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Pincer Ligands Based on α-Amino Acids: IV.* Schiff Bases Derived from Pyridine-2,6-dicarbaldehyde. Synthesis and Intramolecular Dynamics

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Abstract—A number of pincer Schiff base and amine ligands were synthesized from pyridine-2,6-dicarbaldehyde and α-amino acids, L-methionine and L-serine. The Schiff base derived from L-serine was shown to exist as an equilibrium mixture with diastereoisomeric oxazolidines. The ring–chain tautomerism was confirmed by the results of reduction of the azomethine bond. The reduction products, pincer amines, exist in solution as mixtures of conformers differing in the degree of aggregation of the amino acid residues.

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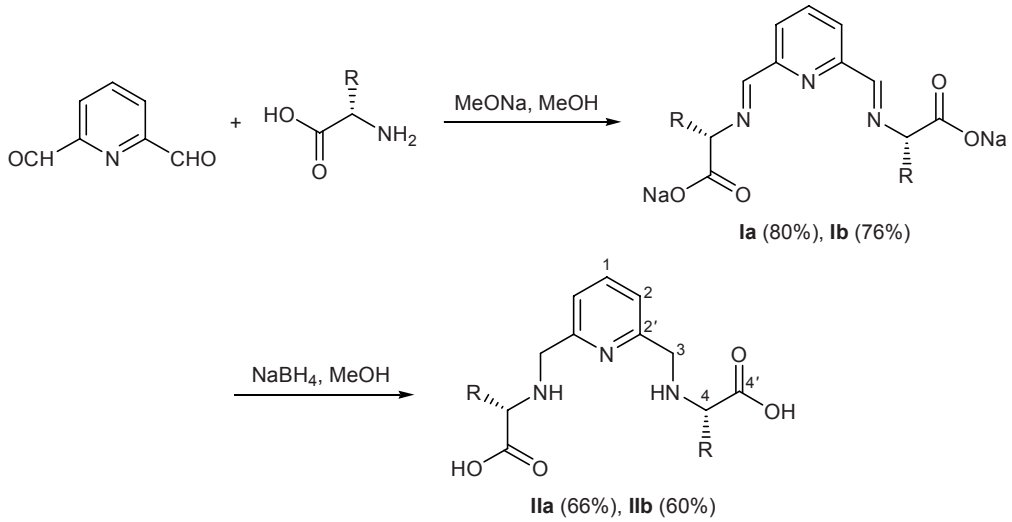
Schiff base ligands obtained on the basis of pyridine derivatives play an important role in coordination chemistry due to their ability to bind and stabilize low-valence metal ions [2]. Complexes formed by these ligands are used in the assembly of various supramolecular structures [3, 4], e.g., helicates and capsules, as well as in the preparation of liquid crystals [5]. In addition, chiral 2,6-bis(dihydrooxazol-2-yl)pyridine derivatives were shown to catalyze enantioselective reactions, such as [2+4]-cycloadditions (Diels–Alder) [6] and cyclopropanation [7]. One more important field of application of optically active complexes of 2,6-bis(dihydrooxazol-2-yl)pyridine derivatives is based on their ability to act as enantioselective receptors for particular enantiomers of amino acids in polar solvents [8]. Only derivatives of pyridine-2-carbaldehyde [9] and complexes derived from 2-acetylpyridine [10] were studied previously, but the corresponding Schiff base ligands were not characterized by NMR spectroscopy, so that their structure in solution was not interpreted unambiguously.

