Interpenetrated networks from a novel nanometer-sized pseudopeptidic ligand, bridging water, and transition metal ions with cds topology†

George E. Kostakis,[ab] Luigi Casella,[a] Nick Hadjiliadis,*[b] Enrico Monzani,[a] Nikolaos Kourkoumelis[c] and John C. Plakatouras*[b]

The combination of a new pseudopeptidic ligand, transition metal ions, and bridging water molecules results in the formation of $[M(\mu\text{-TBG})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ (M: Cu, Co and H_2TBG: terephthaloylbisglycine); both compounds show rare two-fold interpenetrated three-dimensional cds-nets and reversible loss of coordinated and lattice water molecules.

In recent years there has been extensive interest in metal–organic polymer chemistry due to the variety of the composition and topology of the produced compounds, and also to their interesting functional properties and potential applications. The development of rational synthetic routes by self-assembly has afforded an important number of coordination polymers with specific topologies.[1] Metal–ligand coordination has been well used in the directed assembly of extended porous metal–organic networks. The ability to control the design of coordination networks arises from the management of the coupling of the coordination properties of individual metal ions and ligand functionality. One of the key points for such studies is the design or choice of components that organize themselves into desired patterns with useful functions. Considerable use has been made of the rigid linear bridging ligand 1,4-benzenedicarboxylic (terephthalic) acid and also of related ligands in which various spacer groups connect carboxylic pairs.[2]

Our synthetic strategy is to introduce flexibility on the aromatic rigid scaffold in addition to groups that would allow extra stabilizing interactions and eventually to build up a higher dimensional motif through metal–ligand interactions. Our first approach is terephthaloylbisglycine,[3a] which is longer than terephthalate, the carboxylate groups are reasonably free to rotate and the amide bond can be the source of hydrogen bonds that would be able to stabilize a network. Furthermore, bearing in mind that aminoacids and peptides provide the glycine chelate ring for coordination to metal ions, we could expect a bis-chelating bridging behavior that could lead to an unprecedented polymer.

The reaction between equivalent amounts of the corresponding metal nitrate and terephthaloylbisglycine (H_2TBG) in water, at r.t.,

proceeds smoothly and produces crystalline solids formulated as $[M(\mu\text{-TBG})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ [M: Cu (1), Co (2)].[3b] Both compounds were characterized crystallographically and they were found to belong to the $P2/a$ space group with one half molecule in the asymmetric unit.‡ A water molecule is included, and it is connected to the network, eventually formed, with four hydrogen bonds. Each metal ion is coordinated, in a rather regular octahedron (with larger Jahn–Teller distortion in the case of Cu, in 1), to two oxygen atoms belonging to two monodentate carboxylates of two different TBG ligands, two bridging and two terminal water molecules, in *trans* positions (mean M–O distances, 1: 2.092, 2: 2.102 Å). The differences in M–O bonds are also reflecting the two different kinds of H_2O molecules in the coordination sphere and can preclude the existence of hydroxide species. The system's coordination is presented in Fig. 1. The structure of $[M(\mu\text{-TBG})(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]$ is constructed from one-dimensional chains interlinked through bridging water and TBG groups into an open framework, three-dimensional structure. As shown in Fig. 2, the chains consist of square planar nodes (the terminal water molecules are not counted) linked through TBG ligands. There are two different metal–metal distances: (a) a short one for the water bridge (1: 4.0878(8), 2: 3.986(2) Å) and (b) a long one for the TBG bridge (1: 17.207(4), 2: 17.438(9) Å). The structure propagates in one direction as {M(TBG)} chains through the bridging terephthaloylbisglycinate ligands. These linear chains are linked in turn through a $\{M(\text{H}_2\text{O})\}^{2+}$ undulating chain. Adjacent {M(TBG)} chains cross at an angle of $\sim 48°$ to produce the grid pattern seen in projection along c. The water bridges propagate along the a axis, while the TBG bridges propagate alternately parallel to the two diagonal directions of the bc face forming this way a cds network.[4]

The rhombic channels shown in Fig. 3, exhibit a 68-atom connect to generate a cavity of ~ 50 Å^2 cross section area. (Fig. S1)
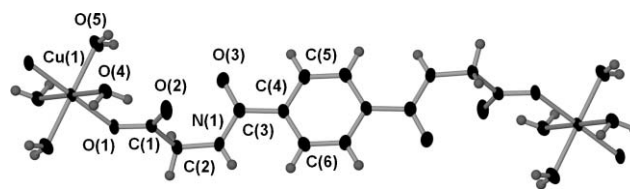

Fig. 1 The coordination sphere of the Cu atoms and the ligand bonding in 1. 2 has a very similar structure. Selected bond lengths/Å and angles/°, 1: Cu(1)–O(1) 1.987(2), Cu(1)–O(4) 2.291(2), Cu(1)–O(5) 1.998(2); O(1)–Cu(1)–O(4) 93.18(8), O(1)–Cu(1)–O(5) 88.80(10), O(4)–Cu(1)–O(5) 89.71(10); 2: Co(1)–O(1) 2.053(3), Co(1)–O(4) 2.182(2), Co(1)–O(5) 2.069(4); O(1)–Co(1)–O(4) 92.09(13), O(1)–Co(1)–O(5) 89.89(15), O(4)–Co(1)–O(5) 90.10(14).

