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Stereochemical Studies of Metal Chelates. IV.[1] Preparation and Stereospecificity of Bis(ethylenediamine)cobalt(III) Complexes with N-Methyl-L-alanine and Related Ligands

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The preparation of crystalline bis(ethylenediamine)cobalt(III) complexes coordinated with N-methyl-L-alanine, D-pipecolic acid, and L-proline is reported. The stereospecific formation of $\Delta(C_2)$ or $\Lambda(C_2)$ isomers of these complexes is correlated with the asymmetric nature of the secondary nitrogen atoms of coordinated N-substituted amino acids. The origin of the stereospecificity in the N-methyl-L-alanine complex is discussed.

The stereospecificity of the metal complexes coordinated with optically active ligands is one of the interesting subjects in coordination chemistry. The stereochemical effects of propylenediamine, one of the simplest optically active bidentate ligands, were clarified thoroughly by Dwyer and his coworkers.[2-4] The experimental results of their studies supported the theoretical conclusion of the conformational analysis of $Co(en)_3^{3+}$ by Corey and Bailar,[5] as illustrated, for example, in the distribution of the diastereoisomers of the mixed cobalt(III) complexes of ethylenediamine and D(−)-propylenediamine.[2,4] The ratio of the $\Lambda(C_2)$ isomer to the $\Delta(C_2)$ isomer of $Co(en)_2(D(-)\text{-}pn)^{3+}$ was found to be 2.1. Optically active amino acids coordinated in the framework $Co(en)_2(L\text{-}aa)^{2+}$ (aaH = amino acid) had, however, been considered to have little stereospecificity, owing to the planarity of the chelate ring of amino acids.[6] Buckingham and his coworkers[7] recently reported the thermodynamically equilibrated ratio of the L to the D isomers of alanine and valine in the fixed absolute configuration of $Co(en)_2(aa)^{2+}$. According to their results, the equilibrium ratio of the $\Delta(C_2)$ to the $\Lambda(C_2)$ isomer of $Co(en)_2(L\text{-}val)^{2+}$ was found to be $\Delta/\Lambda \approx 1/1.7$, while that of $Co(en)_2(L\text{-}ala)^{2+}$ was found to be $\Delta/\Lambda \approx 1$. The value for the L-valine complex ($\Delta/\Lambda \approx 1/1.7$) is not so large as that for the L-propylenediamine complex ($\Delta/\Lambda \approx 2.1$). It is interesting that the preferred configuration is inverted between these complexes, that is, $\Lambda(C_2)$ for the former and $\Delta(C_2)$ for the latter.

An interesting suggestion of the high degree of stereospecificity was given by the recent studies of $Co(en)_2(sar)^{2+}$ (sarH = sarcosine, N-methylglycine).[8,9] Since the secondary nitrogen atom of sarcosine coordinated to the cobalt(III) ion is asymmetric, four isomers are theoretically possible in $Co(en)_2(sar)^{2+}$ arising from the combination of the absolute configuration about the cobalt(III) ion ($\Delta(C_2)$ and $\Lambda(C_2)$) and that of the asymmetric secondary nitrogen center (*R* and *S*), *i.e.*, $\Delta(C_2)$-*R*, $\Delta(C_2)$-*S*, $\Lambda(C_2)$-*R*, and $\Lambda(C_2)$-*S*. In a recent study[8] it was suggested that the sarcosine is coordinated stereospecifically in this complex, indicating that either of the enantiomeric pairs ($\Delta(C_2)$-*R*, $\Lambda(C_2)$-*S*) or ($\Delta(C_2)$-*S*, $\Lambda(C_2)$-*R*) is the sole product. The absolute configuration of $(-)_{589}$-$Co(en)_2(sar)^{2+}$ determined by a total X-ray analysis is the $\Lambda(C_2)$-*S* form.[9] Hence we supposed that if the configuration of the secondary nitrogen atom of N-methylamino acid could be fixed, the absolute configuration of the complex $Co(en)_2(N\text{-}Meaa)^{2+}$ (N-MeaaH = N-methylamino acid) would be controlled to give the $\Delta(C_2)$ or the $\Lambda(C_2)$ isomer stereoselectively, reflecting the configuration of the asymmetric secondary nitrogen center.

