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Molecular tectonics: generation of 1- and 2-D copper coordination networks by positional isomeric tectons based on a phenylenediamine backbone bearing two isonicotinoyl moieties†

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The combination of three isomeric organic tectons **1–3** based on 1,2-, 1,3- and 1,4-phenylenediamine backbones bearing two isonicotinoyl groups with a $Cu(OAc)_2$ neutral complex leads to the formation of 1-D and 2-D coordination networks. Whereas for both tectons **1** and **2** the network is generated through the interconnection of the organic moieties by copper dimers of the paddle-wheel type, in the case of **3**, the 2-D network is formed by another type of connector, a binuclear copper complex for which the two metal centres adopt an octahedral coordination geometry.

Introduction

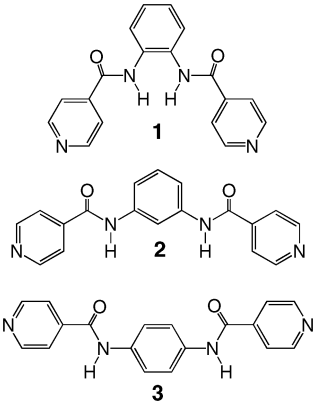
The design of molecular architectures in the solid state is a subject of current interest. In particular, the formation of coordination networks,[1] hybrid metallo-organic molecular assemblies, has been attracting much attention over the last decade.[2] The formation of this type of network results from the establishment of coordination bonds between a metal or a metal complex and a donor atom belonging to an organic building block called a tecton.[3,4] Self-assembly processes are responsible for the formation of such infinite architectures. This construction strategy based on iterative processes may lead to structural complexity even when rather simple tectons are engaged.[5] For that reason, although many types of coordination networks have been reported over recent years, the precise design of these networks in terms of connectivity (type and number of coordination bonds) and dimensionality (depending on the number of translations of the coordination event leading to chains (1-D), sheets (2-D) and three-dimensional arrangements (3-D)) still remains a challenge. In terms of design, in order to reach an acceptable degree of confidence, systematic investigations are needed. In particular, the study of the incidence of (i) the nature of the binding sites and poles of the organic building block, their number and disposition in space, (ii) the number and disposition of available coordination sites on the metal centre, (iii) steric and electrostatic constraints, (iv) the nature and binding ability of anions present, (v) the solvent used, (vi) kinetics or thermodynamic control of crystallisation, must be undertaken. For some time now we have been engaged in a systematic study of these parameters.[6]

We report here our investigation dealing with the possibility of controlling the geometry (bend angle) of stair type 1-D coordination networks using a combination of three isomeric tectons **1–3** (Scheme 1) with copper(II) acetate which generally behaves as a linear connector.

Results and discussion

The goal of this investigation is to study both the correlation between structural features of a rather rigid tecton, such as the angle between two monodentate coordinating sites, with the geometry of the coordination networks generated when combined with the bimetallic copper(II) acetate as connector (Scheme 2), and the connectivity and geometry of the bimetallic unit.

In order to obtain restricted conformational space, rather rigid ligands are required. For that reason, the design of the organic bismonodentate tectons **1–3** (Scheme 1) is based on the aryl group bearing two coordinating pyridine units oriented in a divergent fashion. The aryl backbone is connected to pyridines through amide junctions. The three tectons are positional isomers. Indeed, they only differ by the position of connection of the pyridyl units to the aryl group (*ortho* for **1**, *meta* for **2** and *para* for **3**). Although all three parts (aryl,



Scheme 1

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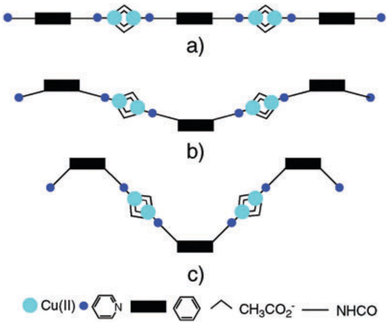
† Dedicated to G. Ourisson on the occasion of his 80th birthday.



