

tion of Co(II) was postulated because the reaction observed with irradiated solutions exposed to air was considerably faster than that of pure Co(acac)<sub>2</sub> solutions under the same conditions. The pink color of pure Co(acac)<sub>2</sub> solutions, however, was rapidly changed to green by the addition of hydrogen peroxide.

The fact that benzil and acetic acid were detected

along with Co(bzac)<sub>2</sub> in the photolysis of Co(bzac)<sub>3</sub> seems to agree with the mechanism suggested above for Co(acac)<sub>3</sub>.

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CONTRIBUTION No. 388 FROM THE DEPARTMENT OF CHEMISTRY,  
TUFTS UNIVERSITY, MEDFORD, MASSACHUSETTS 02155

## The Formation of a Second Coordination Sphere for Tris(L-alaninato)cobalt(III) as Studied by Proton Magnetic Resonance

BY B. M. FUNG AND IRENE H. WANG

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The proton nmr spectra of the four isomers of tris(L-alaninato)cobalt(III) in D<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>O–D<sub>2</sub>SO<sub>4</sub> solutions are reported. The change of the nmr spectra with temperature and solvent composition are explained by the solvation of the complexes. In D<sub>2</sub>SO<sub>4</sub>, the carboxyl group in the ligand has a strong interaction with the acid. When D<sub>2</sub>O is first added to the solvent, the NH protons of the amino acid start to form hydrogen bonds with D<sub>2</sub>O. Further increase of the D<sub>2</sub>O content in the solvent leads to the departure of the acid molecules from the second coordination sphere. Increase of temperature tends to reduce the solvation of the complexes.

### Introduction

It has been recently demonstrated that the formation of a second coordination sphere due to the solvation of a complex can be detected by nuclear magnetic resonance (nmr).<sup>1</sup> For cobalt(III) complexes with ethylenediamine, the formation of hydrogen bonding between the NH protons and basic solvents is reflected in the change of the NH proton signal.<sup>1</sup> Other ligands containing acidic protons are expected to behave similarly. On the other hand, if a ligand contains a proton-accepting site, it may form hydrogen bonding with acidic solvents. The interaction may be detectable under favorable conditions. For ligands with both proton-donating and proton-accepting sites, the interaction of the complex with solvents of varying acidity would be most interesting.

All  $\alpha$ -substituted tris(L-amino acid) complexes of cobalt(III) have at least four isomers. Each of the geometrical (*cis* and *trans*) isomers can be separated into two optical ((+) and (–)) isomers. The geometrical isomers can be identified by their absorption spectra<sup>2–4</sup> and the optical isomers have different rotational properties.<sup>5–7</sup> All four forms for several amino acids have been isolated.<sup>5–7</sup> Of those complexes, Co(L-ala)<sub>3</sub> are the least complicated ones. They have relatively simple structures, and the conformations of the

chelate rings are probably fixed by the existence of the methyl groups. The NH<sub>2</sub> protons in the amino acid can act as proton donors, whereas the carboxyl group can behave as a proton acceptor. The formation of a second coordination sphere with both acids and bases is then expected for those complexes.

Although the proton nmr of *cis*-(–)-Co(L-ala)<sub>3</sub> and *trans*-(–)-Co(L-ala)<sub>3</sub> in D<sub>2</sub>O have been reported,<sup>7</sup> the study did not emphasize the solvent–solute interaction. The present work describes the nmr study on the four isomers of Co(L-ala)<sub>3</sub> in solutions of D<sub>2</sub>SO<sub>4</sub>–D<sub>2</sub>O mixtures. The results demonstrate that information on the second coordination sphere of the complexes with both D<sub>2</sub>O and D<sub>2</sub>SO<sub>4</sub> can be inferred from the results of proton magnetic resonance.

### Experimental Section

The Co(L-ala)<sub>3</sub> complexes were prepared according to the method of Mori, *et al.*,<sup>4</sup> and separated by methods suggested by Denning and Piper.<sup>7</sup> The *cis*-(+) isomer was obtained from ligand exchange of hexaamminecobalt(III) chloride. In preparing the other three isomers, potassium tricarbonylcobaltate(III) was used as the starting material.<sup>4</sup> The less soluble *trans*-(+) complex separated out first; the more soluble *trans*-(–) and *cis*-(–) isomers contained in the remaining mother liquor were separated on an alumina column. D<sub>2</sub>O and D<sub>2</sub>SO<sub>4</sub> (99%) were purchased from Stople Isotope Chemicals.

Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer. The signal of sulfuric acid was used as the external lock. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was added to the samples for measuring chemical shifts. However, it decomposed at elevated temperatures and in concentrated sulfuric acid and could not be used as an internal standard. Therefore in measuring the chemical shifts, we took the methyl peak of DSS in solutions of 1:1 D<sub>2</sub>O–D<sub>2</sub>SO<sub>4</sub> as 0.00 ppm and treated the methyl signals of the complexes as un-

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varying in solvents of other compositions. Actually the methyl signals of the complex did move slightly upfield with respect to added DSS when the D<sub>2</sub>O content in the solvent increased. The choice of an external standard was equally difficult because of the change of the susceptibility of the solvent with composition and temperature. Deuterium exchange was very slow in these systems; the proton spectra did not change after 24 hr or more.

### Results

*cis*-(+)-Co-(L-ala)<sub>3</sub>.—In concentrated D<sub>2</sub>SO<sub>4</sub> solution, the proton nmr spectrum consisted of four peaks of an intensity ratio 1:1:1:3 (Figure 1). The peak at highest

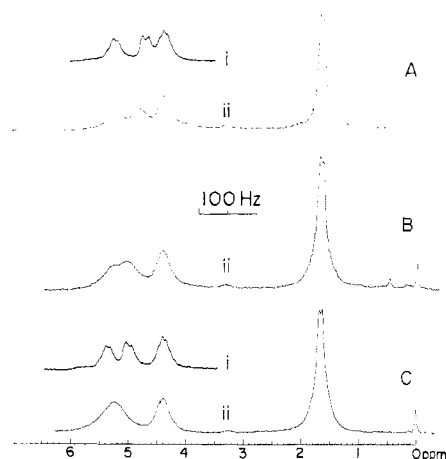


Figure 1.—The 100-MHz proton nmr spectra of *cis*-(+)-Co-(L-ala)<sub>3</sub>. The D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios were: A, 0.0; B, 0.4; C, 1.0. The temperatures were: i, 100°; ii, 25°. DSS was added to the solutions.

field was obviously due to the methyl group, which was split into a doublet by the  $\alpha$ -CH proton. The peak at  $-4.39$  ppm was assigned to the  $\alpha$ -CH proton, because an irradiation at this position decoupled the methyl doublet. The two peaks at  $-4.83$  and  $-5.25$  ppm were of equal intensity. They must arise from the two NH protons, which we will designate as NH <sub>$\alpha$</sub>  and NH <sub>$\epsilon$</sub> , respectively. With the increase of the D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratio in the solvent, the NH <sub>$\alpha$</sub>  signal moved downfield. The NH <sub>$\epsilon$</sub>  peak did not change with solvent composition so that the two NH signals coincided at D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> = 1. Spectra for further decrease of the acid content were not available because of the limited solubility of the complex. When the temperature was raised, the NH <sub>$\alpha$</sub>  peak moved upfield. For concentrated D<sub>2</sub>SO<sub>4</sub> solution, the change of temperature from 25 to 100° caused this peak to shift 0.09 ppm; for a solution of D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> = 1.0, the corresponding change was about 0.25 ppm (Figure 1). The NH <sub>$\epsilon$</sub>  peak and the CH peak stayed almost the same *vs.* the methyl signal through the change of solvent composition and temperature. The  $\alpha$ -CH and NH peaks did not show fine structure at room temperature. The spin-spin splittings were partly resolved at higher temperature, undoubtedly due to the decrease of the viscosity of the solvent. The coupling constants (Table I) were obtained by analyzing spin-decoupled spectra (Figure 2).

