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Metal Complexes with Amino Acid Amides. III. Geometrical Structures and Electronic Spectra of Bis(α-amino-acid-amidato)palladium(II), -nickel(II) and -copper(II)

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Square planar complexes of [ML_2] type were synthesized, where M=Pd^{2+} and Ni^{2+} for L=L-valine-, L-phenylalanine- and L-proline-amidate anions, and M=Pd^{2+}, Ni^{2+} and Cu^{2+} for L=L-leucinemethylamidate anion and for L_2=trimethylenediamine-*N,N'*-diisobutyric acid amidate dianion; the last ligand is a tetradentate one and gives exclusively *cis* type complexes. *Cis* and *trans* isomers were isolated and identified for each of the L-valinamidato and the L-prolinamidato palladium complexes. All the other complexes were inferred to be *trans* isomers from examination of the electronic absorption and circular dichroism spectra. Common solvent effects of the ligand field bands were clearly observed between the *trans* palladium and *trans* nickel complexes. A similar empirical relationship was also found between the ligand field bands of the *trans* palladium complexes and those of the corresponding *cis* isomers. The spectral behavior of the bis(L-amino-acid-amidato)-copper(II) complexes was not so easily related to that of the corresponding nickel or palladium complexes. The ligand field bands of the palladium, nickel, and copper complexes were tentatively assigned.

In the previous papers of this series,[1,2] square planar bis-chelate complexes of palladium(II), nickel(II) and copper(II) with several α-amino acid amidate ligands were reported. A pair of isomers were prepared for each of bis(L-alaninamidato)- and bis(L-leucinamidato)-palladium(II), but only one isomer was isolated for every nickel(II) and copper(II) complex examined. It has been concluded from the electronic, IR, and NMR spectra that all the complexes cited are of square planar [$M(N)_4$] type, and that the pairs of palladium(II) complexes are of *cis* and *trans* isomers. The nickel(II) and copper(II) complexes have been considered to be mostly *trans* in solid state or in solution with a few exceptions.

The most interesting fact found in the study of the electronic absorption (AB) and circular dichroism(CD) spectra of these complexes is the similarity of the ligand field bands of the *trans* nickel complexes to those of the corresponding palladium complexes.[1,3] We believe that a comparative study of CD spectra will useful for the elucidation of the electronic structure of square planar complexes. With this view in mind we decided to extend our work to the complexes with additional ligands.

The purpose of the present study is to confirm the previous conclusion concerning the geometrical structures of the bis(α-amino-acid-amidato) complexes, and to investigate their AB and CD spectra more extensively. Bis(α-amino-acid-amidato) type complexes of palladium(II), nickel(II), and copper(II) were prepared with some optically active L-α-amino-acid amides and with a tetradentate ligand which gives *cis* type complexes exclusively.

Experimental

Materials. 1) Ligands:[4] *Trimethylenediamine*-N,N'-*diisobutyric Acid Amide*: *tndbaH$_2$*: When trimethylenediamine dihydrochloride was used in place of the ethylenediamine analog in Schlesinger's method for ethylenediamine-*N,N'*-diisobutyronitrile,[5] trimethylenediamine-*N,N'*-diisobutylonitrile was obtained from the ether layer as rhombic plates in good yield. This compound is soluble in ether; mp 90—92°C (uncorr.).

Found: C, 63.68; H, 9.81; N, 26.86%. Calcd for $C_{11}H_{20}N_4$: C, 63.43; H, 9.68; N, 26.90%.

The dinitrile (17.7 g) was suspended in 75 m*l* of concentrated hydrochloric acid under ice cooling and the mixture was allowed to stand overnight at room temperature. The dinitrile was then dissolved. When necessary, hydrogen chloride gas was bubbled into the mixture in order to complete the dissolution. The dihydrochloride salt of the desired compound was obtained as white crystals from the solution by diluting with equivolume of water and cooling in an ice bath. The crystals were filtered off and washed with methanol and then ether. Recrystallization was carried out by concentrating the aqueous solution *in vacuo*. The yield was good.

Found: C, 41.44; H, 8.36; N, 17.37%. Calcd for $C_{11}H_{26}N_4O_2Cl_2$: C, 41.64; H, 8.26; N, 17.66%.

The desired amide tndbaH$_2$ was derived from the dihydrochloride by ion exchange chromatography with Amberlite IRA-410 (OH^--type). This was recrystallized from chloroform and dried at 60°C *in vacuo*. Elongated rectangular plates; mp 140.5—141.5°C (uncorr.).

Found: C, 54.03; H, 9.98; N, 22.88%. Calcd for $C_{11}H_{24}N_4O_2$: C, 54.07; H, 9.90; N, 22.93%.

Other Ligands: L-Valinamide, L-Phenylalaninamide and L-prolinamide were prepared as described elsewhere.[2] L-Leucinemethylamide was prepared according to literature;[6] bp 97—106°C/2 mmHg.

2) [Pd(tndba)]·5H$_2$O: Forty milliliters of aqueous solution containing 0.75 g of lithium tetrachloropalladate-

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[1] Part I: T. Komorita, J. Hidaka, and Y. Shimura, This Bulletin, **41**, 854 (1968).

[2] Part II: T. Komorita, J. Hidaka, and Y. Shimura, *ibid.*, **42**, 168 (1969).

[3] T. Komorita, J. Hidaka, and Y. Shimura, *ibid.*, **42**, 1782 (1969).

[4] The following abbreviations are used for ligands: alaaH= alaninamide, leuaH=leucinamide, valaH=valinamide, phalaaH= phenylalaninamide, proaH=prolinamide, leumaH=leucinemethylamide and tndbaH$_2$=trimethylenediamine-*N,N'*-diisobutyric acid amide.

[5] N. Schlesinger, *Ber.*, **44**, 1135 (1911).

[6] A. Rosenberg, *Acta Chem. Scand.*, **11**, 1390 (1957).

(II)[7] was added to a solution of 0.76 g of tndbaH_2 in 35 m*l* of water with stirring. When a clear solution was obtained after stirring for several minutes, the brownish yellow solution was carefully neutralized under pH adjustment with 1 N lithium hydroxide. It took about 100 min for neutralization. The end point was detected when it was observed that the pH was retained at 7.3 for 30 min without further addition of alkali. A crude complex was obtained from the pale yellow solution by concentrating it to near dryness and adding a small amount of ethanol and a large amount of acetone. Purification was performed by ion exchange chromatography with the required amount of 1 : 2 mixture (by volume) of Amberlite IR-120B (H^+-type) and IRA-410 (OH^--type). The eluate was concentrated *in vacuo* below 35°C until the complex began to crystallize and allowed to stand under ice cooling. The pale yellow needles were filtered off, washed with a small volume of cold water twice and dried in air.

Found: C, 30.12; H, 7.34; N, 12.59%. Calcd for $C_{11}H_{32}N_4O_7Pd$: C, 30.11; H, 7.35; N, 12.77%.

3) trans-$[Pd(\text{L-vala})_2]$ *and* cis-$[Pd(\text{L-vala})_2]\cdot 0.5H_2O$: Twenty milliliters of aqueous solution containing 1.48 g of lithium tetrachloropalladate(II)[7] was added to a solution of 1.44 g of L-valaH in 20 m*l* of water with stirring. The resulting brown solution was treated with 0.5 N lithium hydroxide in a similar way to that for 2). The pale yellow solution was concentrated *in vacuo* until it became a syrup. Most of the lithium chloride was removed from the syrup by dissolving it in a few m*l* of ethanol and then by extracting it three times with 30 m*l* of ether each time. The same purification procedure was repeated once more. The residual viscous syrup was dissolved in 50 m*l* of 99% ethanol. To this solution, 450 m*l* of ether was added little by little, and the mixture was kept in a refrigerator overnight. After the supernatant solution was removed by decantation, the precipitate was dissolved in 50 m*l* of 99% ethanol again, and reprecipitated carefully from this solution by adding 500 m*l* of ether. At this stage, the crude complex (a *cis-trans* mixture) was obtained as a fine powder, which was washed with ether and dried *in vacuo*. The mixture was fractionally recrystallized by addition of acetone to the concentrated aqueous solution. All fractions of the fibrous crystals, which were washed with a (1 : 10) water-acetone mixture and then with acetone, were collected (1.23 g). Then the contaminated lithium chloride was completely eliminated with an ion exchange column as described in 2). The eluate was concentrated by a rotary evaporator, and then diluted to about one fifth of the saturated concentration. Isolation of the *cis* and *trans* isomers from this solution was performed by fractional crystallization with acetone. Purity of the isomers was checked by the uniformity of the crystals as well as by the reproducibility of the CD spectrum. The *trans* isomer was isolated as glistening fine plates, which had been suspended in the solution at the beginning of crystallization and grew rather slowly. On the other hand, the cis isomer grew more rapidly from the wall of a beaker as prisms, and its aqueous solution was inclined to be supersaturated.

