

Three unique two-fold interpenetrated three-dimensional networks with PtS-type topology constructed from $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) as “square-planar” building blocks†

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Three unique three-dimensional cyanide-based networks with $\{4^28^4\}$ PtS-type topology, $\text{ZnM}(\text{CN})_4$ ($\text{M} = \text{Ni}(1), \text{Pd}(2), \text{Pt}(3)$), have been synthesized deliberately from $[\text{M}(\text{CN})_4]^{2-}$ as “square-planar” building blocks and characterized by single crystal X-ray diffraction.

Rational design and construction of cyanide-containing coordination frameworks are of great interest and have been attracting increasing attention owing to their intriguing molecular topologies as well as exciting properties, such as, high T_c ,¹ magneto-optics/electronics,² spin crossover,³ catalysis,⁴ molecular sieving,⁵ ion exchange,⁶ luminescence,⁷ nanoparticles,⁸ gas storage,⁹ zero/negative thermal expansion,¹⁰ and so on. The most usual and efficient strategy for synthesizing the above materials is based on a “building block” approach. The topology of the final structure is greatly dependent on the geometry of the nodes (metal centers) and/or the flexibility of the connectors (cyanometallates). Various dimensional polymers with desired functions based on $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$), $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$), $[\text{M}(\text{CN})_6]^{4-/\beta-}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ru}, \text{Os}$), $[\text{Mo}(\text{CN})_7]^{4-}$, and $[\text{M}(\text{CN})_8]^{4-/\beta-}$ ($\text{M} = \text{Mo}, \text{W}, \text{Nb}$) as building blocks have been synthesized and produced numerous fascinating archetypal topologies, including diamondoid,¹¹ quartz,¹² α -Po or ReO_3 ,¹³ and so on, the theory-predicted topologies of which have all been experimentally confirmed. All of these extraordinary structures are of fundamental importance in structural design and in understanding structure–property correlations. Among the successful synthetic strategies reported previously, 2-fold interpenetrating diamondoid network $\text{Zn}(\text{CN})_2$,^{10b} 6-fold interpenetrated quartz network $\text{Zn}[\text{Au}(\text{CN})_2]_2$,^{10c} and 3-fold interpenetrating cubic framework $\text{Ag}_3\text{Co}(\text{CN})_6$ ^{10d} exhibit intriguing negative thermal expansion (namely, NTE) properties.

In our previous work, we have synthesized four diamond networks using $[\text{M}(\text{CN})_8]^{4-}$ as building blocks.^{11a–d} As one part of our ongoing efforts in the design and synthesis of new structural types of cyanide-based functional crystalline materials, we chose the square planar node to react with the tetrahedral node in order to construct networks with a new type topology and interesting physical properties. It is well

known that there are three types of topological nets that have mixed tetrahedral and square building blocks: **pts**, **mog**, and **ptt** net. Among them, the PtS (**pts**) net consists of equal numbers of tetrahedral and square-planar nodes [Schläfli symbol $(4^2 \cdot 8^4)(4^2 \cdot 8^4)$], while the two different nodes in the moganite (**mog**) net are in the ratio of 1 : 2 (square-planar : tetrahedral) [Schläfli symbol $(4^2 \cdot 6^2 \cdot 8^2)(4 \cdot 6^4 \cdot 8_2)$]. Although there are equal numbers of square-planar and tetrahedral nodes in the twisted **pts** net (**ptt**), and each bonds only to the other, there are two types of square-planar node [Schläfli symbol $(4 \cdot 6^3 \cdot 8^2)(4^2 \cdot 6^2 \cdot 8^2)(6^2 \cdot 8^4)$]. Bearing this in mind, we chose $[\text{M}(\text{CN})_4]^{2-}$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) as the square planar node to react with an equivalent molar of metal center Zn acting tetrahedral node in order to construct a PtS-type topological network with the ratio between the two nodes being 1 : 1, in which the square and tetrahedral vertices are linked by just one kind of link (CN ligand). Excitingly, isostructural coordination networks $\text{ZnM}(\text{CN})_4$ ($\text{M} = \text{Ni}(1), \text{Pd}(2), \text{Pt}(3)$) with PtS topology have been obtained successfully.‡

The networks are very unusual in that except for displaying PtS-type topologies, they are also neutral frameworks with 2-fold interpenetration. It should be pointed out that, although examples of interpenetrated PtS-related metal–organic frameworks are becoming more common especially in the recent five years.^{14,15} To the best of our knowledge, only one cyanide-containing network represents PtS-type topology without interpenetration up to now,¹⁶ namely, $[\text{CuPt}(\text{CN})_4]^-$, which is charged due to the inclusion of Cu^I . However, it requires a charge-balancing cation, $[\text{NMe}_4]^+$, which serves to prevent interpenetration.

