

Ethylenebis(isonitrosoethylacetoacetate imine)과 그 유사화합물을 리간드로 하는 팔라듐(II) 착물의 합성 및 성질

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Preparation and Properties of Palladium(II) Complexes with Ethylene- bis(isonitrosoethylacetoacetate imine) and Its Analogue

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요 약. 팔라듐(II)의 새로운 착물인 $[Pd\{(ieaa)_2-en\}]$ 및 $[PdCl\{(ieaa)-l-pn\}]$ 을 합성하였다. 여기서 $(ieaa)_2-en$ 과 $(ieaa)-l-pn$ 은 각각 N, N'-ethylenebis(isonitrosoethylacetoacetate imine) 및 l-N-(2-aminopropyl)-isonitrosoethylacetoacetate imine을 표시한다. 합성된 이들 팔라듐(II) 착물들은 전자흡수(AB) 스펙트럼, 원이색성(CD) 스펙트럼, C-13 핵자기공명스펙트럼, 적외선 및 라만스펙트럼 등의 측정결과를 기초로 그 특성을 연구하였다. 염화팔라듐(II)과 ethylenediamine을 첨가한 isonitrosoethylacetoacetate(ieaa)와의 반응에서 생성된 팔라듐착물에서는 $(ieaa)_2-en$ 형의 Schiff 염기, 한편 ethylenediamine 대신 l-propylenediamine을 사용한 비슷한 반응으로 생성된 착물에서는 $(ieaa)-l-pn$ 형의 Schiff 염기로 나타난다. 이러한 구조형성의 차이를 사용된 diamine의 입체화학적 관점에서 검토한다.

ABSTRACT. Novel palladium(II) complexes, $[Pd\{(ieaa)_2-en\}]$ and $[PdCl\{(ieaa)-l-pn\}]$ ($(ieaa)_2-en$ and $(ieaa)-l-pn$ denote N, N'-ethylenebis(isonitrosoethylacetoacetate imine) and l-N-(2-aminopropyl)-isonitrosoethylacetoacetate imine, respectively), have been prepared. The palladium(II) complexes were characterized on the bases of the electronic absorption, circular dichroism (CD), ¹³C NMR, infrared, and Raman spectra. The reaction of palladium(II) chloride and isonitrosoethylacetoacetate (ieaa) with ethylenediamine gives an $(ieaa)_2-en$ type Schiff base, while similar reaction using l-propylenediamine instead of ethylenediamine gives an $(ieaa)-l-pn$ type Schiff base. The difference in formation is discussed from the stereochemical viewpoint of the diamine employed.

INTRODUCTION

Metal complexes containing α -isonitroso- β -diketone type ligand have been stereochemically remarked because of two probable coordination modes of the isonitroso group in the ligand.¹⁻⁴

The ligand, such as isonitrosoacetylacetone (Hiaa) and isonitrosobenzoylacetone (Hiba), coordinates to cobalt(III) or palladium(II) through the nitrogen of its isonitroso group to form selectively a five-membered chelate ring.²⁻⁴ On the other hand, isonitrosoacetylacetone imine