L-Proline is a typical ligand having a secondary nitrogen atom which becomes asymmetric upon coordination. It was found that the CD and ORD curves of $Co(NH_3)_4(L\text{-}pro)^{2+}$ (proH = proline) are markedly different from those of the corresponding complexes of other L-amino acids.[10] This was considered to be due to the influence of the additional asymmetric center, the asymmetric secondary nitrogen. In a previous paper in this series,[11] the asymmetric nature of the secondary nitrogen of the coordinated N-methyl-L-alanine and pipecolic acid was also demonstrated. An attempt to prepare $Co(en)_2(L\text{-}pro)^{2+}$ was, however, reported to be unsuccessful. In the

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[1] Part III: M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **8**, 358 (1969).

[2] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Am. Chem. Soc.*, **85**, 2913 (1963).

[3] F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

[4] T. E. MacDermott, *Chem. Commun.*, 223 (1968).

[5] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[6] C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[7] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5133 (1967).

[8] D. A. Buckingham, S. F. Mason, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **5**, 1649 (1966).

[9] J. F. Blount, H. C. Freeman, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 324 (1967).

[10] T. Yasui, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **39**, 2417 (1966).

[11] M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **7**, 1890 (1968).

present study, Co(en)$_2$(L-pro)$^{2+}$, Co(en)$_2$(N-Me-L-ala)$^{2+}$ (N-Me-L-alaH = N-methyl-L-alanine), and Co(en)$_2$(D-pipec)$^{2+}$ (pipecH = pipecolic acid) were prepared by the reaction of *trans*-[Co(en)$_2$Cl$_2$]Cl with the corresponding amino acid anions in methanol solution. The ORD curves of these complexes were similar to those of the optically active Co(en)$_2$(aa)$^{2+}$.[6,8] This indicates that the coordinated optically active N-substituted amino acids control the absolute configuration about the cobalt(III) ion.

Experimental Section

Preparation of N-methyl-L-alanine and D-pipecolic acid was described previously.[11] L-Proline was kindly presented by Aji-no-moto Co.

Δ(C$_2$)-N-Methyl-L-alaninatobis(ethylenediamine)cobalt(III) Perchlorate, [Co(en)$_2$(N-Me-L-ala)](ClO$_4$)$_2$.—*trans*-[Co(en)$_2$Cl$_2$]Cl (2.8 g) was added to a solution of LiOH·H$_2$O (0.43 g) and N-methyl-L-alanine (1.1 g) in methanol (30 ml) and the mixture was stirred and heated under reflux for 20 min. The solution was cooled to room temperature and the precipitated [Co(en)$_3$]Cl$_3$ was removed by filtration. The filtrate was allowed to stand at room temperature for 30 min, and the separated crude product ([Co(en)$_2$(N-Me-L-ala)]Cl$_2$) was filtered off, washed with methanol, and air dried. [Co(en)$_2$(N-Me-L-ala)](ClO$_4$)$_2$ was obtained by adding an excess of NaClO$_4$ to an aqueous solution of the crude product and recrystallized from a small volume of water by adding ethanol. *Anal.* Calcd for [Co(en)$_2$(N-Me-L-ala)](ClO$_4$)$_2$: C, 20.01; H, 5.04; N, 14.59. Found: C, 19.85; H, 4.88; N, 14.12.

The corresponding iodide was obtained by adding NaI instead of NaClO$_4$. *Anal.* Calcd for [Co(en)$_2$(N-Me-L-ala)]I$_2$: C, 17.96; H, 4.52; N, 13.09. Found: C, 17.92; H, 4.60; N, 12.87.