The goal of the present work was to synthesize optically active pincer ligands on the basis of pyridine-2,6-dicarbaldehyde and natural amino acids and examine their properties. The ligands were synthesized following the general procedure developed by us previously [1], by reaction of pyridine-2,6-dicarbaldehyde with amino acid sodium salts and subsequent reduction of Schiff bases **I** to amines **II** (Scheme 1). The product structure was determined by NMR and IR spectroscopy. The ^{1}H NMR spectra were recorded in methanol-d_4. Schiff base **Ia** displayed in the ^{1}H NMR spectrum a signal at δ 8.43 ppm from the azomethine CH=N proton. Protons in the pyridine ring had similar chemical shifts and resonated as a multiplet at δ 7.89 ppm. The amino acid fragment gave signals in a stronger field. The 4-H signal was a doublet of doublets at δ 4.1 ppm, while protons in the methionine side chain $CH_2CH_2SCH_3$ appeared as two multiplets at δ 2.2 and 2.5 ppm and a singlet at δ 2.06 ppm (CH_3). Unlike compound **Ia**, Schiff base **Ib** displayed a more complex pattern in the ^{1}H NMR spectrum. The spectrum of **Ib** contained two clearly resolved signals in the region typical of azomethine CH=N protons, at δ 8.36 and 8.41 ppm; a set of overlapping signals with different multiplicities was observed in the region δ 7.5–8.0 ppm; and signals in the aliphatic region (δ 3.5–4.0 ppm) were also overlapped by each other. In addition, two sets of signals were present in the region δ 5.3–5.8 ppm (Fig. 1). According to published data [11], signals in the latter region were observed in the ^{1}H NMR spectrum of Schiff base derived from serine

* For communication III, see [1].

Scheme 1.



R = $MeS(CH_2)_2$ (**a**), $HOCH_2$ (**b**).

methyl ester and ferrocenecarbaldehyde and were assigned to protons in position *2* of the oxazolidine ring in the ring isomer (Scheme 2). However, Schiff base salts obtained by us previously from serine and derivatives of phenol or ferrocene showed no signals in the corresponding region (see [1] and references given therein to our early studies).

Thus the ^{1}H NMR data led us to conclude that salt **Ib** in solution exists as a mixture of ring and chain tautomers (Scheme 3), the latter prevailing (δ 8.41 ppm, s). In keeping with Scheme 3, signals from the CH=N protons in two diastereoisomeric cyclic tautomers (*R*)-**Ib** and (*S*)-**Ib** might be expected to appear in the spectrum. However, we observed only one signal at δ 8.36 ppm, presumably due to similarity of chemical shifts of protons that are distant from the chiral center. The intensity ratio of the signals at δ 8.41 and 8.36 ppm was 2:0.68. This means that the ratio of tautomers **Ib**–[(*R*)-**Ib** + (*S*)-**Ib**] is 1:0.68. Two sets of signals in the region δ 5–6 ppm were assigned to

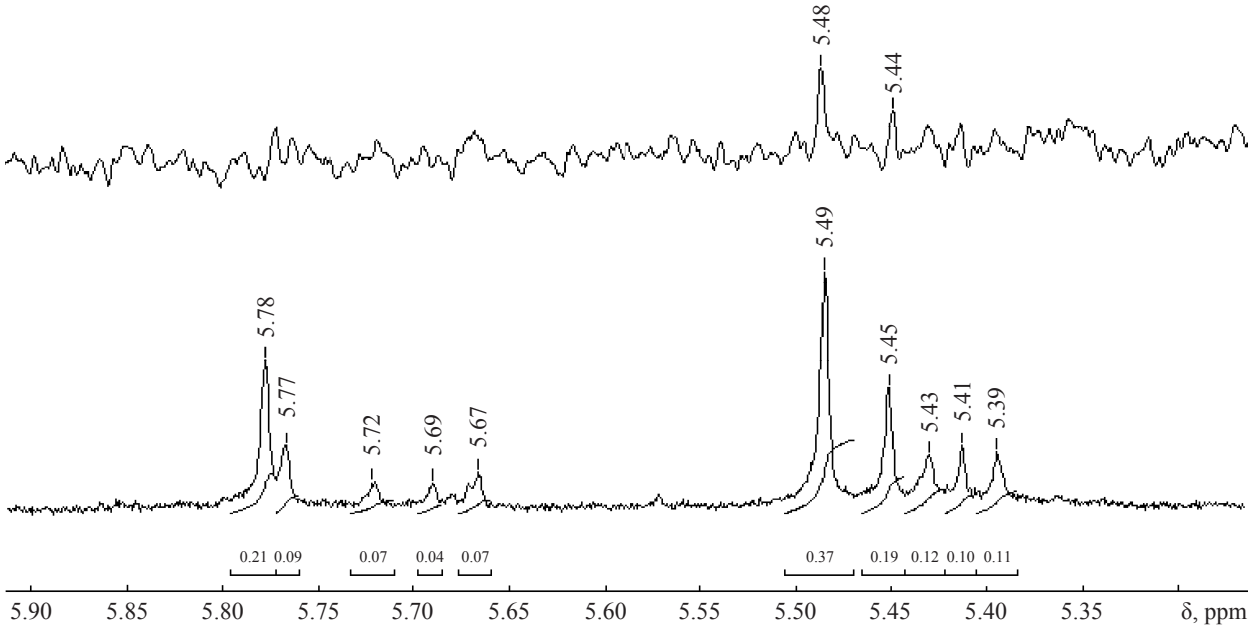
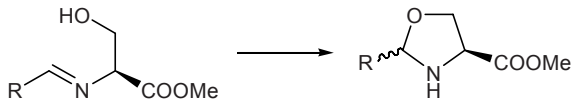


