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Metal Complexes with Amino Acid Amides. IV. Relationship between the CD Spectra of Palladium, Nickel, and Copper Complexes with *cis*-Bis(amino carboxamidato)metal(II) Type

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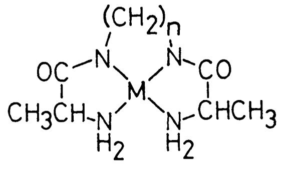
Square planar complexes of [ML] type, where M=Pd^{2+}, Ni^{2+}, and Cu^{2+} for L=*N*,*N'*-bis(L-alanyl)-1,3-propanediaminate anion and M=Ni^{2+} and Cu^{2+} for L=*N*,*N'*-bis(L-alanyl)-1,2-ethanediaminate anion, were synthesized. Their absorption and CD spectra were measured in aqueous, ethanol, and DMF solutions. The results are discussed in comparison with those of *cis*- and *trans*-bis(amino carboxamidato)complexes. Definite correspondence is found between the component d-d bands of *N*,*N'*-bis(L-alanyl)-1,3-propanediaminatopalladium(II) and those of its nickel analog, in line with a similar correspondence for the corresponding *trans*-bis(L-amino carboxamidato) complexes. Assignment of the component d-d bands has been reexamined for the copper complexes of bis(amino carboxamidato) type by comparing their CD data with those for the palladium and nickel analogs.

Solvent effects on CD spectra have been studied for a large number of square planar bis(amino carboxamidato) complexes.[1-4] A definite correspondence has been found between the ligand field bands of trans palladium(II) complexes and those of nickel(II) analogs.[3,4] However, no similar examination has been carried out on the cis type or copper(II) complexes, due to the labile nature of the copper(II) and nickel(II) complexes.

This paper presents spectral relationship found for the nickel(II), palladium(II), and copper(II) complexes of *cis*-bis(L-amino carboxamidato) type. The work was achieved by use of tetradentate ligands, *N*,*N'*-bis(L-alanyl)-1,3-propanediamine and -1,2-ethanediamine, which make the complexes take the *cis* geometry.



Experimental

Materials. The ligands, *N*,*N'*-bis(L-alanyl)diamines were synthesized according to Scheme 1.

N,*N'-Bis(N-benzyloxycarbonyl-*L*-alanyl)-1,2-ethanediamine (**1**)*: *N*-Benzyloxycarbonyl-L-alanine (31.6 g, 0.14 mol) was dissolved in 700 cm^3 of absolute tetrahydrofuran (THF). The resulting solution was cooled to the temperature range −10—−5 °C, and 14.4 g (0.14 mol) of triethylamine was added to it under stirring. The temperature was kept in the range, stirring being continued. A solution of 19.4 g (0.14 mol) of isobutyl chloroformate in 60 cm^3 of absolute THF was added dropwise to the reaction mixture. After the addition had been completed, the mixture was stirred for 20 min, and a solution of 3.3 g (0.055 mol) of 1,2-ethanediamine in 250 cm^3 of absolute THF was added dropwise. The mixture which turned curdy was gradually warmed to room temperature under stirring for several hours and then allowed to stand overnight.

The white precipitate, which contained triethylammonium chloride as well as the desired compound, was separated by a glass filter, washed with water three times and recrystallized from ethanol: the compound crystallizes in needles if it is of adequate purity. The samples for elemental analyses were dried *in vacuo* over $CaCl_2$. Another crop of the product was obtained from the mother liquor. Total yield, 19.1 g (74 %); mp 188.5—190.5 °C (uncorr.).

Found: C, 61.15; H, 6.45; N, 11.82 %. Calcd for $C_{24}H_{30}N_4O_6$: C, 61.26; H, 6.43; N, 11.91 %.

This compound is readily soluble in ethanol, ethyl acetate, chloroform, and THF only when hot.

N,*N'-Bis(*L*-alanyl)-1,2-ethanediamine Dihydrobromide Hemihydrate,* L,L*-balaenH$_2$·2HBr·0.5H$_2$O (**2**)*: A 1:2 mixture (100 g) of hydrogen bromide–acetic acid was added to 23.0 g of **1** previously damped with 50 cm^3 of gracial acetic acid. On stirring the whole mixture for 80 min, the starting material **1** was dissolved and the desired product deposited as a resinous mass. An additional amount of the product was precipitated as a powder by adding 300 cm^3 of ether. Recrystallization of the crude product from ethanol–ether yielded colorless microcrystals. These were washed with a 1:2 mixture of ethanol–ether and dried *in vacuo* over P_2O_5 at about 75 °C overnight. Yield, 15.4 g (86 %); $[\alpha]^{16}_{589}=+4.1°$ (c=0.114; water); mp *ca.* 135 °C (dec).