Scheme 2

pyridine and amide group) are rigid units, nevertheless, due to rotational flexibility, tectons **1–3** may adopt different conformations and configurations.[7–9] The formation of coordination networks by combining **1–3** with a variety of metal cations has already been reported: Hg, Ag and Au for **1**,[9,10] Pd and Pt for **2**[11] and Hg for **3**.[7,12] Other related ligands have been also used for the formation of coordination networks.[13] To the best of our knowledge, no copper coordination network has been reported for tectons **1–3**.

Since all tectons **1–3** are neutral units, in order to avoid the presence of unbound anions and furthermore to control the linear disposition of available coordination sites on the metal centre, copper acetate was chosen as a linear metallotecton. In general, in the presence of ligands offering donor atoms such as nitrogen and oxygen, $Cu(OAc)_2$ forms a binuclear neutral complex with square pyramidal geometry resulting from the bridging of the two Cu(II) centres by four acetate anions occupying the square base of the polyhedron (Fig. 1a). This dimer acts as a linear connector through the two free apical positions.

This dimeric unit has been extensively used for the formation of several coordination networks.[14] A correlation between (i) the nature of the carboxylate ligand, (ii) the nature of the axial ligands, and (iii) the distortion around the copper(II) ions and the amplitude of the antiferromagnetic coupling between both copper(II) ions has been investigated.[15] For binuclear copper units containing carboxylate ligands as bridging ligands and ligands bearing N donor atoms, other coordination modes of carboxylate are observed;[16] however, for the majority of cases reported, the geometry around copper(II) atoms is square pyramidal.

At room temperature, the mixing of each of the three ligands **1–3** (in DMSO) with copper(II) acetate (in MeOH or EtOH) in a 1 : 1 ratio afforded crystalline material that was structurally investigated by X-ray diffraction methods on single-crystals (see Table 1 for details).

Structural analysis

$1 \cdot (Cu(OAc)_2)_2$

The crystal (triclinic, $P\bar{1}$) is composed of one molecule of the tecton **1**, one $(Cu(OAc)_2)_2$ dimer and two DMSO solvent molecules. No specific interactions between the DMSO molecules and the other two components are detected.

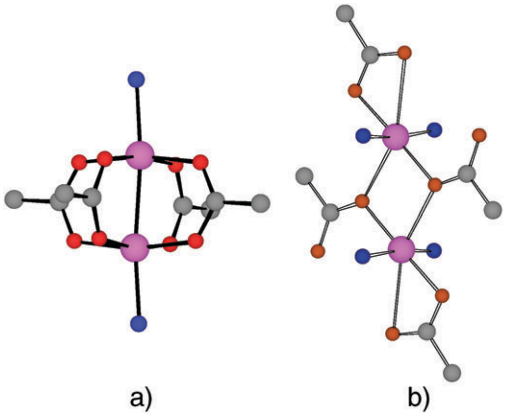


Fig. 1 Two different binuclear copper complexes (a) square pyramidal environment of copper(II) (b) deformed octahedral environment of copper(II).

Tectons **1** are interconnected by $(Cu(OAc)_2)_2$ dimers, leading thus to a 1-D zigzag type coordination network (Fig. 2). Due to the V-shape of the tecton **1**, the geometrical feature of the zigzag chain is rather pronounced (torsion angle of *ca.* 60°). For the organic tecton **1**, both amide junctions ($d_{C=O}$ = 1.228 Å, $d_{N-C(O)}$ = 1.341 Å) are in a *trans* configuration. The two amide groups adopt an antiparallel arrangement. The oxygen and nitrogen atoms of the amide junctions are not coordinated to the copper ions but form two intermolecular H-bonds between the NH and CO moieties (N–O distances of 2.94 Å and 3.08 Å).

The geometry around the copper atoms is square pyramidal (Fig. 1a), with the square base occupied by four oxygen atoms belonging to four acetate groups (Cu–O distance of *ca.* 1.97 Å, $OCuO_{cis}$ angle in the range of 88.6° to 90.7° and $OCuO_{trans}$ angle in the range of 168.5° to 169.0°) and the axial position by a nitrogen atom belonging to the tecton **1** (Cu–N distances of *ca.* 2.15 Å and 2.18 Å, NCuO angle in the range of 91.7° to 99.5°). The Cu–Cu distance in the dimeric core is 2.61 Å. The shortest Cu–Cu distance between two dimers is 8.81 Å.

