A Novel Cis–Trans Isomerism Found in a Sulfur-bridged $Pd^{II}{}_2Au^{I}{}_2$ Tetranuclear Complex with $[Pd(amine)_2(thiolato)_2]$-type Building Units

Mai Taguchi,[1] Yuko Sameshima,[1] Asako Igashira-Kamiyama,[1] Shigehisa Akine,[2] Tatsuya Nabeshima,[2] and Takumi Konno*[1]
[1]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*
[2]*Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571*

(Received November 15, 2007; CL-071269; E-mail: konno@ch.wani.osaka-u.ac.jp)

Treatment of $[Au(D\text{-pen-}S)_2]^{3-}$ (D-H_2pen = D-penicillamine) with $[PdCl_4]^{2-}$ in a 1:1 ratio gave a S-bridged $Pd^{II}{}_2Au^{I}{}_2$ tetranuclear complex, in which two square-planar $[Pd(D\text{-pen-}N,S)_2]^{2-}$ units are linked by two linear Au^{I} ions. This tetranuclear complex was found to form two geometrical isomers that are discriminated by the cis–trans isomerism of $[Pd(D\text{-pen-}N,S)_2]^{2-}$ units.

Over the past decades, there has been considerable research interest in the creation of S-bridged polynuclear complexes composed of square-planar $[M(amine)_2(thiolato)_2]$-type ($M = Ni^{II}$ and Pd^{II}) units because of their rich structural diversity and their relevance to structural models of metalloenzymes.[1–4] The most common approach to synthesize this kind of polynuclear complexes is the use of $[M(amine)_2(thiolato)_2]$-type mononuclear complexes as a S-donating metalloligand, and a variety of S-bridged polynuclear structures with different metal ions and nuclearities have been constructed from this approach.[1–3] Recently, we have shown that the reaction of $[Au(D\text{-pen-}S)_2]^{3-}$ with Ni^{II} gave a S-bridged $Ni^{II}{}_2Au^{I}{}_2$ tetranuclear complex, $[Au_2\{Ni(D\text{-pen-}N,S)_2\}_2]^{2-}$, in which two square-planar $[Ni(D\text{-pen-}N,S)_2]^{2-}$ units are linked by two linear Au^{I} ions, although other $Ni^{II}Au^{I}$ polynuclear complexes, $[Au_3\{Ni(D\text{-pen-}N,S)_3\}_2]^{5-}$, $[Au_2\{Ni(D\text{-pen-}N,O,S)_2\}_2]^{2-}$, and $[Au_3\{Ni(D\text{-Hpen-}O,S)_3\}_2]^{+}$, were also produced by changing the reaction conditions.[4b] This result implies that the use of $[Au(D\text{-pen-}S)_2]^{3-}$ as a N,S-chelating metalloligand in combination with a square-planar metal ion is an alternative approach to construct S-bridged polynuclear structures composed of $[M(amine)_2(thiolato)_2]$-type units. Thus, we investigated the reaction of $[Au(D\text{-pen-}S)_2]^{3-}$ with Pd^{II}, which indeed gave an expected S-bridged $Pd^{II}{}_2Au^{I}{}_2$ tetranuclear complex, $[Au_2\{Pd(D\text{-pen-}N,S)_2\}_2]^{2-}$. To our surprise, however, this $Pd^{II}{}_2Au^{I}{}_2$ tetranuclear complex was found to form an unprecedented geometrical isomer composed of *trans*-$[Pd(D\text{-pen-}N,S)_2]^{2-}$ units, besides an isomer composed of *cis*-$[Pd(D\text{-pen-}N,S)_2]^{2-}$ units. Here, we report on the synthesis, characterization, and properties of the two isomers of $[Au_2\{Pd(D\text{-pen-}N,S)_2\}_2]^{2-}$.

To a colorless aqueous solution of $NH_4[Au(D\text{-Hpen-}S)_2]$,[5] which was adjusted to pH ≈ 8.5 with K_2CO_3, was added 1 molar equiv of $K_2[PdCl_4]$. The mixture was stirred at room temperature for 1.5 h to give a clear orange-yellow solution. This reaction solution was chromatographed on an anion-exchange column (QAE-Sephadex A-25, K^+ form), which afforded two yellow bands by eluting with a 0.15 M aqueous solution of KCl. From the first and second eluates, yellow needle crystals of K_2[**1b**] and K_2[**1a**] were isolated, respectively.[6] X-ray fluorescence spectrometry indicated that K_2[**1a**] and K_2[**1b**] each contain Au and Pd atoms in a 1:1 ratio, and their elemental analytical data were in agreement with the formula for a 1:1 adduct of $[Au(D\text{-pen})_2]^{3-}$ and Pd^{II}.

