Preparation and Characterization of Nickel(II) Complexes with Diethyl *N,N'*-Ethylenebis(2-hydroxyimino-3-iminobutanoate) and Its Analogue

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Synopsis. The reaction of nickel(II) chloride hexahydrate and ethyl α-(hydroxyimino)acetoacetate with ethylenediamine or (*R*)-propylenediamine gives [diethyl *N,N'*-ethylenebis(2-hydroxyimino-3-iminobutanoato)]nickel(II) or {diethyl *N,N'*-[(*R*)-1-methylethylene]bis(2-hydroxyimino-3-iminobutanoato)}nickel(II). The nickel(II) complexes with Schiff base ligands were characterized by their electronic absorption, ^{13}CNMR, infrared, and CD spectra.

In the metal complexes with α-hydroxyimino β-diketone or its derivatives, it has been known that two coordination modes are possible for the hydroxyimino group.[1-8] Namely, the ligands coordinate to a metal ion through the nitrogen of the hydroxyimino group to form a five-membered ring or through the oxygen of the group to form a six-membered one. In the previous paper,[9] we reported some properties of the palladium(II) complexes with diethyl *N,N'*-ethylenebis(2-hydroxyimino-3-iminobutanoate), (ieaa)$_2$-en, and ethyl 3-[(*R*)-2-aminopropylimino]-2-hydroxyiminobutanoate, (ieaa)-(*R*)-pn,[10] in which the hydroxyimino group coordinates to palladium(II) ion through the nitrogens. It is of interest that the (ieaa)$_2$-en was formed as a quadridentate ligand and the (ieaa)-(*R*)-pn as a terdentate one, though a similar reaction was adopted.[9] In order to examine the difference in formation, the preparation of the nickel(II) complexes with Schiff base ligands, which are derived from the reaction of ethyl α-(hydroxyimino)acetoacetate, ieaa, with the ethylenediamine or (*R*)-propylenediamine, was attempted. The resulting nickel(II) complexes are characterized by the electronic absorption, ^{13}CNMR, infrared, and CD spectra.

Experimental

Materials. Ethyl α-(hydroxyimino)acetoacetate was prepared by nitrosation of ethyl acetoacetate with sodium nitrite according to the method of Adams.[11] Nickel(II) chloride hexahydrate and the other reagents used were obtained from the Wako Pure Chemicals Ind. Co., Ltd.

Preparation of Complexes. 1) [Diethyl *N,N'*-Ethylenebis(2-hydroxyimino-3-iminobutanoato)]nickel(II): [Ni{(ieaa)$_2$-en}]. Nickel(II) chloride hexahydrate (0.65 g, 0.005 mol) and ieaa (3.2 g, 0.02 mol) were dissolved in 70 cm^3 of 1-propanol, and 0.7 cm^3 of ethylenediamine was added to it. After reflux for 45 min, the red precipitate which appeared was collected by filtration. The crude product was recrystallized from chloroform and dried in a vacuum desiccator. The orange red needle crystals obtained were insoluble in water, but soluble in methanol, dimethyl sulfoxide (DMSO), and chloroform. Found: C, 41.97; H, 5.02; N, 14.03%. Calcd for $NiC_{14}H_{20}N_4O_6$: C, 42.14; H, 5.05; N, 14.04%.

2) {Diethyl *N,N'*-[(*R*)-1-Methylethylene]bis(2-hydroxyimino-3-iminobutanoato)}nickel(II): [Ni{(ieaa)$_2$-(*R*)-pn}]. Nickel(II) chloride hexahydrate (0.65 g, 0.005 mol) and ieaa (3.2 g, 0.02 mol) were dissolved in 80 cm^3 of absolute ethanol, and 0.8 cm^3 of (*R*)-propylenediamine and 10 drops of 28% aqueous ammonia were added to it. After reflux for 72 h, the reaction mixture was stood in a refrigerator for 48 h. The crystals which appeared were collected by filtration, washed three times with small amounts of cold ethanol, and dried in a vacuum desiccator. The red fine crystals obtained were also insoluble in water, but soluble in methanol, DMSO, and chloroform. Found: C, 43.60; H, 5.35; N, 13.70%. Calcd for $NiC_{15}H_{22}N_4O_6$: C, 43.61; H, 5.36; N, 13.56%.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrophotometers and the CD spectra with a JASCO J-20 and J-500 spectropolarimeters. All measurements were carried out at room temperature. The ^{13}CNMR spectra were recorded in $CDCl_3$ with a JEOL JNM-FX-100 or -FX-90Q 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 elemental analyses were carried out in the Analysis Center of the University of Tsukuba.

