metal-organic compounds

Poly[diaqua(μ-4,4′-bipyridine-$\kappa^2 N$:N')-bis(μ-cyanido-$\kappa^2 C$:N)bis(cyanido-κC)-nickel(II)copper(II)]: a metal–organic cyanide-bridged framework

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The structure of the title compound, $[NiCu(CN)_4(C_{10}H_8N_2)(H_2O)_2]_n$ or $[\{Cu(H_2O)_2\}(\mu\text{-}C_{10}H_8N_2)(\mu\text{-CN})_2\{Ni(CN)_2\}]_n$, was shown to be a metal–organic cyanide-bridged framework, composed essentially of –Cu–4,4′-bpy–Cu–4,4′-bpy–Cu– chains (4,4′-bpy is 4,4′-bipyridine) linked by $[Ni(CN)_4]^{2-}$ anions. Both metal atoms sit on special positions; the Cu^{II} atom occupies an inversion center, while the Ni^{II} atom of the cyanometallate sits on a twofold axis. The 4,4′-bpy ligand is also situated about a center of symmetry, located at the center of the bridging C—C bond. The scientific impact of this structure lies in the unique manner in which the framework is built up. The arrangement of the –Cu–4,4′-bpy–Cu–4,4′-bpy–Cu– chains, which are mutually perpendicular and non-intersecting, creates large channels running parallel to the c axis. Within these channels, the $[Ni(CN)_4]^{2-}$ anions coordinate to successive Cu^{II} atoms, forming zigzag –Cu—N≡C—Ni—C≡N—Cu– chains. In this manner, a three-dimensional framework structure is constructed. To the authors' knowledge, this arrangement has not been observed in any of the many copper(II)–4,4′-bipyridine framework complexes synthesized to date. The coordination environment of the Cu^{II} atom is completed by two water molecules. The framework is further strengthened by O—H···N hydrogen bonds involving the water molecules and the symmetry-equivalent nonbridging cyanide N atoms.

Comment

The synthesis and characterization of multidimensional coordination networks has been an area of rapid growth in recent years. The aim of this intense activity is the deliberate design of materials with specific properties, for example, electronic, magnetic, optical, catalytic, ion exchange and absorption (Chae *et al.*, 2004; Janiak, 2003; Fujita *et al.*, 1994; Noro *et al.*, 2000; Tabares *et al.*, 2001; Coronado *et al.*, 2000). Among these materials, multidimensional cyanide-bridged complexes, prepared by the self-assembly of specifically designed precursors (typically a cyanometallate complex that acts as a ligand and a transition metal complex with available coordination sites), are playing an important role in areas such as molecule-based magnets, magneto-optic materials, ion exchange, materials for storing gases and host–guest chemistry (Dunbar & Heintz, 1997; Ferlay *et al.*, 1995; Cernák *et al.*, 2002). Most approaches to the design of nanoporous coordination polymers have involved the employment of rigid

(I)
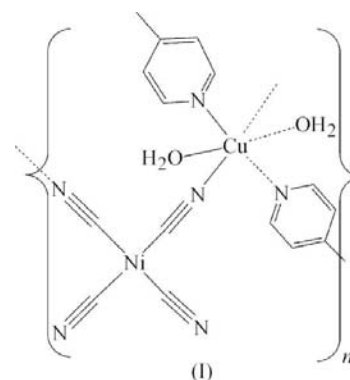
bidentate heteroaromatic N-atom donor ligands, such as pyrazine (pyz) or 4,4′-bipyridine (4,4′-bpy), to connect metal ions, so giving cationic networks (Hagrman *et al.*, 1999). Surprisingly, the 4,4′-bpy ligand has not been used extensively
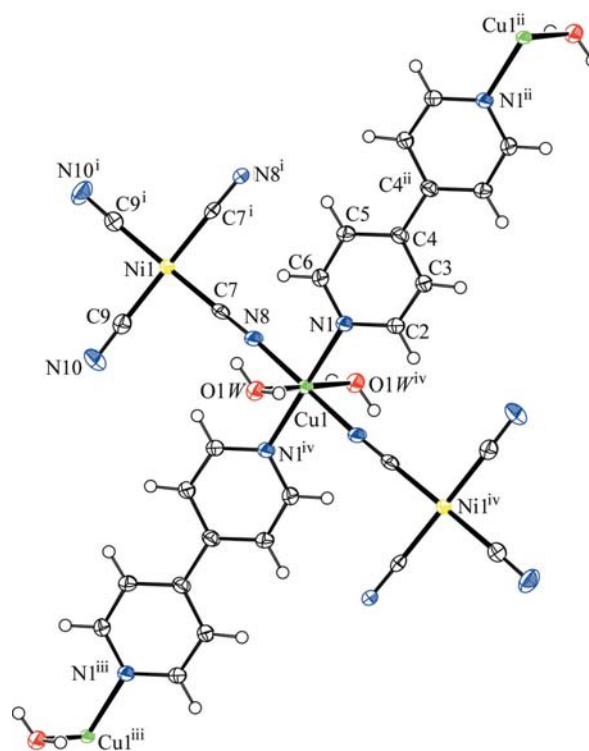
Figure 1
A view of the asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + 1, -y, -z + 1$; (iii) $x - \frac{1}{2}, y + \frac{1}{2}, z - 1$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

