Molecular tectonics: structural and magnetic properties of a discrete copper binuclear complex and a 1-D coordination network

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Two new copper complexes **2** ($[Cu_2(pyS_4)Cl_4]\cdot 2CHCl_3$) and **3** ($[Cu_2(pyS_4)Cl_2]^{2+}\cdot 2BF_4^-$) have been prepared, their crystal structures elucidated and their magnetic properties studied. Compound **2** is a discrete binuclear copper (II) complex. The geometry around the metal centre is a distorted square pyramid. Compound **3**, in contrast, is an infinite coordination network formed upon mutual bridging of binuclear species through chloride atoms. Again, the geometry around each copper atom is closed to a square pyramid. The packing of the 1-D coordination networks generates channels which are occupied by BF_4^- anions. The magnetic behaviour observed for the 1-D network is comparable to the one corresponding to a discrete chloro-bridged copper (II) binuclear complex. In terms of magnetic coupling, whereas a strong ferromagnetic coupling is observed between the two spin bearers within the dimer ($d = 3.467$ Å) ($J/k_B = 337$ K), a weak interdimer antiferromagnetic interaction is measured ($zJ'/k_B = -1.6$ K).

Introduction

The design of molecular architectures in the solid state is a subject of current investigations. In particular, the formation of coordination networks, hybrid metallo-organic molecular assemblies, has attracted much attention over the last decade.[1] These networks, based on the formation of coordination bonds, may be defined as infinite structures resulting from iterative self-assembly processes between organic and metallic tectons (active building blocks). Dealing with structural aspects, the knowledge accumulated over the last years permits with an acceptable degree of confidence the design of coordination networks with defined connectivity and dimensionality. The generation of coordination networks in the solid-state results on one hand from the binding events taking place between the coordinating sites located on the organic tecton and the available coordination sites on the metal centre thus defining the assembling cores, and on the other hand, the iteration of the binding process allowing the translation of the assembling cores which become nodes of the network. The dimensionality of the network, *i.e.* 1-, 2- or 3-D, is defined by the number of translations of one or several assembling cores into one, two or three directions of space respectively.

The majority of coordination networks reported are based on the use of cationic metal centres. This implies, for charge neutrality reasons, either the presence of an anionic organic tecton or the presence of anions in the case of neutral organic tectons. For the latter case, two possibilities based on the coordination ability of the anion may be envisaged. Non coordinating anions will be present in the solid but without interactions with the cationic metallic centres, whereas for coordinating anions they will be located within the coordination sphere of the cationic metals. As previously demonstrated by us, one may use the latter possibility to direct the formation of the network.[2]

Dealing with molecular networks, in particular for coordination polymers, the passage between structural and functional assemblies remains a further and important step to be realised. In other words, the incorporation of physical properties at the level of the building blocks should in principle lead to functional networks. These properties may be in the areas of optics, electronics or magnetism. For the latter case, a variety of materials with various dimensionality ranging from isolated species to 1-D chains, 2-D sheets or three-dimensional networks displaying specific magnetic properties have been produced.[3] Pursuing our efforts in the design of coordination networks in the crystalline phase,[4] we report here the synthesis of a discrete binuclear Cu(II) complex, its extension to a 1-D coordination network as well as magnetic studies on both compounds.

The organic tecton **1** (Scheme 1), a symmetrical bis-tridentate ligand based on two pyridines and four thioether units of Py_2S_4 type was chosen because of its ability to generate 1- and 2-D networks with transition metals, in particular with Cd(II).[5] In the latter case, we have previously demonstrated that depending on the binding ability of the anion used, 1-D or a 2-D coordination networks may be generated. Indeed, whereas in the presence of chloride anion a 1-D network is formed, the use of a mixed cadmium salt ($CdClBF_4$), a 2-D network is generated.[5] For both cases, the metal centre adopts an octahedral coordination geometry and the networks are obtained through bridging of metallic centres by chloride anions.

