doi:10.1246/cl.2010.601

Novel Multinuclear $Ni^{II}Au^{I}_2$ and $Ni^{II}Au^{I}_3$ Complexes Containing D-Penicillaminate and Bis(diphenylphosphino)methane: Rational Expansion of 8-Membered to 12-Membered Chelating Metalloring

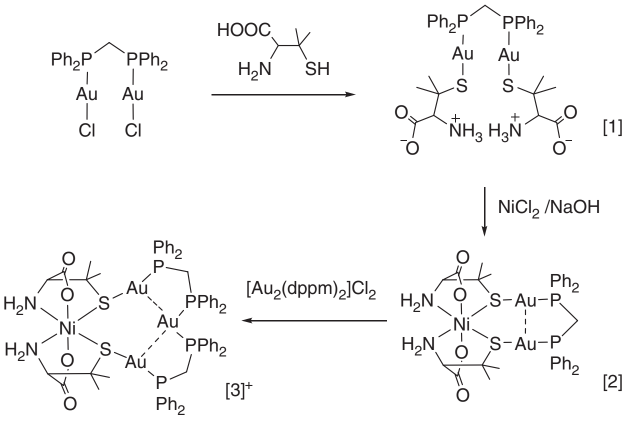
Yuji Hashimoto, Kiyoshi Tsuge, and Takumi Konno*
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

(Received March 17, 2010; CL-100261; E-mail: konno@chem.sci.osaka-u.ac.jp)

A digold(I) complex, $[Au_2(\text{D-Hpen-}S)_2(dppm)]$ ([**1**]), newly prepared from $[Au_2Cl_2(dppm)]$ and D-H_2pen, readily reacted with Ni^{2+} to give a S-bridged $Ni^{II}Au^{I}_2$ trinuclear complex having an 8-membered chelating metalloring, $[Au_2(dppm)\{Ni(\text{D-pen-}N,O,S)_2\}]$ ([**2**]). Complex [**2**] was reversibly converted to a $Ni^{II}Au^{I}_3$ tetranuclear complex having a 12-membered metalloring, $[Au_3(dppm)_2\{Ni(\text{D-pen-}N,O,S)_2\}]Cl$ ([**3**]Cl), retaining the coordination environment about a Ni^{II} center.

Molecular rings, ranging from simple benzene rings to sophisticated supramolecular rings, represent one of the most essential structural motifs in chemistry.[1] In coordination chemistry, ring structures have commonly been observed, as represented by chelate rings, and furthermore, metalloring structures have often been found in coordination oligomers.[2] A representative approach to create a large-membered ring in coordination compounds is the linkage of plural rigid ligands with use of metal ions in a closed form through self-assembly processes,[3] as well as the chelation of long, flexible ligands to a metal center.[4] While these methods enable the formation of intended ring structures with specific sizes, the expansion and contraction of a given ring, which requires the cleavage/formation of coordination bonds, has scarcely been achieved in coordination systems.[5] Thus, the finding of a methodology that leads to metalloring-expansion/contraction reactions is a key concern and a great challenge in coordination chemistry. As part of our ongoing efforts in the development of a gold(I) metalloligand system derived from thiol-containing amino acids,[6] herein we report a novel digold(I) complex, $[Au_2(\text{D-Hpen-}S)_2(dppm)]$ (D-H_2pen = D-penicillamine, dppm = bis(diphenylphosphino)methane), which acts as a hexadentate metalloligand toward Ni^{II} to form an 8-membered chelating metalloring. Remarkably, a $[Au(dppm)]^+$ unit was reversibly inserted into the 8-membered metalloring, allowing the reversible conversion to a 12-membered metalloring, while the coordination environment about a Ni^{II} center remained intact during the reactions (Scheme 1).