The *trans* isomer: dried over calcium chloride.

Found: C, 35.50; H, 6.24; N, 16.49%. Calcd for $C_{10}H_{22}N_4O_2Pd$: C, 35.67; H, 6.59; N, 16.64%.

The *cis* isomer: dried in the atmosphere.

Found: C, 34.78; H, 6.74; N, 16.15%. Calcd for $C_{10}H_{23}N_4O_{2.5}Pd$: C, 34.74; H, 6.71; N, 16.21%.

Both isomers are pale yellow, and soluble in water, methanol, ethanol, and *N,N*-dimethylformamide (DMF).

4) trans-$[Pd(\text{L-phalaa})_2]$: A solution of 1.50 g of L-phalaaH in 25 m*l* of water was slowly added to 60 m*l* of an aqueous solution containing 1.10 g of lithium tetrachloropalladate(II).[7] Together with the brownish precipitate, the whole mixture was subjected to a similar neutralization procedure as in 2). The color of both the precipitate and the supernatant solution then changed to pale yellow. The mixture was continuously stirred for 2 additional hr. Yield of the precipitate, or the desired complex in a crude state, was 1.48 g (82%). This could be recrystallized from a (1 : 2) water-methanol mixture; dried *in vacuo* over phosphorus pentoxide; pale yellow plates; soluble in methanol and ethanol, and slightly soluble in DMF.

Found: C, 50.09; H, 5.17; N, 12.86%. Calcd for $C_{18}H_{22}N_4O_2Pd$: C, 49.95; H, 5.12; N, 12.95%.

5) trans-$[Pd(\text{L-proa})_2]\cdot 0.5H_2O$ *and* trans-$[Pd(\text{L-proa})_2]\cdot CH_3OH$: To a solution containing 1.41 g of L-proaH in 40 m*l* of water was added 1.00 g of a powdered palladium(II) chloride, and the suspension was continuously stirred until most of the palladium(II) chloride was dissolved. This took about 40 min. The mixture was then neutralized with an anion exchange resin, Dowex 1×8 (50—100 mesh) of OH^--type. The resin was added little by little with mechanical stirring so that the pH of the mixture was kept under 8. A precipitate was produced at the beginning of the neutralization procedure, but it disappeared as the reaction proceeded. The end point of the neutralization was determined in the same way as in 2). The whole procedure took about 5 hr, and about twice the calculated amount of anion exchange resin was needed. The resin and the residual starting material were discarded by filtration. From the resulting yellow solution, the desired *trans* complex was isolated as a hemihydrate or a methanol adduct. The total yield of the *trans* complexes was 47%, but we could not isolate the *cis* isomer in this procedure.

Hemihydrate: The yellow solution prepared as above was concentrated *in vacuo*. An appropriate amount of acetone was added to the solution and the mixture was cooled in an ice bath. The yellow microcrystals were collected on a glass filter, washed with (1 : 10) water-acetone mixture and acetone, and dried over calcium chloride. Very long plates.

Found: C, 35.62; H, 5.59; N, 16.15%. Calcd for $C_{10}H_{19}N_4O_{2.5}Pd$: C, 35.15; H, 5.60; N, 16.40%.

Methanol Adduct: The yellow solution prepared as above was concentrated to dryness *in vacuo*. The residuals were dissolved in methanol and the methanol solution was concentrated *in vacuo*. The yellow prisms were washed with a small amount of methanol, acetone, and ether, and dried over phosphorus pentoxide *in vacuo*.

Found: C, 35.85; H, 6.00; N, 15.54%. Calcd for $C_{11}H_{22}N_4O_3Pd$: C, 36.23; H, 6.08; N, 15.36%.

Both the hemihydrate and the methanol adduct are soluble in water, methanol, and ethanol.

6) cis-$[Pd(\text{L-proa})_2]\cdot 3.5H_2O$: A solution containing 1.48 g of lithium tetrachloropalladate(II)[7] in 60 m*l* of water was mixed with a solution of 1.41 g of L-proaH in 20 m*l* of water. The mixture was neutralized with 0.5 N lithium hydroxide in the same way as that in 2). The yellow solution was concentrated to one fifth of its original volume *in vacuo* and treated with an ion exchange column as in 2), where about twice the calculated amount of resin was used. The first fraction of crystalline products was deposited when the eluate was concentrated to a few m*l*. From the mother liquor two additional fractions were obtained by fractional addition of acetone. Each fraction consisted mainly of

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[7] In practice, lithium chloride and palladium(II) chloride were dissolved in water.

needle crystals and was contaminated by a small amount of plates, or the *trans* isomer. The first two fractions, rich in *cis* isomer, were combined and fractionally recrystallized from the aqueous solution by addition of acetone. The pure *cis* complex consisted of fine yellow needles. Its purity was checked by the CD spectrum as it was difficult to distinguish it from the *trans* complex by their crystal forms only. The sample for elemental analyses was dried in air.

Found: C, 30.28; H, 6.34; N, 14.06%. Calcd for $C_{10}H_{25}N_4O_{5.5}Pd$: C, 30.35; H, 6.37; N, 14.16%.

This complex is soluble in water, methanol, ethanol and DMF. Total yield of the crude complex, contaminated with a small amount of the *trans* isomer, was rather low, 0.71 g (*ca.* 32%). It should be added that considerable amounts of both isomers were separated from the column used in the above preparation when eluted with a concentrated sodium chloride solution.

7) trans-*[Pd(*L*-leuma)$_2$]*: A solution containing 1.32 g of lithium tetrachloropalladate(II)[7] in 70 m*l* of water was added to 80 m*l* of an aqueous solution containing 1.58 g of L-leumaH with stirring. The brown solution was neutralized as in 2) by use of 0.5 N lithium hydroxide. When the resulting solution was concentrated *in vacuo*, the desired complex was deposited as yellow hexagonal plates; yield, 1.85 g (94%). It was recrystallized by concentrating the aqueous solution *in vacuo*. The pure crystals were washed with water and then dried over calcium chloride.

Found: C, 42.53; H, 7.78; N, 14.08%. Calcd for $C_{14}H_{30}N_4O_2Pd$: C, 42.81; H, 7.70; N, 14.26%.

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

8) Nickel(II) Complexes: The preparation procedure for these complexes is similar to that for *trans*-bis(L-alaninamidato)nickel(II);[1] an aqueous solution of the ligand (2.2 equivalent amount[8]) and then 1 N sodium hydroxide (2 equiv.) were added to an aqueous solution of nickel(II) acetate (1 equiv.). The desired complex was obtained from the resulting orange colored solution.

[Ni(tndba)]·H$_2$O: The orange yellow solution was concentrated to a small volume (*ca.* 5 m*l*/1 g of the ligand used) and then diluted with a large amount (about 8 times) of ethanol. Sodium acetate and the desired complex were fractionally precipitated from the solution by adding ether gradually. The complex was recrystallized by adding ether to a 95% ethanol solution, the concentration of which had been adjusted to about half as saturated. The sample for elemental analyses was dried over calcium chloride overnight. Deep yellow pillars.

