was obtained from hot butan-1-ol or ethanol solutions and recrystallized from acetone or ethanol under nitrogen. Recrystallization from acetone, ethanol, or methanol under aerial conditions gave Co(H-NNP(O))(NCS)$_2$. From concentrated solutions of Co(H-NNP)(NCS)$_2$ in chloroform or 1,2-dichloroethane, fine red-brown crystals of Co(H-NNP)(NCS)$_3$ separated upon standing.

Materials and Physical Measurements. All solvents were reagent grade. Physical measurements were carried out as described previously.[3] Magnetic susceptibilities at various temperatures were measured with the Gouy balance already described.[17]

Registry No. Cl(CH$_2$)$_2$N(Me)CH$_2$CH$_2$NEt$_2$ · 2HCl, 38127-70-7; Me-NNP, 38127-71-8; Co(H-NNP)Cl$_2$, 38127-72-9; Co(H-NNP)Br$_2$, 38127-73-0; Co(H-NNP)I$_2$, 38127-74-1; Co(H-NNP)(NCS)$_2$, 29993-37-1; Co[H-NNP(O)](NCS)$_2$, 38127-76-3; Co(H-NNP)(NCS)$_3$, 38127-77-4; Co(Me-NNP)Cl$_2$ (5-coordinate), 38127-78-5; Co(Me-NNP)Cl$_2$ (4-coordinate), 38127-79-6; Co(Me-NNP)Br$_2$ (5-coordinate), 38127-80-9; Co(Me-NNP)Br$_2$ (4-coordinate), 38127-81-0; Co(Me-NNP)(NCS)$_2$, 29993-38-2.

Acknowledgments. We thank Dr. J. Gelsomini for microanalyses, Mr. F. Nuzzi for the metal analyses, and Dr. M. A. Gristina and Mr. F. Zanobini for technical assistance.

[17] I. Bertini and F. Mani, *Inorg. Chem.*, 6, 2032 (1967).

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

Stereochemical Studies of *N*-Methyl-(*S*)-alaninatocobalt(III) Complexes with Chiral Tetramines. I. Cobalt(III)-*N*-Methyl-(*S*)-alaninato-5(*R*)- and -5(*S*)-methyl-1,4,7,10-tetraazadecane Systems

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The preparations and structural assignments of *N*-methyl-(*S*)-alaninatocobalt(III) complexes with 5(*R*)- and 5(*S*)-methyl-1,4,7,10-tetraazadecane (abbreviated as 5(*R*)- and 5(*S*)-metrien) are described. The Λ-β_2-*SSR* isomer has been obtained for Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion. The two isomers, which have been observed for the Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion under equilibrium condition at pH 7, are assigned as Δ-β_2-*RRS* and Δ-β_2-*RRR* configurations, based on the stereospecific coordination of 5(*S*)-metrien. The analogous arguments have been applied for the Δ-β_2 isomers of Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion. The individual species noted in pmr measurements are assigned tentatively to Δ-β_2-*RRS* and Δ-β_2-*RRR* structures, respectively.

Introduction

In recent papers, cobalt(III) complexes with bidentate ligands containing coordinated secondary nitrogen atom(s), such as N-substituted amino acidates (sarcosinate,[1,2] (*S*)-prolinate,[3–6] and *N*-methyl-(*S*)-alaninate[6,7]) and N-substituted 1,2-diamines (*N*-methylethylenediamine,[8] *N*-methyl-(*S*)-propylenediamines,[9] and *N,N'*-dimethylethylenediamine[10,11]), have been investigated from stereochemical points of view. The study on the sarcosinatobis(ethylenediamine)cobalt(III) ion[1] first provided the possibility of stereoselective coordination of the N-substituted methyl group in tris chelate complexes due to steric repulsions between the *N*-methyl group and the adjacent chelate rings. It was indicated from an X-ray analysis study[12] that the coordinated secondary N center of sarcosinate takes stereoselectively the *S*[13] configuration in the Δ[14] enantiomer of the Co(en)$_2$(sar)$^{2+}$ ion. The restricted orientation of the *N*-methyl group of sarcosinate chelate was also supposed for the β_2[15] isomer of the Co(trien)(sar)$^{2+}$ ion[2] (trien = triethylenetetramine).

It was observed that the bis(ethylenediamine)cobalt(III) complex of (*S*)-proline arises only in the Δ configuration stereoselectively.[6,16] Corresponding (*S*)-pipecolic acid and *N*-methyl-(*S*)-alanine complexes, in which both the amino acids have the asymmetric secondary N center with *R* configuration, gave rise to the Λ absolute configurations. This suggests that the absolute configuration of bis(en) complexes with N-substituted amino acids is controlled by the configuration of the secondary N center of amino acids.[6] When the asymmetric secondary N atom has the *R* configuration, the Λ absolute configuration is preferred for the bis(en) complex.

