Double Subroutine Self-Assembly; Spontaneous Generation of a Nanocyclic Dodecanuclear Cu^{I} Inorganic Architecture

Daniel P. Funeriu, Jean-Marie Lehn,* Gerhard Baum and Dieter Fenske

Abstract: The newly synthesised ligand **2** combines binding components known to undergo specific and distinct self-assembly processes with Cu^{I} ions. It complexes Cu^{I} to form, in almost quantitative yield, a large inorganic architecture **1** made up from four ligand molecules and twelve metal ions. The structure of **1** was ascertained by X-ray radiocrystallography as well as by NMR spectroscopy and electrospray mass spectrometry. It consists of a macrocycle of nanometric dimension with an external diameter of 28 Å; the central cavity has a diameter of 11 Å, which contains four PF_6^- anions as well as solvent molecules. The spontaneous formation of **1** results from a self-assembly process based on a "program" combining two assembly subroutines, each specific to one of the ligand subunits. Self-assembly through double or, more generally, multiple subroutines can be used to generate a wide variety of highly complex inorganic supramolecular architectures by combination of two or more assembly processes.

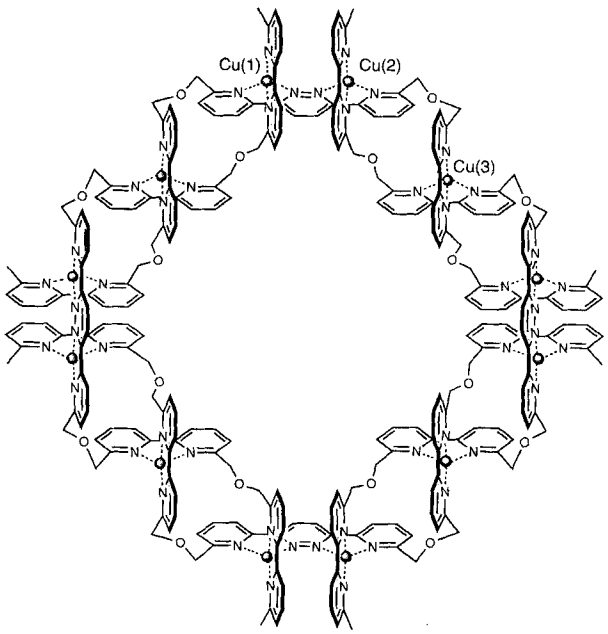
Keywords
bipyridines · copper compounds · self-assembly · supramolecular chemistry

Introduction

Defined self-assembled architectures are formed through a "program" that comprises 1) molecular recognition between the individual components, 2) correct orientation of the initially connected components so as to allow growth and 3) termination, yielding a finite structure. Their syntheses are directed by the information stored in the structure of the precursors that participate in the self-assembly process[1] and processed through the algorithm defined by the interactions between the components. The spontaneous but directed generation of inorganic architectures has thus been achieved, based on the steric information defined by ligand structure and on the operational algorithm determined by the coordination geometry of metal ions. A variety of complex structures have been obtained, such as double,[2] triple[3] and circular[4] helicates,[1, 5, 6] and cylindrical cages[7, 8] and grids.[9]

A further logical step would be to explore how several programs that independently govern the formation of different structures can be combined as subroutines of an overall program. Specifically, it is of interest to investigate whether the system behaves as a linear combination of subroutines with each yielding its predetermined substructure or as a more complex combination with the subroutines interfering and crossing over. We present here such a case involving a two-subroutine self-assembling system that yields the large hollow architecture **1** from four ligands **2** and twelve Cu^{I} ions (see also Figure 1).

It has been established that the bisbipyridine ligand **3a** combines with Cu^{I} ions to form a double-helical structure, the helicate **4**.[2] On the other hand, the bispyridyl–pyridazine ligand **5a**[10] or **5b**[9b] and Cu^{I} ions have been shown to yield a square-shaped species, **6**.[10] Therefore, ligand **2**, which combines both