Found: C, 41.43; H, 7.56; N, 16.94%. Calcd for $C_{11}H_{24}N_4O_3Ni$: C, 41.41; H, 7.58; N, 17.56%.

trans-*[Ni(*L*-vala)$_2$]·2H$_2$O*: The complex was obtained by adding methanol and then ether to the concentrated mother solution; dried in air as orange prisms; soluble in water (not very stable), methanol, ethanol, and DMF.

Found: C, 36.95; H, 7.72; N, 16.98%. Calcd for $C_{10}H_{26}N_4O_4Ni$: C, 36.95; H, 8.06; N, 17.24%.

trans-*[Ni(*L*-phalaa)$_2$]*: Recrystallized from a methanol solution by vacuum evaporation; dried *in vacuo* over phosphorus pentoxide; orange plates; soluble in methanol, ethanol and DMF.

Found: C, 56.16; H, 5.85; N, 14.30%. Calcd for $C_{18}H_{22}N_4O_2Ni$: C, 56.14; H, 5.76; N, 14.55%.

trans-*[Ni(*L*-proa)$_2$]·2H$_2$O*: Recrystallized from an aqueous solution by vacuum evaporation; dried over phosphorus pentoxide; orange pillars; soluble in water, methanol, ethanol, and DMF.

Found: C, 37.56; H, 6.96; N, 17.30%. Calcd for $C_{10}H_{22}N_4O_4Ni$: C, 37.42; H, 6.91; N, 17.45%.

trans-*[Ni(*L*-leuma)$_2$]·H$_2$O*: Recrystallized by adding ether to an ethanol solution; dried over phosphorus pentoxide; orange plates; soluble in methanol, ethanol and DMF, but rapidly decomposed in water.

Found: C, 46.58; H, 8.72; N, 15.45%. Calcd for $C_{14}H_{32}N_4O_3Ni$: C, 46.30; H, 8.88; N, 15.43%.

9) Cu(tndba)·1.5H$_2$O: Copper(II) hydroxide, freshly prepared from 0.93 g of copper(II) sulfate pentahydrate, was added to a solution containing 0.91 g of tndbaH$_2$ in 15 m*l* of water. The mixture was continuously stirred until a homogeneous red solution was obtained; it took about 100 min. It was filtered and concentrated *in vacuo* until it became a viscous syrup. The syrup was mixed with 2 m*l* of absolute ethanol and then with 150 m*l* of acetone, and allowed to stand in a refrigerator after scratching the vessel with a glass rod. Crystallization proceeded very slowly. Brick-red crystals. The sample for elemental analyses was dried over calcium chloride overnight.

Found: C, 40.19; H, 7.71; N, 16.78%. Calcd for $C_{11}H_{25}N_4O_{3.5}Cu$: C, 39.69; H, 7.57; N, 16.83%.

*10) Cu(*L*-leuma)$_2$*: Copper(II) hydroxide freshly prepared from 0.87 g of copper(II) sulfate pentahydrate was added to a solution of 1.00 g of L-leumaH in 20 m*l* of water. The mixture was stirred for 30 min. The residual copper(II) hydroxide was then filtered off. The violet solution was concentrated *in vacuo* below 35°C until the brick-red crystals of the desired complex began to separate out. The whole mixture was then dissolved in 40 m*l* of ethanol. The complex was precipitated from the solution by slow addition of ether, and recrystallized from its 99% ethanol solution by addition of ether. The crystals were dried over calcium chloride and then over phosphorus pentoxide *in vacuo*. Yield, 0.73 g (60%).

Found: C, 47.64; H, 8.64; N, 15.61%. Calcd for $C_{14}H_{30}N_4O_2Cu$: C, 48.05; H, 8.64; N, 16.01%.

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

Measurements. The instruments and solvents employed for measurements of AB and CD spectra were the same as those reported,[2] except for the Shimadzu MPS-50L spectrophotometer used for AB measurements in Nujol mulls. All the measurements were carried out at room temperature.

Both the hemihydrate and the methanol adduct of *trans*-bis(L-prolinamidato)palladium(II) hardly dissolved into DMF, but the AB and CD spectra of the complex in this solvent could be obtained with material prepared by a method analogous to that for *trans*-bis(L-alaninamidato)-palladium(II).[1] The material dissolved somewhat easily in DMF. It was confirmed from its AB and CD spectra in the aqueous and alcoholic solutions and elemental analysis that it is composed of *trans*-[Pd(L-proa)$_2$] and sodium chloride at a mole ratio of about 3 : 1 (Found: C, 34.24; H, 5.30; N, 15.73; Cl, 2.63%.).

Results and Discussion

Spectral data for the complexes newly prepared are given in Tables 1, 2, and 4—7, and in Figs. 1—7 and 9—14. Supplementary data which were obtained for several complexes previously reported are also included in Tables 1, 2 and 4—7. Discussion in this section will be made in reference to the data given in the previous papers for the bis(L-α-amino-

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[8] 1.1 Equivalent amount for tndbaH$_2$.

TABLE 1. AB MAXIMA OF THE PALLADIUM COMPLEXES

Complex	Solvent[a]	Maxima[b,c]		
trans-[Pd(L-alaa)$_2$]	(Me)	~30sh (2.1)	35.5 (2.44)	
trans-[Pd(L-vala)$_2$]	(W)	~30sh (2.1)	35.5 (2.45)	
	(Et)	~29sh (2.0)	35.5 (2.46)	
	(DMF)	28.1 (2.07)	~35sh (2.6)	
trans-[Pd(L-phalaa)$_2$]	(Et)	~29sh (1.95)	35.5 (2.37)	37.4 (2.59) 37.9 (2.70) 38.7sh (2.9)
	(DMF)	28.4 (2.00)	~35sh (2.5)	
trans-[Pd(L-proa)$_2$]·0.5H$_2$O	(W)	~30sh (2.2)	35.5 (2.52)	
	(Et)	~29sh (2.1)	35.5 (2.54)	
	(DMF)[d]	28.1 (2.04)	~35sh (2.6)	
trans-[Pd(L-leuma)$_2$]	(W)	~29sh (2.05)	35.3 (2.43)	
	(Et)	28.7 (2.03)	~35.5sh (2.5)	
	(DMF)	26.9 (2.03)	~35.5sh (2.6)	
cis-[Pd(L-leua)$_2$]·6H$_2$O	(DMF)	~27sh (1.6)	~31sh (2.5)	35.3 (2.79)
cis-[Pd(L-vala)$_2$]·0.5H$_2$O	(W)	~26.7sh (1.3)	~32sh (2.5)	34.8 (2.64)
	(Et)	~26.5sh (1.4)	~31.5sh (2.5)	34.7 (2.65)
	(DMF)	~27sh (1.6)	~31sh (2.5)	35.3 (2.81)
cis-[Pd(L-proa)$_2$]·3.5H$_2$O	(W)	~27sh (1.5)	~31sh (2.3)	35.3 (2.61)
	(Et)	~27sh (1.7)	~31sh (2.3)	35.3 (2.66)
	(DMF)	~27sh (1.8)	~30.5sh (2.3)	35.9sh (2.79)
[Pd(tndba)]·5H$_2$O	(W)	~27sh (1.2)	34.7 (2.59)	

a) W=water, Me=methanol, Et=ethanol, and DMF=*N,N*-dimethylformamide.
b) Wave numbers are given in 10^3 cm^{-1} unit and the intensities, log ε, in parentheses.
c) sh=shoulder. d) For data, see Experimental.

