BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 854—862 (1968)

Metal Complexes with Amino Acid Amides. I. Preparations and Electronic Spectra of the Nickel(II) and Palladium(II) Complexes

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(Received July 31, 1967)

Several planar bis(amino-acid-amidato) complexes of nickel(II) and palladium(II) have been newly synthesized and characterized mainly spectroscopically. The geometrical structures of these $[M(N)_4]$-type complexes have been determined: palladium(II) produced both cis and trans complexes with L-alanine- and L-leucine-amidate ligands, while nickel(II) did only trans forms with glycine-, L-alanine- and L-leucine-amidates. Nickel(II) also produced cationic complexes, Ni(L-alanine-amide)$_2$SO$_4$ and its glycine amide analogue. The circular dichroism spectra and rotatory dispersion of the complexes containing optically active amino acid amide have been measured and discussed as for the assignments of the ligand field absorption bands of the diamagnetic planar complexes. A good correspondence was observed between the circular dichroism spectra of the nickel(II) and the palladium(II) complexes.

A number of reports[1-3] have been presented for the electronic structures of the tetracoordinated planar complexes with d^8 electron configuration. It seems, however, that the attempts have been less successfully carried out, partly because of the rather simple feature of the ligand field bands of these complexes and partly because of the lack of favorable series of complexes suitable to systematic studies. In these circumstances, it is thought of as desirable to study the circular dichroism (CD) and the rotatory dispersion (RD) of the planar complexes containing optically active ligands.[4,5]

It is well known that the bidentate ligand with amide or amidino groups, such as biuret, biguanide, oxamide or dicyandiamidine, is coordinated planarly to copper(II) or nickel(II) through its two nitrogen atoms;[6,7] an authentic example is the bis(biuretato)-cuprate(II) ion whose structure has been established by X-ray analysis of its potassium salt tetrahydrate.[8] The α-amino acid amide, such as L-alanine amide *etc.*, belongs to the category of ligands above shown and furthermore has one asymmetric carbon atom in the structure. Therefore the complexes of optically active α-amino acid amides will be excellently suitable for CD or RD studies of the planar complexes. Such complexes have not been isolated heretofore, except for a few copper(II) complexes, which have been prepared by Rising and Yang,[9] and Rosenberg.[10]

In the present paper, the preparations of several nickel(II) and palladium(II) complexes with glycine amide, L-alanine amide and L-leucine

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amide[*1] are reported, and the electronic absorption and CD spectra of these complexes are discussed in relation to their geometrical structures.

Experimental

Preparation. *1) Glycine Amide, L-Alanine Amide and L-Leucine Amide.* These were derived from the corresponding amino acids by the similar methods described in literature.[11]

2) trans-Bis(glycine-amidato)nickel(II) Monohydrate: trans-[Ni(glya)$_2$]·H$_2$O. To the suspension of 2.43 g of $[Ni(NH_3)_6](ClO_4)_2$ in 20 m*l* of water was added 1.00 g of glycine amide, and the suspension was mechanically stirred for a few minutes. When the solution containing 0.54 g of sodium hydroxide and 5 m*l* of water was dropped into the suspension with stirring, the color of the mixture changed from blue to orange brown. After the mixture was stirred for several minutes and the residue, $[Ni(NH_3)_6](ClO_4)_2$, filtered off, the filtrate was cooled in an ice bath until the desired complex began to crystallize out as orange needles. The crystals obtained were washed with water-methanol mixture (1 : 1) and with methanol and then dried in air.

Found: C, 21.89; H, 5.24; N, 25.21%. Calcd for $C_4H_{12}N_4O_3Ni$: C, 21.56; H, 5.43; N, 25.14%.

An additional crop of the complex was obtained by adding methanol to the mother liquor which was concentrated by evaporation below 35°C. Total yield, 0.7 g.

This complex is soluble in water, but the solution is not very stable. It is slightly soluble in methanol, and insoluble in ethanol, acetone, benzene and chloroform.

In the preparation above, it is also possible to use nickel(II) acetate tetrahydrate instead of $[Ni(NH_3)_6](ClO_4)_2$.

3) trans-Bis(L-alanine-amidato)nickel(II): trans-[Ni(L-alaa)$_2$]. A solution of 0.46 g of sodium hydroxide in 4 m*l* of water was gradually added to a solution containing 1.41 g of nickel(II) acetate tetrahydrate and 1.00 g of L-alanine amide in 7 m*l* of water. After about 60 m*l* of methanol was added to the mixture, the resultant orange solution was filtered. By adding 30 m*l* of methanol and about 300 m*l* of ether to the filtrate, the complex desired was crystallized out as glistening orange plates. The crystals were filtered and washed with methanol-ether mixture and then with ether and dried *in vacuo* over calcium chloride. The complex was recrystallized by adding ether to its methanolic solution. Yield, 0.9 g.

Found: C, 31.26; H, 6.11; N, 24.26%. Calcd for $C_6H_{14}N_4O_2Ni$: C, 30.90; H, 6.06; N, 24.05%.

This complex is soluble in water, but the solution is not very stable. It is soluble in methanol and ethanol, but insoluble in other organic solvents.

4) trans-Bis(L-leucine-amidato)nickel(II): trans-[Ni(L-leua)$_2$]. To a solution containing 0.93 g of purified nickel(II) sulfate heptahydrate in 30 m*l* of water was added a solution of 1.00 g of L-leucine amide in 10 m*l* of water and then the mixture was mechanically stirred. A small fraction of the desired complex already began to deposit in this step. A solution of 0.31 g of sodium hydroxide in 10 m*l* of water was added drop by drop to the mixture with stirring. The orange microplates deposited were filtered out and washed with water, methanol and ether, and then dried *in vacuo* over calcium chloride. The yield was nearly quantitative.