Found: C, 25.81; H, 5.67; N, 15.03 %. Calcd for $C_{16}H_{42}N_8O_5Br_4$: C, 25.75; H, 5.67; N, 15.02 %.

N,*N'-Bis(N-benzyloxycarbonyl-*L*-alanyl)-1,3-propanediamine (**3**)*. A solid product was obtained by a procedure similar to that for the 1,2-ethanediamine analog **1**, except for the use of 1,3-propanediamine in place of 1,2-ethanediamine. It was separated by a glass filter and washed with THF, water, aqueous 5 % $NaHCO_3$ solution, and water, successively. Recrystallization from THF yielded fibrous crystals which were dried *in vacuo* over $CaCl_2$. An addtional amount of the compound was obtained from the mother liquor. Total yield was 8.00 g (88 %) starting with 11.2 g (50 mmol) of *N*-benzyloxycarbonyl-L-alanine and 1.4 g (19 mmol) of 1,3-propanediamine: mp 192.5—193.5 °C (uncorr).

Found: C, 61.86; H, 6.74; N, 11.44 %. Calcd for $C_{25}H_{32}N_4O_6$: C, 61.97; H, 6.66; N, 11.56 %.

This compound is easily soluble only in hot THF, chloroform, and ethanol.

N, *N'-Bis(*L*-alanyl)-1,3-propanediamine Dihydrobromide,* L,L*-balatnH$_2$·2HBr (**4**)*: This compound can be derived from **3** by a similar procedure to that for the 1,2-ethanediamine analog **2**, but does not seem to be so easily crystallizable as **2**: Thus, the resinous mass of the crude product **4** was obtained from an appropriate amount of **3** each time before the preparation of metal complexes.

*Cu(*L,L*-balaen)·2H$_2$O*: A solution containing 1.5 g (4.1

mmol) of **2** in 25 cm^3 of water was poured into a column (1.3 cm×10 cm) packed with Amberlite IRA-410 of OH$^-$ form and the column was eluted with water. To the eluate was added Cu(OH)$_2$ freshly prepared from 1.03 g (4.1 mmol) of CuSO$_4$·5H$_2$O, and the mixture was stirred until it turned red. The solution was evaporated to dryness below 35 °C *in vacuo*. To the residual reddish violet powder was added 20 cm^3 of water, and a small amount of insoluble substances was filtered off. From the filtrate diluted with 80 cm^3 of ethanol, a small amount of less soluble bluish precipitate and a large amount of brick-red needles (or plates), the desired complex, were deposited successively by careful addition of ether. After the supernatant suspension of the bluish precipitate had been decanted, the brick-red crystals were washed with ether by decantation and dried in air. Additional crops of these crystal, were obtained by fractional treatment of the supernatant solution with ether. Total yield, 0.78 g (72 %).

Found: C, 31.97; H, 6.73; N, 18.63 %. Calcd for $C_8H_{20}N_4O_4Cu$: C, 32.05; H, 6.72; N, 18.69 %.

*Cu(*L,L*-balatn)·3H$_2$O*: An aqueous solution (40 cm^3) containing **4** derived from 4.84 g (10 mmol) of **3** was neutralized with an aqueous KOH solution and mixed with Cu(OH)$_2$ prepared from 2.25 g (9 mmol) of CuSO$_4$·5H$_2$O. To the resulting violet solution was added such an amount of aqueous KOH solution as necessary to raise the pH to 8.5, where the color of the solution turned pink. The solution was evaporated to dryness on a rotary evaporator below 35 °C. The desired complex was extracted with ethanol from the residue and recrystallized as shiny reddish violet plates, the trihydrate, by addition of ether. The crystals were dried in air: yield, 1.80 g (64 %).

Found: C, 32.23; H, 7.20; N, 16.94 %. Calcd for $C_9H_{24}N_4O_5Cu$: C, 32.57; H, 7.29; N, 16.88 %.

