

Coordination polymers based on porphyrin and copper: the influence of the crystallization solvents on the dimensionality of the network

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The $\alpha_2\beta_2$ atropisomer of *meso*-tetrakis(*o*-nicotinoylamidophenyl)-copper porphyrin leads in the presence of Cu(II) cation to coordination polymers in the crystalline phase. The networks are generated by interconnection of metalloporphyrin units through the coordination of Cu centres adopting an octahedral coordination geometry by two pyridines belonging to consecutive complexes. Depending on the solvent systems used, the 1-D coordination network based on $1\alpha_2\beta_2$ and Cu dication was shown to form a 3-D network based on a combination of three distinct supramolecular forces.

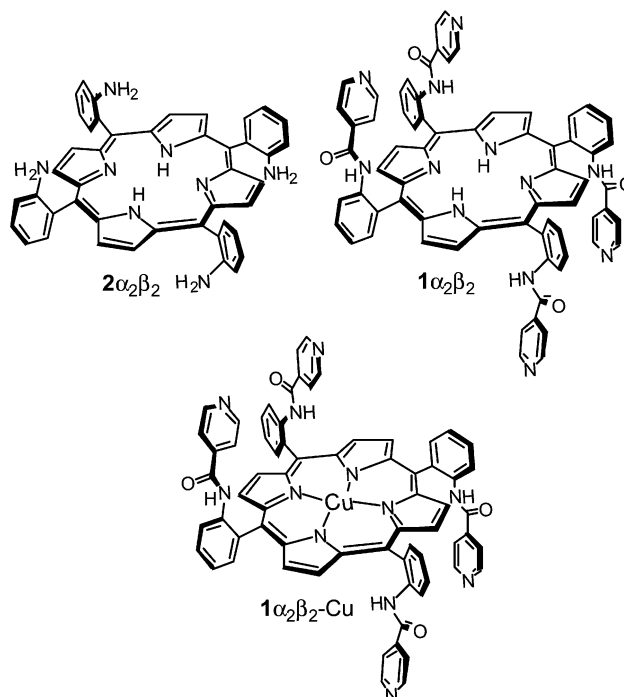
Introduction

Coordination networks¹ are sequenced molecular assemblies composed of organic ligands and metallic centres acting as building blocks or tectons. These infinite structures are obtained upon mutual interconnection of organic tectons bearing coordination sites and metal centres. The guidelines followed for the design of coordination networks are: i) the dimensionality and topology of the network (1-, 2- or 3-D) which is defined by the number of translations operating on the assembling nodes or coordination patterns connecting the organic and the metallic tectons, ii) the nature of the coordination pattern which strongly depends on the metal considered (coordination number and geometry), iii) the nature of the organic tecton (number of coordination sites and the type of hetero atom, the disposition of the coordination sites). When considering a metallic tecton adopting an octahedral coordination geometry, one of the multiple possibilities which may be explored may be to use a tetradentate core capable of occupying the square base of the octahedron and thus leaving the two apical positions free for the generation of a 1-D network. For that purpose, the porphyrin core,² already widely used in materials chemistry,³ appeared as the candidate of choice for many reasons such as its binding ability towards a variety of metal cations and the possibility of fine tuning of the redox and/or photochemical properties of the corresponding metal complex. Another interesting feature associated with porphyrin backbone is the possibility of functionalising the central core at β -pyrrolic and/or *meso* positions. Thus, based on this preorganised tetradentate unit, one may design a variety of tectons by anchoring additional coordination sites such as pyridine, nitrile, carboxylate *etc.* to the porphyrin core. In particular, we have published a class of tectons based on a porphyrin core bearing at the *meso* positions phenylcatechoamido groups.⁴

Although the formation of coordination networks as well as finite polynuclear assemblies based on porphyrin derivatives bearing either pyridine or imidazole moieties directly connected at the *meso* positions has been reported,⁵ to the best of our knowledge, apart from a single example dealing with a polymeric structure obtained in the presence of Fe(III),⁶ the use of atropisomers of *meso*-phenyl porphyrins bearing pyridine units to generate coordination networks has not been explored.

Here we report the formation of two different coordination networks formed upon crystallisation of the isolated copper complex of $1\alpha_2\beta_2$ (Scheme 1).

