tahedral species.[10a] In the limit of "hard" neutral ligands, the substituent in the trans position to the $Tc=O$ is a second oxo group, O^{2-}, leading to the formation of the *trans*-$[O=Tc=O]^+$ group and to nearly regular octahedral structures (the Tc atom lying on the same plane of the ligands cis to the $Tc=O$).[10,30]

Apart from the carbyne ligand, the N^{3-} group is considered the strongest known π-electron donor, and thus it is likely that its trans influence should be greater than that of the oxo group. This should cause a more remarkable lengthening of the metal–ligand bond distance of the substituent trans to the nitrido group. To give support to such an idea, all the Tc–Cl bond distances found in octahedral Tc(V)–oxo and Tc(V)–nitrido complexes have been collected in Table VIII. The analysis of the structural data suggests that the trans influence exerted on the Cl⁻ group by the $Tc\equiv N$ multiple bond (of the order of magnitude of some 0.34 Å) is much greater than that exerted by the isoelectronic $Tc=O$ group, in agreement with experimental data as well as theoretical arguments.[31]

Even though in both the compounds 1 and 2 the Tc–Cl bond distances are abnormally long, it is interesting to notice that the lengths of the $Tc\equiv N$ and Tc—Cl bonds are inversely related, suggesting an incipient transition from square-pyramidal to octahedral geometry of the coordination around the $[Tc\equiv N]^{2+}$ moiety. The observed differences in Tc—Cl and $Tc\equiv N$ distances in the structures reported here might be ascribed to the different strain effects arising from the coordination of the two neutral ligands, although the analysis of the rings puckering and of the Tc—N bond distances has not shown any particular evidence for it.

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Contribution from the Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan, and National Chemical Laboratory for Industry, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan

Crystal Structure of Head-to-Head Bis(μ-α-pyridonato-*N,O*)bis[(ethylenediamine)palladium] Nitrate, [Pd₂(en)₂(C₅H₄NO)₂](NO₃)₂, and ¹³C and ¹H–¹³C COSY NMR Study of Head-to-Head to Head-to-Tail Isomerization in Solution

Kazuko Matsumoto,*,[1a] Hiroshi Moriyama,[1b] and Katsuhiko Suzuki[1a]

Binuclear head-to-head [Pd₂(en)₂(α-pyridonato)₂](NO₃)₂ has been synthesized, and the crystal structure has been solved with a single-crystal X-ray diffraction technique. The crystal is monoclinic, space group $P2_1/a$, with a = 17.201 (8) Å, b = 10.879 (1) Å, c = 12.175 (3) Å, β = 102.96 (3)°, and Z = 4. The binuclear complex cation has head-to-head geometry with a Pd–Pd distance of 2.981 (1) Å. Two binuclear cations are arranged in the crystal as if to form a zigzag chain of four palladium atoms with an inversion center at the midpoint of the central Pd–Pd vector between the two dimers. However, the central Pd–Pd distance is 3.220 (1) Å and is not a Pd–Pd bonding. The ¹³C NMR spectrum of the compound shows two very close signals for every carbon resonance in both D₂O and DMF, which indicates the existence of head-to-head (HH) and head-to-tail (HT) isomers. Although the isolated complex is pure HH complex, which was confirmed with powder X-ray diffraction, the isomerization to the HT isomer after dissolution is very rapid and the equilibrium is established almost instantaneously after dissolution. The present complex is the first example of HH to HT isomerization of a binuclear palladium(II) complex in solution.

Introduction

We have studied the syntheses and chemical properties of amidate-bridged tetranuclear platinum complexes containing Pt(II) and Pt(III), so-called "platinum blues", with the general formula $[Pt_4A_8L_4]^{5+}$ (A is amine ligand, L is deprotonated amide ligand)[2] and revealed their novel redox behavior, i.e., reduction to $[Pt^{II}_2A_4L_2]^{2+}$ by OH^- [3,4] or oxidation to $[Pt^{III}_4A_8L_4]^{n+}$ (n = 6,

8) by dioxygen or persulfate.[5] In a parallel experiment attempting to synthesize "palladium blues", the palladium analogues of platinum blues, it would be reasonable first to synthesize a Pd(II) dimer of the type $[Pd_2A_4L_2]^{2+}$ and examine its oxidizability to binuclear $[Pd^{III}_2A_4L_2L'_2]^{4+}$ (L' is the axial ligand) or to a tetranuclear palladium blue $[Pd^{III}Pd^{II}_3A_8L_4]^{5+}$, similar to the syntheses of amidate-bridged Pt(III) dimer complexes[6] or platinum blues[6b] from amidate-bridged Pt(II) dimers. Dimer complexes containing Pd(III) have so far been little reported with any bridging ligand. $[Pd_2(form)_4]$ (form is *N,N'*-di-*p*-tolylformamidinato), which is reversibly oxidized to $[Pd(form)_4]^{n+}$ (n = 1, 2),[7] is the only example so far as we know. Therefore, it would

(1) (a) Waseda University. (b) National Chemical Laboratory for Industry.
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be valuable to synthesize an amidate-bridged dimer complex of Pd(II) and examine its chemical nature, including its oxidizability to the Pd(III) complex.

