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Two different one-dimensional structural motifs in [*catena*-{Cu(tacn)}$_2$-Pd(CN)$_4$]Br$_2$·[*catena*-Cu(tacn)Pd-(CN)$_4$]$_2$·H$_2$O (tacn is 1,4,7-triazacyclononane)

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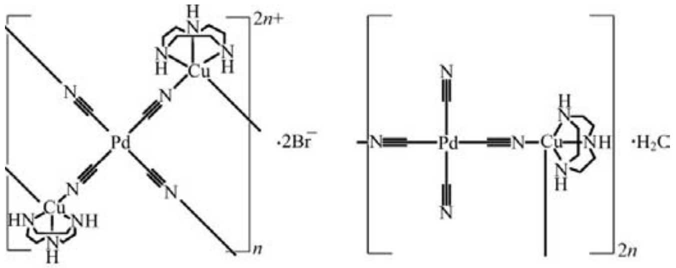
The title compound, *catena*-poly[[bis[(triazacyclononane-κ^3N,N',N'')copper(II)]-di-μ-cyanido-κ^4N:C-palladate(II)-di-μ-cyanido-κ^4C:N] dibromide bis[[(triazacyclononane-κ^3N,N',N'')-copper(II)]-μ-cyanido-κ^2N:C-[dicyanidopalladate(II)]-μ-cyanido-κ^2C:N] monohydrate], $\{[Cu_2Pd(CN)_4(C_6H_{15}N_3)_2]Br_2\cdot[Cu_2Pd_2(CN)_8(C_6H_{15}N_3)_2]\cdot H_2O\}_n$, (I), was isolated from an aqueous solution containing tacn·3HBr (tacn is 1,4,7-triazacyclononane), Cu^{2+} and tetracyanidopalladate(2−) anions. The crystal structure of (I) is essentially ionic and built up of 2,2-electroneutral chains, *viz.* [Cu(tacn)(NC)–Pd(CN)$_2$–(CN)–], positively charged 2,4-ribbons exhibiting the composition $\{[Cu(tacn)(NC)_2–Pd(CN)_2–Cu(tacn)]^{2n+}\}_n$, bromide anions and one disordered water molecule of crystallization. The O atom of the water molecule occupies two unique crystallographic positions, one on a centre of symmetry, which is half occupied, and the other in a general position with one-quarter occupancy. One of the tacn ligands also exhibits disorder. The formation of two different types of one-dimensional structural motif within the same structure is a unique feature of this compound.

Comment

Cyanide complexes exhibit great structural variability because of the bridging ability of the cyanide ligand. This structural variability allied with the presence of paramagnetic central atoms makes cyanide complexes popular among chemists and physicists as materials exhibiting various interesting magnetic properties (Lescouezec *et al.*, 2005; Ohba & Okawa, 2000; Garde *et al.*, 2008; Bernhardt *et al.*, 2005; Klokishner *et al.*, 2007; Herrera *et al.*, 2008).

In the construction of low-dimensional cyanide complexes, the so-called ‘brick-and-mortar’ method can be applied (Willet *et al.*, 1993), in which a metallic central atom coordinated by suitable blocking ligand(s) acts as the ‘brick’ and the cyanide complex anion is used as the ‘mortar’. Previously, following these ideas, we have prepared, structurally characterized and studied the magnetic properties of several low-dimensional cyanide complexes in which various bidentate ligands were used (Hanko *et al.*, 2007; Kuchár *et al.*, 2003, 2004). These complexes are also interesting as models for studies of the role of hydrogen bonds in mediating magnetic exchange interactions.

As a continuation of our efforts to prepare one-dimensional cyanide complexes, we have decided to use a cyclic triaza ligand, namely 1,4,7-triazacyclononane (tacn). This tridentate ligand, connected to a Cu^{II} central atom, promotes mainly five-coordination (Han *et al.*, 2004; Wang *et al.*, 2004), thus leaving two coordination sites free for the polymerization process during crystallization. As a result of our synthetic procedure using tacn·3HBr, prepared according to the literature (White *et al.*, 1979), we have isolated the title compound, (I).