In the lattice, in the *b* direction, the chains are arranged in parallel fashion with van der Waals interactions between the methyl groups of the acetate moieties (C–C distance of *ca.* 4.05 Å) and in the other direction two adjacent chains are disposed in alternate fashion, leading thus to the formation of lozenge-type channels which are filled with DMSO solvent molecules (Fig. 3).

$2 \cdot (Cu(OAc)_2)_2$

The crystal (monoclinic, $C2/c$) is composed of one molecule of the tecton **2**, one $(Cu(OAc)_2)_2$ dimer and two MeOH solvent molecules. No specific interactions between the MeOH molecules and the other components are detected.

Tectons **2** are again interconnected by $(Cu(OAc)_2)_2$ dimers again behaving as linear connectors, generating again a 1-D zigzag type coordination network (Fig. 4). Due to the less pronounced V-shape of the tecton **2**, the zigzag chain is smoother (torsion angle of *ca.* 140°) than in the case of **1** (angle of 60°). For the organic tecton **2**, both amide junctions

Table 1 Data collection and refinements for $\mathbf{1}\cdot(\mathrm{Cu(OAc)_2})_2$, $\mathbf{2}\cdot(\mathrm{Cu(OAc)_2})_2$ and $\mathbf{3}\cdot(\mathrm{Cu(OAc)_2})_2$

	$\mathbf{1}\cdot(\mathrm{Cu(OAc)_2})_2$	$\mathbf{2}\cdot(\mathrm{Cu(OAc)_2})_2$	$\mathbf{3}\cdot(\mathrm{Cu(OAc)_2})_2$
Empirical formula	$C_{18}H_{14}N_4O_2\cdot(Cu(CH_3COO)_2)_2\cdot(CH_3SOCH_3)_2$	$C_{18}H_{14}N_4O_2\cdot(Cu(CH_3COO)_2)_2\cdot(CH_3OH)_2$	$C_{18}H_{14}N_4O_2\cdot(Cu(CH_3COO)_2)_2$
Molecular weight/g mol^{-1}	835.85	745.68	499.96
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2(1)/n$
a/Å	8.2271(2)	33.799(1)	13.6671(13)
b/Å	14.3223(3)	12.7452(5)	11.5908(8)
c/Å	15.7025(4)	8.5671(5)	14.1521(16)
α/°	76.877(4)	90	90
β/°	89.004(4)	95.297(5)	117.785(3)
γ/°	82.816(4)	90	90
V/Å^3	1787.66(7)	3674.7(3)	1983.4(3)
Z	2	4	4
Color	Blue	Blue	Blue
Crystal size/mm	0.16 × 0.06 × 0.04	0.08 × 0.06 × 0.06	0.15 × 0.15 × 0.15
ρ_{calcd}/g cm^{-3}	1.55	1.35	1.674
μ/mm^{-1}	1.372	1.216	1.153
λ/Å	0.710 73	0.710 73	0.710 73
Number of reflections collected	14 823	9707	18 010
Number of data with $I > 2\sigma(I)$	6842	2314	4373
R	0.076	0.105	0.0349
Rw	0.095	0.134	0.0872
GOF	1.149	1.252	1.025

($d_{\mathrm{C=O}}$ = 1.294 Å, $d_{\mathrm{N-C(O)}}$ = 1.331 Å) are again in a *trans* configuration. Once again, the two amide groups adopt the antiparallel conformation.

For the copper dimer, the same square pyramidal geometry with almost the same distances and angles (Cu–O distance of *ca.* 1.96 Å, OCuO_{cis} angle in the range of 88.7° to 88.9° and OCuO_{trans} angle in the range of 168.3° to 168.4°, Cu–N distance of *ca.* 2.18 Å, NCuO angle in the range of 94.5° to 97.0°) as in the case of **1** mentioned above, is observed (Fig. 1a). The Cu–Cu distance in the dimeric core is 2.61 Å. The shortest Cu–Cu distance of 17.80 Å between two dimers is considerably longer than that observed in the case of **1** (8.81 Å).