(a)

(b)

(c)
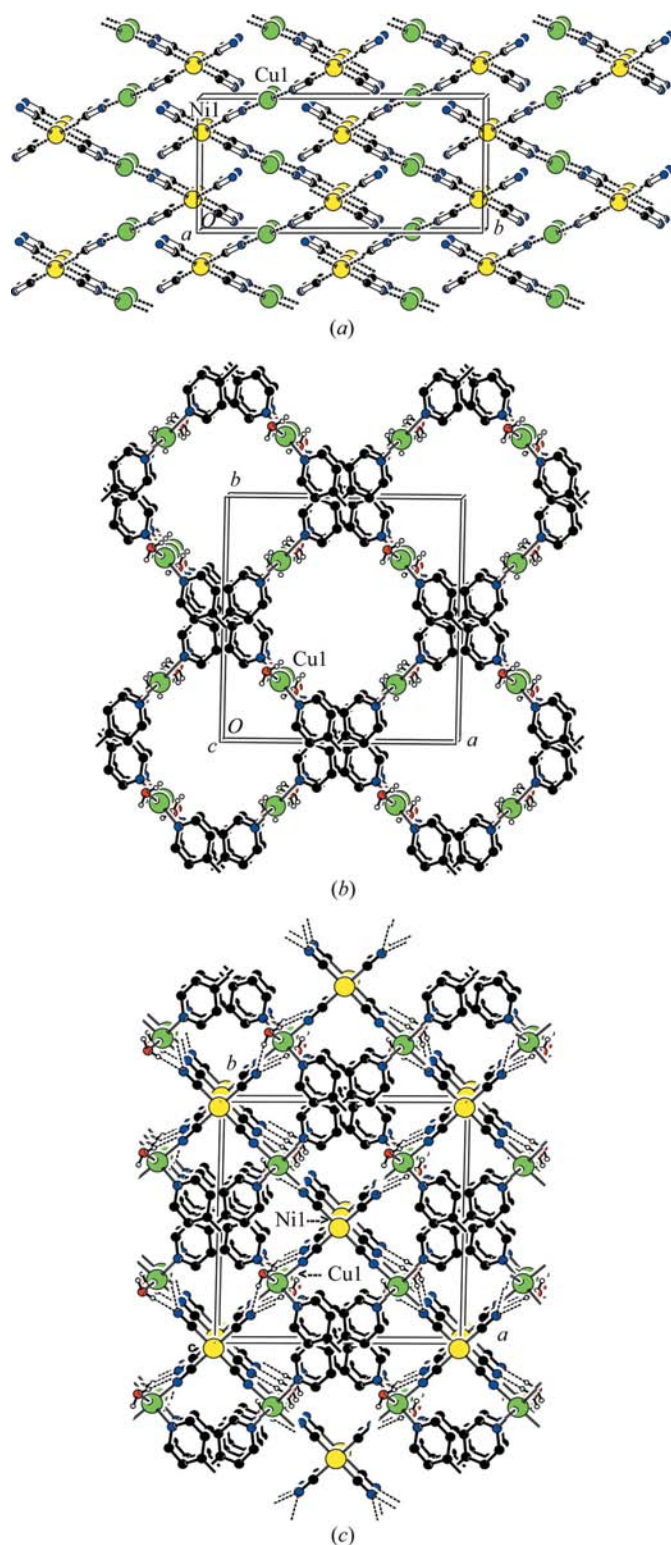
Figure 2
(a) A view down the *a* axis of the zigzag –Cu—N≡C—Ni—C≡N—Cu– chains, extending in the *c* direction. (b) A view down the *c* axis of the mutually perpendicular arrangement of the –Cu–4,4′-bpy–Cu–4,4′-bpy– chains (the 4,4′-bpy H atoms have been omitted for clarity). (c) The crystal packing of (I), viewed along the *c* axis. The O—H···N hydrogen bonds are shown as dashed lines; see Table 2 for details (the 4,4′-bpy H atoms have been omitted for clarity).