Λ(C$_2$)-D-Pipecolinatobis(ethylenediamine)cobalt(III) Iodide, [Co(en)$_2$(D-pipec)]I$_2$.—*trans*-[Co(en)$_2$Cl$_2$]Cl (2.8 g) was added to a solution of D-pipecolic acid (1.3 g; $[\alpha]^{25}\text{D}$ +28.3) and NaOH (0.4 g) in methanol (40 ml) and was stirred and heated under reflux for 40 min. NaI (3.3 g) and 10 ml of methanol were then added, and stirring and heating were continued for 20 min longer. The mixture was cooled to room temperature and the precipitated product was filtered off, washed with a small volume of methanol, and air dried. The crude product was recrystallized from water with NaI giving red needle crystals. *Anal.* Calcd for [Co(en)$_2$(D-pipec)]I$_2$: C, 21.40; H, 4.68; N, 12.48. Found: C, 21.64; H, 5.05; N, 12.61.

Λ(C$_2$)-L-Prolinatobis(ethylenediamine)cobalt(III) Chloride Perchlorate, [Co(en)$_2$(L-pro)]ClClO$_4$.—*trans*-[Co(en)$_2$Cl$_2$]Cl (2.8 g) was added to a solution of LiOH·H$_2$O (0.24 g) and L-proline (1.2 g) in methanol (30 ml) and heated under reflux with stirring for 5–10 min. The solution was cooled to room temperature, and the precipitated impurity ([Co(en)$_3$]Cl$_3$) was filtered off. The filtrate was warmed at 40° for 4 hr and then allowed to stand at room temperature overnight. The crude product which separated was filtered off and washed with methanol. [Co(en)$_2$(L-pro)]ClClO$_4$ was obtained by adding NaClO$_4$ and methanol to an aqueous solution of the crude product. *Anal.* Calcd for [Co(en)$_2$(L-pro)]ClClO$_4$: C, 25.24; H, 5.65; N, 16.36. Found: C, 25.05; H, 5.78; N, 15.84.

Measurements.—Optical rotatory dispersion was measured using a Jasco Model ORD/UV-5 spectrophotometer. The circular dichroism was measured with a Shimazu QV-50 spectrophotometer fitted with a CD attachment. Proton magnetic resonance spectra were measured using a Japan Electronic Model JNN-R-60 spectrometer and sodium trimethylsilylpropanesulfonate as the internal standard.

Results and Discussion

Two typical methods for preparing aminoacidobis(ethylenediamine)cobalt(III) ions have been reported. Liu and Douglas[6] obtained the bis(ethylenediamine)cobalt(III) complexes of glycine and some optically active amino acids by a reaction of the corresponding amino acid anions with *trans*-[Co(en)$_2$Cl$_2$]Cl in aqueous solution. Buckingham and Collman[12] prepared Co(en)$_2$(aa)$^{2+}$ by a reaction of amino acid with Co(en)$_2$OH(H$_2$O)$^{2+}$ at pH 8. In either method, the products were isolated as their iodides by adding excess NaI. An attempt to prepare [Co(en)$_2$(L-pro)]I$_2$ was, however, reported to be unsuccessful, giving only [Co(en)$_3$]I$_3$.[12] Some attempts to prepare the bis(ethylenediamine)cobalt(III) complexes of L-proline, N-methyl-L-alanine, and D-pipecolic acid by the reaction of the amino acid anions with *trans*-[Co(en)$_2$Cl$_2$]Cl in aqueous solution also failed in this study. However, the desired products were isolated by a similar reaction procedure in methanol solution.

