained from these spectra.

UV/Vis studies in CH_3CN revealed, in the case of the species obtained by reaction of **2** with a Cu^{II}/Cu^I mixture, transitions corresponding to eight Cu^I ions complexed each to two bipyridine units and four Cu^{II} (N_6) sites. For this $[Cu^{II}_4Cu^I_8(\mathbf{2})_4]^{16+}$ complex, an MLCT transition is observed at 445 nm ($\varepsilon = 37\,000\,\text{M}^{-1}\text{cm}^{-1}$) as compared with 449 nm ($\varepsilon = 9800\,\text{M}^{-1}\text{cm}^{-1}$) for a dihelicate containing two $[Cu^I(bipy)_2]$ sites;[8] in addition a weak Cu^{II} d–d absorption is found at

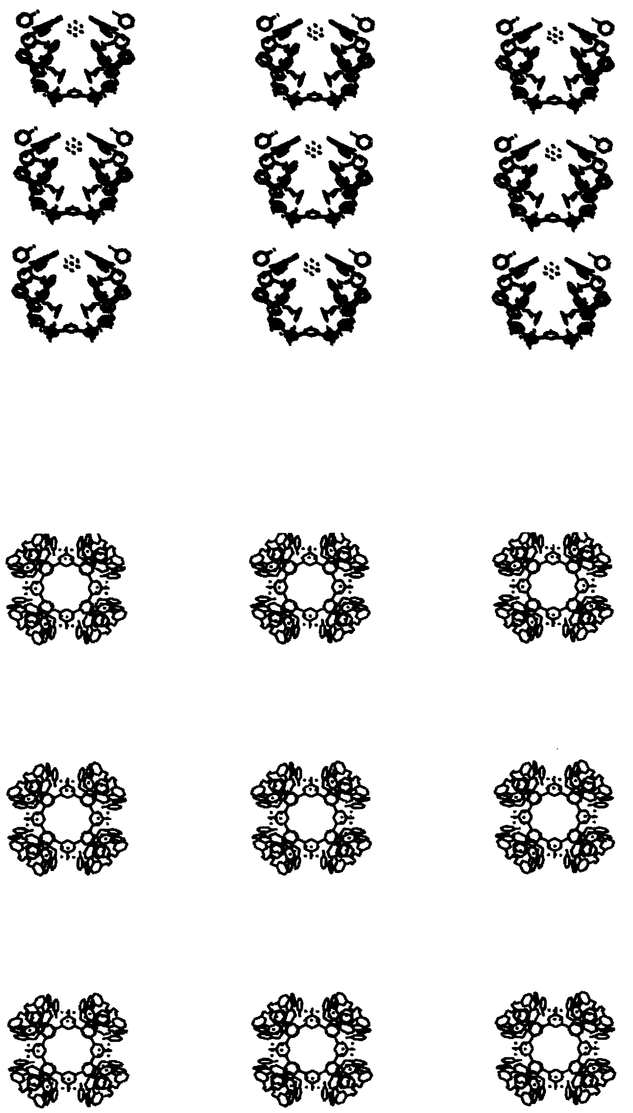

Figure 8. Two views of the arrangement of **D1** molecules within the crystal lattice.