In the present study a head-to-head (HH) binuclear Pd(II) complex with α-pyridonate as bridging ligand, [Pd$_2$(en)$_2$-(C$_5$H$_4$NO)$_2$](NO$_3$)$_2$, has been prepared and the HH structure has been confirmed by single-crystal X-ray diffraction analysis. The preliminary structural result of the complex cation has been briefly reported previously.[8] The fully detailed description of the crystal structure is reported in the present paper, together with the redox behavior of the complex. Although a stable complex containing Pd(III) has not been obtained, very rapid isomerization from the head-to-head (HH) to head-to-tail (HT) isomer in aqueous and DMF solutions was detected with ^{13}C NMR spectroscopy (see I). Similar isomerizations have been reported for analogous Pt(II)

head-to-head (HH) isomer   head-to-tail (HT) isomer

I
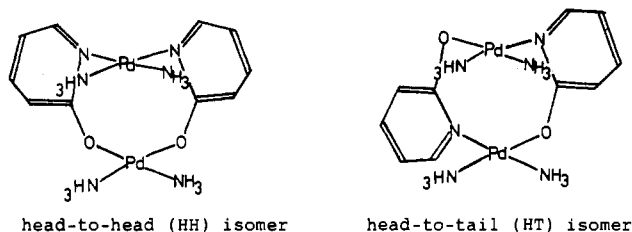
binuclear complexes with the α-pyridonate ligand,[9] HT and HH [Pt$_2$(NH$_3$)$_4$(C$_5$H$_4$NO)$_2$]$^{2+}$, and with the α-pyrrolidonate ligand.[4] The present study is the first synthesis of an amidate-bridged HH isomer and also the first observation of the isomerization from the HH to HT isomer in a binuclear palladium complex.

Experimental Section

Preparation of the Compound. The title compound was prepared as follows. A suspension of 0.5 mmol of Pd(en)Cl$_2$ and 1 mmol of α-pyridone in 10 mL of water was stirred at 60 °C for 1 h, with the pH kept at 11 by adding 1 M NaOH. The suspension gradually became a clear yellow solution while being heated. After it was cooled on an ice–water bath, 1 mmol of AgNO$_3$ in 5 mL of H$_2$O was added to the solution with vigorous stirring. After a few minutes, AgCl was filtered off. Another 0.5 mmol of Pd(en)Cl$_2$ was added to the filtrate, and the mixture was stirred at 60 °C for 2 h. The resulting clear yellow solution was cooled, and 1 mmol of AgNO$_3$ was added. After the mixture was stirred for a few minutes, AgCl was filtered off. Yellow powder of the complex was obtained by concentration of the solution. The complex was recrystallized from water, and orange-yellow plate crystals were obtained. Anal. Calcd for Pd$_2$C$_{14}$H$_{24}$N$_8$O$_8$: C, 26.06; H, 3.75; N, 17.37. Found: C, 26.01; H, 3.63; N, 17.43. The crop seems uniform microscopically and is confirmed to be the pure HH isomer (vide infra).

Physical Measurements. The powder X-ray diffraction pattern was measured on a Rigaku RAD-B with Cu Kα radiation in the range 3° < 2θ < 50°.

The electrochemical measurements were performed on a Fuso 315A potentiostat with either a platinum or a glassy-carbon disk electrode as the working electrode and a platinum wire as the counter electrode. All the measurements were performed with a three-electrode system by using an SCE as the reference electrode.

^{13}C and ^{1}H–^{13}C COSY NMR spectra were acquired on a Bruker AC200P instrument at 50.3 MHz. Both D$_2$O and DMF-d_6 solutions were prepared at room temperature and studied at 25 °C. Chemical shift data are reported relative to TMS, which was set in a sealed coaxial capillary tube in a 5-mm sample tube.

