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Cyano-bridged extended heteronuclear supramolecular architectures with hexacyanoferrates(II) as building blocks

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Abstract

Two cyano-bridged heteronuclear coordination polymers $[\{Cu(bipn)\}_3Fe(CN)_6]_n(ClO_4)_{2n}\cdot 4nH_2O$ (bipn = bis(3-aminopropyl)-amine) (**1**) and $[\{Cd(tet)\}_2Fe(CN)_6]_n\cdot 3nH_2O$ (tet = triethylenetetramine) (**2**) were synthesized and their structures determined. Both complexes were obtained from the assembly reactions of $[ML_n]^{2+}$ (M = Cu, Cd; $n = 1, 2$) and $[Fe(CN)_6]^{4-}$ in aqueous solutions. Complex **1** exhibits a honeycomb structure with twisty rings formed by Cu(II), Fe(II), and cyanides. The anions ClO_4^- weakly coordinate to Cu(II) and form hydrogen bonds with amino groups of bipn, while water molecules link to the 2D network via hydrogen bonds. In complex **2**, the neutral polymer $[\{Cd(tet)\}_2Fe(CN)_6]_n$ forms zigzag chains. The water molecules insert between chains and pull them together to form a layered structure via a series of interchain hydrogen bonds. Thermal analyses over the temperature range 30–700°C show both complexes decompose completely above 460°C. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cyano-bridged complex; Heteronuclear coordination polymer; Hydrogen bond; Honeycomb structure

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1. Introduction

Coordination polymers with supramolecular structures are one of the most interesting topics in current chemistry and crystal engineering, both for the theoretical aspects related to the topologies of novel networks with zeolite-like inner cavities and channels [1], and for their potential applications in catalysis [2], host–guest chemistry [3] and molecular electronics [4]. One of the most successful strategy leading to heterometallic supramolecular architecture is using metal cations to link relatively stable coordination compounds containing potential bridging units. This synthetic strategy offers prospect of rationally designing extended solids with desired properties by linking together molecular building blocks with specific functionality and geometry.

Cyanide is an ambidentate ligand capable of bridging two metal centers in an asymmetric mode. The most outstanding and long-known example of such behavior is represented by the mixed-valence polymeric structure of Prussian blue [5], where cyanide is C-end attached to low-spin Fe(II) and N-end to high-spin Fe(III). Recently, the cyano-bridged polymeric materials have received great attention due to the following aspects. Firstly, Prussian blue analogues, derived from self-assemblies of the anionic block $[M(CN)_6]^{3-}$ (M = Cr [6c], Fe [6a–b,e,g,h], Mn [6f,l]) and the cationic fragment $(M'L_m)^{n+}$ (M′ = Mn [6a,e–l], Ni [6b,c]; L = terminal N-containing ligand; $m, n = 1, 2$ or 3) possessing one to four unsaturated coordination sites, are potential molecular-based magnets [6]. Secondly, the cyano-bridged organometallic coordination polymers [7] formed from the combination of the building blocks $[M(CN)_6]^{n-}$ (M = Co [7a–c,g], Fe [7a–j], Cu [7h]; $n = 3$ or 4) and $R_3M'^+$ (M′ = Sn [7a–j], Pb [7c]; R = aliphatic or aromatic group) represent a series of molecular materials and zeolite-like host–guest systems involved in novel charge-transfer ion pairs with multidimensional electron-donor networks. Thirdly, a series of cyano-bridged cadmium and nickel polymeric com-

