

Nanoporous three-dimensional networks topologically related to Cooperite from the self-assembly of copper(I) centres and the "square-planar" building block 1,2,4,5-tetracyanobenzene

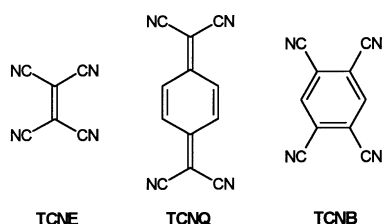
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The deliberate assembly of a Cu^{I} 3D coordination network with the Cooperite (PtS) topology, namely $[\text{Cu}(\mu_4\text{-TCNB})][\text{PF}_6]$ **1**, has been accomplished by using the pseudo-square-planar building block 1,2,4,5-tetracyanobenzene (TCNB). It has been obtained by reacting $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with TCNB (in molar ratio 1 : 1) in solvent mixtures of CH_2Cl_2 and of a poorly basic solvent, like ethanol, isopropanol, benzyl alcohol or acetone. The crystals are orthorhombic, space group *Cccm*, with $a = 8.157(1)$, $b = 18.634(2)$, $c = 11.613(1)$ Å, $Z = 4$. The framework is based on tetrahedral Cu^{I} centres and tetradentate μ_4 -TCNB ligands and presents cavities containing guest solvent molecules. On performing the same reaction in CH_2Cl_2 -THF a 3D three-connected polymeric species, $[\text{Cu}(\mu_3\text{-TCNB})(\text{THF})][\text{PF}_6]$ **2**, is obtained. Compound **2** gives monoclinic crystals, space group *P2₁/c*, with $a = 21.617(2)$, $b = 11.127(3)$, $c = 16.294(2)$ Å, $\beta = 111.61(2)^\circ$, $Z = 8$. In **2** the TCNB ligands are tridentate and the copper centres achieve a tetrahedral coordination on forming a bond with a THF molecule. The network presents an unprecedented topology, $(8^210)\text{-b}$, and the crystals undergo, by thermal activation, an unusual crystal-to-crystal transformation, losing the THF molecules to give the same frame as **1**.

Many efforts in the crystal engineering of networked materials based on polymeric coordination compounds^{1,2} have been devoted to the use of novel suitably tailored polydentate ligands. Polycyano ligands, neutral and anionic, are attracting a growing interest,³ both for their electronic properties and also for their different bonding modes and variable *hapticity*. In particular, some tetracyano species like TCNE (tetracyanoethene) and TCNQ (7,7,8,8-tetracyanoquinodimethane) can potentially act as planar μ_4 -bridging groups, as, indeed, found in some previously reported polymeric species.^{4,5}



The self-assembly of ligands like these with tetrahedral metal centres can produce open nanoporous frameworks related to the prototypical structure of Cooperite (PtS, Fig. 1, top), containing a 1 : 1 ratio of tetrahedral and square-planar nodes. Networked materials with this topology (4^28^4),⁶ have been deliberately assembled by using tetrahedral Cu^{I} ions together with square-planar *metal* centres, like $[\text{Pt}(\text{CN})_4]^{2-}$ ⁷ or metalloporphyrins,⁸ but also a suitable organic group can play the same role of a square-planar coordination centre, as found in the case of the two-fold interpenetrated PtS-like network of $[\text{Ag}(\text{TCNQ})]$,⁹ schematically shown in Fig. 1 (bottom).

Our previous attempts to build a PtS-like net using TCNE together with Ag^{I} or Cu^{I} ions were unsuccessful, resulting in frames of different topology because of the transformation of the ligand, under the reaction conditions, into a non-planar carbanionic acetonide derivative.¹⁰ We report here on the reac-

tions of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with 1,2,4,5-tetracyanobenzene (TCNB), leading to a Cooperite-like framework, $[\text{Cu}(\mu_4\text{-TCNB})][\text{PF}_6]$ **1**, in solution mixtures of CH_2Cl_2 with different poorly basic solvents (like acetone, ethanol, isopropanol, benzyl alcohol), and to a three-connected net of uncommon topology, $[\text{Cu}(\mu_3\text{-TCNB})(\text{THF})][\text{PF}_6]$ **2**, in CH_2Cl_2 -THF