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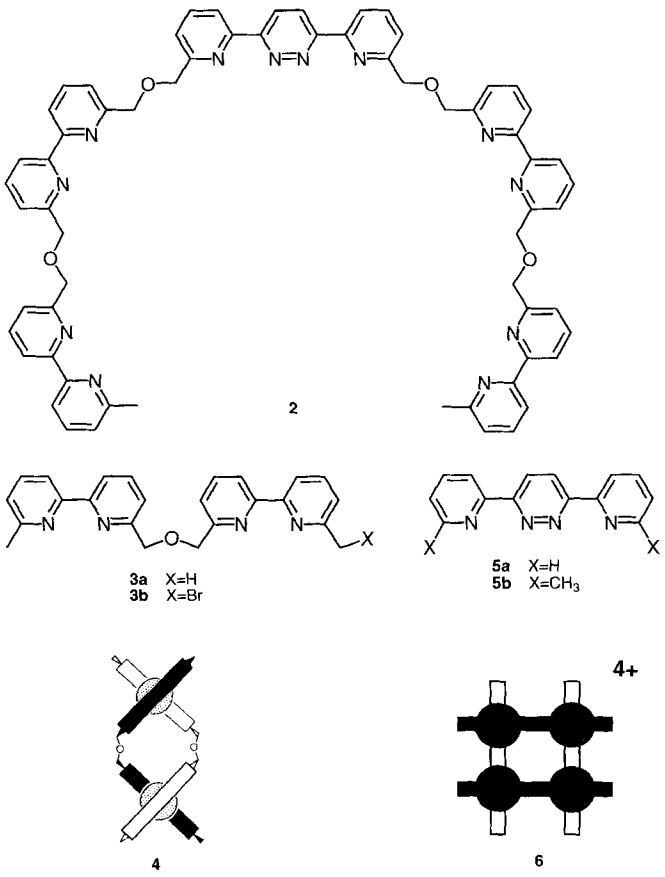
[*] Prof. Dr. J.-M. Lehn, D. P. Funeriu
Laboratoire de Chimie Supramoléculaire
Institut Le Bel, Université Louis Pasteur CNRS URA 422
4, rue Blaise Pascal, F-67000 Strasbourg (France)
Fax: Int. code +(88)41-1020
e-mail: lehn@chimie.u-strasbg.fr
G. Baum, Prof. Dr. D. Fenske
Institut für Anorganische Chemie der Universität Karlsruhe (Germany)



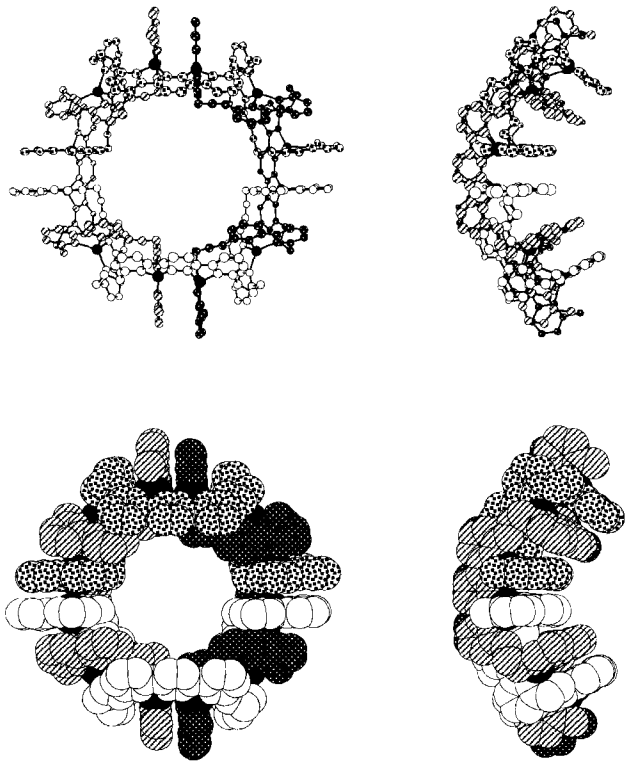


Fig. 1. Crystal structure of complex **1**. Top: ball and stick representation; bottom: space-filling representation (see also colour picture on cover); left: front view; right: side view.

these structural elements, can be used to test how a mixed system "remembers" and expresses the behaviour of its individual components.

Results and Discussion

Synthesis of ligand 2 and Cu^I complexation: Ligand **2** was produced by treating diol **5d** with NaH followed by 2 equiv of the bisbipyridine monobromide **3b**[11] in THF at reflux (65–82% yield; m.p. 221 °C). The diol **5d** itself was obtained as shown in Scheme 1.[12] The bromopyridine **7** was oxidised in 72% yield to the corresponding carboxylic acid **8a** with CrO_3/H_2SO_4. Esterification and reduction of the ester **8b** with $NaBH_4$/ethanol gave the alcohol **9a** (78% yield), which was protected with dihydropyran to afford **9b** in 95% yield. Treatment of **9b** with *n*BuLi in THF followed by $n Bu_3SnCl$ gave the stannylated pyridine **10** in (52% yield; distilled). $Pd(PPh_3)_4$-catalysed coupling of **10** with 3,6-dichloropyridazine in toluene afforded product **5c** (25–35% yield). Deprotection gave diol **5d** in 98% yield.