*Cu(*L,L*-balatn)·2H$_2$O*: The crystals of the trihydrate, described above, released a part of the water of crystallization to give an orange solid upon exposure to dry atmosphere. The sample for elemental analyses was prepared by drying the trihydrate over CaCl$_2$ overnight.

Found: C, 34.06; H, 6.99; N, 17.75 %. Calcd for $C_9H_{22}N_4O_4Cu$: C, 34.44; H, 7.07; N, 17.85 %.

*Ni(*L,L*-balaen)·2H$_2$O*: A solution of 2.00 g (5.5 mmol) of **2** in 10 cm^3 of water was neutralized with a solution containing 0.62 g (11.1 mmol) of KOH in 10 cm^3 of water. To the resulting solution was added a solution of 1.50 g (5.2 mmol) of Ni(NO$_3$)$_2$·6H$_2$O in 10 cm^3 of water. The blue solution was neutralized with a KOH solution (0.62 g in 10 cm^3 of water). A green precipitate appeared immediately, disappearing almost within 40 min under stirring. Desalting was performed from the resulting dark yellow solution by a few cycles of successive procedures: evaporation to dryness and extraction of the desired complex into ethanol. Brown yellow needles were separated from the ethanol extract by adding a small amount of water and a large amount of ether and dried in air: yield, 0.71 g (47 %).

Found: C, 32.26; H, 6.75; N, 18.70 %. Calcd for $C_8H_{20}N_4O_4Ni$: C, 32.57; H, 6.83; N, 18.99 %.

*Ni(*L,L*-balatn)·2H$_2$O*: An ethanol solution containing the complex was prepared by a similar procedure described for the balaen analog, by use of 2.62 g (9 mmol) of Ni(NO$_3$)$_2$·6H$_2$O and 4.84 g (10 mmol) of **3**, the volume being reduced *in vacuo* to a few cubic centimeters. Orange-yellow microcrystals of the desired complex were separated from the concentrated solution by adding several drops of water. These were collected on a glass filter, washed with a mixture of water–ethanol–ether (roughly 1: 4: 3) and dried in air: yield, 1.97 g (71 %).

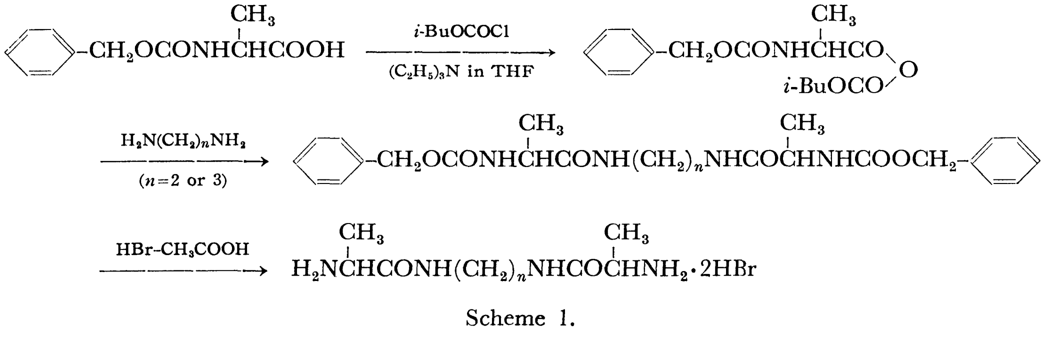
Found: C, 34.73; H, 7.24; N, 18.10 %. Calcd for $C_9H_{22}N_4O_4Ni$: C, 34.98; H, 7.18; N, 18.13 %.

*Pd(*L,L*-balatn)·2.5H$_2$O*: The crude compound **4** derived from 2.42 g (5 mmol) of **3** was dissolved in 25 cm^3 of water and neutralized with 10 cm^3 of a 1 M NaOH solution. To the resulting solution was added a solution containing 1.18 g (4 mmol) of Na$_2$PdCl$_4$ in 10 cm^3 of water. A brownish precipitate was immediately formed. The solution suspending the precipitate was subjected to a similar neutralization procedure, by use of 1 M NaOH.[4] During the course of procedure followed by stirring for 2.5 h, most of the precipitate was dissolved. The residue was then filtered off. Mixed salts and yellow sirup were obtained by evaporating the yellow solution *in vacuo*. Most of the salts were removed by a similar procedure to that described for Ni(L,L-balaen)·2H$_2$O, except for the use of methanol in place of ethanol. The resulting methanol extract was evaporated to dryness. The residue was dissolved in a small amount of water, poured into a column (1.3 cm×23 cm) packed with Amberlite IRA-410 of OH$^-$ form and eluted with water. The eluate was concentrated *in vacuo* below 35 °C to give pale yellow needles which were washed with a small amount of cold water and dried over CaCl$_2$: yield, 0.42 g (29 %).

