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Guest-selective Binding of Z-Amino Acids by a Strapped Metalloporphyrin Receptor with a Hydrogen-bonding Capability.

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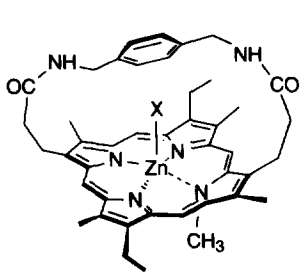
Abstract: In competitive complexation of Z-amino acids (*N*-benzyloxycarbonyl-amino acids) in $CDCl_3$, a synthetic receptor such as zinc *N*-methylmesoporphyrin II having a xylylenediamido strap (**1a**) preferred Z-glycine over other Z-amino acids, where an excellent selectivity (> 90 %) was achieved when Z-β-alanine, Z-sarcosine, Z-leucine, or Z-proline was the competitor. In contrast, in competitive binding of Z-amino acid anions in a $CHCl_3$ / water biphasic system, **1a** preferred substrates with hydrophobic side chains. © 1997 Elsevier Science Ltd.

INTRODUCTION

Design of receptors for selective recognition of amino acids and their derivatives is one of the interesting subjects not only from a practical viewpoint but also in relation to the functions of aminoacyl-tRNA synthase in biological protein synthesis. Although numerous artificial receptors for amino acid derivatives have been synthesized,[1] examples of metal-containing receptors are rather limited.[2] Considering a potential of metal ions for coordination and/or electrostatic interaction with guest molecules, they pose as one of the promising candidates for recognition of amino acids.

Among metal complexes, metalloporphyrins can provide a framework suitable for arranging cooperative binding sites for guest recognition, and have been studied as host molecules.[3] In a previous paper,[4] we have reported that a chiral zinc complex of *N*-methylmesoporphyrin II having a xylylenediamido strap (**1**) is capable of enantioselectively binding Z-amino acid (*N*-benzyloxycarbonyl-amino acid) anions. Spectroscopic studies have



1a X = –O–C(=O)–CH_3

1b X = –O–C(=O)–CH_2–NH–Z

1c X = –O–C(=O)–CH(R^1)–[CH_2]$_n$–N(R^2)–Z

(Z = –$CO_2CH_2C_6H_5$)

shown the formation of two hydrogen bonds between the strap amide functionalities of **1** and the substrate (Figure 1), which play an essential role in the enantioselection. More recently, we have also found that the same chiral receptor can discriminate the helical sense of polyglutamic acid in aqueous media.[5] In these cases, however, no appreciable enantioselection occurred with a non-strapped chiral receptor (**2a**) without hydrogen-bonding capability.[5, 6] These observations prompted us to investigate the potential of the strapped receptor (**1**) for guest-selective binding of *Z*-amino acids.[7] In the present paper, we report results of competitive complexation of *Z*-amino acids under varying conditions, and discussed the guest selectivity of **1** by focusing attention on the hydrogen-bonding and steric interactions.

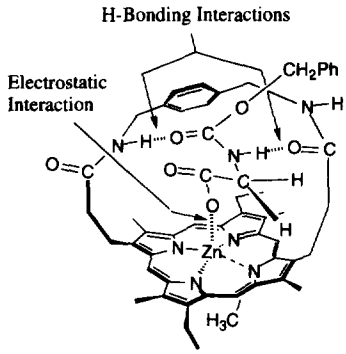
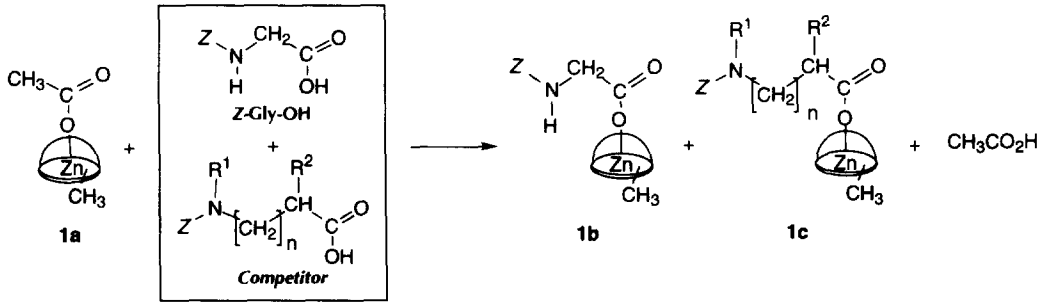


Figure 1. A schematic diagram of the *Z*-glycinate complex (**1b**).

