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STEREOSELECTIVE INTERACTION BETWEEN α-AMINO ACIDS AND THE NICKEL(II) COMPLEXES OF OPTICALLY ACTIVE TETRAMINES INCLUDING TWO PYRROLIDINYL GROUPS

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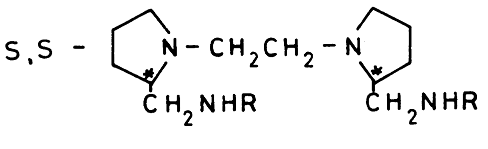
To the nickel(II) complexes of 1,2-bis[2(S)-2-aminomethyl-1-pyrrolidinyl]ethane and 1,2-bis[2(S)-2-N-methylaminomethyl-1-pyrrolidinyl]-ethane, some α-amino acidate ions coordinated stereoselectively. The stereoselectivity was evaluated in terms of the ratio of stability constants, K_L/K_D, by measurements of circular dichroism spectra.

As reported previously$^{1)}$, 1,2-bis[2(S)-2-aminomethyl-1-pyrrolidinyl]ethane(AMPE) and 1,2-bis[2(S)-2-N-methylaminomethyl-1-pyrrolidinyl]ethane(MMPE) coordinate to nickel(II) ion stereospecifically to form octahedral-type complexes. These complexes have two remaining ligation sites to which some bidentate ligands, such as α-amino acids, may coordinate stereoselectively, because of the chirality of the tetramines held around the nickel(II) ion.



R = H : AMPE
R = CH_3 : MMPE

In the present communication, a detailed examination was carried out to see which enantiomer of α-amino acidate ion forms more favorably the mixed complexes with these tetramine complexes. Thus, CD spectra of the systems of L-, D-, and DL-

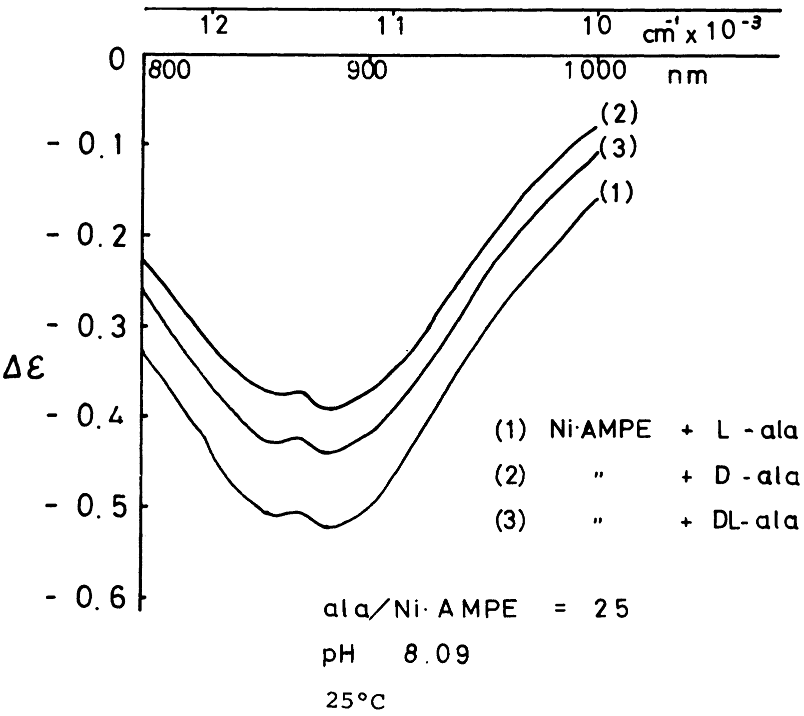


Fig. 1. The CD spectra of the mixtures of L-, D-, and DL-alanine with the AMPE·Ni(II) complexes in aqueous solutions.

amino acids with $[Ni(AMPE)]^{2+}$ or $[Ni(MMPE)]^{2+}$ were compared with each other.