Single-crystal X-ray structural analysis reveals that **1–3** are isomorphous (Fig. S1†), so only the structure of **1**§ will be discussed here. **1** crystallizes in tetragonal space group $P4(2)/mcm$. As illustrated in Fig. 1, the asymmetric unit contains one Zn center and one $[\text{Ni}(\text{CN})_4]^{2-}$ moiety. The Zn atom is at a site with $-42m$ symmetry, while the Ni atom lies at a site with mmm symmetry. In addition, the C and N atoms lie at sites with m symmetry. Each Zn atom displays a tetrahedral geometry with four nitrogen atoms from four bridging cyanide groups, while each $[\text{Ni}(\text{CN})_4]^{2-}$ anion acts as a planar μ_4 -linker and bridges two tetrahedral Zn sites with a $\text{Zn} \cdots \text{Zn}$ separation of 7.433 Å. The length of the Zn–N bond is 1.846(12) Å, while that of the Ni–C bond is 1.140(15) Å. In addition, the bond Ni–CN–Zn rods of length 4.939 Å are close to linear. As a result, the centers Zn and Ni are linked through linear rods, forming a three-dimensional open framework structure. As expected, the network consists of equal numbers of square-planar and tetrahedral species, and thus form an interesting network with the desired PtS-type topology (Fig. 2), in which the Zn atom can be considered as the S vertex, while the $[\text{Ni}(\text{CN})_4]^{2-}$ unit decorates the Pt position in PtS.

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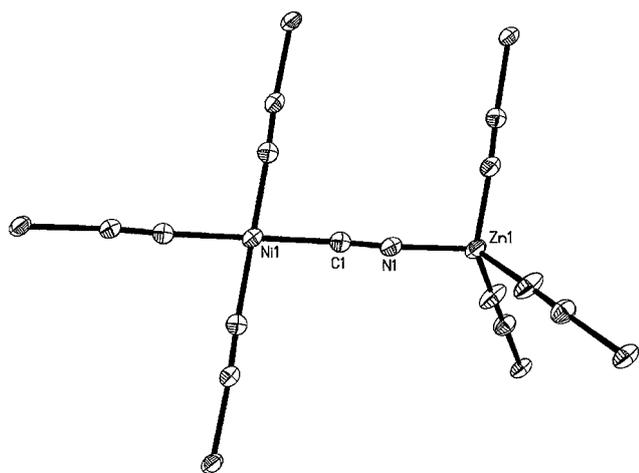


Fig. 1 ORTEP diagram of **1**. Displacement ellipsoids are drawn at the 30% probability level.

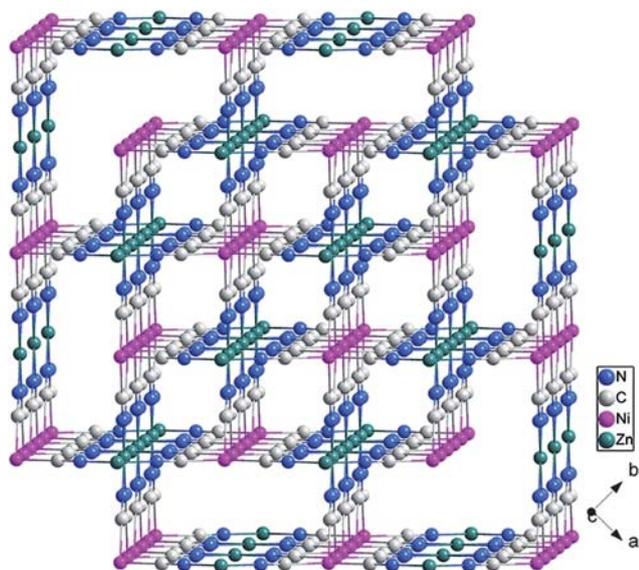


Fig. 2 The 2-fold interpenetrated PtS-type net in **1** viewed along the *c* axis.

For a single PtS net in the structure of **1**, PLATON calculations show that the three-dimensional pore system accounts for approximately 60% of the crystal volume.¹⁷ Due to the large cavities, two such independent porous networks pass through each other, generating the formation of the 2-fold interpenetrated network with the Schläfli symbol of $\{4^28^4\}$, as illustrated in Fig. 2. The shortest Zn \cdots Zn distances within the interpenetrated framework are 7.44 Å. The similar 2-fold interpenetrated modes with PtS-type topology have also been observed in metal–organic frameworks.¹⁴

Notably, the arrangement of the two interpenetrated networks with respect to each other results in the pores in the structure being reduced to a large extent and no solvent molecules occupying the crystal. This is in accord with the fact that tetrahedral, trigonal, and octahedral metal templates have a high tendency to form interpenetrated or self-inclusion compounds, if the cavity created in this way is more than 50% of the crystal by volume.¹⁸ Due to the

