

Poly[tetraphenylphosphonium  
copper(I)-di- $\mu_2$ -dicyanamido]

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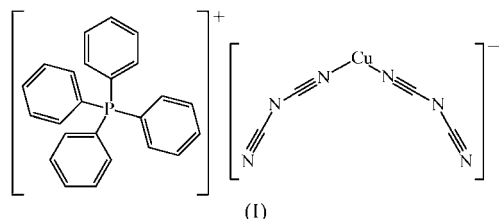
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In the title compound,  $\{(\text{C}_{24}\text{H}_{20}\text{P})[\text{Cu}(\text{C}_2\text{N}_3)_2]\}_n$ , the copper(I) dicyanamido anion forms a distorted three-dimensional single diamondoid network. Templating tetraphenylphosphonium cations reside within the cavities of the polymeric anion.

## Comment

The dicyanamido pseudohalide anion [*i.e.*  $\text{N}(\text{CN})_2^-$ , hereinafter abbreviated dca] has become a component of a growing number of coordination polymers because its large variety of bonding modes enables the formation of a wide range of structural types (Miller & Manson, 2001; Batten & Murray, 2003; Manson, 2005). With divalent first row transition elements, neutral binary  $M(\text{dca})_2$  complexes with rutile-like structures form, in which the dca anion is coordinated in a  $\mu_{1,3,5}$  fashion. Long-range magnetic order is observed in the cobalt and nickel compounds, which order ferromagnetically (Manson *et al.*, 1998; Kurmoo & Kepert, 1998), while the vanadium, chromium, manganese and iron analogs possess antiferromagnetic ground states (Kurmoo & Kepert, 1998; Manson *et al.*, 1999, 2001; Kmety *et al.*, 2000; Batten *et al.*, 1999). The isostructural  $\text{Cu}(\text{dca})_2$  complex is paramagnetic to temperatures as low as 2 K (Kurmoo & Kepert, 1998, 1999).



There has recently been a rapid increase in the study of anionic dca complexes in which the use of diverse cationic templates has led to an increasing variety of structural types with various dimensionalities. Various *trans* and *cis*  $\mu_{1,5}$ -dibridged chains have been reported (Raebiger *et al.*, 2001; Jager *et al.*, 2001; Wang *et al.*, 2002). Ladder-type structures represent an intermediate motif between one- and two-dimensional systems (van der Werff, Batten, Jensen,

Moubaraki, Murray & Tan, 2001; Wang *et al.*, 2003). Three two-dimensional anionic structural types are known, namely square (Raebiger *et al.*, 2001; van der Werff, Batten, Jensen, Moubaraki & Murray, 2001; van der Werff, Batten, Jensen, Moubaraki, Murray & Tan, 2001; Biswas *et al.*, 2006), hexagonal honeycombs (Batten *et al.*, 2000) and triangular (Schlueter, Geiser & Manson, 2004). Three-dimensional topologies with cube-like (Tong *et al.*, 2003; Schlueter, Manson *et al.*, 2004; Schlueter *et al.*, 2005; van der Werff *et al.*, 2005), triple rutile (Schlueter *et al.*, 2005; van der Werff, Batten, Jensen, Moubaraki & Murray, 2001; van der Werff *et al.*, 2004) and lithium antimonate (Schlueter *et al.*, 2005) packing motifs have also been identified. These various structural types differ in the ratio and arrangement of single and double dca bridges. The vast majority of these complexes contain divalent first row transition elements.

Anionic copper dicyanamido complexes are relatively unknown, but we have recently reported the first three structures that contain anionic copper(II) dicyanamido coordination polymers. The  $(\text{PPh}_4)_3[\text{Cu}_4(\text{dca})_{11}]$  salt possesses a novel triple ladder structure, in which the rungs are comprised of single  $\mu_{1,5}$ -dca bridges, while the sides are constructed of double  $\mu_{1,5}$ -dca bridges (Schlueter *et al.*, 2006). We have also found that the  $(\text{PPh}_4)[\text{Cu}(\text{dca})_3(\text{H}_2\text{O})]$  salt contains singly bridged  $\mu_{1,5}$ -dca chains that are linked into a two-dimensional network through coordinated water molecules (Schlueter *et al.*, 2007). Replacement of one of the cation phenyl groups with a butyl group results in the formation of the  $(\text{PPh}_3\text{-Bu})_2[\text{Cu}(\text{dca})_4]$  salt, which contains doubly-bridged  $\mu_{1,5}$ -dca chains (Schlueter *et al.*, 2007). Only two examples of anionic copper(I) dca salts have been reported to date, namely the  $[\text{Rb}(18\text{-crown-6})]_3[\text{Cu}_2(\text{dca})_5]$  salt, which contains both tetrahedrally and triangularly coordinated copper, forming complex one-dimensional chains, while  $[\text{Ti}(18\text{-crown-6})][\text{Cu}(\text{dca})_2]$  contains only tetrahedrally coordinated Cu linked through single  $\mu_{1,5}$ -dca bridges into two-dimensional polymeric sheets (Manskaya *et al.*, 1999). We report here the first example of a three-dimensional copper(I) dicyanamido network, *viz.*  $(\text{PPh}_4)[\text{Cu}(\text{dca})_2]$ , (I). This salt has been used as a precursor (Wang *et al.*, 1990, 1992) for the electrochemical