Found: C, 45.10; H, 8.14; N, 17.60%. Calcd for $C_{12}H_{26}N_4O_2Ni$: C, 45.46; H, 8.27; N, 17.67%.

This complex is soluble in methanol, and insoluble in water and ethanol.

5) Bis(glycine-amide)nickel(II) Sulfate Sesquihydrate: Ni(glyaH)$_2$SO$_4$·1.5H$_2$O and Bis(L-alanine-amide)nickel(II) Ni(L-alaaH)$_2$SO$_4$. These complexes were prepared by adding methanol to an aqueous solution of nickel(II) sulfate containing glycine amide or L-alanine amide. After the desired complex began to appear, the resultant mixture was stirred mechanically for a few hours. The blue crystals were soluble in water and insoluble in methanol and ethanol. The complex sulfate with L-alanine amide was very hygroscopic.

Found: C, 14.73, 14.69; H, 4.75, 4.55; N, 16.33, 16.41%. Calcd for $Ni(glyaH)_2SO_4 \cdot 1.5H_2O = C_4H_{15}N_4O_{7.5}SNi$: C, 14.56; H, 4.58; N, 16.98%.

Found: C, 21.01; H, 4.99; N, 15.18%. Calcd for $Ni(alaaH)_2SO_4 = C_6H_{16}N_4O_6SNi$: C, 21.77; H, 4.87; N, 16.93%.

The elemental analysis data fluctuated slightly, and this may be caused by a partial hydrolysis of the ligands.

An attempt to obtain the complex salt with L-leucine amide was unsuccessful because of the precipitation of insoluble [Ni(L-leua)$_2$].

6) trans-Bis(glycine-amidato)palladium(II): trans-[Pd(glya)$_2$]. Palladium(II) chloride (2.86 g) was dissolved in 130 m*l* of water with stirring and filtered once. By adding a solution of 3.00 g of glycine amide in 20 m*l* of water to the dark brown solution, a light brown precipitate appeared. When an aqueous solution of 1.30 g of sodium hydroxide was dropped into the mixture, the light brown precipitate disappeared. Within several minutes after the dissolution of the precipitate, pale yellow fine needles began to appear. The mixture was mechanically stirred until the crystals did not increase further (about 20 min). The crystals filtered off mainly consisted of the pale yellow needle crystals. The second and third crops of crystals were fractionally obtained from the mother liquor by concentrating it to 10—20 m*l* *in vacuo* at about 30°C. These second and third crops were contaminated by another kind of pale yellow crystals which were prismatic. However, the two kinds of crystals have not been separated as yet. Recrystallization was repeated until the pure *needles* were obtained, by dissolving the crude complex in water and by evaporating the solution *in vacuo* at about 30°C. The needle crystals obtained were washed with cold water and dried *in vacuo* over phosphorus pentoxide. The yield was 1.6 g in total.

Found: C, 19.08; H, 4.16; N, 21.94%. Calcd for $C_4H_{10}N_4O_2Pd$: C, 19.02; H, 3.99; N, 22.19%.

This complex is moderately soluble only in water.

7) trans-Bis(L-alanine-amidato)palladium(II): trans-[Pd(L-alaa)$_2$]. Two grams of palladium(II) chloride was suspended in a solution of 2.00 g of L-alanine amide in 20 m*l* of water, and to this suspension was added a

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[*1] The following abbreviations are used in this paper: glyaH=glycine amide, alaaH=alanine amide, and leuaH=leucine amide.

[11] P. S. Yang and M. M. Rising, *J. Am. Chem. Soc.*, **53**, 3183 (1931); G. Hillmann, *Z. Naturforsch.*, **1**, 682 (1946).

solution containing 0.90 g of sodium hydroxide in 5 m*l* of water with stirring. After the continuous stirring for about 2 hr, the palladium(II) chloride dissolved gradually. The insoluble materials were filtered off and the pale yellow filtrate was concentrated at about 30°C. When a pale yellow microplates began to separate, the mixture was diluted by adding 30 m*l* of ethanol. The whole of them was concentrated to about 10 m*l* by evaporation at about 30°C. The crystals deposited were gathered by filtration and washed with a small amount of ethanol. The mother liquor and the washings were kept for obtaining the cis complex in 8). The crude complex was recrystallized by concentrating its aqueous solution at about 30°C and then by adding methanol and ether to it. Yield, 0.7 g.

Found: C, 26.08; H, 4.96; N, 19.62%. Calcd for $C_6H_{14}N_4O_2Pd$: C, 25.68; H, 5.03; N, 19.97%.

This complex is soluble in water, slightly soluble in methanol and insoluble in ethanol.

8) cis-Bis(L-alanine-amidato)palladium(II) Monohydrate: cis-[Pd(L-alaa)$_2$]·H_2O. The combined mother liquor and washings from 7) was filtered once more. The filtrate was concentrated to half of its original volume under a reduced pressure and a few milliliters of methanol was added to the yellow solution. At this stage, a small amount of *trans*-[Pd(L-alaa)$_2$] and sodium chloride has precipitated. After those were filtered off, the desired complex, which is pale yellow, was formed by adding a large amount of ether to the filtrate. The crude complex obtained was dissolved in a small amount of methanol, and the solution was filtered. An appropriate amount of ether was added to the filtrate, and the vessel was scratched with a glass rod if necessary to obtain crystals. This purification procedure was repeated until a uniform mixture of the pure prisms was obtained. The crystals were washed with ether and dried *in vacuo* over calcium chloride. Yield, 0.6 g.