The reaction of $[Au_2Cl_2(dppm)]$[7] with 2 molar equiv of D-H_2pen in ethanol, followed by the addition of NaOH, gave a colorless solution, from which a white powder ([**1**]•$5H_2O$) was isolated in a high yield.[8] The ^{1}H NMR spectrum of this compound in methanol-d_4 shows a methine and two methyl singlet signals due to D-pen (δ 3.57, 1.76, and 1.43) and aromatic multiplet signals due to dppm (δ 7.74–7.35) in an integral intensity ratio of 1:3:3:10.[8,9] From this spectrum, together with the elemental analysis, [**1**] is assigned to an expected digold(I) complex, $[Au_2(\text{D-Hpen-}S)_2(dppm)]$, in which Cl^- donors in the starting $[Au_2Cl_2(dppm)]$ is replaced by thiolato groups of D-Hpen$^-$. In the IR spectrum, [**1**] gives a strong ν_{CO} band at 1627 cm^{-1},[8] indicative of the presence of deprotonated carboxyl groups.[10] Thus, D-Hpen$^-$ is assumed to exist in a zwitterionic form with COO^- and NH_3^+ groups, like free D-H_2pen.[11]



Scheme 1. Synthesis and conversion of [**1**], [**2**], and [**3**]$^+$.

When [**1**]•$5H_2O$ was treated with 1 molar equiv of $NiCl_2$•$6H_2O$ in ethanol, followed by the addition of NaOH, a colorless solution immediately turned to green in color, and green crystals with a block-like shape ([**2**]•$7H_2O$•0.5EtOH) were obtained from the green solution in a good yield.[8] X-ray fluorescence spectrometry implied that this compound contains Ni and Au atoms in a 1:2 ratio, and its elemental analytical data were in agreement with the formula for a 1:1 adduct of $[Au_2(\text{D-pen})_2(dppm)]^{2-}$ and Ni^{2+}. The electronic absorption spectral behavior of [**2**] in ethanol (Figure 1) is reminiscent of that of $[Au_2\{Ni(\text{D-pen-}N,O,S)_2\}_2]^{2-}$ composed of octahedral $[Ni(\text{D-pen-}N,O,S)_2]^{2-}$ units,[6b] giving a broad near IR band at 1020 nm and a visible band at 589 nm assignable to $^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ transitions. Based on these results, [**2**] is assigned as a $Ni^{II}Au^{I}_2$ trinuclear complex, $[Au_2(dppm)\{Ni(\text{D-pen-}N,O,S)_2\}]$, in which a Ni^{II} center has an $N_2O_2S_2$ octahedral geometry surrounded by two tridentate-N,O,S D-pen ligands. Compatible with this assignment, a ν_{CO} band due to deprotonated carboxyl groups is observed at 1596 cm^{-1} in the IR spectrum of [**2**].[8]

The crystal structure of [**2**]•$7H_2O$•0.5EtOH was determined by single-crystal X-ray crystallography, which revealed the presence of two independent, yet nearly the same complex molecules in the asymmetric unit, besides solvated water and ethanol molecules.[8,12] As shown in Figure 2, [**2**] contains a $[Ni(\text{D-pen-}N,O,S)_2]^{2-}$ unit that is bound to a $[Au_2(dppm)]^{2+}$ moiety to form a S-bridged $Ni^{II}Au^{I}_2$ trinuclear structure with 8-membered $NiAu_2S_2P_2C$ metalloring.[13] The Ni^{II} atom in [**2**]