X-ray structural analysis of a single crystal for K_2[**1a**], which was prepared by vapor diffusion of ethanol into an aqueous solution of K_2[**1a**] at room temperature, revealed the presence of two independent, yet nearly the same complex anions.[7] The presence of two potassium cations per one complex anion in the unit cell implies the dianionic charge of the entire complex anion. As shown in Figure 1a, the entire complex anion $[\mathbf{1a}]^{2-}$ has a S-bridged $Pd^{II}{}_2Au^{I}{}_2$ tetranuclear structure in $[Au_2\{Pd(D\text{-pen-}N,S)_2\}_2]^{2-}$ with a crystallographic C_2 symmetry. In $[\mathbf{1a}]^{2-}$, two square-planar *cis*-$[Pd(D\text{-pen-}N,S)_2]^{2-}$ units are linked by two almost linear Au^{I} atoms through thiolato groups (av Au–S = 2.299(5) Å, Pd–S = 2.284(5) Å, S–Au–S = 176.0(2)°, S–Pd–S = 96.1(2)°, Au–S–Pd = 103.0(2)°). The averaged intramolecular Au···Au distance in $[\mathbf{1a}]^{2-}$ is 2.996(2) Å, suggestive of the presence of an appreciable aurophilic interaction.[8] The overall structure in $[\mathbf{1a}]^{2-}$ is reminiscent of that in the previously reported $[Au_2\{Ni(D\text{-pen-}N,S)_2\}_2]^{2-}$ containing two square-planar *cis*-$[Ni(D\text{-pen-}N,S)_2]^{2-}$ units.[4] However, $[\mathbf{1a}]^{2-}$ adopts a boat-like tetranuclear framework made up of two PdN_2S_2 planes spanned by two S–Au–S linkages, which is distinct from a chair-like framework found in $[Au_2\{Ni(D\text{-pen-}N,S)_2\}_2]^{2-}$. The ^{1}H NMR spectrum of $[\mathbf{1a}]^{2-}$ in D_2O shows four methyl (δ 1.43, 1.69, 1.78, 1.84) and two methine (δ 3.29, 3.40) proton signals due to four D-pen ligands in the complex (Figure 2b). This is consistent with the C_2 symmetrical structure in $[\mathbf{1a}]^{2-}$, although each signal is broadened presumably because of the flexible nature of this S-bridged tetranuclear structure.

While the IR spectrum of K_2[**1b**] is very similar to that of K_2[**1a**],[9] its ^{1}H NMR spectral feature is quite different. That is, K_2[**1b**] exhibits only two methyl (δ 1.36, 1.63) and one methine (δ 3.81) proton signals (Figure 2a), suggestive of a higher symmetrical structure. To isolate X-ray quality crystals for K_2[**1b**], acetone vapor was diffused into a concentrated solution of the

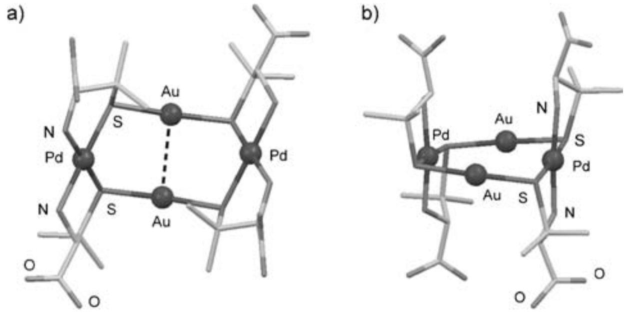

Figure 1. Perspective view of a) $[\mathbf{1a}]^{2-}$ (cis isomer) and b) the trans isomer in K_2[**1c**]. H atoms are omitted for clarity.

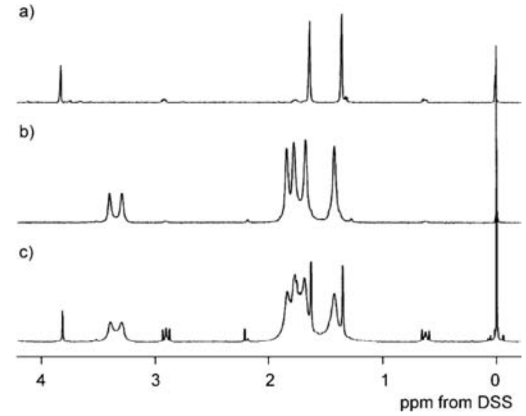

Figure 2. ^{1}H NMR spectra of a) [**1b**]$^{2-}$, b) [**1a**]$^{2-}$, and c) [**1c**]$^{2-}$ in D_2O.

first eluate at room temperature.