Figure 1 shows the CD spectra(10,000 - 12,500 cm^{-1} region) of the mixtures of L-, D-, and DL-alanine with the AMPE complex in aqueous solutions at pH 8.09. The CD band in this region is $^3A_{2g} \rightarrow {}^3T_{2g}$ which is the only one magnetically allowed transition in the octahedral approximation. The CD curve of the DL-alanine system does not lie on the mid-line between the two curves given by L- and D-alanine systems, but, to some extent, close to the D-alanine system's. At 880 nm, for example, the values of $\Delta\varepsilon_D$, $\Delta\varepsilon_L$, and $\Delta\varepsilon_{DL}$ are 0.39, 0.52, and 0.44, respectively, where $\Delta\varepsilon_D$, $\Delta\varepsilon_L$, and $\Delta\varepsilon_{DL}$ are molar circular dichroism of the mixed complexes of the AMPE complex with D-, L-, and DL-alanine ions, respectively. This shows that a stereoselective coordination of D-alanine does occur. Because, if stereoselective coordination did not occur, the value of $\Delta\varepsilon_{DL}$ should be the average value of $\Delta\varepsilon_D$ and $\Delta\varepsilon_L$, i.e. 0.46. In the DL-alanine system, the molar ratios, α_L and α_D, of the mixed complexes of AMPE with L- and D-alaninate ions can be given from the figure(see appendix section, eq. (10)). The ratio of the stability constants of the following equilibria can be determined from α_L

(see appendix section):

$$\mathrm{T{\cdot}Ni + L} \xrightleftharpoons{K_L} \mathrm{T{\cdot}Ni{\cdot}L} \tag{1}$$

$$\mathrm{T{\cdot}Ni + D} \xrightleftharpoons{K_D} \mathrm{T{\cdot}Ni{\cdot}D} \tag{2}$$

where T is the tetramine such as AMPE, L and D are L- and D-amino acidate ions, respectively, and the charge are omitted.

Table I Values of α_L and K_L/K_D.

Tetramine	Amino Acid		Wavelength(nm) 840	860	880	900	920	940	$\bar{\alpha}_L$	K_L/K_D
AMPE	Alanine	$\Delta\varepsilon_D-\Delta\varepsilon_{DL}$	0.049	0.052	0.050	0.044	0.037		0.38	0.59
		$\Delta\varepsilon_D-\Delta\varepsilon_L$	0.123	0.122	0.129	0.123	0.111			
		α_L	0.40	0.43	0.39	0.36	0.33			
	Valine	$\Delta\varepsilon_D-\Delta\varepsilon_{DL}$		0.072	0.076	0.082	0.091	0.085	0.43	0.73
		$\Delta\varepsilon_D-\Delta\varepsilon_L$		0.163	0.182	0.197	0.205	0.206		
		α_L		0.44	0.42	0.42	0.44	0.41		
MMPE	Alanine	$\Delta\varepsilon_D-\Delta\varepsilon_{DL}$		0.059	0.063	0.063	0.057	0.049	0.50	1.0
		$\Delta\varepsilon_D-\Delta\varepsilon_L$		0.117	0.128	0.127	0.114	0.096		
		α_L		0.50	0.49	0.50	0.50	0.51		
	Valine	$\Delta\varepsilon_D-\Delta\varepsilon_{DL}$			0.059	0.064	0.065	0.065	0.52	1.1
		$\Delta\varepsilon_D-\Delta\varepsilon_L$			0.114	0.122	0.124	0.124		
		α_L			0.52	0.52	0.52	0.52		
	Proline*	$\Delta\varepsilon_D-\Delta\varepsilon_{DL}$		0.022	0.030	0.035	0.032	0.030	0.54	1.3
		$\Delta\varepsilon_D-\Delta\varepsilon_L$		0.047	0.057	0.064	0.059	0.052		
		α_L		0.47	0.53	0.55	0.54	0.58		

amino acid/Ni = 25, [Ni] = 2.5 10^{-3}M 25°C
* proline/Ni = 2.5 [Ni] = 2.5 10^{-2}M
The errors for $\Delta\varepsilon$ values are within 2%.

In Table I are summarized the values of α_L and K_L/K_D, which are obtainable under the assumption that all the tetramine-nickel(II) complexes form the mixed complexes with amino acids. From the ν_{max} values of the three spin-allowed d-d bands(Table II), it was found that almost all the AMPE complex formed the mixed complexes of the type $[\mathrm{Ni(N_5O)}]$ with α-amino acids. Therefore, the assumption above is satisfied. From Table I, it can be said that D-enantiomers of alanine and valine are more favorable to coordinate to the AMPE complex 1.7 and 1.4 times as strongly as L-enantiomers, respectively.