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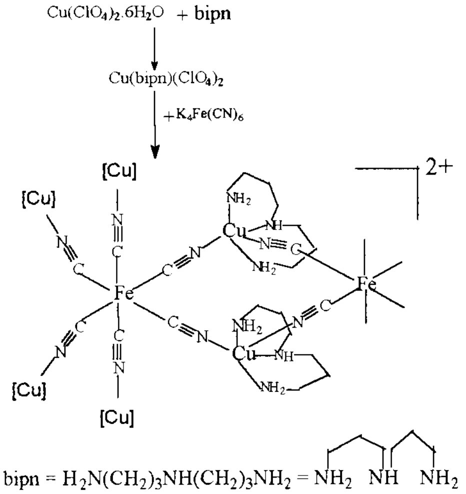
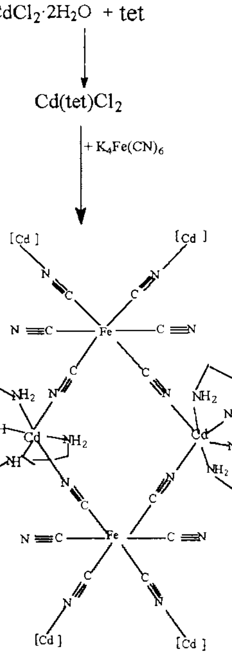
pounds [8] could include organic molecules in a host–guest type relationship. In addition, several cyano-bridged 3D polymers with interpenetrating nets were isolated via the linkage of metal ions and building blocks $[M(CN)_2]^-$ (M = Au [9a], Ag [9b–c]). This paper reports two novel 2D coordination polymers $[\{Cu(bipn)\}_3Fe(CN)_6]_n(ClO_4)_{2n}\cdot4nH_2O$ [bipn = bis(3-aminopropyl)amine] (**1**) and $[\{Cd(tet)\}_2Fe(CN)_6]_n\cdot3nH_2O$ (tet = triethylenetetramine) (**2**).



$[\{Cu(bipn)\}_3Fe(CN)_6]_n^{2+}$

1

Scheme 1.



Scheme 2.

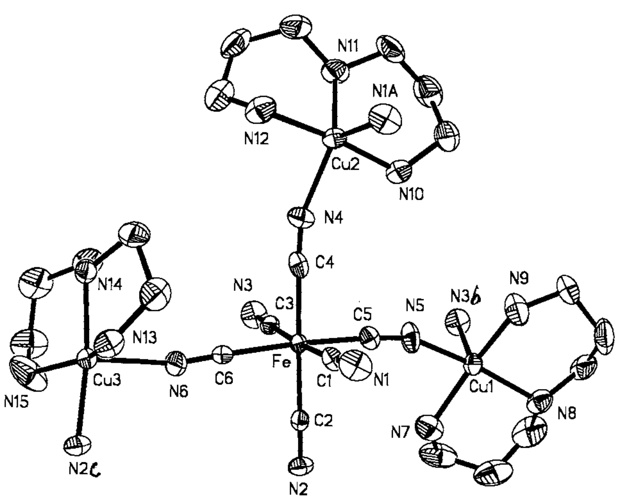


Fig. 1. The asymmetric unit of $[\{Cu(bipn)\}_3Fe(CN)_6]_n^{2n+}$ for **1** with the atom-labeling scheme.

2. Results and discussion

2.1. Syntheses and characterization

Both reactions were performed in aqueous solutions according to the strategies depicted in Schemes 1 and 2, together with the abbreviations of the ligands. Salts of Cu(II) and Cd(II) reacted first with the suitable ligands to give coordinated salts, which then reacted with 0.5 equivalents of the hexacyanoferrate(II) to give products **1** and **2**, respectively. The cyanides exhibit the bidentate bridging nature by forming the pathways M–N≡C–Fe to build up the coordination polymers. However, the cyanides are all bridges in **1** and both bridges and terminal in **2**.

2.2. Structure of $[\{Cu(bipn)\}_3Fe(CN)_6]_n(ClO_4)_{2n}\cdot4nH_2O$ (1)

Crystal **1** contains the cation $[\{Cu(bipn)\}_3Fe(CN)_6]_n^{2n+}$, anions ClO_4^- and solvated water molecules. A perspective view of the asymmetric unit $[\{Cu(bipn)\}_3Fe(CN)_6]^{2+}$ with the atom-labeling scheme is depicted in Fig. 1. Atoms Cu(1) and Cu(3) are both located inside distorted square-based pyramids with the basal plane composed of the three N atoms from one bipn ligand and an atom from a cyanide group, while the apex of the pyramid occupied by the N-end of another cyanide. The bridge pathways Cu(1, 3)–N≡C–Fe are non-linear with angles in the range 158–162°. One of the oxygen atoms (O(8) or O(2)) of an anion ClO_4^- coordinates weakly to the Cu atom (Cu(1) or Cu(3), respectively) on the other side of the basal plane with a distance 3.2–3.4 Å.