as a bridging ligand with metallocyanides to form multi-dimensional complexes. A search of the Cambridge Structural Database (Version 5.18, November 2007 update; Allen, 2002) revealed only 13 crystal structures of metallocyanide complexes involving 4,4′-bpy, and only five of these concerned first-row transition metals. A few three-dimensional coordination polymers based on 4,4′-bpy and cyanide compounds have been reported (Soma *et al.*, 1994; Teichert & Sheldrick, 2000), but none involved tetracyanonickelate(II). We describe here the synthesis and structure of a new metal–organic cyanide-bridged framework, (I), formed from 4,4′-bipyridine, copper sulfate and tetracyanonickelate.

The molecular structure of the asymmetric unit of (I) is shown in Fig. 1, and selected geometrical parameters are given in Table 1. The crystal structure analysis of (I) revealed that it has a neutral three-dimensional framework, built up of $[Cu(4,4'-bpy)(H_2O)_2]^{2+}$ cations and $[Ni(CN)_4]^{2-}$ anions. The Cu^{II} atom is located on an inversion center, while the Ni^{II} atom sits on a twofold rotation axis. The 4,4′-bpy ligand is also situated about a center of symmetry, located at the center of the bridging C—C bond. The Cu atom has a distorted octahedral geometry, being coordinated to four N atoms in the equatorial plane, two from cyanide ligands and two from 4,4′-bpy ligands. The axial positions are occupied by two water molecules. The coordination polyhedron of the Cu atoms can be described as $Cu(N)_2(H_2O)_2(NC)_2$ or CuN_4O_2. Two of the four C≡N groups of the $[Ni(CN)_4]^{2-}$ anion are nonbridging, while the other two bond to the Cu1 atoms, giving rise to Ni—C≡N—Cu bridges and forming zigzag –Cu—N≡C—Ni—C≡N—Cu– chains extending in the *c* direction (Fig. 2a). The Ni atom has a square-planar arrangement, and the mean Ni—C and C≡N bond lengths are similar to the values reported for other tetracyanonickelate salts (Miyoshi *et al.*, 1973; Cernák & Lipkowski,1999; Akitsu & Einaga, 2006; Broring *et al.*, 2007). The Ni—C≡N angles are almost linear, and there is no difference between those involving the bridging N atom (N8) and the nonbridging N atom (N10). The Cu1—N≡C angles are slightly bent.

The centrosymmetric 4,4′-bpy ligands bonded to the Cu atoms in *trans* positions give rise to the formation of –Cu–4,4′-bpy–Cu–4,4′-bpy– chains, which run at right angles to one another (Fig. 2b). They are separated by a distance of *ca* 3.27 Å. These chains are connected to one another *via* two of the four C≡N groups of the $[Ni(CN)_4]^{2-}$ anions, so giving rise to the three-dimensional nature of the compound (Fig. 2c). The shortest Ni···Ni distance is 3.7514 (6) Å. The structure is further stabilized by O—H···N hydrogen bonds involving the coordinated water molecules and the N atoms of the nonbridging cyano groups (Table 2). There are also two C—H···O interactions involving the water molecules and two H atoms of symmetry-related 4,4′-bpy ligands.