In the case of the MMPE complex, as the formation of the mixed complexes with valine and proline was not complete(Table II), the assumption above is not satisfied. Nevertheless, the attempts to evaluate the selectivity were made according to the procedure mentioned at appendix section. The resulting values of α_L and K_L/K_D are listed in Table I. These values indicate that the selectivity is very low for alanine and valine, while L-proline is more favorable to coordinate than D-proline.

Table II Electronic Absorption Frequencies of Nickel(II) Complexes of Tetramines in Aqueous Solutions

Complex System	pH	Absorption Maxima ($cm^{-1}x10^{-3}$)			Ligating Atoms
		$\nu_1(\varepsilon_1)$	$\nu_2(\varepsilon_2)$	$\nu_3(\varepsilon_3)$	
Ni·AMPE		10.5(10.0)	17.2(5.7)	27.8(11.2)	N_4O_2
Ni·AMPE·L-ala	9	10.8(9.6)	17.6(7.8)	28.6(13.5)	N_5O
Ni·AMPE·D-ala	9	10.8(9.3)	17.5(7.8)	28.6(13.5)	N_5O
Ni·AMPE·L-val	10	10.7(9.8)	17.3(8.0)	28.3(15.2)	N_5O
Ni·MMPE		10.4(12.1)	17.0(6.6)	27.8(12.2)	N_4O_2
Ni·MMPE·L-ala	8	10.7(11.8)	17.3(9.0)	28.3(15.3)	N_5O
Ni·MMPE·D-ala	8	10.7(11.8)	17.3(9.0)	28.3(15.7)	N_5O
Ni·MMPE·L-val	10	10.3(11.7)	16.9(7.8)	27.8(17.3)	
Ni·MMPE·L-pro	10	10.2(10.8)	16.7(7.3)	27.5(16.6)	
Ni(en)(gly)$_2$ [a]		10.5(8.7)	17.8(8.0)	27.8(12.7)	N_4O_2
Ni(trien)(H_2O)$_2^{2+}$ [b]		10.2	17.3	28.2	N_4O_2
Ni(en)$_2$(gly)$^+$ [a]		10.8(9.2)	17.9(8.7)	28.6(12.0)	N_5O

a) C.K.Jørgensen, Acta Chim. Scand., 10, 887(1956).

b) N.F.Curtis and D.A.House, J. Chem. Soc., 1965, 6194.

The reverse tendency in the stereoselective coordination of α-amino acidate ions to the AMPE and MMPE complexes may not be attributed to the unidentical chirality of the two tetramine complexes, but to the steric hindrance of the terminal N-methyl groups in the MMPE complex. The similarity of the CD spectra of the two tetramine complexes and their mixed complexes with α-amino acidate ions(Fig. 2) shows that the two tetramines coordinate with the same conformation around the central nickel(II) ion even in the mixed complexes.

Appendix

When both of the equilibria mentioned above(Eqs. (1) and (2)) are attained between racemic amino acidate ion and the nickel(II) complex, the ratio of the equilibrium constants, K_L/K_D, is given by

$$\frac{K_L}{K_D} = \frac{[T\cdot Ni\cdot L]}{[T\cdot Ni][L]} \Big/ \frac{[T\cdot Ni\cdot D]}{[T\cdot Ni][D]} = \frac{[T\cdot Ni\cdot L]}{[T\cdot Ni\cdot D]} \cdot \frac{[D]}{[L]} \qquad (3)$$