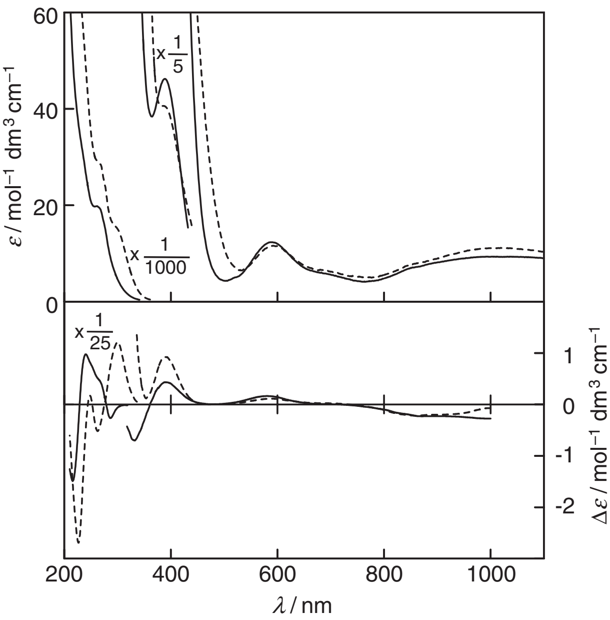


Figure 1. Electronic absorption and CD spectra of [**2**] (—) and [**3**]Cl (- - -) in ethanol.

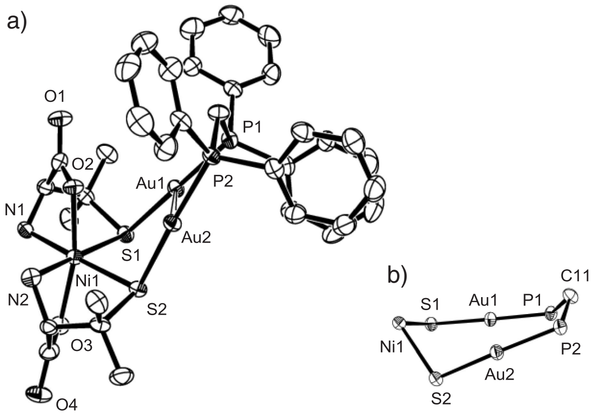


Figure 2. ORTEP drawings of [**2**]. One of two independent complex molecules of [**2**] is selected. a) Entire trinuclear complex molecule, b) 8-membered metalloring structure in [**2**]. Hydrogen atoms are omitted for clarity.

adopts a distorted $N_2O_2S_2$ octahedral geometry with a *trans*(*O*) geometric configuration (av. Ni–N = 2.076(3) Å, Ni–O = 2.093(2) Å, Ni–S = 2.4267(8) Å, N–Ni–S = 175.54(8)°, O–Ni–O = 167.52(13)°). The two Au^I atoms are each situated in a linear geometry coordinated by P and S atoms (av. Au–P = 2.2681(8) Å, Au–S = 2.3172(8) Å, P–Au–S = 174.52(3)°). In [**2**], the intramolecular separation between two Au^I atoms is 3.1346(2) Å, suggestive of the presence of an aurophilic interaction.[14] A similar aurophilic interaction has commonly been observed for other gold(I) species with a $[Au_2(dppm)]^{2+}$ moiety.[15] The two bridging S atoms have *R* and *S* chiral configurations such that the 8-membered metalloring forms a twisted boat-like conformation.

It has been reported that $[Au_3Cl_2(dppm)_2]Cl$ equilibrates with a mixture of $[Au_2Cl_2(dppm)]$ and $[Au_2(dppm)_2]Cl_2$ in solution.[16] This is suggestive of the conversion of a dppm digold(I) species to a dppm trigold(I) species by reacting with $[Au_2(dppm)_2]Cl_2$. Thus, we carried out the reaction of [**2**] with $[Au_2(dppm)_2]Cl_2$ in ethanol to examine whether the digold(I) structure in [**2**] is converted to a trigold(I) structure. Indeed, the initial green solution of [**2**] quickly turned to yellow-green on adding 0.5 molar equiv of $[Au_2(dppm)_2]Cl_2$, and yellow-green crystals with a needle-like shape ([**3**]Cl$\cdot$17H_2O) were isolated from the yellow-green solution in a good yield.[8] X-ray fluorescence and elemental analyses suggested that this compound is a 1:1 adduct of [**2**] and [Au(dppm)]Cl, and its IR spectrum was very similar to that of [**2**] over the whole region. In addition, the absorption spectrum of [**3**]Cl resembles that of [**2**] especially in the d–d absorption region, showing a broad near IR band at 1020 nm and a visible band at 593 nm (Figure 1). However, a marked spectroscopic difference between [**2**] and [**3**]Cl was found in the CD spectra in the region of 250–350 nm. That is, the CD spectrum of [**2**] exhibits negative and positive CD signs from longer wavelengths in this region, while that of [**3**]Cl shows CD signs opposite to [**2**] (Figure 1). Thus, it is assumed that [**3**]Cl has a metalloring structure different from that in [**2**], although the coordination mode of D-pen, as well as the coordination environment of a Ni^{II} ion, is similar.