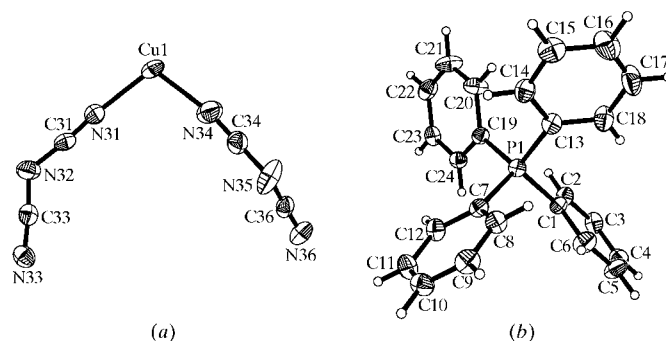
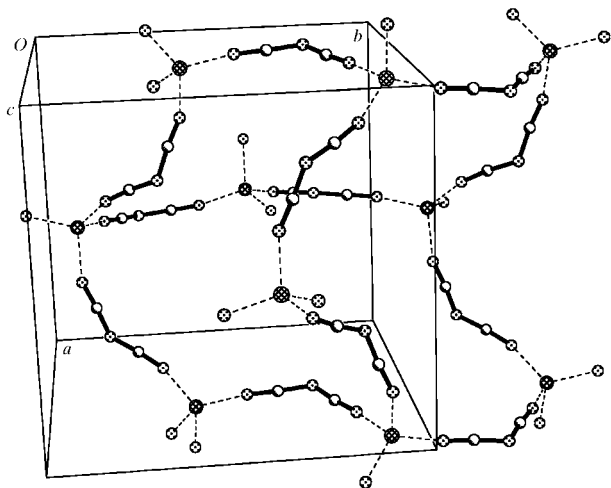


Figure 1

The atom-numbering schemes of (a) a unique fragment of the  $[\text{Cu}(\text{dca})_2]^-$  anion and (b) the molecular structure of the tetraphenylphosphonium cation (different absolute scales). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

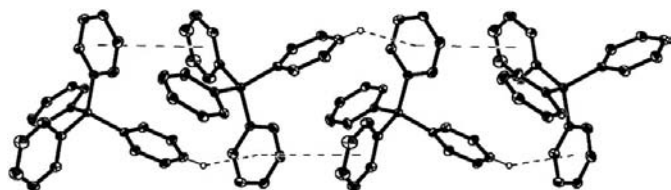
synthesis of the superconducting charge-transfer salts (BEDT-TTF)<sub>2</sub>[Cu(dca)X] [X is Br or Cl; BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene] (Williams *et al.*, 1990; Kini *et al.*, 1990). In order to control the electrocrystallization process better, it is necessary to understand more fully the structure of the anionic network in electrolyte precursors.

The atom-numbering scheme of the tetraphenylphosphonium cation and the copper(I) dicyanamide anion of (I) are illustrated in Fig. 1. The geometry of the dca anions in the (PPh<sub>4</sub>)[Cu(dca)<sub>2</sub>] structure is typical. The nitrile C≡N bond lengths range from 1.148 (4) to 1.157 (4) Å, the amide N—C bond lengths range from 1.299 (4) to 1.320 (4) Å, the C—N—C bond angles are 120.1 (2) and 123.3 (3)°, and the N≡C—N bond angles range from 172.9 (3) to 174.3 (3)°. The displacement ellipsoids of the amide N atoms are elongated, indicating a rocking thermal motion of the dca anion. The coordination about the Cu<sup>I</sup> center is distorted tetrahedral, with the N—Cu—N bond angles ranging from 100.5 (1) to 119.0 (1)°. Two of the Cu—N bond lengths are slightly shorter (0.07 Å) than the other two. A polymeric network is formed by two sets of copper dicyanamide chains; one runs along the *a* axis, while the other runs along the *b* axis. These zigzag chains wind around 2<sub>1</sub> screw axes. The chain along the *a* axis has N—Cu—



**Figure 2**

An adamantane-type fragment of the polymeric [Cu(dca)<sub>2</sub>]<sup>−</sup> anion. Twelve dca<sup>−</sup> anions and ten Cu<sup>I</sup> ions that construct a single cage are illustrated, along with the nitrile N atoms that complete the distorted tetrahedral coordination of the Cu atoms.