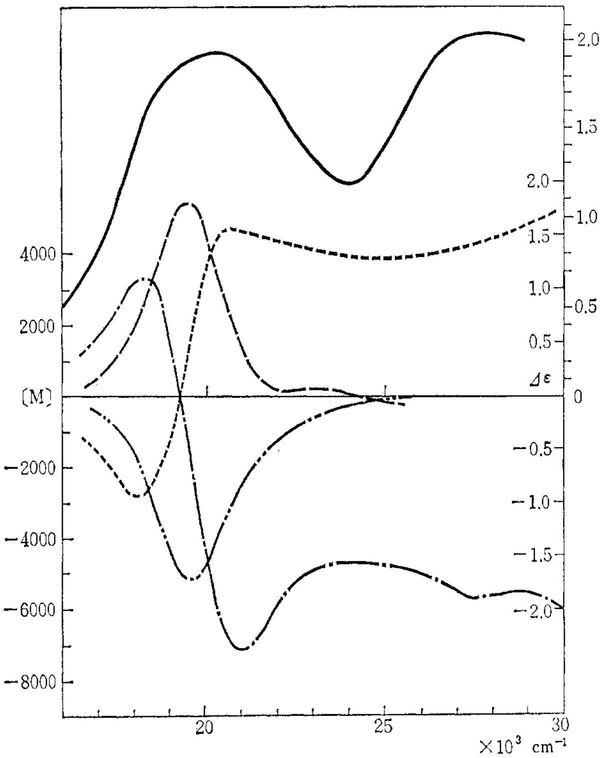

Figure 1.—Visible absorption (———), rotatory dispersion (– · – · –), and circular dichroism (– – – –) curves for the Co(en)$_2$(N-Me-L-ala)$^{2+}$ ion and rotatory dispersion (- - - - -) and circular dichroism (–· · –· · –) curves for the (−)$_{589}$-Co(en)$_2$(sar)$^{2+}$ ion.[8]

The visible absorption, optical rotatory dispersion (ORD), and circular dichroism (CD) curves for Co(en)$_2$(N-Me-L-ala)$^{2+}$ are shown in Figure 1, along with the ORD and CD curves for (−)$_{589}$-Co(en)$_2$(sar)$^{2+}$. The ORD and CD curves for Co(en)$_2$(N-Me-L-ala)$^{2+}$ are closely similar to the corresponding curves for (−)$_{589}$-Co(en)$_2$(sar)$^{2+}$, though the signs of the Cotton effects of these complexes are opposite to each other. This suggests that the diastereomeric isomers having the absolute configuration in a relation to the mirror image of (−)$_{589}$-Co(en)$_2$(sar)$^{2+}$ were stereospecifically

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(12) D. A. Buckingham and J. P. Collman, *Inorg. Chem.*, **6**, 1803 (1967).

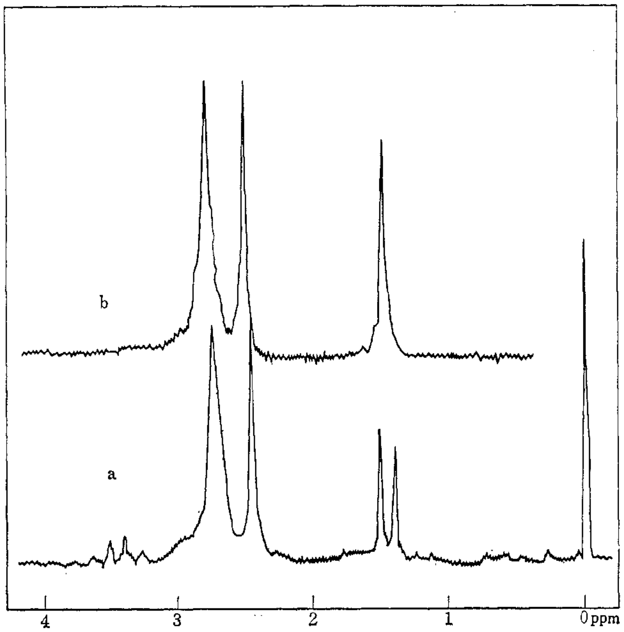

Figure 2.—Pmr spectra for $Co(en)_2(N\text{-}Me\text{-}L\text{-}ala)^{2+}$ in D_2O (a) and for the deuterated complex at the α proton in D_2O after treatment with OD^- (b).

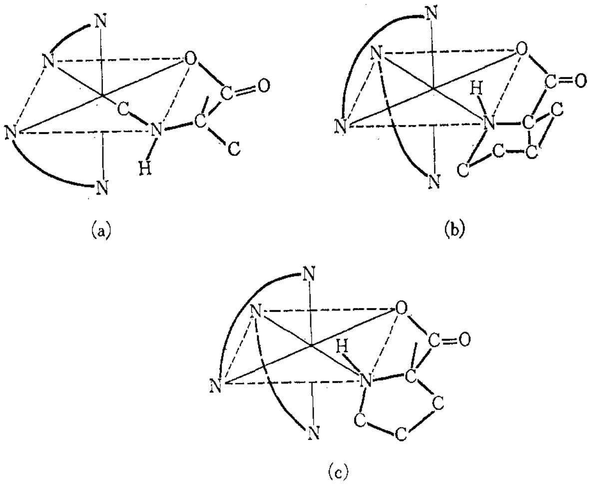

Figure 3.—Structures of coordinated N-methyl-L-alanine (a), D-pipecolic acid (b), and L-proline (c).