The 1-D networks are packed in a parallel fashion within planes perpendicular to the *c* axis. The consecutive planes are tilted by *ca.* 30°. The packing of planes along the *c* axis leads to the formation of rectangular channels (7.8 Å × 14 Å), which are occupied by MeOH molecules. The shortest distance between copper dimers localised in two adjacent planes is 6.98 Å (Fig. 5).

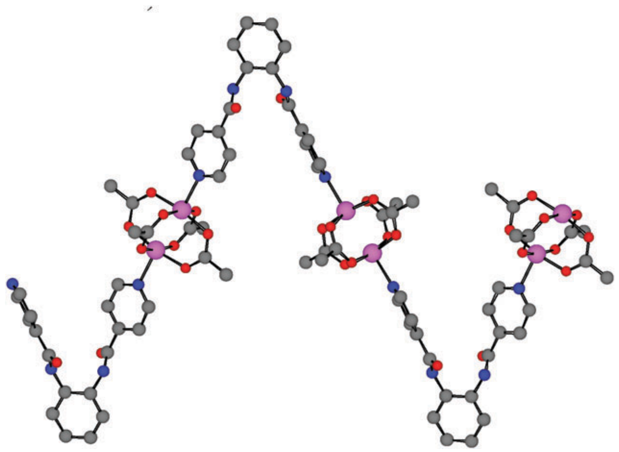


Fig. 2 A portion of the structure of the 1-D coordination network $[\mathbf{1}\cdot(\mathrm{Cu(OAc)_2})_2]$ formed between the tecton **1** and $\mathrm{Cu(OAc)_2}$ complex. H atoms and DMSO solvent molecules are not represented for clarity. For bond distances and angles see text.

$\mathbf{3}\cdot(\mathbf{Cu(OAc)_2})_2$

The crystal (monoclinic, $P2(1)/n$) is composed of one molecule of the tecton **3** and one $(\mathrm{Cu(OAc)_2})_2$ dimer, however of a different type. No solvent molecule is present in the crystal.

The overall structure is a 2-D coordination network with a different role played by the copper dimer (Fig. 6). For the organic tecton **1**, both amide junctions ($d_{\mathrm{C=O}}$ = 1.212 Å, $d_{\mathrm{N-C(O)}}$ = 1.355 Å) are again in a *trans* configuration. The two amide groups again adopt the antiparallel arrangement. The oxygen and nitrogen atoms of the amide junctions do not participate in the coordination of the metal centre.

Interestingly, in marked contrast with the two cases mentioned above, the copper bimetallic unit does not behave as the often observed linear connector.[14] In fact, the coordination geometry around Cu(II), instead of being square pyramidal, is a distorted octahedral as shown in Fig. 1b. The copper centre is hexacoordinate and its coordination sphere is composed of four oxygen atoms occupying the square base of the octahedron and two nitrogen atoms of the pyridine type belonging to two consecutive tectons **3** (N–Cu distances of 2.019 and 2.028 Å). The two nitrogen atoms occupy the apical positions (NCuN angle of 170°). Among the four acetate units forming the dimer, two are terminal with one short (2.000 Å) and one long (2.624 Å) Cu–O distances and an OCuO angle of 55.0°. The other two acetate anions are bridging the two metal centres again with one short (2.030 Å) and one long (2.333 Å) Cu–O distances and with a CuOCu angle of 103.7°. To the best of our knowledge, this coordination mode of acetate and N donor atoms has never been observed before. Consequently, the Cu–Cu distance of 3.436 Å is considerably longer than that of 2.613 Å observed in the case of **1** and **2**. Due to this peculiar

