Inorganic Chemistry
COMMUNICATION
pubs.acs.org/IC

Enantioselective/Anion-Selective Incorporation of Tris(ethylenediamine) Complexes into 2D Coordination Spaces between Tripalladium(II) Supramolecular Layers with D-Penicillaminate

Yusuke Hirai, Yoshinori Nagao, Asako Igashira-Kamiyama, and Takumi Konno*

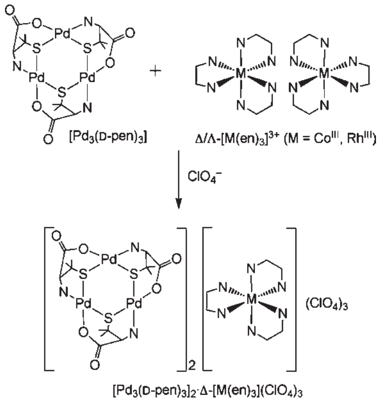
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Supporting Information

ABSTRACT: The formation of a cocrystallized coordination compound, $[Pd_3(\text{D-pen})_3]_2 \cdot [M(en)_3](ClO_4)_3$ (D-H_2pen = D-penicillamine; M = Co^{III} or Rh^{III}), from $[Pd_3(\text{D-pen})_3]$ and $[M(en)_3](ClO_4)_3$ is reported. In this compound, only the Δ-configurational $[M(en)_3]^{3+}$ cations were incorporated when its racemic (Δ/Λ) isomer was employed. Besides this enantioselective incorporation of complex cations, this compound was found to show the selective incorporation of ClO_4^- as the anion species.

Porous coordination compounds, in which molecular building units are linked by coordination bonding and/or hydrogen-bonding interactions, have attracted considerable attention in many research fields including coordination chemistry and supramolecular chemistry.[1−3] This is not only because of the intriguing physical properties based on their framework structures[2] but also because of the utilization of their coordination spaces for various applications such as catalysis, recognition, and adsorption of small molecules.[3] To date, a large number of coordination compounds with a 3D porous structure, some of which are composed of chiral building units,[4] have been prepared and their properties and functionalities have been extensively investigated. On the other hand, coordination compounds having a 2D layer structure are less common despite their potential for the selective incorporation of guest molecules by modification of the interlayer distances and functional groups on layer surfaces.[1a,3a] In particular, there are only a few examples of chiral 2D coordination compounds that show the enantioselective incorporation of chiral guest molecules into their asymmetric coordination spaces.[4b,5] In the course of our investigation on the coordination behavior of metalloligands with D-penicillaminate (D-pen),[6] we encountered a unique cocrystallized compound, $[Pd_3(\text{D-pen})_3]_2 \cdot K_3[Hg_2Br_7]$, in which neutral $[Pd_3(\text{D-pen})_3]$ molecules are self-assembled to construct a 2D supramolecular layer structure with hydrophilic and hydrophobic surfaces.[7] Notably, the supramolecular layers were stacked in a face-to-face fashion to afford hydrophilic interlayer spaces, in which K^+ cations and $[Hg_2Br_7]^{3-}$ anions are accommodated through multiple hydrogen bonds. This observation, together with the fact that $[Pd_3(\text{D-pen})_3]$ is optically active, prompted us to investigate the possibility of the enantioselective incorporation of chiral species into the hydrophilic spaces of this compound. In this Communication, we report that the treatment of $[Pd_3(\text{D-pen})_3]$ with $[M(en)_3](ClO_4)_3$ (M = Co^{III} or Rh^{III}; en = ethylenediamine) gives a cocrystallized compound, $[Pd_3(\text{D-pen})_3]_2 \cdot [M(en)_3](ClO_4)_3$, in which only the Δ isomer is exclusively incorporated into the hydrophilic spaces when the racemic Δ/Λ isomer is used (Scheme 1). A remarkable selectivity of ClO_4^- as the anion species is also reported.

