Synthesis, Characterization, and Crystal Structures of Cis and Trans Isomers of a Platinate(II) Complex with D-Penicillaminate

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Received February 4, 2011
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A square-planar platinate(II) complex, $[Pt(D\text{-pen-}N,S)_2]^{2-}$ (D-H_2pen: D-penicillamine), was newly synthesized by the 1:2 reaction of $[PtCl_4]^{2-}$ with D-pen in water under severe conditions (reflux for 12 h). This complex formed both cis and trans isomers, which were separated, isolated, and crystallographically characterized.

The development of coordination chemistry involving $[M(amine)_2(thiolato)_2]$-type ($M = Ni^{II}$, Pd^{II}, and Pt^{II}) square-planar species has been driven by their utility as an S-donating metalloligand for the rational construction of S-bridged multinuclear structures,[1] as well as their structural similarity to the active centers of nickel-containing metalloproteins.[2] To date, a number of $[Ni^{II}(amine)_2(thiolato)_2]$-type complexes have been prepared and their structures and properties have been extensively investigated.[1e–1g,3] On the other hand, studies on the corresponding Pd^{II}/Pt^{II} complexes are much less common mainly because of the difficulty in isolating these species in a monomeric form.[4] For example, it has been shown that the reaction of $[PdCl_4]^{2-}$ with D-penicillamine (D-H_2pen) in water produces an S-bridged tetranuclear complex, $[Pd_4Cl_4(D\text{-Hpen-}N,S)_4]$, which is convertible to an S-bridged trinuclear complex, $[Pd_3(D\text{-pen-}N,S,O)_3]$,[5] while a similar reaction of Ni^{2+} have been shown to produce a mononuclear Ni^{II} complex, *cis*-$[Ni(D\text{-pen-}N,S)_2]^{2-}$.[3a] Recently, a mononuclear Pd^{II} complex, *cis*-$[Pd(D\text{-pen-}N,S)_2]^{2-}$, analogous to *cis*-$[Ni(D\text{-pen-}N,S)_2]^{2-}$, has been prepared by treating $[Pd_3(D\text{-pen-}N,S,O)_3]$ with additional D-pen in water.[5] However, the corresponding mononuclear Pt^{II} complex with D-pen has not been isolated to date, although attempts to prepare this complex from $[PtCl_4]^{2-}$ and D-pen have been reported previously.[6] In this paper, we report the first isolation and structural characterization of $[Pt(D\text{-pen-}N,S)_2]^{2-}$ that forms not only its cis isomer but also trans isomer.

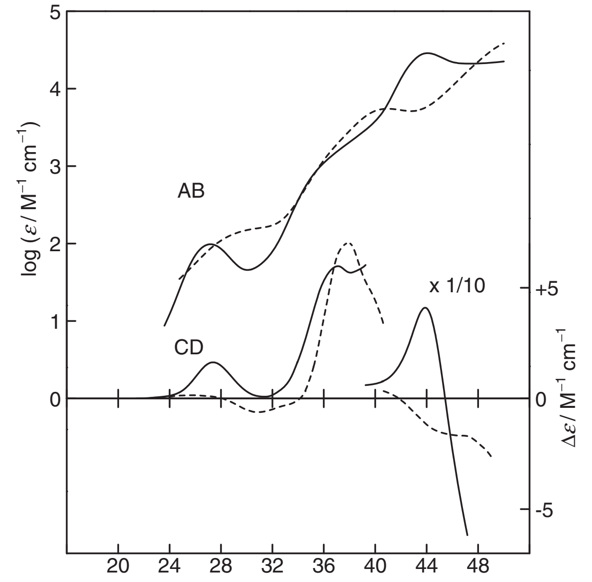

Figure 1. Electronic absorption and CD spectra of $[H_2\mathbf{1a}]$ (—) and $K_2[\mathbf{1b}]$ (- - -) in H_2O.

