A Novel S-bridged $Pd^{II}_2Hg^{II}$ Metallacycle of D-Penicillaminate that Forms a Unique Supramolecular Structure Combined with Tetraamminepalladium(II)

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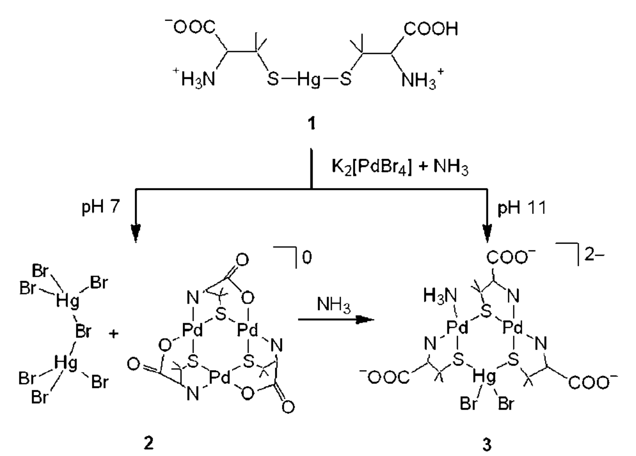
The newly prepared $[Hg(\text{D-Hpen-}S)(\text{D-}H_2\text{pen-}S)]^+$ (D-H_2pen = D-penicillamine) reacted with $[PdBr_4]^{2-}$ in aqueous ammonia to give a $Pd^{II}_2Hg^{II}$ cyclic complex, $[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$, by way of a Pd^{II}_3 cyclic complex, $[Pd_3(\text{D-pen-}N,O,S)_3]$. The $Pd^{II}_2Hg^{II}$ complex was found to aggregate into a cylindrical supramolecular structure in combination with $[Pd(NH_3)_4]^{2+}$, accommodating $[HgBr_3(NH_3)]^-$ in its cavity.

The design and creation of homometallic and heterometallic molecular aggregates that show intriguing supramolecular structures and host–guest interactions have attracted increasing attention over the past decade.[1] While the most common approach to create metalloaggregates is the use of functional organic ligands that can bridge two or more metal centers,[1a–1c] our efforts have been paid for the use of thiolato metal complexes as a S-donating metalloligand.[2] Recently, we have found that the bis(D-penicillaminato)aurate(I) complex, $[Au(\text{D-pen-}S)_2]^{3-}$ (D-H_2pen = D-penicillamine), functions as an effective multidentate metalloligand to construct heterometallic aggregates, using free carboxylate and/or amine groups, besides coordinated thiolato groups.[3] This finding prompted us to synthesize analogous D-penicillaminato metal complexes having several binding sites, with the aim of expanding the range of heterometallic architectures based on thiolato-type metalloligands. Here, we report on the preparation of a new bis(D-penicillaminato)mercury(II) complex, $[Hg(\text{D-Hpen-}S)(\text{D-}H_2\text{pen-}S)]Br$, together with its reactions with $K_2[PdBr_4]$ in aqueous ammonia (Scheme 1). Contrary to our expectation, it was found that the reactions are accompanied by the Hg–S bond cleavage to afford a Pd^{II}_3 cyclic complex with D-penicillaminate, which is converted to a $Pd^{II}_2Hg^{II}$ cyclic complex. A unique metallo-supramolecular structure consisting of $Pd^{II}_2Hg^{II}$ metallacycles and Pd^{II} square planes, which encapsulates a Hg^{II} tetrahedron, is also presented.



Scheme 1. Synthetic routes of **2** and **3** from **1**.