formed for $Co(en)_2(N\text{-}Me\text{-}L\text{-}ala)^{2+}$. Since the absolute configuration of $(-)_{589}$-$Co(en)_2(sar)^{2+}$ was determined to be $\Lambda(C_2)$ by X-ray analysis study,[9] the isolated product of $[Co(en)_2(N\text{-}Me\text{-}L\text{-}ala)](ClO_4)_2$ is considered to take a preferred configuration of $\Delta(C_2)$.

The pmr spectrum of $Co(en)_2(N\text{-}Me\text{-}L\text{-}ala)^{2+}$ in D_2O solution is shown in Figure 2a. The doublet at 1.45 ppm was assigned to C-substituted methyl protons of N-methyl-L-alanine split by the methyne proton, the signal of which was found as a quartet at 3.45 ppm. The signal at 2.45 ppm was assigned to the N-methyl protons and the slightly broadened peak in the vicinity of 3.70 ppm was assigned to the protons of the ethylenediamine chelate rings. Any indication of the existence of fundamental shoulders was not recognized in the signals for the protons of either methyl group. This supports the conclusion that only one species exists in the isolated product of $[Co(en)_2(N\text{-}Me\text{-}L\text{-}ala)](ClO_4)_2$. A similar conclusion has already been drawn from the

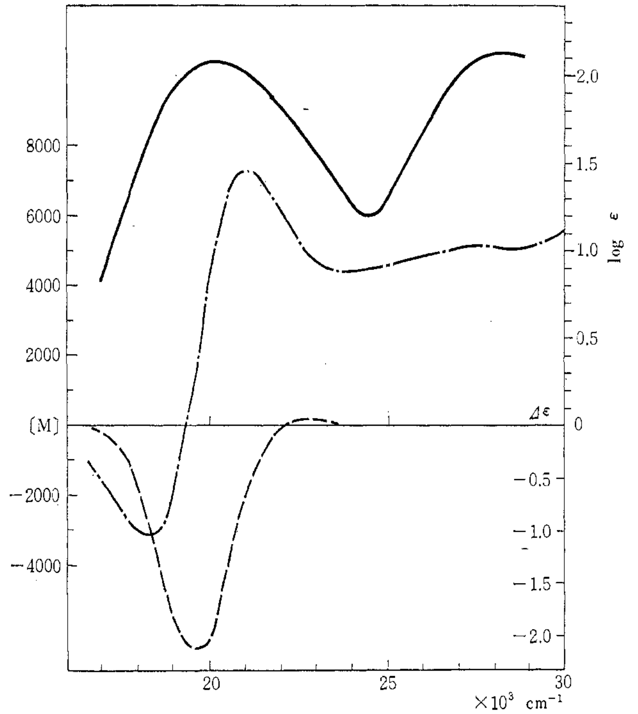

Figure 4.—Visible absorption (———), rotatory dispersion (– · – · –), and circular dichroism (- - - -) curves for the $Co(en)_2(D\text{-}pipec)^{2+}$ ion.