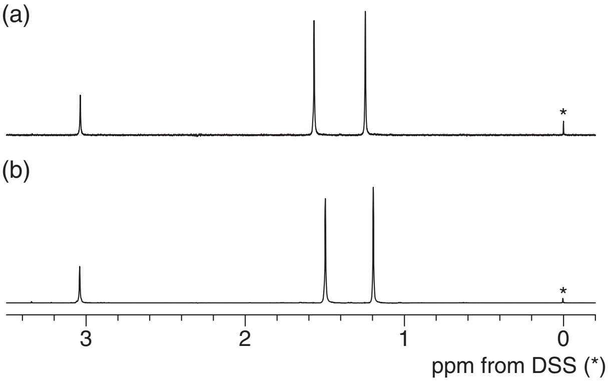

Figure 2. ^{1}H NMR spectra of (a) $[H_2\mathbf{1a}]/Na_2CO_3$ and (b) $K_2[\mathbf{1b}]$ in D_2O.

The 1:2 reaction of $K_2[PtCl_4]$ with D-H_2pen in water, neutralized by K_2CO_3, at reflux temperature for 12 h under a nitrogen atmosphere gave a red-orange solution. When the reaction solution was chromatographed on an anion-exchange column (QAE Sephadex A-25), two pale yellow bands, $[\mathbf{1a}]^{2-}$ and $[\mathbf{1b}]^{2-}$, were eluted with a 0.12 M aqueous solution of KCl in this order. From the two eluates, two pale yellow complexes were isolated as a protonated form ($[H_2\mathbf{1a}]$) and a potassium-salt form ($K_2[\mathbf{1b}]$).[7] The presence of protonated and deprotonated carboxy groups in $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ was confirmed by the appearance of intense C=O stretching bands at 1703 and 1585 cm^{-1}, respectively, in their IR spectra (Figure S1).[8] While the elemental analytical data of $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ are in good agreement with formulas containing Pt^{II} and D-pen in a 1:2 ratio, $[Pt(D\text{-Hpen})_2]\cdot 2H_2O$ and $K_2[Pt(D\text{-pen-}N,S)_2]\cdot 2.5H_2O$, their electronic absorption and CD spectral features are substantially different from each other, as illustrated in Figure 1. In addition, a slight difference in chemical shifts is found in the ^{1}H NMR spectra of $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ in D_2O, although they commonly exhibit a single set of proton signals assignable to D-pen (Figure 2). These results imply that $[\mathbf{1a}]^{2-}$ and $[\mathbf{1b}]^{2-}$ are a pair of isomers of $[Pt(D\text{-pen})_2]^{2-}$. The formation ratio of $[\mathbf{1a}]^{2-}$:$[\mathbf{1b}]^{2-}$ was estimated to be ca. 1:3, based on the NMR spectral measurement of the reaction solution and the absorption spectral measurement of the two eluates obtained by the column chromatography.

Published on the web May 28, 2011; doi:10.1246/bcsj.20110036

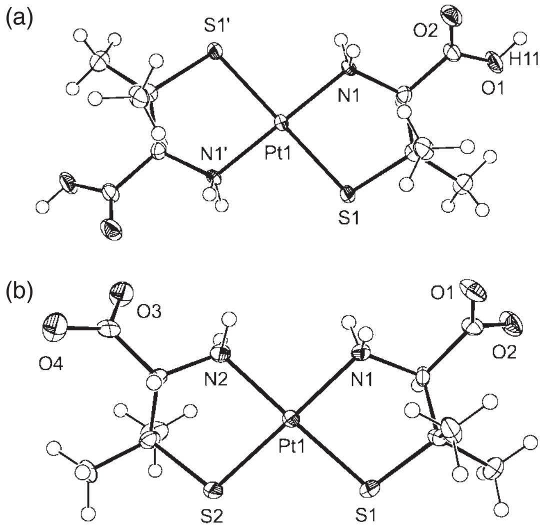

Figure 3. ORTEP drawings of (a) the complex-molecule of $[H_2\mathbf{1a}]$ and (b) one of four independent complex-anions of $[\mathbf{1b}]^{2-}$ with 50% probability ellipsoids. The symbol (′) denotes the symmetry code of $[-x, y, -z]$.