Collection and Reduction of X-ray Data. Unit cell parameters were obtained from a least-squares fit of 21 reflections in the range of 15° < 2θ < 28° measured on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo Kα radiation. The details of the data collection are given in Table I and in supplementary Table S3.

Solution and Refinement of the Structure. The coordinates of the two palladium atoms were found from a Patterson map, and a series of block-diagonal least-squares refinements followed by Fourier synthesis

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chem formula: Pd$_2$C$_{14}$H$_{24}$N$_8$O$_8$	$Z = 4$
fw 645.23	$T = 23$ °C
cryst syst: monoclinic	$\lambda = 0.7107$ Å
space group: $P2_1/a$	$\rho_{obsd} = 1.922$ g cm^{-3}
$a = 17.201$ (8) Å	$\rho_{calcd} = 1.930$ g cm^{-3}
$b = 10.879$ (1) Å	$\mu = 16.55$ cm^{-1}
$c = 12.175$ (3) Å	$T_{max}/T_{min} = 1.04$
$\beta = 102.96$ (3)°	$R(F_o) = 0.0597$
$V = 2220$ (1) Å^3	$R_w(F_o{}^2) = 0.0599$ ($w = 1/\sigma^2(F)$)

Table II. Positional and Thermal Parameters

atom	x	y	z	B_{eq}, Å^2
Pd1	0.35807 (4)	0.19467 (7)	0.19081 (6)	2.05
Pd2	0.45552 (5)	0.04270 (7)	0.37508 (7)	2.27
N1	0.2484 (5)	0.1143 (8)	0.1472 (7)	2.60
N2	0.3762 (5)	0.1170 (8)	0.0457 (7)	2.76
C1	0.2330 (6)	0.0762 (11)	0.0264 (10)	3.37
C2	0.3111 (6)	0.0213 (11)	0.0069 (9)	3.01
N3	0.4147 (6)	−0.1350 (8)	0.3671 (9)	3.43
N4	0.5483 (5)	−0.0292 (9)	0.3162 (9)	3.61
C3	0.4710 (10)	−0.2153 (14)	0.3167 (16)	6.96
C4	0.5188 (9)	−0.1476 (14)	0.2567 (14)	6.10
N11	0.3301 (5)	0.2730 (8)	0.3272 (7)	2.61
O12	0.3628 (4)	0.1013 (6)	0.4407 (6)	3.02
C12	0.3309 (6)	0.2110 (10)	0.4246 (9)	2.55
C13	0.2996 (7)	0.2684 (11)	0.5105 (10)	3.25
C14	0.2699 (7)	0.3870 (12)	0.4960 (10)	3.72
C15	0.2736 (7)	0.4508 (12)	0.3967 (11)	3.98
C16	0.3025 (6)	0.3916 (10)	0.3137 (9)	3.02
N21	0.4612 (4)	0.2946 (8)	0.2243 (6)	2.16
O22	0.5104 (4)	0.2093 (7)	0.4017 (6)	3.11
C22	0.5124 (6)	0.2932 (9)	0.3251 (9)	2.56
C23	0.5697 (7)	0.3908 (11)	0.3538 (10)	3.65
C24	0.5728 (8)	0.4818 (12)	0.2782 (12)	4.25
C25	0.5199 (8)	0.4808 (12)	0.1718 (11)	4.27
C26	0.4656 (7)	0.3864 (11)	0.1476 (10)	3.38
N5	0.2159 (6)	−0.2099 (9)	0.1939 (8)	3.59
O51	0.2558 (5)	−0.1263 (8)	0.2494 (8)	4.91
O52	0.1590 (6)	−0.1822 (10)	0.1166 (9)	6.49
O53	0.2302 (9)	−0.3160 (9)	0.2208 (9)	8.51
N6	0.5881 (6)	0.1700 (9)	0.0971 (9)	3.81
O61	0.5461 (5)	0.0769 (8)	0.0949 (9)	5.27
O62	0.6378 (5)	0.1926 (9)	0.1850 (8)	5.03
O63	0.5858 (7)	0.2372 (10)	0.0154 (9)	6.92

revealed all the remaining atoms except hydrogen atoms. The structure was finally refined with anisotropic temperature factors for all the atoms to the final discrepancy index of $R = 0.0597$ and $R_w = 0.0599$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$ ($w_i = (1/\sigma^2(F))$). Atomic scattering factors and anomalous dispersion corrections were taken from ref 10. All the calculations were performed with the program systems UNICS-III[11] and ORTEP.[12] Absorption correction was made by following the method of North et al.[13] None of the hydrogen atoms were located in the final difference map and therefore were not included in the calculation.