Abstract in French: *Le nouveau ligand **2** combine des unités de coordination connues pour donner lieu à des processus d'autoassemblage spécifiques et différents avec des ions Cu^I. Il complexe Cu^I en formant spontanément et presque quantitativement une architecture inorganique de grande taille **1** à partir de quatre molécules de ligand et douze ions métalliques. La structure **1** a été établie par diffraction des rayons X ainsi que par spectrométrie de RMN et de masse. Elle consiste en un macrocycle de dimension nanométrique ayant un diamètre extérieur de 28 Å et une cavité centrale de 11 Å de diamètre qui contient quatre anions PF_6^- ainsi que des molécules de solvant. La formation de **1** résulte d'un processus d'autoassemblage suivant un programme fondé sur la combinaison de deux sous-routines d'assemblage dont chacune est spécifique d'un des sous-unités du ligand. Un tel autoassemblage à double où, plus généralement, multiple sous-routine ouvre la voie à la génération d'une grande variété d'architectures supramoléculaires inorganiques de haute complexité par combinaison de deux où de plusieurs processus d'assemblage.*

Abstract in Romanian: *Noul sintetizatul ligand **2** combină în structura sa două părți distincte, cunoscute pentru proprietățile complexante față de ionii Cu(I). Ligandul **2** complexează cantitativ cationul Cu(I) dând naștere unei arhitecturi anorganice de mari dimensiuni **1**, formată din patru molecule de ligand și doisprezece cationi metalici. Structura **1** a fost stabilită prin spectroscopie RMN, spectrometrie de masă și difracția razelor X. Această structură constă într-un macrociclu de dimensiuni nanometrice de diametru exterior 28Å, cavitatea centrală având 11Å și incorporând patru anioni PF_6^- și câteva molecule de solvent. Procesul de autoasamblare, în urma căruia rezultă nanociclul **1** este realizat prin "executarea" unui program fondat pe combinarea a două subrutine de asamblare, fiecare subrutină fiind specifică unei subunități a ligandului **2**. Acest nou tip de autoasamblare, având la bază "executarea" unui program molecular format din două sau mai multe subrutine, deschide calea realizării unei varietăți de arhitecturi supramoleculare de mare complexitate.*

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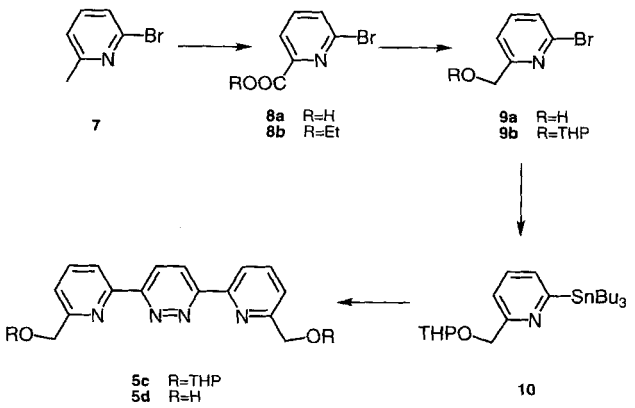

Scheme 1. Synthesis of the diol **5d**.

The complex **1** was obtained by treating a suspension of **2** in acetonitrile with 3 equiv of $Cu(CH_3CN)_4X$ ($X = ClO_4^-$, PF_6^- or BF_4^-) at reflux under argon for twelve hours. Alternatively, the same complex was formed at room temperature over a two-month period.

Spectral data for complex 1: The electrospray mass spectrum is very informative (Figure 2). It displays a set of peaks that correspond to the successive loss of five PF_6^- ions, from $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_9]^{3+}$ to $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_4]^{8+}$; this shows unambiguously the stoichiometry of the complex as being four ligands and twelve Cu^I ions.

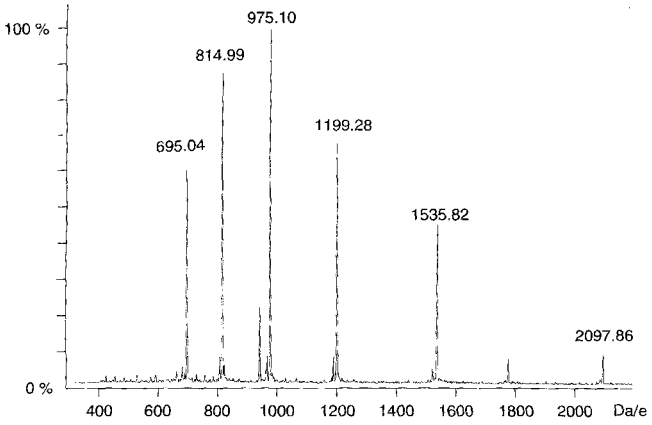

Fig. 2. Electrospray mass spectrum of the PF_6^- salt of the complex **1**. The peaks correspond to the following compositions: 2097.86, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_9]^{3+}$; 1535.82, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_8]^{4+}$; 1199.28, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_7]^{5+}$; 975.10, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_6]^{6+}$; 814.99, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_5]^{7+}$; 695.04, $[\{Cu_{12}(\mathbf{2})_4\}(PF_6)_4]^{8+}$.