RESULTS

Competitive complexation of *Z*-amino acids with the receptor (**1**) was investigated in $CDCl_3$ using *Z*-glycine as a reference guest (Scheme 1), and the guest selectivities (Table 1) were evaluated by means of ^1H NMR. On the basis of the previous study,[4] nine different *Z*-amino acids were chosen as the competitors for *Z*-glycine, which can be classified into two types according to their hydrogen-bonding capability with the strapped receptor **1**. Namely, the first seven *Z*-amino acids in Table 1, including *Z*-glycine, bear a NHCO moiety and can form hydrogen bonds with the strap amido functionalities in **1** (Figure 1), whereas no hydrogen-bonding interactions are operative for the latter two *Z*-amino acids.[4]

Scheme 1



Competition with Z-amino acids having a hydrogen-bonding capability.

Upon mixing of racemic **1a** with an equimolar mixture of *Z*-glycine (*Z*-Gly-OH) and *Z*-*L*-alanine (*Z*-*L*-Ala-OH) ($[\mathbf{1a}]_0$ / [*Z*-Gly-OH]$_0$ / [*Z*-*L*-Ala-OH]$_0$ = 1.25 / 5 / 5 in mM) at 25 °C, the signals due to the axial acetate (δ –1.32) and *N*-methyl groups (δ –4.05) of **1a** completely disappeared, while new signals due to the *Z*-glycinate (**1b**) (δ –2.26 (CH_2CO_2), δ –3.87 (*N*-CH_3)) and *Z*-*L*-alaninate complexes (**1c**, R^1 = H, R^2 = CH_3, n = 0) (δ –1.15 and –1.26 (CH_3CHCO_2), δ –4.02 and –4.12 (*N*-CH_3))[8, 9] appeared together with a singlet signal due to the methyl group of free acetic acid (δ 2.12). The mole ratio of **1b** to **1c**, as determined from the relative intensity of the corresponding *N*-CH_3 signals, was 83 : 17, indicating that *Z*-Gly-OH was preferentially bound to **1** over *Z*-*L*-Ala-OH (run 1). Under similar conditions, *Z*-Gly-OH was preferred (> 80 %) over *Z*-*L*-valine (*Z*-*L*-Val-OH), *Z*-*L*-leucine (*Z*-*L*-Leu-OH), *Z*-*L*-isoleucine (*Z*-*L*-Ile-OH), and *Z*-*L*-phenylalanine (*Z*-*L*-Phe-OH) (runs 3, 4, 6, and 9), where the selectivity for *Z*-Gly-OH was as high as 90 % when the side chain of the competitor was bulky (runs 4 and 6).

The topology of the hydrogen-bonding NHCO functionality relative to the CO_2H group in the guest molecule is also important: In competition of *Z*-Gly-OH with *Z*-β-Ala-OH having two methylene units between the NHCO and CO_2H groups, the selectivity for *Z*-Gly-OH was 94 % (run 2), which is higher than that in the competition with *Z*-*L*-Ala-OH, an isomer of *Z*-β-Ala-OH (run 1). The presence of a proton-donating or -accepting side-chain functionality in the guest molecule also affects the selectivity. For example, with *Z*-*L*-serine (*Z*-*L*-Ser-OH, run 7) or *Z*-*L*-methionine (*Z*-*L*-Met-OH, run 8) as the competitor, the selectivity for *Z*-Gly-OH was only ~70 % under similar conditions.

