CHEMISTRY LETTERS, pp. 317-320, 1989.

Synthesis and Crystal Structure of Head-to-Head Bis(μ-2-pyridonato-N,O)bis[(ethylenediamine)palladium] Nitrate, $[Pd_2(en)_2(C_5H_4NO)_2](NO_3)_2$

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A synthetic method for preparing exclusively the head-to-head isomer of a dimeric compound $[Pd_2(en)_2(C_5H_4NO)_2](NO_3)_2$ has been reported. Single-crystal X-ray analysis of the compound confirmed the head-to-head structure. The complex is the first example of a head-to-head isomer for a doubly amidate-bridged Pd(II) dimer.

Although several dinuclear, quadruply bridged compounds of the type, $M(II)_2$-L_4^{n+} (M = Ni or Pd, n = 0 or 4), have been reported,$^{1-3)}$ there are little example of the oxidation of such complexes to the corresponding M(III) dimers. One example is $Ni_2(S_2CCH_3)_4I$, where the nickel average oxidation state is 2.5,$^{4)}$ and another example is $[M_2(form)_4]$ (M = Ni or Pd form is N,N'-di-p-tolylformamidinato).$^{1)}$ In view of the recent development in the chemistry of dinuclear quadruply bridged compounds of other transition elements$^{5,6)}$ and syntheses of Pt(III) dimers,$^{7,8)}$ the authors think that new dinuclear chemistry of Pd(III) seems possible. In the present study, α-pyridonate ($C_5H_4NO^-$) is selected as a bridging ligand for amidate-bridged Pd(II) dimer complexes. Nitrogen donors in amides and lactams have been shown to decrease the oxidation potentials and stabilize higher oxidation states of the coordinated metals.$^{9,10)}$ Doubly amidate-bridged Pd(II) complexes of the type $[Pd_2A_4L_2]^{2+}$ (A is an ammine ligand and L is a deprotonated amide ligand) like the one reported here are expected to be oxidized to the corresponding Pd(III) dimer and/or to a tetranuclear mixed-valent compound containing Pd(III), which is analogous to tetranuclear platinum blues.$^{9-11)}$

The head-to-head isomer of the title complex was synthesized 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 mol dm^{-3} NaOH. The suspension gradually turned to be a clear solution while heating. After it was cooled on an ice-water bath, 1 mmol of $AgNO_3$ in 5×10^{-3} dm^3 of water was added to the solution with vigorous stirring. After a few minutes, white precipitate of AgCl was removed by filtration. 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 a few minutes' stirring, AgCl was filtered off. Yellow powder of the complex was obtained by concentration of the solution. The complex was recrystallized from water. Found: C, 26.01; H, 3.63; N, 17.43. Anal. Calcd for $Pd_2C_{14}H_{24}N_8O_8$: C, 26.06; H, 3.75; N, 17.37.

An orange yellow plate crystal with approximate dimensions of 0.05 mm × 0.1 mm × 0.3 mm was used for X-ray crystallographic study. The crystal data for the complex are as follows: FW=645.23, monoclinic, space group $P2_1/a$, a=17.201(8), b=10.879(1), c=12.175(3) Å, β=102.96(3)°, V=2220(1) $Å^3$, D_{calcd}=1.930, D_{measd}=1.922 g cm^{-3} and Z=4. The X-ray diffraction intensities were collected in the range of $3° \leqq 2\theta \leqq 55°$ on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo Kα radiation. A total of 3306 independent reflections with $|F_o| \geqq 3\sigma(|F_o|)$, corrected for Lorentz and polarization effects, were used for the calculation. The crystal structure was solved by the standard heavy atom method. All non-hydrogen atoms were refined anisotropically by the block-diagonal least-squares method. The final R and R_w factors were 0.0597 and 0.0599, respectively.