The final positional and thermal parameters are listed in Table II. The anisotropic temperature factors (Table S1) and their standard deviations (Table S2), the details of the crystal data (Table S3), and the observed and calculated structure factors (Table S4) are available as supplementary material.

Results

Structure of the Complex Cation. The structure of the complex cation with the atomic numbering scheme is shown in Figure 1. Each palladium atom is coordinated by two nitrogen atoms of ethylenediamine and either two exocyclic amide oxygens or two deprotonated amide nitrogens. The two α-pyridonate ligands bridge the two palladium atoms in a HH manner, and the dimeric

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Table III. Structural Properties of Amidate-Bridged Dinuclear Palladium and Platinum Complexes

complex	M–M dist, Å	tilt angle,[a] deg	torsion angle,[b] deg	M–M–M angle, deg	ref
[Pd$_2$(en)$_2$(α-pyridonato)$_2$](NO$_3$)$_2$	2.981 (1) 3.220 (1)[d]	39.7	25.5	159.82 (4)	c
[Pt$_2$(en)$_2$(α-pyridonato)$_2$](NO$_3$)$_2$	2.922 (1) 3.236 (1)[d]	39.6	24.9	160.58 (2)	14
[Pd$_2$(C$_6$H$_4$CH=NPh)$_2$(succinimidato)$_2$]·CH$_2$Cl$_2$	2.979 (1)	26.1	1.6		17

[a] Between adjacent coordination planes. [b] About the M–M vector. [c] This work. [d] The distance between the adjacent dimers.
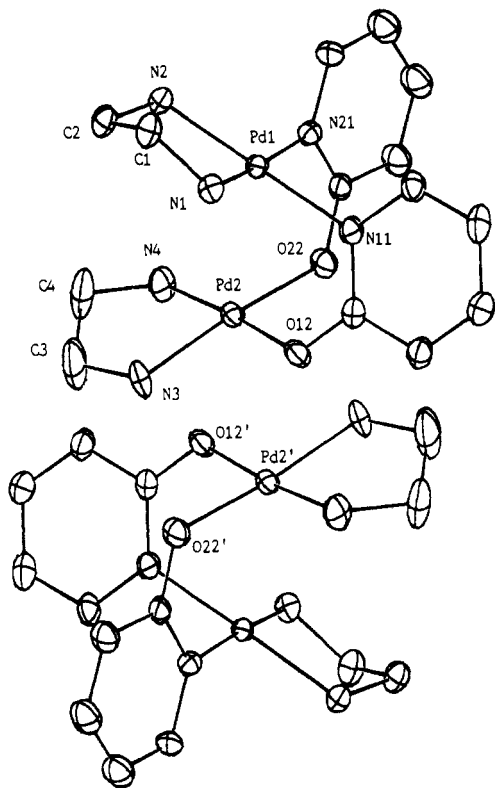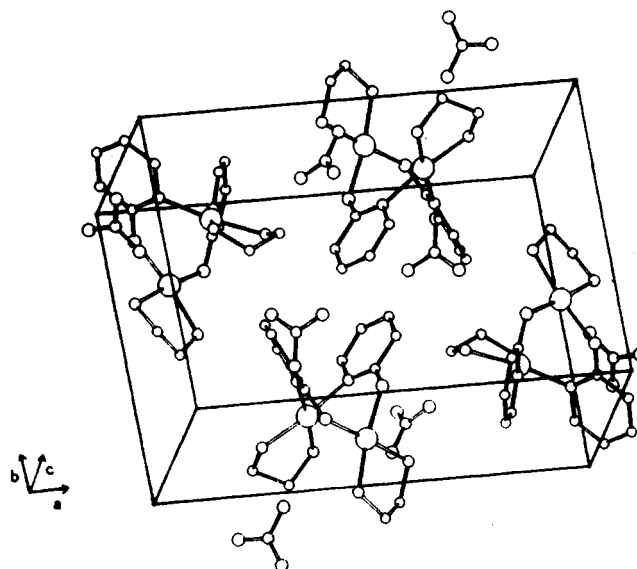

Figure 1. Molecular structure of HH [Pd$_2$(en)$_2$(α-pyridonato)$_2$]$^{2+}$. The thermal ellipsoids are drawn at the 50% probability level.

structure is analogous to the previously reported HH pyridonate-bridged dimeric platinum(II) complex, [Pt$_2$(en)$_2$-(C$_5$H$_4$NO)$_2$]$^{2+}$.[14] Crystal packing in the unit cell is shown in Figure 2.