However, the stereoselective formation has not been observed in the case of trien–cobalt(III) complexes with (*S*)-proline[3] and *N*-methyl-(*S*)-alanine.[7] Under the reported preparative conditions, which are kinetically controlled, the above complexes were yielded in mixtures of Λ and Δ isomers in almost equal amounts. For the latter complex, the base-

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

[2] L. G. Marzilli and D. A. Buckingham, *Inorg. Chem.*, 6, 1042 (1967).

[3] D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Chem. Commun.*, 583 (1969).

[4] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 92, 3617 (1970).

[5] C. Y. Lin and B. E. Douglas, *Inorg. Chim. Acta*, 4, 3 (1970).

[6] M. Saburi, M. Homma, and S. Yoshikawa, *Inorg. Chem.*, 8, 367 (1969).

[7] D. A. Buckingham, I. E. Maxwell, and A. M. Sargeson, *Inorg. Chem.*, 9, 2663 (1970).

[8] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 7, 915 (1968).

[9] M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, 9, 1476 (1970).

[10] J. A. Tiethof and D. W. Cooke, *Inorg. Chem.*, 11, 315 (1972).

[11] S. Yano, M. Saburi, and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, 44, 3486 (1971).

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

[13] *R* and *S* refer to the configuration about the secondary N atoms, following the rules suggested by R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966).

[14] The absolute configuration about the cobalt center is indicated by the prefix Λ or Δ: see *Inorg. Chem.*, 9, 1 (1970).

[15] The use of β, β_1, and β_2 follows that used by L. G. Marzilli and D. A. Buckingham; *cf.* ref 2.

[16] S. K. Hall and B. E. Douglas, *Inorg. Chem.*, 8, 372 (1969).

catalyzed equilibrium reactions were performed at the neutral and basic pH values.[7] The structures of equilibriated species were predicted from strain energy minimization calculations.[7]

The steric factors to be considered for the isomerism of the β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion are as follows: the configuration about the metal ion (Λ or Δ) and the configuration at the *N*-methyl and "planar"[17] secondary N centers (*R* or *S*). As the Λ configuration, only one isomer, represented as Λ-*SSR*(*S*),[18] is probable. For the Δ configuration, the presence of two isomers has been detected from pmr measurements.[7] These isomers have been assigned as Δ-*RRS*(*S*) and Δ-*RSS*(*S*), respectively, and the other possible structure, Δ-*RRR*(*S*), has not been accepted.[7]

In the present paper, *N*-methyl-(*S*)-alaninatocobalt(III) complexes with 5(*R*)- or 5(*S*)-methyl-1,4,7,10-tetraazadecane (abbreviated hereafter as 5(*R*)- and 5(*S*)-metrien; $NH_2CH_2CH_2NHCH(CH_3)CH_2NHCH_2CH_2NH_2$) are examined. These trien derivatives have been proved to prefer the β configuration upon coordination.[19] Further, the methyl group substituted to the central chelate ring controls the absolute configuration of complexes; 5(*R*)- and 5(*S*)-metrien complexes arise stereospecifically in the Λ and Δ absolute configuration, respectively. Furthermore, the possibility of inversion at the "planar" asymmetric N atom of trien, which accompanies the synchronous conformational inversion of the chelate rings, should be ruled out because of the favored equatorial orientation of the methyl group attached to the trien skeleton. Therefore, the equilibrium reaction of *N*-methylalaninato complexes with these tetramines will be simplified compared to that of the corresponding trien complex, since one of the expected isomers in the latter case, that is, the Δ-*RSS*(*S*), is impossible for the 5(*S*)-metrien complex.

Experimental Section

N-Methyl-(*S*)-alanine was synthesized according to the method of Quitt, Hellerbach, and Vogler.[20] 5(*R*)- and 5(*S*)-methyl-1,4,7,10-tetraazadecane (5(*R*)- or 5(*S*)-metrien) and their dichlorocobalt(III) complexes (Λ-*cis*-β-[Co(5(*R*)-metrien)Cl_2]Cl·0.5H_2O and Δ-*cis*-β-[Co(5(*S*)-metrien)Cl_2]Cl·0.5H_2O) were prepared by the method described previously.