Found: C, 24.15; H, 5.34; N, 18.73%. Calcd for $C_6H_{16}N_4O_3Pd$: C, 24.13; H, 5.40; N, 18.76%.

This complex is very soluble in water, methanol and slightly soluble in ethanol.

9) trans-Bis(L-leucine-amidato)palladium(II): trans-[Pd(L-leua)$_2$]. Thirty milliliters of aqueous solution containing 1.25 g of potassium tetrachloropalladate(II) was added little by little to the solution of 1.00 g of L-leucine amide in 30 m*l* of water with stirring. A solution of 0.5 g of potassium hydroxide in 10 m*l* of water was added to the solution. The desired complex, pale yellow precipitate, began to deposit soon after. After the mixture was stirred for about 2 hr, the precipitate was filtered off, washed with water three times, and with methanol, and then with ether. This was dried *in vacuo* over calcium chloride. Yield, 0.7 g.

Found: C, 39.55; H, 7.15; N, 15.39%. Calcd for $C_{12}H_{26}N_4O_2Pd$: C, 39.51; H, 7.18; N, 15.36%.

This complex is very sparingly soluble in water, methanol and ethanol.

10) cis-Bis(L-leucine-amidato)palladium(II) Hexahydrate: cis-[Pd(L-leua)$_2$]·6H_2O. A mixture of 1.40 g of L-leucine amide in 10 m*l* of water and 0.45 g of sodium hydroxide in 15 m*l* of water were added to the suspension of 1.00 g of palladium(II) chloride in 10 m*l* of water with stirring. Being stirred for about 30 min until it became very pasty, the mixture was diluted with 60 m*l* of water. After the continuous stirring for 1 hr further, a mixed precipitate of cis and trans forms appeared: then it was filtered out (ppt. 1). After the mother liquor was concentrated to about 1/5 volume by evaporation at about 30°C, the solution was kept in a refrigerator overnight. A large amount of pale yellow fine needles (desired cis complex) were separated by filtration (ppt. 2).

The ppt. 1 was suspended in an appropriate amount of ethanol: in this procedure only the cis form dissolved. This extraction was repeated several times. When the combined extracts was kept in a refrigerator overnight, a small amount of trans form was deposited, which was discarded by filtration. The pale yellow filtrate was concentrated under reduced pressure at about 30°C until it became yellow syrup. From this syrup crystallization was started by scratching the vessel with a glass rod. This crude cis complex and the ppt. 2 obtained above were dissolved in an appropriate amount of methanol-water mixture (10 : 1). By concentrating the solution to 15 m*l* at about 30°C, a very small amount of the trans complex was deposited and then filtered off. Pure crystals of cis complex were obtained by concentrating the yellow filtrate to about 5 m*l*. The crystals, elongated rectangular plates, were gathered and washed with a little of ice water three times and dried in a desiccator over calcium chloride.

Found: C, 29.82; H, 8.03; N, 11.85%. Calcd for $C_{12}H_{38}N_4O_8Pd$: C, 30.48; H, 8.10; N, 11.85%.

The crystal form of the final product was different from that of ppt. 2, but the infrared absorption (IR) spectra of these two kinds of crystals agreed well with each other (in NaCl region) except for the bands due to crystalline water.

This complex is soluble in water, methanol and ethanol. It was noted that the cis forms of [Pd(L-alaa)$_2$] and [Pd(L-leua)$_2$] are more soluble in water and in alcohols than the corresponding trans forms.

Measurements. The following instruments were employed for the measurements: for the visible and ultraviolet absorption spectra, a Beckman DU spectrophotometer; for the diffuse reflectance spectra, a Hitachi EPU-2A spectrophotometer (in visible region) and a Hitachi EPS-3T recording spectrophotometer (in ultraviolet region); for the CD spectra, a Roussel-Jouan dichrographe; for the RD curves, a Yanagimoto recording spectropolarimeter Model-185; for the IR absorption spectra, a Model DS-402G infrared spectrophotometer of Japan Spectroscopic Co. (700—4000 cm^{-1}) and a Hitachi EPI-2 spectrophotometer (1300—1500 cm^{-1}); and finally for the nuclear magnetic resonance (NMR) spectra, a Japan Electron Optics JNM 3H-60 spectrometer using tetramethylsilane as an internal reference. All the measurements were made at room temperature.

Results and Discussion

1) Palladium(II) Complexes. The five palladium complexes obtained are classified into two groups, (A) and (B), on the basis of their absorption and diffuse reflectance spectra; (A) group consists of [Pd(glya)$_2$], [Pd(L-alaa)$_2$] and [Pd(L-leua)$_2$], and (B) group [Pd(L-alaa)$_2$]·H_2O and [Pd(L-leua)$_2$]·6H_2O. The spectral behavior of the complexes is the same in each group, but is