Scheme 1. Formation of $[Pd_3(\text{D-pen})_3]_2 \cdot \Delta\text{-}[M(en)_3](ClO_4)_3$



The slow evaporation of an aqueous solution containing $[Pd_3(\text{D-pen})_3] \cdot 4H_2O$[8] and 3 times excess of the racemic Δ/Λ-$[Co(en)_3](ClO_4)_3$[9] gave orange plate crystals (**1**·$10H_2O$) in a yield of ca. 90%.[10] X-ray fluorescence spectrometry indicated that **1** contains both Pd and Co atoms, and its elemental analysis data were in agreement with the formula for a 2:1 adduct of $[Pd_3(\text{D-pen})_3]$ and $[Co(en)_3](ClO_4)_3$. The ^{1}H NMR spectrum of **1** in D_2O was essentially the same as that of a 2:1 mixture of $[Pd_3(\text{D-pen})_3]$ and $[Co(en)_3](ClO_4)_3$.[10] From these results, together with the presence of characteristic strong bands due to carboxylate groups (1597 cm^{-1}) and ClO_4^- anions (1120 and 627 cm^{-1}) in the IR spectrum,[10] **1** is confidently assigned to a cocrystallized compound having $[Pd_3(\text{D-pen})_3]$ and $[Co(en)_3](ClO_4)_3$ in a 2:1 ratio. Single-crystal X-ray crystallography revealed that **1**·$10H_2O$ consists of two crystallographically independent, but nearly the same $[Pd_3(\text{D-pen})_3]$ molecules,

Received: September 16, 2010
Published: January 28, 2011

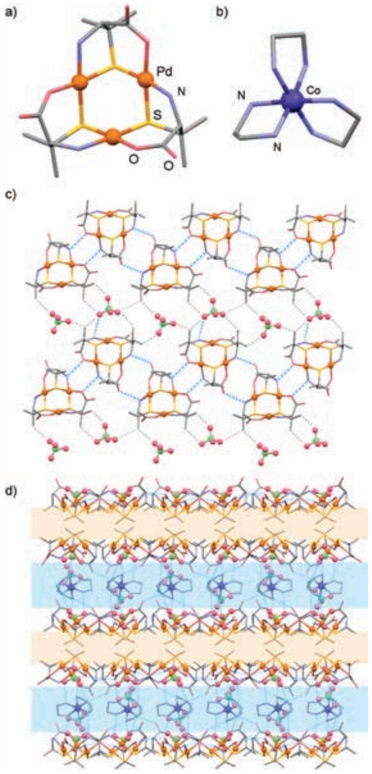


Figure 1. Perspective views of (a) one of the $[Pd_3(\text{D-pen})_3]$ units, (b) the Δ-$[Co(en)_3]^{3+}$ unit, (c) a 2D layer structure, and (d) a packing structure in **1**. Disordered and H atoms are omitted for clarity. Blue and orange bands represent hydrophilic and hydrophobic spaces between the 2D layers. Blue and gray dashed lines represent NH···O and CH···O interactions.

one $[Co(en)_3]^{3+}$ cation, and three ClO_4^- anions in the asymmetric unit, besides water molecules of crystallization.[10] As shown in Figure 1a, each $[Pd_3(\text{D-pen})_3]$ molecule has a cyclic S-bridged tripalladium(II) structure, in which three Pd^{II} atoms are connected by three D-pen ligands that adopt a μ_2-κ^2N,S:κ^2S,O coordination mode [avg Pd−S = 2.267(1) Å, Pd−N = 2.087(4) Å, and Pd−O = 2.050(3) Å]. This tripalladium(II) structure in **1** is essentially the same as that found in the parental $[Pd_3(\text{D-pen})_3]\cdot 4H_2O$,[8] indicative of the retention of its structure during the cocrystallization reaction. In **1**, the $[Pd_3(\text{D-pen})_3]$ molecules are connected to one another through double hydrogen bonds between amine and carboxylato groups [avg $N\cdots O_{\text{coordination}}$ = 3.007(5) Å and $N\cdots O_{\text{noncoordination}}$ = 2.915(5) Å] to form a 1D zigzag chain structure (Figure 1c). The 1D chains are coplanarly linked by ClO_4^- anions through CH···O and NH···O interactions [avg C···O = 3.561(7) Å and N···O = 3.113(5) Å],[11] completing a 2D supramolecular layer structure with a hydrophilic surface covered with amine and carboxylate groups and a hydrophobic surface covered with methyl and μ_2-thiolato groups. These layers are stacked in an $(AB)_n$ fashion such that wide hydrophilic and narrow hydrophobic 2D coordination spaces are alternately formed (Figure 1d). The $[Co(en)_3]^{3+}$ cations, as well as other ClO_4^- anions and water molecules, are accommodated in the hydrophilic interlayer spaces by forming NH···O hydrogen-bonding networks [avg $N_{en}\cdots O_{\text{D-pen}}$ = 2.961(5) Å, $N_{\text{D-pen}}\cdots O_{ClO4}$ = 3.040(5) Å, and $N_{en}\cdots O_{ClO4}$ = 3.122(6) Å]. It should be noted that the $[Co(en)_3]^{3+}$ cations in **1** uniformly adopt the Δ configuration (Figure 1b).