Λ-β_2-[Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)](ClO_4)$_2$. Λ-*cis*-β-[Co(5(*R*)-metrien)Cl_2]Cl·0.5H_2O (2.00 g) was added to 8 ml of water, followed by 0.252 g of LiOH·H_2O. The mixture was gently warmed to 60° until the complex dissolved. To the resultant solution was added 0.618 g of *N*-methyl-(*S*)-alanine and dissolved. After 1.0 g of activated carbon had been added, the mixture was warmed at 70° for 15 min. The activated carbon was removed by filtration and washed with a small volume of water. The filtrate and washings were combined and concentrated on a water bath (70°) to a volume of about 3 ml. Solid $LiClO_4$ (2.5 g) was added to the solution, and the mixture was cooled in an ice bath overnight. The orange-red crystals which separated were collected, washed with $NaClO_4$ solution, methanol, and acetone, successively, and air-dried; yield 1.93 g. The product was recrystallized from hot water. *Anal.* Calcd for [Co($C_7H_{20}N_4$)($C_4H_8NO_2$)](ClO_4)$_2$: C, 25.40; H, 5.42; N, 13.46. Found: C, 25.20; H, 5.39; N, 13.72.

Δ-β_2-[Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)](ClO_4)$_2$·H_2O. This complex was prepared in a procedure identical with that for the above 5(*R*)-metrien complex, except that Δ-*cis*-β-[Co(5(*S*)-metrien)Cl_2]Cl·0.5H_2O was employed in place of corresponding 5(*R*)-metrien complex; yield 1.32 g. *Anal.* Calcd for [Co($C_7H_{20}N_4$)($C_4H_8NO_2$](ClO$_4$)$_2$·H_2O: C, 24.55; H, 5.62; N, 13.01. Found: C, 24.58; H, 5.79; N, 12.91.

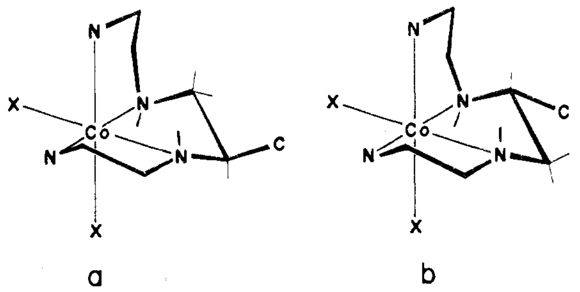

Figure 1. Possible coordination modes of 5(*R*)-metrien in the Λ-β-*RR* configuration.

Δ-β_2-[Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)]I_2·2H_2O. Δ-*cis*-β-[Co(5(*S*)-metrien)Cl_2]Cl·0.5H_2O (1.00 g) was added to 5 ml of water, followed by 0.126 g of LiOH·H_2O. The mixture was warmed to dissolve the complex, and, then, 0.309 g of *N*-methyl-(*S*)-alanine and 0.3 g of activated carbon were added, successively. The mixture was warmed to 70° for 15 min. The activated carbon was filtered off and washed with a small volume of water. The filtrate and washings were combined and concentrated to a volume of 3 ml on a water bath (70°). After 1.5 g of solid NaI was added, the solution was cooled in an ice bath overnight. The orange-red crystals which separated were collected, washed with NaI solution, ethanol, and ether, successively, and air-dried; yield 0.80 g. The product was recrystallized from dilute hydrochloric acid (0.01 *N*). *Anal.* Calcd for [Co($C_7H_{20}N_4$)($C_4H_8NO_2$)]I_2·2H_2O: C, 21.62; H, 5.28; N, 11.46. Found: C, 22.31; H, 5.23; N, 11.32. An attempt to separate the other isomer from the filtrate as the pure crystalline product failed.

Measurements. Visible absorption spectra were measured with a Shimadzu MPS-50L recording spectrophotometer. Circular dichroism curves were obtained with a JASCO J-20 recording spectropolarimeter. Proton magnetic resonance (pmr) spectra (100-MHz) were obtained using a JEOL PS-100 spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard reference.

The perchlorate salts (about 50-mg samples) were suspended in the solvents (0.01 *N* DCl or D_2O; 0.5–0.7 ml) and treated with twice the molar amount of tetraphenylarsonium chloride. The white precipitates were removed by filtration, and the filtrates were employed for pmr measurements. Iodide salts (about 60-mg samples) suspended in the solvents (0.5–0.7 ml) were treated with an equimolar amount of silver nitrate. The precipitated AgI was removed by filtration, and pmr spectra of the filtrates were measured.

Results and Discussion

As described in the Introduction, only one stereoisomer was anticipated for the *N*-methyl-(*S*)-alaninatocobalt(III) complexes with 5(*R*)- and 5(*S*)-metrien, designated as Λ-β_2-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ and Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ions, respectively. However, the possibility of another isomerism still remained for these complexes, arising from the difference of the positions of the *C*-methyl group of 5-metrien. As illustrated in Figure 1, two isomers are possible for 5(*R*)-metrien complexes.