The crystal structures of $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ were determined by X-ray crystallography. As shown in Figure 3a, $[H_2\mathbf{1a}]$ is a mononuclear Pt^{II} complex-molecule having two D-Hpen ligands. A crystallographic C_2 axis passes through a Pt^{II} atom, and thus only a half of the complex molecule is independent. In $[H_2\mathbf{1a}]$, two D-Hpen ligands coordinate to a Pt^{II} center through amine-N and thiolato-S atoms, forming a square-planar mononuclear structure with a trans configuration (Pt–S = 2.298(2) Å, Pt–N = 2.043(4) Å, S–Pt–S = 178.1(3)°, and N–Pt–N = 177.1(9)°). The two carboxy groups in $[H_2\mathbf{1a}]$, which do not participate in the coordination, exist as a protonated form, consistent with the IR spectrum. The two five-membered N,S-chelate rings in $[H_2\mathbf{1a}]$ adopt a δ conformation such that two carboxy groups have an equatorial orientation.

X-ray analysis for $K_2[\mathbf{1b}]$ revealed the presence of four independent, yet nearly the same complex-anions in the asymmetric unit, besides potassium counter-cations. As shown in Figure 3b, the complex-anion consists of a Pt^{II} atom and two D-pen ligands. Like in $[H_2\mathbf{1a}]$, a Pt^{II} atom is coordinated by two N,S-chelating D-pen ligands in a square-planar geometry to form a mononuclear structure in $[\mathbf{1b}]^{2-}$. A notable structural difference is that $[\mathbf{1b}]^{2-}$ has a cis geometry with a molecular C_2 symmetry (av S–Pt–N = 176.82(18)°). The average Pt–N distance in $[\mathbf{1b}]^{2-}$ (2.086(5) Å) is ca. 0.04 Å longer than that in $[H_2\mathbf{1a}]$, while the average Pt–S distance in $[\mathbf{1b}]^{2-}$ (2.271(2) Å) is ca. 0.03 Å shorter than that in $[H_2\mathbf{1a}]$. This is ascribed to the trans influence due to thiolato groups. Considering the trans influence, $[\mathbf{1a}]^{2-}$ with a trans(S) geometry seems to be less favorable than $[\mathbf{1b}]^{2-}$ with a cis(S) geometry, compatible with the fact that $[\mathbf{1b}]^{2-}$ is a major product. In $[\mathbf{1b}]^{2-}$, the two noncoordinated carboxy groups exist as a deprotonated form and adopt an equatorial orientation with a δ conformational N,S-chelate ring. It is noted that $[\mathbf{1b}]^{2-}$ and K^+ are connected to each other through K–O (av 2.835(7) Å) and K···S (av 3.338(3) Å) bonding interactions in crystal. A similar structural feature has been found in *cis*-$K_2[M(\text{D-pen})_2]$ (M = Ni^{II} and Pd^{II}).[3a,5]

To check the functionality of $[\mathbf{1a}]^{2-}$ and $[\mathbf{1b}]^{2-}$ as a metalloligand, $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ were each reacted with $[AuCl\{S(CH_2CH_2OH)_2\}]$, prepared from $Na[AuCl_4]$ and 2,2′-thiodiethanol in situ, in a 1:1 ratio at room temperature in D_2O. The ^1H NMR spectra of the reaction solutions starting from $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ were identical with those of the trans and cis isomers of an S-bridged $Au^I{}_2Pt^{II}{}_2$ tetranuclear complex composed of two $[Pt(\text{D-pen-}N,S)_2]^{2-}$ units ($[Au_2Pt_2(\text{D-pen-}N,S)_4]^{2-}$), respectively, which has been prepared from $[Au(\text{D-pen-}S)_2]^{3-}$ and $[PtCl_4]^{2-}$.[9] This result clearly indicates that $[\mathbf{1a}]^{2-}$ and $[\mathbf{1b}]^{2-}$ do act as an effective metalloligand toward transition-metal ions using two thiolato groups, retaining their trans and cis geometries.