In line with our continued efforts to design new types of tectons for the formation of coordination networks,⁷ the $\alpha_2\beta_2$ atropisomer $1\alpha_2\beta_2$ of the porphyrin based tecton **1** bearing four isonicotinoyl units was designed and prepared. It is worth noting that, owing the bulkiness of the isonicotinoyl amido



Scheme 1 Upon self-assembly of metalloporphyrin $1\alpha_2\beta_2$ -Cu a 3-D network was obtained in the crystalline phase. The network is based on three distinct supramolecular synthons (coordination bonding, π - π stacking, H-bonding).

group, the $\alpha_2\beta_2$ atropoisomer may be obtained in a pure form and that the atropoisomerisation process leading to a mixture is rather slow at room temperature.

The tecton **1** possesses four isonicotinoyl moieties and for the $\alpha_2\beta_2$ atropoisomer of **1**, each face of the porphyrin is occupied by two adjacent isonicotinoyl units. The synthesis of **1** was achieved in 68% yield upon treatment of the pure tetraaminoporphyrin derivative **2** with isonicotinoyl chloride in dry THF and in the presence of Et₃N. This strategy appeared as more viable since the separation of atropoisomers of **1**, obtained upon condensation of a statistical mixture containing all four atropoisomers of **2** with isonicotinoyl chloride, is extremely difficult.⁹

The structure of the free tecton **1** was elucidated in the solid state by X-ray diffraction on a single crystal obtained upon slow diffusion of hexane into a CHCl₃ solution of the compound **1**. The X-ray study was in agreement with ¹H-NMR investigations in solution (Fig. 1). The porphyrin ring is almost planar. The phenyl groups are tilted with respect to the porphyrin ring by 64.2° and 83.7°. The amide junctions between the phenyl groups and the pyridine ring are all in *trans* configuration with $d_{C=O}$ and d_{C-N} distances of 1.22 Å and 1.35 Å respectively. The amide groups are, as expected, planar with CCO, CCN and OCN angles of 121.0°, 115.2° and 123.7° respectively. The pyridine units are almost coplanar with the amide groups (OCNC dihedral angles of −0.4° and −2.9°).

For the formation of the network, Cu(II) was used as the metallic centre. The choice of Cu(II) was related to the possibility of forming the copper–porphyrin complex under mild conditions and thus avoiding atropoisomerisation of the porphyrin derivative. The latter was obtained in 68% yield as an orange powder upon treatment at rt of **1** with Cu(OAc)₂·H₂O in a CH₂Cl₂–MeOH 1 : 1 mixture. As a first trial, single crystals of the metalloporphyrin were obtained by slow diffusion of water into a methanol solution of **1**–Cu. The X-ray diffraction study on a single crystal revealed that the crystal **A** (triclinic system, $P\bar{1}$ as the space group, $Z = 1$) is composed of doubly deprotonated **1**, Cu(II) cation, 4CH₃OH and 3H₂O molecules. The water molecules are disordered over two positions. For the organic tecton **1**, the porphyrin macrocycle is almost planar (maximum deviation of 0.04 Å). The phenyl rings at the *meso* positions are tilted with respect to the plane of the porphyrin by 70.7° and 82.1°. All four amide groups (d_{C-N} : 1.340 Å and 1.346 Å; $d_{C=O}$: 1.224 Å and 1.277 Å; d_{C-C} : 1.505 Å and 1.507 Å; NCO angle of 123.5°; CCO angle of 120.8° and 118.8°; NCC angle of 115.7° and 117.6°) are in *trans* configuration with the C=O fragments outwardly oriented. The pyridine units are not coplanar with the connected phenyl groups but tilted

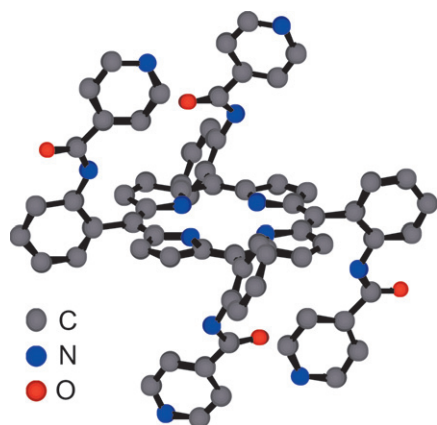


Fig. 1 The crystal structures of **1** showing the localisation of the pyridine groups with respect to the porphyrin backbone. Solvent molecules and H atoms are not represented for clarity. For bond distances and angles see text.