Table 1. Competitive Reaction of *Z*-Gly-OH and *Z*-Amino Acids with **1a**. [a]

Run	Competitor	Solvent	Selectivity for Z-Gly-OH (%) [b]
1	*Z*-*L*-Ala-OH	$CDCl_3$	83
2	*Z*-β-Ala-OH	$CDCl_3$	94
3	*Z*-*L*-Val-OH	$CDCl_3$	81
4	*Z*-*L*-Leu-OH	$CDCl_3$	90
5	*Z*-*L*-Leu-OH	CD_3OD	80
6	*Z*-*L*-Ile-OH	$CDCl_3$	89
7	*Z*-*L*-Ser-OH	$CDCl_3$	67
8	*Z*-*L*-Met-OH	$CDCl_3$	72
9	*Z*-*L*-Phe-OH	$CDCl_3$	81
10	*Z*-Sar-OH	$CDCl_3$	94
11	*Z*-Sar-OH	CD_3OD	60
12	*Z*-*L*-Pro-OH	$CDCl_3$	>99
13 [c]	*Z*-*L*-Pro-OH	$CDCl_3$	>99

[a] $[\mathbf{1a}]_0$ / [Z-Gly-OH]$_0$ / [competitor]$_0$ = 1.25 / 5 / 5 in mM, at 25 °C. [b] By ^{1}H NMR. [c] $[\mathbf{1a}]_0$ / [Z-Gly-OH]$_0$ / [*Z*-*L*-Pro-OH]$_0$ = 1 / 2 / 6 in mM.

Competition with Z-amino acids without hydrogen-bonding capability.

Under similar conditions to the above, competition of Z-Gly-OH with Z-*L*-proline (Z-*L*-Pro-OH) for the complexation with **1** resulted in an exclusive formation of the Z-glycinate complex (**1b**) (run 12). Such a perfect selection of Z-Gly-OH also occurred even in the presence of excess Z-*L*-Pro-OH with respect to Z-Gly-OH ($[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / $[Z\text{-}L\text{-Pro-OH}]_0$ = 1 / 2 / 6 in mM) (run 13). Likewise, in competition of Z-Gly-OH with Z-sarcosine (Z-Sar-OH) ($[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / $[Z\text{-Sar-OH}]_0$ = 1.25 / 5 / 5 in mM), Z-Gly-OH was preferred in 94 % selectivity (run 10).

Guest selection in protic media.

In general, hydrogen-bonding host - guest interactions are prohibited in protic media.[10] Thus, as for the two selected cases of the above guest combinations, Z-Gly-OH / Z-*L*-Leu-OH and Z-Gly-OH / Z-Sar-OH, the competitive complexation with **1** was investigated in CD_3OD. In the competition of Z-Gly-OH with Z-Sar-OH, where only Z-Gly-OH is capable of forming hydrogen bonds with the receptor,[4] the selectivity for Z-Gly-OH was considerably decreased from 94 % ($CDCl_3$, run 10) to 60 % in CD_3OD (run 11). In sharp contrast, in the Z-Gly-OH / Z-*L*-Leu-OH competition, where both guests are eligible for a hydrogen-bonding interaction with **1**, the selectivity for Z-Gly-OH, upon change of the solvent from $CDCl_3$ to CD_3OD, dropped only by 10 % (90 % → 80 %) (runs 4 and 5).

In the previous studies on chiral recognition of Z-amino acid anions with **1**,[4] we have employed a $CHCl_3$ / water biphasic system as the medium. However, in this biphasic medium, the competitive reaction of two Z-amino acid anions with **1a** resulted in a preferential binding of the substrates with hydrophobic side chains. For example, mixing of a $CHCl_3$ solution of racemic **1a** with an aqueous solution of an equimolar mixture of Z-Gly-ONa and Z-*L*-Val-ONa resulted in the formation of the Z-valinate complex (**1c**, R^1 = H, R^2 = $CH(CH_3)_2$, n = 0) in 100 % selectivity. Similarly, Z-*L*-Leu-O^- (93 %), Z-*L*-Phe-O^- (94 %), and Z-*L*-Met-O^- (93 %) were preferred over Z-Gly-O^-. In contrast, the selectivity for less hydrophobic Z-*L*-Ala-O^- was very poor (42 %), and that for Z-Ser-O^- having a hydroxylated side chain was only 14 %. On the

