CHEMCOMM
Communication
www.rsc.org/chemcomm

Interlinked molecular squares with $[Cu(2,2'\text{-bipy})]^{2+}$ corners generating a three-dimensional network of unprecedented topological type

Lucia Carlucci,[a] Gianfranco Ciani,*[b] Davide M. Proserpio[b] and Silvia Rizzato[b]

[a] *Dipartimento di Biologia Strutturale e Funzionale, Università dell'Insubria, Via J. H. Dunant 3, 21100 Varese, Italy*
[b] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica and Centro CNR, Via G. Venezian 21, 20133 Milano, Italy. E-mail: davide@csmtbo.mi.cnr.it*

Received (in Cambridge, UK) 25th April 2001, Accepted 24th May 2001
First published as an Advance Article on the web 13th June 2001

A noteworthy three-dimensional framework, obtained by reacting the preformed molecular corner $[Cu(2,2'\text{-bipy})]^{2+}$ (with BF_4^- counter ions) and 1,2-bis(4-pyridyl)ethane (bpetha) in the presence of chlorides, contains molecular square units $[Cu(2,2'\text{-bipy})(bpetha)]_4$ that are linked *via* chloride bridges into a triconnected architecture of unprecedented topology.

In the rational development of new strategies for the crystal engineering of coordination networks[1] and of supramolecular architectures[2] the use of preformed metal-based units has assumed an increasing relevance in recent times. Molecular corners containing transition metals with programmed coordination angles can been employed for the self-assembly of frameworks and, especially, of macromolecular polygons and polyhedral cages,[3] of potential utility for molecular recognition. In particular, *cis*-protected Pd^{II} and Pt^{II} units have been widely employed for the building of molecular squares.[3,4] We are currently studying the use of a different corner unit, namely $[Cu(2,2'\text{-bipy})]^{2+}$ **1** (2,2′-bipy = 2,2′-bipyridyl), that contains two *cis*-equatorial and, possibly, also two axial free coordination sites, and is produced from the parent complex $[Cu(2,2'\text{-bipy})Cl_2]$ by removing the chlorides with different AgX salts of poorly coordinating anions (X = triflate, tetrafluoroborate or nitrate). These $[(\mathbf{1})X_2]$ species have already been reacted with a variety of bidentate spacer ligands, mainly affording one-dimensional zigzag polymeric chains.[5] Monochloride species $[(\mathbf{1})Cl]X$, obtained by removing only one half of the chloride content from the parent complex, were also employed, and, interestingly, the reaction of $[(\mathbf{1})Cl](BF_4)$ with 1,2-bis(4-pyridyl)ethane (bpetha) has produced the novel polymeric species $[\{(\mathbf{1})(bpetha)\}_2Cl(BF_4)](BF_4)_2\cdot 8.5H_2O$ **2**, containing molecular square units joined by bridging chloride ions into an extended array. We describe here this three-dimensional network, containing large interstitial cavities and exhibiting a topology unprecedented within coordination networks. We report also on a strictly related species, compound **3**, obtained using 1,2-bis(4-pyridyl)ethene (bpethe) as spacer, that, in spite of the similarity of the ligands, shows a completely different frame. Compound **2** is obtained in high yield in a two step process. In the first step the parent $[Cu(2,2'\text{-bipy})Cl_2]$ was treated with $AgBF_4$ in a 2 : 3 molar ratio in EtOH under stirring for 2 h. The solution was then filtered and layered on a solution of bpetha in CH_2Cl_2 (molar ratio Cu : bpetha from 1 : 1 to 1 : 3). After a few days beautiful blue crystals of **2** were obtained. Compound **3**, $[\{(\mathbf{1})(bpethe)\}_2Cl](BF_4)_3\cdot 2.5H_2O\cdot CH_2Cl_2$, was obtained in the same way, using in the second step the bpethe ligand in CH_2Cl_2 solution. Both species have been characterized by single crystal X-ray analysis.†

The crystal structure of **2** consists of $[(\mathbf{1})(bpetha)]_4$ square units interconnected *via* chloride bridges into a three-dimensional non-interpenetrated network. The squares are comprised of $[Cu(2,2'\text{-bipy})]^{2+}$ corners and bpetha edges, with a Cu···Cu separation of 13.23 Å (Fig. 1, top); they are moderately folded about their diagonal axes by *ca.* 27° (Fig. 1, bottom). Similar previously reported macrocyclic motifs, containing Pt^{II} or Pd^{II} corners, are all individual molecules, held together essentially by van der Waals interactions.[4] The peculiar structural feature of **2**, on the other hand, consists in that these square units are organized in an extended architecture sustained by slightly bent chloride bridges [Cu···Cu 5.12 Å, Cu–Cl 2.582(2) Å, Cu–Cl–Cu 164.3(2)°]. Each square is bound to four similar motifs, two