Fig. 1. Signals from diastereotopic protons in the ^{1}H NMR spectra of diastereoisomeric cyclic oxazolidine tautomers of compound **Ib** (0.1 M solution in CD_3OD). The upper plot is a fragment of the NOE spectrum of compound **Ib** (irradiation at a frequency corresponding to resonance of protons in the α-position of the amino acid fragment).

Scheme 2.

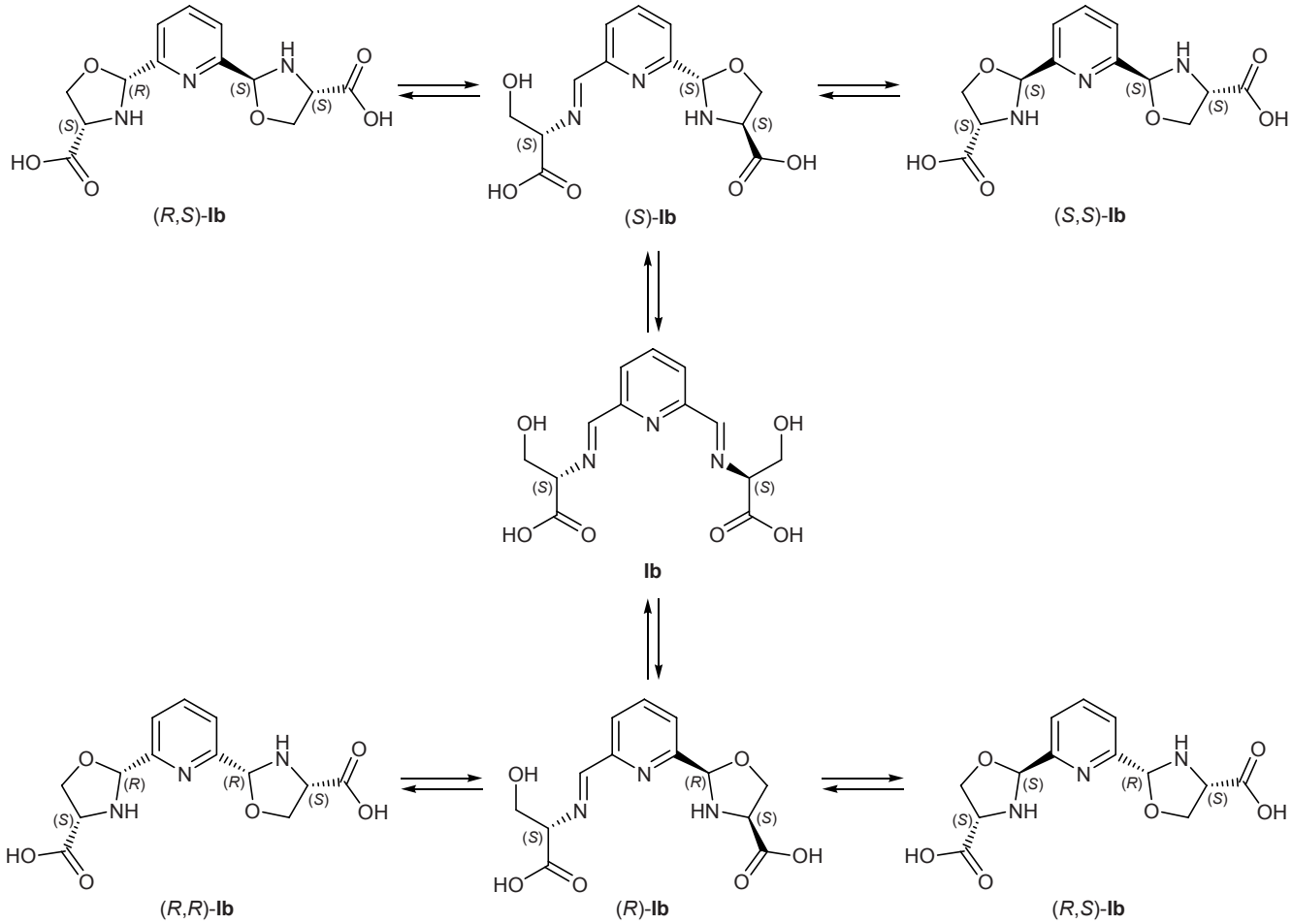


diastereotopic protons on C^2 in the oxazolidine structures (Scheme 3), as well as to diastereotopic protons in isomeric compounds **Ib**-(*R*)-OH and **Ib**-(*S*)-OH formed via addition of water molecule at one CH=N bond (Scheme 4).

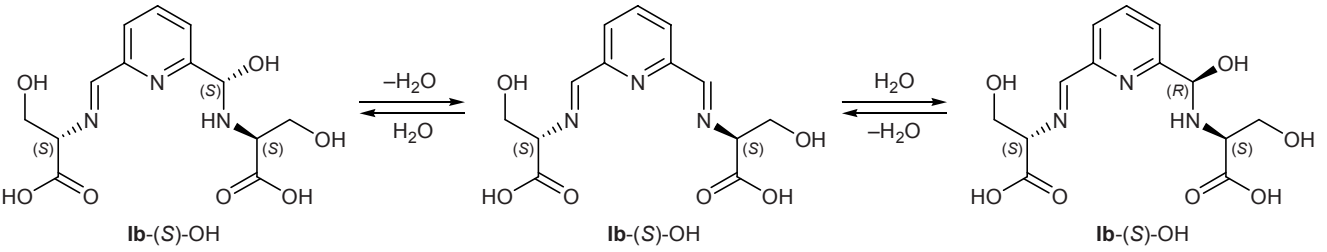
In order to assign signals arising from the adducts with water, we examined variation of the intensity of signals in the region δ 5–6 ppm versus **Ib**–H_2O ratio. For this purpose, ^{1}H NMR spectra of solutions containing compound **Ib** at different concentrations and water at a constant concentration were recorded. Reduction of the concentration of Schiff base **Ib** by a factor of 4 resulted in appearance of a signal at δ 5.77 ppm, while the intensity of the signal at δ 5.39 ppm increased twofold. These findings indicated that the signals at δ 5.77 and 5.39 ppm belong to products of partial hydrolysis of compound **Ib**. The other signals were assigned to cyclic tautomers of **Ib**. The presence of two sets of signals may be rationalized in terms of different steric environments of protons on C^2 in the oxazolidine ring. In the tautomer with *S* configuration of the C^2 chiral center the 2-H proton appears closer to the carboxy group in position *4* of the oxazolidine ring (Fig. 2); therefore, it resonates in a weaker field as compared to the corresponding *R*-diastereoisomer.

