1- and 2-D Coordination Networks Based on Porphyrin and Copper: an Example of Supramolecular Isomerism

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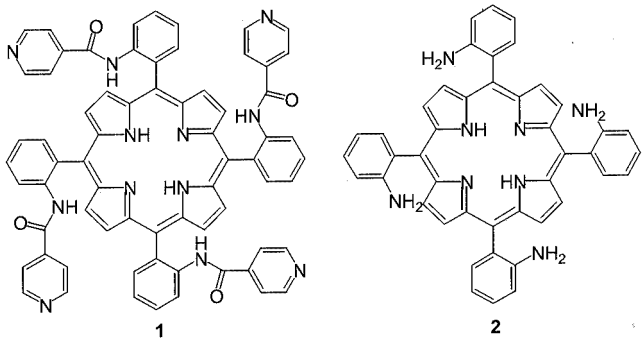
A high-yield synthesis of atropoisomers of the *meso*-tetrakis(*o*-isonicotinoylamidophenyl)porphyrin was achieved. Depending on the crystallising solvent system, the $\alpha_2\beta_2$ atropoisomer leads to the formation of either 1-D or 2-D coordination networks in the presence of $Cu(OAc)_2$.

Introduction

The design of coordination networks, i.e. infinite structures formed upon interconnection of organic tectons by metal centres, is a topic of current interest.[1] The formation of such a molecular assembly results from the interplay between the organic and the metallic tectons. With respect to the design of the organic tecton, one may use the porphyrin core which presents several interesting features. Being a tetradentate macrocycle, it binds a variety of metal cations and the resulting complex offers tuneable redox as well as photochemical properties. Furthermore, the porphyrin backbone may be functionalised either at the β-pyrrolic or *meso* positions. Thus, using this preorganised unit, one may design a variety of tectons upon anchoring additional coordination sites such as pyridine, nitrile, carboxylate etc. The porphyrin core has been widely used in materials chemistry[2] and the formation of coordination networks based on a porphyrin bearing pyridyl units directly connected at the *meso* positions has been demonstrated.[3] On the other hand, discrete polynuclear species have been also obtained when using pyridine-bearing porphyrin derivatives.[4]

Results and Discussion

Continuing our effort towards the formation and design of new types of coordination networks,[5] we thought that the porphyrin-based tecton **1** (Scheme 1) bearing four isonicotinoyl units may be of interest for the formation of coordination networks when associated with connecting transition metal complexes possessing two linearly disposed coordination sites. The tecton **1** is based on the *meso*-tetraphenylporphyrin bearing four pyridyl units. The connection between the latter and the phenyl ring is ensured at the *ortho* position through an amide junction using the *para* position of the pyridyl unit. It is worth noting that, owing to the bulkiness of the isonicotinoyl unit, four separable atropoisomers ($\mathbf{1}\alpha_4$, $\mathbf{1}\alpha_3\beta$, $\mathbf{1}\alpha_2\beta_2$, and $\mathbf{1}\alpha\beta\alpha\beta$) may be formed.[6] In terms of design principles, as previously demonstrated for catechol-bearing porphyrins,[7] this aspect is interesting since using the same units one may generate four different tectons. Although the synthesis of **1**, based on the condensation of a statistical mixture of all four atropoisomers of the amino derivative **2** with isonicotinoyl chloride, was previously reported,[8] as mentioned by the authors, the separation procedure leading to the pure atropoisomers is extremely tedious and may only be achieved by preparative thin layer chromatography affording thus small quantities of the desired species. For those reasons we developed our own strategy based on the condensation, in the presence of Et_3N and in dry THF, of purified atropoisomers of the amino derivative **2** with isonicotinoyl chloride. Thus, $\mathbf{1}\alpha_2\beta_2$,



Scheme 1

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1αβαβ, and **1**α_4 could be obtained in 68, 43 and 78% yields, respectively.

Here we report on the formation of supramolecular isomeric 1-D and 2-D coordination networks formed between **1**$\alpha_2\beta_2$ and copper acetate.

Since the tecton **1**$\alpha_2\beta_2$ possesses four isonicotinoyl moieties (two adjacent pyridine units located on each face of the porphyrin), in order to generate a stair-type network the choice of a metallic tecton adopting a linear coordination geometry was obvious. Therefore, we used $Cu(OAc)_2$ which is present as a binuclear neutral complex formed upon bridging of the two Cu^{II} centres by four acetate anions.[9] This complex has been previously exploited in the formation of coordination networks using urotropine.[10]