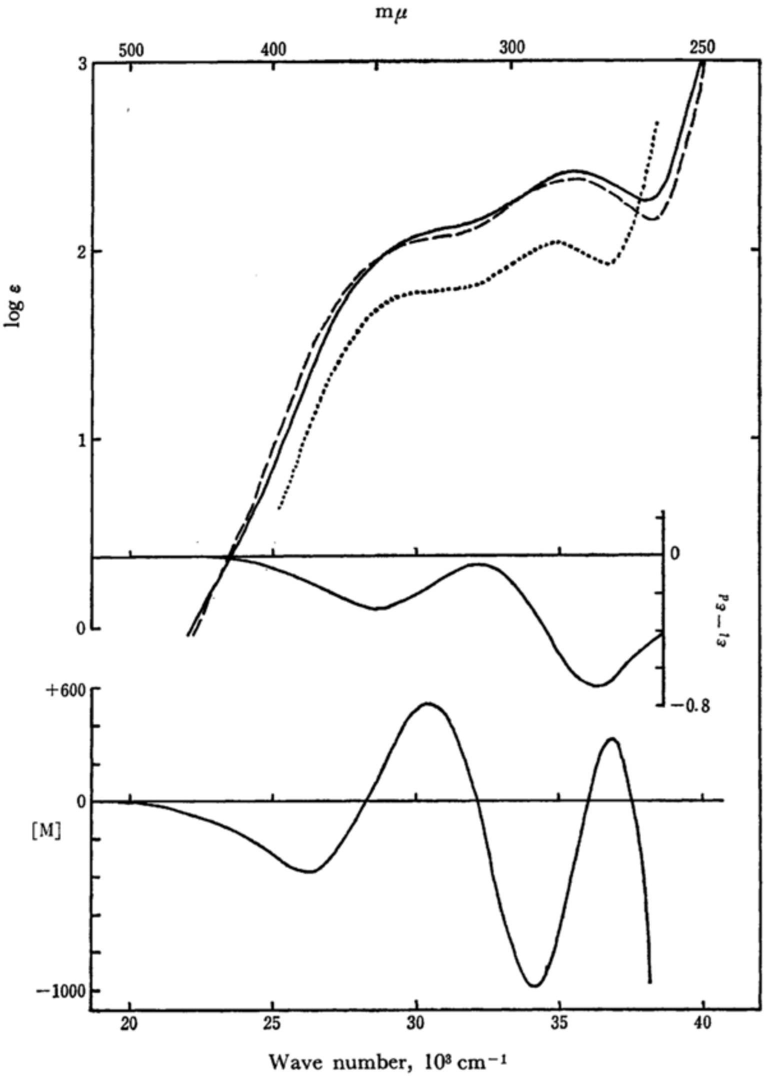


Fig. 1. Absorption and CD spectra, and RD of *trans*-[Pd(amino-acid-amidate)$_2$].

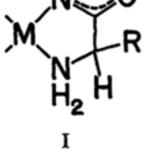
—— L-alaa complex in water; ---- glya complex in water; and ······ L-leua complex in the solid state.

remarkably different from that of the other group, as can be seen in Table 1 and Figs. 1—3.

The NMR spectra of (A) group's [Pd(L-alaa)$_2$] and of (B) group's [Pd(L-alaa)$_2$]·H_2O, in deuterium oxide, show only one kind of sharp doublet line due to the methyl protons of the ligands; τ-value of the former is 8.29 and that of the latter 8.16. This fact confirms, together with the results of the elemental analyses, that two coordinated alanine amidate ligands are not hydrolyzed. The IR spectra also support this conclusion (Table 2).

From these facts, it was concluded that the groups, (A) and (B), represent a couple of geometrical isomers, *i. e.*, cis and trans isomers concerning the two amino groups.

It may be expected that double bond character of the amidate's C–N bond is rich for the coordination type II or III in comparison with the type I.



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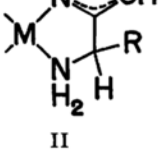

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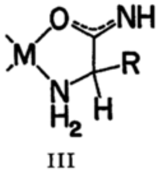

III

In IR spectra of the complexes (Table 2), very intense C–O stretching bands are observed at about 1600 cm^{-1} for both groups of complexes, (A) and (B). This behavior did not contradict[7] the theory that these palladium(II) complexes have structure I. A similar behavior of the amidate's C=O

TABLE 1. ABSORPTION MAXIMA OF THE COMPLEXES
(Wave numbers are give in $10^3\,cm^{-1}$ unit and the intensities, log ε, in parentheses)

Complex	Solvent or condition[a)]	Absorption maximum[b)]
trans-$[Pd(glya)_2]$	(S)	29.5, 34.3
	(W)	~30 sh (2.1), 35.3 (2.39)
trans-$[Pd(L\text{-}alaa)_2]$	(S)	~30 sh, 34.8
	(W)	~30 sh (2.1), 35.5 (2.41)
trans-$[Pd(L\text{-}leua)_2]$	(S)	~30 sh, 34.8
cis-$[Pd(L\text{-}alaa)_2]\cdot H_2O$	(W)	~26.7 sh (1.3), 34.7 br (2.62)
	(Me)	~26.7 sh (1.4), 34.5 br (2.63)
cis-$[Pd(L\text{-}leua)_2]\cdot 6H_2O$	(W)	~26.7 sh (1.3), 34.8 br (2.63)
	(Et)	~26.7 sh (1.4), 34.8 br (2.65)
trans-$[Ni(glya)_2]\cdot H_2O$	(S)	22.9
trans-$[Ni(L\text{-}alaa)_2]$	(S)	23.7
	(Me)	23.4 (1.77)
trans-$[Ni(L\text{-}leua)_2]$	(Me)	23.4 (1.82)
$Ni(glyaH)_2SO_4\cdot 1.5H_2O$	(S)	10.4, 13.6 sh, 15.9, ~27 br
	(W)	9.7 (0.86), 13.5 sh, 16.1 (0.73), 26.5 (0.97)
$Ni(L\text{-}alaaH)_2SO_4$	(W)	9.7, 13.5 sh, 16.0, 26.4

a) Abbreviations: S=solid, W=water, Me=methanol, and Et=ethanol.
b) sh=shoulder, br=broad band.