Experimental

To an aqueous solution of $CuSO_4 \cdot 5H_2O$ (2 mmol, 0.499 g, 20 ml) was added with stirring $K_2[Ni(CN)_4]$ (2 mmol, 0.489 g) in water (20 ml). A blue precipitate formed at once and was dissolved by adding

appropriate amounts of citric acid (1.8 g) and 2-aminoethanol (1.6 ml) to adjust the pH to 9, giving a final volume of *ca* 100 ml. A portion of this solution (30 ml) was very carefully layered onto an ethylene glycol solution (20 ml) of 4,4′-bpy (1 mmol, 0.156 g). Green crystals of (I) appeared at the interface of the two solutions after several weeks. Analysis calculated for $C_{14}H_{12}CuN_6NiO_2$: C 40.18, H 2.89, N 20.08%; found: C 40.64, H 3.09, N 20.72%. IR (KBr disk): ν(O—H) 3513 (*s*), 3456 (*s*), 3379 (*sh*); $\nu(C_{ar}$—H) 3144 (*w*), 3109 (*w*), 3088 (*w*); ν(C—H) 3061 (*s*), 3045 (*s*); ν(C≡N) 2142 (*s*), 2121 (*s*); $\nu(C_{ar}$—C) 1641 (*vs*), 1615 (*vs*), 1537 (*m*), 1493 (*m*), 1435 (*s*); ν(O—H, C—C, C_{ar}—H in-plane) 1388 (*s*), 1369 (*s*), 1238 (*m*), 1212 (*m*), 1153 (*w*), 1099 (*m*), 1012 (*w*); $\nu(C_{ar}$—H out-of-plane) 866 (*w*), 728 (*m*), 688 (*m*), 660 (*sh*); ν(Ni—C, Cu—N) 553 (*w*), 483 (*m*), 454 (*m*).

Crystal data

[NiCu(CN)4(C10H8N2)(H2O)2]
$M_r = 418.55$
Monoclinic, $C2/c$
$a = 15.158$ (2) Å
$b = 14.8108$ (15) Å
$c = 7.4512$ (11) Å
$\beta = 111.892$ (11)°

$V = 1552.2$ (4) Å³
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.60$ mm⁻¹
$T = 173$ (2) K
$0.50 \times 0.45 \times 0.40$ mm

Data collection

Stoe IPDS diffractometer
Absorption correction: multi-scan
  (*MULscanABS*; Spek, 2003)
  $T_{min} = 0.246$, $T_{max} = 0.352$

8011 measured reflections
1389 independent reflections
1248 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.054$
$S = 1.04$
1389 reflections
120 parameters
2 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.22$ e Å⁻³
$\Delta\rho_{min} = -0.26$ e Å⁻³

Water H atoms were located in difference Fourier maps and were refined with O—H distance restraints of 0.88 (2) Å. The remainder of the H atoms were included in calculated positions and treated as riding atoms [C—H = 0.95 Å and U_{iso}(H) = $1.2U_{eq}$(C)].

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

Cu1—O1W	2.4199 (15)	Ni1—C7	1.858 (2)
Cu1—N1	2.0605 (16)	Ni1—C9	1.865 (2)
Cu1—N8	1.9754 (17)		
Ni1···Ni1^{v}	3.7514 (6)		
O1W—Cu1—N1	87.19 (6)	C7—Ni1—C9	89.98 (9)
O1W—Cu1—N8	91.46 (6)	C7—Ni1—C7^{i}	89.30 (9)
O1W—Cu1—O1W^{iv}	180	C7—Ni1—C9^{i}	179.23 (10)
N1—Cu1—N8	90.09 (7)	C9—Ni1—C9^{i}	90.74 (10)
N1—Cu1—N1^{iv}	180	Ni1—C7—N8	178.18 (19)
N8—Cu1—N8^{iv}	180	Ni1—C9—N10	178.6 (2)

Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (v) $-x + 1, -y + 1, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···N10^{vi}	0.85 (2)	2.04 (2)	2.886 (3)	177 (2)
O1W—H2W···N10^{vii}	0.84 (2)	2.15 (2)	2.976 (3)	169 (3)
C2—H2···N8^{iv}	0.95	2.43	2.964 (3)	115
C6—H6···N8	0.95	2.46	2.957 (3)	112

Symmetry codes: (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (vi) $x, -y + 1, z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

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