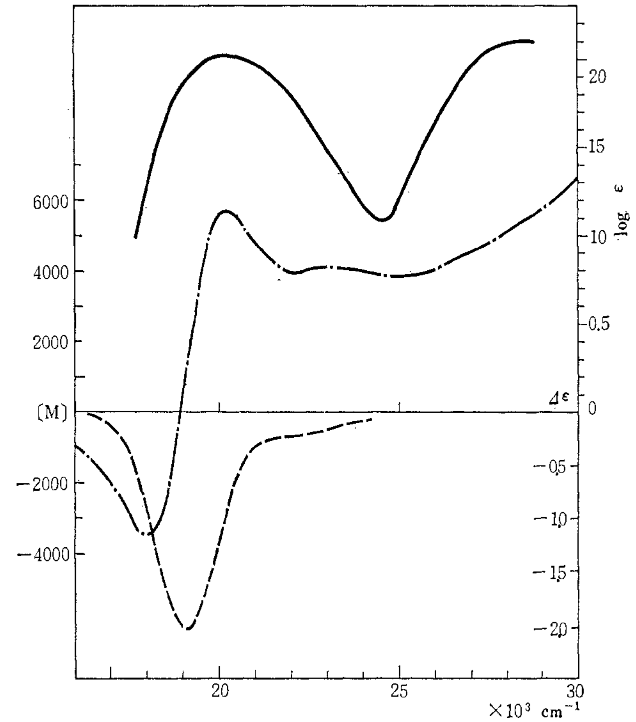

Figure 5.—Visible absorption (———), rotatory dispersion (– · – · –), and circular dichroism (- - - -) curves for the $Co(en)_2(L\text{-}pro)^{2+}$ ion.

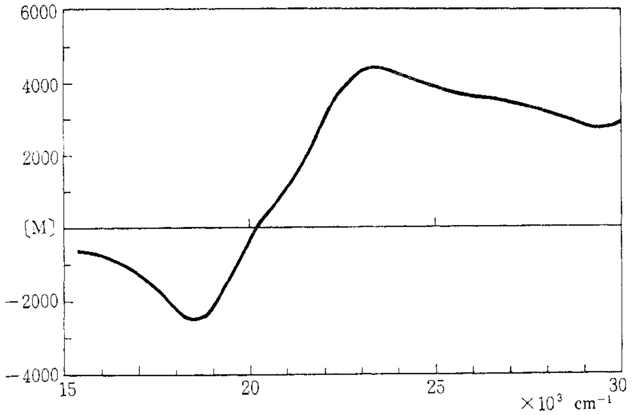

Figure 6.—Rotatory dispersion curve for [Co(trien)(L-pro)]-$I_2 \cdot H_2O$.

pmr measurements in the case of the active $Co(en)_2$-$(sar)^{2+}$ ion.[8] Therefore the pmr spectrum of $Co(en)_2$-$(N\text{-Me-L-ala})^{2+}$ supported the assumption that this complex is formed almost stereospecifically in $\Delta(C_2)$ configuration.

In a previous paper in this series,[11] the asymmetric nature of the secondary nitrogen atom of coordinated N-methyl-L-alanine was demonstrated. The stereospecificity of the secondary nitrogen center of sarcosine in $Co(en)_2(sar)^{2+}$ has also been established.[8,9] Therefore the preferred configuration of $Co(en)_2(N\text{-Me-L-ala})^{2+}$ can be correlated with the absolute configuration of the secondary nitrogen atom. The absolute configurations of the secondary nitrogen of N-methyl-L-alanine, L-proline, and D-pipecolic acid are thought to be *R*, *S*, and *S*, respectively, as shown in Figure 3. The results of a total X-ray analysis study of $(-)_{589}$-$Co(en)_2(sar)^{2+}$ indicated that the absolute configuration about the cobalt(III) ion is $\Lambda(C_2)$ and the absolute configuration of the asymmetric nitrogen center is *S*.[9] Considering these facts, the preferred configurations of $Co(en)_2(N\text{-Me-L-ala})^{2+}$, $Co(en)_2(L\text{-pro})^{2+}$, and $Co(en)_2(D\text{-pipec})^{2+}$ are expected to be $\Delta(C_2)$, $\Lambda(C_2)$, and $\Lambda(C_2)$, respectively. In the case of the N-methyl-L-alanine complex, this anticipation was found to agree with the observation that the present complex showed ORD and CD curves which can be assigned to those for the $\Delta(C_2)$-$Co(en)_2(aa)^{2+}$ ion. The ORD and CD curves for $Co(en)_2(D\text{-pipec})^{2+}$ and $Co(en)_2$-$(L\text{-pro})^{2+}$ are shown in Figures 4 and 5, respectively. These complexes show a large negative Cotton effect in the first absorption band region and are considered to adopt the $\Lambda(C_2)$ absolute configuration as expected.