In this paper, we showed that the 1:2 reaction of $[PtCl_4]^{2-}$ with D-pen under severe conditions affords $[Pt(\text{D-pen-}N,S)_2]^{2-}$ ($[\mathbf{1}]^{2-}$) having two N,S-chelating D-pen ligands. Complex $[\mathbf{1}]^{2-}$ formed both the cis and trans isomers, which were successfully separated, isolated, and structurally characterized. The isolation of *cis*- and *trans*-$[\mathbf{1}]^{2-}$ is in sharp contrast to the fact that only the cis isomer has been produced for the corresponding Ni^{II} and Pd^{II} complexes.[3a,5] Recently, we have shown that the reactions of $[Au(\text{D-pen-}S)_2]^{3-}$ with $[MCl_4]^{2-}$ (M = Pd^{II} and Pt^{II}) afford both the cis and trans isomers of $[Au^I{}_2M_2(\text{D-pen-}N,S)_4]^{2-}$,[9,10] while only the cis isomer is formed for the corresponding $Au^I{}_2Ni^{II}{}_2$ tetranuclear complex.[11] Furthermore, the trans isomer of $[Au_2Pd_2(\text{D-pen-}N,S)_4]^{2-}$ was found to be converted into the cis isomer,[10] while such a trans-to-cis conversion was not observed for $[Au_2Pt_2(\text{D-pen-}N,S)_4]^{2-}$.[9] Thus, it is assumed that both the cis and trans isomers are formed for $[M(\text{D-pen-}N,S)_2]^{2-}$ (M = Ni^{II}, Pd^{II}, and Pt^{II}) at the first stage of the reactions of M and D-pen, but the trans isomer, which is thermodynamically less stable because of the mutual trans influence due to thiolato donors, is converted to the cis isomer for M = Ni^{II} and Pd^{II}. On the other hand, the inertness of coordination bonds between a Pt^{II} center and D-pen ligands prevents the trans-to-cis isomerization, leading to the isolation of both the cis and trans isomers for $[Pt(\text{D-pen-}N,S)_2]^{2-}$. To create multinuclear and metallosupramolecular compounds that show unique structures and properties, the reactions of $[\mathbf{1a}]^{2-}$ and $[\mathbf{1b}]^{2-}$ with transition-metal ions, other than Au^I, are currently underway in our laboratory.

Experimental

Preparation of *trans*-$[Pt(\text{D-Hpen})_2]$ ($[H_2\mathbf{1a}]$) and *cis*-$K_2[Pt(\text{D-pen})_2]$ ($K_2[\mathbf{1b}]$). To a solution containing D-H_2pen (0.60 g, 4.02 mmol) and K_2CO_3 (0.55 g, 4.02 mmol) in water (40 mL) was added $K_2[PtCl_4]$ (0.80 g, 1.93 mmol). The mixture was refluxed at 110 °C under N_2 atmosphere for 12 h, which afforded a reddish-orange solution. After cooling to room temperature, the reddish-orange solution was poured onto a QAE-Sephadex A-25 column (3 × 40 cm, Cl^- form). After washing with water, two pale yellow bands, *trans*-$[Pt(\text{D-pen})_2]^{2-}$ ($[\mathbf{1a}]^{2-}$) and *cis*-$[Pt(\text{D-pen})_2]^{2-}$ ($[\mathbf{1b}]^{2-}$), were separately eluted in this order with a 0.12 M aqueous solution of KCl.