*cis*-(−)-Co(L-ala)<sub>3</sub>.—The proton nmr in D<sub>2</sub>SO<sub>4</sub> was

TABLE I  
PROTON-PROTON COUPLING CONSTANTS (IN HZ) FOR  
*cis*-Co(L-ala)<sub>3</sub>

	CH- NH <sub><math>\alpha</math></sub> <sup>a,b</sup>	CH- NH <sub><math>\epsilon</math></sub> <sup>b</sup>	NH <sub><math>\alpha</math></sub> - NH <sub><math>\epsilon</math></sub> <sup>b</sup>	CH- CH
<i>cis</i> -(+), D <sub>2</sub> SO <sub>4</sub> , 100°	7.6	8.1	8.8	6.5
<i>cis</i> -(−), D <sub>2</sub> SO <sub>4</sub> , 100°	8.2	7.4	8.6	6.5
<i>cis</i> -(−), 10:1 D <sub>2</sub> O-D <sub>2</sub> SO <sub>4</sub> , 60°	8.9	8.4	9.0	6.8

<sup>a</sup> These protons are in *cis* positions for *cis*-(+), and in *trans* positions for *cis*-(−). The subscript  $\alpha$  refers to axial positions with respect to the C<sub>3</sub> axis. <sup>b</sup> Estimated errors are  $\pm 0.5$  Hz because the peaks are quite broad.

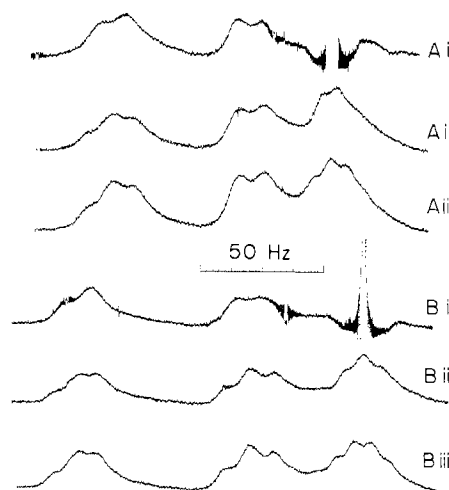


Figure 2.—The 100-MHz nmr spectra of the CH and NH<sub>2</sub> protons in (A) *cis*-(+)-Co(L-ala)<sub>3</sub> and (B) *cis*-(−)-Co(L-ala)<sub>3</sub> dissolved in D<sub>2</sub>SO<sub>4</sub> at 100°: i, the CH signal irradiated; ii, the CH<sub>2</sub> signal irradiated; iii, no irradiation.

very similar to that of the *cis*-(+)-Co(L-ala)<sub>3</sub> complex. The  $\alpha$ -CH proton had a peak at  $-4.24$  ppm, and the two peaks for the NH protons were at  $-4.81$  and  $-5.53$  ppm (Figure 3). They are designated as NH <sub>$\alpha$</sub>  and NH <sub>$\epsilon$</sub> , respectively, as in the previous case. When the composition of the solvent was changed, the  $\alpha$ -CH and the NH signals moved in an interesting way. For D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> = 0 to about 1, the CH and the NH <sub>$\alpha$</sub>  signals stayed almost unshifted with respect to the methyl group, while the NH <sub>$\epsilon$</sub>  signal moved downfield rapidly. Further increase of the D<sub>2</sub>O content in the solvent caused the three kinds of proton to move upfield in different extents: CH most, NH <sub>$\epsilon$</sub>  less, and NH <sub>$\alpha$</sub>  least (Figure 3). Raising the temperature of the samples brought both NH signals upfield, while the CH peak had very little change. The over-all changes for D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> from 0 to 10 were: CH,  $+0.36$  ppm; NH <sub>$\alpha$</sub> ,  $+0.26$  ppm; NH <sub>$\epsilon$</sub> ,  $-0.40$  ppm. These peaks showed fine structure when the viscosity of the solution was lowered by either raising the temperature or reducing the sulfuric acid content (Figure 3). The coupling constants were obtained by analyzing the spectra (Figure 2) with the aid of a double-resonance technique.

