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Sandwich-like octacyanometalate-based cadmium assemblies with the 4,4'-dipyridyl sulfide ligand

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Self-assembly of octacyanotungstate, cadmium ions, and 4,4'-dipyridyl sulfide ligands has isolated the first octacyanometalate-based cadmium compounds, which exhibit novel sandwich-like coordination networks. The effect of solvent and temperature on the formation of products was discussed.

Advances in the field of porous coordination frameworks have been realized in the past few decades because of their robust adsorption/desorption abilities for guest molecules.[1] Among them, cyanide-bridged assemblies such as Hofmann-type clathrates and Prussian blue analogues with lower framework densities and higher specific surface areas have received particular attention, which can be ascribed to high thermal stabilities and easy to manipulate host frameworks with diverse linkers.[2-8]

Recently, octacyanometalate anions $[M(CN)_8]^{n-}$ (M = Mo, W; n = 3, 4) are intensively used as tectons in crystal engineering, due to the fact that their geometries vary between three ideal configurations: square antiprism, dodecahedron, and bicapped trigonal prism.[9.10] However, relatively few studies have reported their porous applications,[11-13] despite the first examples of octacyanometalate-based assemblies $M_2[Mo(CN)_8]\cdot nH_2O$ (M = Mn, Fe, Co, Ni, Cu, Zn; n = 2-9) have been documented as far back as 1973,[14] in comparison to the better known Hofmann-type clathrates and Prussian blue analogues. In fact, the syntheses and characterizations of octacyanometalate-based cadmium assemblies have not been reported to date. Also, the crystallization is a difficult process and the growth of molecular motifs depends on the combinations of many factors, such as reaction solvents and temperature, etc.[15-18] The 4,4'-dipyridyl sulfide (dps) ligand contains a delocalized π system and can bridge two or more remote metal centers to form multi-dimensional structures.[19,20] In the present contribution, we chose $[W(CN)_8]^{3-}$ as the precursor to react with Cd^{2+}

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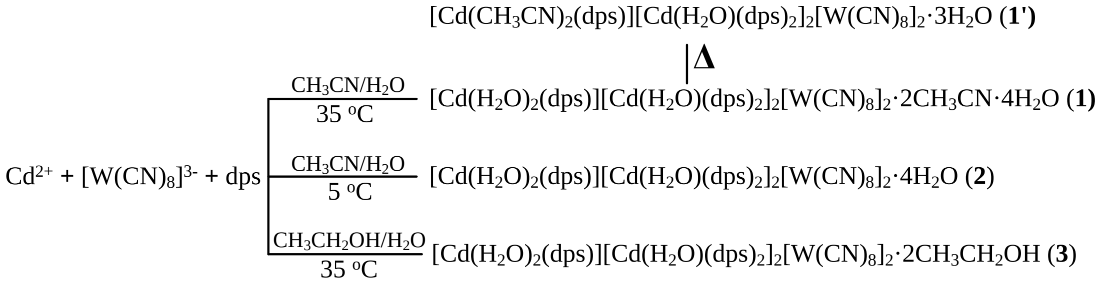
ions and dps ligands in different solvents or at different reaction temperatures (Scheme 1), isolating four cyanide-bridged bimetallic assemblies (**1**, **1'**, **2**, and **3**) with novel sandwich-like structures. Among them, compounds **1** and **3** were obtained under the same experiment condition except for the solvent system, while compounds **1** and **2** were isolated using the identical synthetic method except for the reaction temperature. Furthermore, compound **1'** was prepared upon the single crystal of compound **1** in situ heated to 340 K at ambient atmosphere on the single-crystal diffractometer. Above results indicate that the temperature and reaction solvents have an obvious impact on the formation of final products.


$[Cd(CH_3CN)_2(dps)][Cd(H_2O)(dps)_2]_2[W(CN)_8]_2 \cdot 3H_2O$ (**1'**)

Δ

$Cd^{2+} + [W(CN)_8]^{3-} + dps \xrightarrow[35\ ^oC]{CH_3CN/H_2O} [Cd(H_2O)_2(dps)][Cd(H_2O)(dps)_2]_2[W(CN)_8]_2 \cdot 2CH_3CN \cdot 4H_2O$ (**1**)

$\xrightarrow[5\ ^oC]{CH_3CN/H_2O} [Cd(H_2O)_2(dps)][Cd(H_2O)(dps)_2]_2[W(CN)_8]_2 \cdot 4H_2O$ (**2**)

$\xrightarrow[35\ ^oC]{CH_3CH_2OH/H_2O} [Cd(H_2O)_2(dps)][Cd(H_2O)(dps)_2]_2[W(CN)_8]_2 \cdot 2CH_3CH_2OH$ (**3**)

Scheme 1 The reaction equation of four compounds.