However, the geometry of Cu(2) is a compressed trigonal-bipyramid with atoms N(1a) (Cu(2)–N(1a) 2.125(8) Å), N(4) (Cu(2)–N(4) 2.049(8) Å), and N(11)

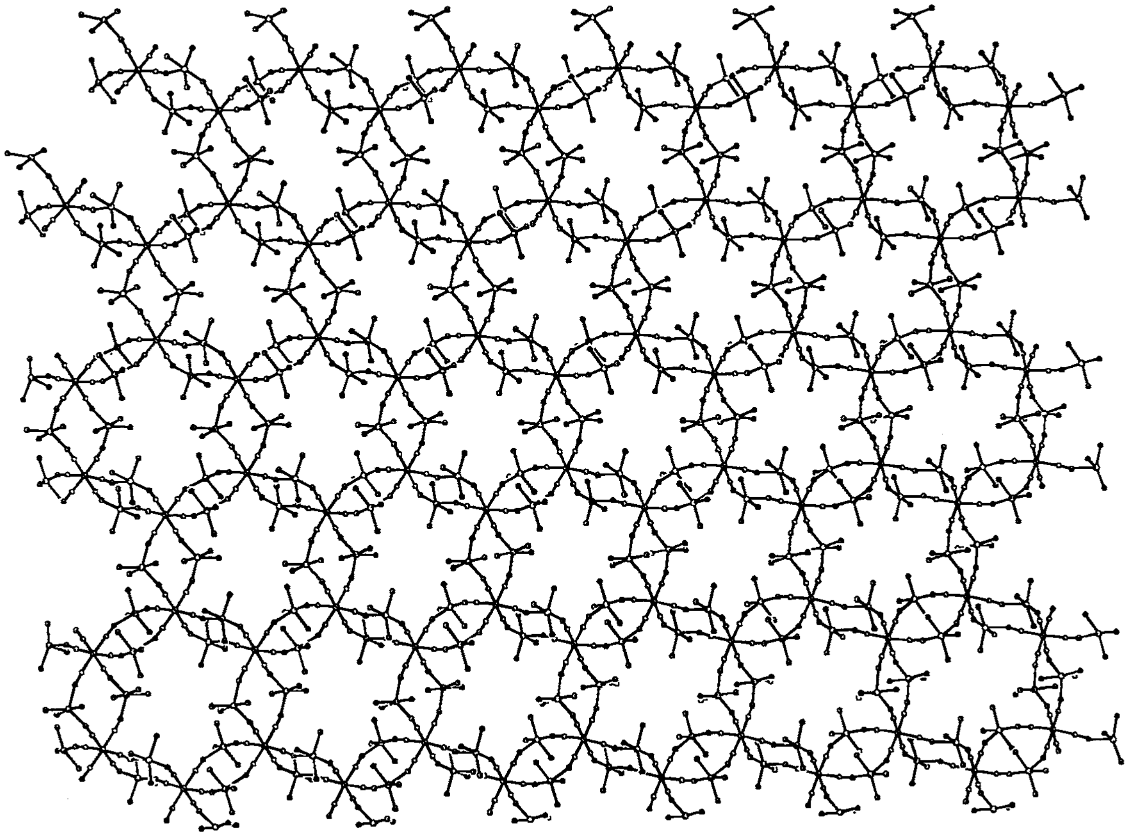


Fig. 2. A simplified view of the 2D honeycomb structure with twisty rings extending along the *ab* plane for $[\{Cu(bipn)\}_3Fe(CN)_6]_n^{2n+}$ of **1**. All the C and H atoms of the bipn ligands have been omitted for clarity.