*trans*-(+)-Co(L-ala)<sub>3</sub>.—All three ligands in both *trans* isomers have slightly different environments and therefore gave rise to more complicated proton nmr spectra. In D<sub>2</sub>O the three methyl groups of the *trans*-(−) isomer have different chemical shifts.<sup>7</sup> However,

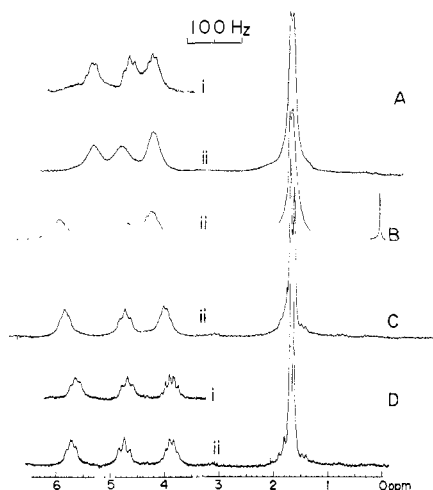


Figure 3.—The 100-MHz proton nmr spectra of *cis*-(-)-Co(L-ala)<sub>3</sub>. The D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios were: A, 0.0; B, 1.0; C, 5.0; D, 10.0. The temperatures were: i, 100°; ii, 25°. DSS was added to the solutions.

in solutions of concentrated and moderately concentrated D<sub>2</sub>SO<sub>4</sub>, there were only two types of methyl protons for both the *trans*-(+) and the *trans*-(-) isomers. Their intensity ratio was 2:1 (Figure 4). The CH protons also separated into two groups, one of them having twice the intensity of the other. There were four peaks in the intensity ratio of 1:1:3:1 for the NH protons. When the D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratio changed from 0.0 to 1.0, the CH signals moved slightly upfield, while all NH peaks moved downfield.

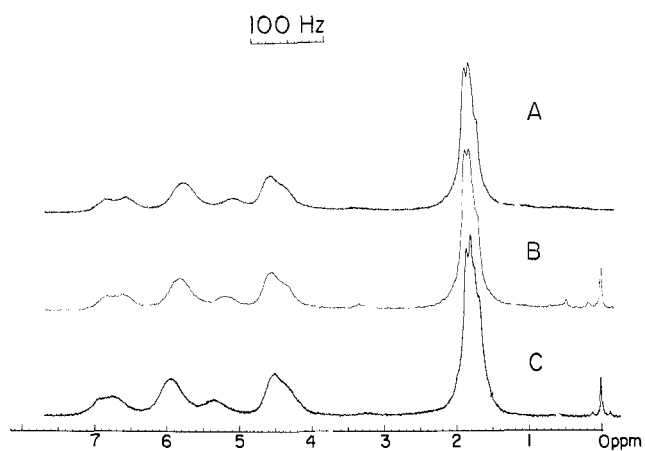


Figure 4.—The 100-MHz proton nmr spectra of *trans*-(+)-Co(L-ala)<sub>3</sub> at 25°. The D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios were: A, 0.0; B, 0.4; C, 1.0. DSS was added to the solutions.

*trans*-(-)-Co(L-ala)<sub>3</sub>.—The *trans*-(-) isomer had proton nmr spectra very similar to those of the *trans*-(+) isomer. However, it is more soluble in D<sub>2</sub>O; therefore spectra in solutions having D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios larger than 1 were obtained. Like the *cis*-(-) isomer, the CH and NH signals shifted slightly upfield when the content of D<sub>2</sub>O in the solvent was increased. Various peaks shifted differently so that the two kinds of CH absorptions crossed each other at D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ≈ 1.5 (Figure 5). Fine structures of the CH and NH ab-

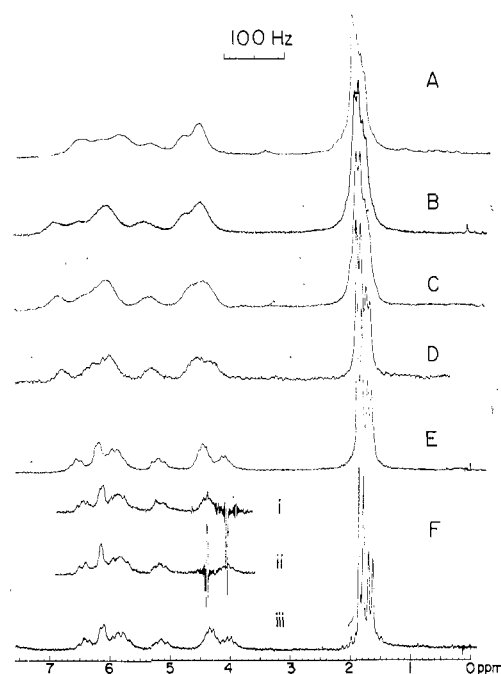


Figure 5.—The 100-MHz proton nmr spectra of *trans*-(-)-Co(L-ala)<sub>3</sub> at 25°. The D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios were: A, 0.0; B, 1.0; C, 1.5; D, 2.0; E, 4.0; F, 10.0. Spectra with irradiation of the CH protons (Fi and Fii) are also shown. DSS was added to the solutions.