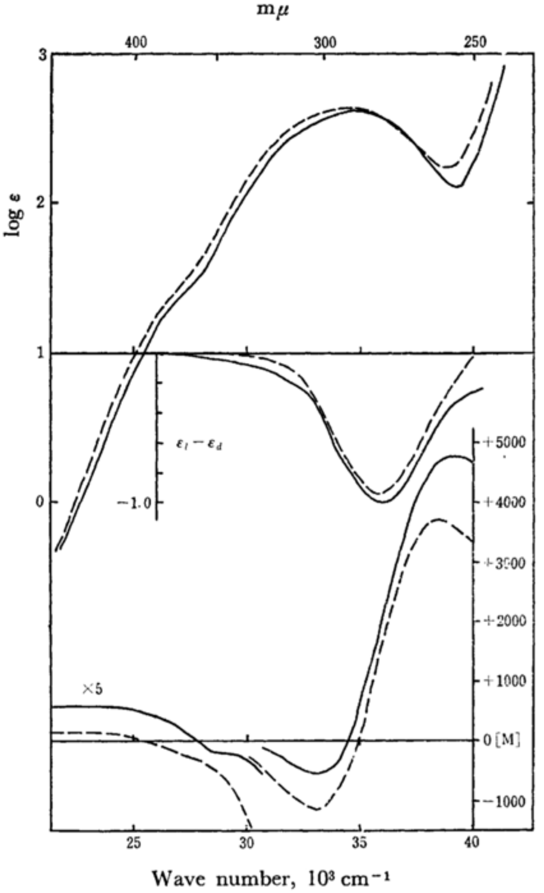

Fig. 2. Absorption and CD spectra, and RD of *cis*-$[Pd(L\text{-}alaa)_2]\cdot H_2O$.
—— in water; and ---- in methanol.

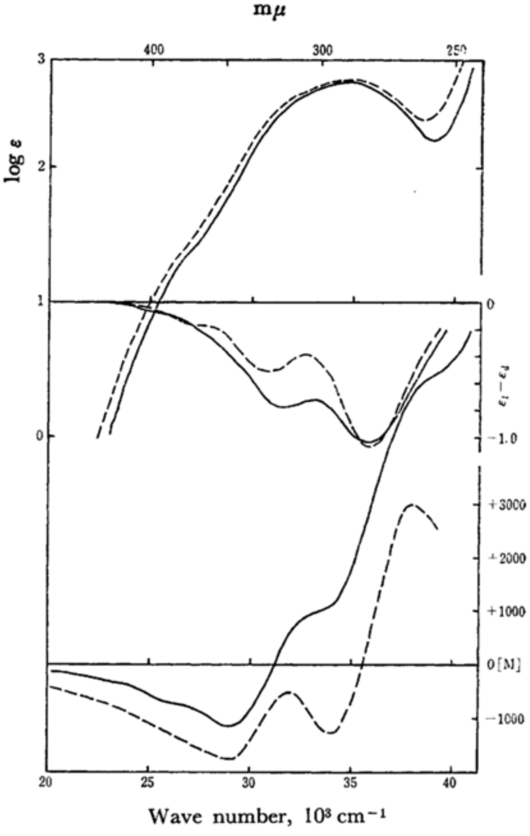

Fig. 3. Absorption and CD spectra, and RD of *cis*-$[Pd(L\text{-}leua)_2]\cdot 6H_2O$.
—— in water; and ---- in ethanol.

Table 2. IR data of the complexes in 3μ and 6μ regions, obtained with Nujol mull method
(C-H Stretching bands are omitted in 3μ region)[a,b]

trans-[Ni(glya)$_2$]·H$_2$O	3328m, 3200s, 3120s, 1630s, 1580vs, 1552s
trans-[Pd(glya)$_2$]	3310sh, 3206s, 3110s, 1620sh, 1575vs, 1552s
trans-[Ni(L-alaa)$_2$]	3300s, 3166s, 3056s, 1597vs
trans-[Pd(L-alaa)$_2$]	3296s, 3158s, 3056s, 1629m 1584vs
cis-[Pd(L-alaa)$_2$]·H$_2$O	3320w, 3250m, 3200s, 3118s, 1630m, 1600sh, 1575vs, 1550sh
trans-[Ni(L-leua)$_2$]	3310m, 3170s, 3078s, 1616s, 1595s, 1555vs
trans-[Pd(L-leua)$_2$]	3312m, 3167s, 3072s, 1605s, 1587s, 1546vs
cis-[Pd(L-leua)$_2$]·6H$_2$O	3250sh, 3210s, 3110s, 1575vs

a) Abbreviations: s=strong, m=medium, w=weak, vs=very strong, and sh=shoulder.
b) Wave number in cm^{-1}.

stretching bands has been reported in several current papers, for example, for bis(biuretato)-cuprate(II),[12] bis(oxamidato)-cuprate(II) and -nickelate(II) complexes,[7] and bis(glycine-amidato)- and bis(L-leucine-amidato)-copper(II) complexes.[10]

Now, considering the absorption spectra, we find those of (B) group's complexes are quite similar to that of tetramminepalladium(II) ion,[13] as shown in Figs. 2 and 3. From the point of view of ligand field theory, it may be concluded that the complexes belonging to (B) group are cis form of the structure I, since the effective field symmetry is approximately D_{4h} in these cis complexes even by considering a moderate π-interaction between the metal d-orbitals and the ligand π-orbitals.

Another support for the geometrical structures can be furnished by comparing their absorption spectra with those of the [Pd(Cl)$_2$(N)$_2$]-type complexes of known geometrical structures. A trans complex, [Pd(Cl)$_2$(1-phenylethylamine)$_2$], has been reported[4] to show two "spin-allowed" ligand field bands at about 25500 and 30000 cm^{-1}, while a cis(N)-type complex, [Pd(Cl)$_2$(1-pn)], shows[5] a broad band at 26200 cm^{-1} with a weak shoulder at the lower wave number side. The comparison of these data with the spectra in Figs. 1—3 clearly shows that (A) group is trans and (B) group cis.