Single crystal X-ray diffraction analysis revealed that compounds **1**, **2**, and **3** have the same sandwich-like structure except for crystallized solvents involved. Here only the crystal structure of compound **1** was described in detail. Compound **1** crystallized in the monoclinic space group *C*2/*c*. The asymmetric unit consists of one $[Cd(H_2O)_2(dps)]^{2+}$ cation, two $[Cd(H_2O)(dps)_2]^{2+}$ cations, two $[W(CN)_8]^{3-}$ anions, and guest acetonitrile and water molecules (Figure 1). The S3 atom in the structure exhibits the crystallographically imposed twofold symmetry, while the Cd2 atom lies on an inversion centre.

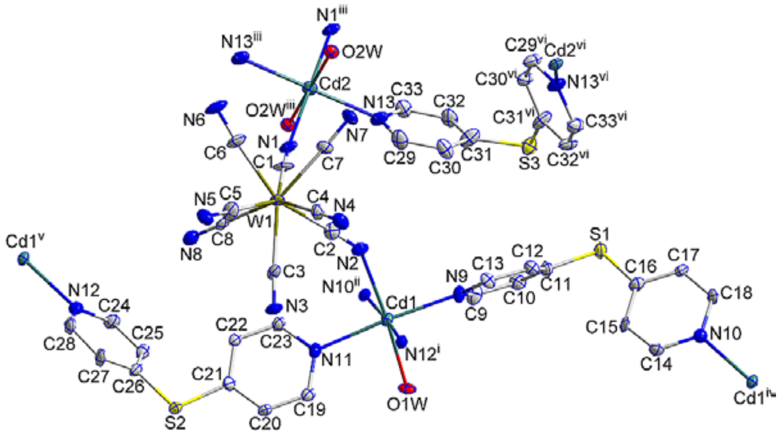
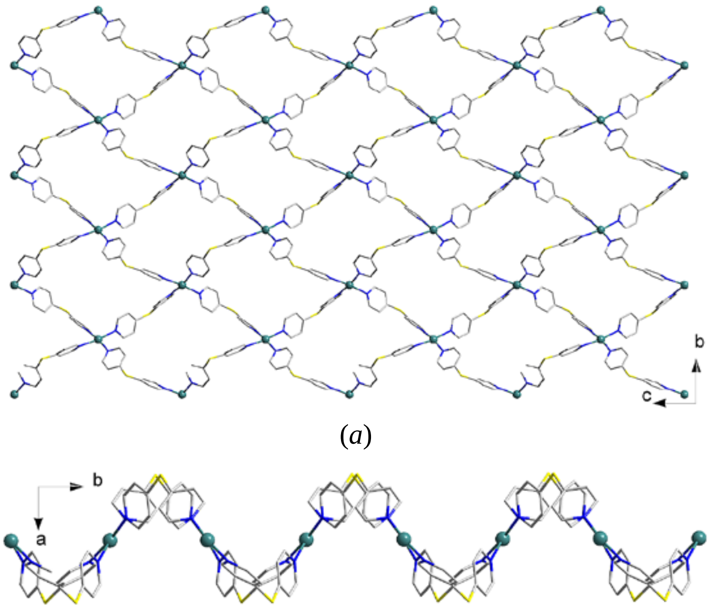


Figure 1 ORTEP diagram of compound **1** with thermal ellipsoids at the 30% probability level. All hydrogen atoms, crystallized acetonitrile and water molecules were omitted for clarity. Symmetry codes: (i) $x, -y, z + 1/2$; (ii) $x, -y + 1, z - 1/2$; (iii) $-x, -y, -z$; (iv) $x, -y + 1, z + 1/2$; (v) $x, -y, z - 1/2$; (vi) $-x, y, -z + 1/2$.

