

A novel μ_3 -cyano-bridged heterotrimetallic 2-D coordination polymer constructed from rectangular grids

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A novel μ_3 -cyano-bridged heterotrimetallic 2-D coordination polymer constructed from rectangular grids was isolated and characterized crystallographically.

Construction of coordination polymers *via* metal coordination directed self-assembly processes was spawned by a fundamental interest in the development of new approaches to the prediction of crystal structures, and has subsequently been fuelled by many promising applications such as bio-mimic models or functional materials for catalysis, absorption, nonlinear optics, and molecular magnetic materials *etc.*^{1–3} Assembly of extended structures by propagating the chemical structure of multifunctional ligands and the coordination geometry of metal ion species may yield a series of network architectures with various topologies. Recently, there has been increasing interest in polynuclear or polymeric metal cyanides owing to their often remarkable structural as well as physical and chemical properties.^{4–7} One of the most prominent characteristics of CN^- is its ability to act either as a terminal or as a bridging ligand. Although many 2-D and 3-D metal cyanides have been reported, most of them are assembled from bimetallic units with μ -bridging. To our surprise, coordination polymers constructed by μ_3 - and μ_4 -cyano-bridging have been crystallographically documented in only two instances, namely the layer-type double salts, $3\text{AgCN}\cdot 2\text{AgF}\cdot 3\text{H}_2\text{O}$ and $\text{AgCN}\cdot 2\text{AgF}\cdot 3\text{H}_2\text{O}$.^{7c} Our work is devoted to obtaining 2-D or 3-D heterometallic compounds based upon the diversity of the bridging modes of the cyanide group, in order to extend the studies on framework structures constructed by CN^- . Herein, we report a novel 2-D framework constructed by rectangular grids, $[\text{Cd}(\text{tren})_2[\text{Fe}(\text{CN})_6]]$ ($\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$), which possesses a trimetallic T-shaped motif consisting of two Cd^{II} and one Fe^{II} atoms. To the best of our knowledge, this is the first example of a heterometallic coordination polymer constructed by μ_3 -bridging cyanides.

To an aqueous solution of sodium silicate (1.5 M), hydrochloric acid (0.5 M) was added until pH 7.0. The resulting gel was placed into a U-tube and allowed to set for one day. Diffusion in opposite directions of the U-tube with aqueous solutions of $\text{K}_4[\text{Fe}(\text{CN})_6]$ (3 mmol) and $\text{Cd}(\text{NO}_3)_2$ (3 mmol) and tren (3 mmol) for three weeks produced light yellow, plate-like single crystals suitable for X-ray structure determination. All crystals were separated from the silica gel manually.† Yield: $\approx 60\%$. The compound was characterized by X-ray structure analysis.‡

The building-block unit of the extended structure is shown in Fig. 1: the two Cd^{II} centers are bridged by two N atoms from $\mu_3\text{-CN}^-$, and each Cd^{II} ion is also coordinated by one $\mu\text{-CN}^-$ and four N atoms of tren to form a distorted pentagonal bipyramid. The Cd-N (2.326–2.653 Å) distances are in accordance with

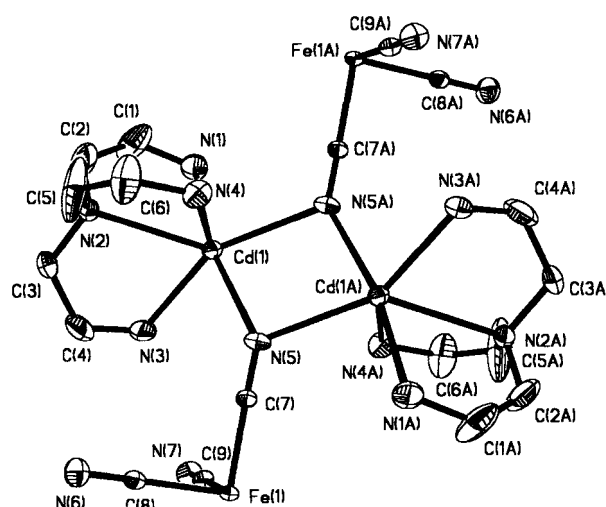


Fig. 1 ORTEP⁹ plot of the μ_3 -cyano-bridged trimetallic building-block, showing 30% probability displacement ellipsoids. The $\text{Cd}(1)$ atom is also coordinated by another $\text{N}(7)$ atom (2.459(4) Å) from $\mu\text{-CN}^-$ generated by the symmetry operation $(-x + 1, -y, -z + 2)$. Bond lengths: $\text{Cd}(1)\text{--N}(1)$ 2.343(5), $\text{Cd}(1)\text{--N}(2)$ 2.653(4), $\text{Cd}(1)\text{--N}(3)$ 2.326(5), $\text{Cd}(1)\text{--N}(4)$ 2.336(5), $\text{Cd}(1)\text{--N}(5)$ 2.526(4), $\text{Cd}(1)\text{--N}(5A)$ 2.575(4), $\text{Fe}(1)\text{--C}(7)$ 1.899(4), $\text{Fe}(1)\text{--C}(8)$ 1.927(5), $\text{Fe}(1)\text{--C}(9)$ 1.912(4), $\text{C}(7)\text{--N}(5)$ 1.154(6), $\text{C}(8)\text{--N}(6)$ 1.151(6), $\text{C}(9)\text{--N}(7)$ 1.172(6) Å. Bond angles: $\text{N}(5)\text{--Cd}(1)\text{--N}(5A)$ 78.00(14), $\text{Cd}(1)\text{--N}(5)\text{--Cd}(1A)$ 102.00(14), $\text{C}(7)\text{--N}(5)\text{--Cd}(1)$ 129.8(4), $\text{N}(5)\text{--C}(7)\text{--Fe}(1)$ 179.1(4)°.

those values previously reported.⁸ The long $\text{Cd}(1)\cdots\text{Cd}(1A)$ distance (3.962 Å) indicates that there is no obvious interaction between the two metal atoms. The Fe^{II} ion is octahedrally coordinated by six C atoms from pairs of μ -, μ_3 -, and terminal CN^- ligands. The C–N bond lengths are $\text{C}(9)\text{--N}(7)$ 1.172(6), $\text{C}(7)\text{--N}(5)$ 1.154(6), $\text{C}(8)\text{--N}(6)$ 1.151(6) Å, respectively.