Electrochemistry. Cyclic voltammetry of the present complex in 0.05 M H$_2$SO$_4$ with a Pt working electrode shows an irreversible wave at E_{pa} = 0.78 V and E_{pc} = 0.42 V vs SCE. Similar voltammetry in 0.1 M NaNO$_3$ with a glassy-carbon electrode also reveals a pair of irreversible waves at E_{pa} = 0.76 V and E_{pc} = 0.25 V. Addition of N-methylimidazole, possibly to stabilize the Pd(III) oxidation state by coordinating to the axial position of the Pd–Pd vector, resulted in no improvement of the reversibility in the cyclic voltammogram. Bulk oxidation of the complex electrochemically at 1.2 V seemed to result in decomposition of the complex.

^{13}C NMR Spectra in Solution. ^{13}C NMR spectra of the present complex in D$_2$O and DMF-d_6 solutions are shown in Figure 3. It should be noted that although both spectra are basically consistent with the solid structure, close examination of each carbon atom peak shows that all the peaks consist actually of two closely lying peaks. The intensity ratios of the two pairing peaks are ca. 1:5 in DMF and ca. 1:2 in D$_2$O. Chemical shifts (ppm) in DMF: C1 173.090, 172.985; C2 117.552; C3 139.050, 139.148; C4 112.283, 112.649; C5 148.453, 148.098; en 49.431, 47.513, 48.587, 48.347. The former values for each carbon are with relative intensities of ca. 1, whereas the latter ones are with relative intensities of ca. 5. For en the former two values are with intensities of ca. 1 and the latter two are with intensities of ca. 5.

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Figure 2. Crystal structure of HH [Pd$_2$(en)$_2$(α-pyridonato)$_2$](NO$_3$)$_2$.
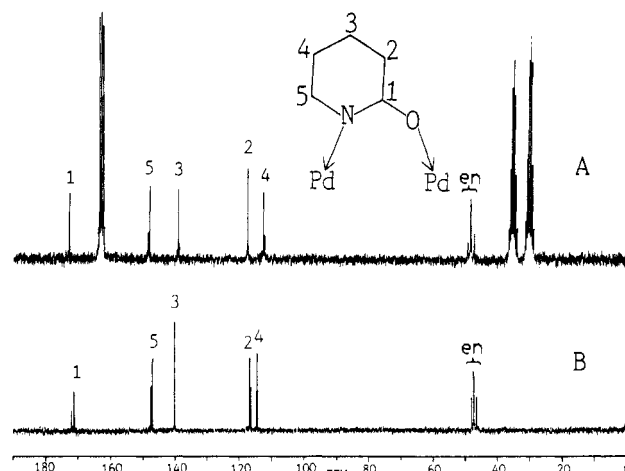
Figure 3. ^{13}C NMR spectra of [Pd$_2$(en)$_2$(α-pyridonato)$_2$](NO$_3$)$_2$: (A) DMF-d_6 solution; (B) D$_2$O solution.

The peak for C2 is not split. Chemical shifts in D$_2$O: C1 171.758, 171.119; C2 116.378, 116.651; C3 140.041; C4 114.297, 114.458; C5 147.413, 147.092; en 47.897, 46.491, 47.381, 47.154. The relative intensity of the two peaks in each couple was ca. 1:2, and the values for smaller peaks are shown first in each couple. The peak for C3 is not split. For en the former two values are with intensities of ca. 1, while the latter two are with intensities of ca. 2. The existence of these two close-lying peaks for each carbon is due to the occurrence of HH to HT isomerization in solution as mentioned in the Discussion.

Discussion

Description of the Structure. The structure of the complex cation is shown in Figure 1. A unit cell contains four dimeric cations, two of which are closely related by an inversion center to form a tetramer as shown in Figure 1. However, the central Pd–Pd distance is not so small as a Pd–Pd bonding. The tetra-
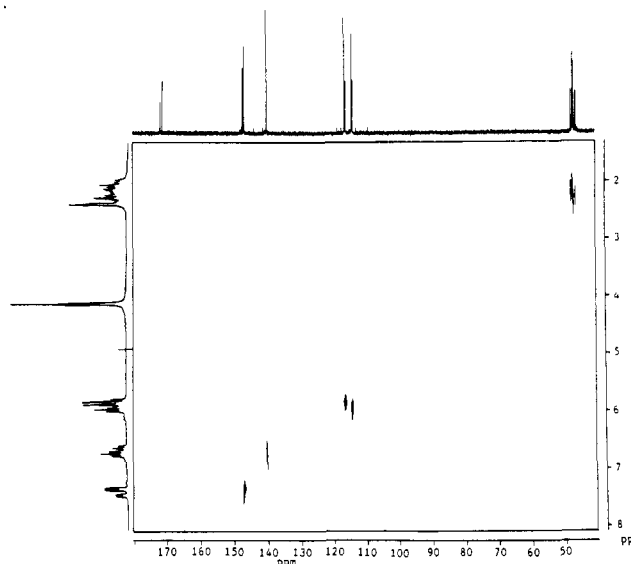
Table IV. Interatomic Distances (Å)