Treatment of $HgBr_2$ with 2 molar equiv. of D-H_2pen in water, followed by storing in a refrigerator, gave hygroscopic colorless crystals **1**.[4] Complex **1** was assigned to be a D-penicillaminatomercury(II) species with a formula of $[Hg(\text{D-}H_{1.5}\text{pen-}S)_2]Br$ by (i) the X-ray fluorescence spectrometry that indicates the existence of Hg^{II} atom, (ii) the IR spectrum that gives two ν(C=O) bands at 1721 and 1580 cm^{-1} and a $\delta(NH_2)$ band at 1626 cm^{-1} for COOH, COO^-, and NH_3^+ groups, respectively,[5] and (iii) the elemental analysis. Furthermore, single-crystal X-ray analysis indicated that the complex cation of **1** is $[Hg(\text{D-Hpen-}S)(\text{D-}H_2\text{pen-}S)]^+$, in which a Hg^{II} center is linearly coordinated by two thiolato S atoms, although a detailed structural discussion is precluded because of the poor crystal quality.[6]

To investigate the ligating ability of **1** toward a thiophilic metal ion, an aqueous solution of **1** was mixed with an aqueous solution of $K_2[PdBr_4]$ in a 1:2 ratio at room temperature, which quickly gave an orange suspension. This suspension became a clear orange solution on adding aqueous ammonia to adjust pH $\approx$7, and from this solution orange crystals **2** were isolated by allowing to stand at room temperature.[7] The X-ray fluorescence spectrometry indicated that **2** contains Pd and Hg atoms, and the presence of fully deprotonated D-penicillaminate ligands is confirmed by its IR spectrum that gives a ν(C=O) band at 1591 cm^{-1}. The structure of **2** was established by single-crystal X-ray analysis,[8] which showed the presence of a neutral $[Pd_3(\text{D-pen-}N,O,S)_3]$ molecule and a $K_3[Hg_2Br_7]$ salt in a 2:1 ratio, besides water molecules.[9] This result clearly indicates that D-penicillaminate bound to Hg^{II} transfers to Pd^{II} owing to the cleavage of Hg–S bonds in the course of the reaction. In the $[Pd_3(\text{D-pen-}N,O,S)_3]$ molecule, each of three D-penicillaminate ligands adopts a μ_2-κ^2N,S:κ^2O,S coordination mode to connect two square-planar Pd^{II} atoms to form a S-bridged tripalladium(II) cyclic structure (Figure 1a). It is noted that Hg^{II} atoms exist in a counter anion of $[Hg_2Br_7]^{3-}$, in which two trigonal $[HgBr_3]^-$ moieties (av. Hg–Br = 2.5638(5) Å, Br–Hg–Br = 116.60(10)°) are bridged by a Br^- ion (av. Hg–Br = 2.823(3) Å, Hg–Br–Hg = 101.08(14)°) (Scheme 1).

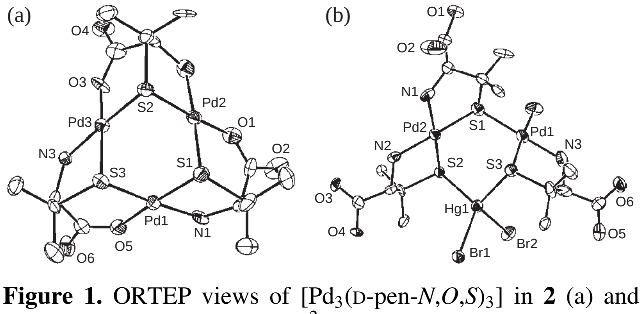


Figure 1. ORTEP views of $[Pd_3(\text{D-pen-}N,O,S)_3]$ in **2** (a) and $[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$ in **3** (b).

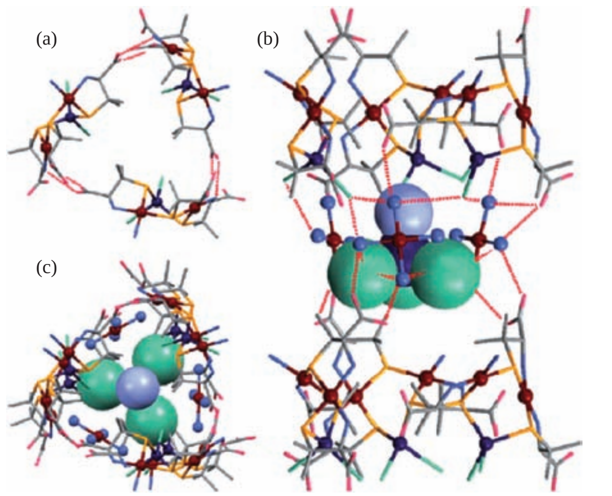


Figure 2. Perspective views of the trimer structure (a) and the supramolecular structure (b, c) of **3**: Hg, purple; Pd, brown; Br, green; S, yellow; N, blue; O, pink.