The electronic absorption spectrum (in acetonitrile) shows a metal-to-ligand charge transfer (MLCT) band in the visible region at $\lambda = 429$ nm ($\varepsilon = 34000$), as expected from literature data for related complexes.[2, 10]

The ^1H NMR spectrum (500 MHz) (Figure 3) shows a marked upfield shift (more than 1 ppm) of the signals of the methylene protons with respect to the uncomplexed ligand as well as a more complicated pattern in this region (AB systems). Such features are commonly observed for the formation of helicoidal complexes of oligobipyridine ligands.[2, 13] The aromatic part consists of sixteen peaks, which were all assigned by means of ROESY (Figure 4) and COSY NMR data (Figure 5); this data indicates that the symmetry of the ligand is conserved during the complexation process.

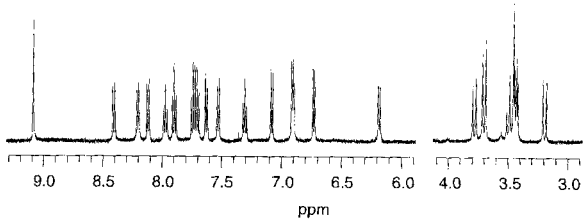

Fig. 3. ^1H NMR spectrum (500 MHz) of the PF_6^- salt of the complex **1** in CD_3CN.

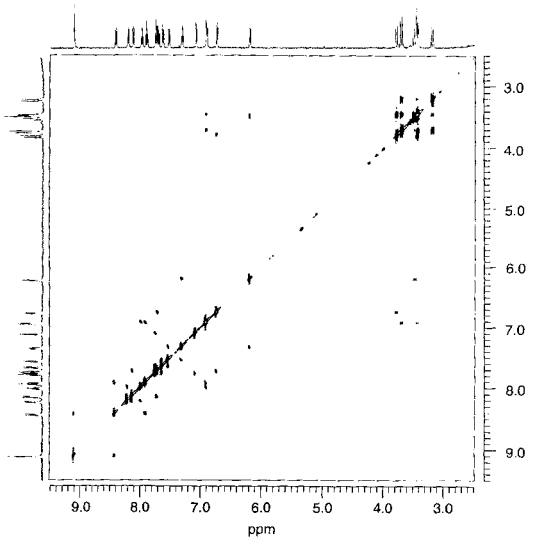

Fig. 4. ROESY spectrum of the PF_6^- salt of the complex **1** in CD_3CN.

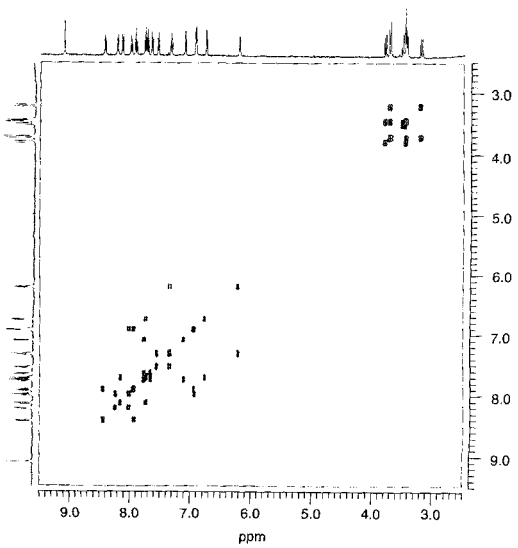

Fig. 5. COSY NMR spectrum (500 MHz) of the PF_6^- salt of the complex **1** in CD_3CN.

The data obtained in solution agree with the complex having either structure **A** or **B**. The cruciform geometry **A** corresponds to the linear combination of the processes governing the formation of complexes **4** and **6**, whereas the intertwined geometry **B**

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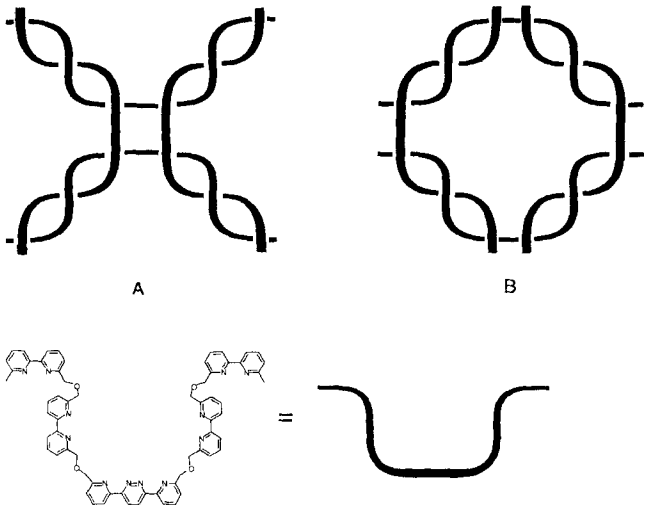

implies a more complex operation of the two programs. These two cases may also be considered respectively as the diagonal and the off-diagonal elements of a matrix combination of the subroutines.