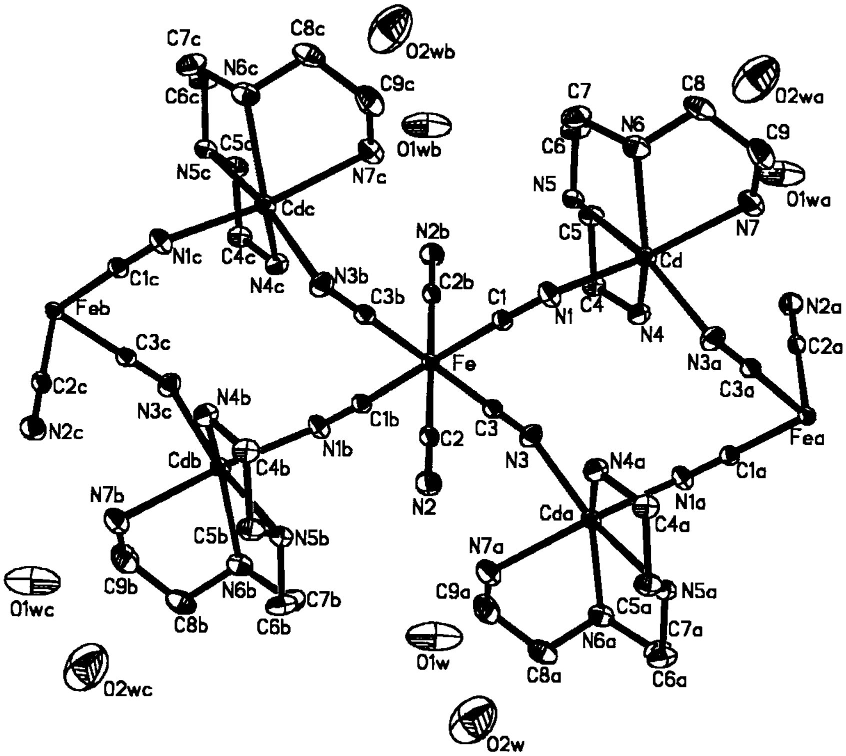


Fig. 3. View of two asymmetric units of $[\{Cd(tet)\}_2Fe(CN)_6]_n \cdot 3nH_2O$ (**2**) with atom-labeling scheme.

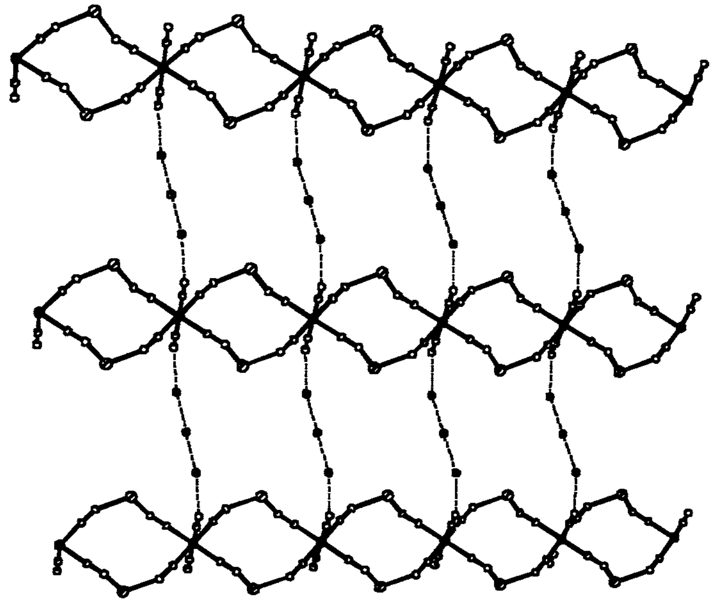


Fig. 4. The layer structure of $[\{Cd(tet)\}_2Fe(CN)_6]_n \cdot 3nH_2O$ (**2**) formed by zigzag chains joining together via H-bonding linkages –N···H–O···H–O–H···O–H···N– with the ligand tet omitted for clarity.

(Cu(2)–N(11) 2.093(8) Å) in the trigonal plane and N(10) (Cu(2)–N(10) 1.990(8) Å and N(12)(Cu(2)–N(12) 2.010(8) Å) in the axial sites. The bridging pathways Cu(2)–N≡C–Fe are non-linear with the angles Cu(2)–N(4)–C(4) and Cu(3)–N(1a)–C(1a) being 158.8 and 166.3°, respectively. The Fe(II) atom exhibits an octahedral geometry with six C donors (Fe–C = 1.902(8)–1.935(8) Å) from the cyanides which are bound to six nearest $[Cu(bipn)]^{2+}$ units. The angles C–Fe–C(*cis*) and C–Fe–C(*trans)* are close to 90 and 180°, respectively. The distances of Cu···Fe through the bridging pathways are in the range 4.494–5.183 Å.

As shown in Fig. 2, the bimetallic rings, which is derived from the linkage of six Fe(II) centers and twelve Cu(II) centers via twenty-four cyanides, are entwined with one another and extend along the *ab* plane to produce the 2D honeycomb-like sheets. The inner cavity of the distorted bimetallic ring has the dimension 14.7 × 10.8 Å.

The anions ClO_4^- form hydrogen bonds with amino groups of bipn with O···N distance in the range 3.055–3.184 Å. Hydrogen bonds are also present between H_2O and H_2O and amino groups of bipn with the distances $H_2O \cdots OH_2$ and $H_2O \cdots NH_2$ in the range 2.754–3.153 Å.