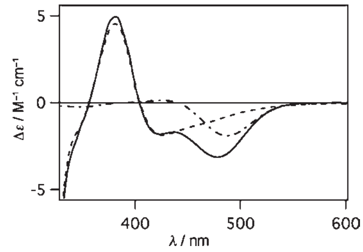


Figure 2. CD spectra of **1** (—), $[Pd_3(\text{D-pen})_3]\times 2$ (- - -), and Δ-$[Co(en)_3]^{3+}$ (—·—) in water.

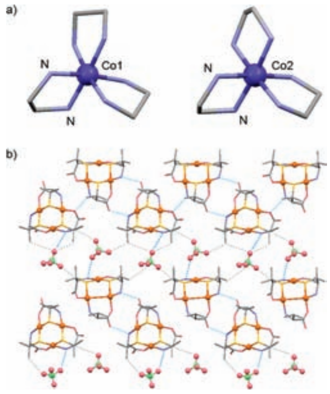


Figure 3. Perspective views of (a) independent Λ-$[Co(en)_3]^{3+}$ units and (b) a 2D layer structure in **2**.

To ensure the enantioselective incorporation of the Δ isomer of $[Co(en)_3]^{3+}$, the bulk sample of **1** was chromatographed on a cation-exchange column of SP-Sephadex C-25. After an orange-yellow band of $[Pd_3(\text{D-pen})_3]$ was eluted with water, an orange band containing $[Co(en)_3]^{3+}$ was eluted with 0.3 M aqueous NaCl. The CD spectrum of this eluate was identical with that of the optically pure Δ-$[Co(en)_3]^{3+}$ [9] not only in its spectral pattern but also in its intensity (Figure 2). This result clearly indicates that $[Pd_3(\text{D-pen})_3]$ has an ability to uptake only the Δ isomer of $[Co(en)_3]^{3+}$ from a 1:1 mixture of its Δ and Δ enantiomers, giving the diastereomerically pure cocrystallized compound $[Pd_3(\text{D-pen})_3]_2\cdot\Delta$-$[Co(en)_3](ClO_4)_3$.[12]

When a large excess of Λ-$[Co(en)_3](ClO_4)_3$,[9] instead of Δ/Λ-$[Co(en)_3](ClO_4)_3$, was mixed with $[Pd_3(\text{D-pen})_3]\cdot 4H_2O$ in water, orange plate crystals ($\mathbf{2}\cdot 10H_2O$) were obtained in a yield of ca. 50%.[10] This compound was confidently assigned to $[Pd_3(\text{D-pen})_3]_2\cdot\Lambda$-$[Co(en)_3](ClO_4)_3$, based on the absorption, circular dichroism (CD), IR, and ^1H NMR spectroscopies, together with X-ray fluorescence and elemental analyses.[10] Single-crystal X-ray analysis indicated that the overall structure in **2** is similar to that in **1**, except the presence of Λ-$[Co(en)_3]^{3+}$ in place of Δ-$[Co(en)_3]^{3+}$ (Figure 3a), although its asymmetric unit contains four crystallographically independent $[Pd_3(\text{D-pen})_3]$ molecules, two Λ-$[Co(en)_3]^{3+}$ cations, and six ClO_4^- anions, besides water molecules of crystallization.[10] Like in **1**, the $[Pd_3(\text{D-pen})_3]$ molecules in **2** are arranged in parallel in a coplane to form a 2D layer structure and, furthermore, the Λ-$[Co(en)_3]^{3+}$ cations are incorporated in hydrophilic interlayer spaces in combination with ClO_4^- anions and water molecules by forming multiple hydrogen bonds. A slight, but significant structural difference between **1** and **2** is observed in hydrogen-bonding interactions among the $[Pd_3(\text{D-pen})_3]$ molecules.