A recent X-ray analysis study[21] revealed that the actual structure of the Λ-*cis*-β-Co(5(*R*)-metrien)(NO_2)$_2$$^+$ ion is confined solely to the structure depicted as Figure 1a (X = NO^-). Hence, it may be reasonable to expect that 5(*R*)- and 5(*S*)-metrien adopt the single coordination mode even in the *N*-methyl-(*S*)-alaninato complexes, where the methyl groups of 5-metrien orient adjacent to the "planar" secondary N atom.

The pmr spectrum of the Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, which was isolated as the perchlorate salt, was obtained in 0.01 *N* DCl. The spectrum is shown in Figure 2a. The *N*-methyl signal appeared as a doublet at 2.61 ppm (standard, DSS), because deuterium exchange of N-bonded protons is

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(17) The designations of "planar" and "angular" secondary N atoms follow the nomenclature by D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 5, 1032 (1967).

(18) The order of the secondary N atoms designated by *R* and *S* is as follows: the "angular" and "planar" N atoms of trien and the secondary N atoms of *N*-methyl-(*S*)-alanine. The fourth letter, represented in parentheses, designates the absolute configuration of the amino acid; *cf.* ref 7.

(19) M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, 8, 358 (1969).

(20) P. Quitt, J. Hellerbach, and K. Vogler, *Helv. Chim. Acta*, 46, 327 (1963).

(21) K. Tanaka, M. Ito, F. Marumo, and Y. Saito, unpublished result.