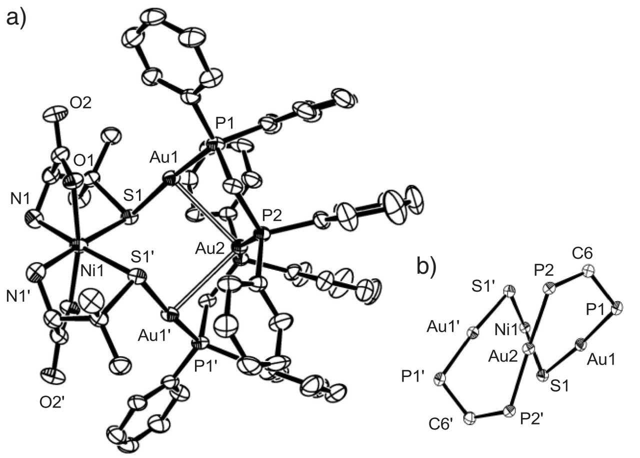


Figure 3. ORTEP drawings of complex-cation [**3**]$^+$. a) Entire tetranuclear complex-cation, b) 12-membered metalloring structure in [**3**]$^+$. Hydrogen atoms are omitted for clarity. Symmetry code: (′) $-x + 1$, $-y$, z.

Single-crystal X-ray analysis of [**3**]Cl$\cdot$17H_2O revealed the presence of a $Ni^{II}Au^{I}_3$ complex-cation and a chloride anion in a 1:1 ratio, besides solvated water molecules.[8,17] As shown in Figure 3, the complex-cation [**3**]$^+$ contains an octahedral [Ni(D-pen-*N*,*O*,*S*)$_2$]$^{2-}$ unit with a *trans*(*O*) geometry (Ni–N = 2.061(4) Å, Ni–O = 2.076(3) Å, Ni–S = 2.4624(15) Å, N–Ni–S = 177.48(13)°, O–Ni–O = 167.7(2)°), the structure of which is almost the same as that in [**2**]. However, [**3**]$^+$ possesses a $[Au_3(dppm)_2]^{3+}$ linker, in place of $[Au_2(dppm)]^{2+}$ in [**2**], constructing a S-bridged $Ni^{II}Au^{I}_3$ tetranuclear structure bearing a 12-membered $NiAu_3S_2P_4C_2$ metalloring.[13] This metalloring forms a skewed conformation with two S atoms being fixed to *R* configuration. In [**3**]$^+$, each of the two terminal Au atoms is coordinated by P and S atoms to form a linear geometry (Au–P = 2.2737(14) Å, Au–S = 2.3262(13) Å, P–Au–S =

174.30(5)°), while the geometry of the central Au atom is considerably distorted from linearity with two P donor atoms (Au–P = 2.3347(12) Å, P–Au–P = 162.49(6)°). This distortion appears to result from Au1···Au2 and Au1′···Au2 aurophilic interactions (2.9774(3) Å), which sustain this unique 12-membered metalloring structure.