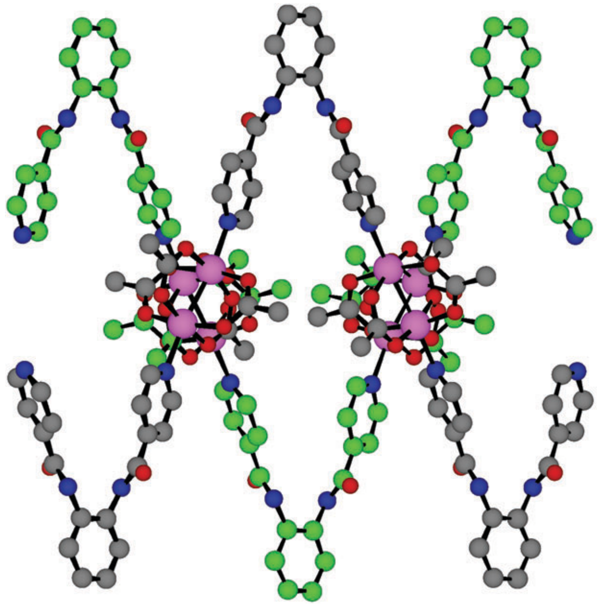


Fig. 3 A portion of structures of [**1** · $(Cu(OAc)_2)_2$] showing the packing of two 1-D networks generating lozenge-type channels. The two networks are differentiated by the colour of the carbon atoms (grey and green). H atoms and DMSO molecules are not represented for clarity.

mode of coordination, the 2-D network may be described as 1-D copper networks obtained upon bridging of tectons **3** by copper ions and their interconnection by the bridging of Cu(II) ions by acetate anions (Fig. 6). The arrangement of the 2-D networks leads to a compact structure with no cavity available for the inclusion of solvent molecules.

Conclusions

For both bismonodentate tectons **1** and **2** which are V-shaped, copper diacetate behaves as a linear connector leading thus to two analogous 1-D coordination networks of the zigzag type. Based on the geometrical features of tectons **1** and **2**, as expected, the zigzag chain observed with tecton **2** possesses a smoother angle than that observed with tecton **1**. This observation confirms the existence of a correlation between geometrical characteristics of the organic tecton such as the bend angle between the two coordinating sites (Scheme 2b and c) and the bend angle of the zigzag type 1-D networks generated upon interconnection of tectons **1** and **2** by a linear connector such as copper diacetate (Fig. 2a). However, interestingly but unexpectedly, in the case of the tecton **3** which should have behaved as a linear construction unit (Fig. 1a), instead of a 1-D network, a 2-D network is obtained. Although the tecton **3** behaves as an almost linear unit, probably due to packing effects, the nature of the connecting metallic part is different. Indeed, in that case, the copper centre still forms a binuclear complex; however it changes its coordination geometry from square pyramidal to octahedral. This mode of connectivity is rather unusual for binuclear copper(II) carboxylate complexes. This change in the coordination mode leads to the formation of a 2-D network. The

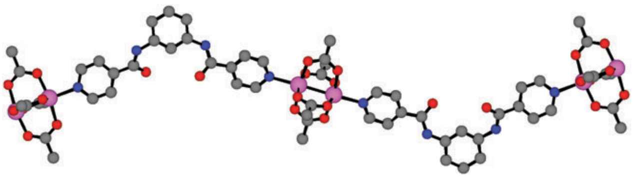


Fig. 4 A portion of the structure of the 1-D coordination network [**2** · $(Cu(OAc)_2)_2$] formed between the tecton **2** and $Cu(OAc)_2$ complex. H atoms and MeOH solvent molecules are not represented for clarity. For bond distances and angles see text.

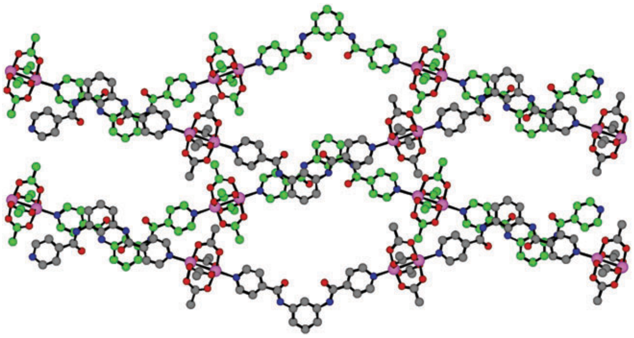


Fig. 5 A portion of structures of [**2** · $(Cu(OAc)_2)_2$] showing the packing of 1-D networks generating lozenge-type channels. The 1-D networks are differentiated by the colour of the carbon atoms. Networks with the same colour (grey or green) are in the same plane. H atoms and MeOH molecules are not represented for clarity.