sorptions started to appear in solutions of D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> > 4. Decoupling experiments were performed to determine which groups are coupled to each other. Coupling constants were not assigned because of the complexity of the spectra for the three overlapping six-spin system.

The two *trans* isomers isomerized to the *cis* forms at elevated temperatures<sup>5</sup> so that their nmr spectra were not clear.

Some of the proton nmr results are summarized in Tables II and III. The assignment of the NH protons will be discussed in the next section.

### Discussion

The structures of the four isomers of Co(L-ala)<sub>3</sub> are shown schematically in Figure 6. The *cis* compounds have a C<sub>3</sub> symmetry axis with all three ligands in geometrically equivalent positions. The *trans* compounds do not have any symmetry element, but the axis passing through the cobalt atom and facing the reader in Figure 6 can be regarded as a pseudo-C<sub>3</sub> axis. All three methyl groups in the (+) isomers are in equatorial arrangement with respect to the C<sub>3</sub> or pseudo-C<sub>3</sub> axis. In the (-) isomers, there are methyl groups in pseudo-axial positions with respect to those axes.<sup>7</sup> The methyl groups in all isomers are most likely all in the equatorial positions with respect to the corresponding five-membered rings.<sup>7</sup> There was no evidence of detectable conformational equilibria.

The three chelate rings in the *cis* isomers are all geometrically and magnetically equivalent. Therefore their nmr spectra had only one kind of methyl and one kind of α-CH signals. The methyl group is coupled to

TABLE II  
PROTON CHEMICAL SHIFTS (IN PPM) OF THE LIGANDS IN  
*cis*-Co(L-ala)<sub>3</sub><sup>a</sup>

D <sub>2</sub> O:D <sub>2</sub> SO <sub>4</sub>	Temp, °C	CH	NH <sub>α</sub>	NH <sub>ε</sub>
<i>cis</i> -(+)				
0.0	25	-4.39	-4.83	-5.25
0.0	100	-4.40	-4.72	-5.27
0.4	25	-4.43	-5.05	-4.24
1.0	25	-4.40		-5.23
1.0	100	-4.39	-4.99	-5.33
<i>cis</i> -(-)				
0.0	25	-4.24	-4.81	-5.33
0.0	100	-4.21	-4.63	-5.29
1.0	25	-4.25	-4.75	-5.95
5.0	25	-4.04	-4.74	-5.85
10.0	25	-3.88	-4.75	-5.73

<sup>a</sup> Estimated error: ±0.02 ppm.

TABLE III  
PROTON CHEMICAL SHIFTS (IN PPM) OF THE LIGANDS IN  
*trans*-Co(L-ala)<sub>3</sub> at 25°<sup>a</sup>

D <sub>2</sub> O:D <sub>2</sub> SO <sub>4</sub>	CH	NH <sub>ε</sub> ( <i>cis</i> )		NH <sub>ε</sub> ( <i>trans</i> )
		NH <sub>α</sub> ( <i>cis</i> )	NH <sub>α</sub> ( <i>trans</i> )	
<i>trans</i> -(+)				
0.0	-4.33, -4.54	-5.03	-5.71	-6.50, -6.76
0.4	-4.31, -4.51	-5.16	-5.78	-6.57, -6.78
1.0	-4.33, -4.52	-5.38	-5.97	-6.57, -6.73
<i>trans</i> -(-)				
0.0	-4.44, -4.68	-5.28	-5.76	-6.09, -6.36
1.0	-4.42, -4.66	-5.36	-5.95	-6.45, -6.86
1.5	-4.46	-5.37	-6.05	-6.90
2.0	-4.27, -4.51	-5.32	-5.99	-6.26, -6.77
4.0	-4.11, -4.47	-5.10	-5.96	-6.18, -6.56
10.0	-4.08, -4.38	-5.18	-5.90	-5.96, -6.45

<sup>a</sup> Estimated error: ±0.02 ppm.