Bryant, Hu, and Glaze[13] prepared [Co(trien)(L-pro)]$I_2 \cdot H_2O$ (trien = triethylenetetramine), and they indicated that all of the fractions of this complex are essentially the same, according to the measurement of optical rotation at 546 mμ. The result of obtaining only one isomer of the "internal" diastereoisomers which has an optical rotation $[\alpha]_{546}$ −460° was attributed by these authors to the consequence of the fractional crystallization, and the other diastereoisomer which was not isolated was considered to remain in the filtrate. Furthermore, they also claimed the isolation of $[Co(en)_2(L\text{-pro})]I_2 \cdot H_2O$ and that a phenomenon similar to that in the triethylenetetramine complex was also observed in the bis(ethylenediamine) complex. However, it has been elucidated that both internal diastereoisomers were isolated in the case of the analogous complexes containing optically active amino acids except L-proline.[6] We consider therefore that the isolation of the single diastereoisomers only in the L-proline complex is due to the stereospecific formation of the $\Lambda(C_2)$ isomers. The ORD curve for [Co(trien)-(L-pro)]$I_2 \cdot H_2O$ obtained by the method of Bryant, *et al.*, is shown in Figure 6; it shows a negative Cotton effect in the first absorption band region. Therefore $Co(trien)(L\text{-pro})^{2+}$ is considered to have the $\Lambda(C_2)$ absolute configuration, similar to $Co(en)_2(L\text{-pro})^{2+}$.

L-Valine coordinated in either absolute configuration of $Co(en)_2(L\text{-val})^{2+}$ was found from the polarimetric and pmr measurements to be partially racemized to give an equilibrium mixture of $Co(en)_2(L\text{-val})^{2+}$ and $Co(en)_2(D\text{-val})^{2+}$ in alkaline solution.[7] From the pmr spectra for valine and alanine complexes in D_2O solution containing OD^-, the methyne protons of amino acids were reported to be deuterated during the simultaneous partial racemization reaction.[7] A similar treatment with OD^- was carried out for $[Co(en)_2$-$(N\text{-Me-L-ala})](ClO_4)_2$ in D_2O solution, and the pmr spectrum of the resultant complex deuterated at the α proton of N-methyl-L-alanine is shown in Figure 2b. In this spectrum the signal of the methyne proton observed as a quartet in Figure 2a has disappeared and the signal of the C-methyl protons is converted to a singlet by deuterium exchange. The pmr signals of the methyl protons of alanine in $\Delta(C_2)$-$Co(en)_2(L$-$ala)^{2+}$ and $\Delta(C_2)$-$Co(en)_2(D\text{-ala})^{2+}$ were reported to show slightly different chemical shifts.[7,14] We consider that the C-methyl group of $\Delta(C_2)$-$Co(en)_2(N$-$Me\text{-D-ala})^{2+}$ is in a circumstance slightly different from that of the original complex owing to the difference of the steric influence from the N-methyl group (the absolute configuration of the asymmetric nitrogen center should be fixed here as well as in $(-)_{589}$-$Co(en)_2$-$(sar)^{2+}$), and therefore both methyl groups should be in the slightly different magnetic fields. However, the pmr signals for the methyl groups in Figure 2b gave no indication of splitting into two peaks. This means that the racemization of the asymmetric carbon of coordinated N-methyl-L-alanine did not occur during the alkaline treatment. It was observed, moreover, that the ORD curve for $Co(en)_2(N\text{-Me-L-ala})^{2+}$ treated with alkali (0.02 *N* NaOH) was almost identical with that for the original complex. After a similar treatment, the ORD curve for $\Delta(C_2)$-$Co(en)_2(L\text{-val})^{2+}$ was found to convert into that for the equilibrium mixture

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(13) B. E. Bryant, H. J. Hu, and W. H. Glaze, *Inorg. Chem.*, **5**, 1373 (1966).

(14) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

of $\Delta(C_2)$-$Co(en)_2$(L-val)$^{2+}$ and $\Delta(C_2)$-$Co(en)_2$(D-val)$^{2+}$.[7] Thus it was suggested that [$Co(en)_2$(N-Me-L-ala)](ClO_4)$_2$ was produced stereospecifically in the $\Delta(C_2)$ absolute configuration.