[a]*Dipartimento di Chimica Generale, Universitá di Pavia, Via Taramelli 12, 27100, Pavia, Italy*
[b]*Department of Chemistry, University of Ioannina, 451 10, Ioannina, Greece. E-mail: iplakatu@cc.uoi.gr*
[c]*Department of Physics, University of Ioannina, 451 10, Ioannina, Greece*

† Electronic supplementary information (ESI) available: Figures, H-bond Tables for the structures, vibrational, electronic and EPR spectra, thermal analyses, XRPD patterns for original, dehydrated and rehydrated samples and a vrml file with the topological presentation of the structures. See http://dx.doi.org/10.1039/b502788h
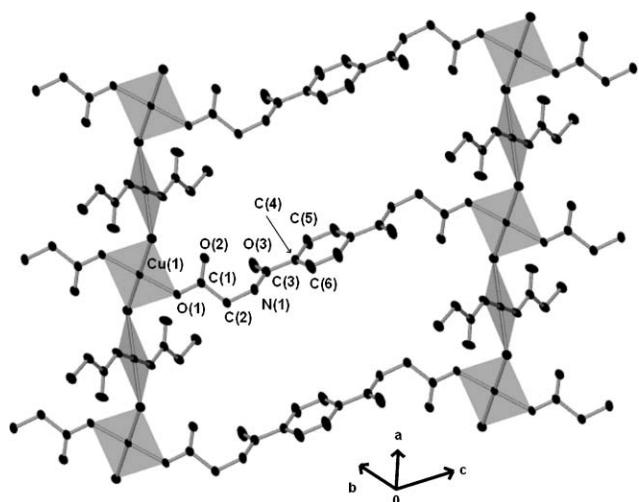
Fig. 2 The infinite 2D-layers based on {Cu$_3$(TBG)(H$_2$O)$_2$}$_2$ rings as part of a 3D network in the structure of **1**.

Although these channels have significant size there is no significant void space as a consequence of the interpenetration of a second three-dimensional gridwork, as illustrated in Fig. 3. (See also Fig. S2) Interpenetration obviously is due to the length of the TBG ligand. The two networks, dependent crystallographically, are chemically connected through the lattice water, which forms four H-bonds, two as a donor to the non-bonded oxygen atom of a carboxylic group and to the amide oxygen of a different ligand but of the same grid and two as acceptor from a terminal water molecule of the previous grid and a peptide nitrogen of the other grid. (Fig. 4, Tables S1–2)

Despite the coordination and the extended H-bonding network, thermogravimetric analyses, under nitrogen, for **1** and **2** indicate complete and rapid loss of all water molecules. Both ligated and non-bonded water loss occur simultaneously in the temperature ranges 80–120 and 75–125 °C for **1** and **2**, respectively. The anhydrous intermediates are stable up to 200 and 310 °C, respectively, around where the decomposition begins, to give metal oxides as final residues. (Fig. S3)

X-ray powder diffraction on the stable intermediates suggests that the initial structure collapses on heating. Infrared and electronic spectroscopies provide useful tools for the elucidation of the dehydrated structures. The carboxylate group is not
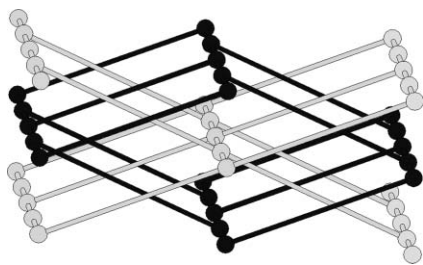
Fig. 3 Schematic presentation of the interpenetrating cds networks as derived from the crystallographic data of **1**. Spheres represent metal centres while short and long bars represent water and TBG bridges, respectively. The distortion of the cds network can be seen from the differences in bridge lengths as well as from the dihedral angles defined by the metal centres.
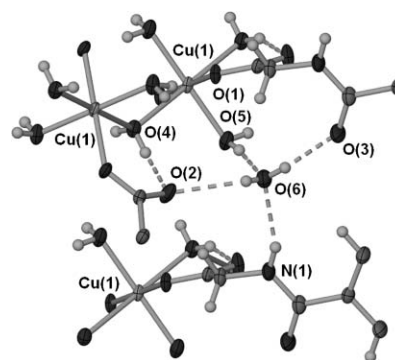
Fig. 4 A part of the H-bonding network in **1** showing the interaction between the interpenetrating nets.