That is, in **2**, some of the intermolecular N···O distances between amine and carboxylato groups are too long to be considered as an effective hydrogen bond [N···O = 3.103(16)−3.142(15) Å], and thus the $[Pd_3(D\text{-pen})_3]$ units are not connected to one another through a rigid double hydrogen bonding as found in **1** (Figure 3b). Because there exist no other substantial structural differences between **1** and **2**, it is most likely that the incorporation of the Λ-$[Co(en)_3]^{3+}$ cations in place of the Δ-$[Co(en)_3]^{3+}$ ones partially breaks the hydrogen-bonding interactions between the $[Pd_3(D\text{-pen})_3]$ molecules, which results in the weaker packing force of crystals.

To check whether the enantioselective incorporation occurs only for $[Co(en)_3](ClO_4)_3$, Δ/Λ-$[Rh(en)_3](ClO_4)_3$[13] was treated with $[Pd_3(D\text{-pen})_3]$ under similar conditions, which gave orange plate crystals (**3**·$10H_2O$) in a yield of ca. 90%.[10] This compound was assigned to $[Pd_3(D\text{-pen})_3]_2\cdot[Rh(en)_3](ClO_4)_3$, based on the absorption, IR, and ^1H NMR spectroscopies, together with X-ray fluorescence and elemental analyses. It was found, from the SP-Sephadex C-25 column chromatography of the bulk sample of **3** and the subsequent absorption and CD spectral measurements of the eluate, that only the Δ isomer of $[Rh(en)_3]^{3+}$ is incorporated in **3**.[10] The enantioselective incorporation of Δ-$[Rh(en)_3]^{3+}$ in **3** was also confirmed by single-crystal X-ray analysis,[10] which revealed that **3**·$10H_2O$ is isomorphorous with **1**·$10H_2O$, containing two crystallographically independent $[Pd_3(D\text{-pen})_3]$ molecules, one Δ-$[Rh(en)_3]^{3+}$ cation, and three ClO_4^- anions in the asymmetric unit.

On the other hand, when $[Co(en)_3]Cl_3$ was treated with $[Pd_3(D\text{-pen})_3]$ in water, only rod crystals of $[Pd_3(D\text{-pen})_3]\cdot 4H_2O$ appeared and the formation of crystals composed of $[Pd_3(D\text{-pen})_3]$ and $[Co(en)_3]^{3+}$ was not noticed until the solution reached dryness. This was also the case for $[Co(en)_3](NO_3)_3$. Furthermore, the addition of a large excess of $NaCF_3SO_3$, Na_2SO_4, or Na_3PO_4 to an aqueous solution containing $[Co(en)_3]Cl_3$ and $[Pd_3(D\text{-pen})_3]$ gave only crystals of $[Pd_3(D\text{-pen})_3]\cdot 4H_2O$, while the addition of $NaClO_4$ led to the formation of crystals of **1**·$10H_2O$.[10,14] Thus, this system is highly selective toward ClO_4^- as an anion species when $[Pd_3(D\text{-pen})_3]$ forms a cocrystallized compound with $[Co(en)_3]^{3+}$. The formation of rigid hydrogen-bonding networks by the existence of ClO_4^- anions, which sustain the interactions between $[Pd_3(D\text{-pen})_3]$ and Δ-$[Co(en)_3]^{3+}$, seems to account for this result.

In summary, we demonstrated the completely enantioselective incorporation of the chiral complex salts, Δ-$[M(en)_3](ClO_4)_3$ (M = Co^{III} or Rh^{III}), into the hydrophilic 2D coordination spaces between the supramolecular layers made up of the neutral, optically active $[Pd_3(D\text{-pen})_3]$ molecules. Besides the enantioselectivity for the Δ-configurational $[M(en)_3]^{3+}$ cations, the interlayer spaces were found to possess an anion selectivity for ClO_4^-. To our knowledge, this is the first enantioselective/anion-selective incorporation of chiral complex salts into 2D interlayer coordination spaces of supramolecular compounds,[15] which should provide insight not only into the classical chiral resolution chemistry but also into the functional supramolecular chemistry. To further investigate the enantioselectivity and/or ion selectivity of this system, the reactions of $[Pd_3(D\text{-pen})_3]$ and other complex salts are currently underway.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data in CIF format and detailed experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: konno@chem.sci.osaka-u.ac.jp.