Crystal structure of complex 1: Crystals of compound **1** were grown by diffusion of benzene into a solution of the complex in CH_3NO_2 (2.5 mg mL^{-1}). The X-ray crystal structure data indicate that the compound consists of a large complex cation $[Cu_{12}(\mathbf{2})_4]^{12+}$, **1** (Figure 1) of toroidal shape, having an external diameter of 28 Å and a central cavity with an 11 Å diameter into which $4PF_6^-$ anions are incorporated. In addition the structure contains uncoordinated PF_6^- anions and solvent molecules, some of which are also located within the central cavity. The overall appearance of the structure is not "flat" but bowl-shaped. This feature probably results, at least in part, from the position of attachment of the bisbipyridine subunits to the central bispyridylpyridazine group in ligand **2**.

The complex cation contains a macrocyclic array of twelve Cu^I ions.[16] One can distinguish two types of Cu^I ions according to their environment. Four of them are complexed by two 2,2′-bipyridine units (bipy), while the eight others are bound to a bipy and to a pyridine–pyridazine (pypz) unit. The distance between Cu(1) and Cu(2) (see structural formula of **1**) is 3.621 Å, whereas the distance between Cu(2) and Cu(3) is 6.306 Å. All Cu^I cations are in a distorted tetrahedral environment.

The ligand strands are wrapped around each other as schematically represented by structure **B**, forming four linked double helical sections with twelve crossing points. The duplexes in **B** are, in their pairs and alternating around the ring, of opposite (+) and (−) helicity so that the structure is an achiral, *meso* form with two planes of symmetry cutting through the middle of the pyridazine rings of the central components **5a**. The structure is unusual in that it combines four chiral double-helical elements into an achiral object. Structure **B** can also be viewed as two pairs of strings intertwined into a "perpendicular braid". Appropriate connection of the termini of the strands would yield a knotted figure with 12 crossings, that is, a 12-knot.[17]

The generation of structure **B** rather than **A** from ligand **2** and Cu^I ions could result from the appreciably weaker basicity and binding affinity of pyridazine (pz) nitrogens compared to pyridine (py) nitrogens. The constitution of the Cu^I sites of **B** [$8(N_3^{py}N^{pz})$, $4(N_4^{py})$] may thus lead to stronger total binding than that of **A** [$4(N_2^{py}N_2^{pz})$, $8(N_4^{py})$], owing to the presence of four comparatively disfavourable ($N_2^{py}N_2^{pz}$) sites in the latter.

Conclusion

The self-assembly of the inorganic architecture **1** of type **B** has a number of interesting features:

1) The crossover of two different assembly subroutines generates a novel structure representing a combination of those generated independently by these processes.
2) Complex **1** is an inorganic macrocyclic architecture of nanometric size containing a large internal cavity, which allows the inclusion of four PF_6^- anions; varying the size and the charge of the guest anions might lead to a change in cavity size and shape, as has been observed in the self-assembly of circular helicates and along the lines of the "virtual combinatorial library" concept.[4]
3) Such highly charged cationic entities should act as receptors possessing strong association constants with anionic substrates.
4) The formation pathway(s) of such a highly intertwined structure from its components (involving a multidimensional hypersurface with multiple intermediates, sequences and bifurcations) presents analogous problems to the complex process of protein folding.
5) Modifications of the ligand **2** as well as the combination of several different components should provide further insight into multisubroutine self-assembly and yield a variety of architectures of increasing complexity.

Experimental Procedure

General Methods: Unless specified, the solvents were technical grade. Dry THF was obtained by distillation over Na and benzophenone. All commercially available compounds were purchased from Aldrich, except DHP (Fluka). Yields were calculated on isolated compounds, unoptimised unless specified. NMR spectra were recorded on a Bruker 200 or 300 MHz spectrometer. TLC plates used were Macherey Nagel POLYGRAM® ALOX N/UV_{254} and Macherey Nagel POLYGRAM® SIL N/UV_{254}. Aluminium oxide used for preparative chromatographic separations was "Aluminium oxide 90 standardised (activity II–III) particle size 0.063–0.200 mm (70–230 mesh ASTM)" from Merck.