(*iaa-NH*), isonitrosobenzoylacetone imine (*iba-NH*), and their *N*-alkyl derivatives (*iaa-NR* and *iba-NR*; R, alkyl group (CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, and so on)) coordinate to palladium (II) and nickel (II) to form the square planar $[\text{M}(\text{N})_4]$ (M: Pd(II) or Ni(II)) and/or $[\text{M}(\text{O})(\text{N})_3]$ type complexes, depending on the *N*-substituted group in the ligand.^{1,5-8} Namely, in the $[\text{Ni}(\text{iaa-NH or } iaa\text{-NR})(\text{iaa-NH}')]_2$, $[\text{Ni}(\text{iba-NH or } iba\text{-NR})(\text{iba-NH}')]_2$, $[\text{Pd}(\text{iaa-NH})(\text{iaa-NH}')]_2$, and $[\text{Pd}(\text{iba-NH})(\text{iba-NH}')]_2$ type complexes, *iaa-NH*, *iba-NH*, *iaa-NR*, or *iba-NR* coordinates to palladium(II) or nickel(II) through the nitrogen of the isonitroso group to form the five-membered N-N chelate ring. While, *iaa-NH'* or *iba-NH'* coordinates through the oxygen of the isonitroso group to form the six-membered N-O one. In contrast to these facts, the isonitroso group in the palladium (II) complexes of the bis type, $[\text{Pd}(\text{iaa-NR})_2]$ and $[\text{Pd}(\text{iba-NR})_2]$, coordinates dominantly through the nitrogen. Quite similar coordination behavior was confirmed for the palladium(II) and nickel (II) complexes with isonitrosoethylacetoacetate imine (*ieaa-NH*) and its *N*-alkyl derivative (*ieaa-NR*);⁹ namely, in the $[\text{M}(\text{ieaa-NR})_2]$ (M: Pd (II) or Ni (II)) and $[\text{M}(\text{ieaa-NH})(\text{ieaa-NH}')]_2$ type complexes, the isonitroso group in *ieaa-NR* and *ieaa-NH* coordinates through the nitrogen and that in *ieaa-NH'* through the oxygen.

The present work is concerned with the preparation and stereochemistry of palladium (II) complexes with a Schiff base which is derived from the reaction of the isonitrosoethylacetoacetate (*ieaa*) with the ethylenediamine (*en*) or *l*(-)-589-propylenediamine (*l-pn*).¹⁰ The resulting palladium (II) complexes, yellow for *en* and orange yellow for *l-pn*, are characterized from their electronic absorption, circular dichroism(CD), ¹³C nuclear magnetic resonance

(NMR), infrared, and Raman spectra, and the structural difference between the two complexes is discussed from the stereochemical viewpoint of the diamine employed.

EXPERIMENTAL

Materials. Isonitrosoethylacetoacetate (α -oximinoethylacetoacetate, *ieaa*) was prepared by the method of Adams.¹¹ Palladium (II) chloride and the other reagents used were obtained from the Wako Pure Chemicals Ind. Co., Ltd.

Preparation of Complexes. (*l*-*N*-(2-Aminopropyl)-isonitrosoethylacetoacetate imino) chloropalladium(II) 0.5 Hydrogen Chloride ($[\text{PdCl}(\text{ieaa})\text{-}l\text{-pn}] \cdot 0.5\text{HCl}$): Palladium(II) chloride (0.35g, 0.002 mol) and *ieaa* (1.28g, 0.008 mol) were dissolved in 80cm³ of absolute methanol, and 0.34cm³ of *l*-propylenediamine was added. The solution was adjusted to pH 3~4 by the addition of acetic acid. After reflux for 48 h, the orange yellow precipitate resulted was collected by filtration and washed with small amount of methanol, and recrystallized from chloroform and dried in vacuum desiccator. The complex is insoluble in water but soluble in methanol, dimethylsulfoxide (DMSO), and chloroform. *Anal.* Found: C, 28.77; H, 4.48; N, 11.21%. Calcd for $[\text{PdCl}(\text{ieaa})\text{-}l\text{-pn}] \cdot 0.5\text{HCl} = \text{PdC}_9\text{H}_{17}\text{N}_3\text{O}_3\text{Cl} \cdot 0.5\text{HCl}$: C, 28.88; H, 4.44; N, 11.23%.