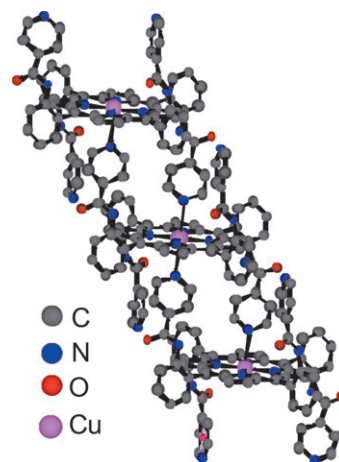


Fig. 2 A portion of the crystal structure **A** showing the formation of a 1-D coordination network obtained upon mutual interconnection of **1**–Cu complexes through Cu–pyridine coordination bonds. Solvent molecules (H₂O and MeOH) and H atoms are not represented for clarity. For the crystallisation conditions as well as bond distances and angles see text.

by 28.5° and 34.0°. The angles between the pyridines and the porphyrin ring are 53.3° and 87.9°. The Cu²⁺ cation, occupying the centre of symmetry, adopts a distorted octahedral coordination geometry and is coordinated to the set of four N atoms belonging to the porphyrin core (d_{Cu-N} of ca. 2.01 and 2.02 Å). The two apical positions on the Cu cation are occupied by two pyridine units belonging to two consecutive porphyrins (d_{Cu-N} of ca. 2.59 Å) leading thus to a 1-D coordination network (Fig. 2). It is worth noting that no structural study dealing with a Cu–porphyrin complex adopting an octahedral geometry has been reported so far.

Interestingly, the 1-D networks are interconnected through π – π and dipole–dipole interactions leading thus to a 2-D network. Indeed two adjacent pyridine units belonging to two consecutive 1-D networks are arranged in a head-to-tail fashion with a distance of 3.67 Å between their centroids (Fig. 3).

Furthermore, the 2-D networks thus formed are again interconnected through H-bonds engaging water molecules and O atoms of the amide junctions with the O–O distance varying between ca. 2.67–2.83 Å (Fig. 4). Although the MeOH molecules are H-bonded to each other and to H₂O molecules, they do not participate in the formation of the 3-D network.

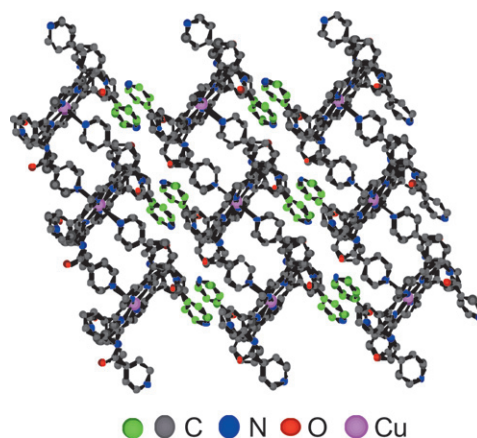


Fig. 3 A portion of the crystal structure **A** showing the formation of a 2-D network. The latter is obtained upon π – π stacking of pyridine rings (shown in green) belonging to adjacent 1-D coordination networks and not involved in coordination bonds with Cu cations. Solvent molecules and H atoms are not represented for clarity. For the bond distances and angles see text.

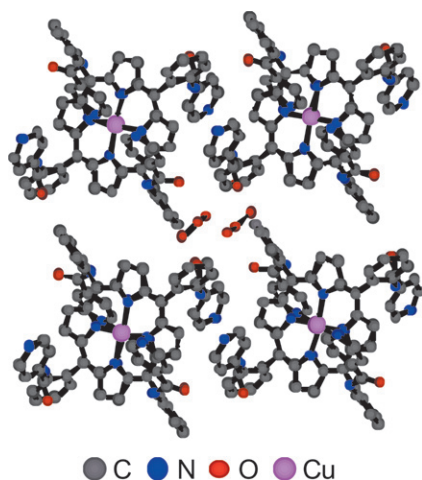


Fig. 4 A portion of the crystal structure **B** showing the formation of a 3-D network. The latter is obtained upon interconnection of the 2-D networks through H-bonding between O atoms belonging to the C=O groups of the metalloporphyrin $1\alpha_2\beta_2$ -Cu and water molecules (disordered). MeOH molecules and H atoms are not represented for clarity. For the bond distances and angles see text.