Found: C, 29.46; H, 6.37; N, 15.19 %. Calcd for $C_{18}H_{46}N_8O_9Pd_2$: C, 29.56; H, 6.34; N, 15.32 %.

Measurements. The absorption and CD measurements were made with a Shimadzu UV-200 spectrophotometer and a JASCO MOE-1 spectropolarimeter, respectively, at room temperature. The solvents employed were the same as those reported.[2]

Gaussian Analyses. Gaussian analyses for selected absorption and CD curves were performed by use of a slightly modified version of program LGNS:[5,6] best fit between the observed and calculated curves was obtained by use of 35—49 spectral points per curve; each point was weighted with the square of ε in the least-squares treatment in absorption-curve analyses, but not in CD analyses. The number of components of ligand field ansorption and CD bands was fixed to three and four for the nickel and palladium complexes, respectively. All the calculations were performed at Computation Center, Osaka University.



Scheme 1.

Results and Discussion

Absorption and CD data of the complexes are shown in Tables 1 and 2 and Figs. 1—5. The absorption and CD spectra of [Cu(L,L-balaen)] in aqueous solution have been recorded by Parris and Hodges, without isolation of the complex.[7] Our data do not differ much from theirs.

Gaussian Analyses. Gaussian analyses were performed for the CD spectra of the palladium and nickel complexes and for the absorption spectra of [Ni(L,L-balatn)] in three kinds of solvents. The results are given in Table 3.

For the analysis of CD curves of the palladium complex, the position of the first component, a spin-forbidden band,[1] was assumed to be equal to the corresponding output value[8] of *cis*-bis(L-valinamidato)-palladium(II). This does not seem to affect the overall results seriously, since the component is small enough. Overlapping of the intense charge transfer bands might affect the results seriously if inappropriate data in the overlapping region were chosen as inputs.

All the standard deviations of $\Delta\varepsilon$ values (Table 3) are within experimental error. On the other hand, those of ε values are, seemingly, of considerable magnitude, but the deviations in the region of relatively large ε values should be much smaller due to the weight scheme adopted.

The results of absorption- and CD-curve analyses for [Ni(L,L-balatn)] coincide with each other as regards the positions. This shows the validity of the assumption of three components in the ligand field band region of this or similar nickel complexes.

Absorption Spectra. The complex, [Ni(L,L-balatn)], exhibits an absorption maximum with a little higher intensity at a slightly lower wave number than the *trans*-bis(amino carboxamidato)nickel(II) complexes,[1,4] in each of the solvents (Table 1 and Fig. 1). This behavior is in line with that found between the absorption spectra of *cis*- and *trans*-bis(amino carboxamidato)-palladium(II) complexes.[1,4] Consequently, the absorp-

TABLE 1. ABSORPTION DATA OF THE COMPLEXES

Complex	Solvent[a]	Maxima[b]
Pd(L,L-balatn)·2.5H_2O	(W)	*ca.* 27sh 34.8br(2.64)
	(Et)	*ca.* 27sh *ca.* 32sh 34.9(2.68)
	(DMF)	*ca.* 29sh 35.3(2.81)
Ni(L,L-balatn)·2H_2O	(W)	22.8(1.85)
	(Et)	*ca.* 21sh 22.9(1.88)
	(DMF)	*ca.* 20.5sh 23.1(1.88)
Ni(L,L-balaen)·2H_2O	(W)	*ca.* 22sh 24.5(2.36)
	(Et)	*ca.* 21.5sh 24.6(2.41)
	(DMF)	*ca.* 21.5sh 24.7(2.46)
Cu(L,L-balatn)·3H_2O	(W)	19.8(1.81)
	(Et)	20.6(1.85) *ca.* 22.5sh
	(DMF)	21.0br(1.83)
Cu(L,L-balaen)·2H_2O	(W)	19.6(2.24)
	(Et)	20.2(2.24) *ca.* 23sh
	(DMF)	20.4(2.35) *ca.* 23sh

a) W: water, Et: ethanol. b) Wave numbers given in 10^3 cm^{-1} unit; intensities, log ε, in parentheses. sh: shoulder, br: broad peak.