Based on the above mentioned observation, demonstrating the important role played by the anion in the formation and dimensionality of coordination network, the approach was further extended to the design of a functional network based on Cu(II) as magnetically active centre. The approach was further supported by the rather short distance (3.94 Å) observed between chloro bridged diamagnetic cadmium

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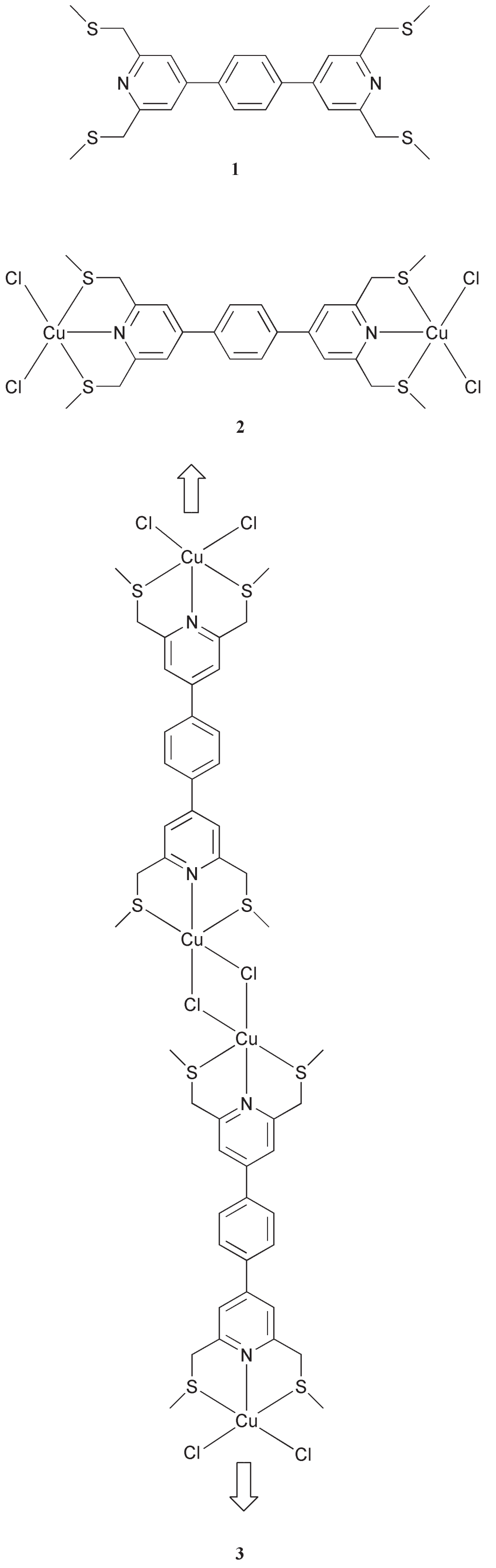

Scheme 1

cations which, in the case of Cu(II) could lead to reasonable magnetic interactions between paramagnetic centres.

Many extended coordination networks based on bridging of transition metal ions by halogen atoms or organic ligands have been reported.[6] Both in terms of intermolecular and intramolecular magnetic interactions between paramagnetic metal centres bridged by multi-atomic units (halogens, organic ligand), Cu(II) based networks containing N donor sites have been extensively studied.[7] As an example, an antiferromagnetic coupling constant of *ca.* -200 cm^{-1} was reported for a chain containing a 2,2′-bipyrimidine ligand and octahedral Cu(II) atoms, with the shortest Cu–Cu distance of 3.60 Å.[6b] For the majority of dimeric species studied antiferromagnetic interactions have been observed.[8] However, few examples of ferromagnetic coupling for dimeric species have been reported. In particular, recently, a ferromagnetic coupling with a J value of *ca.* $+50$ cm^{-1} has been reported for a distorted square pyramidal binuclear copper complex.[9]

Results and discussion

Structural analysis

Both solid materials **2** and **3** were obtained as single crystals upon slow liquid–liquid diffusion (see Table 1 for X-ray data). Both solids have been also synthesised as polycrystalline samples and characterised by elemental synthesis which revealed the presence of water molecules in the case of **3**.