(I)

The crystal structure of (I) is essentially ionic (Figs. 1–3). It is built up of positively charged 2,4-ribbons exhibiting the composition $\{[Cu(tacn)(NC)_2–Pd(CN)_2–Cu(tacn)]^{2n+}\}_n$ and running along the (100) direction, bromide anions, electroneutral 2,2-CT chains (for details, see Černák *et al.*, 2002), *viz.* [Cu(tacn)(NC)–Pd(CN)$_2$–(CN)–], running along the (001) direction, and one water molecule of crystallization. An alternative view of the structure is that it is formed of the above-mentioned chains, with ribbons running perpendicularly between the chains, and with bromide anions and water molecules of crystallization placed in the free space between the chains and ribbons.

This type of 2,4-ribbon incorporating cyanide ligands and Cu^{II} central atoms has not been described previously, but a similar ribbon structural motif was found in $[Mn_6(tptz)_6(MeOH)_4(DMF)_2W_4(CN)_{32}]_8\cdot 2H_2O\cdot 2.3MeOH$ [tptz is 2,4,6-tris(2-pyridyl)-1,3,5-triazine and DMF is *N*,*N*-dimethylformamide; Zhao *et al.*, 2007]. On the other hand, chains built up of cyanide complex anions and Cu^{II} ions are not uncommon; examples are [Cu(en)$_2$Ni(CN)$_4$] or [Cu(dmen)$_2$Pd(CN)$_4$] (en is ethylenediamine and dmen is *N*,*N*-dimethylethylenediamine; Seitz *et al.*, 2001; Kuchár *et al.*, 2004). The presence of both one-dimensional structural motifs within the same structure is, however, a unique feature of (I).

Both the ribbon and the chain parts of the structure contain five-coordinated Cu^{II} ions. As expected, three coordination sites are occupied by the blocking tacn ligand, with Cu—N bonds within the range 1.917 (11)–2.216 (4) Å and with

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intrachelate N—Cu1—N angles of 83.38 (17), 83.47 (18) and 83.7 (2)° (Table 1). The remaining two coordination sites around the Cu^{II} central ions are occupied by N atoms from bridging cyanide ligands, with Cu—N distances in the range 1.976 (4)–1.998 (4) Å. As calculated following the suggestion of Addison *et al.* (1984), the τ parameters of atoms Cu1 (chain) and Cu2 are 0.98 and $\frac{1}{3}$, respectively, indicating that the polyhedron around atom Cu1 is close to ideal trigonal bipyramidal, while that around atom Cu2 is closer to square pyramidal. The geometric parameters within the tacn ligands are as expected (Schwindinger *et al.*, 1980).

There are three crystallographically independent Pd^{II} ions in the structure. Each of them occupies a special position (centre of symmetry). All Pd^{II} ions exhibit square-planar coordination by four cyanide ligands with a mean Pd—C bond length of 2.004 (3) Å; this value is close to that of 1.994 (1) Å found in $[Cu(tn)Pd(CN)_4]$ (tn is 1,3-diaminopropane; Legendre *et al.*, 2008). All of the cyanide ligands within the ribbon exhibit bridging character, while amongst those in the