It has been reported that the stereoselective formation of the $\Delta(C_2)$ isomer of [$Co(en)_2$(glu)]ClO_4 from the reaction of glutamic acid with the racemic $Co(en)_2(H_2O)_2^{3+}$ ion is kinetic in origin.[15,16] On the contrary, the results of the pmr and ORD measurements of $\Delta(C_2)$-[$Co(en)_2$(N-Me-L-ala)](ClO_4)$_2$ treated with alkali suggested that the stereospecificity induced by the coordinated N-methyl-L-alanine is thermodynamic in origin. However, the possibility that the unstable $\Lambda(C_2)$ isomer was formed during the reaction of the N-methyl-L-alanine anion with *trans*-[$Co(en)_2Cl_2$]Cl cannot be excluded conclusively. In order to examine this possibility, the reaction mixture for the preparation of the $Co(en)_2$(N-Me-L-ala)$^{2+}$ complex was deposited directly on a cation-exchange resin column (Dowex 50W-X8, 50–100 mesh, H^+ form) and eluted slowly. The eluent was collected in several fractions. In a preliminary examination using 1 *N* $NaClO_4$ as the eluting agent, all of the fractions showed ORD curves similar to that for isolated $\Delta(C_2)$-[$Co(en)_2$(N-Me-L-ala)](ClO_4)$_2$, though the crystalline products could not be obtained from these fractions. However, when 1 *N* NH_4Br was used as the eluent, a crystalline product was isolated from each fraction. The pmr spectra and the ORD curves of these complexes were identical with those for $\Delta(C_2)$-[$Co(en)_2$(N-Me-L-ala)](ClO_4)$_2$ (Figures 2a and 1, respectively). The existence of the unstable $\Lambda(C_2)$ isomer was not recognized. It is indicated that the stereospecificity incorporated with the coordinated N-methyl-L-alanine is not only perfect but thermodynamic in origin. A similar conclusion could be applied to the stereospecificity of the bis(ethylenediamine) complexes of L-proline and D-pipecolic acid.

It is noteworthy that L-alanine which has no contribution to the stereospecific formation of the bis(ethylenediamine) complex[6,7] shows complete stereospecificity by introducing only the N-substituted methyl group. The stereoselective formation of the ($\Delta(C_2)$-*R*, $\Lambda(C_2)$-*S*) enantiomeric pair in the $Co(en)_2$(sar)$^{2+}$ ion, rather than ($\Delta(C_2)$-*S*, $\Lambda(C_2)$-*R*), was attributed to the preferred nonbonded interactions between the hydrogen atoms of the N-methyl groups and those on the adjacent ethylenediamine chelate rings. The stereospecific formation of the $\Delta(C_2)$ isomer in the case of $Co(en)_2$(N-Me-L-ala)$^{2+}$ could be caused by similar nonbonded interactions, since the configuration of the secondary nitrogen of coordinated N-methyl-L-alanine is considered to be in the *R* absolute configuration.

More recently, the preparation and the detailed stereochemistry of [Co(trien)(L-pro)]$I_2 \cdot H_2O$ were reported by Lin and Douglas.[17] These authors obained only one isomer ($\Lambda(C_2)$-*RR* form) by a procedure similar to that by Bryant *et al.*,[18] which supports our conclusion described previously. However, the other isomer which was considered as the $\Delta(C_2)$-*SS* form was also obtained by a slightly different method. This suggests that the stereospecificity induced by the N-substituted amino acids may not be so perfect in the triethylenetetramine complexes as in the bis(ethylenediamine) complexes. The triethylenetetraminecobalt(III) complexes coordinated with N-methyl-L-alanine and D-pipecolic acid have now been isolated in our laboratory, and a study of the detailed stereochemistry of these complexes is in progress.

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(15) J. H. Dunlop, R. D. Gillard, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 874 (1966).

(16) J. H. Dunlop and R. D. Gillard, *J. Chem. Soc., A*, 1469 (1967).

(17) C.-Y. Lin and B. E. Douglas, *Inorg. Nucl. Chem. Letters*, **4**, 15 (1968).