**Figure 3**

The PPh<sub>4</sub><sup>+</sup> cationic chain running along the *b* axis; P···P separations are 7.2621 (7) Å. Aromatic interactions of the offset-face-to-face (*off*) and edge-to-face (*ef*) types are illustrated with dashed lines. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii.

N bond angles of 111.0 (1)°, while for the *b* axis chain this angle is 110.6 (1)°. As illustrated in Fig. 2, each Cu atom is joined to four equivalent Cu atoms through dca linkages, resulting in Cu···Cu separations of 7.9641 (7) and 8.1075 (7) Å, thus forming a highly distorted single diamondoid net.

As seen in Fig. 1, the molecular structure of the tetraphenylphosphonium cation that templates the anionic pores is typical of that commonly described in the literature. The P—C bond lengths range from 1.795 (3) to 1.804 (3) Å, with C—P—C bond angles slightly distorted from tetrahedral and ranging from 108.3 (1) to 110.8 (1)°. The C—C distances within the aromatic rings range from 1.375 (4) to 1.396 (4) Å and the C—C—C bond angles range from 119.2 (2) to 120.6 (3)°.

As illustrated in Fig. 3, zigzag chains of PPh<sub>4</sub><sup>+</sup> cations form along the *b* axis, with P···P separations of 7.2621 (7) Å. These chains are stabilized through multiple phenyl embraces of both the offset-face-to-face (*off*) and edge-to-face (*ef*) types. The most prominent *off* interaction is between phenyl rings defined by atoms C1—C6 and C13—C18. The centroid-to-centroid distance between these rings is 4.4080 Å, with a dihedral angle of 15.51° between their respective planes, confirming the presence of π—π interactions (Spek, 2003). The most significant *ef* interaction is between atom H10 and the phenyl ring defined by atoms C1—C6. The associated hydrogen-to-centroid distance is 3.28 Å. This type of concerted supramolecular motif is not one of the modes commonly observed for tetraphenylphosphonium salts (Dance & Scudder, 1996; Scudder & Dance, 1998*a,b*).

We conclude that, although the three-dimensional [Cu(dca)<sub>2</sub>]<sup>−</sup> lattice of the PPh<sub>4</sub><sup>+</sup> salt breaks down in solution prior to electrocrystallization of (BEDT-TTF)<sub>2</sub>[Cu(dca)X], the one-dimensional zigzag anionic chain structure is retained in these BEDT-TTF salts. The presence of coordinating Br<sup>−</sup> or Cl<sup>−</sup> anions and the two-dimensional templating effect of the (BEDT-TTF)<sub>2</sub><sup>+</sup> cations likely cause the anionic structural transformation.

## Experimental

Tetraphenylphosphonium copper(I) dicyanamide was prepared according to the literature procedure of Wang *et al.* (1990). An acetonitrile solution containing CuBr and two equivalents of PPh<sub>4</sub>(dca) was refluxed for 16 h. Upon slow cooling, crystals of (PPh<sub>4</sub>)[Cu(dca)<sub>2</sub>] formed.

### Crystal data

(C<sub>24</sub>H<sub>20</sub>P)[Cu(C<sub>2</sub>N<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 535.01  
 Orthorhombic, *P*<sub>2</sub><sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 12.7929 (12) Å  
*b* = 13.4006 (12) Å  
*c* = 14.4847 (14) Å

*V* = 2483.1 (4) Å<sup>3</sup>  
*Z* = 4  
 Mo *K*α radiation  
 μ = 0.97 mm<sup>−1</sup>  
*T* = 150 (2) K  
 0.40 × 0.06 × 0.06 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 Absorption correction: integration (SHELXTL; Sheldrick, 2001)  
*T<sub>min</sub>* = 0.787, *T<sub>max</sub>* = 0.951

21614 measured reflections  
 5978 independent reflections  
 4855 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.049

## Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.039$$

$$wR(F^2) = 0.083$$

$$S = 1.03$$

5978 reflections

325 parameters

H-atom parameters constrained

$$\Delta\rho_{\max} = 0.89 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.63 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack (1983),

with 2581 Friedel pairs

Flack parameter: 0.061 (12)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu—N33	1.985 (3)	Cu—N31	2.068 (2)
Cu—N30	1.995 (2)	Cu—N32	2.080 (3)
N33—Cu—N30	118.95 (11)	N31—Cu—N32	100.46 (11)
N33—Cu—N31	106.27 (11)	C30—N30—Cu	171.0 (3)
N30—Cu—N31	110.55 (10)	C31—N31—Cu	172.4 (2)
N33—Cu—N32	110.96 (12)	C32—N32—Cu	148.9 (3)
N30—Cu—N32	108.09 (11)	C33—N33—Cu	164.4 (3)

H atoms on aromatic C atoms were positioned geometrically, with C—H = 0.93  $\text{\AA}$ , and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3036). Services for accessing these data are described at the back of the journal.

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