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

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A noteworthy three-dimensional framework, obtained by reacting the preformed molecular corner [Cu(2,2'-bipy)]²⁺ (with BF₄⁻ counter ions) and 1,2-bis(4-pyridyl)ethane (bpetha) in the presence of chlorides, contains molecular square units [Cu(2,2'-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 networks¹ and of supramolecular architectures² 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 be 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 PdII and PtII 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'-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'-bipy)/Cl]₂ by removing the chlorides with different AgX salts of poorly coordinating anions (X = triflate, tetrafluoroborate or nitrate). These [(I)X₂] species have already been reacted with a variety of bidentate spacer ligands, mainly affording one-dimensional zigzag polymeric chains.⁵ Monochloride species [(I)Cl]X, obtained by removing only one half of the chloride content from the parent complex, were also employed, and, interestingly, the reaction of [(I)Cl]BF₄ with 1,2-bis(4-pyridyl)ethane (bpetha) has produced the novel polymeric species [(I)(bpetha)]₂Cl[BF₄] with 8.5H₂O 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 (bpetha) 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'-bipy)/Cl]₂ was treated with AgBF₄ 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 CH₂Cl₂ (molar ratio Cu:bpetha from 1:1 to 1:3). After a few days beautiful blue crystals of 2 were obtained. Compound 3, [(I)(bpetha)]₂Cl[BF₄] with 2.5H₂O-CH₂Cl₂, was obtained in the same way, using in the second step the bpetha ligand in CH₂Cl₂ solution. Both species have been characterized by single crystal X-ray analysis.⁷ The crystal structure of 2 consists of [(I)(bpetha)]₄ square units interconnected via chloride bridges into a three-dimensional non-interpenetrated network. The squares are comprised of [Cu(2,2'-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 PtII or PdII 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](image1.png)

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

![Fig. 2](image2.png)

**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.
above and 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 4–12, a relatively simple topological type already considered by Wells in his enumeration, 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 the large interconnected cavities. The overall packing in Fig. 4 shows the surface of the large interconnected cavities.

The higher rigidity of the bpethe ligand and the presence of similar framework stoichiometries, are difficult to rationalize. However, attempts to disentangle the squares of 3 by dissolution were made impossible by its poor solubility in all common solvents.

Notes and references


8 An analysis of the holes was performed with the PLATON program: A. L. Spek, 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.