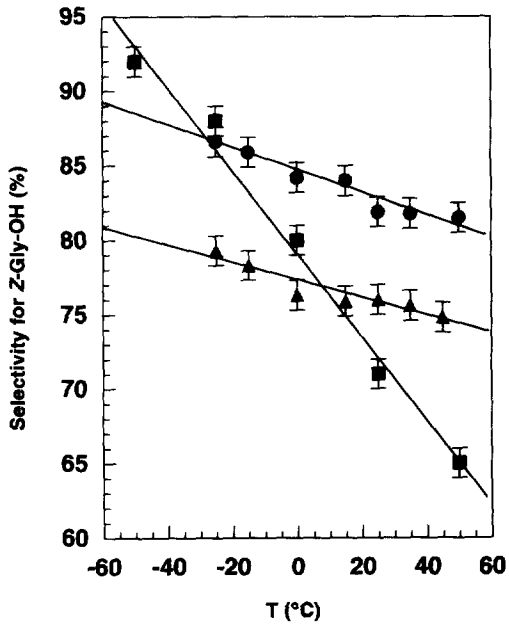


Figure 2. Temperature effects on the selectivity of **1** for Z-Gly-OH in competition with Z-Sar-OH (■), Z-*L*-Leu-OH (●), and Z-*L*-Ile-OH (▲) in $CDCl_3$. Conditions: $[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / $[Z\text{-Sar-OH}]_0$ = 1 / 1.5 / 4 in mM; $[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / [Z-*L*-Leu-OH or Z-*L*-Ile-OH]$_0$ = 1.25 / 2.5 / 7.5 in mM.

other hand, in such a $CHCl_3$ / water biphasic system, a similar, high selectivity for Z-amino acids with hydrophobic side chains was observed for the non-strapped receptor (**2a**) without hydrogen-bonding capability. For example, in a competitive complexation of Z-Gly-O^- and Z-*L*-Val-O^- ($[\mathbf{2a}]_0$ / $[Z\text{-Gly-ONa}]_0$ / $[Z\text{-}L\text{-Val-ONa}]_0$ = 1.25 / 5 / 5 in mM), the Z-valinate complex was formed in almost 100 % selectivity.

Temperature effects on guest selection.

In the competitive binding of Z-Gly-OH and Z-Sar-OH with **1a**, the guest selectivity was clearly dependent on the temperature (Figure 2, ■): At 25 °C, the competition of Z-Gly-OH and a 2.7-fold excess of Z-Sar-OH in complexation with **1a** ($[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / $[Z\text{-Sar-OH}]_0$ = 1 / 1.5 / 4 in mM, $CDCl_3$) resulted in 71 % selectivity for the Z-glycinate complex (**1b**). On the other hand, when the temperature for the complexation was lowered to –50 °C, the selectivity for Z-Gly-OH was considerably increased to 92 %. From these selectivities, the relative association constants (*Krel*) for Z-Gly-OH / Z-Sar-OH at 25 and –50 °C were evaluated to be 17.7 ($\Delta\Delta G$ = –1.7 kcal·mol^{-1}) and 117 ($\Delta\Delta G$ = –2.2 kcal·mol^{-1}), respectively. Plotting of Ln (*Krel*) versus 1/T (van't Hoff - type fitting) gave a straight line, which afforded $\Delta\Delta H$ and $\Delta\Delta S$ of –3.4 kcal·mol^{-1} and –5.5 cal·mol^{-1}·K^{-1}, respectively. In sharp contrast to the above, in competition of Z-Gly-OH with Z-*L*-Leu-OH or Z-*L*-Ile-OH ($[\mathbf{1a}]_0$ / $[Z\text{-Gly-OH}]_0$ / $[\text{competitor}]_0$ = 1.25 / 2.5 / 7.5 in μM), where both guests have a hydrogen-bonding capability with the receptor, the temperature dependency of the guest selectivity was much smaller (Figure 2, ● and ▲).