(*N, N'*-Ethylenebis(isonitroso ethylacetoacetate imino))-palladium(II) ($[\text{Pd}(\text{ieaa})_2\text{-en}]$):

This complex was prepared by the procedure similar to that described for $[\text{PdCl}(\text{ieaa})\text{-}l\text{-pn}] \cdot 0.5\text{HCl}$, using ethylenediamine instead of *l*-propylenediamine. Palladium(II) chloride(0.35 g, 0.002 mol) and *ieaa* (1.28g, 0.008 mol) were dissolved in 50cm³ of absolute methanol, and 0.3cm³ of ethylenediamine (99%) was added. The solution was acidified to pH 3~4 with acetic acid. After reflux for 48h, the golden

yellow precipitate resulted was collected by filtration and washed with small amount of methanol, and recrystallized from methanol and dried in vacuum desiccator. This complex is also insoluble in water but soluble in methanol, DMSO, and chloroform. *Anal.* Found: C, 36.91; H, 4.47; N, 12.54%. Calcd for $[\text{Pd}((\text{ieaa})_2\text{-en})] = \text{PdC}_{14}\text{H}_{20}\text{N}_4\text{O}_6$: C, 37.64; H, 4.51; N, 12.54%.

Measurements. All measurements were carried out at room temperature. The electronic absorption spectra were recorded with a JASCO UVIDEK-1 and UVIDEK-610 spectrophotometers, and the CD spectra with JASCO J-20 and J-500 spectropolarimeters. The ^{13}C NMR spectra were recorded in dimethylsulfoxide- d_6 with a JEOL JNM-FX-100 NMR spectrometer at the probe temperature. Tetramethylsilane was used as an internal reference. The infrared spectra were recorded with a Hitachi 260-50 infrared spectrophotometer using the KBr disk method. The Raman spectra were recorded with a JASCO R-800 Laser Raman spectrophotometer by an excitation of the He-Ne Laser (632.8nm, 50mV) in disk. The elemental analyses were carried out in Analysis Center of the University of Tsukuba in Japan.

RESULTS AND DISCUSSION

One yellow complex was formed by the reaction of palladium(II) chloride and *ieaa* with ethylenediamine in methanol, and its analytical result suggests the formation of the palladium(II) complex with an $(\text{ieaa})_2\text{-en}$ type Schiff base (Fig. 1). On the other hand, similar reaction with *l*-propylenediamine gave one orange yellow complex and its analytical result suggests the coordination of an $(\text{ieaa})\text{-l-pn}$ type Schiff base and a chloride ion. Their electronic absorption spectra are shown in Fig. 2 and 3, and the data are summarized in Table 1.

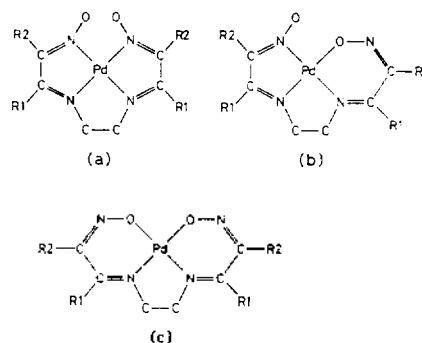


Fig. 1. The possible geometrical isomers of $[\text{Pd}((\text{ieaa})_2\text{-en})]$; $\text{R}_1 = \text{CH}_3$ and $\text{R}_2 = \text{CO}_2\text{C}_2\text{H}_5$.

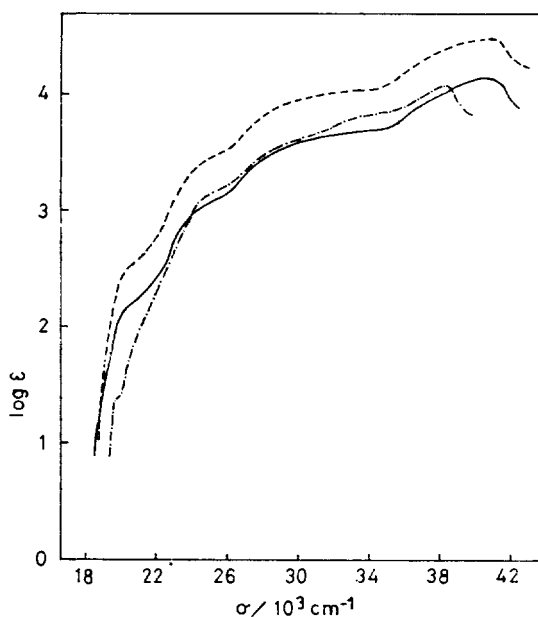


Fig. 2. Absorption spectra of $[\text{Pd}((\text{ieaa})_2\text{-en})]$ in chloroform (-----), in DMSO (— · — · —), and in methanol (————).

