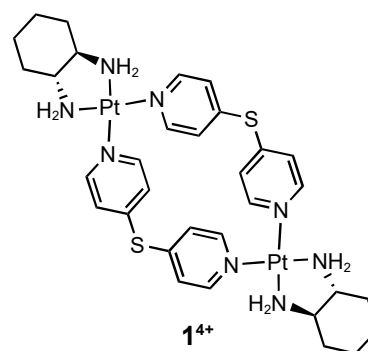


Synthesis of a wavy MX-tube complex

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MX-tube family is a novel class of metal–organic nanotube based on the mixed-valence halogen-bridged transition-metal complex (MX-chain), which shows unique electronic states, sorption properties, and proton conduction.^{1–4} In this work, we have successfully synthesized a two-legged MX-tube type complex from a diamond-shaped platinum complex having a sulfide based organic ligand, [Pt(dach)(dpsf)]₂(NO₃)₄ (**1**; dach: (1R, 2R)-(–)-1,2-Diaminocyclohexane; dpsf: 4,4'-dipyridyl sulfide).



The target complex was synthesized from following two steps:

(a) $\text{Pt}(\text{dach})(\text{NO}_3)_2 + \text{dpsf} \rightarrow [\text{Pt}^{\text{II}}(\text{dach})(\text{dpsf})]_2(\text{NO}_3)_4$ (**1**)

(b) $\mathbf{1} + \text{I}_2 + \text{ex. NO}_3^- \rightarrow [\text{Pt}^{\text{II/IV}}(\text{dach})(\text{dpsf})\text{I}]_2(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (**2**)

Figure 1 shows the X-ray crystal structure of **2** at 100 K. **2** crystallizes in orthorhombic space group $P2_12_12_1$ ($a = 17.0370(6)$, $b = 23.3704(8)$, $c = 24.4124(8)$ Å, $V = 9720.1(5)$ Å³). Each diamond-shaped platinum unit is bridged by an iodide ion to form two-legged MX-tube structure, and a nitrate anion is trapped inside a pore. Due to the flexibility of the ligand and the existence of trapped nitrate anion, **2** has a uniquely wavy nanotube structure. In addition, bridging-iodide ions are three-dimensionally ordered between adjacent Pt ions, resulting in an in-phase charge-density-wave state. Details are presented.

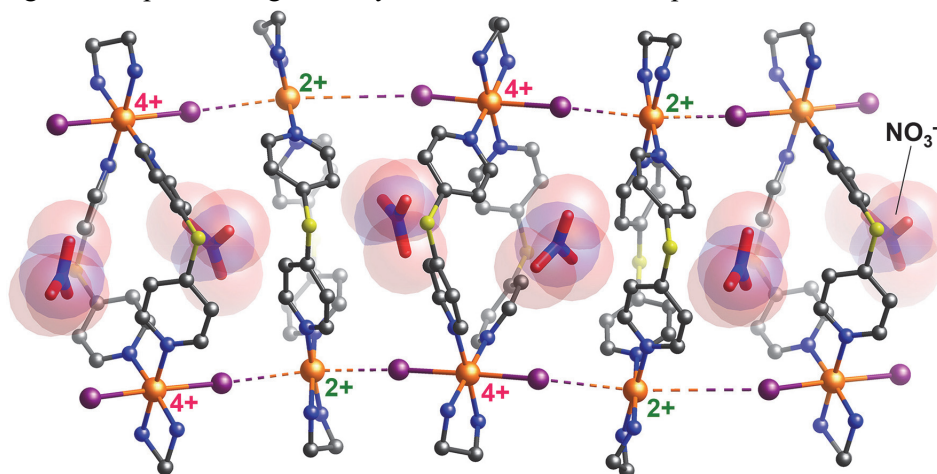


Figure 1. Nanotubular structure of **2** at 100 K. Pt, I, C, S, N, and O atoms are shown in orange, purple, grey, yellow, blue, and red, respectively. Cyclohexane rings of dach ligand and H atoms are omitted. The valence state of Pt ions is also shown in green and pink.

- (1) K. Otsubo, H. Kitagawa *et al.* *Nature Materials*, **2011**, 10, 291. (2) K. Otsubo, H. Kitagawa *CrystEngComm* **2014**, 16, 6277. (3) K.-i. Otake, K. Otsubo, H. Kitagawa *et al.* *Angew. Chem. Int. Ed.* **2016**, 55, 6448. (4) K.-i. Otake, K. Otsubo, H. Kitagawa *et al.* *Nature Communications*, **2020**, 11, 843.