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Molecular tectonics: design of coordinating tectons based on diazamacrocycles bearing pyridine units and formation of 1D copper coordination networks

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Four new bis monodentate tectons **1–4** based on the diazadioxa (**5**)- and diazatetraoxa (**6**)-macrocyclic backbones bearing two pyridine units as coordinating sites have been designed and prepared. In the presence of copper diacetate, their ability to form coordination networks was demonstrated by structural studies based on X-ray diffraction methods. Both tectons **1** and **2** behave as bis monodentate units and their bridging by copper diacetate dimer behaving as a linear metallatecton leads to the formation of analogous 1D coordination networks.

Although the prediction of crystal structures based on knowledge of the molecular components is not feasible today,[1,2] nevertheless, in some cases, based on precise design of tectons[3] (active building blocks), one may predict with an acceptable degree of confidence some of the connectivity between molecular constituents. By considering these connections as recognition patterns, one may describe crystals as molecular networks.[4] In the case of H-bonding and van der Waals interactions, the complete prediction of all connections is rather difficult because of the weak nature of these interactions. However, for combinations of organic and metallic tectons, due to the stronger nature of the interactions and the more directional feature of the coordination bond, the prediction of the connectivity and thus the design of networks appear to be more reliable. For that reason and because of properties associated with such molecular organisations, the design, formation and characterisation of coordination networks in the crystalline phase have been attracting much attention over the last two decades.[5–15]

These infinite molecular architectures are formed upon mutual bridging between organic tectons and metallic centres. The connectivity between these two building blocks defines the dimensionality of the network (1D, 2D or 3D).

In order to increase our knowledge of factors guiding the formation of coordination networks in the crystalline phase, we have undertaken a systematic study dealing with the design of a variety of organic tectons.[16–35] This study covers the exploration of a variety of structural and electronic features such as geometry and topology of the tecton, the number, the nature and the localisation of coordinating sites within the backbone of the tecton *etc.*

In the continuation of our effort, we have designed new organic tectons based on macrocyclic backbones bearing pyridine units as coordinating sites and investigated their ability to generate coordination networks in the presence of metallic tectons.

Here we report the synthesis of four new tectons **1–4** (Scheme 1) and the formation of two new 1D coordination networks formed upon crystallisation of tectons **1** and **2** in the presence of $Cu(OAc)_2$.

Diaza macrocycles in general and compounds **5** and **6** in particular (Scheme 1) are interesting cyclic backbones for the design of tectons. Indeed, through the use of the two secondary amines, these cyclic entities offer the possibility of introducing in a symmetrical fashion two exocyclic coordinating units such as pyridine, bipyridine, phenanthroline catechol *etc.* (Scheme 2). We have previously reported the synthesis of catechol bearing derivatives of **5**[36–38] and **6**[39] as well as pyridine bearing diaza macrocycles.[40,41]

All four tectons **1–4** are based on the $[12]N_2O_2$ macrocycle **5** (compounds **1** and **3**) or $[18]N_2O_4$ macrocycle **6** (compounds **2** and **4**) bearing two pyridine moieties as monodentate coordinating sites (Scheme 1). For all four tectons the connection between the macrocyclic backbone and the pyridine moiety is achieved through an amide junction. The difference between tectons **1** and **3** and between **2** and **4** results from the connecting position of the pyridinecarbonyl moiety to the backbone (position 4 for **1** and **2** and position 3 for **3** and **4**).

The rather straightforward synthesis of all four tectons was achieved in high yield upon condensation at room temperature of the macrocyclic units **5** or **6** with the hydrochloride salt of isonicotinoyl chloride **7** or of nicotinoyl chloride **8** in the presence of Et_3N in dry THF (see Experimental section).

