Reversible Conversion of Tetranuclear, Trinuclear, and Mononuclear Palladium(II) Complexes with D-Penicillaminate

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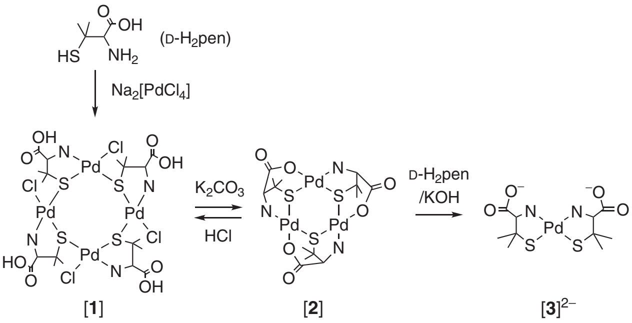
The 1:1 reaction of $[PdCl_4]^{2-}$ with D-penicillamine (D-H_2pen) gave a S-bridged tetranuclear complex, $[Pd_4Cl_4$(D-Hpen)$_4]$ ([**1**]). Complex [**1**] was converted to a S-bridged trinuclear complex, $[Pd_3$(D-pen)$_3]$ ([**2**]), which was further converted to a mononuclear complex, $K_2[Pd$(D-pen)$_2]$ (K_2[**3**]). The reverse conversion of [**2**] to [**1**] was also achieved.

Penicillamine (H_2pen), which is a thiol-containing amino acid analogous to cysteine (H_2cys), has been recognized to act as a multitopic chiral ligand toward a variety of metal ions using amine, carboxylate, and/or thiolate groups.[1–3] In 1998, Cervantes et al. reported that D-penicillamine reacts with $K_2[PdCl_4]$ to produce two kind of 1:1 complexes, $[Pd_2Cl_2$(D-Hpen)$_2]$ ([**1**]) and $[Pd_3$(D-pen)$_3]\cdot7/8KCl$ ([**2**]$\cdot7/8KCl$).[2] The former complex was obtained as an orange solid from the reaction mixture and the latter was isolated as red crystals from the filtrate of [**1**]. While [**2**] was crystallographically determined to have a S-bridged tripalladium(II) structure in $[Pd_3$(D-pen-*N,O,S*)$_3]$, [**1**] was characterized to have a Cl-bridged dipalladium(II) structure only by spectroscopic methods, and thus its accurate composition and structure have remained unclear. Recently, we have found that the reaction of $[Hg$(D-$H_{0.5}$pen-*S*)$_2]Br$ with $K_2[PdBr_4]$ in aqueous ammonia is accompanied by Hg–S bond cleavage to afforded a cyclic $Pd^{II}{}_2$-Hg^{II} trinuclear structure in $[Pd_2HgBr_2$(D-pen-*N,S*)$_3(NH_3)]^{2-}$, by way of [**2**].[3] This observation was indicative of the flexible binding nature of D-penicillamine toward a Pd^{II} center. In this context, we thought it worthwhile to reexamine the coordination system of palladium(II) and D-penicillamine, with the aim of finding a key factor to control S-bridged polynuclear structures with thiol-containing amino acids. Here we report that [**1**] does not have a proposed dinuclear structure but a S-bridged tetranuclear structure in $[Pd_4Cl_4$(D-Hpen-*N,S*)$_4]$. Notably, treatment of the tetranuclear [**1**] with K_2CO_3 in water was found to give the trinuclear [**2**], which is further converted to the mononuclear $K_2[Pd$(D-pen-*N,S*)$_2]$ by treatment with D-H_2pen/KOH in H_2O (Scheme 1). The reversible conversion of [**2**] to [**1**], which was achieved by treatment with HCl, is also reported.



Scheme 1. Synthesis and interconversion of [**1**], [**2**], and $[\mathbf{3}]^{2-}$.

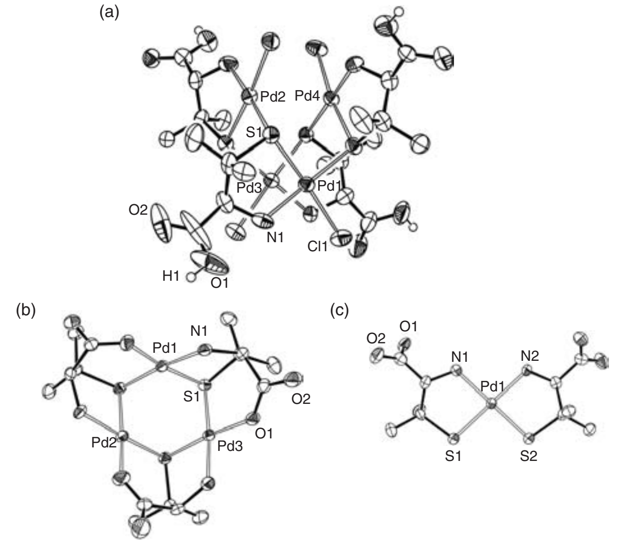


Figure 1. Perspective views of each complex unit of (a) [**1**], (b) [**2**], and (c) K_2[**3**]. H atoms except for COOH in [**1**] are omitted for clarity.