Assuming that the yellow complex contains an $(\text{ieaa})_2\text{-en}$ type Schiff base, three geometrical isomers with respect to the coordination mode of the isonitroso group of *ieaa* moiety are possible for the square planar palladium (II) complex, as shown in Fig. 1. For the palladium (II) complexes such as $[\text{Pd}(\text{iaa-NR})_2]$,⁶ $[\text{Pd}(\text{iba-NR})_2]$,⁸ and $[\text{Pd}(\text{ieaa-NR})_2]$ ($\text{R}: \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, \text{etc}$),⁹ it has been known that each

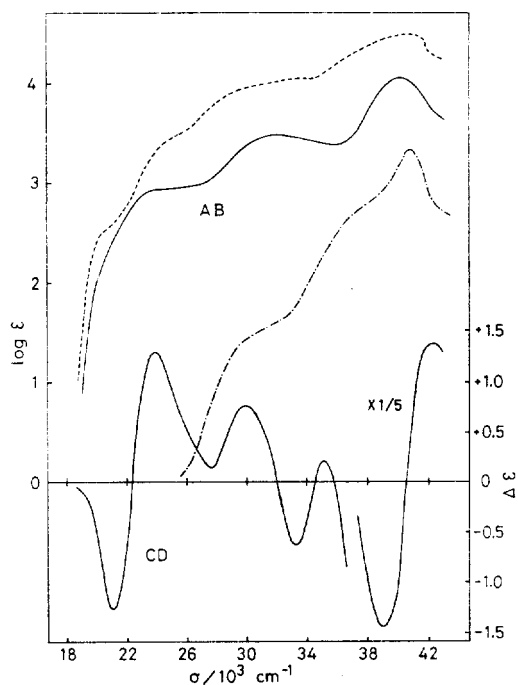


Fig. 3. Absorption and CD spectra of $[\text{PdCl}((\text{ieaa})\text{-}1\text{-pn})]$ (—): $[\text{Pd}((\text{ieaa})_2\text{-en})]$ (-----) and ieaa (-·-·-) in chloroform.

isonitroso group of the ligands coordinates to the palladium(II) through the nitrogen rather than the oxygen on the basis of their infrared spectral investigation. The infrared spectrum of the yellow complex exhibits the N-O, C=O, and Pd-N stretching vibration bands, $\nu_{\text{N-O}} = ca. 1210 \text{ cm}^{-1}$, $\nu_{\text{C=O}} = ca. 1700 \text{ cm}^{-1}$, and $\nu_{\text{Pd-N}} = ca. 505 \text{ cm}^{-1}$. These spectral bands are quite similar to those of $[\text{Pd}(\text{ieaa-NR})_2]$ (R: CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, etc) whose isonitroso groups coordinate to palladium (II) through the nitrogen atom;⁹ especially, the spectral behavior of the N-O stretching vibration band suggests the nitrogen coordination of the isonitroso group in the yellow complex. These considerations lead us to the conclusion that the yellow complex is (a) in Fig. 1.