2-Bromo-6-pyridinecarboxylic acid (8a): Compound **7** (11 g; 64 mmol) was dissolved in conc. H_2SO_4 (70 mL), and CrO_3 (20.4 g; 204 mmol) was slowly added under vigorous stirring. The temperature was kept under 75 °C by cooling in an ice–water bath when necessary. After the CrO_3 addition was complete, the reaction mixture was stirred at room temperature overnight, then poured over crushed ice (60 g). Filtration and washing of the solid with cold water (3 × 15 mL) afforded **8a** (9.3 g; 72%) as a pale yellow solid. M.p. 197 °C; ^{1}H NMR: (200 MHz, [D$_6$]DMSO): $\delta = 8.1$ (dd, $^3J = 6.5$ Hz, $^4J = 1.5$ Hz, 1H), 7.90–7.70 (m, 2H); ^{13}C NMR (50 MHz, [D$_6$]DMSO): $\delta = 164.6$, 149.2, 141.0, 140.6, 131.4, 124.2; FAB$^-$: 202.

Ethyl 2-bromo-6-pyridinecarboxylate (8b): Acid **8a** (5 g; 24.7 mmol) was dissolved in ethanol (200 mL), and conc. H_2SO_4 (10 mL) was cautiously added. The mixture was refluxed overnight and then cooled to 0 °C and neutralised with aqueous sat. $NaHCO_3$. The ethanol was evaporated under reduced pressure, and the residual aqueous mixture extracted with $CHCl_3$ (3 × 100 mL). The organic layers were dried over $MgSO_4$, filtered and evap-

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orated under reduced pressure to afford the ester **8b** as a colourless oil (5.23 g; 92%). $R_f = 0.54$ (alox, $CHCl_3$/hexane 1/1). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.07$ (dd, $^3J = 6.5$ Hz, $^4J = 1.8$ Hz, 1H, H5), 7.72–7.64 (m, 2H, H3, H4), 4.47 (quadruplet, $^3J = 7.1$ Hz, 2H, CH_2CH_3), 1.42 (t, $^3J = 7.1$ Hz, 3H, CH_2CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 164$, 149.2, 142.2, 139.2, 131.7, 124, 62.3, 14,4; FAB^+: 230.1.

2-Bromo-6-hydroxymethylpyridine (9a): The ester **8b** (2.3 g; 10 mmol) was dissolved in ethanol (50 mL), and $NaBH_4$ (3.5 g) was added. After 1 h at room temperature, TLC analysis (alumina, $CHCl_3$) showed that all the starting material had been consumed. The reaction mixture was carefully acidified to pH 6 with 2M HCl, and the ethanol evaporated under reduced pressure. The residual aqueous solution was extracted with $CHCl_3$ (3 × 50 mL). The organic phases were dried with $MgSO_4$, filtered and evaporated in vacuo to afford the alcohol **9a** as a colourless oil (1.71 g; 91%). $R_f = 0.23$ (alox, $CHCl_3$), ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.55$ (t, $^3J = 7.7$ Hz, 1H, H4), 7.38 (d, $^3J = 7.7$ Hz, 1H), 7.28 (d, $^3J = 7.7$ Hz, 1H), 4.74 (s, 2H, CH_2OH), 3.14 (b, 1H, CH_2OH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 139.1$, 126.7, 119.3, 64.3; FAB^+: 187.9.

(2-Bromo-6-pyridyl)methyl 2-tetrahydropyranyl ether (9b): The alcohol **9a** (1.86 g; 9.9 mmol) in $CHCl_3$ (10 mL) was treated with dihydropyran (1.25 g; 14.8 mmol) and *p*-toluenesulfonic acid (PTSA; 60 mg) at reflux overnight. The reaction mixture was partitioned twice between 10% aqueous $NaHCO_3$ and $CHCl_3$. The organic layers were concentrated in vacuo to give an oily residue (2.56 g; 95%). $R_f = 0.53$ (alox, $CHCl_3$/hexane 1/1), ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.55$ (t, $^3J = 7.6$ Hz, 1H, H4), 7.44 (dd, $^3J = 7.6$ Hz, $^4J = 0.5$ Hz, 1H), 7.36 (dd, $^3J = 7.6$ Hz, $^4J = 0.5$ Hz, 1H), 4.85 (d, $^2J = 14.2$ Hz, 1H, CH_2OTHP), 4.75 (t, $^3J = 3.2$ Hz, 1H, CH in THP ring), 4.60 (d, $^2J = 14.2$ Hz, 1H, CH_2OTHP), 3.87 (m, 1H, OCH_2 in THP ring), 3.56 (m, 1H, OCH_2 in THP ring), 2–1.5 (m, other CH_2 protons from the THP ring), ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 160.6$, 141.34, 139, 126.6, 120, 98.6, 69.2, 62.4, 30.6, 25.5, 19.4; FAB^+: 271.9.