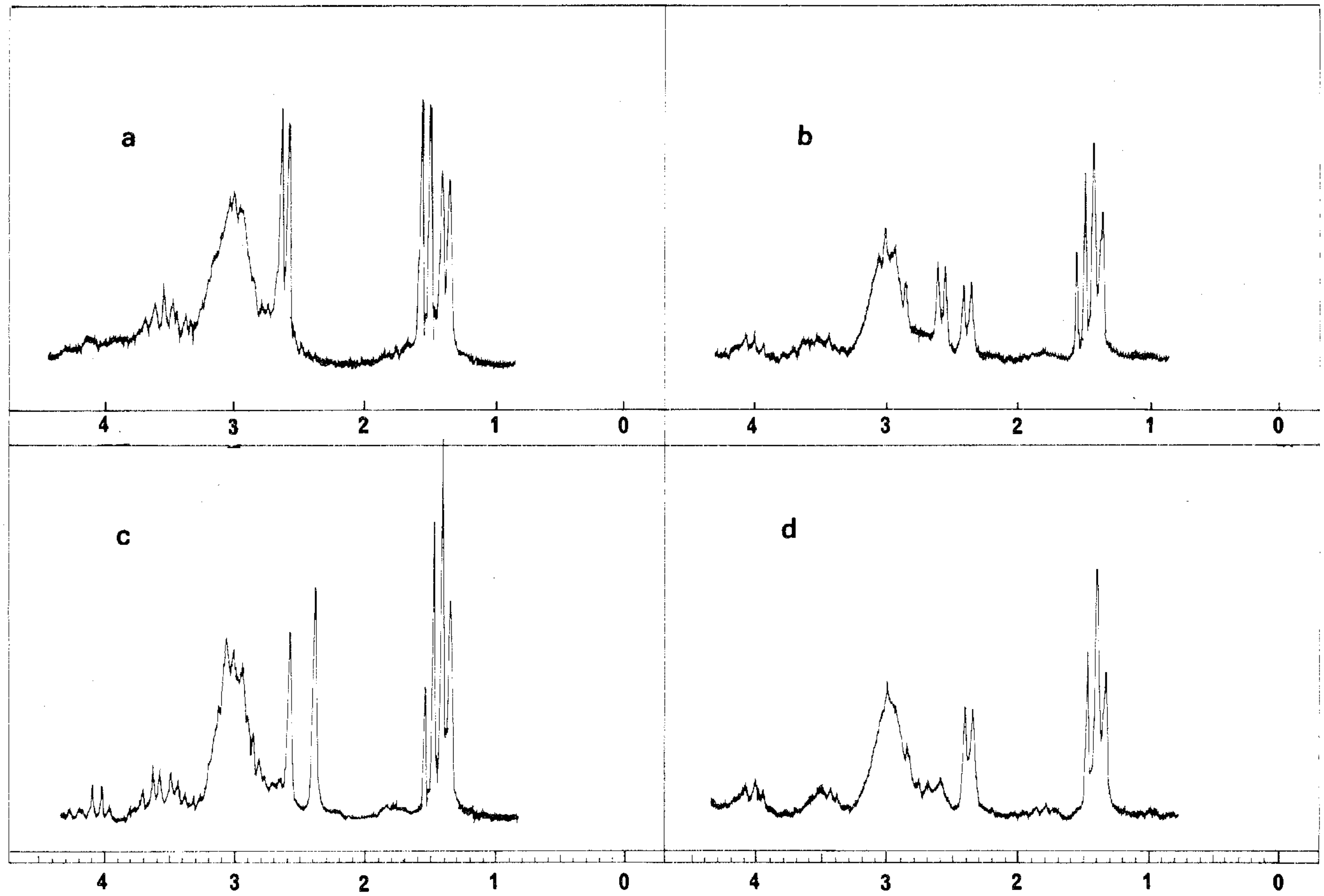

Figure 2. 100-MHz pmr spectra: (a) Λ-β_2-[Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)]$(ClO_4)_2$ in 0.01 *N* DCl; (b) Λ-β_2-[Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)]-$(ClO_4)_2 \cdot H_2O$ in 0.01 *N* DCl; (c) Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers in neutral D_2O after equilibration of Δ-β_2-[Co(5(*S*)-metrien)-(*N*-Me-(*S*)-ala)]$(ClO_4)_2 \cdot H_2O$ and -$I_2 \cdot 2H_2O$ at pH 7 (in D_2O); (d) Δ-β_2-[Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)]$I_2 \cdot 2H_2O$ in 0.01 *N* DCl.

retarded under the acidic condition. The two doublets centered at 1.37 and 1.53 ppm were assigned to either of the *C*-methyl groups of 5(*R*)-metrien and *N*-Me-(*S*)-ala, respectively. The assignment of these signals will be described later.

Observation of a single pmr signal for the *N*-methyl and two *C*-methyl groups indicates the presence of largely one species for the Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion. The visible absorption and CD spectra of this ion in 0.1 *N* $HClO_4$ solution are shown in Figure 3. No change was observed when these curves were measured in neutral aqueous solution (at pH 7). These spectra are similar to those of the Λ-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion.[7] On this basis, the 5(*R*)-metrien complex should be assigned as Λ-β_2-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, as was expected.

Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion was first isolated as the perchlorate salt. However, the pmr spectrum of this complex, obtained in 0.01 *N* DCl, showed two *N*-methyl resonances at 2.58 and 2.38 ppm (Figure 2b). The pmr spectrum of the same complex after equilibration at pH 7.0 in D_2O is also shown (Figure 2c). At this pH the protons attached to the N atoms have exchanged with solvent D_2O, and the pmr signals for the *N*-methyl groups have collapsed to singlets. The two *N*-methyl signals appear to vary slightly their relative intensities before and after equilibration.

The visible absorption and CD curves of [Co(5(*S*)-metrien)-(*N*-Me-(*S*)-ala)]$(ClO_4)_2$, obtained under the acidic (0.1 *N* $HClO_4$) and neutral (pH 7) conditions, are shown in Figure 3. These CD curves are slightly different from each other. This spectral change is considered to correspond to the above pmr spectral change. The CD pattern of the present complex after equilibration at pH 7 is closely similar to the corresponding curve of the Δ-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ isomers.

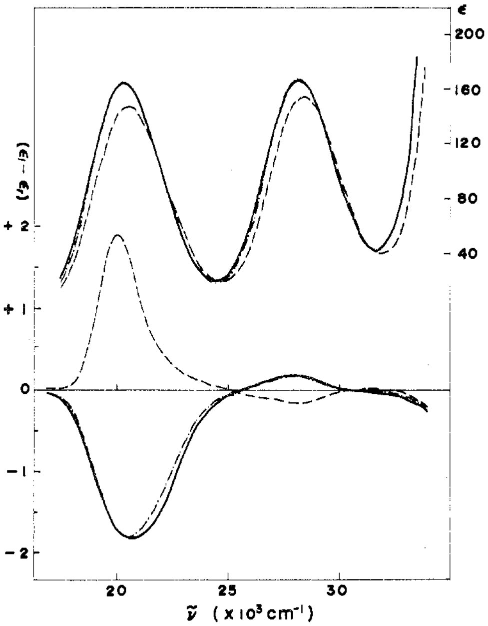

Figure 3. Visible absorption and CD spectra of Λ-β_2-[Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)]$(ClO_4)_2$ in 0.1 *N* $HClO_4$ (- - -), Δ-β_2-[Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)]$(ClO_4)_2 \cdot H_2O$ in 0.1 *N* $HClO_4$ (- · -), and in H_2O after equilibration at pH 7 (———).