Unexpectedly, yellow crystals thus obtained (K_2[**1c**]) showed the ^{1}H NMR spectrum corresponding to a 2:1 mixture of [**1a**]$^{2-}$ and [**1b**]$^{2-}$ (Figure 2c).[9] X-ray analysis revealed that K_2[**1c**] contains five independent complex anions in the unit cell.[10] The molecular structures of four of five complex anions, each of which possesses a crystallographic C_2 symmetry, are essentially the same as the S-bridged $Pd^{II}_2Au^I_2$ tetranuclear structure in [**1a**]$^{2-}$ (av Au–S = 2.284(4) Å, Pd–S = 2.270(4) Å, S–Au–S = 174.9(1)°, S–Pd–S = 96.4(1)°). The remaining complex anion also has a S-bridged $Pd^{II}_2Au^I_2$ tetranuclear structure in $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$ (av Au–S = 2.266(4) Å, S–Au–S = 177.6(1)°), but the two square-planar $[Pd(\text{D-pen-}N,S)_2]^{2-}$ units assume a trans configuration (av Pd–S = 2.274(4) Å, S–Pd–S = 174.1(2)°), as illustrated in Figure 1b. While the trans complex anion has no crystallographically imposed symmetry, its idealized molecular symmetry is D_2, compatible with the ^{1}H NMR spectral behavior observed for [**1b**]$^{2-}$.[11] In this structure, the two *trans*-$[Pd(\text{D-pen-}N,S)_2]^{2-}$ units face each other and are connected by linear Au^I atoms to form a $Pd^{II}_2Au^I_2S_4$ square ring. The Au···Au, Pd···Pd, and Au···Pd separations are 4.508(1), 4.740(2), and 3.271(2) Å, respectively, and thus no significant metal–metal attractive interactions exist in this structure. It should be noted that the Au–S–Pd angles (av 92.2(2)°) in the trans structure are much deviated from the regular tetrahedral angle compared with those in the cis structure (av 101.3(2)°). This is ascribed to the steric constraint imposed by the formation of the $Pd^{II}_2Au^I_2S_4$ square ring.

The generation of crystals K_2[**1c**] from a solution of K_2[**1b**] implies that [**1b**]$^{2-}$ converts into [**1a**]$^{2-}$ in solution, accompanied by the trans-to-cis isomerization of the $[Pd(\text{D-pen-}N,S)_2]^{2-}$ units. To confirm this, the ^{1}H NMR spectral change with time was monitored for a 1:1 reaction mixture of $NH_4[Au(\text{D-Hpen})_2]$ and $K_2[PdCl_4]$ in the presence of K_2CO_3 in D_2O at room temperature. Indeed, the proton signals for [**1b**]$^{2-}$ decreased with time with the increase of the signals for [**1a**]$^{2-}$, and the NMR spectrum after 3 weeks turned to be identical with that of [**1a**]$^{2-}$.[9] This is indicative of the thermodynamic instability of [**1b**]$^{2-}$ composed of the *trans*-$[Pd(\text{D-pen-}N,S)_2]^{2-}$ units relative to [**1a**]$^{2-}$ composed of the *cis*-$[Pd(\text{D-pen-}N,S)_2]^{2-}$ units. The strained thiolato-bridged structure and the absence of a metal–metal attractive interaction in [**1b**]$^{2-}$, together with the mutual trans influence due to thiolato donors, seem to be responsible for this result.

In summary, we showed that $[Au(\text{D-pen-}S)_2]^{3-}$ acts as a bis(bidentate-*N*,*S*) metalloligand toward Pd^{II} to give a S-bridged $Pd^{II}_2Au^I_2$ tetranuclear complex composed of two square-planar $[Pd(amine)_2(thiolato)_2]$-type units, $[Au_2\{Pd(\text{D-pen-}N,S)_2\}_2]^{2-}$ ([**1**]$^{2-}$). Remarkably, not only the expected $Pd^{II}_2Au^I_2$ structure with *cis*-$[Pd(\text{D-pen-}N,S)_2]^{2-}$ units ([**1a**]$^{2-}$) but also the structure with *trans*-$[Pd(\text{D-pen-}N,S)_2]^{2-}$ units ([**1b**]$^{2-}$), which converts into [**1a**]$^{2-}$ in solution, was formed for [**1**]$^{2-}$. This appears to be the first observation and isolation of two geometrical isomers for S-bridged polynuclear species, which are discriminated by geometrical isomerism of their building units. In addition, S-bridged polynuclear complexes composed of *trans*-$[M(amine)_2(thiolato)_2]$-type units have never been found in the literature.[12] It is expected that another novel stereoisomerism is created in polynuclear systems if one employs a multidentate metalloligand such as $[Au(\text{D-pen-}S)_2]^{3-}$ in combination with a transition-metal ion that adopts a defined coordination geometry.