Unfortunately, because of the disorder observed for all three H_2O molecules (occupancy of 1/2), the network can not be described in a simple fashion. It is of interest to point out that for the structure described above, different types of supramolecular interaction (coordination bonding, π - π and dipole-dipole interactions and hydrogen bonding) are operating in concert to generate a 3-D network.

Upon slow diffusion of MeOH into a DMF solution containing the $1\alpha_2\beta_2$ -Cu complex a different type of single crystal was obtained and studied by X-ray diffraction. The crystal **B** (triclinic system, $P\bar{1}$ as the space group, $Z = 1$) is composed of the $1\alpha_2\beta_2$ -Cu complex and 2 DMF molecules. The solvent molecules are H-bonded to the porphyrin complex through the O atom of DMF and the NH moiety of the amide group of $1\alpha_2\beta_2$ ($d_{\text{N-O}} = 2.869 \text{ \AA}$). The porphyrin core of $1\alpha_2\beta_2$ is again almost planar (maximum deviation of 0.09 Å). The phenyl rings are tilted with respect to the plane of the porphyrin by 63.9° and 70.8°. All four amide groups (CN, CO and CC distances of *ca.* 1.36 Å, 1.21 Å and 1.50 Å respectively and NCO angles of 123.4° and 124.6°; CCO angle of 119.0° and 121.0° and NCC angle of 114.3° and 117.4°) are again in *trans* configuration with the C=O fragments outwardly oriented. The pyridine units are not coplanar with the connected phenyl groups but tilted by 37.7° and 46.7°. The angles between the pyridines and the porphyrin ring are 75.6° and 85.8°. The Cu^{2+} cation, again lying on the centre of symmetry, is coordinated to the set of four N atoms belonging to the porphyrin core ($d_{\text{Cu-N}}$ of *ca.* 2.01 Å) and to two pyridine units belonging to two consecutive porphyrins ($d_{\text{Cu-N}}$ of *ca.* 2.58 Å). Thus, again the same type of 1-D coordination network (Fig. 5) as the one observed when crystals were obtained in the presence of water is formed. However, in marked contrast with the previous case, no stacking interactions nor H-bonding are observed.

In summary, upon treatment of the $\alpha_2\beta_2$ atropoisomer of the porphyrin **1** bearing four isonicotinoyl moieties and $\text{Cu}(\text{OAc})_2$ the corresponding metalloporphyrin $1\alpha_2\beta_2$ -Cu was synthesised. The X-ray diffraction study revealed that the Cu(II) cation is hexacoordinated and adopts a distorted octahedral coordination geometry. Depending on the solvent systems used, the $1\alpha_2\beta_2$ -Cu complex leads either to a 1-D coordination network (mixture of DMF and MeOH) or to a 3-D network (H_2O and MeOH). For the latter case, the 3-D network may be described as a combination of different supramolecular forces, *i.e.* coordination bonding, π - π stacking and dipole-dipole interactions and H-bonding, operating simultaneously.

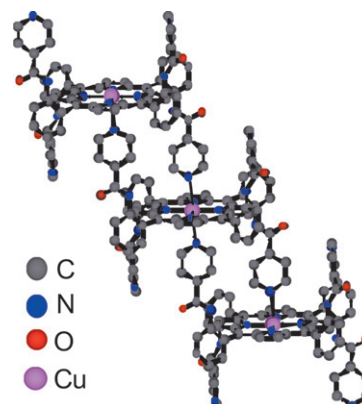


Fig. 5 A portion of the crystal structure **B** showing the formation of a 1-D coordination network obtained upon mutual interconnection of $1\alpha_2\beta_2$ -Cu complexes through Cu-pyridine coordination bonds. Solvent molecules (DMF) and H atoms are not represented for clarity. For the crystallisation conditions as well as bond distances and angles see text.