2.3. Structure of $[\{Cd(tet)\}_2Fe(CN)_6]_n \cdot 3nH_2O$ (2)

This complex contains neutral zigzag chains $\{[Cd(tet)]_2Fe(CN)_6\}_n$ and solvated water molecules. As shown in Fig. 3, atom Cd(II) adopts a distorted octahedral geometry with atoms N(4), N(5), N(6), N(7) from one tet ligand and atoms N(1), N(3a) from two cyanides. The average Cd–N distance is 2.362 Å. The Fe(II) atom also exhibits an octahedral geometry with six C donors (the Fe–C bond distances are in the range 1.903–1.927 Å) from six cyanides, four of which are bridges bound to four nearest Cd(II) ions while the other two are terminals forming hydrogen bonds with solvated water molecules. The bridging pathway Cd–N≡C–Fe is bent with the angles Cd–N(1)–C(1) and Cd–N(3a)–C(3a) being 131.4 and 119.4°, respectively.

In Fig. 3, the pseudo-rhombic units, all edges of which are bridging pathways Cd–N≡C–Fe, join one another through the apex Fe(II) to form doubly cyano-bridged zigzag chains. The solvated water molecules, inserted between chains, form a series of hydrogen bonds with one another and with nitrogen of the terminal cyanides. Consequently, the 2D structure is constructed by chains via interchain hydrogen bonds (Fig. 4). The hydrogen bonding pathway is N(2) ···O(1w)···O(2w)···O(1wd)···N(2d) with the distances N(2)···O(1w), O(1w)···O(2w), O(2w)···O(1wd), O(1wd)···N(2d) being 2.929, 2.647, 2.647 and 2.929 Å, respectively.

Plenty of extended polymers formed through cyanide bridges have been reported [10–15]. In these polymers the ambidentate coordination of cyanide always leads to the bridging pathway M_A–C≡N–M_B which may be linked in different ways to form a crystal lattice. Examples are represented by complexes $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [16a,c] and $[\{Cu(dien)\}_2 \cdot Fe(CN)_6] \cdot 6H_2O$ [16b] where both linear and non-linear modes of the bridging pathway Cu–N≡C–Fe exist. In complex $[Cu(dien)]_3[Fe(CN)_6]_2 \cdot 6H_2O$ [16a,c], *cis* cyanides occur in both linear and non-linear orientations when attached to the copper atoms, whereas it is the *trans* cyanides which occur in linear and bent linkages in [{Cu(dien)}$_2$·Fe(CN)$_6$]·6H$_2$O [16b]. This leads to one- and two-dimensional polymers, respectively. In our present work, all the bridging pathways Cu–N≡C–Fe in compound **1** are bent with the angles Cu–N–C in the narrow range 156.8–166.3° which is half-way between the average values for linear (about 170°) and non-linear (about 140°) modes in literatures [16]. The coordinate geometries of Cu(1) and Cu(3) are distorted square-basal pyramid whereas that of Cu(2) is trigonal-bipyramid. In compound **2**, The bridging pathways Cd–N≡C–Fe bend severely with the angles Cd–N(1)–C(1) and Cd–N(3a)–C(3a) being 131.4 and 119.4°, respectively. The coordinate geometry of Cd is a distorted octahedron. The bent linkages of Cu (or Cd)–N≡C–Fe and the coordination behaviors of Cu(II) and Cd(II) lead to two different 2D structures in **1** and **2**. Therefore, we can conclude that non-linear linkage M_A–N≡C–M_B and suitable coordination geometry of M_A and M_B can induce different network structures.

2.4. Thermal behavior

The thermal gravimetric analysis shows that **1** will be oxidized to CuO and Fe$_2$O$_3$ near the temperature 460°C. Before that temperature, the solvated water molecules are lost first. The TG curve of [{Cu(bipn)}$_3$Fe(CN)$_6$]$_n$(ClO$_4$)$_{2n}$·4nH$_2$O (**1**) suggests a weight loss of 6.84% in the temperature range 87–123°C, corresponding to the degradation of the four solvated water molecules (theoretical value 6.7%). A rapid loss of weight in the narrow temperature range 190–200°C, reveals that the ligand bipn and anion ClO$_4^-$ are removed at the same time, which may be accompanied by partial loss of bridging cyanides, since the measured weight loss (64.7%) is higher than the theoretical value (55.6%) calculated for bipn and ClO$_4^-$ only. The TG analysis for [{Cd(tet)}$_2$Fe(CN)$_6$]$_n$·3nH$_2$O (**2**) indicates that the solvated water molecules are lost first in the temperature range 115–150°C. At about 280°C, the polymeric chain structure begins to break down and the ligands are released. Above 300°C, the