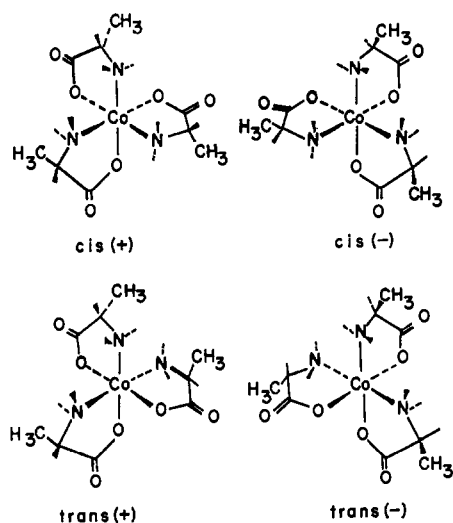


Figure 6.—The schematic representation of the four isomers of Co(L-ala)<sub>3</sub>. Of the two NH protons in the amino group, the one on the dotted line is in equatorial position with respect to the C<sub>3</sub> or pseudo-C<sub>3</sub> axis and is designated as NH<sub>ε</sub> in the text.

the α-CH proton only, and the splitting showed up even in concentrated D<sub>2</sub>SO<sub>4</sub>. The α-CH proton is coupled to the CH<sub>3</sub> and NH<sub>2</sub> groups; the splitting was obvious only in less viscous media (high temperature or low acid content). For the amino group, the two protons

have different environments in the chelate ring: one is *cis* to the methyl group and the other is *trans* to it. They gave rise to two different NH absorptions. The difference in chemical shift for the two NH protons is, with little doubt, due to the magnetic anisotropy of the neighboring groups.<sup>8</sup> Since the anisotropy of the Co-N and Co-O bonds is considerably larger than that of the C-C bond,<sup>8</sup> it is more significant to discuss the conformation of the amino group in the whole complex rather than in an individual ring. The carbonyl group in the amino acid may have considerable anisotropy, but it is farther away from the amino group and forms approximately the same angle with the two NH protons; consequently its contribution to the difference in their chemical shifts is not important. In each ring there is one NH proton in the axial position *with respect to the C<sub>3</sub> axis*; the other NH proton is in the equatorial position. They are designated as NH<sub>α</sub> and NH<sub>ε</sub>, respectively (Greek subscripts are used to emphasize the unique reference axis). Because of the lack of information on the exact geometry of the complexes and values of bond anisotropies, *a priori* calculation on the chemical shift between the two NH protons is not possible. We assign the peak at higher field to the NH<sub>α</sub> protons for the following reasons. In the *cis*-(+) complex, each NH<sub>α</sub> is *trans* to the methyl group. It is less sterically hindered than the NH<sub>ε</sub> proton and forms a hydrogen bond with a proton acceptor more easily. Therefore when the D<sub>2</sub>O content in the solvent was reduced or the temperature was raised, its nmr signal moved upfield (Figure 1). For the *cis*-(-) isomer, the NH<sub>α</sub> proton is *cis* to the methyl group. Then the less hindered NH<sub>ε</sub> proton had a larger downfield shift when the D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratio increased from 0 to 1. Since the *cis*-(-) isomer has a larger solubility, its nmr in solutions with higher D<sub>2</sub>O:D<sub>2</sub>SO<sub>4</sub> ratios was measurable. The upfield shift of the proton signals in those solutions (Table II) can be explained by considering another aspect of the solvent effect. It is well known that sulfuric acid is a very strong proton donor to many organic molecules.<sup>9</sup> In concentrated and moderately concentrated sulfuric acid, the carboxyl group in the complex would form strong hydrogen bonding with sulfuric acid or may even be protonated. The interaction would be weakened when the acid content is reduced. It would then cause a reduction of the positive charge in the chelate ring and an upfield shift of the proton signals. This interpretation is in accordance with the previous observations of the effect of a positive charge in the carboxyl group on the chemical shift of other groups in the molecule.<sup>10-12</sup> The CH proton is closest to the carboxyl group and influenced most by the departure of D<sub>2</sub>SO<sub>4</sub> from the second coordination sphere. Although the NH<sub>2</sub> and the CH<sub>3</sub> groups have approximately the same distance from the carboxyl group, the NH<sub>ε</sub> proton

