Drastic Change in Dimensional Structures of D-Penicillaminato $(Au^{I}_2Pt^{II}_2Zn^{II})_n$ Coordination Polymers by Moderate Change in Solution pH

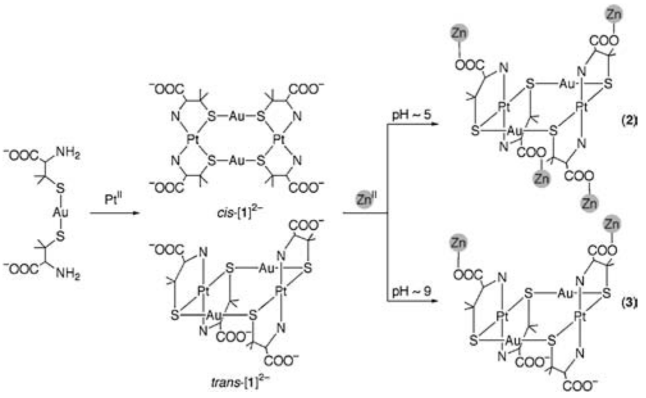
Takumi Konno,* Nobuto Yoshinari, Mai Taguchi, and Asako Igashira-Kamiyama
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received March 11, 2009; CL-090250; E-mail: konno@chem.sci.osaka-u.ac.jp)

Treatment of an aqueous solution containing cis and trans isomers of a S-bridged tetranuclear $Au^{I}_2Pt^{II}_2$ complex, $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$), newly prepared from $[Au(\text{D-pen-}S)_2]^{3-}$ and $[PtCl_4]^{2-}$, with Zn^{2+} at pH $\approx$ 5 gave a 3D porous $(Au^{I}_2Pt^{II}_2Zn^{II})_n$ coordination polymer **2**, in which *trans*-$[\mathbf{1}]^{2-}$ units are linked by Zn^{2+}. On the other hand, a 1D helix $(Au^{I}_2Pt^{II}_2Zn^{II})_n$ coordination polymer **3**, in which *trans*-$[\mathbf{1}]^{2-}$ units are linked by $[Zn(H_2O)_2]^{2+}$, was produced by similar treatment at pH $\approx$ 9.

There has been considerable research interest in the design and creation of coordination polymers that show attractive structures and properties.[1] One-step assembly of multidentate organic ligands assisted by transition-metal ions is the most common approach to construct coordination polymers.[2] However, this approach often encounters difficulty in the rational construction of heterometallic systems, as well as difficulty in the control and modification of their dimensional structures by external factors. An alternative approach that could overcome these difficulties is the use of discrete metal complexes as metalloligands, which have several potential donor groups available for coordination to metal centers.[3] Our interest has been directed to this approach based on thiolato metal complexes with sulfur-containing aminocarboxylate ligands, such as L-cysteinate (L-cys) and D-penicillaminate (D-pen).[4] Recently, we have shown that the two-coordinate aurate(I) complex with two D-pen ligands, $[Au(\text{D-pen-}S)_2]^{3-}$, binds to Pd^{II} ions through thiolato and amine groups to afford two stereoisomers (cis and trans) of a S-bridged tetranuclear $Au^{I}_2Pd^{II}_2$ complex, $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$.[5] This tetranuclear $Au^{I}_2Pd^{II}_2$ complex possesses four free carboxylate groups, and thus is expected to act as a chiral O-donating metalloligand to construct heterometallic coordination polymers consisting of three different metal ions. However, a rapid trans-to-cis isomerization was observed for $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$, which made it difficult to investigate the functionality of this complex as a metalloligand. In this paper, we report that an analogous tetranuclear $Au^{I}_2Pt^{II}_2$ complex, $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$), newly prepared from $[Au(\text{D-pen-}S)_2]^{3-}$ and Pt^{II}, is fairly stable toward the trans-to-cis isomerization and is assembled into heterotrimetallic coordination polymers in combination with Zn^{2+}. Remarkably, only the trans isomer of $[\mathbf{1}]^{2-}$ was assembled into coordination polymers, the structures of which were drastically changed by moderate change in solution pH (Scheme 1).