Table 1
Crystallographic data for complexes **1** and **2**

Complex	**1**	**2**
Formula	$C_{24}H_{59}Cl_2Cu_3FeN_{15}O_{12}$	$C_{18}H_{42}N_{14}O_3Cd_2Fe$
M_w	1067.23	783.30
Color and habit	Black purple prism	Yellow prism
Crystal size (mm)	0.22 × 0.26 × 0.48	0.32 × 0.48 × 0.50
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.799(2)	7.7570(10)
b (Å)	13.292(3)	8.8390(10)
c (Å)	14.496(2)	10.9850(10)
α (°)	81.190(10)	89.370(10)
β (°)	85.710(10)	88.450(10)
γ (°)	61.840(10)	77.690(10)
U (Å^3)	2148.6(7)	735.58(14)
Z	2	1
T (K)	295(2)	295(2)
λ (Mo–K$_\alpha$) (Å)	0.71073	0.71073
$D_{calc.}$ (g cm^{-3})	1.650	1.768
μ (cm^{-1})	19.90	19.65
F(000)	1102	394
2θ Range (°)	4.20 to 50.00	3.70 to 58.00
h, k, l Ranges	0–14, −13 to 15, −17 to 17	0–10, −11 to 12, −14 to 14
Independent reflections	7425	3920
Observed reflections ($I > 2\sigma(I)$)	5728	3565
R [a]	0.0678	0.0189
wR_2 [b]	0.1957	0.0457
No. of variables	515	259
S	1.079	1.024
Residual extreme (e Å^{-3})	1.660 to −0.596	0.431 to −0.309
$(\Delta/\sigma)_{max}$	0.002	0.002
R_{int}	0.0206	0.0141

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma\, w(|F_o|^2 - |F_c|^2)^2/\Sigma\, w(F_o^2)^2]^{1/2}$. $w = [\sigma^2(F_o^2) + (0.0671P)^2 + 29.0790P]^{-1}$ **1**. $w = [\sigma^2(F_o^2) + (0.0281P)^2 + 0.061P]^{-1}$ **2**. $P = [|F_o^2| + 2|F_c^2|]/3$.

Table 2
Selected atomic distances (Å) and bond angles (°) for complex **1** [a]

Cu(1)–N(5)	2.001(8)	Cu(1)–N(7)	2.016(9)	Fe–C(4)	1.917(9)
Cu(1)–N(9)	2.019(8)	Cu(1)–N(8)	2.081(8)	Fe–C(6)	1.921(8)
Cu(1)–N(3b)	2.160(8)	Cu(2)–N(10)	1.990(8)	Fe–C(5)	1.905(9)
Cu(2)–N(12)	2.010(8)	Cu(2)–N(4)	2.049(8)	Fe–C(2)	1.920(8)
Cu(2)–N(11)	2.093(8)	Cu(2)–N(1a)	2.125(8)	Fe–C(1)	1.935(8)
Cu(3)–N(2c)	1.998(7)	Cu(3)–N(15)	2.032(9)	Fe–C(3)	1.902(8)
Cu(3)–N(13)	2.041(7)	Cu(3)–N(14)	2.049(7)	Cu(3)–N(6)	2.173(8)
N(5)–Cu(1)–N(7)	86.2(4)	N(5)–Cu(1)–N(9)	84.9(3)		
N(7)–Cu(1)–N(9)	158.7(4)	N(5)–Cu(1)–N(8)	165.8(3)		
N(7)–Cu(1)–N(8)	91.2(4)	N(9)–Cu(1)–N(8)	92.7(3)		
N(5)–Cu(1)–N(3b)	98.4(3)	N(7)–Cu(1)–N(3b)	99.5(4)		
N(9)–Cu(1)–N(3b)	100.9(4)	N(8)–Cu(1)–N(3b)	95.7(3)		
N(10)–Cu(2)–N(12)	173.8(4)	N(10)–Cu(2)–N(4)	86.2(3)		
N(12)–Cu(2)–N(4)	88.3(4)	N(10)–Cu(2)–N(11)	91.1(3)		
N(12)–Cu(2)–N(11)	91.0(3)	N(4)–Cu(2)–N(11)	136.6(3)		
N(10)–Cu(2)–N(1a)	92.4(3)	N(12)–Cu(2)–N(1a)	92.3(4)		
N(4)–Cu(2)–N(1a)	113.0(3)	N(11)–Cu(2)–N(1a)	110.4(3)		
N(2c)–Cu(3)–N(15)	84.1(4)	N(2c)–Cu(3)–N(13)	90.4(3)		
N(15)–Cu(3)–N(13)	151.1(4)	N(2c)–Cu(3)–N(14)	173.1(3)		
N(15)–Cu(3)–N(14)	90.8(4)	N(13)–Cu(3)–N(14)	91.9(3)		
N(2c)–Cu(3)–N(6)	95.5(3)	N(15)–Cu(3)–N(6)	113.9(4)		
N(13)–Cu(3)–N(6)	94.8(3)	N(14)–Cu(3)–N(6)	90.8(3)		
C(3)–Fe–C(5)	88.9(3)	C(3)–Fe–C(4)	89.7(4)		
C(5)–Fe–C(4)	92.1(4)	C(3)–Fe–C(2)	91.8(3)		
C(5)–Fe–C(2)	87.7(3)	C(4)–Fe–C(2)	178.5(4)		
C(3)–Fe–C(6)	87.5(3)	C(5)–Fe–C(6)	173.8(4)		
C(4)–Fe–C(6)	92.9(3)	C(2)–Fe–C(6)	87.4(3)		
C(3)–Fe–C(1)	176.6(3)	C(5)–Fe–C(1)	89.9(3)		
C(4)–Fe–C(1)	87.2(4)	C(2)–Fe–C(1)	91.3(3)		
C(6)–Fe–C(1)	94.0(3)				