The solution absorption spectra of *trans*-[Pd·(glya)$_2$] and *trans*-[Pd(L-alaa)$_2$] are quite similar to those in their solid states (Table 1). It may be concluded that the structures of these complexes in solution and in solid state are not very different each other. This conclusion may also be supported by the two cis complexes, though their absorption spectra slightly depended upon the solvents used (Figs. 2 and 3).

It seems likely that the σ-lone pair electrons of an amidate nitrogen alone do not give effects to the electronic structure of the complex much different from those of an amino nitrogen. Consequently, to explain the significant difference between the absorption spectra of cis and trans forms, it is necessary to consider π-interactions between the palladium 4d- and the ligand π-orbitals through metal-amidate linkages. By an inspection of the orbital overlaps, it is expected that the most sensitive one to this kind of π-interaction is the d_{xz}- or d_{yz}-orbital. If the antibonding effects are predominant, only the d_{xz}-orbital will be strongly instabilized in trans form, while both the d_{xz} and d_{yz} will be moderately instabilized in cis form. The d_{yz}-orbital of the trans form will be nearly non-interacted. Accordingly, the energy order, $\nu_4 > \nu_3' \sim \nu_4' > \nu_3$, is expected.*2 Thus the band at about 30000 (CD, 28700) cm^{-1} in *trans*-[Pd(L-alaa)$_2$] may be assigned to ν_3 while the band at about 34500 (CD, 36000) cm^{-1} in the cis form and one at 35500 (CD, 36400) cm^{-1} in the trans form to (ν_3', ν_4') and ν_4' respectively (Figs. 1 and 2).

The *cis*-[Pd(L-leua)$_2$] has two CD components at about 31300 and 36000 cm^{-1} corresponding to one broad ordinary absorption band at 24800 cm^{-1}. The component at 36000 cm^{-1} is considered to be a combined peak of ν_3' and ν_4' corresponding to 36000 cm^{-1} band of *cis*-[Pd(L-alaa)$_2$]. Therefore the CD component at 31300 cm^{-1} should be another component, ν_1' or ν_2', whose absorption component is also included in the lower wave number side of the broad absorption band at 34800 cm^{-1}. In the CD spectra of *cis*- and *trans*-[Pd(L-alaa)$_2$], the band at about 31000 cm^{-1} did not appear clearly, but it seems likely that a positive CD band is canceled out almost completely by the strong negative CD bands. These bands at about 31000 cm^{-1} may be ν_1 and ν_1', or ν_2 and ν_2'. Theoretically,[1-3] it is expected that the order is $\nu_1 > \nu_2$, and $\nu_1' > \nu_2'$. But the absorption and CD bands at the region lower than 27000 cm^{-1} in the cis complexes and the CD tail in lower wave numbers of the trans complex may be assigned to "spin-forbidden" ligand field transitions, judging from their band intensities. Also a theoretical consideration expects that the Cotton effect in

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*2 ν_1, ν_2, ν_3 and ν_4 mean transitions $(z^2)\rightarrow(x^2-y^2)$, $(xy)\rightarrow(x^2-y^2)$, $(xz)\rightarrow(x^2-y^2)$ and $(yz)\rightarrow(x^2-y^2)$ in trans form respectively, and ν_i' (i=1—4) means corresponding transition in cis form. Here, (k) means a molecular orbital composed mainly of d_k-orbital. Coordinate systems adopted for cis and trans forms are different, as in Ref. 1.