The reaction of a colorless aqueous solution containing $NH_4[Au(\text{D-Hpen-}S)_2]$ and K_2CO_3 with equimolar $K_2[PtCl_4]$ gave a clear yellow solution (pH $\approx$ 9). The ^{1}H NMR spectrum of this reaction solution showed two sets of proton signals in a ca. 5:4 integration ratio,[6] which correspond well with those of cis and trans isomers of the previously reported $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$.[5] This spectral feature is suggestive of the presence of cis and trans isomers of the analogous $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$) in the reaction solution. Indeed, *cis*- and *trans*-$[\mathbf{1}]^{2-}$ were both successfully isolated as a potassium salt from the reaction solution by fractional crystallization, the assignment of which was made by IR and ^{1}H NMR spectroscopy, together with elemental and X-ray fluorescence analyses.[6] It is worth mentioning that no significant ^{1}H NMR spectral change was noticed for this reaction solution at room temperature for 1 month, indicating that both the cis and trans isomers of $[\mathbf{1}]^{2-}$ are fairly stable toward isomerization in solution. This is in contrast to the fact that the trans isomer of $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$ was completely converted to its cis isomer within 3 weeks under similar conditions.[5]



Scheme 1. Synthetic routes of *cis*- and *trans*-$[\mathbf{1}]^{2-}$, **2**, and **3**.

To create heterotrimetallic coordination polymers that contain $[\mathbf{1}]^{2-}$ as building units, equimolar $Zn(NO_3)_2$ was added to the yellow reaction solution, which was adjusted to pH $\approx$ 5 by HCl. After filtration, the mixture was allowed to stand at room temperature for several weeks in a closed glass vessel, which produced pale-yellow block-like crystals **2** that were insoluble in water.[7] The ^{1}H NMR spectrum of the filtrate after removal of the crystals showed only one set of signals corresponding to *cis*-$[\mathbf{1}]^{2-}$, suggestive of the selective uptake of the trans isomer of $[\mathbf{1}]^{2-}$ into **2**.[6] The presence of Au, Pt, and Zn atoms in **2** was confirmed by X-ray fluorescence spectrometry, and its elemental analytical result was consistent with the formula for a 1:1 adduct of $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ and Zn^{2+}. The structure of **2** was determined by single-crystal X-ray analysis,[8] which showed the existence of $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$) units and Zn^{2+} ions in a 1:1 ratio. As shown in Figure 1, each of the $[\mathbf{1}]^{2-}$ units adopts the trans structure with an idealized D_2 symmetry, in which two *trans*-$[Pt(\text{D-pen-}N,S)_2]^{2-}$ square planes are connected by two linear Au^{I} linkers to form a $Pt^{II}_2Au^{I}_2S_4$ square ring (Au–S = 2.295(2) Å, Pt–S = 2.303(2) Å, S–Au–S = 178.81(9)°, S–Pt–S = 176.60(9)°, and Au–S–Pt = 91.33(6)°).

Copyright © 2009 The Chemical Society of Japan

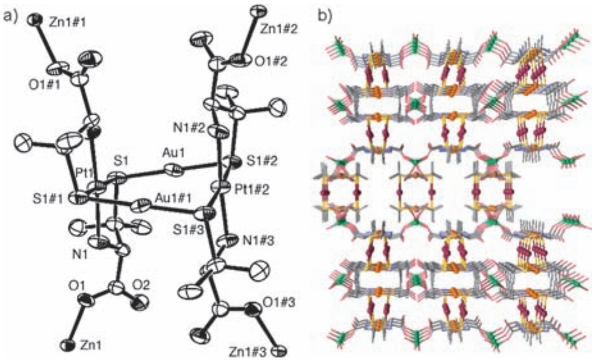


Figure 1. Perspective view of **2**. H atoms are omitted for clarity. Au: purple-red, C: gray, N: blue, O: pale red, Pt: orange, S: yellow, Zn: green.