Coordination networks are generated under self-assembly conditions upon mutual interconnection between an organic tecton and a metallic centre. The connectivity pattern and the dimensionality of the network depend on the combination of the organic tecton and the metallic centre. Although one may envisage a variety of combinations between different metallic centres and bis monodentate tectons such as **1–4**, here we shall focus only on metal centres allowing linear bridging of consecutive organic moieties. For that purpose, copper diacetate appeared to us as a possible candidate. Indeed, $Cu(OAc)_2$ exists as a neutral dimer for which the two Cu(II) centres are bridged by four acetate ligands.[42] Because of the square-based pyramidal geometry adopted by the copper centres, this dimeric unit offers on each metal centre a single coordination site and thus may take part in formation of coordination networks as a linear metallatecton. We[30] and others[43,44] have previously

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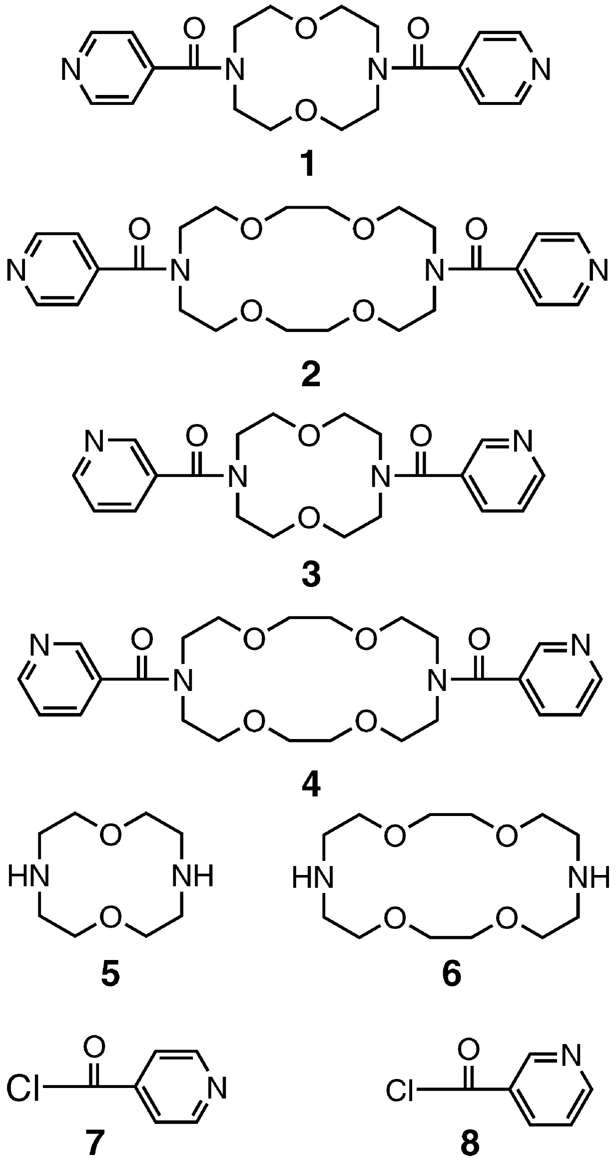
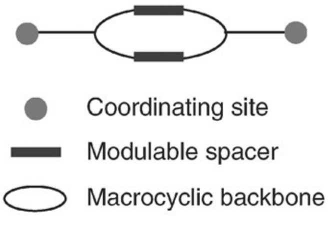


Scheme 1

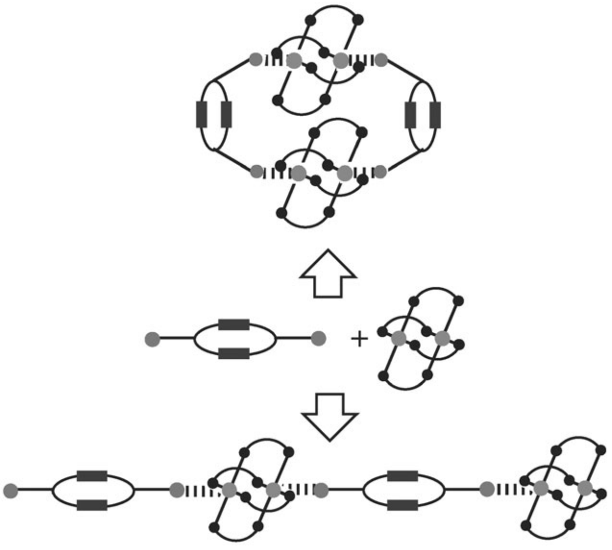
used copper diacetate dimer for the formation of coordination networks.

Depending on the flexibility and the conformation adopted the macrocyclic moiety of the bis monodentate organic tectons such as **1–4**, their combination with the above mentioned dimeric copper unit may lead to the formation of either discrete complexes of the metallamacrocyclic type or infinite coordination networks (Scheme 3).