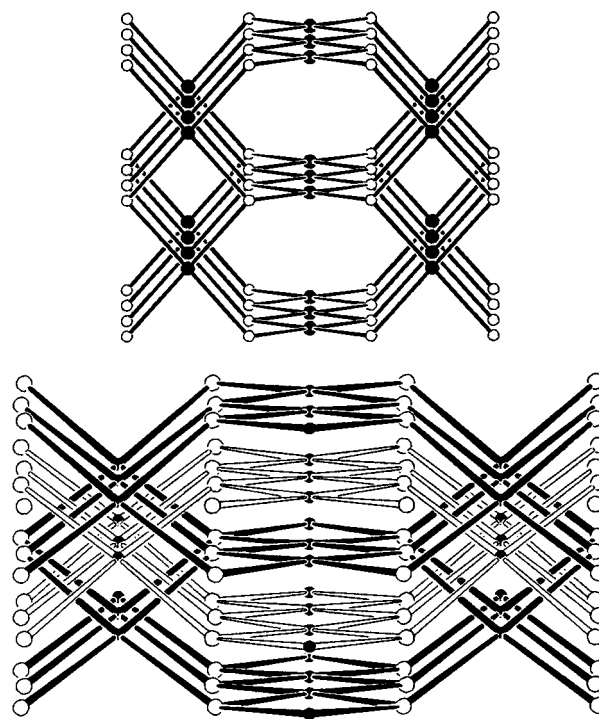


Fig. 1 The prototypical network of Cooperite (PtS) viewed down the [1 0 0] direction (top) and a schematic view of the two-fold interpenetrated PtS-like net of $[\text{Ag}(\text{TCNQ})]$ (bottom, black balls = baricentres of the TCNQ ligands).

(THF = tetrahydrofuran). Compounds **1** and **2** can be inter-converted and the noteworthy crystal-to-crystal transformation of **2** into **1** under thermal activation is also demonstrated. During the preparation of this manuscript another study on the reactivity of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with TCNB has been reported by Munakata *et al.*,¹¹ leading to quite different polymeric products, of composition $[\text{Cu}_2(\text{TCNB})_3][\text{PF}_6]_2$, due to the use of a large stoichiometric excess of the TCNB ligand.

Results and discussion

Reactivity of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with TCNB

The reactions of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with TCNB were performed in different solvents using a 1 : 1 molar ratio of the reagents. The metal complex was dissolved in CH_2Cl_2 and treated with solutions of TCNB in ethanol, isopropanol, benzyl alcohol, acetone or THF. A yellow microcrystalline product is rapidly formed under stirring, which gives, after filtration and drying, rather variable analyses corresponding approximately to the 1 : 1 adduct $[\text{Cu}(\text{TCNB})][\text{PF}_6]$ **1**. Crystals were grown in few days by slow diffusion, upon carefully layering the solution of the ligand on that of the metal complex. Similar elongated yellow crystals were obtained from the acetone, ethanol, benzyl alcohol or isopropanol solutions, containing the same 3D polymeric network, as confirmed by X-ray diffraction analyses performed on crystals of all the samples.

From the CH_2Cl_2 –THF system, on the other hand, by slow diffusion beautiful flattened hexagonal shaped orange-yellow crystals separated, corresponding to $[\text{Cu}(\mu_3\text{-TCNB})(\text{THF})][\text{PF}_6]$ **2**, containing a different 3D polymeric network, characterized by X-ray analysis.

It is interesting to note that the reactions of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ with a large excess (five-fold) of TCNB give two different polymeric species on varying the solvent, *i.e.* $[\text{Cu}_2(\mu_2\text{-TCNB})(\mu_4\text{-TCNB})_2][\text{PF}_6]_2 \cdot 4\text{Me}_2\text{CO}$ in acetone and $[\text{Cu}_2(\mu_2\text{-TCNB})(\mu_4\text{-TCNB})_2][\text{PF}_6]_2$ in methylethyl ketone.¹¹ The former contains 2D undulated layers while the latter consists of a two-fold interpenetrated 3D net topologically related to the SiO_2 polymorph moganite.¹²

The three-dimensional networks of **1** and **2**

The crystal structure of **1** consists of a 3D net based on an equal number of planar tetradentate organic centres and distorted tetrahedral Cu^{I} ions [$\text{Cu}-\text{N}$ 1.969(4) Å, $\text{N}-\text{Cu}-\text{N}$ 95.2(3)–117.2(2)°], with the desired PtS-like topology (see Fig. 2). The TCNB ligands (as well as TCNE and TCNQ) can be better described as “rectangular” rather than square centres (with intraligand $\text{N}\cdots\text{N}$ long and short rectangular edges having a ratio of *ca.* 1.8 : 1). The channels of the network are occupied by the PF_6^- anions and by highly disordered solvent molecules, which are difficult to rationalize (see below). In contrast to what was observed for the two-fold interpenetrated $[\text{Ag}(\text{TCNQ})]$ (Fig. 1, bottom), compound **1** contains a single net, very probably due both to the smaller dimensions of the TCNB ligand and to the presence of the counter ions.