The addition of 1 molar equiv of D-H_2pen to an aqueous solution of $Na_2[PdCl_4]$ immediately gave a red-orange suspension, which turned to a clear red-orange solution on stirring at 60 °C for 30 min. From this reaction solution, orange crystals of [**1**] were isolated by allowing it to stand at room temperature for several days.[4,5] Single-crystal X-ray analysis revealed that [**1**] is a neutral complex consisting of four {PdCl(D-Hpen)} units (av Pd–S = 2.251(2), Pd–N = 2.063(19), and Pd–Cl = 2.372(2) Å), which are linked by sulfur bridges [av Pd–S = 2.302(2) Å] to construct a C_2 symmetrical tetrapalladium(II) structure in $[Pd_4Cl_4$(D-Hpen-*N,S*)$_4]$ (Figure 1a).[6,7] The four Pd^{II} atoms are connected through four S atoms, giving a Pd_4S_4 eight-membered ring that has a folded conformation. Each Pd^{II} atom is situated in a square-planar geometry with a NS_2Cl donor set, and the $PdNS_2Cl$ square planes are pairwise parallel with an average Pd···Pd distance of 3.18 Å. In [**1**], each D-Hpen ligand adopts a μ_2-$\kappa^2 N,S$:$\kappa^1 S$ coordination mode, with its carboxyl group being protonated and noncoordinated. This is compatible with the appearance of a sharp $\nu_{C=O}$ band at 1724 cm^{-1} in the IR spectrum of [**1**].[8]

Complex [**1**] is insoluble in water but soluble in aqueous K_2CO_3, which is explained by the deprotonation of carboxyl groups to afford an anionic species. To investigate the stability of the tetrapalladium(II) structure in solution, [**1**] was dissolved in D_2O by adding K_2CO_3, and its ^1H NMR spectrum was monitored at room temperature.[4] Just after the dissolution, the spec-

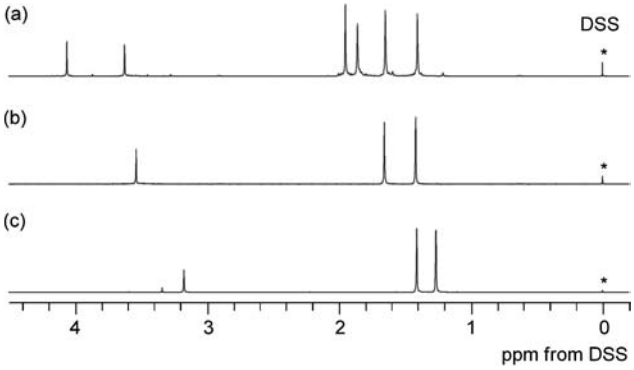


Figure 2. ^{1}H NMR spectra of (a) [**1**], (b) [**2**], and (c) K_2[**3**] in D_2O.

trum showed four methyl (δ 1.40, 1.65, 1.86, and 1.95) and two methine (δ 3.62 and 4.06) proton signals due to D-pen ligands in the complex (Figure 2a), consistent with the C_2 symmetrical structure of [**1**]. However, these proton signals gradually decreased with time and completely disappeared after three days, accompanied by the appearance and growth of a set of new signals (δ 1.42 and 1.66 for methyl and δ 3.53 for methine protons). The species newly generated in solution was isolated as orange crystals ([**2**]) by treatment of [**1**] with K_2CO_3 in water (Figure 2b).[4,9] The presence of deprotonated carboxyl groups in [**2**] was implied by its IR spectrum that shows an intense $\nu_{C=O}$ band at 1610 cm^{-1}.[8] X-ray analysis indicated that [**2**] has a C_3 symmetrical S-bridged tripalladium(II) structure in [Pd_3(D-pen-N,O,S)$_3$] (Figure 1b).[10] In [**2**], three Pd^{II} atoms are spanned by three D-pen ligands in a μ_2-κ^2N,S:κ^2S,O coordination mode to form a Pd_3S_3 six-membered ring with a chair form. This S-bridged structure in [**2**] is essentially the same as that found in [Pd_3(D-pen)$_3$]•7/8KCl and ([Pd_3(D-pen)$_3$])$_2$•K_3[Hg_2Br_7],[2,3] although inorganic salts are not included in crystal [**2**]. Interestingly, [**2**] was quickly and quantitatively reverted back to [**1**] by adding aqueous HCl to its aqueous solution, which was indicated by the ^{1}H NMR spectroscopy. It seems that this easy conversion is related to the much distorted S-bridged structure in [**2**] compared with that in [**1**]; the Pd–S–Pd angles in [**2**] (av 86.91(5)°) are far from the ideal tetrahedral angle of 109.3°, while the corresponding angles in [**1**] (av Pd–S–Pd = 112.80(18)°) are nearly ideal.