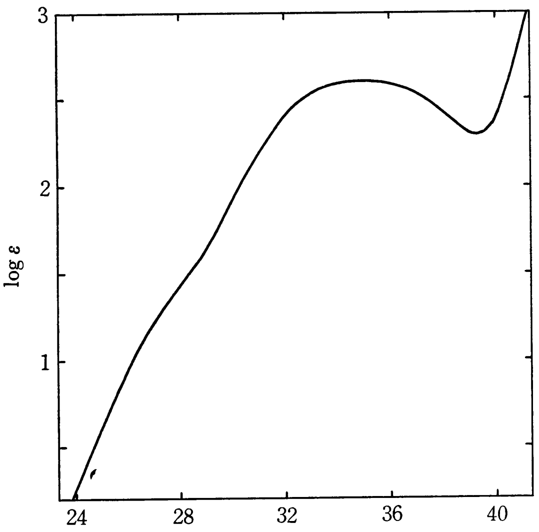

Fig. 1. AB spectrum of [Pd(tndba)] in water.

acid-amidato) complexes. Several AB and CD curves are reproduced in Figs. 5 and 14.

Cis-Trans *Isomerism and Spectral Behavior.* *1) Palladium(II) Complexes*: The absorption spectrum of [Pd(tndba)] given in Fig. 1 and Table 1 is analogous to the spectra of the bis(amino-acid-amidato)palladium(II) complexes, which have been classified into group (B) in Part I.[1] This indicates definitely that the latter complexes have *cis* structures, because the two amino groups of the tndba moiety must be *cis* to each other in the former complex. This is just the conclusion drawn in Part I.[1]

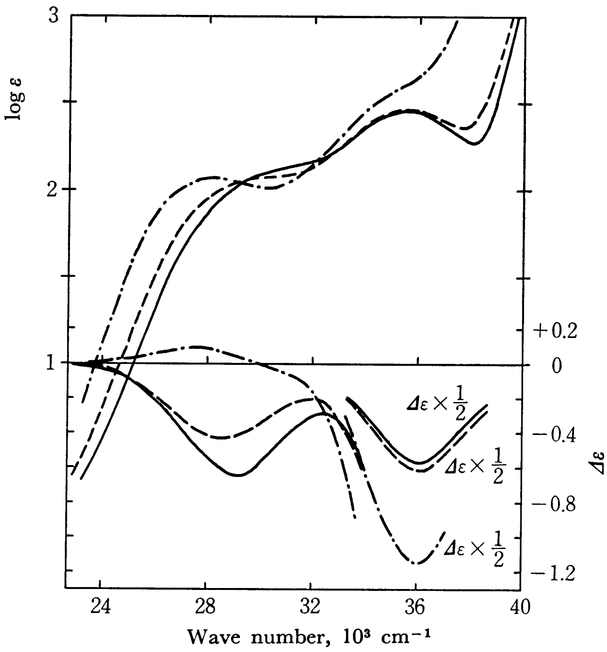

Fig. 2. AB and CD spectra of *trans*-[Pd(L-vala)$_2$] in water (——), in ethanol (----), and in DMF (—·—·).

It was well confirmed by the CD spectra in Table 2, Fig. 4 and Fig. 2 of Ref. 3 that the *trans*-bis(α-amino-acid-amidato)palladium(II) complexes generally have three bands in the ligand field band region: at 26.8—29.2, 31.4—32.3 and 35.5—36.4 kK (kK=10^3 cm^{-1}). These bands (as well as the corresponding components of AB band) will be called tI, tII and tIII, respectively, in this paper.

Table 2. CD extrema of the palladium complexes

Complex	Solvent	Extrema[a)] tI	tII	tIII	Benzenoid
trans-[Pd(L-alaa)$_2$]	(Me)	27.1(−0.03)	31.6(+0.05)	36.4(−0.79)	
trans-[Pd(L-vala)$_2$]	(W)	29.2(−0.65)		36.1(−1.15)	
	(Et)	28.6(−0.43)		36.1(−1.21)	
	(DMF)	27.6(+0.08)		36.1(−2.31)	
trans-[Pd(L-phalaa)$_2$]	(Et)	28.4(−0.32)		36.1(−1.12)	37.4(−1.25) 38.3(−1.17)
	(DMF)	27.2(+0.20)		36.2sh(−2.46)	
trans-[Pd(L-proa)$_2$]·0.5H$_2$O	(W)	28.8(−1.15)		36.3(−1.16)	
	(Et)	28.1(−0.98)	32.0(+0.04)	36.2(−1.74)	
	(DMF)[b)]	26.8(−0.39)	31.4(+0.15)	36.0(−3.0)	
trans-[Pd(L-leuma)$_2$]	(W)	28.1(−0.80)	32.3(+0.01)	36.1(−0.85)	
	(Et)	27.3(−0.55)		35.8(−1.15)	
	(DMF)	27.1(+0.26)		35.5(−2.15)	
		c0	cI	cII	cIII
cis-[Pd(L-leua)$_2$]·6H$_2$O	(DMF)	~27sh(−0.06)	29.6(−0.12)	32.4(+0.05)	36.4(−0.58)
cis-[Pd(L-vala)$_2$]·0.5H$_2$O	(W)	~27sh(−0.2)	31.7(−0.96)		35.7(−1.23)
	(Et)	~27sh(−0.2)	30.7(−0.82)		36.1(−1.26)
	(DMF)	~27sh(−0.1)	30.1(−0.28)		36.3(−0.83)
cis-[Pd(L-proa)$_2$]·3.5H$_2$O	(W)	~27sh(−0.2)	30.8(−0.91)		36.8(+0.33)
	(Et)	~27sh(−0.3)	30.7(−0.90)		36.8(+0.12)
	(DMF)	~26.5sh(−0.3)	30.0(−0.62)		36.5(−0.2)

a) Wave numbers are given in 10^3 cm^{-1} unit and the intensities, $\Delta\varepsilon=\varepsilon_l-\varepsilon_d$, in parentheses.
b) For data, see Experimental.

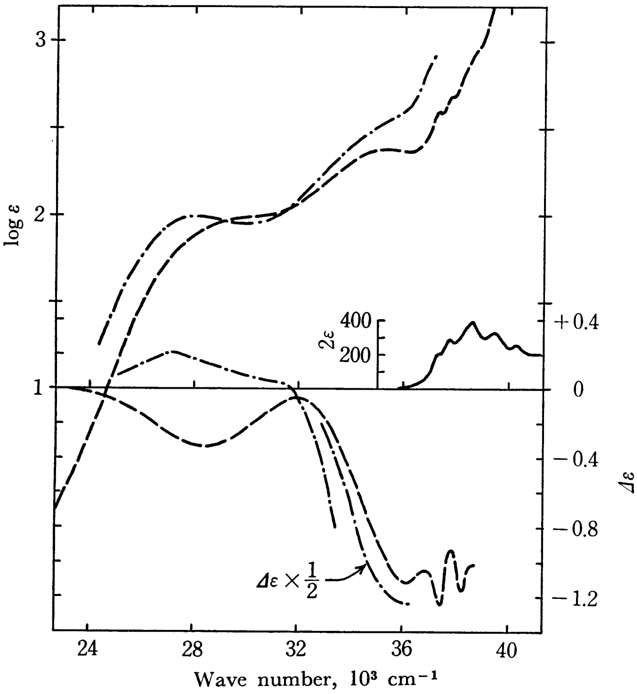

Fig. 3. AB and CD spectra of *trans*-[Pd(L-phalaa)$_2$] in ethanol (———) and in DMF (—·—·), and AB spectrum of L-phalaaH in ethanol (——).

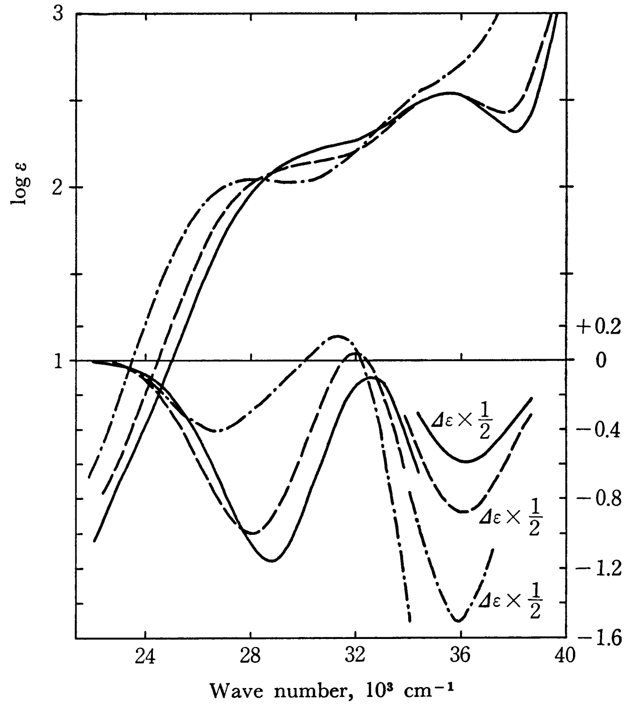

Fig. 4. AB and CD spectra of *trans*-[Pd(L-proa)$_2$] in water (——), in ethanol (———) and in DMF (—·—·).