Taking into account the ^{1}H NMR spectra of (–)-ephedrine derivatives whose structure was determined by X-ray analysis, the downfield signals were assigned to the (*R*)-isomers, and the upfield signals, to the (*S*)-isomers [12]. On the other hand, NOE experiments showed the opposite signal arrangement for norephedrine and norpseudoephedrine: in the latter case, the signal belonging to the (*R*)-isomer appeared in a stronger field relative to the corresponding signal of the (*S*)-isomer [13]. Also, there are discrepancies in the assignment of signals from protons on C^2 in 2-substituted (4*S*)-carboxyoxazolidines. Khrushcheva et al.

Scheme 3.



Scheme 4.



[11] assigned the downfield signal at δ 5.43 ppm to the (2*R*)-isomer, and the signal at δ 5.10 ppm, to the (2*S*)-isomer (Fig. 2), whereas Ando et al. [14] believed that the downfield signal belongs to the (2*S*)-isomer. We performed NOE experiments [15, 16] to assign signals from protons in the oxazolidine rings to particular diastereoisomers (Fig. 2). Irradiation at a frequency corresponding to resonance of 4-H showed response at the upfield signal (δ 5.4–5.5 ppm), whereas no response was observed at the downfield signal at δ 5.6–5.8 ppm (Fig. 1). Thus the results of NOE experiments led us to conclude that signals in the region δ 5.4–5.5 ppm belong to 2-H of the (2*R*)-isomeric oxazolidine fragments in cyclic tautomers.

Taking into account that the intensities of signals at δ 5.78 and 5.48 ppm are 0.21 and 0.37, respectively, these signals may be assigned to cyclic tautomers (*S*)-**Ib** and (*R*)-**Ib**. Therefore, we can estimate diastereoselectivity of intramolecular cyclization. The formation of (2*R*)-isomers appears to be preferred, as was reported previously for the Schiff base derived from benzaldehyde and serine methyl ester [14]. The reason may be more favorable conformation of the oxazolidine ring, where both substituents on C^2 and C^4 occupy equatorial positions [(2*R*), Fig. 2]; in the (2*S*)-diastereoisomers, one of these substituents should inevitably occupy axial position. However, the diastereoselectivity in the cyclization is not high (36:64).

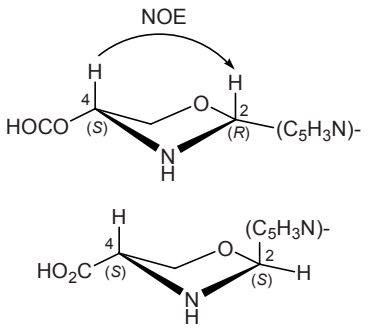


Fig. 2. Nuclear Overhauser effect for cyclic oxazolidine tautomer of compound **Ib** with *R* configuration of the C^2 atom.

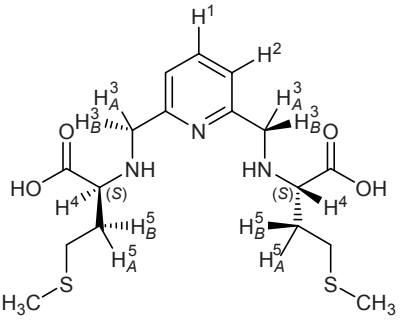
As noted in [12] for substituted benzaldehyde derivatives, the presence of electron-withdrawing substituents reduces the diastereoselectivity and fraction of the cyclic tautomers [12]. The other signals in the region δ 5–6 ppm belong to cyclic tautomers (*S*,*R*)-**Ib**, (*S*,*S*)-**Ib**, (*R*,*R*)-**Ib**, and (*R*,*S*)-**Ib** (Scheme 3), but we failed to perform complete assignment of signals to these stereoisomers because of their low concentration.

The equilibrium in DMSO solution is displaced toward the open-chain isomer, while signals from the corresponding cyclic tautomers had intensities comparable to background so that their concentration could not be estimated.