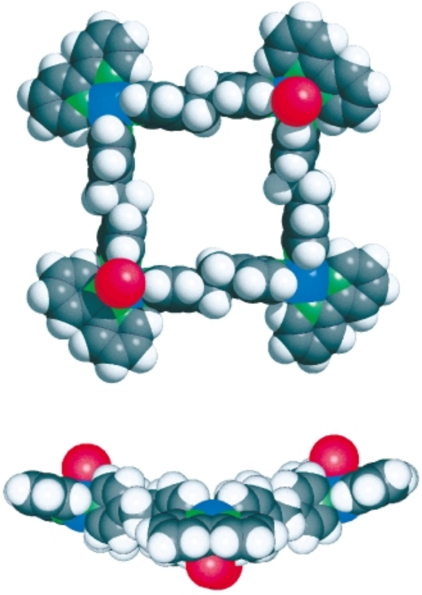

Fig. 1 Two views of the molecular squares in compound **2**.

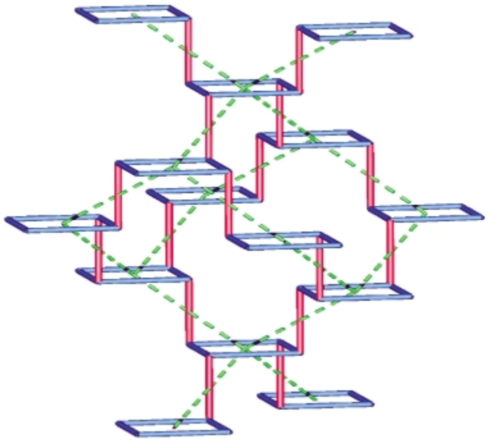

Fig. 2 A schematic view of the three-dimensional network in **2**, with the chloride bridges in red. The broken lines show the underlying diamondoid net, obtained by connecting the baricentres of the squares.

DOI: 10.1039/b103736f

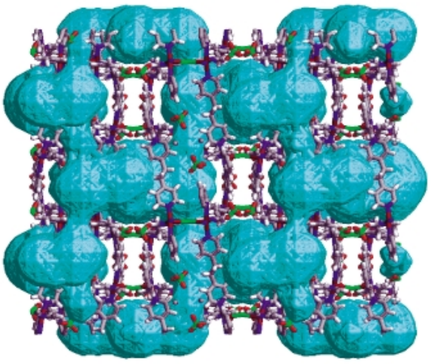

Fig. 3 The overall packing in **2** (down *a*, horizontal *c*) showing the surface of the large interconnected cavities.

above and two below the molecular plane, in an alternate fashion. The Cu^{II} coordination geometry is octahedral, with four equatorial Cu–N(pyridyl) bonds [in the range 2.00(1)–2.04(1) Å], one axial Cu–Cl bond and one axial weak interaction with a BF_4^- anion [Cu–F 2.79(1) Å].

The topology of this uninodal triconnected three-dimensional frame (Fig. 2) is $4{\cdot}14^2$, a relatively simple topological type already considered by Wells in his enumeration,[6] but completely new within coordination polymer chemistry. Interestingly, the baricentres of the squares define a diamondoid network (see Fig. 2), so that the net of **2** can be defined, according to O'Keeffe,[7] as an '*augmented diamond*' net.

The network contains large voids (38% of the cell volume),[8] with connected chambers (Fig. 3) that are filled by water molecules. Samples of **2** start to lose the solvated water at room temperature and TGA analyses show that all the water content (*ca.* 13% weight loss) is completely removed on heating up to *ca.* 120 °C, without demolition of the array (as confirmed by X-ray powder diffraction). Decomposition starts at *ca.* 180 °C, leading to copper metal above *ca.* 400 °C. The desolvated network, however, seems stable as such for an extended period and appears unable to regain solvated molecules to a significant extent even after immersion in different solvents (*e.g.* water, ethanol, isopropyl alcohol, toluene, CCl_4) for some days.

The structure of compound **3**, obtained under reaction conditions quite similar to those leading to **2** but using the bpethe ligand, consists of zigzag polymeric chains all running along the [3 0 1] direction (Cu···Cu contacts of 13.31 Å av.) connected by chloride bridges [Cu–Cl 2.511(1) Å, Cu–Cl–Cu 139.5(1)°] into two-dimensional sheets of six-membered rings (6^3 topology). The Cu^{II} coordination is of the square pyramidal type, with the axial Cu–Cl interaction and four equatorial Cu–N(pyridyl) bonds [in the range 2.012(5)–2.025(5) Å]. The layers are highly undulated, with crankshaft-like sections (Fig. 4, top) and exhibit two-fold parallel interpenetration (Fig. 4, bottom). Moreover, these double-layers are superimposed with high interdigitation involving the nearest neighbours. Again, the array contains large channels along [1 0 0] (28% of the cell volume), located inside the double-layers.