With respect to the *cis* complexes, four kinds of CD band were observed; these (and the corresponding components of AB band) are labeled c0, cI, cII and cIII as shown in Table 2. Since the situation of the four bands would not differ much among the complexes (Figs. 5—7, and Fig. 2 of Ref. 1), it is conceivable that cII bands are hidden in the CD spectra of all of the *cis* complexes other than the leua complex.

No reliable method for AB and CD band analyses

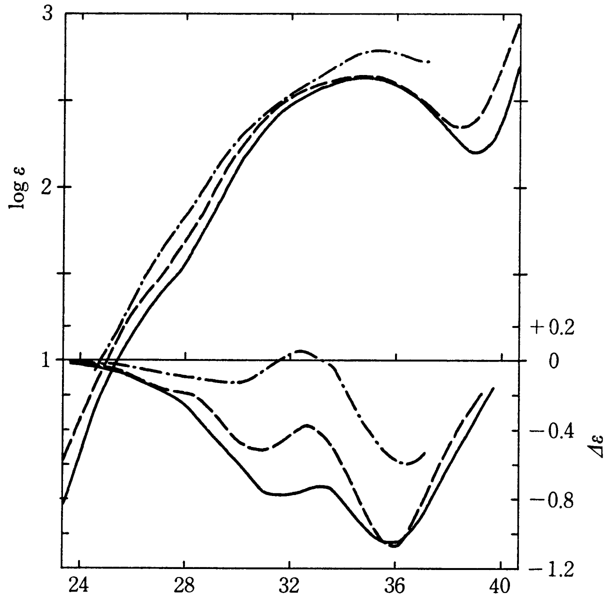

Fig. 5. AB and CD spectra of *cis*-[Pd(L-leua)$_2$] in water (——), in ethanol (– – –), and in DMF (—·—·).

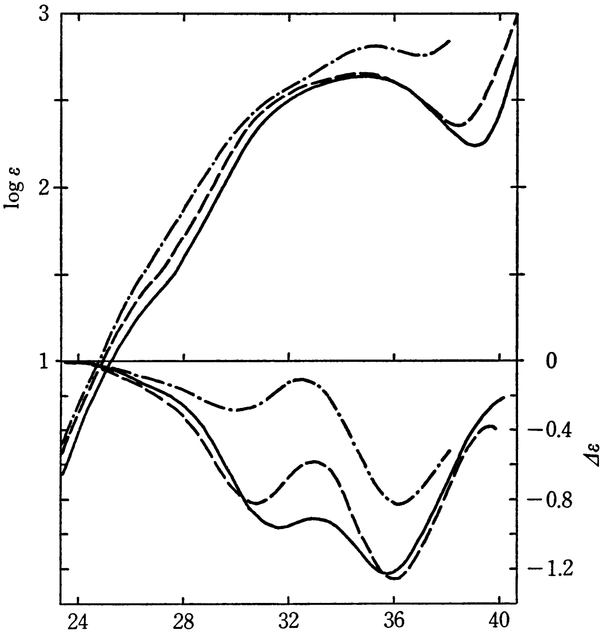

Fig. 6. AB and CD spectra of *cis*-[Pd(L-vala)$_2$] in water (——), in ethanol (– – –), and in DMF (—·—·).

has so far been established, especially for the bands which contain three or more components with comparable intensities. The results of band analyses given in Table 3 are accordingly somewhat arbitrary, but probable at the present stage since they were obtained from the data for a series of closely related complexes. The molar extinction coefficients estimated for cII and tII are the most unreliable of the numerical values in Table 3 but nevertheless seem to be comparable to those for cI and tI, respectively.

Figure 8 illustrates the general CD behavior exhibited by the palladium complexes as the solvent was changed from water, ethanol to DMF; only a significant deviation from the general CD behavior was found in the cIII band of the proa complex (See Fig. 7).

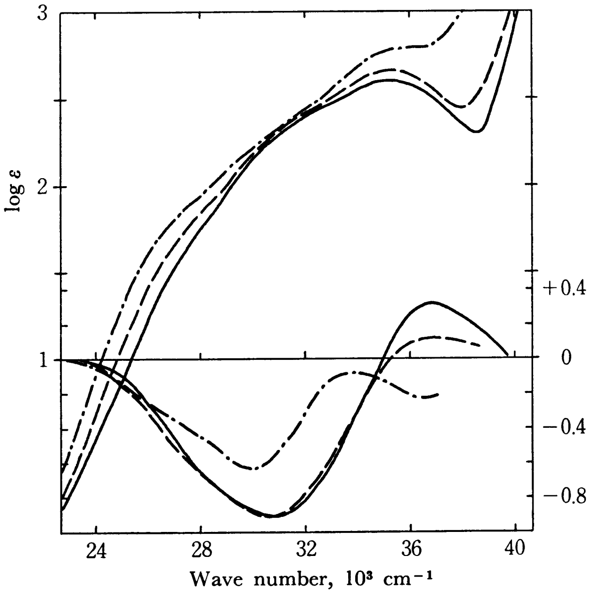

Fig. 7. AB and CD spectra of *cis*-[Pd(L-proa)$_2$] in water (——), in ethanol (– – –), and in DMF (—·—·).

Table 3. General feature of the ligand field bands of the palladium complexes

Band component	Wave number, 10^3 cm^{-1}	ε
tI	~28.5	~100
tII	~32.3	~100
tIII	~36.0	~300
c0	~27.0	~25
cI	~31.2	~200
cII	~33.3	~150
cIII	~36.0	~350

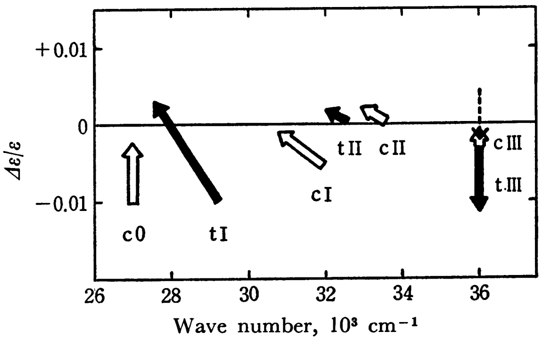

Fig. 8. Changes in the CD of the palladium complexes caused by the change of solvent from water, ethanol to DMF. The broken arrow shows the exceptional behavior of the cIII band of the proa complex.

Two important facts found in Table 3 and Fig. 8 are that characteristics of tI, tII and tIII bands show a close resemblance to those of cI, cII and cIII, respectively, and that the sign inversion for a single CD band is actually caused in the tI and the cIII bands of a few complexes by change of only the solvent.

2) *Nickel(II) Complexes*: The CD band with the lowest wave number of the bis(L-amino-acid-amidato)nickel(II) with vala, phalaa or leuma was negative in the alcoholic solution and positive in DMF (Table 5, Figs. 9 and 10, and Fig. 1 of Ref. 3). This is analogous to the behavior exhibited by the tI bands of the *trans* palladium complexes with those ligands (Figs. 2 and 3, and Fig. 2 of Ref. 3). There is a close correspondence between the whole ligand field (AB and CD) spectra of these nickel complexes (Tables 4 and 5) and those of the corresponding *trans* palladium ones. Thus, the three nickel complexes are inferred to be *trans* isomers both in solution and in solid state. It is strongly suggested therefore that the CD band at 24.0 kK corresponds to tIII (Table 5), and the small positive band at 20.8 kK, detected for *trans*-[Ni(L-alaa)$_2$] in methanol,[1] to tII. It may be noted in this connection that the tI CD extrema of the nickel complexes appear to correspond to the AB shoulder (or peak) at about 20.0 kK but that the tIII situates at considerably higher wave number than the AB peak (Tables 4 and 5, Figs. 9—11, Fig. 1 of Ref. 3 and Fig. 4 of Ref. 1).