The eight-coordinated $[W(CN)_8]^{3-}$ unit adopts a slightly distorted square antiprism, typical for octacyanotungstates.[21-25] Two cyanide groups bridged to adjacent Cd(II) atoms in a *cis* fashion and the others are terminal. The W1-C bond distances range from 2.131(5) to 2.187(4) Å, and the W1-CN angels remain almost linear with the maximum deviation from linearity of 5.3°. There are two crystallographically independent Cd(II) centers (Cd1 and Cd2). The Cd1 atom exhibits a six-coordinated octahedral environment {CdN5O} with one cyano-nitrogen atom, four nitrogen atoms from dps ligands, and one water molecule. The Cd1-O and average Cd1-N bond lengths are 2.314(3) and 2.354 Å respectively. Opposite to the linear W1-CN bonds, the Cd1-NC bond is significantly bent with the angle of 145.2(4)°. The geometrical data of the Cd-O and Cd-N bonds conform to those reported for the monometric Cd(II)-dps compounds.[26,27]

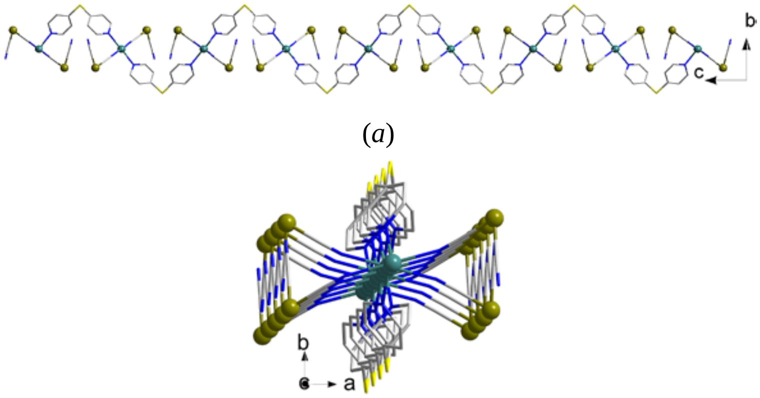
As shown in Figure 2, the Cd1 centers are linked alternatively by dps ligands in the *bc* plane to form a waved grid-type layer $[Cd(H_2O)(dps)_2]^{2+}$ with the diagonal distances of 12.005 and 19.003 Å. The Cd2 atom also adopts a six-coordinated octahedral environment {CdN4O2} with two cyano-nitrogen atoms, two nitrogen atoms from dps ligands, and two water molecules. The Cd2-O and average Cd2-N bond lengths are 2.326(3) and 2.314 Å, respectively, while the Cd2-NC bonds are obviously bent with the angle of 158.2(4)°. The Cd2 atoms are connected alternatively by dps ligands along the *c* axis to generate a zigzag chain $[Cd(H_2O)_2(dps)]^{2+}$ (Figure 3).



(*a*)

(*b*)

Figure 2 The $[Cd(H_2O)(dps)_2]^{2+}$ waved grid-type layer viewed from the (*a*) *a*, and (*b*) *c* axis for compound **1**. All hydrogen atoms and coordinated water molecules were omitted for clarity.



(*a*)

(*b*)

Figure 3 The $[Cd(H_2O)_2(dps)]^{2+}$ zigzag chain viewed from the (*a*) *a*, and (*b*) *c* axis for compound **1**; yellow balls: W, green balls: Cd, thin lines: dps and bridged cyanide ligands; all hydrogen atoms, coordinated water molecules and terminal cyanide ligands were omitted for clarity.

As a result, the $[Cd(H_2O)(dps)_2]^{2+}$ layers and $[Cd(H_2O)_2(dps)]^{2+}$ chains are further connected by two *cis* cyanide groups of $[W(CN)_8]^{3-}$ to generate a sandwich-like layer in the *bc* plane with the thickness of about 21.439 Å (S···S distance), in which the two face-to-face $[Cd(H_2O)(dps)_2]^{2+}$ sheets act as slices of breads, while the $[Cd(H_2O)_2(dps)]^{2+}$ chains and guest molecules act as the fillings (Figure 4). Similar sandwich-like structures have been also observed in other compounds.[28-30] Notably, to the best of our knowledge, compound **1-3** represent the first examples of octacyanometalate-based assemblies with the sandwich-like structure and also the first octacyanometalate-based cadmium compounds characterized structurally to date.