Metal–Metal			
Pd1–Pd2	2.981 (1)	Pd2–Pd2′	3.220 (1)

Coordination Bond			
Pd1–N1	2.039 (8)	Pd2–N3	2.052 (9)
Pd1–N2	2.045 (9)	Pd2–N4	2.046 (11)
Pd1–N11	2.019 (9)	Pd2–O12	2.039 (8)
Pd1–N21	2.042 (8)	Pd2–O22	2.036 (7)

Ligand Geometry			
N1–C1	1.49 (1)	N3–C3	1.53 (2)
C1–C2	1.54 (2)	C3–C4	1.42 (3)
C2–N2	1.52 (1)	C4–N4	1.51 (2)
N11–C12	1.36 (1)	N21–C22	1.34 (1)
C12–O12	1.31 (1)	C22–O22	1.31 (1)
C12–C13	1.42 (2)	C22–C23	1.44 (2)
C13–C14	1.38 (2)	C23–C24	1.36 (2)
C14–C15	1.41 (2)	C24–C25	1.41 (2)
C15–C16	1.38 (2)	C25–C26	1.38 (2)
C16–N11	1.37 (1)	C26–N21	1.38 (2)

Anion Geometry			
N5–O51	1.24 (1)	N6–O61	1.24 (2)
N5–O52	1.23 (2)	N6–O62	1.24 (1)
N5–O53	1.21 (2)	N6–O63	1.23 (2)

Hydrogen Bond			
N3–O22′	2.93 (1)	N2–O61	2.88 (1)
N4–O12′	3.11 (1)	N4–O61	2.92 (2)
N1–O51	2.89 (1)	N2–O52″	2.92 (1)
N3–O51	2.79 (1)	N1–O62″	2.94 (1)

Table V. Interatomic Angles (deg)

Coordination Bond			
N1–Pd1–N2	84.8 (4)	N3–Pd2–N4	84.8 (4)
N1–Pd1–N11	91.0 (4)	N3–Pd2–O12	91.3 (4)
N1–Pd1–N21	172.7 (3)	N3–Pd2–O22	171.2 (3)
N2–Pd1–N11	175.0 (3)	N4–Pd2–O12	175.4 (4)
N2–Pd1–N21	95.7 (3)	N4–Pd2–O22	91.5 (4)
N11–Pd1–N21	88.1 (3)	O12–Pd2–O22	92.0 (3)

Ligand Geometry			
N1–C1–C2	107.0 (9)	N3–C3–C4	113.6 (15)
C1–C2–N2	107.1 (9)	C3–C4–N4	111.5 (14)
Pd1–N11–C12	123.3 (7)	Pd1–N21–C22	122.7 (7)
Pd1–N11–C16	116.0 (7)	Pd1–N21–C26	115.3 (6)
Pd2–O12–C12	124.4 (7)	Pd2–O22–C22	126.3 (6)
N11–C12–C13	119.4 (10)	N21–C22–C23	119.3 (10)
N11–C12–O12	120.2 (9)	N21–C22–O22	122.8 (9)
O12–C12–C13	120.4 (10)	O22–C22–C23	117.8 (10)
C12–N11–C16	120.4 (9)	C22–N21–C26	120.1 (9)
C12–C13–C14	120.4 (11)	C22–C23–C24	120.1 (11)
C13–C14–C15	118.8 (12)	C23–C24–C25	120.1 (13)
C14–C15–C16	119.5 (12)	C24–C25–C26	118.2 (13)
C15–C16–N11	121.5 (10)	C25–C26–N21	122.2 (11)