At room temperature, upon slow diffusion of a toluene solution of **1** into a MeOH solution of $Cu(OAc)_2$, blue crystals suitable for X-ray diffraction studies were obtained after several days and studied by X-ray diffraction (see Experimental section).



Scheme 2



Scheme 3

The crystal (triclinic system, $P\bar{1}$ as the space group, $Z = 1$) is composed of **1**, Cu atoms, acetate anions, CH_3OH and toluene solvent molecules (Fig. 1). The latter is disordered. Among the two methanol molecules, one of them is H-bonded to an oxygen atom of the amide junction ($d_{O\text{–}O}$ = 2.674 Å). For the amide junction ($d_{C\text{–}N}$ = 1.334 Å, $d_{C=O}$ = 1.239 Å, NCO angle of 122.5°) between the cyclic moiety of the organic tecton **1** ($d_{C\text{–}O}$ = 1.429 Å and 1.430 Å, $d_{C\text{–}N}$ = 1.474 Å and 1.476 Å) and the pyridine unit ($d_{C\text{–}N}$ = 1.327 Å and $d_{C\text{–}C}$ varying between 1.372 and 1.392 Å) bonds distances and angles are in the range of expected values. The pyridine units are not coplanar with the amide junctions but tilted (NCCC dihedral angle of −95. 7° and 95.7°). The consecutive tectons **1** are interconnected by neutral $Cu_2(OAc)_4$ dimers through the nitrogen atoms of the pyridine moieties and copper centres ($d_{N\text{–}Cu}$ = 2.197 Å) leading thus to a linear type 1D neutral coordination network. For the bridging $Cu(OAc)_2$ dimer (O–Cu distance varying between 1.963 and 1.983 Å and Cu–Cu distance of 2.628 Å), the coordination sphere is composed of four oxygen atoms belonging to the four bridging acetate anions and a nitrogen atom belonging to the pyridine unit. The coordination geometry around Cu(II) is a distorted square-based pyramid [OCuO angle varying between 88.5° and 90.4° (*cis*) and 168.6° (*trans*)]. These values are similar to those previously observed.[37] The 1D networks are packed in a parallel fashion with solvent molecules occupying the free space.

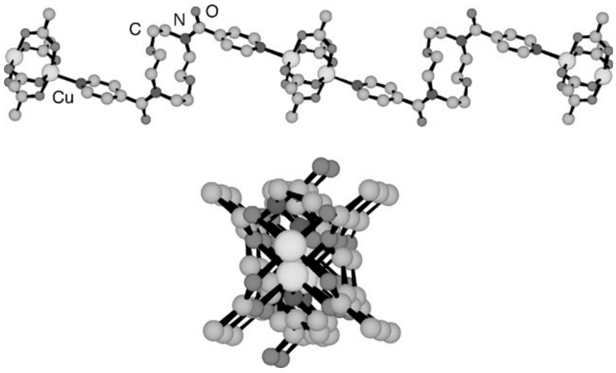


Fig. 1 A portion of the neutral 1D network obtained upon self-assembly of the tecton **1** with $Cu(OAc)_2$: (a) view perpendicular to the axis of the network, (b) view almost parallel to the axis of the network. H atoms are not represented for clarity. For bond distances and angles see text.

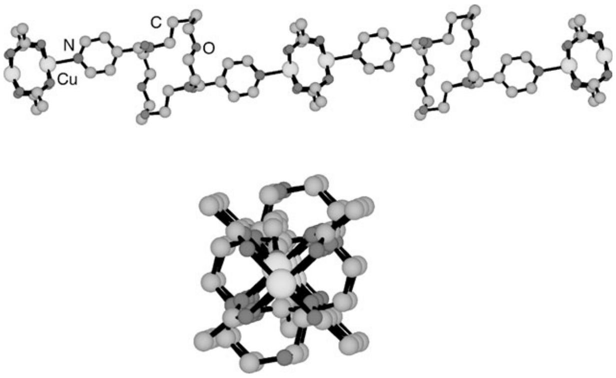


Fig. 2 A portion of the neutral 1D network obtained upon self-assembly of the tecton **2** with $Cu(OAc)_2$: (a) view perpendicular to the axis of the network, (b) view almost parallel to the axis of the network. H atoms are not represented for clarity. For bond distances and angles see text.

In the case of **2**, again high quality crystals were obtained at room temperature after several days upon slow diffusion of a toluene solution of **2** into a MeOH solution of $Cu(OAc)_2$ (see Experimental section).