This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 19027035) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 For example see: A. C. Marr, D. J. E. Spencer, M. Schröder, *Coord. Chem. Rev.* **2001**, *219–221*, 1055; R. Krishnan, J. K. Voo, C. G. Riordan, L. Zahkarov, A. L. Rheingold, *J. Am. Chem. Soc.* **2003**, *125*, 4422; P. V. Rao, S. Bhaduri, J. Jiang, D. Hong, R. H. Holm, *J. Am. Chem. Soc.* **2005**, *127*, 1933.

2 For example see: A. J. Amoroso, S. S. M. Chung, D. J. E. Spencer, J. P. Danks, M. W. Glenny, A. J. Blake, P. A. Cooke, C. Wilson, M. Schröder, *Chem. Commun.* **2003**, 2020; P. V. Rao, S. Bhaduri, J. Jiang, R. H. Holm, *Inorg. Chem.* **2004**, *43*, 5833; S. P. Jeffery, K. N. Green, M. V. Rampersad, J. H. Reibenspies, M. Y. Darensbourg, *Dalton Trans.* **2006**, 4244.

3 D. J. Jicha, D. H. Busch, *Inorg. Chem.* **1962**, *1*, 872; D. J. Jicha, D. H. Busch, *Inorg. Chem.* **1962**, *1*, 878; T. Konno, K. Yonenobu, J. Hidaka, K. Okamoto, *Inorg. Chem.* **1994**, *33*, 861; H.-W. Xu, Z.-N. Chen, S. Ishizaka, N. Kitamura, J.-G. Wu, *Chem. Commun.* **2002**, 1934; T. Konno, M. Usami, A. Toyota, M. Hirotsu, T. Kawamoto, *Chem. Lett.* **2005**, *34*, 1146; T. Yoshimura, A. Shinohara, M. Hirotsu, K. Ueno, T. Konno, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1745.

4 a) P. J. M. L. Birker, G. C. Verschoor, *Inorg. Chem.* **1982**, *21*, 990. b) M. Taguchi, A. Igashira-Kamiyama, T. Kajiwara, T. Konno, *Angew. Chem., Int. Ed.* **2007**, *46*, 2422.

5 A. Toyota, T. Yamaguchi, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Angew. Chem., Int. Ed.* **2005**, *44*, 1088.

6 Calcd for K_2[**1a**]$\cdot 14H_2O$: C, 15.74; H, 4.23; N, 3.67%. Found: C, 15.79; H, 4.02; N, 3.72%. Yield: 38%. Calcd for K_2[**1b**]$\cdot 9H_2O$: C, 16.73; H, 3.79; N, 3.90%. Found: C, 16.99; H, 4.00; N, 3.77%. Yield: 24%.

7 Crystal data for K_2[**1a**]$\cdot EtOH \cdot 6H_2O$: fw 1427.86, Orthorhombic, $P2_12_12$, $a = 14.977(5)$, $b = 23.975(6)$, $c = 13.504(4)$ Å, $V = 4849(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.956\,g/cm^3$, 6098 reflections measured, 6098 independent. $R_1 = 0.0445$ ($I > 2\sigma(I)$), $wR_2 = 0.1475$ (all data). CCDC: 666972.

8 P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

9 Supporting Information is available electronically on the CSJ-Journal Web site; http://www.csj.jp/journals/chem-lett/.

10 Crystal data for K_2[**1c**]$\cdot 10H_2O$: fw 1453.86, Monoclinic, $C2$, $a = 34.479(10)$, $b = 27.294(14)$, $c = 14.238(2)$ Å, $\beta = 99.849(17)°$, $V = 13201(8)$ Å^3, $Z = 12$, $D_{calcd} = 2.194\,g/cm^3$, 6148 reflections measured, 6010 independent. $R_1 = 0.0616$ ($I > 2\sigma(I)$), $wR_2 = 0.1953$ (all data). CCDC: 666973.

11 Only half of each cis complex anion is independent, and thus the crystal K_2[**1c**] contains the cis and trans complex anions in a 2:1 ratio.

12 Even for the reactions using *trans*-$[Ni(aet)_2]$ (Haet = 2-aminoethanethiol), only S-bridged polynuclear complexes composed of *cis*-$[Ni(aet)_2]$ units have been produced.[3]