Upon slow diffusion of compound **1**$\alpha_2\beta_2$ (5 mg) in $CHCl_3$ (0.6 mL) into a solution of $Cu(OAc)_2$ (19 mg, 25-fold excess) in 2-propanol (1.8 mL) violet crystals were obtained at room temp. over a period of one month and studied by X-ray diffraction (Figure 1). The crystal (triclinic system, $P\bar{1}$ as the space group) is composed of **1**$\alpha_2\beta_2$, Cu atoms, acetate anion, $CHCl_3$, H_2O and 2-propanol solvent molecules. Both $CHCl_3$ molecules present in the unit cell are disordered with all Cl atoms distributed over two positions. Among the 10 water molecules present, two of them are also disordered over two positions. For the organic tecton **1**$\alpha_2\beta_2$, the planar porphyrin macrocycle binds a Cu^{2+} cation adopting a square-planar coordination geometry (d_{Cu-N} = 1.99 Å). The Cu^{2+} ion, generated upon decomplexation of the copper acetate, occupies the centre of symmetry. The phenyl rings at the *meso* positions are, as expected, tilted with respect to the plane of the porphyrin with C−C−C−C dihedral angles of −67.3 and 76.6°. All four amide junctions (d_{C-N} = 1.31 and 1.36 Å; $d_{C=O}$ = 1.21 and 1.25 Å, N−C−O angle of 123 and 124°) are in *trans* configuration with the C=O fragments outwardly oriented. The pyridine units are not coplanar with the amide junctions but tilted (N−C−C−C dihedral angle of −18.2 and 44.2°). The consecutive substituted porphyrins are interconnected through the binding by all four isonicotinoyl moieties to the copper centres (average N−Cu distance of 2.17 Å) of four neutral $Cu_2(OAc)_4$ dimers leading thus to a stair-type 1-D coordination network. The structural characteristics of the bridging $Cu(OAc)_2$ dimer (O−Cu distance varying between 1.94 and 2.00 Å and Cu−Cu distance of 2.62 Å) are similar to those previously observed.[9] The 1-D networks are packed in a parallel fashion (Figure 1) with solvent molecules occupying the free space with no specific interactions between the networks and solvents. The same 1-D network was also obtained when *i*PrOH was replaced by MeOH. However, in that case the MeOH molecules were also strongly disordered.

In order to study the role played by the solvent system, the crystallisation of the same molecular components was carried out using different solvent mixtures. Upon slow diffusion of the compound **1**$\alpha_2\beta_2$ (5 mg) in 1,1′,2,2′-tetrachloroethane (TCE) (0.6 mL), or 1,2-dichlorobenzene or a TCE/$CHCl_3$ (1:1) mixture, into a solution of $Cu(OAc)_2$ (19 mg, 25 fold excess) in EtOH (1.8 mL) reddish crystals were obtained at room temp. over a period of 1 month. The single crystals were subject to X-ray diffraction which revealed, unexpectedly, the formation of a 2-D coordination network in all three solvent systems used (Figure 2).

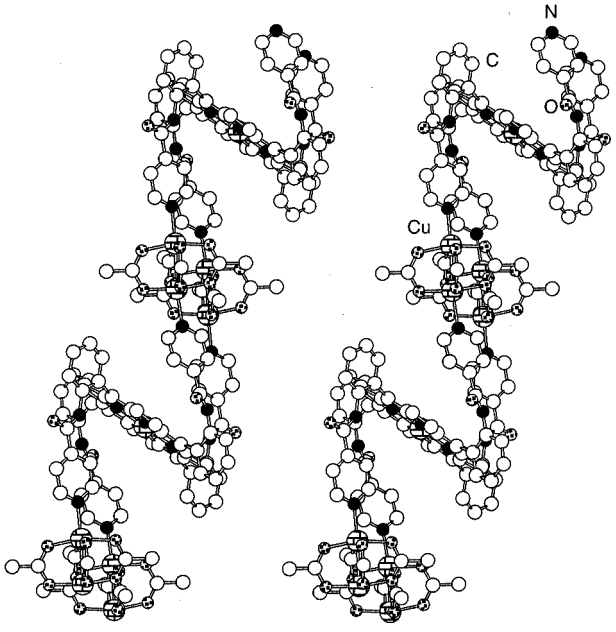

Figure 1. A portion of the crystal structures of the 1-D coordination network formed by the self-assembly of **1**$_{\alpha2\beta2}$ and copper in *i*PrOH/$CHCl_3$ showing the stair-type arrangement and the packing of two consecutive networks; solvent molecules and H atoms are not represented for clarity; for bond lengths and angles see text