The isolated crystalline Schiff bases were characterized by IR spectroscopy. The IR spectra of **Ia** and **Ib** turned out to be very similar to each other. The spectra contained broad absorption bands at 1593 (**Ia**) and 1597 cm^{-1} (**Ib**), belonging to stretching vibrations of the CH=N bonds conjugated with the aromatic system and overlapped by absorption bands due to asymmetric stretching vibrations of the carboxylate ion. This assignment is consistent with the data reported previously [9] for the Schiff base (potassium salt) obtained from pyridine-2-carbaldehyde and valine [9]. Symmetric stretching vibrations of the carboxylate group gave rise to absorption at 1399 (**Ia**) and 1407 cm^{-1} (**Ib**). The difference in the asymmetric and symmetric stretching vibration frequencies is 194 (**Ia**) and 190 cm^{-1} (**Ib**), which confirms ionic character of bonds in the salt molecules. This means that both compounds **Ia** and **Ib** in the solid state have open-chain structure and that cyclic oxazolidine tautomers are formed only in solution. Furthermore, the position of the ring–chain equilibrium depends on the solvent nature, as was reported previously for ephedrine derivatives [17].

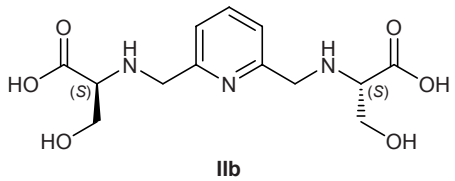
The reduction of compounds **Ia** and **Ib** with sodium tetrahydridoborate in methanol gave the corresponding diamines **IIa** and **IIb** (Scheme 1). Despite the existence of tautomeric equilibrium in methanol solution, the reduction of Schiff base **Ib** gave only amine **IIb**, in keeping with the dynamic character of tautomeric

transformations of the initial Schiff base. The ^{1}H NMR spectra of **IIa** and **IIb** lacked signals from CH=N protons, but those assignable to protons in methylene group attached to nitrogen (CH_2N) were present. The ^{1}H NMR spectrum of compound **IIa** should be considered in detail. Owing to the presence of electron-donating substituent, signals from protons in the pyridine ring are displaced upfield, the strongest shift being observed (as might be expected) for 2-H. Insofar as molecule **IIa** possesses chiral centers, not only the 5-H_A and 5-H_B protons (nearest to the asymmetric center) but also the 3-H_A and 3-H_B protons in the aminomethyl group become nonequivalent. The proton signals were unambiguously assigned on the basis of the NOE data which revealed interactions between the following spatially close protons: 3-H_B–4-H–5-H_B and 3-H_A–4-H–5-H_A. The nuclear Overhauser effect for 3-H_B–4-H–5-H_B was greater by a factor of 1.5 than for 3-H_A–4-H–5-H_A. Therefore, the most favorable conformation of molecule **IIa** is that in which the 4-H proton is located closer to 3-H_B and 5-H_B, whereas 3-H_A and 5-H_A are spatially closer to the carboxy group; as a result, the latter protons resonate in a slightly weaker field (by 0.1 ppm).



IIa

Unlike amine **IIa**, the 3-H protons in molecule **IIb** are not diastereotopic: only one signal is present at δ 4.54 ppm with an intensity corresponding to four protons (CH_2). Presumably, the predominant conformer of **IIb** in solution has a different structure in which the amino acid fragments are turned about the CH–NH bonds in such a way that the carboxy group appears maximally distant from the aminomethyl fragment.



IIb

Thus we have revealed reversible diastereoselective formation of oxazolidine fragments as a result of intramolecular attack by the serine hydroxy group on the azomethine carbon atom. The position of the ring–chain tautomeric equilibrium depends on the solvent nature. Signals from protons in the diastereoisomeric oxazolidines were assigned using NOE experiments. The reversible character of ring–chain tautomerism of Schiff bases derived from pyridine-2,6-dicarbalehyde and α-amino acid was confirmed by reduction of the CH=N bonds. Diastereoselective formation of a dynamic combinatorial library of chiral product attracts interest from the viewpoint of design of enantioselective sensor systems. We have also demonstrated that reduction products of pincer Schiff bases, the corresponding pincer amines, exist in solution as conformers differing by the degree of aggregation of the amino acid residues, which may be promising for enantioselective recognition.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Nicolet Protégé-460 spectrometer with Fourier transform. The ^{1}H and ^{13}C NMR spectra were measured at 20°C on a Bruker Avance-400 instrument using tetramethylsilane as reference. The ^{13}C signals are given according to the numbering shown in Scheme 1. The ^{1}H NMR signals of tautomers of **Ib** were assigned using two-dimensional COSY experiments. The signals from C^2 in diastereoisomeric oxazolidine structures were assigned using ^{13}C–^{1}H heteronuclear correlation technique (with protons resonating at δ 5.0–6.0 ppm).