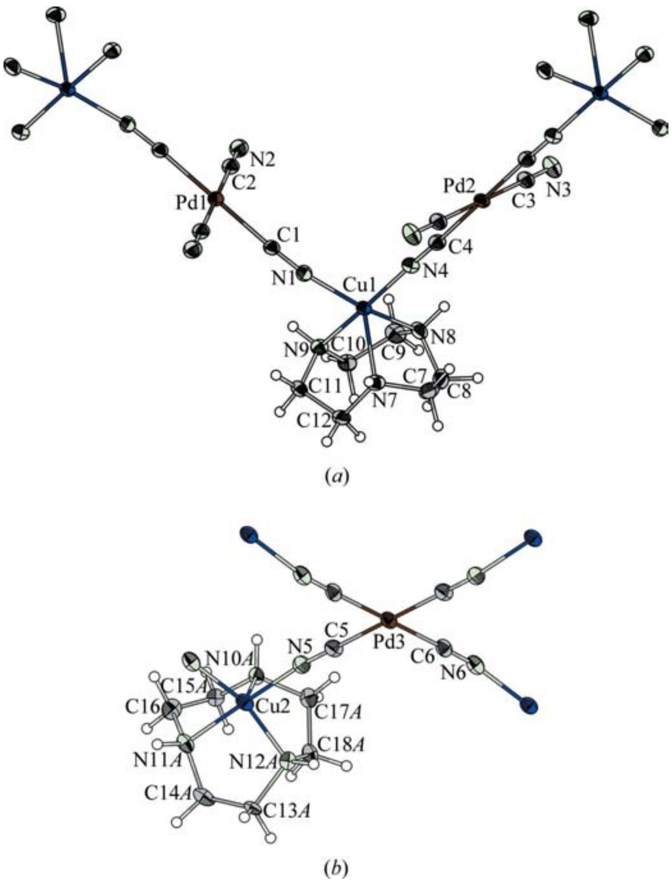

Figure 1
(*a*) The chain and (*b*) the 2,4-ribbon in the title compound, together with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only one conformation of the disordered tacn ligand is shown in (*b*).

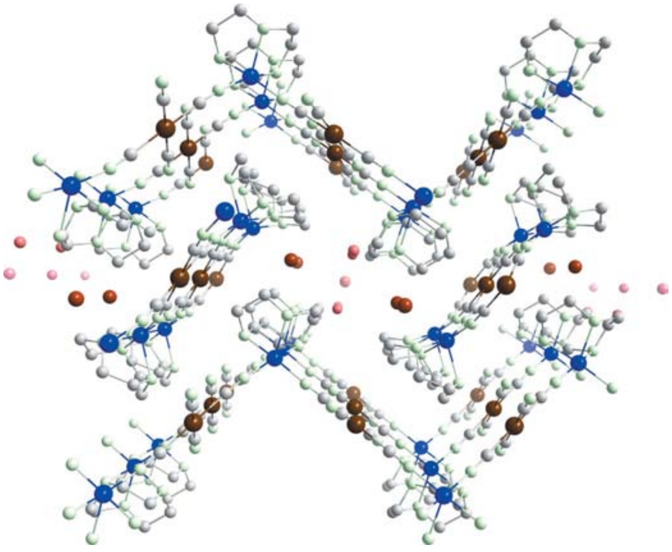

Figure 2
A perspective view of the crystal structure of (I), displaying the chains and ribbons, as well as the bromide anions and water molecules of crystallization. H atoms have been omitted for clarity.