Prompted by the observation that [**2**] is easily converted to [**1**] by treatment with HCl, we investigated the reactivity of [**2**] toward additional D-H_2pen. On adding 3 molar equiv of D-H_2pen and KOH to a D_2O solution of [**2**], its ^{1}H NMR spectrum quickly changed to give only two methyl (δ 1.26 and 1.41) and one methine (δ 3.17) proton signals (Figure 2c). This new species was isolated as yellow crystals (K_2[**3**]) by treatment of [**2**] with 3 molar equiv D-H_2pen neutralized by KOH in methanol/1-butanol.[4,11] X-ray analysis revealed that K_2[**3**] contains complex anions and K^+ cations in a 1:2 ratio.[12] As shown in Figure 1c, the complex anion of K_2[**3**] is a square-planar mononuclear complex with a C_2 symmetry, $cis(S)$-[Pd(D-pen-N,S)$_2$]$^{2-}$, in which two D-pen ligands bind to a Pd^{II} center through amine and thiolato groups [av Pd–S = 2.263(4) and Pd–N = 2.084(5) Å]. Each carboxyl group in K_2[**3**] is deprotonated, as supported by the appearance of an intense $\nu_{C=O}$ band at 1592 cm^{-1} in the IR spectrum.[8] Note that this carboxylate group contacts with a K^+ cation with an average distance of 2.824(6) Å.

In summary, we demonstrated that the reaction product of [$PdCl_4$]$^{2-}$ and D-penicillamine has a S-bridged tetrapalladium(II) structure in [Pd_4Cl_4(D-Hpen)$_4$] (**1**), which is converted to a S-bridged tripalladium(II) structure in [Pd_3(D-pen)$_3$] (**2**) by treatment with base. Remarkably, [**1**] reverted back to [**2**] by treatment with HCl and furthermore converted to a monopalladium(II) structure in [Pd(D-pen)$_2$]$^{2-}$ ([**3**]$^{2-}$) by treatment with additional D-penicillamine.[13] Thus, the three palladium(II) species with different nuclearities were created in a controlled manner, the result of which is attributed to the versatile coordination modes of D-penicillamine in conjunction with the protonation/deprotonation of its carboxyl group. Current efforts are focusing on the creation of chiral metalloaggregates based on [**1**], [**2**], or [**3**]$^{2-}$ that possess functional groups available for the formation of coordination and hydrogen bonds.

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4 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

5 Calcd for [**1**]•$6H_2O$: C, 18.94; H, 4.13; N, 4.42%. Found: C, 18.86; H, 4.07; N, 4.38%. Yield: 47%. This complex was obtained in a high yield (86%) by adding aqueous HCl.[4]

6 Crystal data for [**1**]•$7H_2O$, Tetragonal, $P4_1$, $a = 12.8102(7)$, $c = 52.813(3)$ Å, $V = 8666.7(8)$ Å^3, $Z = 8$, $D_{calcd} = 1.972$ g cm^{-3}, 85859 reflections measured, 19834 independent ($R_{int} = 0.092$), $R_1 = 0.041$ ($I > 2\sigma$), $wR_2 = 0.084$ (all data). CCDC: 743567.

7 An analogous S-bridged tetrapalladium(II) complex with L-cysteinate, [Pd_4Cl_4(L-Hcys-N,S)$_4$], has been prepared from K_2[$PdCl_4$] and L-H_2cys•HCl. X. Chen, L. Zhu, C. Duran, Y. Liu, N. M. Kostc, *Acta Crystallogr., Sect. C* **1998**, *54*, 909.

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9 Calcd for [**2**]•$4H_2O$: C, 21.63; H, 4.24; N, 5.04%. Found: C, 21.52; H, 4.26; N, 4.98%. Yield: 71%.

10 Crystal data for [**2**]•$4.5H_2O$, Orhorhombic, $P2_12_12$, $a = 13.033(3)$, $b = 17.704(3)$, $c = 24.952(4)$ Å, $V = 5753.3(18)$ Å^3, $Z = 4$, $D_{calcd} = 1.942$ g cm^{-3}, 54550 reflections measured, 13040 independent ($R_{int} = 0.066$), $R_1 = 0.041$ ($I > 2\sigma$), $wR_2 = 0.094$ (all data). CCDC: 743568.

11 Calcd for K_2[**3**]•$3H_2O$: C, 22.53; H, 4.54; N, 5.26%. Found: C, 22.76; H, 4.58; N, 5.26%. Yield: 80%.

12 Crystal data for K_2[**3**]•$3.625H_2O$, Monoclinic, $P2_1$, $a = 11.048(3)$, $b = 18.528(7)$, $c = 20.155(7)$ Å, $\beta = 91.622(10)$°, $V = 4124(2)$ Å^3, $Z = 8$, $D_{calcd} = 1.753$ g cm^{-3}, 65413 reflections measured, 18760 independent ($R_{int} = 0.086$), $R_1 = 0.053$ ($I > 2\sigma$), $wR_2 = 0.121$ (all data). CCDC: 743569. This is the first example of a structurally characterized monopalladium(II) complex with thiol-containing amino acid(s).

13 It was found that [**3**]$^{2-}$ is partially reverted back to [**2**] by adding Na_2[$PdCl_4$] to an aqueous solution of Na_2[**3**].[4]

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