TABLE 2. CD DATA OF THE COMPLEXES

Complex	Solvent[a]	Extrema[b]
Pd(L,L-balatn)·2.5H_2O	(W)	29.7(+0.07) 36.4(−0.80)
	(Et)	*ca.* 32sh(−) 36.7(−0.72)
	(DMF)	*ca.* 31.5br(+0.16) 36.8(−0.29)
Ni(L,L-balatn)·2H_2O	(W)	23.7(−0.62)
	(Et)	*ca.* 21sh(−) 24.0(−0.54)
	(DMF)	21.0(+0.15) 24.3(−0.42)
Ni(L,L-balaen)·2H_2O	(W)	21.9(−0.70) *ca.* 24.5sh(−)
	(Et)	21.6(−0.51) 24.9(−0.47)
	(DMF)	20.0(−0.02) 22.4(+0.13) 25.5(−0.19)
Cu(L,L-balatn)·3H_2O	(W)	19.7(−0.48)
	(Et)	19.9(−0.50) 23.9(+0.008)
	(DMF)	20.1(−0.30) 23.3(+0.05)
Cu(L,L-balaen)·2H_2O	(W)	20.0(−0.80)
	(Et)	20.1(−0.80)
	(DMF)	16.3(+0.004) 19.9(−0.37) 24.9br(+0.008)

a), b) See footnotes of Table 1.

Table 3. Results of Gaussian analyses[a)]

Solvent[b)]	[Ni(L,L-balatn)]						[Pd(L,L-balatn)][e)]			[Ni(L,L-balaen)]		
	Absorption components			CD components			CD components			CD components		
	σ_{max}	ε_{max}	Band-width[c)]	σ_{ext}	$\Delta\varepsilon_{ext}$	Band-width	σ_{ext}	$\Delta\varepsilon_{ext}$	Band-width	σ_{ext}	$\Delta\varepsilon_{ext}$	Band-width
(W)							27.00[f)]	+0.011	3.25			
	21.38	13.5	3.48	21.44	−0.066	3.31	31.24	+0.130	4.44	21.52	−0.462	2.36
	21.99	22.9	3.86	21.98	+0.111	3.93	32.79	−0.239	3.10	22.54	−0.068	3.63
	23.58	46.2	4.38	23.60	−0.658	3.94	36.50	−0.792	5.17	24.53	−0.485	4.85
	SD[d)]=1.4			SD=0.009			SD=0.003			SD=0.007		
(Et)							26.83[f)]	+0.047	3.31			
	20.80	8.5	3.57	20.90	−0.175	2.45	31.35	−0.053	4.25	21.39	−0.439	2.43
	21.98	29.1	4.10	21.89	+0.336	2.73	34.42	+0.153	3.14	22.93	+0.112	3.31
	23.59	50.5	4.45	23.65	−0.622	3.99	36.46	−0.770	4.43	24.59	−0.511	4.67
	SD=1.8			SD=0.004			SD=0.007			SD=0.006		
(DMF)							26.80[f)]	−0.011	3.43			
	20.54	27.8	3.32	20.59	+0.147	3.06	29.49	+0.140	4.57	20.81	−0.072	2.33
	22.10	16.0	3.82	22.20	+0.291	2.29	33.51	+0.155	3.96	22.47	+0.228	3.17
	23.68	59.3	4.02	23.60	−0.481	4.27	36.63	−0.313	4.10	25.08	−0.215	4.44
	SD=2.2			SD=0.005			SD=0.002			SD=0.003		

a) σ's and band widths are given in 10^3 cm^{-1} unit. b) See footnote a) of Table 1. c) Half-value width. d) Standard deviation of the calculated values of ε or $\Delta\varepsilon$ from the corresponding observed values. e) For the input data used, see Fig. 5. f) Fixed values; see text.