When excess aqueous ammonia was added to the reaction mixture of **1** and $K_2[PdBr_4]$, the orange suspension turned to a clear yellow solution (pH $\approx$11), from which yellow crystals **3** were isolated by the diffusion of ethanol vapor at room temperature.[10] It is considered that this reaction involves **2** as an intermediate, because **3** was also obtained by treatment of **2** with aqueous ammonia.[11] Again, the presence of Pd and Hg atoms and fully deprotonated D-penicillaminate ligands in **3** was confirmed by X-ray fluorescent spectrometry and IR spectrum (ν(C=O) = 1595 cm^{-1}). However, X-ray analysis revealed that **3** contains $[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$, $[Pd(NH_3)_4]^{2+}$, $[HgBr_3(NH_3)]^-$, and NH_4^+ in a 6:6:1:1 ratio, besides water molecules.[12] The $[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$ trinuclear anion consists of $\{Pd(\text{D-pen-}N,S)_2\}^{2-}$, $\{Pd(\text{D-pen-}N,S)(NH_3)\}$, and $\{HgBr_2\}$ moieties, which are linked by sulfur bridges to form a $Pd^{II}{}_2Hg^{II}$ cyclic structure (Figure 1b). This S-bridged $Pd^{II}{}_2Hg^{II}$ structure in **3** is comparable with the $Pd^{II}{}_3$ structure in **2**, but each D-penicillaminate ligand adopts a μ_2-$\kappa^2N,S{:}\kappa^1S$ coordination mode, and its carboxylate group does not participate in the coordination. Moreover, the $Pd^{II}{}_2Hg^{II}S_3$ six-membered ring in **3** has a twist-boat-like conformation, which is markedly distinct from a chair-like conformation of the $Pd^{II}{}_3S_3$ ring found in **2**. The most interesting structural feature of **3** is the construction of a unique supramolecular structure made up of six $[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$, three $[Pd(NH_3)_4]^{2+}$, and one $[HgBr_3(NH_3)]^-$ complex-ions. As shown in Figure 2, the three $Pd^{II}{}_2Hg^{II}$ anions aggregate into a cyclic trimer through N–H···O hydrogen bonds (av. 2.915(5) Å). Furthermore, three square-planar $[Pd(NH_3)_4]^{2+}$ cations connect two cyclic trimers through N–H···O and N–H···Br hydrogen bonds to complete a cylindrical metallo-supramolecular structure (av. N–H···O = 3.065(4) Å, N–H···Br = 3.572(4) Å), which accommodates a tetrahedral $[HgBr_3(NH_3)]^-$ ion inside its cavity.

In summary, we showed that the reactions of [Hg(D-Hpen-*S*)(D-H_2pen-*S*)]Br (**1**) with $K_2[PdBr_4]$ in aqueous ammonia are accompanied by the transfer of D-penicillaminate from Hg^{II} to Pd^{II}, producing $Pd^{II}{}_3$ ($[Pd_3(\text{D-pen-}N,O,S)_3]$) and $Pd^{II}{}_2Hg^{II}$ ($[Pd_2HgBr_2(\text{D-pen-}N,S)_3(NH_3)]^{2-}$) metallacyclic structures in **2** and **3**, respectively. In addition, it was found that **3** is formed by way of **2**, which involves the replacement of Pd^{II} by Hg^{II} in the S-bridged metallacyclic structure. These results indicate the flexible binding nature of D-penicillaminate toward Pd^{II} and Hg^{II} centers. Notably, the cyclic $Pd^{II}{}_2Hg^{II}$ anions were found to aggregate into a unique cylindrical supramolecular structure in combination with square-planar $[Pd(NH_3)_4]^{2+}$ cations so as to accommodate a tetrahedral $[HgBr_3(NH_3)]^-$ anion. To the best of our knowledge, such an ingenious organization of three different kinds of complex-ions into a discrete supramolecular architecture is unprecedented. Thus, this work paves the way for the construction of fascinating metallo-supramolecular structures based on the aggregation of metal complexes with carboxylate groups in combination with those with amine/ammine groups.