The discrete neutral binuclear complex **2** was formed in a mixture of solvents using a 1 : 1 ratio of **1** and $CuCl_2$ (see experimental section for details). The structural study on single crystal revealed the following features (Fig. 1): the crystal is composed of discrete binuclear complexes **2** and $CHCl_3$ solvent molecules. The binuclear complex presents a centre of symmetry. For the organic ligand, both pyridine rings are tilted by *ca.* 47° with respect to the phenyl group. The CS

Table 1 Data collection and refinements for **2** and **3**

	2	**3**
Empirical Formula	$C_{24}H_{28}Cl_4Cu_2N_2S_4\cdot 2CHCl_3$	$C_{24}H_{28}Cl_2Cu_2N_2S_4\cdot 2BF_4$
Molecular weight [g mol^{-1}]	980.41	844.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a [Å]	9.7076(3)	32.475(3)
b [Å]	12.6420(3)	13.496(2)
c [Å]	16.1419(3)	8.7380(5)
α [°]		
β [°]	98.468(2)	96.335(6)
γ [°]		
V [Å^3]	1959.4(2)	3806(1)
Z	2	4
Color	Blue	Blue
Crystal size [mm]	0.20 × 0.15 × 0.10	0.20 × 0.12 × 0.04
ρ_{calcd} [g cm^{-3}]	1.66	1.47
$F(000)$	984	1696
μ [mm^{-1}]	2.003	1.534
Temperature [K]	173	294
λ [Å]	0.71073	0.71073
Radiation	MoK_α graphite monochromated	MoK_α graphite monochromated
Diffractometer	KappaCCD	KappaCCD
Scan mode	phi scans	phi scans
h/k/l ranges	0,11/0,15/−18,17	0,42/−17,17/−11,11
φ range for collection [°]	2.5/28.06	2.5/27.54
Number of reflections collected	13 947	9265
Number of data with $I > 3$ s(I)	3042	2330
Weighting scheme	$4Fo^2/(\sigma^2(Fo^2) + 0.0064Fo^4)$	$4Fo^2/(\sigma^2(Fo^2) + 0.0009\ Fo^4) + 1.0$
Number of variables	199	199
R	0.033	0.057
Rw	0.063	0.102
GOF	1.327	1.616
Largest peak in final difference (eÅ^{-3})	0.607	0.432

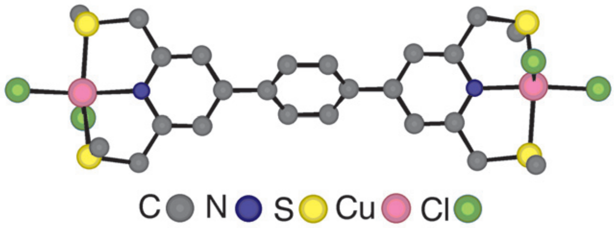

Fig. 1 X ray structure of the discrete binuclear copper complex **2** formed upon mixing the ligand **1** with $CuCl_2$. Solvent molecules and H atoms are not represented for the sake of clarity. For bond distances and angles see text.

and CN distances of 1.797 Å and of 1.345 Å and NCCS dihedral angles of −4.2° and −25.7° are roughly the same as those observed for the free ligand **1**.[5] For both Cu(II) atoms, the coordination sphere around the metal is composed of one N atom ($d_{N–Cu}$ = 2.015 Å), two S atoms ($d_{S–Cu}$ = 2.349 Å and 2.355 Å) and two terminal Cl^- anions with one short and one long Cu–Cl distances ($d_{Cl–Cu}$ = 2.248 Å and 2.462 Å). The coordination geometry for both metal centres is a distorted square pyramid (SCuN angles of 84.7° and 83.9°, NCuCl angles of 95.3° and 162.6°, SCuS angle of 157.5° and ClCuCl angle of 102.0°). The Cu–Cu distance is 15.343 Å. $CHCl_3$ solvent molecules are located between the dimeric units **2** with no specific interactions with them.

The one-dimensional network **3** was generated in a mixture of solvents using an equimolar ratio of tecton **1** and a mixed Cl^- and BF_4^- Cu(II) salt ($CuClBF_4$) (see experimental section). The single crystal structural study revealed the following features (Fig. 2): the crystal is exclusively composed of **1**, Cu(II) atoms, Cl^- and BF_4^- anions. No solvent molecule is present in the solid. Tecton **1**, Cu(II) dication and Cl^- anion form a cationic 1-D coordination network. The 1-D network **3** results from the translation into one direction of space of the assembling cationic core defined by $[pyS_4Cu_2Cl_2]^{2+}$ unit. In other words, the network is generated through bridging of binuclear complexes **2** by both chloride centres. The charge neutrality is then achieved by BF_4^- anions occupying the empty space in the lattice.