The cyanide groups bridge the $\text{Cd}^{\text{II}}\text{--Fe}^{\text{II}}$ heterotrimetallic centers in two different fashions, namely μ - and μ_3 -, respectively, and thus result in two types of $\text{Fe--C}\equiv\text{N--Cd}_2$ sequences which construct the rectangular grids and further extend into a 2-D network along the ac plane, as shown in Fig. 2. The cross-sectional area of the rectangular grid is about 4.3×6.4 Å. The overall packing structure is shown in Fig. 3, which indicates that solvent water molecules are located between two 2-D sheets, and some of them form intermolecular hydrogen bonds to the N atoms of the terminal cyanides. There are two layers packed along the b axis in the unit cell, which makes the inter-layer distances about half of the b length, *ca.* 14 Å.

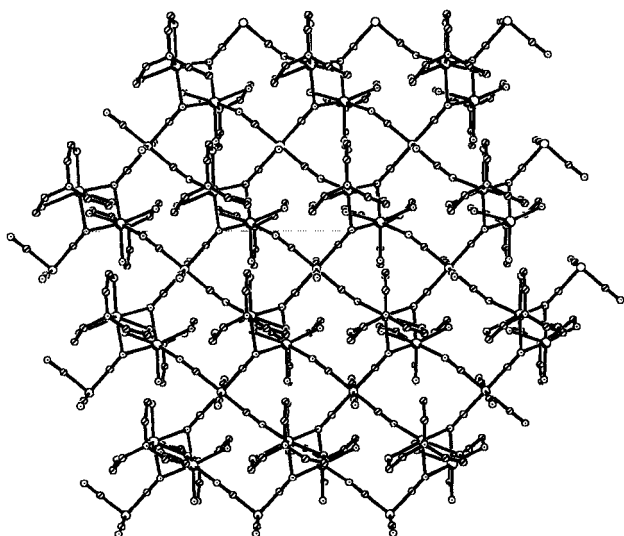


Fig. 2 2-D layer structure projecting along the *ac* plane.

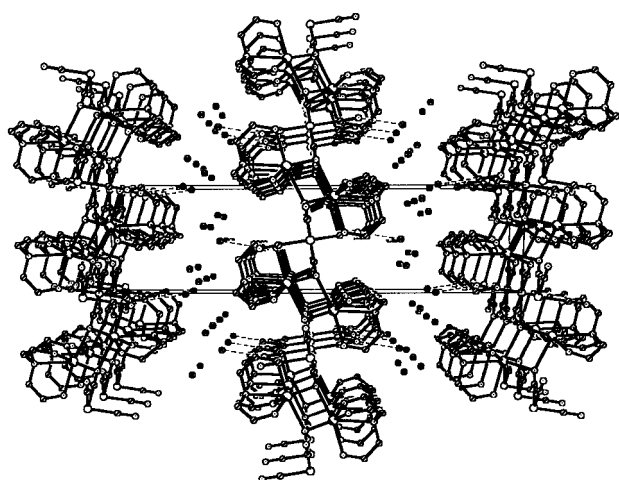


Fig. 3 Packing of the layers along the *b* axis. Hydrogen bonds are shown by dashed lines.

We are currently exploring the physical properties of this reported heterotrimetallic coordination polymer based on electronic interactions between adjacent metals mediated through μ_3 -bridging cyanide ligands.

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Notes and references

† The presence of three water molecules per unit was confirmed by single-crystal X-ray analysis, while four water molecules were found from elemental analysis. The water of crystallization was partly lost upon drying. Elemental analysis: $C_{18}H_{44}N_{14}O_4Cd_2Fe$: calcd.: C, 26.98; H, 5.53; N, 24.47; found: C, 26.73; H, 5.57; N, 24.16%. Selected IR data (KBr): $\nu(CN)$ 2065s, 2031s, 2010s cm^{-1} .

‡ Crystal data: light yellow, $C_{18}H_{42}N_{14}O_3Cd_2Fe$, $M = 783.28$, monoclinic, $P2_1/n$, $a = 7.5219(19)$, $b = 28.593(7)$, $c = 7.7246(19)$ Å, $\beta = 106.345^\circ$, $U = 1594.2(7)$ Å³, $Z = 2$, $D_c = 9.621$ g cm⁻³, $F(000) = 4396$. Crystal dimensions: $0.20 \times 0.15 \times 0.05$ mm, $\mu(Mo-K) = 12.212$ mm⁻¹, $T = 293$ K; $R1 = 0.0441$, $wR2 = 0.1093$. 9264 reflections measured, 3464 unique ($R_{int} = 0.0217$) which were used in all calculations. The structure was solved using direct methods and refined by full-matrix least-squares on F^2 . CCDC reference number 186/1939. See <http://www.rsc.org/suppdata/dt/b0/b003058i/> for crystallographic files in .cif format.

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