TABLE 4. AB MAXIMA OF THE NICKEL COMPLEXES

Complex	Solvent or state[a)]	Maxima		
trans-[Ni(L-alaa)$_2$]	(Et)	~20sh	23.3(1.77)	
trans-[Ni(L-vala)$_2$]·2H$_2$O				
	(N)	~20sh	23.6	
	(Me)	~20sh	23.3(1.75)	
	(Et)	~20sh	23.3(1.77)	
	(DMF)	~20sh	23.6(1.81)	
trans-[Ni(L-phalaa)$_2$]	(N)	~20sh	23.7	
	(Me)	~20sh	23.2(1.80)	
	(Et)	~20sh	23.1(1.82)	
	(DMF)	~20sh	23.5(1.90)	
trans-[Ni(L-proa)$_2$]·2H$_2$O				
	(N)	~19sh	23.1	
	(W)	~20sh	23.0(1.83)	
	(Et)	~20sh	23.1(1.83)	
	(DMF)	~20sh	23.4(1.89)	
trans-[Ni(L-leuma)$_2$]·H$_2$O				
	(N)	~19sh	23.1	
	(Et)	~19sh(1.5)	22.8(1.79)	
	(DMF)	19.2(1.52)	23.1(1.83)	
[Ni(tndba)]·H$_2$O	(Refl)	~22sh	24.0	~32sh
	(W)	23.3(1.92)	~32.5sh(1.2)	
	(Et)	23.3(1.93)	~31.5sh(1.3)	

a) N=Nujol mull, Refl=powder (diffuse reflectance spectrum).

TABLE 5. CD EXTREMA OF THE NICKEL COMPLEXES

Complex	Solvent	Extrema	
		tI	tIII
trans-[Ni(L-alaa)$_2$]	(Et)	18.8(−0.04)	24.1(−0.65)
trans-[Ni(L-vala)$_2$]·2H$_2$O			
	(Me)	20.0(−0.32)	24.0(−0.76)
	(Et)	20.1(−0.36)	24.0(−0.81)
	(DMF)	18.8(+0.07)	24.0(−0.80)
trans-[Ni(L-phalaa)$_2$]	(Me)	20.2(−0.28)	24.0(−0.65)
	(Et)	20.1(−0.38)	24.0(−0.68)
	(DMF)	18.9(+0.13)	24.1(−0.75)
trans-[Ni(L-proa)$_2$]·2H$_2$O			
	(W)	20.1(−1.17)	24.4(−0.17)
	(Et)	19.8(−1.13)	24.2(−0.54)
	(DMF)	20.1(−0.68)	24.1(−0.57)
trans-[Ni(L-leuma)$_2$]·H$_2$O			
	(Et)	18.9(−0.40)	23.5(−0.71)
	(DMF)	19.1(+0.35)	23.4(−1.44)

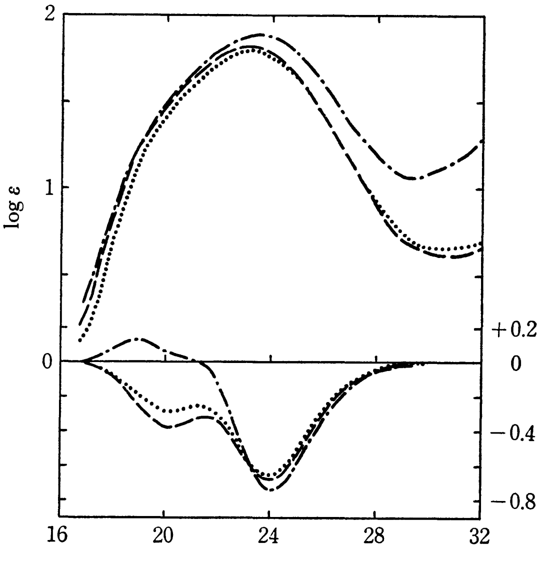

Fig. 9. AB and CD spectra of *trans*-[Ni(L-vala)$_2$] in methanol (……), in ethanol (———) and in DMF (—·—·).

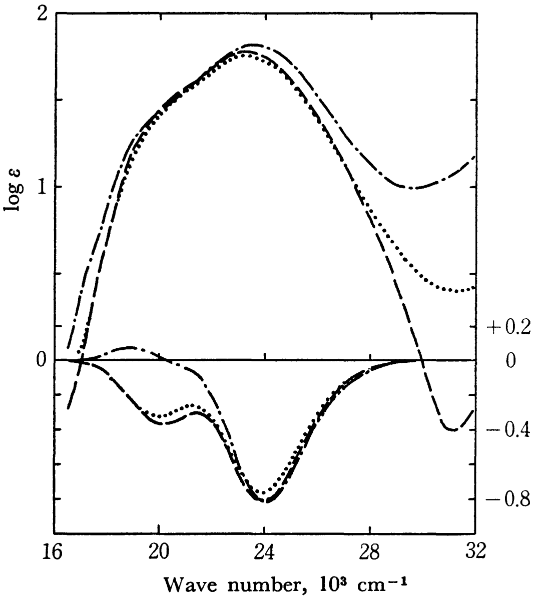

Fig. 10. AB and CD spectra of *trans*-[Ni(L-phalaa)$_2$] in methanol (……), in ethanol (———) and in DMF (—·—·).

The CD behavior of the proa complex seems to be an intermediate of the behaviors of the correspond-

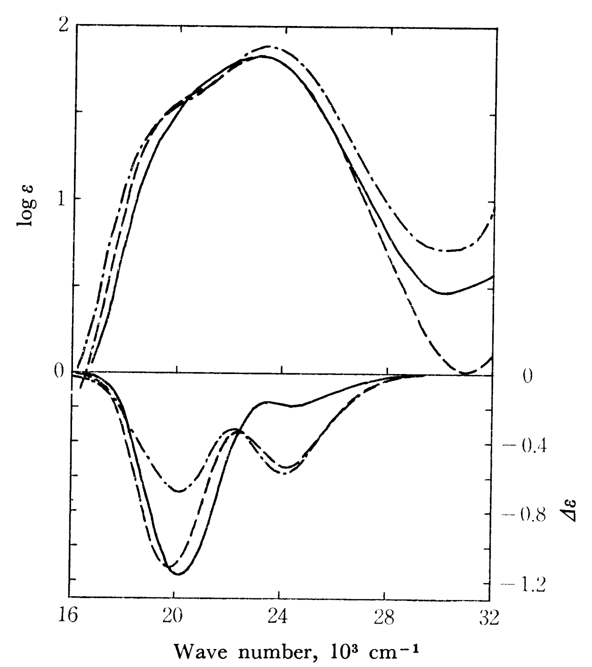

Fig. 11. AB and CD spectra of *trans*-[Ni(L-proa)$_2$] in water (——), in ethanol (– – –), and in DMF (—·—·).