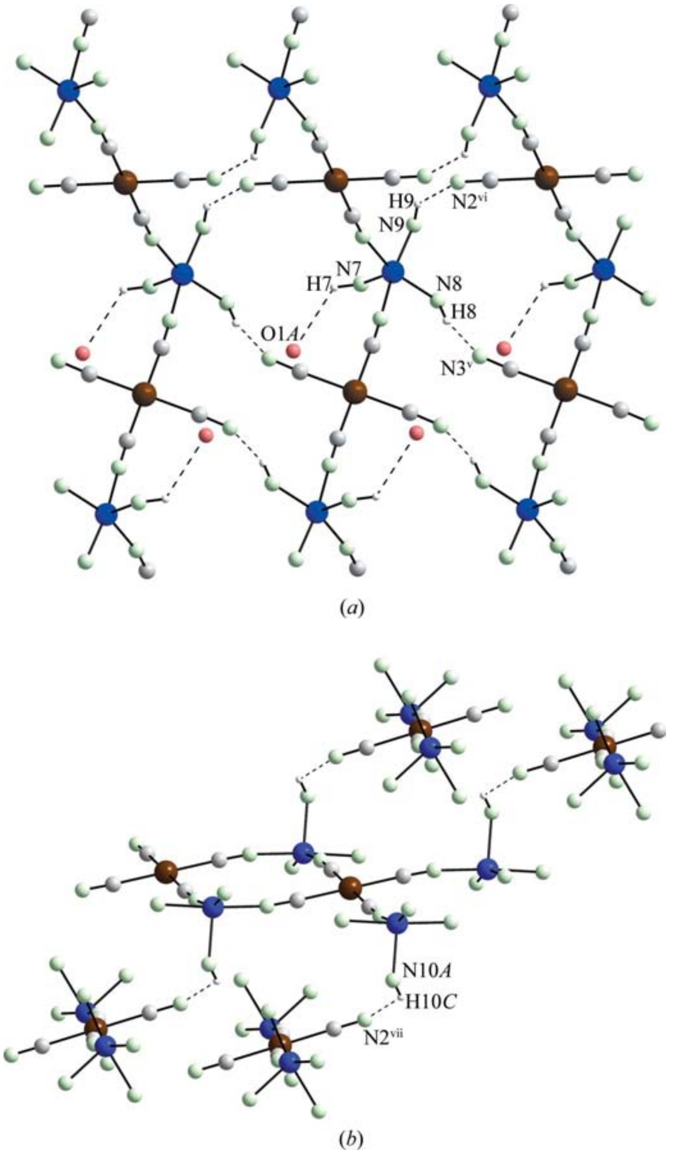

Figure 3
The hydrogen-bond system in (I), connecting (*a*) neighbouring chains and (*b*) chains and ribbons. [Symmetry codes: (v) $-x + 1, -y + 1, -z + 2$; (vi) $-x + 1, -y + 1, -z + 1$; (vii) $x - 1, y - 1, z$.]

$[Pd(CN)_4]^{2-}$ anion within the chain, two are terminal and two link Cu and Pd ions. The C$\equiv$N bonds are in the range 1.126 (7)–1.151 (7) Å, which are normal values (Legendre *et al.*, 2008). The Cu—N$\equiv$C angles formed by bridging cyanide ligands exhibit values in the range 167.1 (4)–177.6 (5)°. The presence of both bridging and terminal cyanide ligands in the structure was also detected by IR spectroscopy; in the spectrum there are absorption bands at 2183 and 2145 cm^{-1}, which were attributed to the stretching vibrations of the bridging (higher wavenumbers) and terminal cyanide ligands. The absorption band at higher wavenumbers exhibits greater intensity, in line with the larger number of bridging cyanide ligands in the structure.

There is one noncoordinated bromide anion that occupies a general position, which hydrogen bonds to NH groups of the tacn ligands (Table 2). Two unique crystallographic positions are occupied by the O atom of the water molecule, one on a centre of symmetry, which is half occupied, and the other in a general position, 1.432 (2) Å away, with one-quarter occupancy. The water molecule, the N atoms from the tacn ligands and the terminal N atoms from the cyanide groups are involved in N—H···O and N—H···N($\equiv$C) hydrogen bonds (Table 2 and Fig. 3).

The N—H···N($\equiv$C) hydrogen bonds connect the electroneutral chains to one another as well as to the chains of negatively charged ribbons, with N···N distances in the range 2.942 (6)–3.282 (11) Å. The water molecule interacts *via* an N—H···O hydrogen-bond interaction with H atoms from the electroneutral chain. At the same time, the O1*B*···Br1 [2.9923 (8) Å] and O1*A*···Br1 distances [3.249 (16) and 3.384 (15) Å] suggest the presence of further hydrogen-bonding interactions. The bromide anions form further weak hydrogen-bonding interactions of the N—H···Br type, with H···Br distances in the range 2.35–2.66 Å.

Experimental

A solution formed by mixing a warm 0.1 *M* solution of $CuSO_4$ (10 ml, 1 mmol) and tacn·3HBr in 10 ml of methanol and 10 ml of water (0.22 ml, 2 mmol) was mixed with a warm aqueous 0.1 *M* solution of $K_2[Pd(CN)_4]$ (10 ml, 1 mmol). The resulting precipitate was dissolved by addition of a concentrated aqueous solution of ammonia (25%). Finally, the solution was filtered and left to crystallize at ambient temperature (291 K). The first single crystals appeared as blue prisms after one day. Analysis found: C 26.95, H 4.05, N 21.05%; calculated: C 27.36, H 3.95, N 21.27%. FT–IR (cm^{-1}, KBr): ν(OH) 3507 (*s*), 3437 (*s*); ν(NH) 3302 (*s*); ν(CH) 2959 (*m*), 2924 (*m*); ν(CN) 2183 (*vs*), 2145 (*vs*); $\delta(OH_2)$ 1651 (*m*); $\delta(CH_2)$ 1485 (*m*), 1454 (*m*); ν(C—N) 1153 (*w*); ν(C—C) 1099 (*m*).