The crystal (triclinic system, $P\bar{1}$ as the space group, $Z = 2$) is exclusively composed of **2**, Cu atoms and acetate anions. In contrast with the above mentioned case, no solvent molecules are present in the lattice (Fig. 2). For the amide junction ($d_{C–N}$ = 1.352 Å, $d_{C=O}$ = 1.230 Å, NCO angle of 119.8°) between the cyclic moiety of the organic tecton **2** ($d_{C–O}$ varying between 1.409 Å and 1.437 Å, $d_{C–N}$ varying between 1.472 Å and 1.476 Å) and the pyridine unit ($d_{C–N}$ = 1.321 Å and 1.341 Å and $d_{C–C}$ varying between 1.384 and 1.393 Å) bonds distances and angles are almost identical to those observed for the above mentioned case. The pyridine units are again tilted with respect to the amide junctions (NCCC dihedral angle of −84. 0° and 84. 0°). Again, as in the case of the tecton **1**, the consecutive tectons **2** are interconnected by neutral $Cu_2(OAc)_4$ dimers through the nitrogen atoms of the pyridine moieties and copper centres ($d_{N–Cu}$ = 2.188 Å) leading again to a linear type 1D neutral coordination network. For the bridging $Cu(OAc)_2$ dimer (O–Cu distance varying between 1.968 and 1.974 Å and Cu–Cu distance of 2.611 Å), the coordination sphere is composed of four oxygen atoms belonging to the four bridging acetate anions and a nitrogen atom belonging to the pyridine unit. The coordination geometry around Cu(II) is again a distorted square-based pyramid [OCuO angle varying between 88.7° and 90.2° (*cis*) and 169.0° and 169.6° (*trans*)]. These values are close to those observed in the case of **1**. Again, the 1D networks are packed in a parallel fashion.

In summary, the synthesis of four new neutral bis monodentate tectons **1–4** based on diazamacrocyclic units connected to two pyridine units through amide junctions was achieved. Two out of the four tectons, mainly the two bearing isonicotinoyl moieties, were shown by X-ray diffraction on single crystal to generate neutral 1D coordination networks in the crystalline phase in the presence of dimeric copper diacetate behaving as a linear metallatecton. The 1D networks are packed in a parallel fashion. The generation of coordination networks and discrete metallamacrocycles based on the reported tectons and other metal centres is currently under investigation.

Experimental

Synthesis of tectons 1–4

General. All commercially available reagents were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers at 300 MHz and at 75.48 MHz, respectively. Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université Louis Pasteur, Strasbourg.

General procedure for the preparation of compounds 1–4. At room temperature, to a suspension of the hydrochloride salt of **7** or **8** in dry THF (15 ml) was added dropwise (20 min) a dry THF solution (15 ml) of **5** or **6** and Et_3N (1 ml, 7.2 mmoles). The mixture was stirred overnight before the solvent was evaporated to dryness affording a solid residue which was dissolved in CH_2Cl_2. The solution was washed with neutral water (30 ml) and then basic water (pH 10, 30 ml). The organic layer was dried over $MgSO_4$ and the solvent removed affording the desired pure compounds **1–4** as a white powders.

Compound 1 (0.08 g, 72%). 7 · HCl (0.112 g, 0.63 mmoles); **5** (0.05 g, 0.19 mmoles). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 3.42–3.93 (m, 16H, NCH_2 and OCH_2), 7.38–7.45 (m, 4H, CHarom.), 8.63–8.69 (m, 4H, CHarom.); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 47.2, 48.3, 50.9, 51.7 (NCH_2); 68.3, 68.8, 69.4, 69.6 (OCH_2); 121.8, 144.0, 150.2 (C arom.); 170.2 (CO); Anal. for $C_{20}H_{32}N_4O_4$ calc. C 62.49, H 6.29, N 14.57, found C 62.09, H 6.29, N 14.39%. Mp = 192–194 °C.