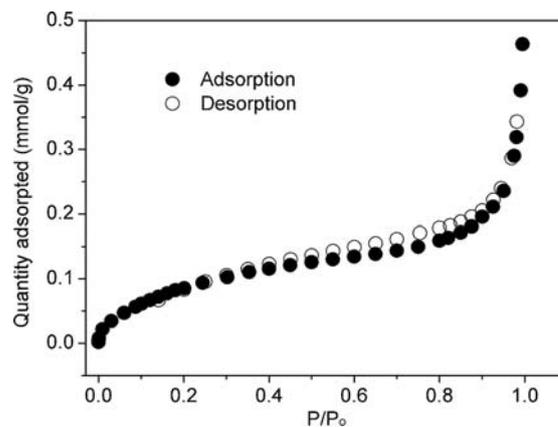


Fig. 3 N₂ adsorption and desorption isotherms for **1**.

condensed structure, **1** exhibits high stability without any weight loss up to 400 °C, above which thermal decomposition occurs (Fig. S2†). Furthermore, N₂ adsorption experiments (Fig. 3) show the surface area was 8.32 m²/g (BET model, Fig. S4) at 77 K compared with 720–870 m²/g for dehydrated Prussian blue analogues M₃[Co(CN)₆]₂,^{9e} and 3362 m²/g for Zn₄O(BDC)₃ (BDC = 1,4-benzenedicarboxylate),¹⁹ respectively. The relatively small apparent surface area can be rationalized by the observation that 2-fold interpenetration exists in the structure.

In summary, three unique 2-fold interpenetrated three-dimensional coordination polymers with PtS-type topologies, ZnM(CN)₄ (M = Ni(**1**), Pd(**2**), Pt(**3**)), have been rationally designed and structurally characterized. The networks have four-connecting tetrahedral metal nodes and square planar [M(CN)₄]²⁻ linkers. We regard this work as important because the present research provides a new strategy to construct the interpenetrated PtS-type networks using simple [M(CN)₄]²⁻ (M = Ni, Pd, Pt) as square planar building blocks rather than the commonly used organic ligands. In addition, it remains to be seen if the 2-fold interpenetrated PtS-type networks reported here can exhibit NTE properties related in some ways to the much studied cyanide-based materials,^{10b–10d} which is an issue we are currently addressing.

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Notes and references

† *Synthesis* of ZnM(CN)₄ (M = Ni(**1**), Pd(**2**), Pt(**3**)): ZnSO₄·7H₂O, K₂[Ni(CN)₄], K₂[Pd(CN)₄], and K₂[Pt(CN)₄] were purchased from commercial sources and used as received. *Caution!* Cyanide complexes are potentially poisonous and should be handled with great care. Colorless block-shaped single crystals of **1–3** were obtained at room temperature by slow diffusion of a mixed solution (2 mL) of EtOH/H₂O = 1:1 containing ZnSO₄·7H₂O (0.05 mmol) into a mixed solution (20 mL) of EtOH/H₂O = 1:1 containing K₂[M(CN)₄]·xH₂O (0.05 mmol). The crystals were found to pulverize as soon as they were removed from the mother liquor. Surprisingly, when the reaction was conducted in aqueous or ethanol solution, no crystals were found, which indicated that the solution may play an important role in the formation of the crystals. Yield (based on Zn): 33% (**1**), 31% (**2**), and 35% (**3**). Anal. Calcd for **1**: C₄N₄NiZn: C, 21.06; N, 24.55. Found: C, 20.90; N, 25.59. EDS for **1**: Zn,

52.81; Ni, 47.19. Anal. Calcd for **2**: C₄N₄PdZn: C, 17.41; N, 20.31. Found: C, 17.20; N, 21.16. EDS for **2**: Zn, 37.90; Pd, 62.10. Anal. Calcd for **3**: C₄N₄PtZn: C, 13.18; N, 15.37. Found: C, 13.30; N, 15.22. EDS for **3**: Zn, 25.23; Pt, 74.77.

§ *Crystal data for 1*: C₄N₄NiZn, $M_r = 228.16$, tetragonal, space group $P4(2)/mcm$, $a = b = 5.2629(15)$, $c = 12.987(8)$ Å, $V = 359.7(3)$ Å³, $Z = 2$, $D_c = 2.106$ g cm⁻³, $R_1 (wR_2) = 0.0512 (0.1238)$ and $S = 1.080$ for 221 reflections with $I > 2\sigma(I)$. *Crystal data for 2*: C₄N₄PdZn, $M_r = 275.85$, tetragonal, space group $P4(2)/mcm$, $a = b = 5.3718(3)$, $c = 13.4271(17)$ Å, $V = 387.46(6)$ Å³, $Z = 2$, $D_c = 2.364$ g cm⁻³, $R_1 (wR_2) = 0.0469 (0.1279)$ and $S = 1.036$ for 232 reflections with $I > 2\sigma(I)$. *Crystal data for 3*: C₄N₄PtZn, $M_r = 364.54$, tetragonal, space group $P4(2)/mcm$, $a = b = 5.3592(4)$, $c = 13.455(2)$ Å, $V = 386.45(7)$ Å³, $Z = 2$, $D_c = 3.133$ g cm⁻³, $R_1 (wR_2) = 0.0264 (0.0856)$ and $S = 1.057$ for 233 reflections with $I > 2\sigma(I)$.

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