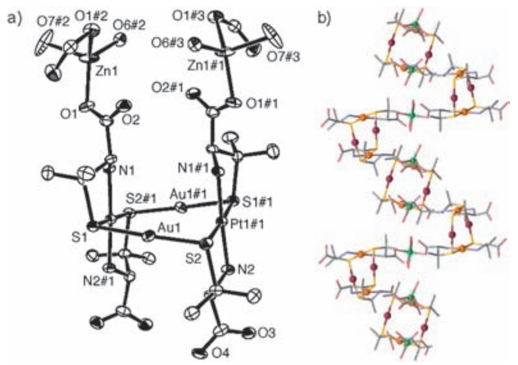


Figure 2. Perspective views of **3**. H atoms and disordered Zn atoms are omitted for clarity. Au: purple-red, C: gray, N: blue, O: pale red, Pt: orange, S: yellow, Zn: green.

Four COO^- groups in each *trans*-$[\mathbf{1}]^{2-}$ unit coordinate to four Zn^{2+} ions, while each Zn^{2+} ion is coordinated by four COO^- groups from four different *trans*-$[\mathbf{1}]^{2-}$ units in a tetrahedral geometry (Zn–O = 1.928(5) Å and av O–Zn–O = 110.3(4)°).[6] As a result, **2** constructs a porous 3D polymeric structure with a neutral formal charge, which is responsible for its insolubility in water. In **2**, a number of solvated water molecules are accommodated in the 3D pores.[6]

When the yellow reaction solution (pH ≈ 9) containing *cis*- and *trans*-$[\mathbf{1}]^{2-}$ was treated with equimolar of $Zn(NO_3)_2$ without adjusting solution pH, pale-yellow plate-like crystals **3** that are also insoluble in water were produced.[9] X-ray fluorescence spectrometry indicated the presence of Au, Pt, and Zn atoms in **3**, and its elemental analytical data were in agreement with the formula for a 1:1 adduct of $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ and Zn^{2+}, as in the case for **2**. In addition, the IR spectrum of **3** was very similar to that of **2** over the whole region.[6] From these results, it was speculated that **3** has a polymeric structure analogous to that found in **2**. However, X-ray structural analysis revealed that **3** does not have a 3D structure but adopts a 1D helix structure (Figure 2).[10] Crystal **3** consists of $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$) units and Zn^{2+} ions in a 1:1 ratio, as does **2**. Each of the $[\mathbf{1}]^{2-}$ units in **3** also has trans structure, in which two *trans*-$[Pt(\text{D-pen-}N,S)_2]^{2-}$ square planes are connected by linear Au^{I} linkers (av Au–S = 2.296(2) Å, Pt–S = 2.294(2) Å, S–Au–S = 177.30(5)°, S–Pt–S = 176.72(6)°, and Au–S–Pt = 91.70(6)°). In **3**, however, only two of four COO^- groups in each *trans*-$[\mathbf{1}]^{2-}$ unit coordinate to Zn^{2+} ions, and each tetrahedral Zn^{2+} ion is coordinated by two water molecules, besides two COO^- groups from two *trans*-$[\mathbf{1}]^{2-}$ units (av Zn–O = 2.01(1) Å and O–Zn–O = 108.7(7)°).[6] As a result, *trans*-$[\mathbf{1}]^{2-}$ units are alternately linked by $[Zn(H_2O)_2]^{2+}$ ions in **3**, constructing a neutral helix structure with a right-handed threefold screw axis. There exist a number of solvated water molecules between the grooves of each helix, which seems to sustain this unique heterotrimetallic structure.[6]

In summary, we showed that $[Au_2\{Pt(\text{D-pen-}N,S)_2\}_2]^{2-}$ ($[\mathbf{1}]^{2-}$) can act as a O-donating multibridging metalloligand to construct heterotrimetallic coordination polymers. Of two stereoisomers formed for $[\mathbf{1}]^{2-}$, only the trans isomer was exclusively assembled into polymeric structures in combination with Zn^{2+} ions, presumably because of the suitable arrangement and orientation of carboxylate groups in the trans isomer for the construction of dimensional coordination networks. Interestingly, the drastic change in dimensional structures (3D porous for **2** vs. 1D helix for **3**) was induced by the moderate change in solution pH (pH ≈ 5 vs. pH ≈ 9), with the change of carboxylate numbers (4 vs. 2) bound to each tetrahedral Zn^{II} center. Finally, the present results point out that a variety of heterotrimetallic coordination polymers with different dimensional structures could be created in a controlled manner if one employs heterobimetallic metalloligands bearing free carboxylate groups and oxophilic transition metal ions.