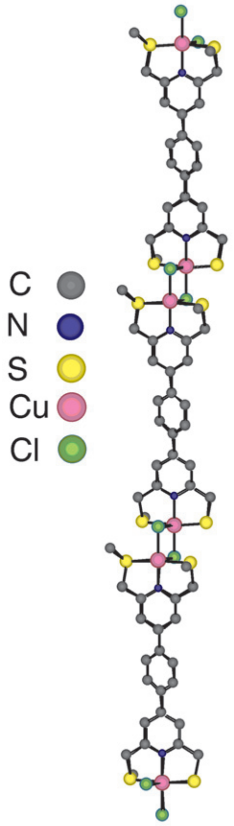

Fig. 2 A portion of the X ray structure of the infinite 1-D coordination network **3** obtained upon self-assembly between tecton **1** and $CuClBF_4$ mixed salt. Only one 1-D network is represented. BF_4^- anions and H atoms are not represented for the sake of clarity. For bond distances and angles see text.

For the ligand part, the pyridine rings are again tilted by about 30° and 33° with respect to the phenyl group. The CS and CN distances of 1.812 Å and of 1.352 Å are roughly the same as those observed for the free ligand **1**[5] and for the discrete binuclear complex **2** mentioned above. The NCCS dihedral angles are 23.5° and 21.2°.

The copper(II) cation is again surrounded by five donor atoms with its coordination sphere composed of one N atom ($d_{N–Cu}$ = 1.971 Å), two S atoms ($d_{S–Cu}$ = 2.314 Å and 2.325 Å) and two bridging Cl^- anions with again one short and one long Cu–Cl distance ($d_{Cu–Cl}$ = 2.239 Å and 2.828 Å). The coordination geometry around the Cu(II) centre is again a distorted square pyramid (SCuN angles of 86.4° and 85.6°, NCuCl angles of 89.2° and 176.3°, SCuS angle of 171.9° and ClCuCl angle of 94.5°). The distance between two Cu atoms located at each extremity of the tecton **1** of 15.323 Å is close to the one mentioned above for the discrete binuclear complex **2** (15.343 Å). The Cu–Cu distance between halide bridged centres is 3.467 Å. This distance is shorter than the one observed for $[Cu_2(dpt)_2Cl_2]Cl_2$ dimeric analogue compound (3.55 Å).[8] Both Cu(II) cations and chloride anions are coplanar forming thus a rectangle with CuClCu angle of 85.5°.

Within a layer, perpendicular to the c axis, the 1-D networks are packed in a parallel fashion. For consecutive layers, the 1-D networks are tilted by 30° (Fig. 3). This arrangement of layers in the crystal leads to the formation of large channels with a diameter of *ca.* 10.8 Å. The tubular space thus generated is occupied by BF_4^- anions. The analysis of the packing of 1-D networks reveals a distance of *ca.* 4.2 Å between superimposed phenyl rings of the tecton **1**. The shortest interchain Cu–Cu distance is 7.6 Å.

The main difference between the discrete binuclear complex **2** and the 1-D coordination network **3** generated in the presence of **1** and the 1- and 2-D networks obtained with Cd(II)[5] is due to the coordination geometry around the metallic centre. Indeed, whereas in the case of Cd(II), the metal centre adopts an octahedral coordination geometry thus allowing the formation of 1- and 2-D networks depending on the number of bridging chloride anions, in the case of Cu(II) adopting a square pyramidal geometry, one would expect either the discrete binuclear complex **2** in the absence of any bridging or the infinite 1-D network **3** for the bridging situation.

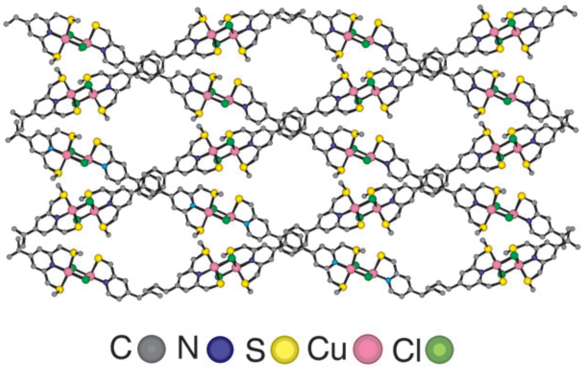

Fig. 3 A portion of the X ray structure of **3** showing the packing of consecutive 1-D networks leading to the formation of channels. BF_4^- anions and H atoms are not represented for sake of clarity.