DISCUSSION

As already reported,[4] Z-amino acids having a hydrogen-bonding NHCO functionality is bound to the receptor (**1**) via two hydrogen bonds in addition to the electrostatic force (Figure 1), and such a multi-point interaction is quite essential for the enantioselection. In the present study on the competitive complexation of Z-amino acids with **1a** in $CDCl_3$, the considerably low selectivities for Z-*L*-Pro-OH and Z-Sar-OH without NHCO functionality (runs 10, 12, and 13) again indicate that the hydrogen-bonding interaction is one of the important factors for the guest selection. This is also supported by the low guest selectivity in the Z-Gly-OH / Z-Sar-OH competition in CD_3OD as solvent (run 11), where the host - guest interaction via hydrogen bonds is considered to be very weak or negligible. On the other hand, when the two competing guests both possess a hydrogen-bonding NHCO functionality, a steric repulsion between the strapped receptor (**1**) and the side chain of the guest seems to be a primary factor for the guest selection, taking into account the small solvent effect on the selectivity (runs 4 and 5) together with the higher selectivities for Z-Gly-OH in competition with Z-amino acids having bulkier side chains (runs 4 and 6). Consistently, in sharp contrast with the competition between guests with and without hydrogen-bonding capability (Z-Gly-OH / Z-Sar-OH [■], Figure 2), the guest selection in such cases (Z-Gly-OH / Z-Leu-OH (●) and Z-Gly-OH / Z-Ile-OH (▲)) remains virtually intact on elevating the temperature where hydrogen-bonding interactions are weaken.

In the $CDCl_3$ / water biphasic system, on the other hand, the guest selectivity of the strapped receptor

(**1a**) is apparently dominated by a hydrophobic host - guest interaction, rather than the hydrogen-bonding or steric interaction, since the non-strapped receptor (**2a**) showed the same guest preference as **1a**.

CONCLUSION

In the present paper, we have demonstrated that the metalloporphyrin receptor (**1**) with a hydrogen-bonding strap cavity on the metal ion center, is capable of discriminating *Z*-amino acids, and exhibits a high selectivity for *Z*-glycine in $CDCl_3$. The solvent and temperature effects on the guest selectivity clearly indicates an important role of the hydrogen-bonding or steric interaction in the guest selection. Addition of catalytic functions to the receptor may be the subject worthy of further investigation.

EXPERIMENTAL

General.

Zinc acetate complexes, **1a** and **2a**, were prepared as reported.[4] $CDCl_3$ used for guest selection was distilled over CaH_2 and stored under argon. *Z*-Amino acids from Tokyo Kasei or Sigma were used as received. ^{1}H NMR spectra were recorded on a JEOL Type GSX-270 spectrometer operating at 270 MHz. Chemical shifts (ppm) were determined with respect to $CHCl_3$ (δ 7.28) or CH_3OD (δ 3.3) as an internal standard.

Competitive complexation of Z-amino acids.

Typically, to a $CDCl_3$ solution (0.8 mL) of a mixture of *Z*-Gly-OH and a competitor (40 μmol each) was added racemic **1a** (10 μmol) under dry argon, and the mixture after stirred at room temperature for 30 min was subjected to ^{1}H NMR analysis. The selectivities for *Z*-Gly-OH in runs 1 - 4, 6 - 9, 12, and 13 (Table 1) were determined from the relative intensity of the *N*-methyl signals of **1b** and **1c** (Table 2), where the assignments were made by reference to the authentic samples prepared as reported previously.[4] For the *Z*-Gly-OH / *Z*-Sar-OH competition in $CDCl_3$ (run 10) and the competitions in CD_3OD (runs 5 and 11), the relative intensity of the signals due to the axial ligands of **1b** to **1c** was used to evaluate the guest selectivity, since the corresponding *N*-methyl signals were overlapped with each other. Selected ^{1}H NMR signals due to the axial ligands were as follows. For **1b** ($CDCl_3$, 25 °C): δ –2.26

Table 2. ^{1}H NMR Chemical Shifts of *N*-Methyl Groups of **1** at 25 °C.