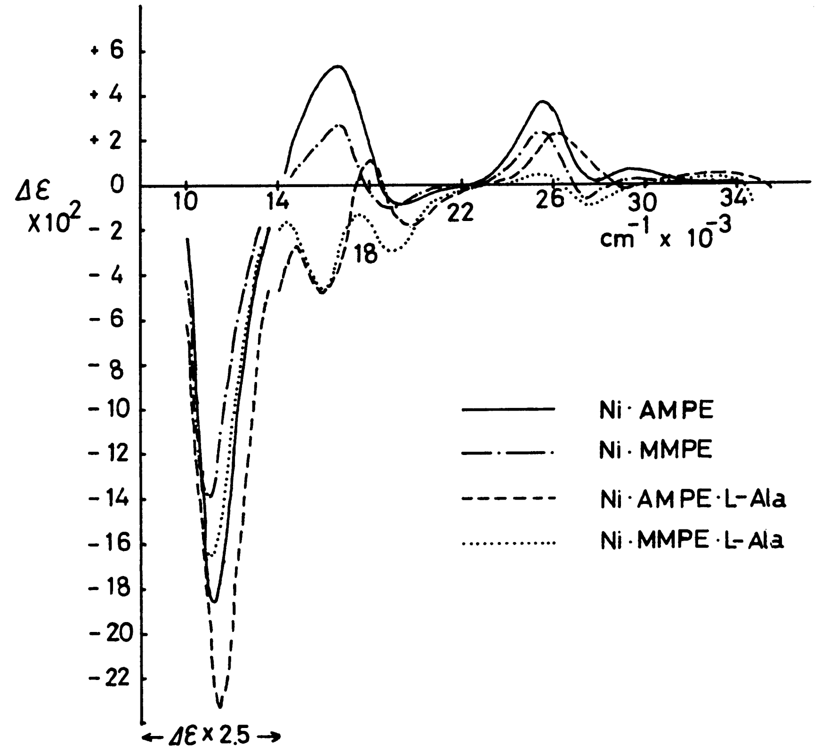


Fig. 2 The CD spectra of the AMPE and MMPE complexes and their mixed complexes with L-alanine.

The molar ratios, α_L and α_D, of the coordinated L- and D-amino acidate ions are given by

$$\alpha_L = \frac{[T\cdot Ni\cdot L]}{[T\cdot Ni\cdot L] + [T\cdot Ni\cdot D]}, \qquad \alpha_D = \frac{[T\cdot Ni\cdot D]}{[T\cdot Ni\cdot L] + [T\cdot Ni\cdot D]} \tag{4}$$

From Eq. (4), Eq. (3) can be rewritten as follows:

$$\frac{K_L}{K_D} = \frac{\alpha_L}{\alpha_D}\cdot\frac{[D]}{[L]} = \frac{\alpha_L}{1-\alpha_L}\cdot\frac{[D]}{[L]} \tag{5}$$

When $[L]_o$, $[D]_o$, and $[T\cdot Ni]_o$ are written for the initial concentrations of L- and D-amino acidate ions and the nickel(II) complex of the tetramine, respectively, and if all the tetramine complex forms the mixed complex with amino acidate ion, the followings are obtained:

$$[L] = [L]_o - [T\cdot Ni\cdot L], \qquad [D] = [D]_o - [T\cdot Ni\cdot D] \tag{6}$$

$$[T\cdot Ni\cdot L] + [T\cdot Ni\cdot D] = [T\cdot Ni]_o \tag{7}$$

From Eqs. (4), (5), (6), and (7), we obtain Eq. (8)

$$\frac{K_L}{K_D} = \frac{\alpha_L}{1-\alpha_L}\cdot\frac{[D]_o - (1-\alpha_L)[T\cdot Ni]_o}{[L]_o - \alpha_L[T\cdot Ni]_o} \tag{8}$$

When racemic amino acid is used n times excess to T·Ni, Eq. (8) results in

$$\frac{K_L}{K_D} = \frac{\alpha_L}{1-\alpha_L} \cdot \frac{(n/2-1) + \alpha_L}{n/2 - \alpha_L} \qquad (9)$$

From the CD spectra α_L is given as follows:2)

$$\alpha_L = \frac{\Delta\varepsilon_D - \Delta\varepsilon_{DL}}{\Delta\varepsilon_D - \Delta\varepsilon_L} \qquad (10)$$

Where $\Delta\varepsilon_D$, $\Delta\varepsilon_L$, and $\Delta\varepsilon_{DL}$ are the CD magnitude at the same wavenumber of the mixtures of the nickel(II) complex with D-, L-, and DL-amino acids, respectively.

Reference

1) S. Kitagawa, T. Murakami, and M. Hatano, Chem. Lett., 1974, 925.

2) V.A.Davankov and P.R.Mitchell, J. Chem. Soc. Dalton, 1972, 1012.

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