Compound 2 (0.07 g, 75%). 7 · HCl (0.075 g, 0.42 mmoles); **6** (0.05 g, 0.19 mmoles). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 3.49–3.80 (m, 24H, CH_2), 7.25–7.30 (td, 4H, J = 5 Hz and 1,5 Hz, CH arom.), 8.65–8.69 (td, 4H, J = 5 Hz and 1,5 Hz, CH arom.); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 46.1, 46.2, 49.7 (NCH_2); 69.4, 69.7, 70.5, 70.6 (OCH_2); 1201.0, 144.2, 150.2, (C arom.); 169.6 (CO); Anal. for $C_{24}H_{32}N_4O_6$ calc. C 61.00, H 6.83, N 11.86, found C 61.01, H 6.86, N 11.92%. Mp = 138–140 °C.

Compound 3 (0.06 g, 54%). 8 · HCl (0.112 g, 0.63 mmoles); **5** (0.05 g, 0.19 mmoles). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 3.48–3.94 (m, 16H, NCH_2 and OCH_2), 7.31–7.35 (m, 2H, CH arom.), 7.81–7.94 (m, 2H, CH arom.), 8.63–8.64 (m, 2H, CH arom.), 8.65–8.85 (m, 2H, CHarom.); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 47.3, 48.6, 51.1, 52.1 (NCH_2); 68.4, 68.9, 69.5 (OCH_2); 123.2, 132.3, 135.5, 148.7, 150.6 (C arom.); 170.1 (CO); Anal. for $C_{24}H_{32}N_4O_6$ calc. C 62.49, H 6.29, N 14.57, found C 62.09, H 6.29, N 14.33%. Mp = 184–187 °C.

Compound 4 (0.06 g, 67%). 8 · HCl (0.076 g, 0.43 mmoles); **6** (0.05 g, 0.19 mmoles). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm): 3.53–3.78 (m, 24H, CH_2), 7.28–7.33 (m, 2H, CH arom.), 7.67–7.73 (m, 2H, CH arom.), 8.60–8.63 (m, 4H, CH arom.); ^{13}C (75.48 MHz, $CDCl_3$, 25 °C), δ (ppm): 46.3, 50.0 (NCH_2); 69.4, 69.7, 70.6 (OCH_2); 123.3, 132.4, 134.6, 147.5, 150.3 (C arom.); 169.5 (CO); Anal. for $C_{24}H_{32}N_4O_6$ calc. C 61.00, H 6.83, N 11.86, found C 60.74, H 6.87, N 11.74%. Mp = 113–117 °C.

Crystallisation conditions

In a crystallisation tube (15 cm long, 0.4 mm diameter) upon slow diffusion of a toluene (0.5 ml) solution of the tecton **1** or **2** (1 mg) into a MeOH (1 ml) solution of $Cu(OAc)_2$, H_2O (6 mg) in large excess, blue crystalline materials were obtained after several days.

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-Kα radiation. For both structures, diffraction data were corrected for absorption and analysed using SHELXL-97. All non-H atoms were refined anisotropically.

Crystal data for: $(\mathbf{1 \cdot CuOAc_2}) \cdot \mathbf{2CH_3OH \cdot C_7H_8}$ (blue crystals, 173 K). $C_{37}H_{52}Cu_2N_4O_{14}$, $M = 903.91$, triclinic, space group $P\bar{1}$, $a = 8.6452(2)$, $b = 11.4949(3)$, $c = 12.4095(3)$ Å, $\alpha = 108.692(2)°$, $\beta = 93.096(2)°$, $\gamma = 107.264(2)°$, $V = 1100.27(5)$ Å^3, $Z = 1$, $D_c = 1.36$ g cm^{-3}, $\mu = 1.032$ mm^{-1}, 9964 data with $I > 2\sigma(I)$, $R = 0.0531$, $Rw = 0.1707$.

Crystal data for: $(\mathbf{2 \cdot CuOAc_2})$ (blue crystals 173 K). $C_{16}H_{22}Cu_1N_2O_7$, $M = 417.90$, triclinic, space group $P\bar{1}$, $a = 8.8868(6)$, $b = 9.9720(7)$, $c = 10.5256(8)$ Å, $\alpha = 75.286(3)°$, $\beta = 81.777(3)°$, $\gamma = 85.916(3)°$, $V = 892.31(11)$ Å^3, $Z = 2$, $D_c = 1.55$ g cm^{-3}, $\mu = 1.265$ mm^{-1}, 5510 data with $I > 2\sigma(I)$, $R = 0.0696$, $Rw = 0.1750$. CCDC reference numbers 252123 and 252124 . See http://www.rsc.org/suppdata/nj/b4/b416145a/ for crystallographic data in .cif or other electronic format.

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