The deliberate construction of a PtS-like framework, using proper building blocks, has thus been successfully carried out. The same topology has also been obtained by the self-assembly of TCNB and AgSbF_6 .¹³ Significantly, these networks (both in the Cu^{I} and in the Ag^{I} species) are not interpenetrated.

The structure of compound **2**, $[\text{Cu}(\mu_3\text{-TCNB})(\text{THF})][\text{PF}_6]$, reveals a different 3D frame. The TCNB ligands use only three of the four nitrile groups for bonding to Cu^{I} ions, which are connected to three such groups [$\text{Cu}-\text{N}$ 1.915(7)–1.999(7) Å] and to the oxygen atom of a THF molecule [$\text{Cu}-\text{O}$ 2.117(7)

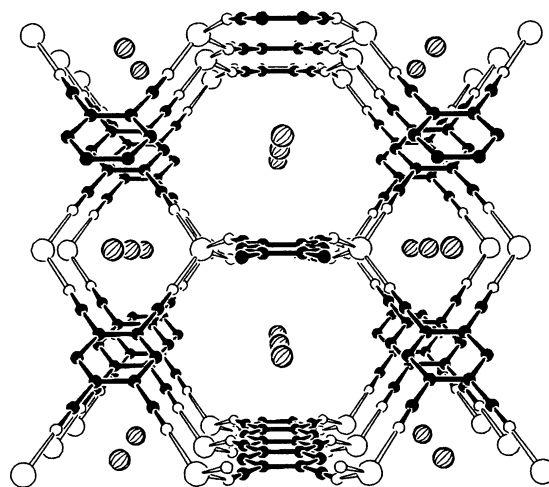


Fig. 2 A SCHAKAL perspective view of the framework of **1** down $[1\ 1\ 0]$, oriented to show the PtS topology (*cf.* Fig. 1 top). Hatched spheres represent the P atoms of the PF_6^- anions.

and 2.119(7) Å] in a distorted tetrahedral geometry. In this case, in contrast to **1**, the solvent molecules are able to enter into the metal coordination sphere, replacing a bound CN group. The coordination is illustrated in Fig. 3, which shows the shortest circuit in the net, consisting of alternated four Cu^{I} ions and four TCNB ligands.

From a topological point of view, the 3D frame is comprised of three-connected metallic and organic centres in equal ratio, which form a system of alternating 4_1 and 4_3 interconnected parallel helices, extending in the *b* direction. It was classified by Wells⁶ as the Archimedean 3D net $(8^210)\text{-b}$ (see Fig. 4) and, to the best of our knowledge, no example of this type has been previously reported.

In spite of the different topology, the structure of **2** displays a great resemblance to that of **1**, as can be seen on comparing the projection of the frame of **1** down *c* with that of **2** down *b* (Fig. 5). This structural similarity can account for the crystal-to-crystal transformation of the two species, that is described below.

The nanoporous network of compound **1**

When compound **1** is rapidly precipitated under stirring it gives polycrystalline samples whose X-ray powder diffraction patterns are almost identical whichever solvent system is used; this is also the case for the THF– CH_2Cl_2 mixture, if the precipitate is immediately removed from the mother-liquor. Single crystals are grown within a few days by slow mixing of the solution of the metal complex in CH_2Cl_2 and the solution of TCNB in the second solvent. All these single crystals give very similar cell parameters, with the exception of those obtained from THF– CH_2Cl_2 (compound **2**). Structure

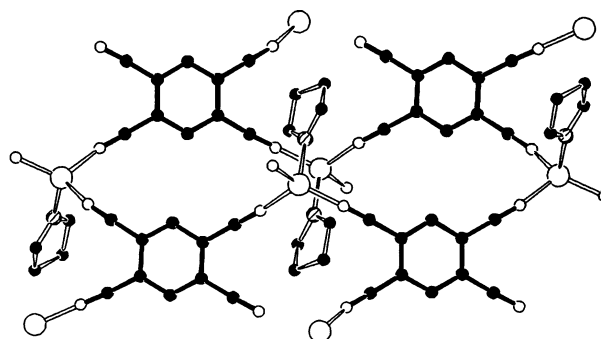


Fig. 3 The shortest circuit in the network of **2**, showing the tri-connected TCNB ligands and the distorted tetrahedral coordination of the Cu^{I} ions.