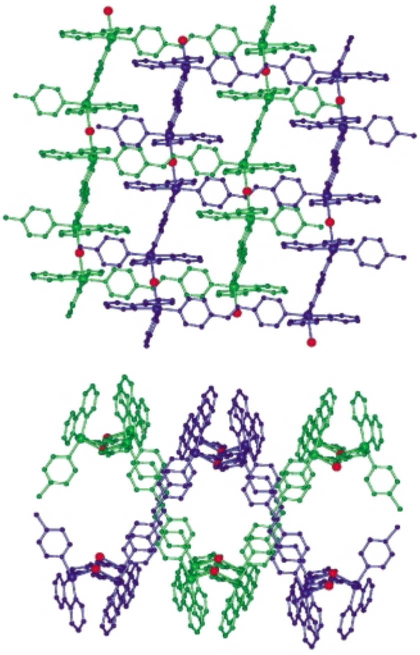

Fig. 4 A side view of the double-layer of **3** (top), showing the highly undulated shape of the sheets, and a view approximately down *b* showing the two-fold interpenetration (bottom). The Cl$^-$ ions are in red.

Such different structures for **2** and **3**, in the presence of similar framework stoichiometries, are difficult to rationalize. The higher rigidity of the bpethe ligand and the presence of solvated CH_2Cl_2 molecules in **3** can play some role. While the *ideal* elimination of the chloride ions from **3** leaves polymeric zigzag chains, similar to those recently reported,[5] in the case of **2** this process should result in isolated molecular motifs. However, attempts to disentangle the squares of **2** by dissolution were made impossible by its poor solubility in all common solvents.

Notes and references

† *Crystal data*: for **2**: $C_{44}H_{57}B_3ClCu_2F_{12}N_8O_{8.50}$, M = 1256.94, tetragonal, space group $I\bar{4}2d$ (no. 122), a = 21.479(2), c = 29.303(3) Å, U = 13519(2) Å^3, T = 223 K, Z = 8, μ(Mo-Kα) = 0.749 mm^{-1}, 25456 reflections measured, 5073 unique (R_{int} = 0.071) which were used in all calculations. The final agreement index $R1$ was 0.0982 for 2933 independent significant [$I > 2\sigma(I)$] absorption corrected data. All but one of the solvated water molecule were refined with partial occupancy.

For **3**: $C_{45}H_{43}B_3Cl_3Cu_2F_{12}N_8O_{2.50}$, M = 1229.73, monoclinic, space group $C2/c$ (no. 15), a = 11.457(5), b = 40.814(17), c = 14.502(6) Å, β = 111.42(1)°, U = 6313(5) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 0.875 mm^{-1}, 14189 reflections measured, 4937 unique (R_{int} = 0.054) which were used in all calculations. The final agreement index $R1$ was 0.0851 for 3240 independent significant [$I > 2\sigma(I)$] absorption corrected data. All the solvated water molecules were refined with half occupancy and suitable disordered models were applied to both anions.

CCDC 164240–164241. See http://www.rsc.org/suppdata/cc/b1/b103736f/ for crystallographic data in CIF or other electronic format.

1 R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, in *Supramolecular Architecture*, ACS, Washington DC, 1992, ch. 19; M. J. Zaworotko, *Chem. Soc. Rev.*, 1994, 283; O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474; M. Munakata, L. P. Wu and T. Kuroda-Sowa, *Adv. Inorg. Chem.*, 1999, **46**, 173; P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.

2 *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, Pergamon Press, Oxford, 1995.

3 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; M. Fujita, *Acc. Chem. Res.*, 1999, **32**, 53; M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509.

4 M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645; M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249; M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535; S. B. Lee, S. Hwang, D. S. Chung, H. Yun and J.-I. Hong, *Tetrahedron Lett.*, 1998, **39**, 873.

5 L. Carlucci, G. Ciani, A. Gramaccioli, D. M. Proserpio and S. Rizzato, *CrystEngComm*, 2000, **29**.

6 A. F. Wells, *Three-dimensional Nets and Polyhedra*, J. Wiley & Sons, New York, 1977, p. 80.

7 Complete symbol is $4{\cdot}14_{12}{\cdot}14_{12}$ see: M. O'Keeffe and B. G. Hyde, *Crystal Structures I. Patterns and Symmetry*, Mineralogical Society of America, Washington, DC, 1996; M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3.

8 An analysis of the holes was performed with the PLATON program: A. L. Speck, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, 1999. The graphic representation of the surfaces of the cavities was obtained with SURFNET: R. A. Laskowski, *J. Mol. Graph.*, 1995, **13**, 323.