The first eluate containing $[\mathbf{1a}]^{2-}$ was concentrated to dryness with a rotary evaporator, and then the residue was dissolved in methanol (10 mL). After removing a solid of KCl by filtration, the pale yellow filtrate was concentrated to dryness with a rotary evaporator. The residue was dissolved in water (2 mL), followed by the addition of an aqueous solution of 1 M HCl (2 mL). The mixture was allowed to stand at room temperature for 10 min, and the resulting pale yellow crystalline powder was collected by filtration. Yield: 0.19 g (18%). Anal. Calcd for $[H_2\mathbf{1a}]\cdot 2H_2O = C_{10}H_{24}N_2O_6PtS_2$: C, 22.77; H, 4.59; N, 5.31%. Found: C, 22.81; H, 4.53; N, 5.31%. IR (KBr, cm^{-1}): 1703 (COOH). ^{1}H NMR (D_2O/Na_2CO_3, ppm from DSS (DSS: sodium 4,4′-dimethyl-4-silapentane-1-sulfonate)): 1.25 (s, CH_3), 1.57 (s, CH_3), 3.04 (s, CH). Electronic absorption spectrum in H_2O [$\tilde{\nu}$, $10^3\,cm^{-1}$ (log ε, $M^{-1}\,cm^{-1}$)]: 27.19 (1.99), 37.30 (3.22 sh), 44.09 (4.46). CD spectrum in H_2O [$\tilde{\nu}$, $10^3\,cm^{-1}$ ($\Delta\varepsilon$, $M^{-1}\,cm^{-1}$)]: 27.38 (+1.63), 37.09 (+5.98), 43.89 (+41.0). Pale yellow block crystals of $H_2[\mathbf{1a}]\cdot 2H_2O$ suitable for X-ray analysis were obtained by the recrystallization of the powder sample from water at room temperature.

The second eluate containing $[\mathbf{1b}]^{2-}$ was concentrated to dryness with a rotary evaporator, and then the residue was dissolved in methanol (10 mL). After removing a solid of KCl by filtration, 1-butanol (3 mL) was added to the pale yellow filtrate. The mixture was allowed to stand at room temperature for 1 day, and the resulting pale yellow crystalline powder was collected by filtration. Yield: 0.38 g (33%). Anal. Calcd for $K_2[\mathbf{1b}]\cdot 2.5H_2O = C_{10}H_{23}K_2N_2O_{6.5}PtS_2$: C, 19.60; H, 3.78; N, 4.57%. Found: C, 19.70; H, 3.80; N, 4.43%. IR (KBr, cm^{-1}): 1585 (COO^-). ^{1}H NMR (D_2O, ppm from DSS): 1.19 (s, CH_3), 1.49 (s, CH_3), 3.04 (s, CH). Electronic absorption spectrum in H_2O [$\tilde{\nu}$, $10^3\,cm^{-1}$ (log ε, $M^{-1}\,cm^{-1}$)]: 31.17 (2.21 sh), 36.98 (3.28 sh), 40.95 (3.74). CD spectrum in H_2O [$\tilde{\nu}$, $10^3\,cm^{-1}$ ($\Delta\varepsilon$, $M^{-1}\,cm^{-1}$)]: 26.01 (+0.14), 30.83 (−0.62), 37.91 (+7.03). Pale yellow plate crystals of $K_2[\mathbf{1b}]\cdot 3.75H_2O$ suitable for X-ray analysis were obtained by the recrystallization of the powder sample from MeOH/1-butanol (3:1) at room temperature.

Measurements. The electronic absorption spectra were recorded on a JASCO V-660 spectrophotometer, and the CD spectra on a JASCO J-600 spectropolarimeter. The IR spectra were recorded on a JASCO FT/IR-4100 infrared spectrophotometer using KBr disks at room temperature. The ^{1}H NMR spectra were measured on a JEOL JNM-A400 NMR spectrometer at 30 °C, using DSS as an internal reference. The elemental analyses (C, H, N) were performed at Osaka University.

X-ray Structural Determinations. Single-crystal X-ray diffraction measurements for $[H_2\mathbf{1a}]\cdot 2H_2O$ and $K_2[\mathbf{1b}]\cdot 3.75H_2O$ were made on a Rigaku RAXIS-RAPID imaging plate area detector with a graphite monochromated Mo Kα radiation. The intensity data were collected by the ω scan mode. The intensities were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied. The structures were refined with full-matrix least-squares on F^2. All calculations were performed using the Yadokari-XG software package[12] except for the refinement that was performed using SHELXL-97.[13] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-815205 and -815206. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information

The IR spectra of $[H_2\mathbf{1a}]$ and $K_2[\mathbf{1b}]$ are listed in Figure S1. Crystallographic data for $[H_2\mathbf{1a}]\cdot 2H_2O$ and $K_2[\mathbf{1b}]\cdot 3.75H_2O$ are listed in Tables S1, S2, and S3. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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