monodentate, and according to the IR spectrum is at least bidentate chelating. The carbonyl oxygen appears to interact with the metal ions, while the amide bond remains protonated.[5] (Table S3) The electronic spectra for the intermediate of **1** suggest reduction of the coordination number, while for **2**, distorted pseudotetrahedral geometry of the coordination sphere about Co(II).[6] (Fig. S5)

When a dehydrated sample of either **1** or **2** is exposed in "wet" media,[7] it reabsorbs the lost water molecules and reforms its original structure, as shown from XRPD patterns.

We believe that this is due to the fact that above 140 °C, though the 3D network is destroyed, the ligand remains intact and coordinated to the metal ions, forming probably a lower dimensional motif. There is an interaction which may not be important for the stabilization of the initial interpenetrated motif but could assist the stabilization of the dehydrated structure. The distance of the least square planes of the phenyl rings of the two different nets is 3.49 Å, but we cannot characterize it as stacking due to the large offset of the ring centroids (2.12 Å). Perhaps dehydration reduces this offset and the interaction becomes stacking and the metal ions remain close. This way the water bridge can be easily formed upon rehydration.

The liquid He temperature EPR spectrum for a powder of **1** (Fig. S6) is characterized by a split broad signal centered at $g \sim 2$. It is indicative of pairs of interacting Cu^{II} paramagnetic centers. The $g = 4$ "semiforbidden" transitions which are predicted in the case of a pure $S = 1$ triplet, are not resolved even at high microwave power.[8] This indicates that the Cu–Cu coupling is comparable to or smaller than the microwave energy *i.e.* 0.3 cm^{-1} in our case. The spectrum for **2** is characterized by g values at 5.8, 3.9 and a weak trough at $g = 2$. This is typical of high-spin monomeric Co^{2+} $S = 3/2$ centers with no resolvable magnetic coupling between them. The g values at 5.8 and 3.9 indicate a severe deviation from axial symmetry. This is due to the rhombicity of the ligand field imposed by the three different kinds of ligands in *trans* positions, as can be seen in the crystal structure.

To our knowledge complexes **1** and **2** are unique in metal organic hybrid polymer chemistry with a number of novel features which can be separated into two different categories. Those of structural interest: (i) Though the cds topology possesses a fundamental place in 4-connected networks and has received considerable attention, our case is the most distorted.[9] (ii) They are the first examples of interpenetrated networks built by metal ions

and two different linkers with such an immense difference in size (one monoatomic and one nanometer-sized bridge). The closest example we could find is [Cu(bpe)(H$_2$O)(SO$_4$)] (bpe = *trans*-1,2-bis(4-pyridyl)ethylene),[9b,10] and those related with important advances in metal organic framework chemistry: (iii) They are the first examples in the literature of 3D metal organic polymers derived from a pseudopeptidic ligand. (iv) Bridging water molecules occur in several crystal hydrates[11] but, when unsupported by other bridging ligands, are very rare in metal organic polymers. A characteristic example is [Ni$_3$(CTC)$_2$(μ-H$_2$O)(H$_2$O)]$_n$ (CTC^{3-} = *cis,cis*-1,3,5-cyclohexanetricarboxylate), where the water bridge is supported by a carboxylate bridge.[12] A search in the CSD[13] reveals only two examples of unsupported water bridges in 1D polymers. These are the carboxylates [CoL$_2$(μ-H$_2$O)(H$_2$O)$_2$] (L = 3,4-dimethoxybenzoate[14a] and 3-hydroxy-4-methoxybenzoate[14b]). (v) Reversible loss of solvated molecules is rather common in metal organic hybrid materials but the reversible loss of bridging ligands is certainly rare.

Encouraged by the structure and properties of complexes **1** and **2**, we are currently exploring the reactions of the TBGH$_2$ ligand with other metals in a variety of conditions, as well as the magnetic and catalytic properties of the complexes presented here.