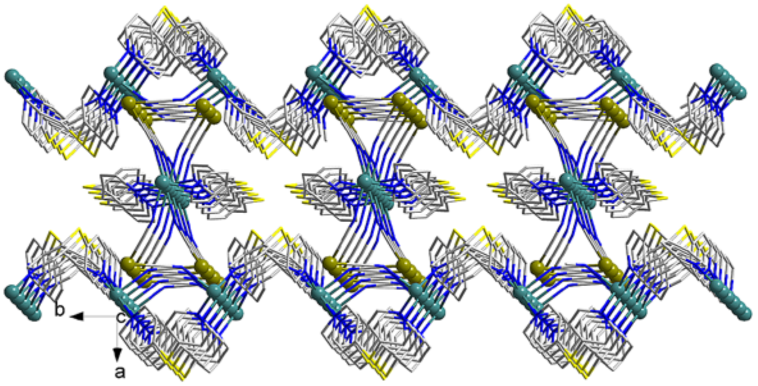


Figure 4 The sandwich-like structure of compound **1**; yellow balls: W, green balls: Cd, thin lines: dps and bridged cyanide ligands; all hydrogen atoms, coordinated and crystallized solvents and terminal cyanide groups were omitted for clarity.

Interestingly, both the formula and overall structural symmetry of compound **1** changed when the same single crystal was heated slowly to 340 K under the ambient atmosphere. The single crystal X-ray diffraction result collected at 340 K of compound **1** showed that the crystal of compound **1'** belongs to the monoclinic $P2_1/c$

space group, different from *C*2/*c* at 100 K for the same single crystal. The coordinated and uncoordinated solvents in the structure of compound **1'** also changed. As shown in Figure 5, the asymmetric unit of compound **1'** consists of one $[Cd(CH_3CN)_2(dps)]^{2+}$ cation, two $[Cd(H_2O)(dps)_2]^{2+}$ cations, and three crystallized water molecules.

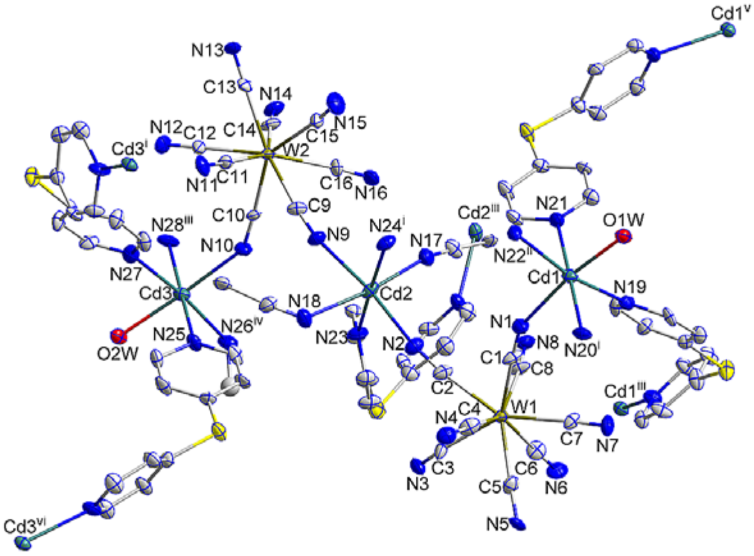


Figure 5 ORTEP diagram of compound **1'** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and crystallized water molecules were omitted for clarity. Symmetry codes: (i) *x*, −*y* + 1/2, *z* + 1/2; (ii) *x*, −*y* − 1/2, *z* + 1/2; (iii) *x*, −*y* + 1/2, *z* − 1/2; (iv) *x*, −*y* + 3/2, *z* − 1/2; (v) *x*, −*y* − 1/2, *z* − 1/2; (vi) *x*, −*y* + 3/2, *z* + 1/2.

There are three crystallographically independent Cd(II) centers (Cd1, Cd2, and Cd3) in compound **1'**. The significant difference between structures of compounds **1** and **1'** is the coordination geometry of Cd2 atom. The Cd2 center in compound **1'** adopts an octahedral environment {Cd2N6} with two cyano-nitrogen atoms, two nitrogen atoms from dps ligands, and two acetonitrile molecules. Obviously, the two water molecules coordinated to Cd2 atom in compound **1** has been substituted by two acetonitriles in compound **1'** after the heat treatment. Recent studies on $[M(CN)_6]$-, $[M(CN)_7]$- or $[M(CN)_8]$-based coordination networks revealed that hydration-dehydration processes may lead to significant structural modifications, and then drastic changes in magnetic properties.[31-35] In our case, however, the variety of solvents does not result in an obvious change of the overall network resulting from the WCN→Cd connections. The corrugated grid-type sheet for compound **1'** is formed on the *bc* plane in a similar way to compound **1**. Similar to compounds **1-3**, compound **1'** also exhibited a sandwich-like structure. It should be noted that the thickness of the resulting sandwich-like layer for compound **1'** was 21.160 Å (S···S distance), slightly less than 21.439 Å observed in compound **1**. In fact, this exchange of solvent molecules has caused the structural adaptation, which is reflected by the difference in the cell parameters. The cell volume of compound **1'** was reduced by *ca*. 1.5% compared with that of compound **1** with slight shrinking along the *a* axis, which can be reasonably ascribed to the reduction in the space occupied by solvent molecules. Different to compound **1**, the above phase transformation process was not observed in compounds **2** and **3**.