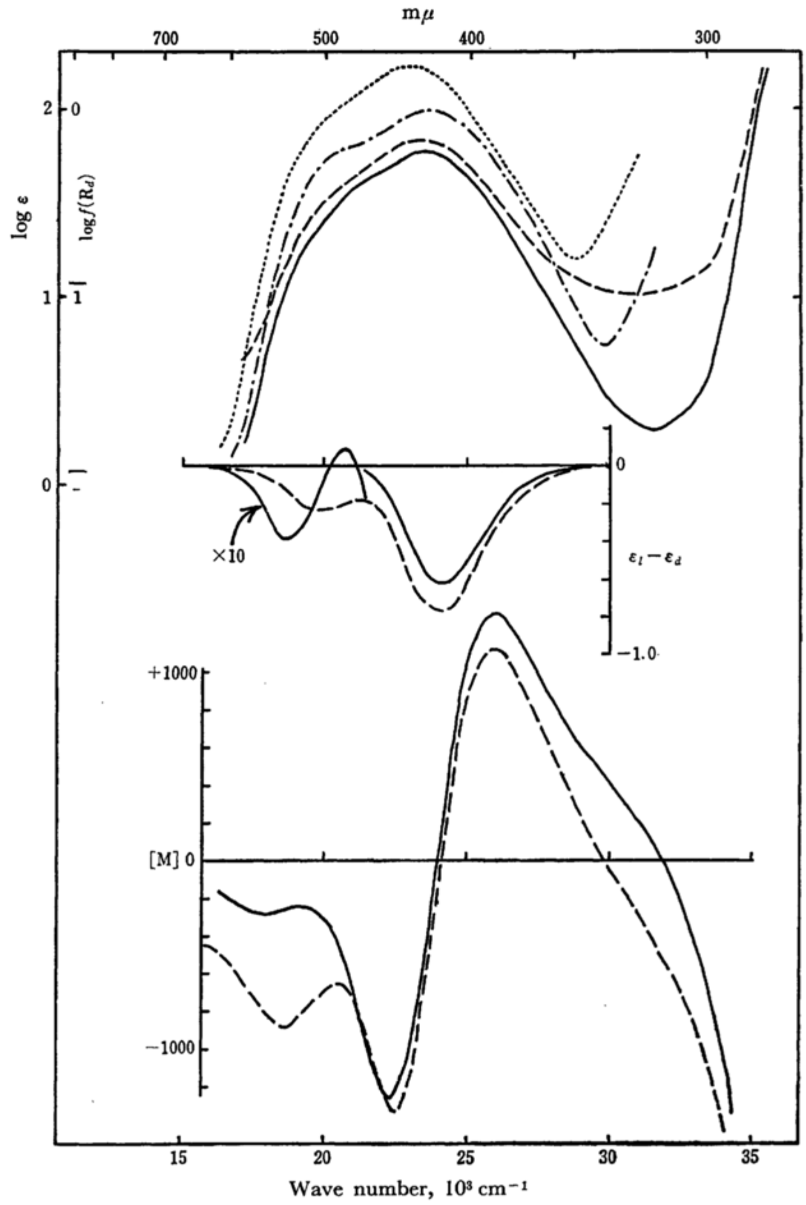

Fig. 4. Absorption and CD spectra and RD of *trans*-[Ni(amino-acid-amidate)$_2$]·xH$_2$O.
—— L-alaa complex in methanol; ---- L-leua complex in methanol; ······ glya complex in the solid state; and -·-·- L-alaa complex in the solid state. As for the x-values, see Table 2.

transitions ν_1 and ν_1' are forbidden under an appropriate approximation.*3 Therefore the present CD measurements suggest that the bands at about 31000 cm^{-1} are ν_2 and ν_2' and the transitions ν_1 and ν_1' are located in the region of higher wave numbers.

The ordering of d-levels assumed above (Table 3) agrees essentially with that proposed recently for tetrachloropalladate(II) ion.3)

2) Bis(amino-acid-amidato)nickel(II) Complexes. The diffuse reflectance spectra of the three neutral nickel(II) complexes in their solid states are very similar to those of the diamagnetic planar [Ni(N)$_4$]-type complexes,6,14) as may be seen in Fig. 4 and Table 1. Their IR spectra (Table 2 and Fig. 5) indicate that also the structure I is suitable to these complexes by the similar

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*3 Pure d-orbitals can not produce magnetic moment for transitions ν_1 and ν_1' without configuration interaction.

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TABLE 3. CD EXTREMA OF THE COMPLEXES AND THE TENTATIVE BAND ASSIGNMENTS FOR THEM
(Wave numbers are given in $10^3\,cm^{-1}$ unit and the intensities, $\varepsilon_l - \varepsilon_d$, in parentheses)

Complex	Solvent[a)]	Observed extrema and their assignments			
		ν_3	ν_2 or ν_2'	ν_4	(ν_3', ν_4')
trans-[Pd(L-alaa)$_2$]	(W)	28.7 (−0.27)		36.4 (−0.69)	
cis-[Pd(L-alaa)$_2$]·H_2O	(W)				36.0 (−1.00)
	(Me)				35.9 (−0.96)
cis-[Pd(L-leua)$_2$]·$6H_2O$	(W)		31.5 (−0.77)		36.0 (−1.06)
	(Et)		31.1 (−0.50)		36.0 (−1.07)
trans-[Ni(L-alaa)$_2$]	(Me)	18.7 (−0.04)	20.8 (+0.01)	24.1 (−0.62)	
trans-[Ni(L-leua)$_2$]	(Me)	20.0 (−0.22)		24.1 (−0.77)	

a) Abbreviations: see Table 1.

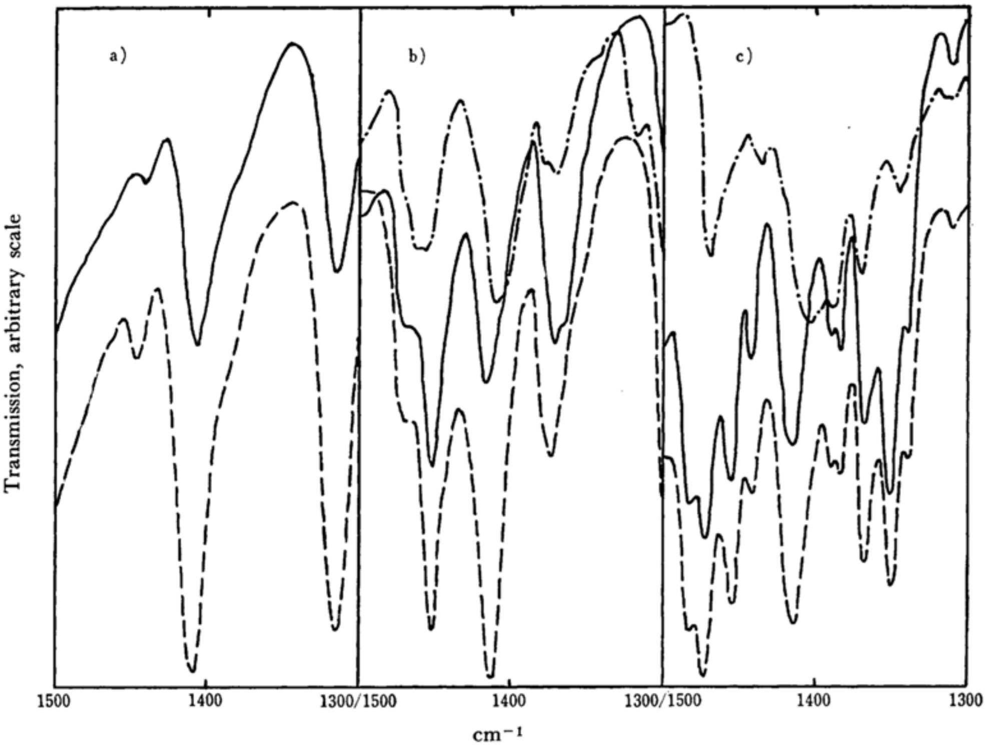

Fig. 5. IR spectra of the *cis*- and *trans*-[M(amino-acid-amidate)$_2$]·xH_2O in 1500—1300 cm^{-1} region (hexachlorobutadiene mull). a) glya-, b) L-alaa-, and c) L-leua-complexes; —— *trans*-Pd, ---- *trans*-Ni, and -·-·- *cis*-Pd complexes. As for the *x*-values, see Table 2.