Results and Discussion

Only an orange red needle crystalline complex was formed by the reaction of nickel(II) chloride hexahydrate and ieaa with ethylenediamine in 1-propanol. The elemental analytical result suggests the formation of the nickel(II) complex containing (ieaa)$_2$-en type Schiff base as a quadridentate ligand, [Ni{(ieaa)$_2$-en}], as in the case of [Pd{(ieaa)$_2$-en}].[9] Although two kinds of structure, square planar and tetrahedral, are possible for this nickel(II) complex, the ^{1}H and ^{13}CNMR spectral behaviors seem to prefer the former to the latter (vide infra). This is supported by the fact that the present nickel(II) complex exhibits a quite similar absorption spectral behavior to the square planar nickel(II) complexes with Schiff base ligands such as 3-hydroxyimino-4-imino-2-pentanone (iaa-NH),[5] 2-hydroxyimino-3-imino-1-phenyl-1-butanone (iba-NH),[6] ethyl 2-hydroxyimino-3-iminobutanoate (ieaa-NH),[12] their *N*-alkyl derivatives (iaa-NR, iba-NR, and ieaa-NR; R=CH_3, C_2H_5, *n*-C_3H_7, and so on),[5,6,12] (*R*)-*N,N'*-disalicylidene-1,2-propanediamine, and its derivatives (Fig. 1).[13,14]

For the square planar nickel(II) complex, three geometrical isomers with respect to the coordination modes of the hydroxyimino groups of the ieaa moieties are possible as shown in Fig. 2. The ^{13}CNMR spectrum of [Ni{(ieaa)$_2$-en}] exhibits eight resonance lines for the four methyl (14.1, 14.2, 17.4, and 18.5 ppm) and four

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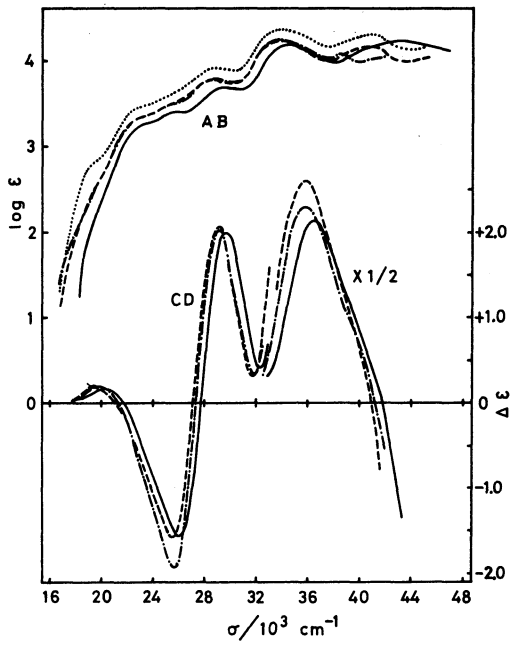

Fig. 1. Absorption spectrum of [Ni{(ieaa)$_2$-en}] in chloroform (·····), and absorption and CD spectra of [Ni{(ieaa)$_2$-(*R*)-pn}] in chloroform (------), in DMSO (—·—·—·—), and in methanol (———).

methylene carbon atoms (48.6, 59.4, 60.4, and 61.7 ppm). As seen in Fig. 2, eight resonance lines for the methyl and methylene carbon atoms are expected for the ^{13}CNMR spectrum of (b) and four resonance lines for the carbon atoms are expected for that of (a) or (c), since (b) is C_1 symmetry and (a) or (c) C_2 one. The infrared spectrum of this complex exhibits the stretching vibration bands, $\nu_{N\text{-}O}$=1260 cm^{-1}, $\nu_{C=O}$=1688 and 1706 cm^{-1}, $\nu_{Ni\text{-}N}$=503 and 541 cm^{-1}, and $\nu_{Ni\text{-}O}$=ca. 315 cm^{-1}. The infrared spectral characteristics coincide well with those of [Ni(iaa-NH)(iaa-NR)][5] or [Ni(ieaa-NR)$_2$][12] (R; H and alkyl groups), in which one ligand coordinates through the nitrogen of the hydroxyimino group and the other through the oxygen. These ^{13}CNMR and infrared spectral characteristics indicate that the present nickel(II) complex takes the form (b) in Fig. 2, namely, one of the two hydroxyimino groups coordinates to nickel(II) ion through the nitrogen to form a five-membered chelate ring and the other through the oxygen to form a six-membered one.