REFERENCES

(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781–2804. (b) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214. (c) Prakash, M. J.; Lah, M. S. *Chem. Commun.* **2009**, 3326–3341. (d) Férey, G. *Dalton Trans.* **2009**, 4400–4415.

(2) (a) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770–818. (b) Murray, K. S. *Aust. J. Chem.* **2009**, *62*, 1081–1101. (c) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.

(3) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375. (b) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695–704. (c) Kuppler, R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J.-R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.-C. *Coord. Chem. Rev.* **2009**, *253*, 3042–3066.

(4) (a) Brissard, M.; Gruselle, M.; Malézieux, B.; Thouvenot, R.; Guyard-Duhayon, C.; Convert, O. *Eur. J. Inorg. Chem.* **2001**, 1745–1751. (b) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305–326. (c) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273–282. (d) Morris, R. E.; Bu, X. *Nat. Chem.* **2010**, *2*, 353–361.

(5) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982–986. (b) Evans, O. R.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396. (c) Yuan, G.; Zhu, C.; Xuan, W.; Cui, Y. *Chem.—Eur. J.* **2009**, *15*, 6428–6434.

(6) (a) Toyota, A.; Yamaguchi, T.; Igashira-Kamiyama, A.; Kawamoto, T.; Konno, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 1088–1092. (b) Taguchi, M.; Igashira-Kamiyama, A.; Kajiwara, T.; Konno, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 2422–2425.

(7) Hirai, Y.; Igashira-Kamiyama, A.; Kawamoto, T.; Konno, T. *Chem. Lett.* **2007**, *36*, 434–435.

(8) Yoshinari, N.; Hirai, Y.; Kawamoto, T.; Igashira-Kamiyama, A.; Tsuge, K.; Konno, T. *Chem. Lett.* **2009**, *38*, 1056–1057.

(9) (a) Work, J. B. *Inorg. Synth.* **1946**, *2*, 221–222. (b) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183–186. (c) Judkins, R. R.; Royer, D. J. *Inorg. Chem.* **1974**, *13*, 945–950. (d) Kaneko, H.; Wada, N. *J. Solution Chem.* **1978**, *7*, 19–25.

(10) See the Supporting Information.

(11) (a) Desiraju, G. R. *Chem. Commun.* **2005**, 2995–3001. (b) Nishio, M.; Umezawa, Y.; Honda, K.; Tsuboyama, S.; Suezawa, H. *CrystEngComm* **2009**, *11*, 1757–1788.

(12) The ^1H NMR spectrum of a D_2O solution containing $[Pd_3(D\text{-pen})_3]$ and *rac*-$[Co(en)_3]^{3+}$ gave a single set of signals that are entirely identical with those containing $[Pd_3(D\text{-pen})_3]$ and Δ- or Λ-$[Co(en)_3]^{3+}$, indicative of the absence of the selective interaction between $[Pd_3(D\text{-pen})_3]$ and Δ-$[Co(en)_3]^{3+}$ in aqueous solution.

(13) Galsbol, F. *Inorg. Synth.* **1970**, *12*, 269–280.

(14) When $[Co(en)_3]X_3$ (X = BF_4^- or ReO_4^-) was treated with $[Pd_3(D\text{-pen})_3]$ in water, $[Co(en)_3]X_3$ was crystallized first, followed by crystallization of $[Pd_3(D\text{-pen})_3]$.

(15) The enantioselective incorporation of $[Co(L)_3]^{3+}$ (L = en or tn) by using α- or β-cyclodextrin has recently been investigated: (a) Ohta, N.; Fuyuhiro, A.; Yamanari, K. *Chem. Commun.* **2010**, *46*, 3535–3537. (b) Ohta, N.; Fuyuhiro, A.; Yamanari, K. *Inorg. Chem.* **2010**, *49*, 9122–9124.