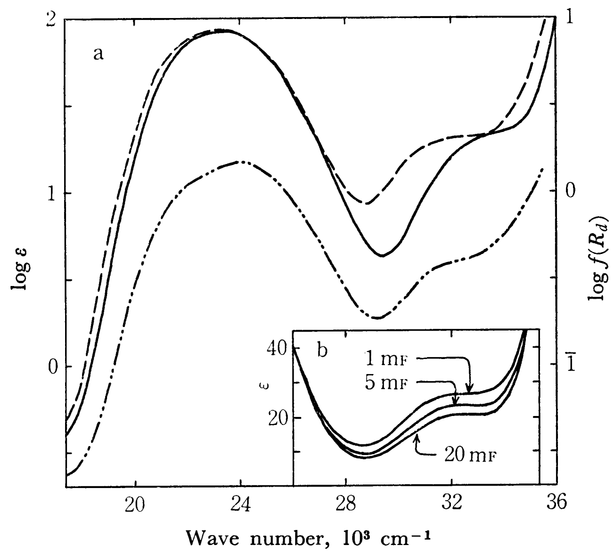

Fig. 12. AB spectrum of [Ni(tndba)]: a, in water (——), in ethanol (– – –), and in solid state (reflectance, —··—··); b, in ethanol.

ing *cis* and *trans* palladium complexes, in the respective solvents (Fig. 11). The wave numbers of the CD extrema, however, do not differ much from those for the other nickel complexes inferred to be *trans* (Table 5). Moreover, the AB spectrum of the proa complex is very similar to spectra of the *trans* complexes and significantly differs from that of the tndba complex, the structure of which is restricted to *cis*-type (Fig. 12). On the whole, it is concluded that the proa complex is also a *trans* isomer. Thus, no *cis* isomer of bis(amino-acid-amidato)nickel(II) has been found so far.

3) Copper(II) Complexes: The six bis(α-amino-acid-amidato)copper(II) complexes showed a broad ligand field band at 18.7—19.5 kK ($\log \varepsilon =$ 1.67—1.76, except for the proa complex) in aqueous solution.[2] These complexes are considered to be *trans* or to be predominantly so in aqueous and alcoholic solutions. This conclusion is supported to some extent by the following observations; Cu(tndba) is slightly higher either in its intensity or in the wave number than the bis(amino-acid-amidato) complexes. The former has no vague shoulder at its lower wave number side in contrast to the latter (Fig. 13 and Table 6). The spectral difference between the tndba and the bis(amino-acid-amidato) complexes seems to be analogous to that between *cis* and *trans* complexes of palladium(II) or of nickel(II).

The above and the previous[2] discussion concerning the geometrical structure can be applied also to the copper complex with L-leuma in the aqueous, ethanol, and DMF solutions as well as to all the bis(α-amino-acid-amidato)copper(II) complexes dissolved in DMF. Though the leuma complex exhibits the ligand field band at considerably lower wave numbers than the other bis(L-amino-acid-amidato)copper(II) complexes in respective solvents (Table 6), the red shift can be attributed to an effect of the methyl group attached to the amido nitrogen. Actually, similar shifts were also observed in the corresponding *trans* complexes of palladium and nickel (Tables 1 and 4).

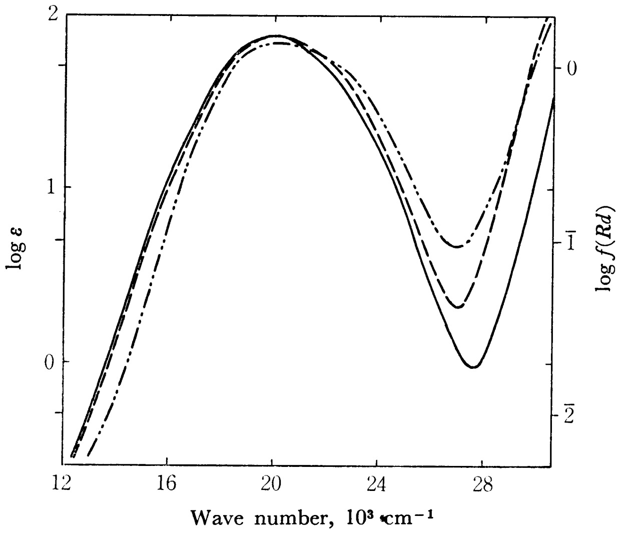

Fig. 13. AB spectrum of Cu(tndba): in water (——), in ethanol (– – –), and in solid state (reflectance, —··—··).

The CD behavior of the bis(L-amino-acid-amidato)-copper(II) complexes is apparently very complicated (Table 7, Fig. 14, and Table 4 of Ref. 2 and Fig. 2 of Ref. 2) in contrast to that of the corresponding nickel or palladium complexes. On the other hand, the shapes and the solvent dependencies of the AB bands of the copper complexes do not differ much from each other (Fig. 14, Fig. 2 of Ref. 2, and Fig. 3 of Ref. 2). It can be accepted that the relative ordering of the components of the band is independent of the kind of ligand. It seems reasonable from an examination of the CD data that the ordering is also independent of the kind of solvent. It is inferred from these considerations that the ligand field band

Table 6. AB data of the copper complexes

Complex	Solvent or state	Maxima		Band-width[a]	Concn.[b]
Cu(L-vala)$_2$·2H$_2$O	(DMF)	20.4(1.81)		6.3	2.4
Cu(L-phalaa)$_2$	(DMF)	20.5(1.85)		5.9	2.5
Cu(L-leuma)$_2$	(W)	18.1(1.74)	~29sh(2.1)	6.1	5.0
	(Et)	19.4(1.87)	~27sh(2.2)	6.2	5.0
	(DMF)	~18sh(1.5)	19.9(1.89)	6.7[c]	5.0
Cu(tndba)·1.5H$_2$O	(Refl)	20.1	~22.5sh	5.7	—
	(W)	20.0(1.86)		5.2	2.0
	(Et)	20.1(1.88)		5.2	2.0

a) Apparent band-with at half extinction in 10^3 cm^{-1} unit.
b) Concentration in 10^{-3} F unit. c) By extrapolation.

Table 7. CD data of the copper complexes

Complex	Solvent	Extrema			Concn.
Cu(L-vala)$_2$·2H$_2$O	(DMF)	14.7(+0.02)	19.0(−0.33)	22.5(+0.05)	5.0
Cu(L-phalaa)$_2$	(DMF)	16.9(+0.02)	20.8(−0.20)		2.5
Cu(L-leuma)$_2$	(W)	16.6(−0.31)	19.8(−0.25)		10
	(Et)	16.1(−0.33)	20.9(−0.18)		10
	(DMF)	15.0(−0.09)	19.9(−0.24)		10

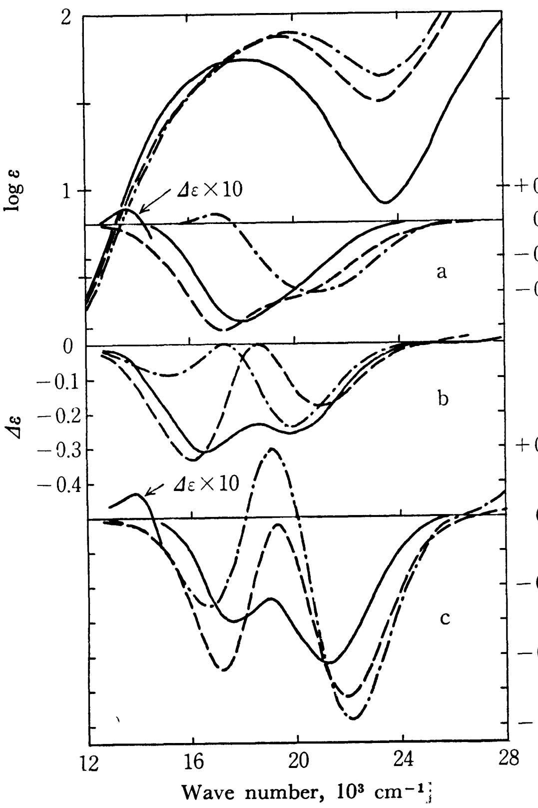

Fig. 14. AB spectrum of Cu(L-leuma)$_2$ and CD spectra of: a, Cu(L-phalaa)$_2$; b, Cu(L-leuma)$_2$; c, Cu(L-proa)$_2$. ——, in water; – – –, in ethanol; —·—·, in DMF.

of the bis(α-amino-acid-amidato)copper(II) complexes generally consists of at least three components which are roughly at 17, 19, and 21—22 kK; these are labeled A, B and C, respectively. Only the leuma complex seems to exhibit each of the three components at lower wave numbers by 0.5—1 kK than the other complexes (Fig. 14b).