2-Tetrahydropyranyl [2-{tri(*n*-butyl)stannyl}-6-pyridyl]methyl ether (10): Compound **9b** (2.26 g; 8.3 mmol) was dissolved in dry THF (10 mL) under an Ar atmosphere and cooled to −75 °C. *n*BuLi in hexane (1.6M, 6 mL) was added dropwise, and the mixture turned a pale red. After 1 h at −75 °C, nBu_3SnCl (3.55 g; 10.9 mmol) was added dropwise, and the reaction mixture was allowed to reach room temperature overnight. The solvent was evaporated in vacuo, and the mixture obtained partitioned between H_2O and $CHCl_3$. The organic layer was dried over $MgSO_4$, filtered and evaporated in vacuo. The oily residue was distilled at 0.4 mm Hg to afford a fraction boiling at 124 °C, which was identified as compound **10** (2.1 g; 52%). $R_f = 0.77$ (alox, $CHCl_3$/hexane 1/1), ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.50$ (t, $^3J = 6.9$ Hz, 1H, H4), 7.45 (d, $^3J = 6.9$ Hz, 1H), 7.27 (d, $^3J = 6.9$ Hz, 1H), 4.90 (d, $^2J = 13.5$ Hz, 1H, CH_2OTHP), 4.81 (t, $^3J = 3.3$ Hz, 1H, CH in THP ring), 4.66 (d, $^2J = 13.5$ Hz, 1H, CH_2OTHP), 3.95 (m, 1H, OCH_2 in THP ring), 3.58 (m, 1H, OCH_2 in THP ring), 2–1.5 (m, $SnCH_2CH_2CH_2CH_3$ and other CH_2 protons from the THP ring), 1.32 (sextuplet, $^3J = 7.4$ Hz, 6H, $SnCH_2CH_2CH_2CH_3$), 1.10 (t, $^3J = 7.4$ Hz, 6H, $SnCH_2CH_2CH_2CH_3$), 0.87 (t, $^3J = 7.4$ Hz, 9H, $SnCH_2CH_2CH_2CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 173.2$, 158.9, 133.6 (s, and d due to $^{119}Sn-^{13}C$ coupling, C2, $^2J_{Sn-C} = 60$ Hz), 130.8, 119.5, 98.4, 70.4, 62.2, 30.7, 29.1, 27.3 (s, and d due to $^{119}Sn-^{13}C$ coupling, $SnCH_2$, $^2J_{Sn-C} = 80$ Hz), 25.6, 19.5, 13.7, 10; FAB^+: 482.

Di-2-tetrahydropyranyl ether of 3,6-di(6-hydroxymethyl-2-pyridyl)pyridazine (5c): 3,6-Dichloropyridazine (60 mg; 0.43 mmol) and tetrakis(triphenylphosphine)palladium(0) (50 mg; 0.043 mmol) in dry toluene (10 mL) were added to the stannylpyridine **10** (0.5 g; 1.03 mmol) under an Ar atmosphere. The reaction mixture was refluxed overnight. Chromatographic workup (alumina, CH_2Cl_2/hexane 1/1) afforded compound **5c** (3rd fraction) as an oil (51 mg; 25.6%) that slowly solidified. The compound could be recrystallised from hexane. M.p. 104 °C. $R_f = 0.32$ (alox, ethyl acetate/hexane 1/4), ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.68$ (s, 2H, CH pyridazine), 8.64 (dd, $^3J = 7.5$ Hz, $^4J = 0.5$ Hz, 2H), 7.90 (t, $^3J = 7.5$ Hz, $^4J = 0.5$ Hz, 2H), 7.59 (dd, $^3J = 7.5$ Hz, $^4J = 0.5$ Hz, 2H), 4.99 (d, $^2J = 13.6$ Hz, 2H, CH_2OTHP), 4.85 (t, $^3J = 3.5$, 2H, CH in THP ring), 4.76 (d, $^2J = 13.6$ Hz, 2H, CH_2OTHP), 3.96 (m, 2H, OCH_2 in THP ring), 3.60 (m, 2H, OCH_2 in THP ring), 2–1.5 (m, other CH_2 protons from the THP ring), ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 158.4$, 157.8, 152.3, 137.3, 124.8, 122.0, 119.7, 98.1, 69.5, 61.9, 30.3, 25.1, 19.0; FAB^+: 463.3 Analysis: calcd for $C_{26}H_{30}N_4O_4$ (462): C 67.5, H 6.53, N 12.11; found C 67.66, H 6.61, N 12.05.