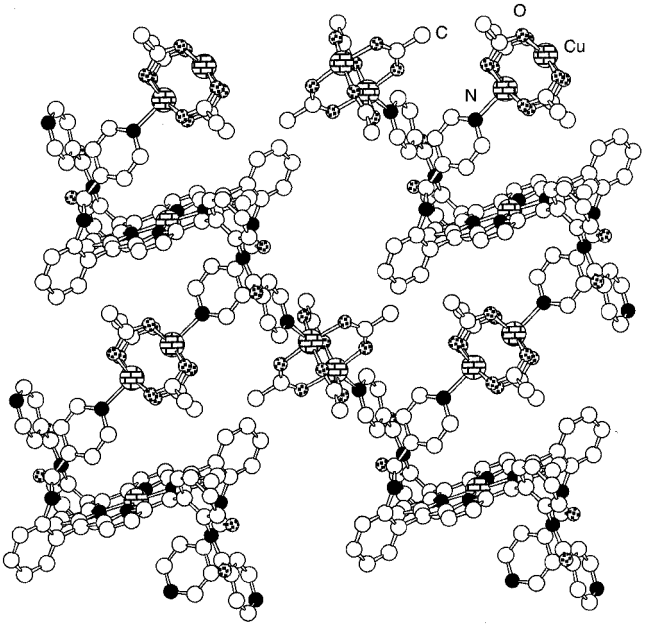

Figure 2. A portion of the crystal structures of the 2-D coordination network formed by the self-assembly of **1**$_{\alpha2\beta2}$ and copper ions in EtOH/TCE showing the connection of Cu−metallaporphyrin by $Cu_2(OAc)_4$ dimers; solvent molecules and H atoms are not represented for clarity; for bond lengths and angles see text:

The crystal (triclinic system, $P\bar{1}$ as the space group) is composed of $\mathbf{1}\alpha_2\beta_2$, Cu atoms, AcO^- anions, and TCE solvent molecules. In that case, the TCE molecules present in the lattice are not disordered and no specific interactions between them and the network structure can be spotted. Dealing with the organic tecton $\mathbf{1}\alpha_2\beta_2$, again the porphyrin macrocycle remains planar and binds a Cu^{2+} cation, formed upon decomplexation of the acetate complex, which occupies the centre of symmetry and again adopts a square-planar coordination geometry (d_{Cu-N} = 1.99 Å). The phenyl rings at the *meso* positions are differently tilted (C−C−C−C dihedral angles of −114.4 and 77.5°) with respect to the above-mentioned case . All four amide junctions (average $d_{C-N} \approx 1.35$ Å; average $d_{C=O} \approx 1.21$ Å, average N−C−O angle of ca. 124.4°) are again in *trans* configuration. The pyridine units are again not coplanar with the amide junctions but tilted (N−C−C−C dihedral angle of −17.0 and 33.3°). In marked contrast with the above-mentioned case for which the pyridine units located on the same face of the porphyrin ring are oriented almost parallel to each other, in the present case, whereas one of the two pyridine rings is almost perpendicular to the porphyrin plane, the other one is strongly tilted. As the consequence of this peculiar disposition of the coordination sites on each face of the tecton, the consecutive units are again interconnected through coordination bonds between the nitrogen atom of the isonicotinoyl moieties and the copper centres (average N−Cu distance of ca. 2.15 Å) of four neutral $Cu_2(OAc)_4$ dimers leading to a 2-D coordination network (Figure 2). Again, the structural characteristics of the bridging $Cu(OAc)_2$ dimer are similar to those obtained in the case of the 1-D network mentioned above. The packing of the 2-D networks generates channels which are filled with TCE solvent molecules with no specific interactions between the networks and the solvents molecules. As mentioned above, the same 2-D network was also obtained when TCE was replaced by 1,2-dichlorobenzene or by a mixture of TCE/$CHCl_3$ (1:1) while using EtOH.

The two networks obtained are clearly not polymorphs since they differ in their composition. However, they constitute an example of supramolecular[11] or structural[12] isomerism since both networks are based on the same molecular units and the passage from the 1-D to the 2-D network takes place through a rotational process (Figure 3).

In summary, upon self-assembly of the $\alpha_2\beta_2$, atropoisomer of the porphyrin **1** bearing four isonicotinoyl moieties and $Cu(OAc)_2$, depending on the solvent systems used, 1-D and 2-D coordination networks containing two different types of Cu^{2+} centres were formed and structurally characterised by X-ray diffraction on single crystals. The two networks obtained may be regarded as supramolecular or structural isomers. The formation of coordination networks using the other atropoisomers of **1** as well as other transition metal cations is under current investigation.