Anion Geometry			
O51–N5–O52	118.8 (11)	O61–N6–O62	117.9 (11)
O51–N5–O53	119.7 (12)	O61–N6–O63	123.7 (12)
O52–N5–O53	121.3 (12)	O62–N6–O63	118.3 (11)

nuclear zigzag chain structure in Figure 1 is basically identical with the so-called platinum α-pyridone blue[15] and the platinum blue related complexes.[2,16] Table III summarizes geometric comparisons of binuclear amidate-bridged palladium and platinum complexes. The complex [Pd₂(C₆H₄CH=NPh)₂(succin-imidato)₂]·CH₂Cl₂[17] is the only doubly bridged amidate Pd(II) dimer complex previously reported; however it has head-to-tail configuration. The tilt angles and the torsion angles in the analogous [M₂(en)₂(α-pyridonato)₂](NO₃)₂ (M = Pd, Pt) are similar to each other but are different from those of head-to-tail [Pd₂(C₆H₄CH=NPh)₂(succinimidato)₂]. Two aromatic phenyl ring ligands in the latter complex stack and overlap, possibly contributing to a decrease in the torsional angle about the Pd–Pd vector. The Pd–Pd distances in the present complex are comparable to those in doubly bridged Pd(II) dimers with other bridging ligands, such as [(π-C₃H₅)Pd(CH₃COO)]₂[18] and [(Me₂PhP)ClPd(CH₃COO)]₂[19] with Pd–Pd values of 2.94 and 2.946 (2) Å, respectively. On the other hand, quadruply bridged Pd(II) dimers of the type Pd^II₂L₄ have shorter metal–metal distances: 2.622 (3), 2.546 (1), 2.715 (3), and 2.563 (1) Å for L-ditolylformamidinate,[7] 6-methyl-α-pyridonate,[20] phenyldithio-acetate,[21] and diphenyltriazenide,[22] respectively. Interatomic distances and bond angles are summarized in Tables IV and V, respectively. Four hydrogen bonds between oxygen atoms of α-pyridonate and hydrogen atoms at the nitrogens of ethylene-diamine shown in Table IV seem to contribute to the close as-
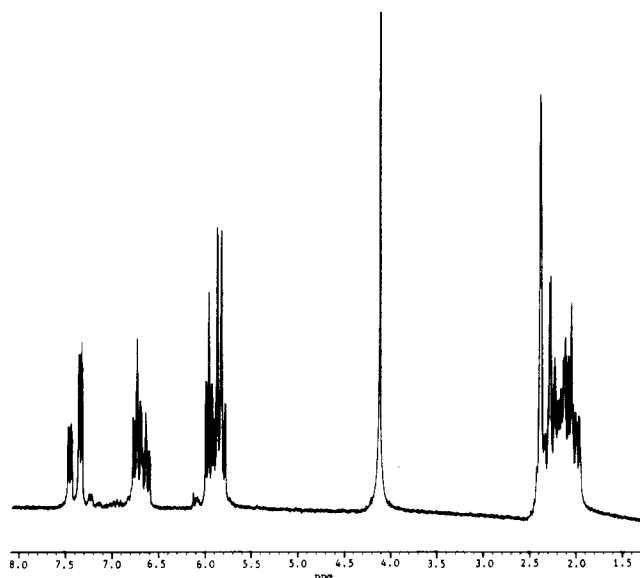
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Figure 4. ¹H–¹³C COSY spectrum of [Pd₂(en)₂(α-pyridonato)₂](NO₃)₂ in D₂O.

sembly of the two dimeric units with a Pd–Pd distance of 3.220 (1) Å. The axial sites of both palladium atoms are not occupied by any terminal ligands. There is not significant trans effect of the α-pyridonate nitrogen observed on the Pd–N(en) distances, which contrasts to the analogues [Pt₂(en)₂(α-pyridonato)₂] complex,[3,14] where Pt–N(en) distances trans to the α-pyridonate nitrogen atoms are longer than those trans to α-pyridonate oxygen atoms. The latter fact indicates the trans influence of heterocyclic nitrogen atoms is stronger than that of the oxygen atoms in amidate ligands. The two ethylenediamine chains are twisted around the Pd–Pd vector so that the repulsion between the two en chains is minimized. Crystal packing in the unit cell is shown in Figure 2. Nitrate anions occupy the intercationic vacancies and some of the nitrate oxygen atoms are hydrogen-bonded to ethylenediamines, as shown in Table IV. All the Pd–N and Pd–O coordination distances and the ligand dimensions are normal.

¹³C NMR Study of the Head-to-Head to Head-to-Tail Conversion in Solution. The peak splittings for each carbon in the ¹³C NMR spectra, as already mentioned under Results, suggest that isomerization from HH to HT occurs on dissolution of the complex, which is similar to the previously reported isomerization in analogous α-pyrrolidonate-[4] or α-pyridonate-bridged[9] Pt(II)

Figure 5. ¹H NMR spectrum of [Pd₂(en)₂(α-pyridonato)₂](NO₃)₂ in D₂O.