The absorption spectral pattern of the yellow complex in the region of $18 \sim 35 \times 10^3 \text{ cm}^{-1}$ is not

affected by each of the solvents employed, chloroform, dimethylsulfoxide, and methanol (Fig. 2 and Table 1), and this fact reveals that the complex is structurally stable in these solvents. In Fig. 3, an intense band at $ca. 41 \times 10^3 \text{ cm}^{-1}$ is assigned to $\pi\text{-}\pi^*$ transition of the coordinated $(\text{ieaa})_2\text{-en}$ and another intense band at $ca. 33 \times 10^3 \text{ cm}^{-1}$ to the charge transfer band, in comparison with the absorption spectra of the free ieaa and $[\text{Pd}(\text{ieaa-NR})_2]$.⁹ The shoulders (at $ca. 20$ and $25 \times 10^3 \text{ cm}^{-1}$) are due to the $d\text{-}d$ transition and they can be correlated to the band at $34.8 \times 10^3 \text{ cm}^{-1}$ of $[\text{Pd}(l\text{-pn})_2]^{2+}$ ¹² and $[\text{Pd}(\text{amino carboxamidato})_2]$,¹³ which belong to $[\text{Pd}(\text{N})_4]$ type, since the $d\text{-}d$ transition in the most Schiff base cobalt (III) complexes shifted to lower energy side.¹⁴

The infrared spectrum of the orange yellow complex exhibits the N-O, C=O, and Pd-N stretching vibration bands, $\nu_{\text{N-O}} = ca. 1200 \text{ cm}^{-1}$, $\nu_{\text{C=O}} = ca. 1700 \text{ cm}^{-1}$, and $\nu_{\text{Pd-N}} = ca. 510 \text{ cm}^{-1}$, as in the case of $[\text{Pd}((\text{ieaa})_2\text{-en})]$. Further, the stretching vibration band of the Pd-Cl bond appears at $ca. 320 \text{ cm}^{-1}$ as reported for the palladium(II) complexes with the chloride coordination.¹⁵ The Raman spectrum of the orange yellow complex exhibits only the Pd-N stretching vibration band at $ca. 500 \text{ cm}^{-1}$ but similar bands at $270 \sim 300 \text{ cm}^{-1}$ to those of PdCl_2 , suggesting the Pd-Cl bonding. These infrared and Raman spectral behaviors for the orange yellow complex indicate that the chloride and the nitrogen of the isonitroso group coordinate to the palladium(II). The shoulders at $ca. 24 \times 10^3 \text{ cm}^{-1}$ of the orange yellow complex somewhat shift to lower energy side than that of $[\text{Pd}((\text{ieaa})_2\text{-en})]$ (Fig. 3 and Table 1), though the absorption spectral pattern is similar each other in the whole region. This absorption spectral behavior for the orange yellow complex also suggests the chloride coordination to the palla-

Table 1. Absorption and CD data of palladium (II) complexes

Compound	Absorption $\sigma/10^3\text{cm}^{-1}$ ($\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)		
	in CHCl_3	in DMSO	in MeOH
ieaa	29.94 (1.43sh)	26.88 (0.71sh)	
	38.17 (2.82sh)	32.89 (2.34sh)	35.97 (3.08sh)
	40.65 (3.34)	38.17 (3.09)	42.74 (3.76)
[Pd((ieaa) ₂ -en)]	20.08 (2.04sh)	19.84 (1.36sh)	19.69 (3.72sh)
	25.38 (3.11sh)	25.51 (3.17sh)	25.51 (3.82sh)
	33.33 (3.67sh)	33.78 (3.81sh)	32.63 (3.87sh)
	40.65 (4.11)	38.46 (4.08)	43.10 (4.05)
[PdCl((ieaa)- <i>l</i> -pn)]			19.31 (1.52sh)
	24.27 (2.93sh)	24.88 (2.98sh)	25.25 (3.06)
	31.85 (3.47)	31.85 (3.65)	32.47 (3.64)
	40.32 (4.05)	38.46 (3.94)	41.32 (4.21)
	CD $\sigma/10^3\text{cm}^{-1}$ ($\Delta\epsilon/\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$)		
[PdCl((ieaa)- <i>l</i> -pn)]	21.01 (-1.19)	21.55 (-0.56)	21.74 (-0.49)
	23.93 (+1.24)	24.51 (+0.69)	25.13 (+0.73)
	29.94 (+0.76)	31.45 (+0.50)	31.65 (+0.44)
	33.11 (-0.64)	34.48 (-0.11)	35.21 (-0.16)
	34.97 (+0.21)	37.88 (+0.38)	37.59 (+0.26)
	39.06 (-1.46)		40.98 (+0.08)
	42.37 (+1.39)		