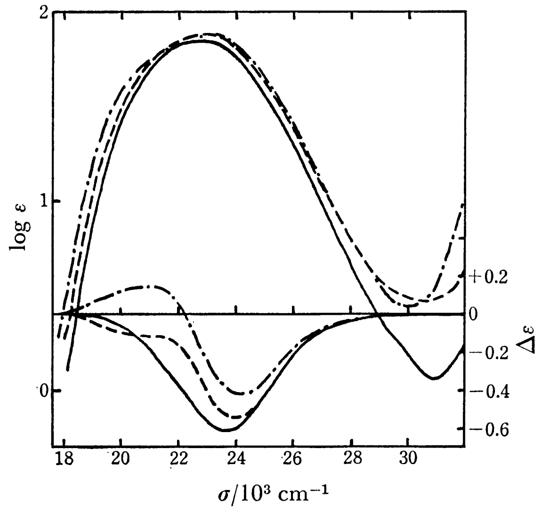


Fig. 1. Absorption and CD spectra of [Ni(L,L-balatn)] in water (——), in ethanol (----), and in DMF(-•-•).

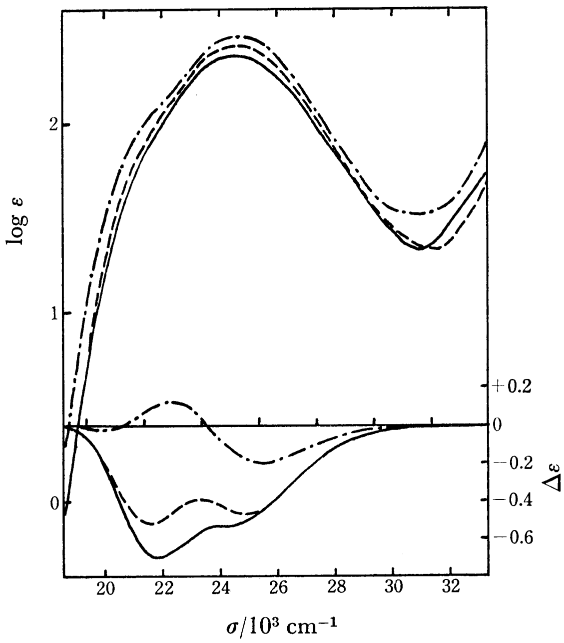


Fig. 2. Absorption and CD spectra of [Ni(L,L-balaen)] in water (——), in ethanol (----), and in DMF (-•-•).

tion spectra of [Ni(L,L-balatn)] are considered to correspond to those of a *cis*-bis(amino carboxamidato)-nickel(II) complex, which has not been isolated so far.

The absorption spectra of [Ni(L,L-balaen)] (Table 1 and Fig. 2) suggest an abnormally strong ligand field in this complex. The absorption maximum shifts toward blue by 1000—1500 cm^{-1} as compared with those of the *trans*-bis(amino carboxamidato)nickel(II) complexes, in each solvent. Such a blue shift is found also for each component band of the balaen complex (Table 3). This suggests that the ligand fits a nickel(II) ion so closely as to cause a constrictive effect found in different kinds of macrocyclic complexes.[9)]

In contrast with the complexes of nickel(II) ion, both ligands, balatn and balaen, give ligand field strengths of the same order of magnitude as the copper(II) ions. The absorption peak of [Cu(L,L-balaen)] lies near that of the balatn analog in each solvent (Table 1 and Figs. 3 and 4). This is in line with the fact that metal–nitrogen bonds are longer for copper(II) than for nickel(II) by roughly 8 pm[10)] in square-planar complexes of similar type.

The absorption spectra of [Pd(L,L-balatn)] (Table 1 and Fig. 5) essentially coincide with those of the *cis*-bis(amino carboxamidato)palladium(II) complexes in