[a] Symmetry transformations used to generate equivalent atoms: $a = -x+1, -y+1, -z+1$; $b = -x+2, -y+1, -z+1$; $c = -x+2, -y, -z+1$.

thermal behavior is quite complicated since there could be a number of decomposition processes. The thermogravimetric results are consistent with the structural findings. The water molecules in compounds **1** and **2** link to the frameworks via only weak hydrogen bonds, so that dehydration is easy. The anions ClO_4^- in **1** link to the honeycomb framework via not only hydrogen bonds but also weak coordination bonds to Cu(II). Perhaps the loss of group ClO_4^- causes changes in the coordinate geometry of Cu(II) and leads to breakdown of the network.

3. Experimental

Bis(3-aminopropyl)amine, triethylenetetramine, $K_4Fe(CN)_6{\cdot}3H_2O$, and $CdCl_2{\cdot}2H_2O$ were used as purchased. $Cu(ClO_4)_2{\cdot}6H_2O$ was synthesized by reacting $CuCO_3{\cdot}Cu(OH)_2$ with $HClO_4$. IR spectra were recorded on a Nicolet FT-IR-170SX spectrophotometer with KBr pellets in the range 4000–400 cm^{-1}.

CAUTION: Though no danger was encountered in this experiment, perchlorate salts containing organic ligands should be prepared in small amounts and handled with care.

3.1. $[\{Cu(bipn)\}_3Fe(CN)_6]_n(ClO_4)_{2n}{\cdot}4nH_2O$ (**1**)

To the aqueous solution (25 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1.0 mmol) was added bis(3-aminopropyl)-amine (bipn) (0.14 ml, 1.0 mmol) with stirring while the solution changed color from pale blue to violet–blue. An aqueous solution (10 ml) of $K_4Fe(CN)_6{\cdot}3H_2O$ (0.211 g, 0.5 mmol) was then added. Several minutes later, the mixture was filtered and the dark-purple filtrate was allowed to stand at room temperature for several days to give black purple crystals. Yield: 53%. Anal. for $C_{24}H_{59}N_{15}O_{12}Cl_2Cu_3Fe$: Found C, 27.31; H, 5.27; N, 20.21%. Anal. Calc. C, 26.98; H, 5.53; N, 19.68%. IR (KBr pellet)/cm^{-1}: 3592 m, 3346 w, 3240 m, 2945 w, 2889 w, 2066 s, 1651 w, 1588 m, 1419 w, 1117 s, 1082 s, 1025 m, 892 w, 625 m, 589 m, 512 w, 421 w.