Magnetic properties

The $\chi_M T$ values at room temperature are equal to 0.78 and 0.83 $cm^3\,K\,mol^{-1}$ for the discrete binuclear complex **2** and for the infinite network **3** respectively. These values are in accordance with two non interacting 1/2 spins centred on Cu(II) cations.

For the complex **2**, the two paramagnetic Cu(II) centres behave as two almost isolated spins. However, below 25 K, a decrease of the χT product is observed indicating a weak antiferromagnetic interaction.

For the infinite network **3**, the $\chi_M T$ *vs.* T curve is shown on Fig. 4. The $\chi_M T$ value increases continuously when temperature decreases, with a maximum value of 0.92 $cm^3\,K\,mol^{-1}$ at *ca.* 80 K. This is in agreement with a ferromagnetic interaction between both Cu(II) spin bearers. Below this maximum, $\chi_M T$ value decreases with temperature, which is consistent with a weak interchain antiferromagnetic interaction. Since the origin of such possibly efficient magnetic interchain contacts is not well addressed, the overall behaviour was simulated by introducing a mean field correction to the dimer equation representing the singlet–triplet (ST) equilibrium:

$$\chi T = \frac{\chi_{ST} T}{1 - \frac{\chi_{ST} zJ'}{k_B}}$$

with $\chi_{ST} = \frac{3C}{T\left(3 + e^{\frac{J}{k_B T}}\right)}$ where $C = \frac{2Ng^2\beta^2}{3k_B}$

A rather good fit is obtained ($R = 0.997$) with a triplet ground state and a ST gap $J/k_B = 337 \pm 10$ K and an antiferromagnetic mean field correction $zJ'/k_B = -1.6 \pm 0.1$ K and $g = 2.04$.

Magnetisation *vs.* field experiments, performed at 4 K up to a field at 60 000 G for compounds **2** and **3**, exhibit a Brillouin function behaviour close to the one expected for a S = 1 ground state. For both **2** and **3** systems, no hysteresis was observed.

The EPR spectra of a polycrystalline sample of **2** or **3** recorded at room temperature are assigned to isolated Cu(II) species with an axial g tensor ($g_\perp = 2.060$; $g_\parallel = 2.015$; $g_{av} = 2.045$ for both compounds). It is worth noting that the measured value of the average g-factor is close to the value given for the fit of the magnetic susceptibility data.

In the case of the 1-D network **3**, a relatively strong ferromagnetic interaction between two μ-chloro bridged Cu(II) atoms was obtained. The high value of 337 K given by the fit is substantially higher than the 50 cm^{-1} reported for the analogous $Cu_2(dpt)_2Cl_2]Cl_2$ complex for which the Cu(II) atom adopts the same square pyramidal geometry.[9] This may be explained by the short distance (3.46 Å) between the Cu(II) atoms observed in the case of the infinite network **3** instead of 3.55 Å for the $[Cu_2(dpt)_2Cl_2]Cl_2$ complex, as well as a different CuClCu angle (85.5° in the case of **3** and 90.1° for the $[Cu_2(dpt)_2Cl_2]Cl_2$ complex).

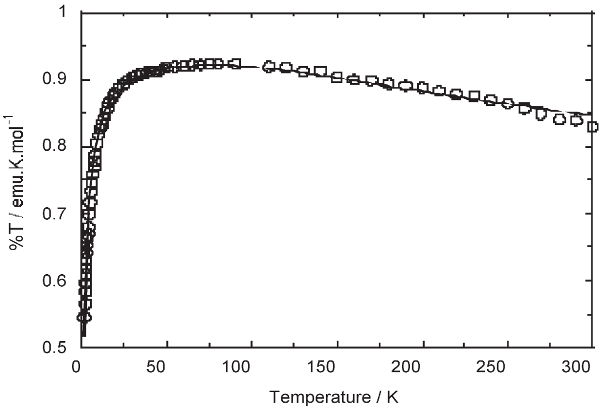

Fig. 4 $\chi_M T$ *vs.* T experimental data for the infinite 1-D coordination network **3**. The best fit is represented by the solid line.