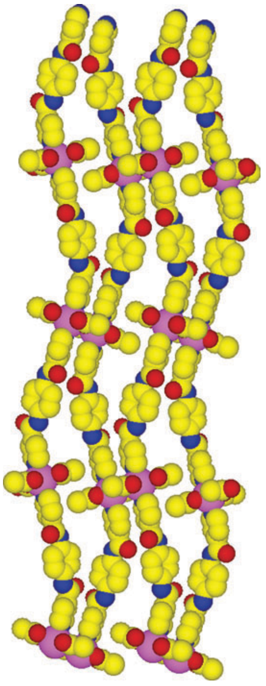


Fig. 6 A portion of the structure of the 1-D coordination network [**3** · $(Cu(OAc)_2)_2$] formed between the tecton **3** and $Cu(OAc)_2$ complex. H atoms are not represented for clarity. For bond distances and angles see text.

magnetic properties of crystalline materials obtained with tectons **1–3** will be investigated. Furthermore, the use of tectons **1–3** for the formation of coordination networks with other metal cations such as cobalt and iron is currently under investigation.

Experimental

The synthesis of ligands **1**[9], **2**[11a] and **3**[7,12] has been previously reported.

The generation of $\mathbf{1}\cdot(\mathrm{Cu(OAc)_2})_2$ coordination network was achieved in a crystallisation tube (height = 15 cm, diameter = 0.4 cm) by slow diffusion at room temperature of a EtOH solution (1 ml) containing $\mathrm{Cu(OAc)_2\cdot H_2O}$ (6×10^{-6} moles) into a DMSO solution (1 ml) of the ligand **1** (6×10^{-6} moles). After one week, blue crystals were obtained which were filtered and dried under vacuum. Molecular formula: $(\mathbf{1}\cdot(\mathrm{Cu(OAc)_2})_2)\cdot(\mathrm{CH_3SOCH_3})_2$ (837.8 g mol^{-1}). Elemental analysis: calcd: C: 43.0%, H: 4.6%, N: 6.7%; found: C: 42.6%, H: 4.2%, N: 6.6%.

The generation of $\mathbf{2}\cdot(\mathrm{Cu(OAc)_2})_2$ coordination network was achieved in a crystallisation tube (height = 15 cm, diameter = 0.4 cm). Upon slow diffusion at room temperature of a MeOH solution (1 ml) containing $\mathrm{Cu(OAc)_2\cdot H_2O}$ (6×10^{-6} moles) into a DMSO solution (1 ml) of the ligand **2** (6×10^{-6} moles) blue crystals were obtained after *ca.* one week. They were filtered and dried under vacuum. Molecular formula: $(\mathbf{2}\cdot(\mathrm{Cu(OAc)_2})_2)\cdot(\mathrm{CH_3OH})_2$ (725.7 g mol^{-1}). Elemental analysis: calcd: C: 45.1%, H: 4.6%, N: 7.5%; found: C: 45.0%, H: 4.1%, N: 7.4%.

The generation of $\mathbf{3}\cdot(\mathrm{Cu(OAc)_2})_2$ coordination network was also achieved in a crystallisation tube (height = 15 cm, diameter = 0.4 cm). Upon slow diffusion at room temperature of a EtOH solution (1 ml) containing $\mathrm{Cu(OAc)_2\cdot H_2O}$ (6×10^{-6} moles) into a DMSO solution (1 ml) of the ligand **3** (6×10^{-6} moles). However, in marked contrast with the two above mentioned cases, few blue crystals were obtained after several weeks. Owing to the small quantities of collected crystals, no elemental analysis has been performed.

Crystallography

Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid $\mathrm{N_2}$ device, using graphite-monochromated Mo-Kα (λ = 0.710 73 Å) radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using the APEX (1.022) package. All hydrogen atoms have been calculated except those connected to disordered atoms. CCDC reference numbers 299702–299704. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600193a

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