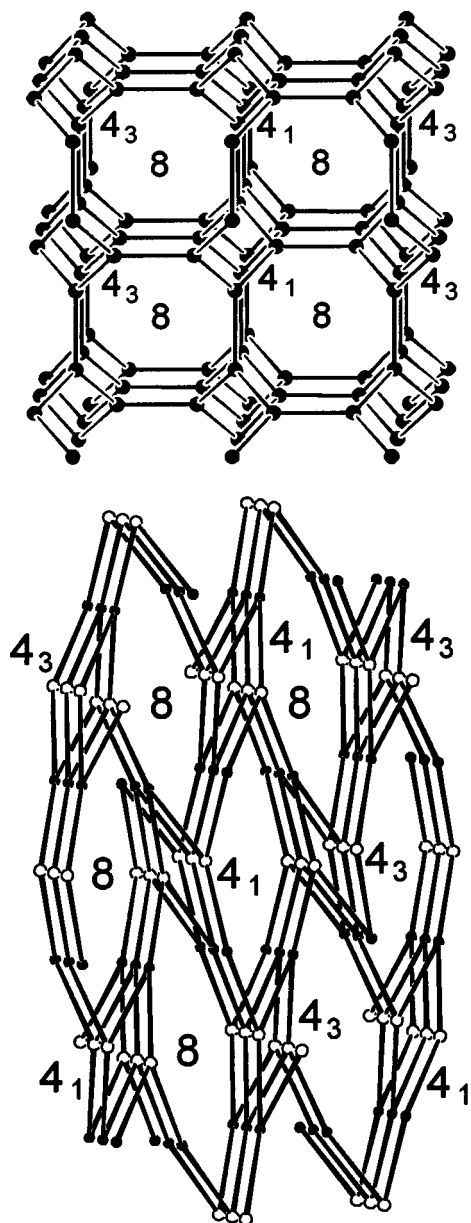


Fig. 4 The ideal triconnected ($8^2 10$)-b network (top) and the topologically equivalent schematized net of **2** (bottom), in which the black balls represent the baricenters of the TCNB ligands.

analyses of crystals of **1** from different solvents, both at room temperature and at -30°C , gave similar results, showing the presence of some variable residual electron density peaks due to highly disordered solvent molecules, that are difficult to rationalize on the basis of the X-ray data only, located within the cavities (of approximate volume 239 \AA^3)¹⁴ illustrated in Fig. 6 by big spheres. These solvent regions are disposed down $[0\ 0\ 1]$, along rhombic channels topologically equivalent to the square ones down the tetragonal axis of PtS. Different experiments have been carried out in order to characterize the guest solvent molecules. IR microscopy on the crystals shows bands due to the presence of both CH_2Cl_2 and the second solvent, and, in the case of the crystals obtained from CH_2Cl_2 -acetone, monitoring of the acetone $\nu(\text{CO})$ stretching reveals that this band rapidly decreases and disappears on heating the sample to 80°C . ^1H NMR spectra of different samples from CH_2Cl_2 -ethanol, collected after drying the crystals under N_2 flux and dissolution in acetone- d_6 , show signals at δ 8.93 (2H, TCNB), 5.63 (2H, CH_2Cl_2) and 1.5 (t, 3H, CH_3 ethanol), of variable relative intensities (TCNB- CH_2Cl_2 from 1 : 1 to 1 : 0.33; TCNB-ethanol from 1 : 0.33 to 1 : 0.20). Ther-