Prompted by the successful conversion of [**2**] to [**3**]Cl by treatment with $[Au_2(dppm)_2]Cl_2$, we also investigated the possibility of the reverse conversion. Based on the idea that the removal of a $[Au(dppm)]^+$ moiety from $[\mathbf{3}]^+$ ($[Au_3(dppm)_2\{Ni(\text{D-pen-}N,O,S)_2\}]^+$) leads to the formation of [**2**] ($[Au_2(dppm)\{Ni(\text{D-pen-}N,O,S)_2\}]$) and that the formula for [**2**] is equal to the 1:1:1 combination of $[Au(\text{D-pen})_2]^{3-}$, Ni^{2+}, and $[Au(dppm)]^+$, 1 molar equiv each of $(NH_4)[Au(\text{D-Hpen-}S)_2]$ and $NiCl_2$ was added to an ethanolic solution containing [**3**]Cl, together with NaOH.[8] Interestingly, this procedure caused the solution color change from yellow-green to green in a few minutes, and the absorption and CD spectra of the resulting green solution were identical with those of [**2**]. Thus, it is concluded that $[\mathbf{3}]^+$ is quickly reverted back to [**2**] by reacting with $[Au(\text{D-pen-}S)_2]^{3-}$ in combination with Ni^{2+}.

In summary, we designed and synthesized a new digold(I) complex ([**1**]), in which two D-penicillaminates are spanned by a bended $[Au_2(dppm)]^{2+}$ linker through thiolato groups. The functionality of [**1**] as a hexadentate-$N_2O_2S_2$ metalloligand was evidenced by the reaction with Ni^{2+}, which gave a S-bridged $Ni^{II}Au^{I}_2$ trinuclear complex with an 8-membered chelating metalloring ([**2**]). Of note is the quick, reversible conversion of the 8-membered metalloring to the larger 12-membered metalloring by simple treatment with $[Au_2(dppm)_2]^{2+}$, retaining the coordination environment about a Ni^{II} center.[18] As far as we know, such an expansion reaction of chelating metalloring has not been reported so far. To develop this attractive chemistry, the reactions of [**2**] with other $[Au_2(diphosphine)_2]^{2+}$ complexes, together with the creation of other metalloligands analogous to [**1**], are underway in our laboratory.

This work was partially supported by Grants-in-Aid for Scientific Research C (No. 20550053) from Japan Society for the Promotion of Science.

References and Notes

1 a) J. A. Semlyen, *Large Ring Molecules*, Wiley, Chichester, **1996**. b) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, **2000**. c) W. Zhang, J. S. Moore, *Angew. Chem., Int. Ed.* **2006**, *45*, 4416. d) H. Oike, *React. Funct. Polym.* **2007**, *67*, 1157.

2 a) J. R. Gispert, *Coordination Chemistry*, Wiley, Chichester, **2008**. b) Y.-F. Han, W.-G. Jia, W.-B. Yu, G.-X. Jin, *Chem. Soc. Rev.* **2009**, *38*, 3419. c) R. J. Puddephatt, *Chem. Soc. Rev.* **2008**, *37*, 2012. d) M. J. Prakash, M. S. Lah, *Chem. Commun.* **2009**, 3326.

3 a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853. b) M. Fujita, M. Tominaga, A. Hori, B. Therrien, *Acc. Chem. Res.* **2005**, *38*, 369. c) Y. Kobuke, *Struct. Bond.* **2006**, *121*, 49.

4 a) H. Ogino, *J. Coord. Chem.* **1987**, *15*, 187. b) J.-C. Chambron, J.-P. Collin, V. Heitz, D. Jouvenot, J.-M. Kern, P. Mobian, D. Pomeranc, J.-P. Sauvage, *Eur. J. Org. Chem.* **2004**, 1627. c) N. Yoshinari, T. Konno, *Inorg. Chem.* **2008**, *47*, 7450.

5 a) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi, K. Ogura, *Chem. Commun.* **1996**, 1535. b) M. Schweiger, S. R. Seidel, A. M. Arif, P. J. Stang, *Inorg. Chem.* **2002**, *41*, 2556. c) F. A. Cotton, C. A. Murillo, R. Yu, *Dalton Trans.* **2006**, 3900.