Figure 6. Powder X-ray diffraction pattern of HH [Pd₂(en)₂(α-pyridonato)₂](NO₃)₂.

dimer complexes. The ¹H–¹³C COSY spectrum in D₂O (Figure 4) enables the assignment of ¹H signals and reveals the existence of the two isomers also in the ¹H spectrum (Figure 5); i.e., each peak is split into several closely lying peaks. The isomerization is most apparent in the signals of the proton attached to C5 in the α-pyridonate ring: there are seemingly two sets of doublets with ca. 1:2 intensity ratios; however, each peak in each set is a close-lying doublet. Therefore, each set is actually a doublet of doublets and there are eight lines altogether for the C5 proton. The two sets with ca. 1:2 ratios correspond to the HH and HT isomers, as judged from the intensity ratios. The doublet of doublets in each set corresponds to the splitting due to the neighboring protons. In order to observe the isomerization process in solution, ¹³C NMR measurements were made just after the dissolution and were repeated on both D₂O and DMF solutions every 1 h up to 19 h; however, no intensity change was observed. Therefore, it seems that the isomerization is very rapid and equilibrium is established just after the dissolution. Similar very rapid isomerization has been reported for the α-pyrrolidonate-bridged Pt(II) dimer complex [Pt₂(NH₃)₄(C₄H₆NO)₄]²⁺.[4]

The definite assignment of HH and HT isomers in ¹³C NMR spectra seems impossible; however the following fact is very much suggestive for the assignment of both isomers. When the solvent is DMF instead of D₂O, the relative intensity of the smaller peak is further decreased from ca. 1:2 to 1:5, as shown in Figure 3. Due to the steric crowding at one side of the axial site in the HH isomer, compared to that of the HT isomer, it seems probable that the HT isomer is more favored in DMF than in D₂O, since a bulkier DMF molecule would be more difficult than D₂O to solvate or coordinate to the complex at the more crowded axial site in the
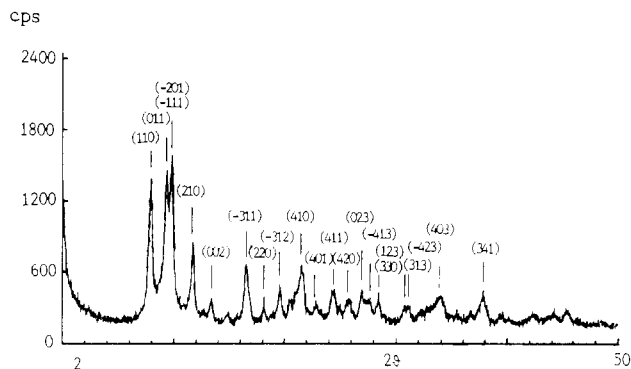
HH isomer. On the assumption that the larger peak is the HT isomer, the equilibrium constant K_{eq} (=[HT]/[HH]) is 2.2 in D₂O, which was obtained from the average integrated intensities for both isomers.

The crystalline material synthesized as described in the Experimental Section is pure HH isomer, which was confirmed by the powder X-ray diffraction study of the crystalline solid. The diffraction pattern is shown in Figure 6, which indicates that the Miller indices and diffraction angles calculated from the unit cell parameters obtained by the single-crystal diffraction study are in good agreement with the powder diffraction data. The intensities in Figure 6 are also in good agreement with those of the single-crystal data. The crystalline material is therefore pure HH isomer.

Conclusion

The present study is the first synthesis of a doubly bridged HH palladium(II) dimer complex and the first observation of the isomerization from the HH to the HT isomer. It should also be mentioned here that no HT isomer can be isolated as a solid under the present conditions because of the rapid isomerization. The solid material obtained from the solution is always pure HH isomer because of its lower solubility compared to that of the HT isomer and very rapid isomerization from the HH to the HT isomer in solution. This fact was confirmed by dissolving crystalline pure HH isomer in H₂O, drying the solution, and obtaining the X-ray powder diffraction pattern of the dried powder. The diffraction pattern showed no difference before and after the dissolving and drying process; therefore the powder is pure HH isomer.

Supplementary Material Available: Anisotropic temperature factors (Table S1) and their standard deviations (Table S2) and detailed crystal data and data collection conditions (Table S3) (3 pages); a listing of observed and calculated structure factors (Table S4) (15 pages). Ordering information is given on any current masthead page.