Experimental Section

Synthesis of $\mathbf{1}_{a2b2}$: 0.10 g (0.15 mmol) of $\mathbf{2}_{a2b2}$ [13] and 0.40 g (2.23 mmol, 15 equiv.) of the hydrochloride salt of isonicotinoyl chloride were placed in a round-bottom flask. 620 μL of NEt_3 (4.44 mmol, 30 equiv.) and 50 mL of freshly distilled and degassed THF were added under argon. The mixture was cooled to 0 °C and sonicated to obtain a clear solution. The course of the reaction was monitored by TLC (SiO_2, CH_2Cl_2). After ca. 3.5 h, the starting porphyrin was completely consumed. Volatiles were removed and the residue was dissolved in CH_2Cl_2 (100 mL), washed with 10% aqueous NaOH (1 × 100 mL), H_2O until neutralisation (5 × 500 mL) and finally dried with Na_2SO_4. Interestingly, due to the low solubility of $\mathbf{1}_{a2b2}$, the purification could be achieved simply by washing the solid with Et_2O (500 mL) and hexane (100 mL). The pure compound $\mathbf{1}_{a2b2}$ was obtained as a purple solid in 68% yield (0.11 g). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ = −2.65 (s, 2 H, NH pyrrole), 6.47 (dd, 8 H, J = 1.5 Hz and J = 4.4 Hz, $H_{pyridine}$), 7.61 (m, 8 H, $H_{phenyl+NHCO}$), 7.64 (broad s, 4 H, NHCO), 7.85 (dd, 8 H, J = 1.5 Hz and J = 4.4 Hz, $H_{pyridine}$), 7.90 (m, 8 H, H_{phenyl}), 8.79 (d, 4 H, J = 7.8 Hz, H_{phenyl}), 8.92 (s, 4 H, $H_{β\text{-}pyrrolic}$), 8.95 (s, 4 H, $H_{β\text{-}pyrrolic}$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ = 114.9, 119.7, 121.9, 124.2, 130.3, 131.2, 135.2, 137.4, 140.9, 149.8, 163.3 (NH**C**O) ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 423 (1.8 × 10^5), 517 (1.2 × 10^4), 550 (4.3 × 10^3), 590 (4.4 × 10^3), 650 (2.3 × 10^3) nm. $C_{68}H_{46}N_{12}O_4{\cdot}CH_2Cl_2$ (1180.14): calcd. C 70.21, H 4.11, N 14.24; found C 70.12, H 4.25, N 14.06.

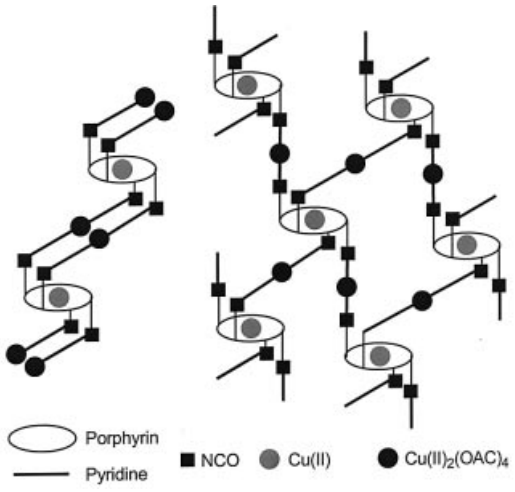

Figure 3. Schematic representation of the two supramolecular isomers based on the 1-D (left) and 2-D (right) coordination networks obtained with the same molecular components but in two different solvent systems

Crystal Structure Characterisation: X-ray diffraction data collection was carried out with a Kappa CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-K_α radiation. For all structures, diffraction data were corrected for absorption and analysed using the OpenMolen package.[14] All non-H atoms were refined anisotropically. Crystallographic data for the 1-D network based on $\mathbf{1}_{\alpha2\beta2}$ and $Cu_2(OAc_4)$ (violet crystals, 173 K): $C_{84}H_{68}Cu_5N_{12}O_{20}{\cdot}2CHCl_3{\cdot}10H_2O{\cdot}4C_3H_7O$, M = 2538.51, triclinic, a = 214.7082(4), b = 15.9643(4) c = 17.8289(6) Å, α = 106.851(5), β = 97.638(5), γ = 117.560(5)°, V = 3371.4(2) Å^3, space group $P\bar{1}$, Z = 1, $D_{calcd.}$ = 1.25 g cm^{-3}, μ = 0.964 mm^{-1}, 6534 data with $I > 3\sigma(I)$, R = 0.109, Rw = 0.142. Crystallographic data for the for 2-D network based on $\mathbf{1}_{\alpha2\beta2}$ and $Cu_2(OAc_4)$ (red crystals, 173 K): $C_{84}H_{68}Cu_5N_{12}O_{20}{\cdot}8C_2H_2Cl_4$, M = 3226.05, triclinic, a = 12.2094(4), b = 16.1597(5), c = 17.6546(6) Å, α = 76.557(5), β = 73.767(5), γ = 83.554(5)°, V = 3248.6(2) Å^3, space group $P\bar{1}$,

$Z = 1$, $D_{calcd.} = 1.65\ g\ cm^{-3}$, $\mu = 1.529\ mm^{-1}$, 6049 data with $I > 3\sigma(I)$, $R = 0.072$, $Rw = 0.102$. CCDC-185378 and -185379 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic data Center, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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