This work was partially supported by Grants-in-Aid for Young Scientists B (No. 20750047) from Japan Society for the Promotion of Science.

References and Notes

1 a) A. Kumar, S.-S. Sun, A. J. Lees, *Coord. Chem. Rev.* **2008**, *252*, 922. b) R. W. Saalfrank, H. Maid, A. Scheurer, *Angew. Chem., Int. Ed.* **2008**, *47*, 8794.

2 a) S. J. Dalgarno, N. P. Power, J. L. Atwood, *Coord. Chem. Rev.* **2008**, *252*, 825. b) B. H. Northrop, H.-B. Yang, P. J. Stang, *Chem. Commun.* **2008**, 5896.

3 a) S. R. Halper, L. Do, J. R. Stork, S. M. Cohen, *J. Am. Chem. Soc.* **2006**, *128*, 15255. b) E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y. Journaux, F. Lloret, M. Julve, *Dalton Trans.* **2008**, 2780.

4 a) T. Konno, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 627. b) A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Angew. Chem., Int. Ed.* **2005**, *44*, 1088. c) T. Aridomi, K. Takamura, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Chem.—Eur. J.* **2008**, *14*, 7752. d) T. Aridomi, A. Igashira-Kamiyama, T. Konno, *Inorg. Chem.* **2008**, *47*, 10202.

5 M. Taguchi, Y. Sameshima, A. Igashira-Kamiyama, S. Akine, T. Nabeshima, T. Konno, *Chem. Lett.* **2008**, *37*, 244.

6 See Supporting Information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

7 Calcd for $[Zn\{Au_2Pt_2(\text{D-pen})_4\}]\cdot 10H_2O$ ($\mathbf{2}\cdot 10H_2O$): C, 14.84; H, 3.49; N, 3.46%. Found: C, 14.72; H, 3.46; N, 3.39%. Yield: 27% based on $NH_4[Au(\text{D-Hpen})_2]$.

8 Crystal data for $\mathbf{2}\cdot 9H_2O$: fw 1600.40, hexagonal, $P6_422$, $a = 12.458(3)$, $c = 24.673(5)$ Å, $V = 3316.5(13)$ Å^3, $Z = 3$, $D_{\text{calcd}} = 2.404$ g/cm^3, 31523 reflections measured, 2546 independent. $R_1 = 0.0261$ ($I > 2\sigma(I)$), $wR_2 = 0.0679$ (all data). CCDC: 723309.

9 Calcd for $[\{Zn(H_2O)_2\}\{Au_2Pt_2(\text{D-pen})_4\}]\cdot 5.5H_2O$ ($\mathbf{3}\cdot 5.5H_2O$): C, 15.27; H, 3.27; N, 3.56%. Found: C, 15.04; H, 3.24; N, 3.61%. Yield: 25% based on $NH_4[Au(\text{D-Hpen})_2]$.

10 Crystal data for $\mathbf{3}\cdot 8H_2O$: fw 1618.41, trigonal, $P3_121$, $a = 14.729(3)$, $c = 16.069(5)$ Å, $V = 3019.2(13)$ Å^3, $Z = 3$, $D_{\text{calcd}} = 2.670$ g/cm^3, 25317 reflections measured, 4603 independent. $R_1 = 0.0228$ ($I > 2\sigma(I)$), $wR_2 = 0.0405$ (all data). CCDC: 723310.

Published on the web (Advance View) April 25, 2009; doi:10.1246/cl.2009.526