Initial pyridine-2,6-dicarbaldehyde was synthesized according to the procedure described in [18]. Methanol was preliminarily distilled over CaH_2 in a stream of argon. The other reagents and solvents were commercial products used without additional purification.

(*S*,*S*)-2,6-Bis{[1-carboxy-3-(methylsulfanyl)-propyl]iminomethyl}pyridine disodium salt (Ia). L-Methionine, 2.98 g (20 mmol), was added to a solution of sodium methoxide prepared from 0.46 g (20 mmol) of metallic sodium and 100 ml of methanol. The mixture was stirred for 1 h, 1.35 g (10 mmol) of pyridine-2,6-dicarbaldehyde and 5 g of 3-Å molecular sieves were added, and the mixture was stirred for 30 h. The mixture was filtered, the filtrate was concentrated under reduced pressure to a volume of 15 ml, 70 ml of acetone was added to the residue, and the precipitate was filtered off, washed with acetone and diethyl ether, and dried under reduced pressure. Yield

3.52 g (80%), yellow powder, mp 140–143°C (decomp.). IR spectrum, ν, cm^{-1}: 1593, 1399, 1372, 1312, 809. ^1H NMR spectrum (CD_3OD), δ, ppm: 2.06 s (6H, SCH_3), 2.2 m (4H, CH_2), 2.5 m (4H, CH_2), 4.1 d.d (2H, CH), 7.89 m (3H, pyridine), 8.43 s (2H, HC=N). Found, %: C 46.41; H 5.03; N 9.39. $C_{17}H_{21}N_3Na_2O_4S_2$. Calculated, %: C 46.25; H 4.79; N 9.52.

(*S*,*S*)-2,6-Bis[(1-carboxy-2-hydroxyethyl)iminomethyl]pyridine disodium salt (Ib) was synthesized in a similar way from 2.1 g of L-serine and 1.35 g of pyridine-2,6-dicarbaldehyde. Yield 2.68 g (76%), mp 84–86°C (decomp.). IR spectrum, ν, cm^{-1}: 1597, 1407, 1036.

Tautomer **Ib**. ^1H NMR spectrum, δ, ppm: in CD_3OD: 7.81 d (2H, CH, ^3J = 7.83 Hz), 8.00 t (1H, CH, ^3J = 7.83 Hz), 8.41 s (2H, CH=N); in DMSO-d_6: 3.55 d.d (2H, CH, ^3J = 5.05, 6.80 Hz), 3.72 d.d (2H, CHN, ^2J = –13.48, ^3J = 6.80 Hz), 3.75 d.d (2H, CHN, ^2J = –13.48, ^3J = 5.04 Hz), 7.90 m (3H, CH), 8.26 s (2H, CH=N). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 65.37 (C^5), 78.90 (C^4), 127.16 (C^2), 140.02 ($C^{2'}$), 154.44 (C^1), 162.59 (C^3), 177.91 ($C^{4'}$).

(*S*)-**Ib**, (*R*)-**Ib**. ^1H NMR spectrum (CD_3OD), δ, ppm: 5.48 s (0.37H, CH, *R*), 5.78 s (0.21H, CH, *S*), 7.62 d (0.79H, CH, ^3J = 7.58 Hz), 7.70 d (0.91H, CH, ^3J = 7.58 Hz), 8.04 d (0.71H, CH, ^3J = 7.58 Hz), 8.36 s (0.67H, CH=N). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 93.27 (CH, *S*), 93.55 (CH, *R*). The aliphatic region contained overlapped signals from the CH_2CH fragment, which were not assigned. Found, %: C 44.00; H 3.95; N 11.77. $C_{13}H_{13}N_3Na_2O_6$. Calculated, %: C 44.20; H 3.71; N 11.90.