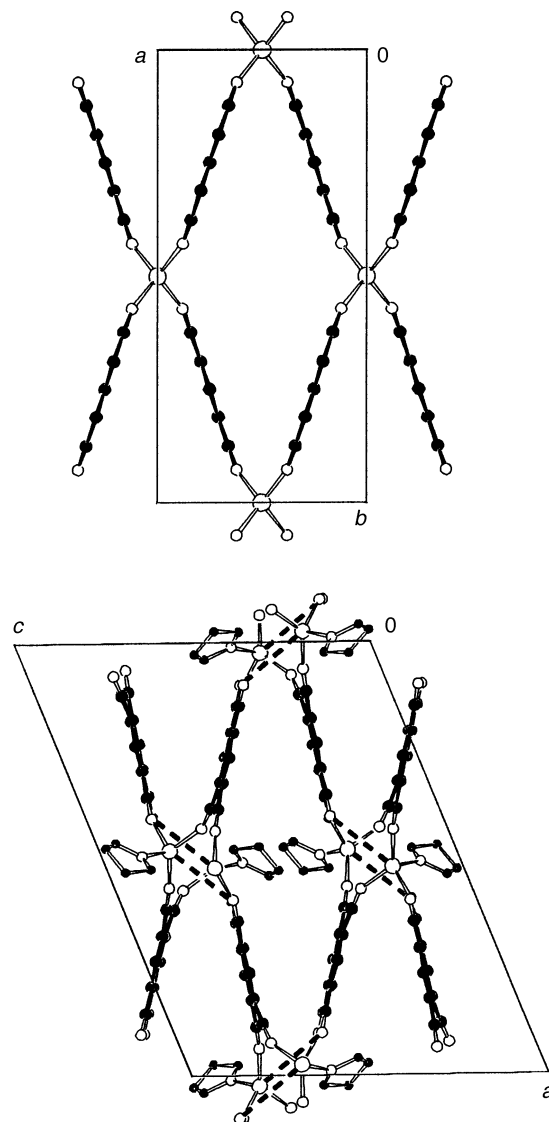


Fig. 5 A comparison of the networks in the structures of **1**, down c (top) and of **2**, down b (bottom). The dashed lines in the case of **2** represent the directions of Cu-N bond formation in the course of the $2 \rightarrow 1$ transformation (see text).

mogravimetric analyses of **1** show a loss of solvent (not constant), not exceeding *ca.* 4% of the mass, in the range 80 – 100°C . The network is stable up to *ca.* 280°C and above this temperature it loses the TCNB ligands. Almost constant elemental analyses for **1**, corresponding to the solvent-free network, can be obtained after heating the samples in an oven at 80°C for some hours. The X-ray powder diffraction spectra of these samples show patterns quite similar to the original one, confirming that the polymeric network is not destroyed on removing the solvents.

Crystal-to-crystal $2 \rightarrow 1$ conversion

Thermal analyses (DSC and TGA) have shown that **2** loses the coordinated THF molecule at 110 – 130°C and starts to decompose above 280°C . Examination under the microscope of the samples previously heated to *ca.* 140°C and cooled at room temperature revealed that the macroscopic crystal shape and colour seem almost unchanged in the process. These crystals, submitted to single crystal X-ray diffraction, showed marked broadening of the peaks and lack of diffraction above θ *ca.* 10° , but gave an orthorhombic cell [$a = 8.30(1)$, $b = 18.66(5)$, $c = 11.60(4) \text{ \AA}$, $V = 1797(8) \text{ \AA}^3$] similar to that of **1**. The same conversion has been confirmed on bulk samples

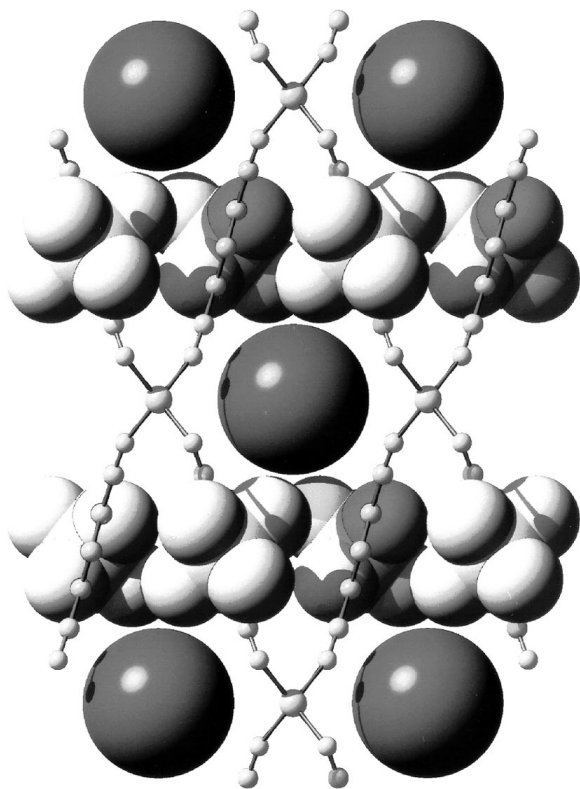


Fig. 6 A view of the frame of **1** that illustrates the rhombic channels down *c* containing the regions (big spheres) occupied by the disordered solvent molecules. The PF_6^- anions are also shown with van der Waals radii.