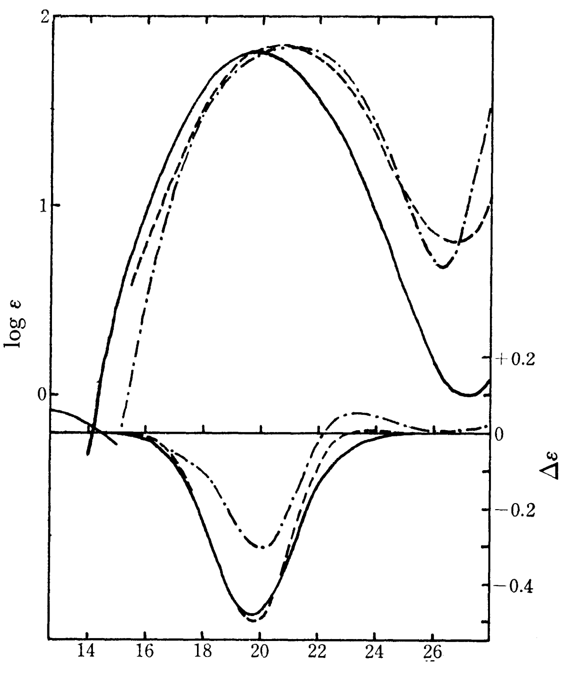


Fig. 3. Absorption and CD spectra of [Cu(L,L-balatn)] in water (———), in ethanol (– – – –), and in DMF (–·–·).

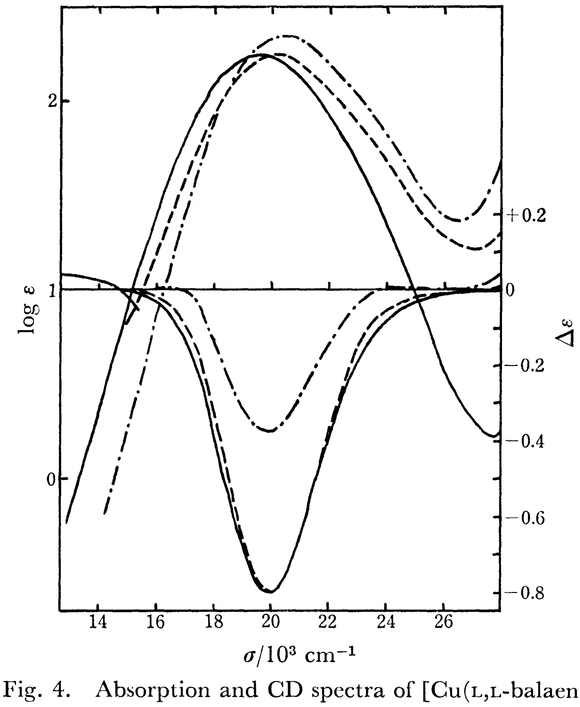


Fig. 4. Absorption and CD spectra of [Cu(L,L-balaen)] in water (———), in ethanol (– – – –), and in DMF (–·–·).

respective solvents. However, attempts to prepare the monomeric balaen complex, [Pd(L,L-balaen)], under similar conditions to those adopted for the balatn analog, have so far been unsuccessful. The results are understandable if palladium(II) ion were of favorable size for balatn to form a stable mononuclear complex but not for balaen. However, this is not the case, since available data of X-ray analyses[11] show that metal–nitrogen distances are nearly equal to each other

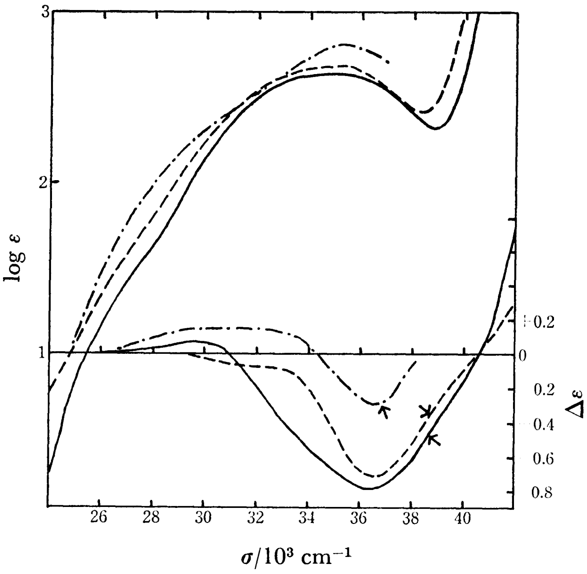


Fig. 5. Absorption and CD spectra of [Pd(L,L-balatn)] in water (———), in ethanol (– – – –), and in DMF (–·–·). Arrows signify the terminal points of input data used in the Gaussian analyses.

between some square-planar complexes of palladium(II) and of copper(II).