Crystal data

$[Cu_2Pd(CN)_4(C_6H_{15}N_3)_2]Br_2\cdot$-
$[Cu_2Pd_2(CN)_8(C_6H_{15}N_3)_2]\cdot H_2O$
M_r = 1580.28
Triclinic, $P\overline{1}$
a = 7.3214 (8) Å
b = 12.9466 (14) Å
c = 14.5178 (16) Å
α = 83.699 (9)°
β = 84.378 (9)°
γ = 82.878 (9)°
V = 1352.3 (3) $Å^3$
Z = 1
Mo *Kα* radiation
μ = 4.05 mm^{-1}
T = 193 K
0.40 × 0.12 × 0.10 mm

Data collection

Stoe IPDS-II diffractometer
Absorption correction: multi-scan (*WinGX*; Farrugia, 1999)
T_{min} = 0.410, T_{max} = 0.667
22649 measured reflections
5903 independent reflections
4826 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.115
S = 1.03
5903 reflections
394 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.18 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.36 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Pd1—C1	2.010 (5)	Cu1—N9	2.033 (4)
Pd1—C2	2.002 (6)	Cu2—N5	1.983 (5)
Pd2—C3	2.003 (6)	N6—Cu2^{i}	1.980 (5)
Pd2—C4	2.003 (5)	Cu2—N10*A*	2.125 (8)
Pd3—C5	2.000 (5)	Cu2—N11*A*	2.029 (10)
Pd3—C6	2.007 (6)	Cu2—N12*A*	1.917 (11)
Cu1—N1	1.998 (4)	Cu2—N10*B*	2.195 (8)
Cu1—N4	1.976 (4)	Cu2—N11*B*	2.022 (8)
Cu1—N7	2.216 (4)	Cu2—N12*B*	2.137 (11)
Cu1—N8	2.024 (5)		
C2—Pd1—C1^{ii}	91.0 (2)	N7—Cu1—N9	83.38 (17)
C2—Pd1—C1	89.0 (2)	N5—Cu2—N12*A*	93.0 (3)
C3^{iii}—Pd2—C4	86.6 (2)	N11*A*—Cu2—N12*A*	86.9 (5)
C3—Pd2—C4	93.4 (2)	N10*A*—Cu2—N12*A*	88.5 (5)
C5^{iv}—Pd3—C6	89.8 (2)	N5—Cu2—N10*A*	99.7 (4)
C5—Pd3—C6	90.2 (2)	N10*A*—Cu2—N11*A*	84.4 (4)
N1—Cu1—N4	92.42 (18)	N5—Cu2—N12*B*	89.5 (3)
N4—Cu1—N8	91.79 (19)	N11*B*—Cu2—N12*B*	80.4 (4)
N1—Cu1—N9	90.27 (17)	N10*B*—Cu2—N11*B*	84.3 (4)
N8—Cu1—N9	83.47 (18)	N10*B*—Cu2—N12*B*	80.7 (4)
N7—Cu1—N8	83.7 (2)		

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+1, -z+1$; (iii) $-x, -y+1, -z+2$; (iv) $-x, -y, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O1*A*	0.93	2.57	3.233 (15)	129
N8—H8···N3^{v}	0.93	2.05	2.960 (6)	165
N9—H9···N2^{vi}	0.93	2.15	2.942 (6)	142
N10*A*—H10*C*···N2^{vii}	0.93	2.62	3.282 (11)	129
N10*B*—H10*D*···N2^{vii}	0.93	2.26	3.076 (10)	146
N11*A*—H11*C*···Br1	0.93	2.66	3.513 (10)	153
N11*B*—H11*D*···Br1	0.93	2.42	3.327 (9)	163
N12*A*—H12*C*···Br1^{i}	0.93	2.35	3.254 (10)	165
N12*B*—H12*D*···Br1^{i}	0.93	2.61	3.461 (10)	153

Symmetry codes: (i) $x+1, y, z$; (v) $-x+1, -y+1, -z+2$; (vi) $-x+1, -y+1, -z+1$; (vii) $x-1, y-1, z$.

All H-atom positions were calculated using the appropriate riding model, with U_{iso}(H) values 1.2 times U_{eq} of the parent atoms, and with C—H distances of 0.99 Å and N—H distances of 0.93 Å. H atoms that belong to the water molecule were not modelled. During structure solution, several peaks appeared in the Fourier difference map that could be assigned to the N and C atoms of the tacn ligand in the 2,4-ribbon. By careful assignment of the observed maxima in the electron map to the N and C atoms, two different orientations could be modelled. The overall site-occupation factors of the two conformations were refined while constraining their sum to 1.0, giving a major occupancy of 50.6 (10)%.

Data collection: *X-AREA* (Stoe & Cie, 2003); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3023). Services for accessing these data are described at the back of the journal.

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