The structure of the cation is shown in Fig. 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 head-to-head manner and the structure is analogous to the previously reported head-to-head α-pyridonate-bridged dimeric platinum complex, $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$.[12] A unit cell contains four dimeric cations, two of which are closely related by an inversion center to form a tetramer as shown in Fig. 1. However, the central

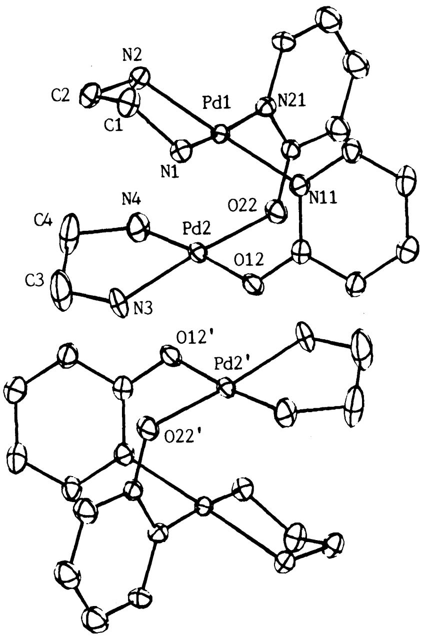

Fig. 1. Structure of $[Pd_2(en)_2(\alpha\text{-pyridonato})_2]^{2+}$.

Pd-Pd distance is not so small as to say the existence of a Pd-Pd bonding.

Structural features of the Pd(II) dimer are summarized in Table 1 together with those of the analogous Pt(II) dimer.[12] These complexes seem to have essentially similar structures. The intra-dimer metal-metal distance, 2.981(1) Å, is comparable to those observed in doubly-bridged Pd(II) dimers, such as $[(\pi\text{-}C_3H_5)Pd(CH_3COO)]_2$,[13] $[(Me_2PhP)ClPd(CH_3COO)]_2$,[14] and $[Pd(o\text{-}C_6H_4CH{=}NPh)(succinimidato)]_2$[15] with the Pd-Pd values of 2.94, 2.946(2), and 2.979(1) Å, respectively. On the other hand, quadruply-bridged Pd(II) dimers of the type, $Pd(II)_2L_4$, have shorter metal-metal distances; 2.622(3), 2.546(1), 2.715(3), and 2.563(1) Å for L = ditolylformamidinate,[1] 6-methyl-α-pyridonate,[16] phenyldithioacetate[17] and diphenyltriazenide,[18] respectively. Selected interatomic distances are summarized in Table 2. Four hydrogen bonds between oxygen atoms of α-pyridonate and hydrogen atoms at the nitrogens of ethylenediamine seem to contribute to the close assembly of the two dimeric units with Pd-Pd distance of 3.220(1) Å (Table 2). Nitrate anions occupy the inter-cationic vacancies and some of the nitrate oxygen atoms are hydrogen-bonded to ethylenediamines as shown in Table 2.

Table 1. Structural Features of $[Pd_2(en)_2(\alpha\text{-pyridonato})_2](NO_3)_2$

Complex	M-M dist. / Å	$\tau^{a)}$/°	$\omega^{a)}$/°	M-M-M angle/°	Ref.
$[Pd_2(en)_2(\alpha\text{-pyridonato})_2](NO_3)_2$	2.981(1) 3.220(1)	39.7	25.5	159.82	this work
$[Pt_2(en)_2(\alpha\text{-pyridonato})_2](NO_3)_2$	2.992(1) 3.236(1)	39.6	24.9	160.58	12

a) τ is the tilt angle between adjacent platinum coordination planes and ω is the torsion angle about the M-M vector.

Table 2. Selected Interatomic Distances (Å) and Angles (°)

Metal-Metal			
Pd1-Pd2	2.981(1)	Pd2-Pd2'	3.220(1)
Coordination sphere			
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)
Hydrogen bond			
N3-O22'	2.934(12)	N4-O12'	3.113(12)
N1-O51	2.889(13)	N3-O51	2.789(12)
N2-O61	2.881(12)	N4-O61	2.923(15)
N2-O52	2.917(14)	N1-O62	2.938(14)

O51, O52, O61, and O62 are nitrate oxygen atoms.

Cyclic voltammogram of the present complex in 0.05 mol dm^{-3} H_2SO_4 shows an irreversible wave at E_{pa} = 0.78 V and E_{pc} = 0.42 V vs. SCE. Bulk oxidation of the complex electrochemically at 1.2 V resulted in decomposition of the complex.

The present study has established for the first time an effective synthetic method for selectively preparing the head-to-head isomer of a doubly amidate-bridged Pd(II) dimer. The other example of a doubly amidate-bridged Pd(II) dimer so far reported is a head-to-tail [Pd(o-C_6H_4CH=NPh)(succinimidato)$]_2$$^{15)}$ and therefore, the present complex is the first example of a head-to-head isomer.

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(Received November 29, 1988)