A very small positive CD band which is seriously eclipsed by large negative ones was observed at about 14 kK for the copper complexes with L-vala, L-phalaa and L-proa (Figs. 14a and 14c, and Fig. 2 of Ref. 2). The reflectance spectrum of Cu(L-proa)$_2$·2H$_2$O reveals a weak but distinct shoulder at about 13 kK.[2,9] Similar CD bands have been found for bis(L-aminoacidato)copper(II) complexes.[10]

The CD behavior of the proa complex is somewhat specific as discussed in Part II[2] but more or less resembles that of the leuma or of the phalaa complex as demonstrated in Fig. 14.

Nature of the Ligand Field Band. The *trans* palladium as well as the *trans* nickel complexes have three components in the ligand field band; each of the components exhibits a behavior common to both palladium and nickel complexes. Thus, each band labeled tI, tII or tIII for both complexes should be assigned to a common *d-d* transition. Such was the case in the tentative assignment made in Part I.[1] On the other hand, a new kind of CD band, cII, was found in this work for the *cis* palladium complexes other than those previously reported. This requires us to reconsider the band assignment for both *cis* and *trans* palladium complexes.

Three of the possible assignments are listed as the preferable ones in Table 8; the bands labeled with the same Roman numeral are assigned to the transitions derived from a certain transition in D_{4h} symmetry, in each possible assignment of the three, because those bands show a very similar behavior to

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[9] If the AB and CD bands at 13—14 kK were neither of A, B nor C, it should be assigned to ν_1; see footnote 11 and the following discussion.

[10] T. Yasui, This Bulletin, **38**, 1746 (1965); T. Yasui, J. Hidaka, and Y. Shimura, *J. Amer. Chem. Soc.*, **87**, 2762 (1965).

each other. The assignment for the *trans* complexes in Part I[1] is revived in assignment (1), whereas that for *cis* complexes in (2) apart from cII. However, another possibility (3) is not so easily omitted. The c0 band is assigned to a spin-forbidden transition in every case for the following reasons (*cf.* Ref. 1). First, it has a significantly lower absorption coefficient than the other bands (Table 3). Secondly, it is very unlikely that the band is assigned to ν_1',[11] because it scarcely ever shifts by change of the solvent. Thirdly, it seems that the three bands of the *trans* complexes are reasonably assigned to ν_2, ν_3, and ν_4. From this it follows that ν_2', ν_3', and ν_4', are to be assigned to the three bands other than c0 in the *cis* complexes.

Table 8. Possible band assignments for the palladium and the nickel complexes

Band	Possible assignments[a,b]		
	(1)	(2)	(3)
tI	ν_3	ν_2	ν_2
tII	ν_2	ν_1	ν_3
tIII	ν_4	ν_3, ν_4	ν_4
c0	sf	sf	sf
cI	ν_3'	ν_2'	ν_2'
cII	ν_2'	ν_1'	ν_3'
cIII	ν_4'	ν_3', ν_4'	ν_4'

a) For the definition of the transitions, see footnote 11.
b) sf = a spin forbidden transition.

Let us examine the validity of each of the three assignments. If assignment (2) were valid, the spectral data would indicate that ν_1 is more slightly shifted than ν_2 as the solvent is changed. This is unlikely under a simple ligand field theory. Moreover, the three bands of the *trans* complexes seem to be reasonably assigned to ν_2, ν_3, and ν_4 since only ν_1 is magnetic dipole forbidden.[12] Thus assignment (2) seems unreasonable. Next, assignment (3) is in conflict with the theoretical expectation that the splitting energies would be influenced most seriously between (xz) and (yz) orbitals by the *cis-trans* isomerism. In conclusion, assignment (1) is the most preferable, but still does not seem unambiguous. A similar assignment has been given for bis(β-ketoenolato) copper(II) complexes.[13]

It can be roughly estimated that contributions of interelectronic repulsion energy are less by 3B to ν_3 and ν_4 than to ν_2, where B is Racah's parameter. If assignment (1) is valid, the energy difference $\nu_2-\nu_3$ can be estimated from the experimental results to be some 1000 cm^{-1} for the nickel complexes; this may be smaller than 3B.[14] It is therefore likely that the contributions of ligand field energy to respective transitions are in the order $\nu_2<\nu_3<\nu_4$ for the nickel complexes. The energy order is expected to be realized in the electronic spectra of the corresponding copper complexes as it is, because there is no contribution of interelectronic repulsion energy to any transition in the d^9 chromophore. With respects to the copper complexes, all the A, B and C bands seem to be magnetic dipole allowed. Actually, the largest CD band is A or C in the complexes with phalaa, proa and leuma (Fig. 14), whereas B in those with alaa, leua and vala. Thus three bands A, B, and C may be tentatively assigned, to ν_2, ν_3, and ν_4, respectively.[9] Definitive assignment of ligand field bands has not been given in the CD studies of the copper(II) complexes with optical active amino acids and peptides.[10,15]

The Benzenoid Absorption. A typical band series of phenyl groups was observed in 38000 cm^{-1} (260 mμ) region in both AB and CD spectra of *trans*-bis(L-phenylalaninamidato)palladium(II) in ethanol. These spectra are given in Fig. 3, together with the AB spectrum of L-phenylalaninamide in ethanol (10 mM), and the numerical data in Table 1 and 2. Measurements of the CD spectra were carefully repeated both for the complex and for the ligand, but for the latter $|\Delta\varepsilon|$ was too small ($\leq$0.03) in this region to give reliable results. The AB and CD spectra were also measured in an ethanol solution containing the ligand (10 mM) and sodium ethoxide (10 mF). The results, however, were indistinguishable from those without alkali. Though the benzenoid absorption of the complex is overlapped by the other absorption, it seems to be scarcely affected by the complex formation. We conclude from this observation that there is no first order interaction between the phenyl π and the metal d orbitals in the complex. Thus, we exclude the possibility that apical coordination of the phenyl groups exists and causes the about ten times enhanced CD of the benzenoid absorption in the complex.

The 32000 cm^{-1} Band of [Ni(tndba)]. The electronic spectrum of [Ni(tndba)] shows another weak band at about 32000 cm^{-1} (Fig. 12). This band shifted to lower wave numbers when the solvent was changed from water to ethanol. It became slightly more intense when the ethanol solution was diluted (Fig. 12b). Its peak is at a wave number about 9000 cm^{-1} higher than that of the main ligand field band maximum. These characteristics are very similar to those of Band II of bis(α-amino-acid-amidato)copper(II) complexes described in Part II,[2] and hence these two kinds of band seem to have a common origin. However, the following facts appear

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[11] ν_1, ν_2, ν_3, and ν_4 mean transitions from (z^2), (xy), (xz) and (yz) to (x^2-y^2), and ν_1', ν_2', ν_3' and ν_4' mean those from (z^2), (x^2-y^2), (xz) and (yz) to (xy), respectively, where (k) means a molecular orbital composed mainly of d_k-orbital. The x axis is fixed to be nearly colinear with metal-N(amido) linkage in the *trans* complex, but to bisect N-metal-N angle within each chelate ring in the *cis* complex. The y axis is fixed also within coordination square in both *trans* and *cis* complexes.

[12] ν_1 can become magnetic dipole allowed by configuration interaction or mixing of p-orbitals under C_2 symmetry.

[13] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 917 (1967).

[14] The value of B in gaseous Ni^{2+} ion is 1041 cm^{-1}, C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962), p. 137.

[15] J. M. Tsangaris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 4255 (1970).

to be somewhat in conflict with this conclusion: Such a kind of band has not been observed in either the *trans*-bis(α-amino-acid-amidato)nickel(II) complexes or in Cu(tndba), and the intensity of the band of [Ni(tndba)] was not so seriously dependent on concentration and on the kind of solvent (including solid state) as in Band II of the copper complexes.

The authors thank Dr. Seiko Komorita for measurements of the AB spectra in Nujol mulls.