CD Correspondence between Palladium and Nickel Complexes. The CD spectra of [Pd(L,L-balatn)] apparently resemble those of the nickel analog (Figs. 1 and 5). Thus Gaussian analyses (Table 3) are expected to disclose the relationship between the spectra of both complexes in more detail. Since the three component bands of the nickel complex have comparable absorption intensities, they should correspond to the second, third, and fourth components (Table 3) of the palladium complex. For the corresponding components of *cis*-bis(amino carboxamidato)palladium(II) complexes, three of the four spin-allowed d-d transitions, ν_3', ν_2', and ν_4', respectively, have already been assigned.[4,12] As regards the three components, the CD sign patterns for the nickel complex coincide with those for the palladium complex in ethanol and in DMF solutions.[13] It might be concluded that the first, second, and third components of [Ni(L,L-balatn)] should correspond to the second, third, and fourth of the palladium analog, respectively. Thus a definite correspondence was found between the ligand field bands of nickel(II) and of palladium(II) complexes with *cis*-bis(amino carboxamidato) type, as already found for the trans analogs.

The CD-sign patterns of [Ni(L,L-balaen)] differ from those of the balatn analog in aqueous and DMF solution (Table 3 and Figs. 1 and 2), but differ from that of *cis*-bis(L-valinamidato)palladium(II) only in aqueous solution. Gaussian analyses for the last complex showed (−,+,−) pattern in water, ethanol and DMF. A question still remains about the (−,−,−) pattern of the balaen complex in aqueous solution.

Band Assignment for the Copper Complexes. There are at least three components at roughly 17000, 19000, and 21000—22000 cm^{-1} in the ligand field band region of bis(amino carboxamidato)copper(II) complexes and the three components have been tentatively assigned to the electronic transitions, ν_2, ν_3, and ν_4, respectively.[4] However, there are many copper complexes that exhibit a small positive extremum on the longer wavenumber end of CD spectrum.[2,4] In most cases it seems inadequate to regard the extremum as a residue of compensation among those three components. This is also the case for [Cu(L,L-balaen)] in DMF (Fig. 4).

Let us reexamine the four components inferred to exist in the ligand field band region of the copper complexes. The balatn and the balaen complexes (Figs. 3 and 4) display similar CD patterns to the bis(L-amino carboxamidato) complexes with alaninamidato, leucinamidato, and valinamidato ligands, although the latter complexes may be trans or predominantly so in the solutions. It seems reasonable to assume that the d-level orderings are essentially the same for the *trans* and *cis* complexes of bis(amino carboxamidato) type.

The order $\nu_2 < \nu_3 < \nu_4$ has been inferred for the trans complexes.[4] The corresponding order $\nu_2' < \nu_3' < \nu_4'$ should hold for the *cis*-type complexes with balatn and balaen.

The second and third CD components, which closely overlap each other to give a negative extremum in most of the complexes including [Cu(L,L-balatn)] and [Cu(L,L-balaen)], are much larger than the others, having net negative sign.[2] For most of the similar nickel or palladium complexes, the two components due to ν_3 and ν_4 (or ν_3' and ν_4') exhibit large and net negative CD, irrespective of the geometrical structures.

Thus it is preferable to assign the four components of the copper complexes to the transitions ν_2', ν_3', ν_4', and ν_1' (or ν_2, ν_3, ν_4, and ν_1), respectively, in the order of increasing wavenumbers.

The assignment is supported by the following observations: (1) The component due to ν_2 corresponds to a positive CD band in most of the bis(L-amino carboxamidato)-type complexes irrespective of the central metal ions and geometrical structures, (2) the component due to ν_1, which can be found only in the copper complexes, exhibits a small positive CD extremum or none in most cases (Table 2 and Figs. 3 and 4).[2] This is in line with the theory that the transition ν_1 is magnetically forbidden in first-order approximation.[14] Remarkable exceptions to (2) are the ν_1 components of the L-prolinamidato, L-phenylalaninamidato, and (*S*)-2-amino-4-methyl-*N*-methylpentanamidato complexes; the ν_1 component seems to correspond to a large negative CD extremum in these complexes.

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

13) The output data of CD analysis for [Ni(L,L-balatn)] in aqueous solution may be relatively unreliable regarding the first two components since these heavily overlap each other.

14) This means that the matrix element of electronic angular momentum, $\langle d_{x^2-y^2}|l_i|d_{z^2}\rangle$, is equal to zero irrespective of chromophore symmetries, where $i = x$, y, or z.