References and Notes

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4 Calcd for $\mathbf{1}\cdot3.5H_2O$ = [Hg(D-Hpen)(D-H_2pen)]Br$\cdot3.5H_2O$: C, 18.74; H, 4.40; N, 4.37%. Found: C, 18.64; H, 4.03; N, 4.21%. Yield: 47%.

5 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley Interscience, Chichester, **1997**, Part B, pp. 62–67.

6 Crystal data for [Hg(D-Hpen)(D-H_2pen)]Br$\cdot3.5H_2O$: Orthorhombic, *C*222, $a = 41.840(3)$, $b = 42.639(3)$, $c = 17.6872(11)$ Å, $V = 31554(4)$ Å^3. $R_1 = 0.085$ ($I > 2\sigma(I)$).

7 Calcd for $\mathbf{2}\cdot5H_2O = [Pd_3(\text{D-pen})_3]_2\cdot K_{1.5}(NH_4)_{1.5}[Hg_2Br_7]\cdot5H_2O$: C, 13.56; H, 2.65; N, 3.95%. Found: C, 13.30; H, 2.72; N, 3.85%. Yield: 50%.

8 A single crystal used for X-ray analysis was prepared by using KOH, instead of NH_3. Crystal data for $\mathbf{2}\cdot59/8H_2O = [Pd_3(\text{D-pen})_3]_2\cdot K_3[Hg_2Br_7]\cdot59/8H_2O$, Hexagonal, $P6_3$, $a = 25.683(2)$, $c = 25.661(3)$ Å, $V = 14658(2)$ Å^3, $Z = 6$, $D_{calcd} = 2.476$ g/cm^3, 139851 reflections measured, 22258 independent ($R_{int} = 0.126$). $R_1 = 0.053$ ($I > 2\sigma(I)$), $wR_2 = 0.086$ (all data). Averaged distances of $Pd^{II}{}_3$ molecule: Pd–O = 2.043(9), Pd–N = 2.073(10), Pd–S = 2.268(3) Å. CCDC: 631461.

9 An analogous compound consisting of $[Pd_3(\text{D-pen-}N,O,S)_3]$ and KCl, $[Pd_3(\text{D-pen-}N,O,S)_3]\cdot7/8KCl$, has been prepared and structurally characterized. G. Cervantes, V. Moreno, E. Molins, M. Quirós, *Polyhedron* **1998**, *17*, 3343.

10 Calcd for $\mathbf{3}\cdot15H_2O = (NH_4)_{1/3}[Pd_2HgBr_2(\text{D-pen})_3(NH_3)]_2$-$[Pd(NH_3)_4]_2[HgBr_3(NH_3)]_{1/3}\cdot15H_2O$: C, 12.68; H, 4.13; N, 8.22%. Found: C, 12.88; H, 4.08; N, 8.20%. Yield: 46%.

11 The addition of aqueous ammonia to the reaction mixture of **1** and $K_2[PdBr_4]$ gave an orange solution at pH $\approx$7, the absorption and CD spectra of which coincided well with those of **2**, and this orange solution turned to a yellow solution containing **3** on further adding aqueous ammonia to pH $\approx$11. This fact also implies that **2** is an intermediate of the reaction from **1** to **3**.

12 Crystal data for $\mathbf{3}\cdot10H_2O = (NH_4)_{1/3}[Pd_2HgBr_2(\text{D-pen})_3(NH_3)]_2$-$[Pd(NH_3)_4]_2[HgBr_3(NH_3)]_{1/3}\cdot10H_2O$, Trigonal, $R3$, $a = 26.963(3)$, $c = 29.261(4)$ Å, $V = 18423(4)$ Å^3, $Z = 9$, $D_{calcd} = 2.232$ g/cm^3, 44452 reflections measured, 18445 independent ($R_{int} = 0.055$). $R_1 = 0.052$ ($I > 2\sigma(I)$), $wR_2 = 0.107$ (all data). Averaged distances of $Pd^{II}{}_2Hg^{II}$ anion: Pd–N = 2.061(3), Pd–S = 2.274(1), Hg–S = 2.502(1), Hg–Br = 2.6574(5) Å. CCDC: 631462.

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