Nickel(II) chloride hexahydrate reacted with ieaa and (*R*)-propylenediamine in basic ethanol to give one product as in the case of [Ni{(ieaa)$_2$-en}]. The analytical result of this complex suggests that one diethyl *N,N'*-[(*R*)-1-methylethylene]bis(2-hydroxyimino-3-iminobutanoate) ligand, (ieaa)$_2$-(*R*)-pn, coordinates to a nickel(II) ion, and the nickel(II) complex exhibits a quite similar absorption spectrum to [Ni{(ieaa)$_2$-en}] (Fig. 1). Further, its infrared spectral bands also agree well with those of the (ieaa)$_2$-en complex; $\nu_{N\text{-}O}$=1255 cm^{-1}, $\nu_{C=O}$=1673 and 1710 cm^{-1}, $\nu_{Ni\text{-}N}$=506 and 538 cm^{-1}, and $\nu_{Ni\text{-}O}$=ca. 325 cm^{-1} (stretching vibrations). These facts suggest that the quadridentate ligand in [Ni{(ieaa)$_2$-(*R*)-pn}] takes a similar coordination mode to that in [Ni{(ieaa)$_2$-en}] ((b) in Fig. 2). The ^{13}CNMR spectrum

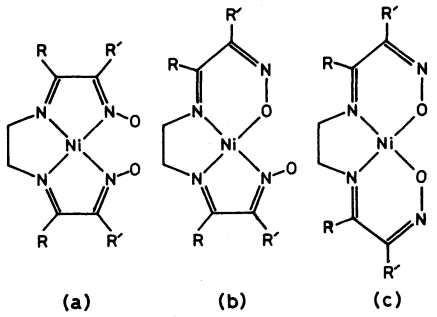

Fig. 2. Possible geometrical isomers of the square planar configuration for [Ni{(ieaa)$_2$-en}]; R=CH_3 and R'=$CO_2C_2H_5$.

of [Ni{(ieaa)$_2$-(*R*)-pn}] exhibits seven resonance lines due to the methyl carbon atoms and eight resonance ones due to the methylene carbon atoms. This ^{13}CNMR spectral behavior seems to indicate that the nickel(II) complex is a composite of two possible isomers, which are caused by the configuration due to the methyl group of the (*R*)-propylenediamine moiety of (b) in Fig. 2.

When the absorption and/or CD spectra of [Ni{(ieaa)$_2$-en}] and [Ni{(ieaa)$_2$-(*R*)-pn}] are compared with those of the square planar nickel(II) complexes with the quadridentate Schiff base ligands such as (*R*)-*N,N'*-disalicylidene-1,2-propanediamine (sal-(*R*)-pn),[10,13,14] their absorption bands are assigned as follows; the intense bands at ca. 34 and 40×10^3 cm^{-1} originate from the π-π* transitions due to the coordinated (ieaa)$_2$-en or (ieaa)$_2$-(*R*)-pn, other three intense bands at 22—29×10^3 cm^{-1} from the charge transfer, and the shoulder at ca. 19.5×10^3 cm^{-1} from the d-d transition. In the region of 18—38×10^3 cm^{-1}, the absorption and/or CD spectral patterns of [Ni{(ieaa)$_2$-en}] and [Ni{(ieaa)$_2$-(*R*)-pn}] were almost unaffected by nature of the solvents such as chloroform, dimethyl sulfoxide, methanol, and pyridine (Fig. 1).

In contrast to [Ni{(ieaa)$_2$-(*R*)-pn}], the corresponding palladium(II) complex, [Pd{(ieaa)$_2$-(*R*)-pn}], could not be formed by a reaction similar to that for the nickel(II) complex, but the palladium(II) complex with a terdentate Schiff base ligand, [Pd(Cl){(ieaa)-(*R*)-pn}], was formed.[9] This difference in the formation of the (*R*)-pn Schiff base ligand between the palladium(II) and nickel(II) complexes is presumably related to the affinity of chloride,[15] which is lower to nickel(II) ion than to palladium(II) ion, and to the adaptability of the strained quadridentate Schiff base ligand with (*R*)-propylenediamine backbone ring, which coordinates more easily to nickel(II) ion capable of taking distorted square planar structure than to palladium(II) ion.

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