reason for the palladium(II) complexes. Moreover, the IR spectra of the nickel(II) complexes show good correspondence to those of the trans palladium(II) complexes throughout NaCl region (700—4000 cm^{-1}). In Fig. 5 amidate's C–N stretching and C–H bending bands are shown; these kinds of bands have been believed to be less sensitive to the hydrogen bonding in crystal lattices. For instance, the spectra of [Ni(glya)$_2$]·H_2O and *trans*-[Pd(glya)$_2$] are very similar to each other in the region, 1300—1500 cm^{-1}. It may be concluded, therefore, that the remarkable difference between the IR spectra of the cis and the trans palladium(II) complexes in 1300—1500 cm^{-1} region should not be assigned to the difference due to the waters of hydration, but to the difference of geometrical configurations of the complexes. These observations strongly suggest that the three nickel(II) complexes concerned are the trans forms. It was confirmed, from the absorption data of Fig. 4 and in Table 1, that these trans structures were retained in their solutions also.

The band assignments of these nickel(II) complexes may be in parallel with those for the trans palladium(II) complexes. Thus the CD extrema of [Ni(L-alaa)$_2$], 18700, 20800 and 24100 cm^{-1},

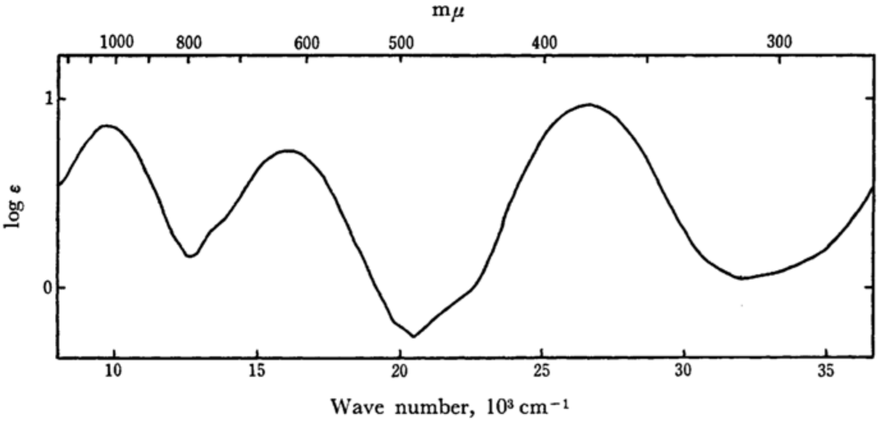

Fig. 6. Absorption spectrum of $Ni(glyaH)_2SO_4 \cdot 1.5H_2O$ in water.

are assigned to transitions ν_3, ν_2 and ν_4 respectively. It is most probable that the ν_2 band is hidden at about 21000 cm^{-1} in the CD spectrum of [Ni(L-leua)$_2$], since this complex should have an electronic structure which is not so different from that of [Ni(L-alaa)$_2$]. The rotatory strength of the band, which is assigned to ν_2 or ν_2', is strongly dependent upon the terminal alkyl groups of the ligands in both nickel(II) and palladium(II) complexes.

3) Bis(amino-acid-amide)nickel(II) Complexes. From the absorption spectra given in Table 1 and Fig. 6, it was inferred[15] that these two cationic complexes have approximately octahedral configurations, with spin triplet ground states, in the solutions and in the solid states. This hexacoordinated configuration will become possible by the coordination of sulfate ions or water molecules besides the amino acid amide ligands.

The structures of nickel(II) complexes with various amino acids[16,17] or with picoline amide,[18,19] which belong to [Ni(N)$_2$(O)$_4$]-type, have been studied previously, and it has been known that most of those complexes are of trans(N) structures. The absorption spectra of $Ni(glyaH)_2SO_4$ and Ni(L-alaaH)$_2$SO$_4$ in water (Table 1 and Fig. 6) are very similar to those of bis(glycinato)nickel(II) dihydrate[20] and of bis(picoline-amide)nickel(II) chloride dihydrate,[18] the structures of which have been determined by X-ray analyses.[16,19] In conclusion, it may be said that an oxygen of amide and an amino nitrogen are coordinated to nickel(II) in the blue complexes with glycine amide and with L-alanine amide.

It will be worthwhile to note that picoline amide, as amino acid amides, also produces a diamagnetic nickel(II) complex, bis(picoline-amidato)nickel(II) dihydrate,[18] the planar [Ni(N)$_4$]-structure of which has also been established by an X-ray analysis.[21]

The authors express their sincere thanks to Assistant Professor Tetsuo Shiba and Mr. Shuji Futakawa of Osaka University for their helpful suggestions about the preparations of amino acid amides. The authors wish to thank also Assistant Professor Fukiko Yamada of Kansai University for her measurements and discussion of the NMR spectra. Their thanks are also due to Dr. Seiko Komorita of Osaka University for her continuing interest.

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