However, no real one-dimensional magnetic behaviour is observed for the network **3**, although a weak interdimer antiferromagnetic interaction resulting probably from the interchain distance of *ca.* 7 Å could be detected.

Conclusion

In conclusion, using the tecton **1**, a symmetrical bis-tridentate unit of the Py_2S_4 type and Cu(II) cation, the binuclear discrete complex **2** as well as the infinite 1-D coordination network **3** have been obtained and structurally characterised in the solid state by X-ray diffraction method on single crystals. Whereas for the discrete complex **2**, the two paramagnetic Cu(II) cations behaved as almost independent centres, for the infinite network **3**, the magnetic study revealed strong ferromagnetic interactions between the Cu(II) centres, probably the highest observed for a square pyramidal μ-chloro bridged copper system. However, no cooperative phenomenon was observed between the dimers.

Experimental section

The synthesis of the ligand **1** has been previously described.[5] The synthesis of the mixed Cl^- and BF_4^- Cu(II) salt, ($CuClBF_4 \cdot xH_2O$), was achieved by mixing an equimolar ratio of $CuCl_4 \cdot 2H_2O$ and $NaBF_4$.

Synthesis of the discrete binuclear complex 2. Slow diffusion at room temperature of a MeOH solution containing $CuCl_2 \cdot 2H_2O$ (6×10^{-6} moles) into a $CHCl_3$ solution of the ligand **1** (6×10^{-6} moles) afforded green crystals after 24 h. The microcrystalline material could also be obtained at room temperature upon mixing a MeOH solution of $CuCl_2 \cdot 2H_2O$ (6×10^{-3} moles) with a $CHCl_3$ solution of the ligand **1** (6×10^{-3} moles). The green precipitate was then filtered and dried under vacuum. Molecular formula: $C_{24}H_{28}Cl_4Cu_2N_2S_4 \cdot 2CHCl_3$ (980.41 g mol^{-1}). Elemental analysis: calcd: C: 31.9%, H: 3.1%, N: 2.9%; found: C: 31.0%, H: 3.1%, N: 2.9%.

Generation of the 1-D network 3. Slow diffusion at room temperature of an EtOH solution containing $CuClBF_4 \cdot H_2O$ (6×10^{-6} moles) into a $CHCl_3$ solution of the ligand **1** (6×10^{-6} moles) afforded blue-green crystals. The microcrystalline material could also be obtained by mixing an EtOH solution of $CuClBF_4 \cdot H_2O$ (6×10^{-3} moles) with a $CHCl_3$ solution of **1** (6×10^{-3} moles). The blue-green precipitate was then filtered and dried under vacuum. Molecular formula for the crystals: $C_{24}H_{28}Cl_2Cu_2N_2S_4 \cdot 2BF_4$ (844.36 g mol^{-1}). Elemental analysis: calcd (with 5 supplementary H_2O molecules): C: 30.9%, H: 4.1%, N: 3.0%; found: C: 31.6%, H: 3.2%, N: 2.9%.

Characterisation and physical measurements

The EPR spectra of polycrystalline powders were recorded at 100 K and at room temperature using an ESP 300 E spectrometer (BRUKER). A TE102 rectangular cavity was used, and all spectrometers parameters were adjusted so as to reach the best S/N ratio without distorting the signal.

Magnetic susceptibility data of the powdered samples were collected with a MPMS Quantum Design SQUID magnetometer in the temperature range of 300–1.8 K at a field of 1000 G. The sample holder was a quartz tube. The output data were corrected for the experimentally determined diamagnetism of the sample holder and the diamagnetism of the samples calculated from Pascal's constants.

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 all structures, diffraction data were corrected for absorption and analysed using OpenMolen package.[10] All non-H atoms were refined anisotropically. CCDC reference numbers 215577 and 215578 See http://www.rsc.org/suppdata/nj/b3/b308944b/ for crystallographic data in .cif or other electronic format.

X-ray data for the discrete binuclear complex **2** and the infinite network **3** are summarised in Table 1.

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