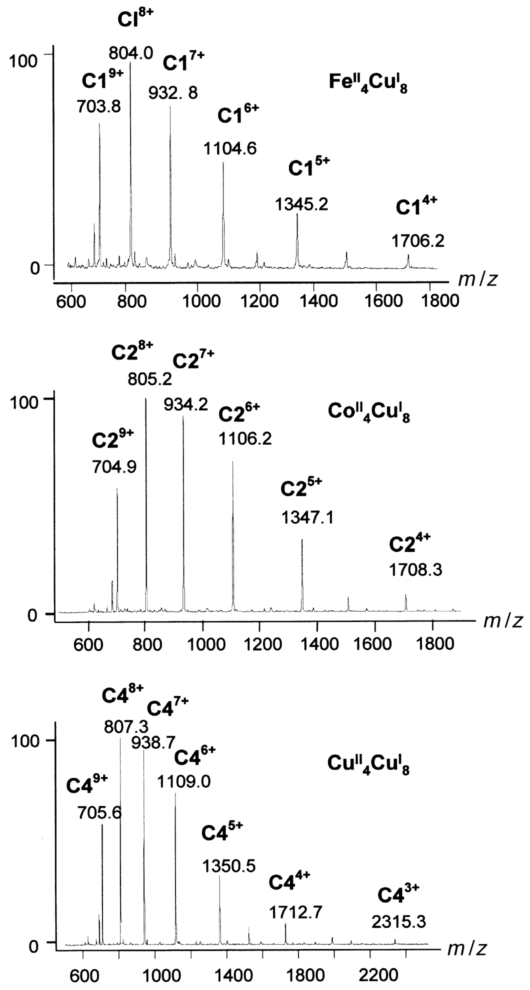

Figure 9. Electrospray mass spectra of the complexes $[M_4Cu_8(\mathbf{2})_4](ClO_4)_{16}$: top **C1** (M = Fe^{II}), center **C2** (M = Co^{II}), bottom **C4** (M = Cu^{II}). The peaks observed correspond to the successive loss of four to nine perchlorate anions from the parent complex.

711 nm($\varepsilon = 430\,\text{M}^{-1}\text{cm}^{-1}$), to be compared with 687 nm ($\varepsilon = 100\,\text{M}^{-1}\text{cm}^{-1}$) or 693 nm ($\varepsilon = 70\,\text{M}^{-1}\text{cm}^{-1}$) for hexacoordinated [Cu^{II}(terpy)$_2$] sites.[9b] The shift towards longer wavelength and the higher absorption for the Cu^{II} sites in the present case is in line with coordination to the central pyrimidine group of the ligand. For the $[Fe^{II}_4Cu^{I}_8(\mathbf{2})_4]^{16+}$ complex two bands are observed at 447 nm ($\varepsilon = 35\,000\,\text{M}^{-1}\text{cm}^{-1}$) and at 630 nm ($\varepsilon = 10\,000\,\text{M}^{-1}\text{cm}^{-1}$) for the Cu^{I} and Fe^{II} sites, respectively; two differently substituted Fe$_4$ [2 × 2] grid complexes of type **4** have absorptions at 585 nm ($\varepsilon = 17\,000\,\text{M}^{-1}\text{cm}^{-1}$) and 622 nm ($\varepsilon = 9900\,\text{M}^{-1}\text{cm}^{-1}$).[14]

All the spectrometric results obtained agree with the formation of complexes with four M^{II} (N$_6$) sites and eight Cu^{I} (bipy)$_2$ sites. Together with the earlier data on the formation of helicates[8] and of [2 × 2] grids,[7] they lead us to propose for these species the general structure **C**, which combines a central [2 × 2] grid (of type **4**) and four dihelicate units (of type **6**), located at the corners of the grid, as represented schematically in Figure 10. This probably holds for all four cases **C1**–**C4** involving Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} ions, respectively. In order to confirm the structure in the solid state, crystallization experiments are being pursued. All the crystals obtained so far were of unsuitable quality. Perhaps the less compact structure of a complex of type **C** with respect to the circular structure **D** is the source of the crystallization difficulties encountered.

Electrochemically induced interconversion of complexes D1 and C4: It should in principle be possible to electrochemically interconvert the complexes **C4** and **D1**, containing [4Cu^{II}, 8Cu^{I}] and [8Cu^{II}, 4Cu^{I}] ions, respectively, by exchange of four electrons. Indeed, preliminary experiments of coulometric oxidation and reduction (in acetonitrile) of **C4** and **D1**, respectively, followed by refluxing the solutions for about ten hours, yielded complexes that displayed the expected ESMS and electronic absorption spectral features; this indicated that the interconversion between the **C4** and **D1** structures (Figure 11) had been achieved.

These results indicate that the **C4/D1** pair represents a bistable system undergoing an electrochemically induced switching by multielectronic exchange, which corresponds to the interconversion of two highly complex inorganic archi-