6 a) A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Angew. Chem., Int. Ed.* **2005**, *44*, 1088. b) M. Taguchi, A. Igashira-Kamiyama, T. Kajiwara, T. Konno, *Angew. Chem., Int. Ed.* **2007**, *46*, 2422. c) Y. Sameshima, N. Yoshinari, K. Tsuge, A. Igashira-Kamiyama, T. Konno, *Angew. Chem., Int. Ed.* **2009**, *48*, 8469.

7 H. Schmidbaur, A. Wohlleben, F. Wagner, O. Orama, G. Huttner, *Chem. Ber.* **1977**, *110*, 1748.

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

9 A triplet signal due to methylene protons of dppm appears at δ 4.21 in the ^{1}H NMR spectrum of [**1**].

10 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, Chichester, **1997**.

11 H. E. Howard-Lock, C. J. L. Lock, P. S. Smalley, *J. Chem. Crystallogr.* **1983**, *13*, 333.

12 Crystal data for [**2**]$\cdot 7H_2O \cdot 0.5EtOH$: fw 1280.54, Monoclinic, $P2_1$, $a = 11.6706(4)$ Å, $b = 31.7998(11)$ Å, $c = 12.7354(5)$ Å, $\beta = 105.9110(10)°$, $V = 4545.3(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.871$ g cm^{-3}, 45203 reflections measured, 20663 independent. $R_1 = 0.0385$ ($I > 2\sigma(I)$), $wR_2 = 0.0813$ (all data). CCDC: 769659.

13 The ESI mass spectra of [**2**] and $[\mathbf{3}]^+$ in ethanol gave main signals at m/z 1153 and 1711, the calculated molecular mass and the isotopic distribution of which match well with those for $\{Na[\mathbf{2}]\}^+$ and $[\mathbf{3}]^+$, respectively,[8] suggesting that the structures in [**2**] and $[\mathbf{3}]^+$ are retained in solution.

14 a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597. b) C.-M. Che, S.-W. Lai, *Coord. Chem. Rev.* **2005**, *249*, 1296. c) H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931. d) M. J. Katz, K. Sakai, D. B. Leznoff, *Chem. Soc. Rev.* **2008**, *37*, 1884.

15 a) R. Usón, A. Laguna, M. Laguna, E. Fernandez, M. D. Villacampa, P. G. Jones, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1983**, 1679. b) R. M. Davila, A. Elduque, T. Grant, R. J. Staples, J. P. Fackler, Jr., *Inorg. Chem.* **1993**, *32*, 1749. c) V. W.-W. Yam, E. C.-C. Cheng, K.-K. Cheung, *Angew. Chem., Int. Ed.* **1999**, *38*, 197. d) Z. Li, Z.-H. Loh, K. F. Mok, T. S. A. Hor, *Inorg. Chem.* **2000**, *39*, 5299.

16 I. J. B. Lin, J. M. Hwang, D.-F. Feng, M. C. Cheng, Y. Wang, *Inorg. Chem.* **1994**, *33*, 3467.

17 Crystal data for [**3**]Cl$\cdot 17H_2O$: fw 2054.45, Orthorhombic, $P2_12_12$, $a = 20.4371(6)$ Å, $b = 11.5371(4)$ Å, $c = 16.7630(6)$ Å, $V = 3952.5(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.726$ g cm^{-3}, 38372 reflections measured, 9013 independent. $R_1 = 0.0360$ ($I > 2\sigma(I)$), $wR_2 = 0.0695$ (all data). CCDC: 769660. A half of the tetranuclear cation is crystallographically independent.

18 The reaction of [**1**] with $[Au_2(dppm)_2]Cl_2$ in a 2:1 ratio in methanol was found to produce $[Au_3(\text{D-pen})(\text{D-Hpen})(dppm)_2]$, accompanied by the conversion of a $[Au_2(dppm)]^{2+}$ core to a $[Au_3(dppm)_2]^{3+}$ core. This result will be published elsewhere.