3.2. $[\{Cd(tet)\}_2Fe(CN)_6]_n{\cdot}3nH_2O$ (**2**)

The ligand triethylenetetramine (tet) (0.3 ml, 2.0 mmol) was added to the water solution (40 ml) of

Table 3
Selected atomic distances (Å) and bond angles (°) for complex **2** [a]

Cd(a)–N(3)	2.313(2)	Cd–N(1)	2.322(2)
Cd–N(4)	2.364(2)	Cd–N(5)	2.389(2)
Cd–N(7)	2.391(2)	Cd–N(6)	2.393(2)
Fe–C(1)	1.903(2)	Fe–C(1b)	1.903(2)
Fe–C(3b)	1.917(2)	Fe–C(3)	1.917(2)
Fe–C(2)	1.927(2)	Fe–C(2b)	1.927(2)
N(3a)–Cd–N(1)	91.23(6)	N(3a)–Cd–N(4)	93.99(6)
N(1)–Cd–N(4)	101.79(6)	N(3a)–Cd–N(5)	166.53(5)
N(1)–Cd–N(5)	85.72(6)	N(4)–Cd–N(5)	73.87(6)
N(3a)–Cd–N(7)	83.10(8)	N(1)–Cd–N(7)	158.40(7)
N(4)–Cd–N(7)	99.40(7)	N(5)–Cd–N(7)	104.30(7)
N(3a)–Cd–N(6)	118.33(6)	N(1)–Cd–N(6)	90.66(6)
N(4)–Cd–N(6)	145.23(6)	N(5)–Cd–N(6)	74.87(6)
N(7)–Cd–N(6)	74.05(7)	C(1)–Fe–C(1b)	180.0
C(1)–Fe–C(3b)	92.18(7)	C(1b)–Fe–C(3b)	87.82(7)
C(1)–Fe–C(3)	87.82(7)	C(1b)–Fe–C(3)	92.18(7)
C(3b)–Fe–C(3)	180.0	C(1)–Fe–C(2)	90.80(7)
C(1)–Fe–C(2)	89.20(7)	C(3b)–Fe–C(2)	89.83(7)
C(3)–Fe–C(2)	90.17(7)	C(1b)–Fe–C(2)	89.20(7)
C(1b)–Fe–C(2b)	90.80(7)	C(3b)–Fe–C(2b)	90.17(7)
C(3)–Fe–C(2b)	89.83(7)	C(2)–Fe–C(2b)	180.000(1)

[a] Symmetry transformations used to generate equivalent atoms: $a = -x+1, -y, -z+1$; $b = -x+2, -y, -z+1$; $c = -x+2, -y-1, -z$.

$CdCl_2 \cdot 2H_2O$ (0.457 g, 2.0 mmol) while stirring, then an aqueous solution (10 ml) of $K_4Fe(CN)_6 \cdot 3H_2O$ (0.422 g, 1.0 mmol) was added to the mixture. After stirring for a few minutes, the solution was filtered and the filtrate stood at ambient temperature for a week to give yellow crystals. Yield: 53.8%. Anal. for $C_{18}H_{42}N_{14}O_3FeCd_2$: Found C, 27.87; H, 5.37; N, 26.95%. Anal. Calc. C, 28.24; H, 5.27; N, 25.62%. IR (KBr pellet)/cm^{-1}: 3374 m, 3339 s, 3282 m, 3254 w, 2938 w, 2910 m, 2868 m, 2038 s, 1630 w, 1588 m, 1454 m, 1363 w, 1096 w, 1011 m, 948 m, 828 m, 582 m, 505 w, 421 w.

3.3. Crystal structure determination

Single crystals with suitable dimensions were mounted on glass fibers and data collections were performed on a Siemens P4 diffractometer for both complexes by ϖ scan technique using the graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The crystallographic data are summarized in Table 1.

The coordinates of the metal atoms were determined by direct methods for **1** and by Patterson method for **2** and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structures were refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the hydrogen atoms were mostly isotropically added to the structure factor calculations but not refined, except those described otherwise. For **1**, all the hydrogen atoms were added theoretically except those of solvated water molecules, which remained undetermined. The final density maximum is 1.071 and 1.412 Å for N(7) and C(7), respectively. For **2**, the site occupancy factor of O(2) is 0.5. The calculations for both complexes were performed on an IBM PC/486 computer with the Siemens SHELXL/PC program package [17]. The final *R* values were 0.0678 and 0.0189 for **1** and **2**, respectively. Selected atomic distances and bond angles are presented in Tables 2 and 3 for **1** and **2**, respectively.

4. Supplementary material

Complete crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles are available. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 131490 for compound **1** and CCDC no. 131491 for compound **2**.

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