Sh denotes a shoulder.

dium(II), referring the absorption spectral data of [Pd(*l*-pn)₂]²⁺ and [PdCl₂(*l*-pn)].¹² In the *d-d* transition band region (20~24×10³cm⁻¹), the orange yellow complex exhibits two CD bands (a negative band at 21.0×10³cm⁻¹ and a positive one at 23.9×10³cm⁻¹) as shown in Fig. 3 and Table 1. This CD spectral pattern is quite similar to that in the *d-d* transition band region of the square planar palladium(II) complex with a *l*-propylenediamine, [PdCl₂(*l*-pn)],¹² whose optically active source arises from a coordinated *l*-propylenediamine. The ¹³C NMR spectrum of the orange yellow complex exhibits three resonance lines (13.9, 15.4, and 18.1 ppm from TMS) due to the three methyl carbon atoms in the ligand, indicating that the complex is not a mixture such as (a)~(d) in Fig. 4. From these facts, the orange yellow complex is

assigned to one of (a)~(d) of [PdCl((ieaa)-*l*-pn)] as shown in Fig. 4.

In contrast to the case of the yellow complex, [Pd((ieaa)₂-en)], the reaction of palladium(II) chloride and ieaa with *l*-propylenediamine does not give an (ieaa)₂-*l*-pn type Schiff base. This difference in formation can be related to that in rigidity between the gauche forms of the ethylenediamine and *l*-propylenediamine moieties. In the case of the yellow complex, the ethylenediamine can span favorably the *cis* coordination sites of the square planar [Pd(ieaa)₂] because of its flexible gauche form, though the ethylenediamine chelate ring coordinated to the palladium(II) take a rigid gauche form in crystalline state.¹⁶ On the other hand, it is well known that *l*-propylenediamine coordinates to a metal ion such as palladium(II) and platinum

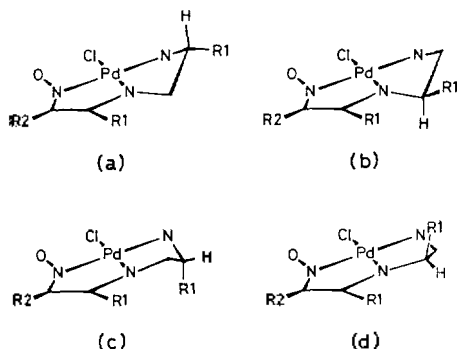


Fig. 4. The possible isomers of $[\text{PdCl}((\text{ieaa})\text{-}l\text{-pn})]$; $\text{R1}=\text{CH}_3$ and $\text{R2}=\text{CO}_2\text{C}_2\text{H}_5$.

(II) to take a λ gauche form depending strongly on the equatorial orientation of its methyl group and brings about a non-planar chelate ring.^{12,17} Here, taking into consideration that the CD spectral pattern of the orange yellow complex in the $d\text{-}d$ transition band region is quite similar to that of $[\text{PdCl}_2(l\text{-pn})]$,¹² it can be deduced that the chelate ring of the l -propylenediamine moiety takes the λ gauche form, (a) or (b) in Fig. 4. It is considered, therefore, that the rigid λ gauche conformation of the l -propylenediamine chelate ring hinders the amino-exchange reaction of (ieaa)- l -pn with another ieaa, namely, N-H orientation depending strongly on the λ gauche conformation does not fit for the reaction with another ieaa. The methine carbon atom bound to the equatorially orientated methyl group of the l -propylenediamine shows more remarkable displacement from the N-Pd-N plane than the methylene carbon atom, accordingly, the amino group remote from the methyl group may react selectively with ieaa to form (a) in Fig. 4.

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