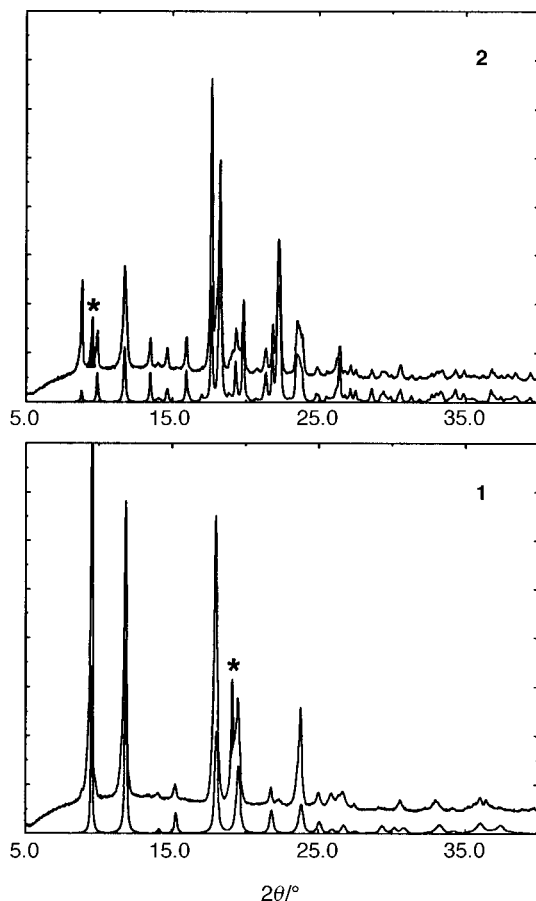


Fig. 7 X-Ray powder diffraction spectra showing the transformation of a polycrystalline sample of **2** (see top) left at 110 °C for one night to give **1** (see bottom). Each XRPD trace is in the $5 < 2\theta < 30^\circ$ range (Cu-K α); observed (top) and calculated (bottom) patterns. Starred peaks arise from mutual sample contaminations.

of **2** by monitoring the heating process by X-ray powder diffraction methods (Fig. 7). A crystal-to-crystal transformation takes therefore place, leading from **2** to **1**, with the cavities and channels along the *c* axis (see Fig. 5, top and Fig. 6) left empty. The process is made possible by the limited extent of the required rearrangements: the displacement of the THF molecules of **2**, which can travel through the crystal channels, is accompanied by the formation of the fourth Cu–N bond (the relevant Cu...N contact varying from *ca.* 3.8 Å in **2** to *ca.* 2.0 Å in **1**, along the directions illustrated by the dashed lines in Fig. 5, bottom). So Fig. 5 gives the extreme situations of the solid-state displacement reaction path $\text{CN}\cdots\text{Cu}\cdots\text{THF}$. Crystal-to-crystal reactions are in general rare,¹⁵ particularly in coordination polymer chemistry.^{16,17} Some evidence of the reverse **1** → **2** solid state transformation has also been achieved: for instance, samples of **1** left in THF at room temperature for a week gave X-ray powder diffraction patterns which can be ascribed to a *ca.* 50% mixture of **1** and **2**.

Experimental

All manipulations were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were distilled under nitrogen from Na– Ph_2CO (THF) or P_2O_5 (CH_2Cl_2). $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ was prepared and purified according to the literature method.¹⁸ All the other reagents were used as purchased from Aldrich. IR spectra in Nujol and IR microscopy data were collected on a Perkin–Elmer FT-IR Paragon 1000 spectrometer. ^1H NMR spectra were recorded on a Bruker AC200 instrument. Thermal analyses were performed on DSC 7 and TGA 7 Perkin–Elmer instruments with a heating rate of 10 °C per min. X-Ray powder diffraction spectra were collected on a Rigaku D/Max horizontal-scan diffractometer. Elemental analyses were carried out at the Microanalysis Laboratory of this University.