Notes and references

‡ Single crystal X-ray data: **1**: C$_{12}$H$_{20}$CuN$_2$O$_{11}$, M = 431.85, monoclinic, a = 8.1755(6), b = 6.8256(14), c = 15.795(2) Å, $β$ = 102.996(7)°, V = 858.8(2) Å^3, T = 295(2) K, space group $P2/a$ (no. 13), Z = 2, $μ$(Mo-Kα) = 1.334 mm^{-1}, 2713 reflections measured, 2504 unique (R_{int} = 0.0255), 1541 ($I \geq 2σ_I$) used for refinement. Final $R(F^2)$ = 0.0471. **2**: C$_{12}$H$_{20}$CoN$_2$O$_{11}$, M = 427.22, monoclinic, a = 7.971(5), b = 6.907(5), c = 16.012(5) Å, $β$ = 103.899(19)°, V = 855.7(5) Å^3, T = 295(2) K, space group $P2/a$ (no. 13), Z = 2, $μ$(Mo-Kα) = 1.065 mm^{-1}, 2656 reflections measured, 2484 unique (R_{int} = 0.0217), 1632 ($I \geq 2σ_I$) used for refinement. Final $R(F^2)$ = 0.0660. Despite the room temperature data, all hydrogen atoms were located from difference Fourier maps. The C–H protons were placed in idealized positions and treated as riding on the parent carbon atoms. The amide and the water protons were refined isotropically leading to small isotropic displacement parameters. For **2**, restraints provided by SHELX (DFIX and EADP (proton pairs)) were applied for the isotropic refinement. CCDC 265226 and 267859. See http://dx.doi.org/10.1039/b502788h for crystallographic data in CIF or other electronic format.

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3 (a) TBGH$_2$ was synthesized by the reaction of a solution of glycine methyl ester hydrochloride (2.51 g, 0.02 mol) and Et$_3$N (5.6 ml, 0.04 mol) in CHCl$_3$ (30 ml) with a solution of terephthaloyl chloride (2.03 g,

0.01 mol) in CHCl$_3$ (20 ml), which was added slowly while maintaining the temperature at 0 °C. After 2 h at r.t., the solution was evaporated, yielding a yellow powder that was recrystallized from H$_2$O. The purity of the intermediate was checked with TLC (CHCl$_3$: AcOEt, 4 : 1). The yellow powder was dissolved in MeOH (50 ml) and KOH (1.7 g, 0.03 mol) in MeOH (20 ml) was added slowly. After 48 h at r.t., the solution was stripped to dryness, and the white residue was dissolved in H$_2$O and acidified down to pH = 2 with HCl. After 5 h at 4 °C the product was filtered and dried *in vacuo*. Yield 2.7 g, 95%. mp/°C 273(1) (dec). Elemental analysis of TBGH$_2$ (calc) C: 51.13(51.43) H 4.20(4.32) N 9.87(10.00)%. IR (KBr), v/cm^{-1} 3358, 3307 (N–H) (s), 3086 (w), 2944 (w), 2749 (w) (O–H), 2637 (w), 2563 (w), 1711 (s) (C=O), 1639 (s) (C=O amide), 1554 (s) (δ N–H), 1501(w), 1408 (m), 1355 (m), 1328 (m), 1275 (w), 1228 (s) (C–O), 1002 (w), 936 (m), 866 (w), 832 (w), 730 (m). ^{1}H NMR (250 MHz, DMSO)/ppm 3.94 (d, J = 5.92 Hz, 4H), 7.96 (s, 4H), 8.97 (t, J = 5.86 Hz, 2H), 12.62 (bs, 2H). ^{13}C NMR (100 MHz, DMSO)/ppm 42.1, 128.2, 137.1, 166.7, 172.1. ESI-MS m/z 560.9 (2M + H)$^+$, 319.0 (M + H + K)$^+$, 281.2 (M + H)$^+$; (b) **1**: TBGH$_2$ (0.2 g, 0.71 mmol) was suspended in H$_2$O (10 ml) and to this NaOH 0.5 M solution was added until the solution became clear (*ca.* 1.5 ml). To this a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.35 g, 1.43 mmol) in 5 ml of H$_2$O was added. Greenish microcrystalline solid was formed after 3 h, which was filtered, washed with ethanol and diethyl ether, and dried *in vacuo*. Yield: 0.22 g, 71% based on TBGH$_2$. For the preparation of crystals 50 mg of TBGH$_2$ were dissolved in a mixture of 10 ml H$_2$O and 3 ml DMF. To this Cu(NO$_3$)$_2$·3H$_2$O (85 mg in 5 ml of H$_2$O) was added and the resulting solution was left to evaporate slowly. A few crystals were isolated after almost 7 weeks, washed with ethanol and dried in air. Similar procedures were followed for the preparation of **2**.

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7 In a typical experiment, a quantity *ca.* 50 mg of a sample of **1** or **2** is heated at 140 °C in the oven, for 30 min. After the identity of the intermediate is checked, the dry sample is placed in a glass desiccator, beside a water filled beaker or is suspended in a 'wet' solvent like diethyl ether or chloroform. The initial weight of the sample is restored faster in the solvents, and this procedure can be repeated at least three times without any significant background in the XRPD patterns of the rehydrated samples.

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