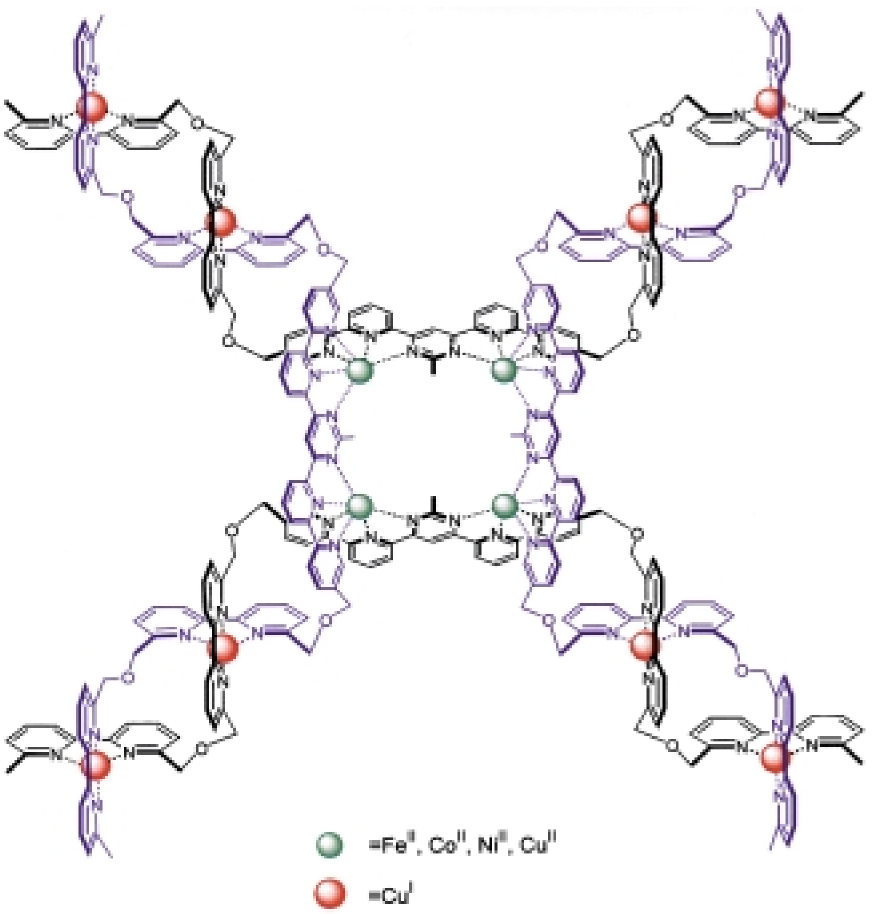

Figure 10. Representation of the structure of the complexes **C1**–**C4**.

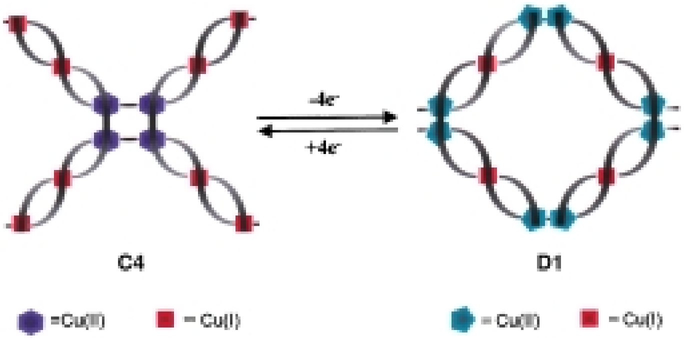

Figure 11. Scheme for the reversible electrochemically induced interconversion between the complexes **C4** [4 Cu^{II}, 8 Cu^{I}] and **D1** [8 Cu^{II}, 4 Cu^{I}] by exchange of four electrons (see text).

tectures. The processes are expected to be kinetically very slow due to the deeply intertwined nature of these structures. Further electrochemical and kinetic investigations are required in order to more quantitatively assess these transformations.

Conclusion

The combination within a ligand strand of different coordination subunits of specific complexation properties with given metal ions has prooved to be a powerful method for generating, in a spontaneous but controlled manner through self-organisation, large supramolecular architectures virtually impossible to create in stepwise fashion. Thus, ligand **2**, containing bidentate and terdentate coordination units capable of discriminating between different cations based on their coordination abilities, has enabled us to place Cu^{I} and M^{II} (M = Fe, Co, Ni, Cu) ions at predictable, well-defined sites within a specific structure. One can take advantage of this approach for introducing specific ions at desired positions in a complex supramolecular architecture in order to finely tune its physical properties. A range of ligands containing other combinations of coordination units may be envisaged. A number of them have been synthesized and their ion binding properties have been studied. These results will be described in future reports.

The functionalization of the ligands at well-defined positions would generate complexes bearing functional groups in precise locations with respect to each other, a feature of much interest for instance for generating specific arrays of complexes through recognition events, for interaction with surfaces, or for binding to biologically relevant molecules. Such self-organization processes present, in principle, much potential for nanotechnology, since highly complex architectures become spontaneously accessible in a controlled fashion, thus offering means of bypassing intricate nanofabrication procedures.

The formation pathway of these highly intertwined architectures presents analogies with the protein folding problem and is being investigated.