Synthesis of the compounds

Compound 1. In a typical preparation a solution of TCNB (0.021 g, 0.12 mmol) in ethanol (5–6 mL) was added to a solution of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (0.044 g, 0.12 mmol) in CH_2Cl_2 (8 mL). The solution was left to stir for 1 h. A yellow precipitate of **1** was obtained, which was filtered off, washed with ethanol and then with hexane and dried under vacuum (*ca.* 0.025 g, yield 55%). Crystals were grown by slow diffusion of a solution of TCNB in ethanol into a solution of the copper complex in CH_2Cl_2 . The crystals are air stable for few days. Constant elemental analyses, corresponding to the solvent-free product, were obtained after heating at 80 °C for some hours (Calc. for $\text{C}_{10}\text{H}_2\text{CuF}_6\text{N}_4\text{P}$: C 31.06, H 0.52, N 14.49. Found: C 30.94, H 0.75, N 14.10%. IR (Nujol, cm^{-1}): CH 3117, 3044, CN 2269, PF_6^- 832.

Compound 2. A solution of TCNB (0.028 g, 0.16 mmol) in THF (5 mL) was added to a solution of $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$ (0.058 g, 0.16 mmol) in CH_2Cl_2 (7–8 mL). After stirring for one night the orange-yellow precipitate of **2** was filtered off, washed with ethanol and then with hexane and dried under vacuum (*ca.* 0.052 g, yield 71%) (Calc. for $\text{C}_{14}\text{H}_{10}\text{CuF}_6\text{N}_4\text{OP}$: C 36.65, H 2.20, N 12.21. Found: C 36.12, H 2.06, N 11.96%. IR (Nujol, cm^{-1}): CH 3128, 3059; CN 2262, 2252; THF 1043, PF_6^- 833.

X-Ray crystallography

Single crystals of **1** and **2** were mounted under a coating of cyanoacrylic glue, to prevent decomposition, on a Siemens SMART CCD area-detector diffractometer. Crystal data for **1**: $\text{C}_{10}\text{H}_2\text{CuF}_6\text{N}_4\text{P}$, $M = 386.67$, orthorhombic, space group *Cccm* (no. 66), $a = 8.157(1)$, $b = 18.634(2)$, $c = 11.613(1)$, $V = 1765.1(3) \text{ Å}^3$, $Z = 4$, $D_c = 1.455 \text{ Mg m}^{-3}$, Mo-K α radi-

ation ($\lambda = 0.71073 \text{ \AA}$), $\mu = 1.381 \text{ mm}^{-1}$. Crystal data for **2**: $\text{C}_{14}\text{H}_{10}\text{CuF}_6\text{N}_4\text{OP}$, $M = 458.77$, monoclinic, space group $P2_1/c$ (no. 14), $a = 21.617(2)$, $b = 11.127(3)$, $c = 16.294(2) \text{ \AA}$, $\beta = 111.61(2)^\circ$, $V = 3643.8(11) \text{ \AA}^3$, $Z = 8$, $D_c = 1.673 \text{ Mg m}^{-3}$, Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), $\mu = 1.356 \text{ mm}^{-1}$. The data collections were performed at 243 K, within the limits $2 < \theta < 28^\circ$ for **1** and at 293 K within the limits $2 < \theta < 26^\circ$ for **2**. The structures were solved by direct methods (SIR97)¹⁹ and refined by full-matrix least-squares (SHELX-97)²⁰ against F_o^2 . In both cases the anions were found disordered and a suitable doubled model [F atoms with 83–17% occupancy (**1**) and 50% (**2**)] was refined. Final residual peaks do not exceed 0.795 e \AA^{-3} for **1** and 0.440 e \AA^{-3} for **2**. All the results here reported for **1** refer to a sample obtained from CH_2Cl_2 –ethanol. Three other single crystal analyses, based on data collected at room temperature on samples obtained from different solvent systems, gave similar results with greater residual peaks around $2/m$ special positions which were not easily rationalized, indicative of disordered solvent molecules. The final agreement indexes R_1 were 0.0614 for 735 independent significant [$F_o > 4\sigma(F_o)$] absorption corrected data for **1** and 0.0647 for 3365 independent significant [$F_o > 4\sigma(F_o)$] absorption corrected data for **2**. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms, but to the atoms of the minor component of the disordered anion in **1**. All the drawings were produced with SCHAKAL 97.²¹

CCDC reference number 440/103.

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