In summary, the first octacyanometalate-based cadmium compounds were prepared and characterized structurally, using dps as bridging ligands. The temperature has an obvious impact on the overall structural symmetry, while the novel sandwich-like coordination network was not tuned by reaction solvents. Further research along this line is in progress in our lab.

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Notes and references

‡ *Syntheses of compounds **1-3***: Single crystals of compounds **1** and **2** were prepared at 35 ^{o}C and 5 ^{o}C, respectively, by slow diffusion of an acetonitrile/water (V/V = 1/1) solution (3 mL) containing $CdSO_4·8/3H_2O$ (0.10 mmol) and dps (0.10 mmol) into an acetonitrile/water (V/V = 1/1) solution (20 mL) of $[HN(n\text{-}C_4H_9)_3]_3W(CN)_8$ (0.05 mmol). Pale-yellow rod-shaped crystals were obtained after about two weeks. IR for compound **1**: $\nu_{C\equiv N}$ = 2149, 2143, 2124, 2096 cm^{-1}; IR for compound 2: $\nu_{C\equiv N}$ = 2149, 2145, 2124, 2097 cm^{-1}. Substituting ethanol/water (V/V = 2/1) for acetonitrile/water (V/V = 1/1) in the synthesis procedure of compound **1** resulted in the formation of pale-yellow rod-shaped crystals of compound **3**. IR: $\nu_{C\equiv N}$ = 2143, 2105, 2099 cm^{-1}.

§ *Crystal data* for **1**: $C_{70}H_{62}Cd_3N_{28}O_8S_5W_2$, M_r = 2288.68, monoclinic, space group $C2/c$, a = 38.4736(12), b = 12.0047(10), c = 19.0031(16) Å, α = 90.00^{o}, β = 104.334(3)^{o}, γ = 90.00^{o}, V = 8503.6(10) Å^3, Z = 4, D_c = 1.788 g cm^{-3}, R_1 (wR_2) = 0.0461 (0.1163) and S = 1.073 for 9722 reflections with $I > 2\sigma(I)$. *Crystal data* for **1'**: $C_{70}H_{56}Cd_3N_{28}O_5S_5W_2$, M_r = 2234.63, monoclinic, space group $P2_1/c$, a = 38.0659(11), b = 11.9553(12), c = 18.9714(10) Å, α = 90.00^{o}, β = 103.9361(12)^{o}, γ = 90.00^{o}, V = 8379.5(10) Å^3, Z = 4, D_c = 1.771 g cm^{-3}, R_1 (wR_2) = 0.0409 (0.1001) and S = 1.017 for 16359 reflections with $I > 2\sigma(I)$. *Crystal data* for **2**: $C_{66}H_{56}Cd_3N_{26}O_8S_5W_2$, M_r = 2206.57, monoclinic, space group $C2/c$, a = 37.855(5), b = 11.8053(15), c = 18.885(2) Å, α = 90.00^{o}, β = 104.534(2)^{o}, γ = 90.00^{o}, V = 8169.3(18) Å^3, Z = 4, D_c = 1.794 g cm^{-3}, R_1 (wR_2) = 0.0389 (0.0869) and S = 1.071 for 7656 reflections with $I > 2\sigma(I)$. *Crystal data* for **3**: $C_{70}H_{60}Cd_3N_{26}O_6S_5W_2$, M_r = 2226.64, monoclinic, space group $C2/c$, a = 37.571(5), b = 11.9361(15), c = 19.196(2) Å, α = 90.00^{o}, β = 104.686(2)^{o}, γ = 90.00^{o}, V = 8327.4(18), Å^3, Z = 4, D_c = 1.776 g cm^{-3}, R_1 (wR_2) = 0.0259 (0.0622) and S = 1.044 for 7815 reflections with $I > 2\sigma(I)$. CCDC numbers: 1001207(**1**), 1001208(**1'**), 1001209(**2**), and 1001210(**3**).

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Graphical Abstract

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