Finally, and probably most importantly, a deeper analysis of the generation of two different inorganic architectures from the same ligand by means of two different sets of metal ions shows that the process has wide implications within the general framework of programmed chemical systems:[1, 15]

1) it corresponds to a case of double subroutine self-assembly involving a ligand strand containing two subunits that code for different structures, one of grid-type and one of double-helicate type;
2) it demonstrates that the processing of the *same* ligand information by *different* coordination algorithms (through the use of different sets of metal ions) allows the controlled generation of *different* output architectures;
3) it indicates that molecular information is, in principle, *pluripotent*, inasmuch as its reading through different interactional algorithms generates different output entities, thus opening perspectives towards the operation of artificial or biological systems with *multiple processing* capacity, by which a given code may yield several products.

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Experimental Section

General techniques: NH_4PF_6 was purchased from Aldrich. The metal salts for the complexation experiments were used as obtained from Strem Chemicals. $[Cu(CH_3CN)_4]ClO_4$ was prepared according to the procedure in ref. [16]. Solvents were used as purchased, except acetonitrile which was distilled over CaH_2. The electrospray mass spectra were recorded on a VG BioQ triple quadrupole mass spectrometer (Micromass, Manchester) upgraded to Quattro II performance. UV spectra were obtained on a Cary 3 spectrometer. The synthesis of the ligands used in this work will be described in detail elsewhere.

Preparation of the complexes C1–C4: A typical complexation experiment was run as follows. Ligand **2** (16.2 mg, 0.0132 mmol) was suspended in acetonitrile (4 mL) at room temperature under Ar. Addition of $M(ClO_4)_2 \cdot 6H_2O$ (1 equiv, M = Fe, Co, Ni, Cu) and $[Cu(CH_3CN)_4]ClO_4$ (2 equiv) led to solubilization and formation of highly colored solutions. The solution was stirred under reflux for 14 hours, and the small amount of insoluble material (less than 2% of mass balance) was separated by centrifugation. All the measurements described in this work were performed on the materials obtained by this method, without further purification. Anion exchange was performed as described for **D1** hereafter.

Preparation of the complex D1: A typical complexation experiment was run as follows. Ligand **2** (14.6 mg, 0.0119 mmol) was suspended in acetonitrile (3.5 mL) at room temperature. Addition of $[Cu(CH_3CN)_4]ClO_4$ (1 equiv, 4.44 mg) and of $Cu(ClO_4)_2 \cdot 6H_2O$ (2 equiv, 8.63mg) led to solubilization and to a change in color from green to brown. The solution was stirred under reflux for 14 hours, and a small amount of insoluble material (removed by centrifugation) was observed (less than 2% of mass balance). ESMS was performed on this sample without further purification. In order to perform anion-exchange, the brown solution obtained was added dropwise to a concentrated aqueous solution of NH_4PF_6. The precipitate was filtered, washed abundantly with water, methanol and diethyl ether to give a brown powder (96% mass recovery). X-ray structural analysis was performed on a crystal grown from this sample without further purification.

Crystal structure data for D1: Formula: $[Cu_{12}(C_{75}H_{62}N_{14}O_4)_4] \cdot 20PF_6 \cdot 12C_6H_6 \cdot 4CH_3NO_2 \cdot 8CH_3CN$; diffractometer and data collection: STOE IPDS (−70 °C), graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), tetragonal, space group $I4(1)/a$, $a = b = 45.775(7)$, $c = 23.580(5)$ Å, $V = 49408(14)$ Å^3, $Z = 4$, $\mu = 0.659$ mm^{-1}, $F(000) = 19144$, $\rho = 1.282$ mg m^{-3}, $2\Theta_{max} = 48.4°$. Structure solution and refinement: primary structure solution by direct methods (SHELXS-92).[17] Anisotropic refinement for all non-hydrogen atoms of the cationic complex except for one terminal bipyridine unit for which disorder was observed and which was refined on two split positions (SHELXL-93).[18] 74519 measured reflections, 18479 independent [R(int) = 0.1273] of which 18475 were used to refine 1063 parameters. The solvent and anionic structure part show multifold disorder. Therefore atoms of solvent and PF_6^- anions were refined isotropically on split positions. The structure was refined against F^2 (full-matrix least-squares). $R1 = 0.1337$ (for 5506 reflections with $F > 4\sigma F$) [$R1 = 0.2882$ (all data)] and $wR2 = 0.3294$ [$wR2 = 0.5073$ (all data)]. GooF on $F^2 = S = 0.976$; max./min. residual density $+1.05/-0.59$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- CCDC-138813. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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