The above CD results suggested that the two isomers of the 5(*S*)-metrien complex could not be ascribed to the difference of absolute configuration about the cobalt(III) center. If the Δ and Λ isomers coexist, the CD due to the absolute configuration about the central cobalt ion would be approximately cancelled since the two isomers must be present in nearly equal amounts from the pmr results, and, consequently, a rather weak CD curve due to the vicinal effect of the N-methyl-(S)-alaninate group would be observed.

It has been noted[7] that the Co(trien)(N-Me-(S)-ala)$^{2+}$ ion gives rise to a mixture of Δ-β_2 isomers, along with Λ-β_2 isomer, as the perchlorate salt, while one of the Δ-β_2 isomers can be isolated as the iodide salt. As mentioned previously, only Δ isomers are possible for the 5(S)-metrien complex. Hence, isolation of the iodide salt of the Δ-β_2-Co(5(S)-metrien)(N-Me-(S)-ala)$^{2+}$ complex was attempted, based on the assumption that the 5(S)-metrien complex yields a mixture of the Δ-β_2 isomer as perchlorate and only one Δ-β_2 isomer as iodide.

The pmr spectrum of [Co(5(S)-metrien)(N-Me-(S)-ala)]I_2 showed only one N-methyl doublet at 2.38 ppm in 0.01 N DCl, as is shown in Figure 2d. This signal coincides with one of the N-methyl signals observed for the perchlorate. The C-methyl signals for the iodide were observed as an apparent triplet, which was assigned to the overlap of two doublets centered at 1.34 and 1.42 ppm. This indicates that the iodide salt of the 5(S)-metrien complex consists of a single species.

The pmr spectrum of the above iodide measured in D_2O after equilibration at pH 7 was found to be identical with the corresponding spectrum of the perchlorate shown in Figure 2c. These results exclude the possibility that the two isomers of the Δ-β_2-Co(5(S)-metrien)(N-Me-(S)-ala)$^{2+}$ ion observed for the perchlorate are attributed to the difference of the location of the methyl group of 5(S)-metrien, either adjacent to or apart from the "planar" secondary N atom. The C-methyl signals, which appeared additional to the signals in Figure 2d, were the doublets at 1.50 ppm and, further, at 1.34 ppm (*cf.* Figure 2c). The latter signal is superimposed with the doublet (1.34 ppm) previously observed in the spectrum obtained in 0.01 N DCl (Figure 2d). In the case of the Δ-β_2-Co(trien)(N-Me-(S)-ala)$^{2+}$ ion, the pmr signals of the C-methyl region appeared as a triplet after equilibration at pH 7. When one more doublet due to the methyl group of 5(S)-metrien was added to such an apparent triplet signal of the N-Me-(S)-ala moiety in the higher field and the highest peak of triplet and the lower peak of doublet overlapped, the signals of the C-methyl region found in Figure 2c (1.3–1.5 ppm) should occur. Therefore, the pmr changes of [Co(5(S)-metrien)(N-Me-(S)-ala)]I_2 caused by the pH variation correspond well to those of the Δ-β_2-[Co(trien)(N-Me-(S)-ala)]I_2.

The CD curve of the iodide of the 5(S)-metrien complex showed a spectral change due to pH change of the solvent, as shown in Figure 4. This change also corresponds to CD behaviors of the Δ-β_2 isomer of the trien complex. The CD curves in H_2O are almost identical between the iodide and perchlorate of the 5(S)-metrien complex, as was expected.

It was concluded from the pmr and CD results that the iodide salt of 5(S)-metrien has a Δ-β_2 structure which isomerizes to another Δ-β_2 form at equilibrium in aqueous solution at pH 7. These two Δ-β_2 isomers crystallized out as a mixture of perchlorate salt, but the second Δ-β_2 form could not be isolated in a pure state. It was probable, further, that the Δ-β_2 isomers of the Co(trien)(N-Me-(S)-ala)$^{2+}$ ion and the Co(5(S)-metrien)(N-Me-(S)-ala)$^{2+}$ ion, both the isomers isolated as iodides and their isomerized forms, have identical structures except for the methyl group of 5(S)-metrien because of the similarity in the pmr and CD changes.