Compound	Solvent	Chemical Shifts (δ, ppm) [a]
1a	$CDCl_3$	–4.05
1a	CD_3OD	–4.03
1b	$CDCl_3$	–3.87
1b	CD_3OD	–4.02
1c (X = Z-β-Ala-O)	$CDCl_3$	–4.16
1c (X = Z-*L*-Ala-O)	$CDCl_3$	–4.12, –4.02
1c (X = Z-*L*-Val-O)	$CDCl_3$	–4.13, –4.03
1c (X = Z-*L*-Leu-O)	$CDCl_3$	–4.19, –4.13
1c (X = Z-*L*-Leu-O)	CD_3OD	–4.27, –4.00
1c (X = Z-*L*-Ile-O)	$CDCl_3$	–4.16, –4.09
1c (X = Z-*L*-Ser-O)	$CDCl_3$	–4.08, –4.17
1c (X = Z-*L*-Met-O)	$CDCl_3$	–4.13, –4.08
1c (X = Z-*L*-Phe-O)	$CDCl_3$	–4.07, –4.01
1c (X = Z-Sar-O)	$CDCl_3$	–3.91
1c (X = Z-Sar-O)	CD_3OD	–3.99
1c (X = Z-*L*-Pro-O)	$CDCl_3$	–4.14, –4.02

[a] Paired signals are due to the Z-*L*-amino acid complexes of (*R*)- and (*S*)-**1**, respectively (see ref 8).

(CH_2CO_2). For **1b** (CD_3OD, 25 °C): δ –2.28 (CH_2CO_2). For **1c** (X = Z-*L*-Leu-O (R^1 = H, R^2 = $CH_2CH(CH_3)_2$, n = 0)) ($CDCl_3$, 25 °C): δ –1.65 and –1.23 (CH_2CHCO_2).[4] For **1c** (X = Z-Sar-O ($R^1 = CH_3$, $R^2 = CH_2$, n = 0)) ($CDCl_3$, 25 °C): δ –1.88 and –0.64 (CH_2CO_2, diastereotopic). For **1c** (X = Z-Sar-O (R^1 = CH_3, $R^2 = CH_2$, n = 0)) (CD_3OD, 25 °C): δ –2.07 and –0.89 (CH_2CO_2, diastereotopic).

The association constant for Z-Gly-OH relative to that for the competitor (*Krel*) was determined according to eqs. 1 - 3 (Scheme 2), where K_G, and K_{AA} denote the association constants of **1** with Z-Gly-OH

Scheme 2

$$\mathbf{1a} + \text{Z-Gly-OH} \underset{}{\overset{K_G}{\rightleftharpoons}} \mathbf{1b} + CH_3CO_2H$$

$$\mathbf{1a} + \text{Z-AA-OH} \underset{}{\overset{K_{AA}}{\rightleftharpoons}} \mathbf{1c} + CH_3CO_2H$$

$$K_G = \frac{[\mathbf{1b}]\,[CH_3CO_2H]}{[\mathbf{1a}]\,[\text{Z-Gly-OH}]} \quad (1) \qquad K_{AA} = \frac{[\mathbf{1c}]\,[CH_3CO_2H]}{[\mathbf{1a}]\,[\text{Z-AA-OH}]} \quad (2)$$

$$K_{rel} = K_G / K_{AA} = \frac{[\mathbf{1b}]\,[\text{Z-AA-OH}]}{[\mathbf{1c}]\,[\text{Z-Gly-OH}]} \quad (3)$$

and with the competitor, respectively.

Competitive single - extraction of Z-amino acid anions.

A $CHCl_3$ (5 mL) solution of racemic **1a** (10 μmol) was stirred at room temperature for 2 h with an aqueous solution (5 mL) of a mixture of two Z-amino acid sodium salts (100 μmol each). The organic phase separated was washed with water, dried over Na_2SO_4, and filtered, then the residue after stripping off volatile fractions was subjected to ^1H NMR analysis in $CDCl_3$ (0.5 mL), where the ratio of **1b** to **1c** was determined in a manner similar to the above.

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8. Paired signals are due to the two diastereoisomers.

9. For (*R*)-**1** / *Z*-*L*-Ala, δ –1.15 and –4.12; for (*S*)-**1** / *Z*-*L*-Ala, δ –1.26 and –4.02.

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