3,6-Di(6-hydroxymethyl-2-pyridyl)pyridazine (5d): Compound **5c** (40 mg; 0.086 mmol) in methanol (10 mL) was treated with PTSA (5 mg) at reflux overnight. The solvent was evaporated in vacuo, and the oily residue partitioned between $CHCl_3$ and water. The aqueous solution was washed with $CHCl_3$ (3 × 15 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. After 15 h under 0.05 mm Hg of pressure the diol **5d** was obtained (24,8 mg; 98%). The compound could be recrystallised from ethanol. M.p. 186 °C; $R_f = 0.33$ (alox, CH_2Cl_2/methanol 95/5); ^1H NMR (200 MHz, [D$_6$]DMSO): $\delta = 8.66$ (s, 2H, pyridazine CH), 8.51 (d, $^3J = 7.8$ Hz, 2H), 8.07 (t, $^3J = 7.8$ Hz, 2H, pyridine H4), 7.66 (d, $^2J = 7.8$ Hz, 2H), 5.59 (t, $^3J = 5.6$ Hz, 2H, OH), 4.71 (d, $^3J = 5.6$ Hz, 4H, CH_2OH); ^{13}C NMR (50 MHz, [D$_6$]DMSO): $\delta = 162.2$, 157.7, 151.6, 138.3, 124.9, 121.6, 119.2, 64.2; FAB^+: 294; Analysis: calcd for $C_{16}H_{14}N_4O_2$ (294): C 65.29, H 4.80, N 19.04; found C 65.02, H 4.75, N 19.31.

Bipyridine–pyridazine ligand 2: The diol **5d** (101 mg; 0.34 mmol) was dissolved in dry THF (10 mL) under an Ar atmosphere. NaH (50% suspension in oil, 50 mg) was added, and the mixture refluxed for 2 h. The monobromide **3b** [11] (317 mg; 0.687 mmol) in dry THF (5 mL) was then added over a period of 3 h, and the reaction mixture was refluxed for 48 h. The solvent was evaporated, and the solid residue washed $CHCl_3$ (3 × 10 mL) and boiling $CHCl_3$ (10 mL). The solid residue was extracted in a Soxhlet apparatus with $CHCl_3$ to afford, after the evaporation of the solvent, a light brown solid (258 mg; 72%), which was pure by TLC and NMR analysis. M.p. 221 °C; $R_f = 0.2$ (alox, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.67$ (d, $^3J = 7.8$ Hz, 1H), 8.66 (s, 1H), 8.32 (m, 3H), 8.19 (d, $^3J = 7.8$ Hz, 1H), 7.83 (t, $^3J = 7.8$ Hz, 1H), 7.81 (t, $^3J = 7.8$ Hz, 3H), 7.67 (d, $^3J = 7.8$ Hz, 1H) 7.66 (t, $^3J = 7.8$ Hz, 1H), 7.57 (d, $^3J = 7.8$ Hz, 2H), 7.55 (d, $^3J = 7.8$ Hz, 1H), 7.15 (d, $^3J = 7.8$ Hz, 1H), 4.93, 4.90 (s, s, 8H), 2.63 (s, 3H, CH_3); FAB^+: 1055.

Complex 1: Typical complexation experiment: Ligand **2** (11.5 mg; 0.0109 mmol) was suspended in acetonitrile (2 mL) at room temperature. Addition of 3 equiv of Cu^I salt led to an instantaneous solubilisation and to the appearance of a red colour. The solution was stirred under reflux overnight. The solvent was evaporated under reduced pressure, and the solid residue suspended in toluene, filtered and dried under reduced pressure (10^{-2} mm Hg, overnight). Complex **1** was thus isolated as a red powder (97% yield). ES-MS, NMR and X-ray structural analyses were performed on this sample without further purification.

X-ray structure of $Cu_{12}[C_{65}H_{54}N_{12}O_4]\cdot 4C_6H_6\cdot 10CH_3NO_2\cdot 2CH_3OH\cdot 7H_2O$: diffractometer and data collection: STOE·IPDS (−70 °C), graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), tetragonal, space group $P\text{-}42_1c$ (no. 114), $a = 31.050(3)$, $c = 18.088(2)$ Å, $V = 17439$ Å^3, $Z = 2$, $\mu = 0.882$ mm^{-1}, $F(000) = 7912$, $\rho = 1.487$ Mgm^{-3}, $2\theta_{max} = 48.26°$. Structure solution and refinement: Primary structure solution by direct methods (SHELXS-92) [14]. Anisotropic refinement for all non-hydrogen atoms of the cationic complex molecule (SHELXL-93) [15]. 40475 measured reflections, 13282 independent [R(int) = 0.0800], 13281 of which were used for the refinement of 943 parameters. The solvent structure shows multifold disorder; therefore, atoms of the solvent molecules were refined isotropically using split positions. The structure was refined against F^2 (full-matrix least-squares). $R1 = 0.0952$ (for 8721 reflections with $F > 4\sigma F$) [$R1 = 0.132$ (all data)] and $wR2 = 0.2935$ (all data), GooF on $F^2 = S = 1.068$, max/min residual density: +0.570/−0.659 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 = no. of reflections and p = no. of parameters). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-44. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

Acknowledgements: We thank Dr. P. N. Baxter for supplying a sample of **5b** and **5d** used for preliminary experiments and useful remarks concerning the synthesis, Dr. A. Dupont for ES-MS studies, P. Maltèse and Dr. R. Graff for NMR work, and Dr. B. Hasenknopf for help in the generation of the pictures.

Received: September 18, 1996 [F469]

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