(*S*,*S*)-2,6-Bis{[1-carboxy-3-(methylsulfanyl)propyl]aminomethyl}pyridine (IIa). A solution of 2.21 g (5 mmol) of compound **Ia** in 100 ml of methanol was cooled to –30°C, 0.57 g (15 mmol) of sodium tetrahydridoborate was added, and the mixture was stirred for 1 h at –30°C and for 2 h at room temperature and filtered. Trifluoroacetic acid, 2.85 g (25 mmol), was added, the mixture was stirred for 2 h, and the product was filtered off, washed with acetone and diethyl ether, and dried under reduced pressure. Yield 1.33 g (66%), white powder, mp 228–230°C. IR spectrum, ν, cm^{-1}: 1690, 1637, 1596, 1455, 1389, 1336, 1527. ^1H NMR spectrum (CD_3OD), δ, ppm: 1.89 d.d (2H, CHN, ^2J = –14.18, ^3J = 7.83, 6.35 Hz), 1.95 d.d (2H, CHN, ^2J = –14.18, ^3J = 7.83, 6.35 Hz), 2.07 s (6H, SCH_3), 2.59 t (4H, CH_2, ^3J = 7.83 Hz), 3.19 d.d (2H, CH, ^3J = 6.35, 6.51 Hz), 3.75 d (2H, CHN, ^2J = –13.45 Hz), 3.85 d (2H, CHN, ^2J = –13.45 Hz), 7.28 d (2H, CH, pyridine, ^3J = 7.58 Hz), 7.70 t (1H, CH, pyridine, ^3J = 7.58 Hz). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 13.87 (C^7), 30.43 (C^6), 33.20 (C^5), 53.06 (C^3), 63.25 (C^4), 120.93 (C^2), 137.43 (C^1), 159.01 ($C^{2'}$), 180.29 ($C^{4'}$). Found, %: C 51.04; H 6.95; N 10.22. $C_{17}H_{27}N_3O_4S_2$. Calculated, %: C 50.85; H 6.78; N 10.46.

(*S*,*S*)-2,6-Bis[(1-carboxy2-hydroxyethyl)aminomethyl]pyridine (IIb). A solution of 1.77 g (5 mmol) of compound **Ib** in 100 ml of methanol was cooled to –30°C, 0.57 g (15 mmol) of sodium tetrahydridoborate was added, and the mixture was stirred for 1 h at –30°C and for 2 h at room temperature. The mixture was filtered, 10 ml of a 2.5 N solution of hydrogen chloride in methanol was added to the filtrate, the mixture was stirred for 2 h, and the solvent was distilled off under reduced pressure. The residue was extracted with ethanol, the extract was filtered and concentrated until crystallization started, 75 ml of acetone was added, and the precipitate was filtered off, washed with acetone and diethyl ether, and dried under reduced pressure. Yield 0.94 g (60%), white powder, mp 204–206°C. IR spectrum, ν, cm^{-1}: 1633, 1581, 1410, 1363, 1203, 1088, 1046. ^1H NMR spectrum (CD_3OD), δ, ppm: 3.83 d.d (2H, CH, ^3J = 4.15, 3.18 Hz), 3.96 d.d (2H, CHN, ^2J = –11.98, ^3J = 4.15 Hz), 4.08 d.d (2H, CHN, ^2J = –11.98, ^3J = 3.18 Hz), 7.39 d (2H, CH, pyridine, ^3J = 7.58 Hz), 4.54 s (4H, CH_2N), 7.85 t (1H, CH, pyridine, ^3J = 7.58 Hz). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 49.83 (C^5), 60.18 (C^3), 64.55 (C^4), 123.09 (C^2), 139.49 (C^1), 153.03 ($C^{2'}$), 172.69 ($C^{4'}$). Found, %: C 49.99; H 6.27; N 13.33. $C_{13}H_{19}N_3O_6$. Calculated, %: C 49.84; H 6.11; N 13.41.

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