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shifted upfield with respect to the methyl protons. This may indicate that the effect depends more on the geometry and structure of the ring than the number of bonds from the carboxyl group. For the more hindered  $\text{NH}_\alpha$  proton, the formation of hydrogen bonding with  $\text{D}_2\text{O}$  may start only in media with large  $\text{D}_2\text{O}:\text{D}_2\text{SO}_4$  ratios; this would then compete with the effect of reducing positive charge and cause a small over-all chemical shift when the acid content is reduced. The above argument can explain the data in Table II satisfactorily. (The numbers are, however, only relative values because of the difficulty in choosing a reference, as mentioned in the Experimental Section. The chemical shift of the methyl group seemed to change slightly with solvent and temperature but could not be accurately measured.) It is of interest to note that a rise of temperature caused one of the NH protons to move slightly upfield, but the other NH proton and the  $\alpha$ -CH proton were influenced less. This indicates that in concentrated and moderately concentrated sulfuric acid, the hydrogen bond between the less hindered NH proton and the solvent is more susceptible to the influence of temperature than the hydrogen bond between the carboxyl group and the solvent, which is understandable because the solvents were very acidic in those cases.

The coupling constants between various protons of the *cis* complexes were obtained from the spectra at elevated temperatures (Figure 2) and are listed in Table I. It is expected that the coupling between vicinal protons in the CH-NH fragment is dependent upon the dihedral angle between them, just as for the hydrocarbons.<sup>13</sup> The data in Table I show that the conformations of the rings in the two optical isomers were almost identical at the same temperature, despite their different spatial arrangements.<sup>7</sup> The conformation seems to change slightly with temperature, which also substantiates the argument for the existence of definite solvent-solute interaction.

The nmr spectra of the *trans* complexes are more complicated because all three rings are different. For the amino groups, there are two amino groups *trans* to each other and *cis* to the third  $\text{NH}_2$ . Since the chemical

shifts of the NH protons are functions of the neighboring groups,<sup>8,14</sup> the nmr properties of the two amino groups that are *trans* to each other would be quite similar. The third amino group, which is *trans* to an oxygen, is different from the other two. We will call it the *cis* group. The CH protons have similar characteristics and showed two resonance peaks with intensity ratio 1:2 for both optical isomers. The NH resonances partly overlapped, giving four peaks in the ratio 1:3:1:1. The assignment in Table III was made by considering the intensity and the decoupling results. For example, irradiation of the CH group of smaller intensity simplified the structure of the two high-field NH signals; those NH peaks are then assigned to the *cis* amino group. Three peaks at lower field (one of which was superimposed on the *cis* signals) are assigned to the *trans* amino groups because their structure simplified upon the irradiation of the CH group of larger intensity. The assignment of  $\alpha$  and  $\epsilon$  protons is analogous to that for the *cis* isomers. Again we observe that when the  $\text{D}_2\text{O}:\text{D}_2\text{SO}_4$  ratio changed from 0 to 1.5, the less hindered protons ( $\text{NH}_\alpha$  for *trans*-(+) and  $\text{NH}_\epsilon$  for *trans*-(-)) moved downfield more rapidly. In solutions of larger  $\text{D}_2\text{O}$  content, all CH and NH peaks moved upfield. Those changes in the proton signals can be readily explained by the formation of hydrogen bonding between the amino group and  $\text{D}_2\text{O}$ , followed by the departure of  $\text{D}_2\text{SO}_4$  from the second coordination sphere, a mechanism similar to that for the *cis* isomers. Finally, it is interesting to notice that the CH peaks shifted differently so that the two resonances crossed each other at  $\text{D}_2\text{O}:\text{D}_2\text{SO}_4 = 1.5$ . We cannot offer a satisfactory explanation for that.

In the above discussion we have demonstrated that an amino acid can act as a proton donor as well as a proton acceptor when it is coordinated to a metal ion. The formation of a second coordination sphere *via* hydrogen bonding is dependent upon the composition of the solvent.

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