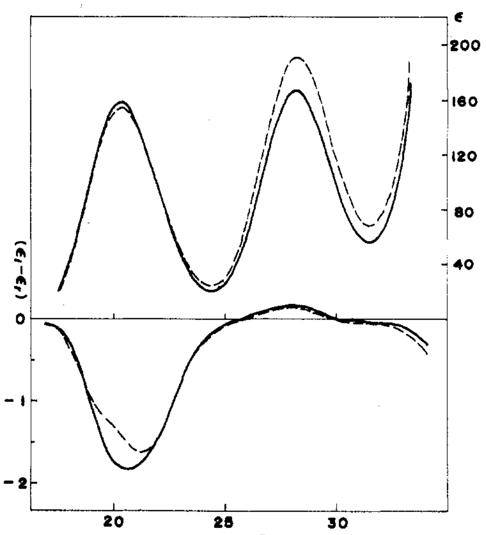

Figure 4. Visible absorption and CD spectra of Δ-β_2-[Co(5(S)-metrien)(N-Me-(S)-ala)]$I_2 \cdot 2H_2O$ in 0.1 N $HClO_4$ (— — —) and in H_2O after equilibration at pH 7 (———).

Therefore, the isomerization at pH 7 may be ascribed to the same origin for the Δ-β_2 isomers of trien and 5(S)-metrien complexes. It has been suggested that the rate constant of the isomerization at pH 6.5–7.0 corresponds to that expected for mutarotation at an asymmetric N center and that two possibilities exist for such mutarotation: inversion at the N-methyl group or at the "planar" secondary N center of β-trien.[7] The former possibility has been ruled out on a stereochemical point of view, and the coexistence of Δ-β_2-(*RRS*)- and Δ-β_2-(*RSS*)-Co(trien)(N-Me-(S)-ala)$^{2+}$ at equilibrium has been concluded for these trien complexes in a previous study.[7]

It is difficult for the 5(S)-metrien complex to have a Δ-β-*RS* form because of unfavorable axial orientation of the methyl group. Therefore, it is very improbable that the Δ-β_2-*RRS* and Δ-β_2-*RSS* forms of Co(5(S)-metrien)(N-Me-(S)-ala)$^{2+}$ ion have similar stabilities. If the latter species coexists at equilibrium, its abundance will be appreciably low relative to the former species. This assumption conflicts with the previous pmr observations. Hence, the other possibility of inversion at the N center seems to be the more probable reason for isomerization; that is, inversion at the N-methyl group of N-methyl-(S)-alaninate.

The most stable configuration for the chelated N-methyl-(S)-alanine moiety should be that in which the two adjacent methyl groups are trans to each other. This configuration has been proposed for complexes Co$(NH_3)_4$(N-Me-(S)-ala)$^{2+}$,[22] Λ-Co$(en)_2$(N-Me-(S)-ala)$^{2+}$, and Λ-β_2-Co(trien)(N-Me-(S)-ala)$^{2+}$.[7] The N-methyl groups have the R configuration in these complexes. Therefore, the above trien complex has been represented as Λ-β_2-(*SSR*)-Co(trien)(N-Me-(S)-ala)$^{2+}$. The trans configuration should be applied for the 5(R)-metrien complex, which can be expressed as Λ-β_2-(*SSR*)-Co(5(R)-metrien)(N-Me-(S)-ala)$^{2+}$.

In the cis configuration, however, the N-methyl and C-methyl groups are in a sterically less favorable, eclipsed configuration. A strain energy minimization study has indicated that the Λ-β_2-(*SSR*)-Co(trien)(N-Me-(S)-ala)$^{2+}$ ion, with trans configuration, is 0.5 kcal/mol in favor of the Δ-β_2-*RRS* isomer with cis configuration.[7] In the Δ-β_2-*RRR* configuration, such stereochemical disadvantage will

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

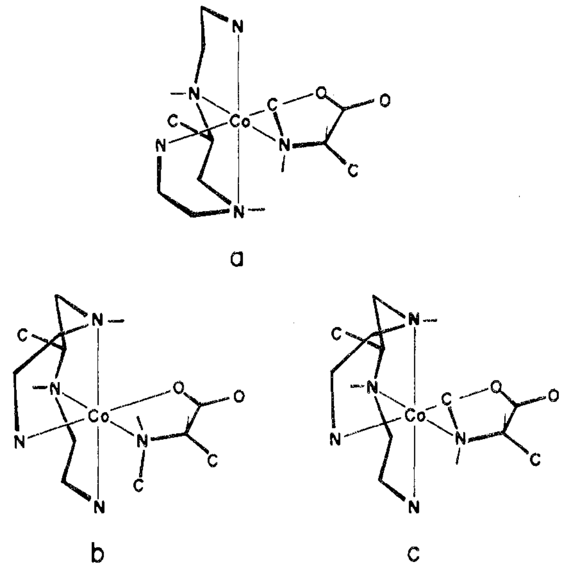

Figure 5. Probable structures of (a) Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$, (b) Δ-β_2-(*RRS*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$, and (c) Δ-β_2-(*RRR*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$.

vanish, though unfavorable steric interactions between the *N*-methyl group and the adjacent trien chelate ring must appear instead of interactions between *N*- and *C*-methyl groups. The pmr results of Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ suggest that the Δ-β_2-*RRR* configuration has approximately equal stabilities as compared with the Δ-β_2-*RRS* configuration.