Further studies along the same lines using other atropoisomers of **1** and a variety of metal centres are currently under investigation.

Experimental

Synthesis of $1\alpha_2\beta_2$ -Cu

In a round bottomed flask (100 ml), a mixture of the porphyrin $1\alpha_2\beta_2$ (0.10 g, 0.092 mmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.19 g, 0.95 mmol) in 50 ml of CH_2Cl_2 -MeOH (1 : 1) was stirred at room temperature for 1 hour. The solvents and volatiles were removed under reduced pressure. The crude material was dissolved in CH_2Cl_2 (100 ml), washed with H_2O ($2 \times 100 \text{ ml}$) and dried over Na_2SO_4 . After filtration and evaporation of the solvent, the orange powder was dried overnight under vacuum affording the copper complex $1\alpha_2\beta_2$ -Cu in 68% yield which was characterised by absorption spectroscopy (UV-VIS (CH_3OH , $\lambda_{\text{max}}/\text{nm}$; ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)): 418 (2.7×10^5), 544 (1.9×10^4), 573 (6.2×10^3)).

Crystal structure characterisation

X-Ray diffraction data collection was carried out on 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.¹⁰ All non-H atoms were refined anisotropically.

CCDC reference numbers 190193–190195. See <http://www.rsc.org/suppdata/nj/b2/b206661k/> for crystallographic files in CIF or other electronic format.

Crystallographic data for free $1\alpha_2\beta_2$ (red crystals, 173 K). $\text{C}_{68}\text{H}_{46}\text{N}_{12}\text{O}_4 \cdot 5\text{CHCl}_3$, $M = 1692.09$, triclinic, $a = 12.8117(2)$, $b = 13.0953(2)$, $c = 13.5473(3) \text{ \AA}$, $\alpha = 104.664(5)$, $\beta = 111.913(5)$, $\gamma = 104.738(5)^\circ$, $U = 1879.54(6) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $D_c = 1.49 \text{ g cm}^{-3}$; $\mu = 0.607 \text{ mm}^{-1}$, 4617 data with $I > 3\sigma(I)$, $R = 0.069$, $R_w = 0.083$. All H atoms were located except the two NH of the porphyrin ring, the two NH of the amide groups and those belonging to CHCl_3 solvent molecules.

Crystallographic data for 3-D network A based on $1\alpha_2\beta_2$ -Cu (red crystals, 173 K). $\text{C}_{68}\text{H}_{44}\text{CuN}_{12}\text{O}_4 \cdot 4\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$, $M = 1338.94$, triclinic, $a = 9.9533(2)$, $b = 13.2375(4)$, $c = 13.3971(3) \text{ \AA}$, $\alpha = 88.813(5)$, $\beta = 69.005(5)$, $\gamma = 88.363(4)^\circ$, $U = 1647.20(7) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $D_c = 1.35 \text{ g cm}^{-3}$.

cm^{-3} ; $\mu = 0.403 \text{ mm}^{-1}$, 4876 data with $I > 3\sigma(I)$, $R(\text{int}) = 0.04$, $R = 0.054$, $R_w = 0.068$. All H atoms were located except those belonging to solvent molecules which were found to be disordered.

Crystallographic data for 1-D network B based on $1\alpha_2\beta_2\text{-Cu}$ (brown crystals, 173 K). $\text{C}_{68}\text{H}_{44}\text{CuN}_{12}\text{O}_4 \cdot 2\text{C}_3\text{H}_7\text{NO}$, $M = 1302.92$, triclinic, $a = 11.0102(2)$, $b = 11.3676(2)$, $c = 13.6847(3) \text{ \AA}$, $\alpha = 76.117(5)$, $\beta = 82.625(5)$, $\gamma = 65.319(5)^\circ$, $U = 1510.07(5) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $D_c = 1.43 \text{ g cm}^{-3}$; $\mu = 0.433 \text{ mm}^{-1}$, 4301 data with $I > 3\sigma(I)$, $R(\text{int}) = 0.04$, $R = 0.044$, $R_w = 0.063$. All H atoms were located.

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