The Δ-β_2-*RSS* configuration, alternative to the Δ-β_2-*RRR* form, has been shown to be less stable than the Δ-β_2-*RRS* form in terms of 3.2 kcal/mol.[7] It seems to be rather unlikely that the Δ-β_2-*RSS* and Δ-β_2-*RRS* isomers have comparable stabilities, even if the entropy term affects appreciably the free-energy difference. We concluded, therefore, that the Δ-β_2-Co(trien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, as well as the Δ-β_2-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion, adopts the *RRS* and *RRR* configurations at equilibrium. The probable structures for 5(*S*)-metrien complexes are illustrated in Figure 5, along with that for the 5(*R*)-metrien complex.

Table I. Assignments of *C*- and *N*-Methyl Proton Resonances[a] of *N*-Me-(*S*)-ala Complexes

	C–CH$_3$ (5-metrien)	C–CH$_3$ (*N*-Me-(*S*)-ala)	N–CH$_3$
Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.37	1.53	2.61
Δ-β_2-(*RRS*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.34	1.42	2.38
Δ-β_2-(*RRR*)-Co(5(*S*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$	1.34	1.50	2.58

[a] Parts per million from DSS.

It is somewhat difficult to assign individual species for the *RRS* and *RRR* configurations. The only remarkable difference between these isomers is the relative orientations of the *N*- and *C*-methyl groups. The pmr signals of the *N*-methyl groups were observed at 2.58 and 2.38 ppm for an isomeric mixture of the 5(*S*)-metrien complex (Figure 2c). The corresponding signal for the Λ-β_2-(*SSR*)-Co(5(*R*)-metrien)(*N*-Me-(*S*)-ala)$^{2+}$ ion was observed at 2.61 ppm. We assign here the *N*-methyl signal at 2.38 ppm, apart from the other signals, for that with the *S* (cis) configuration. Then, the signal at 2.58 ppm for the 5(*S*)-metrien complex and that at 2.61 ppm for the 5(*R*)-metrien complex are simultaneously assigned to the *R* (trans) configuration. The assignments of pmr signals are summarized in Table I.

In order to confirm the conclusions in this study, we have examined *N*-methyl-(*S*)- and *N*-methyl-(*R*)-alaninatocobalt(III) complexes with *N,N'*-bis(β-aminoethyl)-(1*R*,2*R*)-diaminocyclohexane. The trien derivative employed here has no possibility of conformational inversion at the central diamine linkage. The results on these systems will be reported in a subsequent paper.

Registry No. Λ-β_2-[Co[5(*R*)-metrien](*N*-Me-(*S*)-ala)](ClO$_4$)$_2$, 38671-62-4; Δ-β_2-[Co[5(*S*)-metrien](*N*-Me-(*S*)-ala)](ClO$_4$)$_2$, 38671-64-6; Δ-β_2-[Co[5(*S*)-metrien](*N*-Me-(*S*)-ala]I$_2$, 38671-65-7; Δ-β_2-[Co[5-(*S*)-metrien](*N*-Me-(*S*)-ala)]$^{2-}$, 38671-66-8.

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Spin-Triplet Cobalt Complexes of Biuret and Related Ligands

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A number of planar Co^{III}N$_4$ complexes have been prepared with biuret and N-substituted biurets. They are shown to have triplet electronic ground states in the temperature range 6.4–293°K. The zero-field splitting is estimated to be about 40 cm^{-1}. The triplet ground state is consistent with molecular orbital energies obtained from extended Huckel calculations. The d_{xz} and $d_{x^2-y^2}$ orbitals both have the same energy and are both occupied by one electron. Polarographic measurements show that these complexes can be reversibly reduced in a one-electron step. With amines, diamagnetic six-coordinated mixed-ligand species are obtained, whose uv-vis spectra can be interpreted as for Co(III) in an octahedral environment.

Introduction

In previous communications from our laboratory the rather unique properties of biuret as a ligand were discussed. It was shown that the well-known Cu(II) and Ni(II) complexes could be oxidized with various oxidizing agents yielding the corresponding Cu(III) and Ni(III) compounds.[1,2] With cobalt the very remarkable planar bis(biuretato)cobalt-

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