indicate that the rate of exchange, should it occur, is too slow to observe on the nmr time scale over the temperature range investigated. The reactivity of the amine function toward methyl iodide may be quite sensitive to electronic perturbations caused by even a slow exchange process.

An examination of molecular models indicates the third possibility to be the most likely explanation. The two ethyl groups on the uncoordinated nitrogen and the bulkiness of the rest of the molecule make attack by methyl iodide sterically inaccessible. The differences in the geometries of the two potentially tridentate ligands may account for the ability of NPN to add methyl iodide and the inability of T-NPN to do the same. An X-ray investigation of $PdCl_2$(T-NPN) is currently underway.

Conclusions

The polydentate ligands investigated in the course of this study did not yield five-coordinate palladium(II) and platinum(II) halide complexes. When compared with other group Va polydentate ligands[14,15] substitution of a nitrogen atom for a heavier group Va atom drastically reduces the chances for five-coordination. This trend appears to result from both electronic effects and (in the case of our ligands) steric effects. These conclusions agree with those reached by Venanzi.[4]

Acknowledgment.—Partial support of this research by the Petroleum Research Fund is gratefully acknowledged.

(15) J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 3930 (1963).

CONTRIBUTION FROM THE FACULTY OF ENGINEERING, UNIVERSITY OF TOKYO, BUNKYO-KU, TOKYO, JAPAN

Stereochemical Studies of Metal Chelates. II. Stereospecific Coordination of N-Methyl-L-alanine to the Cobalt(III) Ion

BY MASAHIKO SABURI AND SADAO YOSHIKAWA

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Cobalt(III) complexes containing N-methyl-L-alanine and related N-substituted amino acids have been prepared. Rotatory dispersion, circular dichroism, and pmr evidence has been collected to show that N-methyl-L-alanine is coordinated stereospecifically with regard to the secondary nitrogen atom. The contributions to optical activity from the vicinal effects of asymmetric carbon and asymmetric secondary nitrogen were found to be qualitatively additive.

In a recent study, three possible geometrical isomers of the dichlorotriethylenetetraminecobalt(III) ion, that is, the *cis*-α, *cis*-β, and *trans* isomers, were prepared under controlled conditions.[1] The first study of a triethylenetetramine cobalt(III) complex[2] pointed out that the violet dichloro complex was obtained by a method similar to that for preparing green *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$. One of the present authors observed that the green *trans* isomer was isolated in the same procedure using L,L-3,8-dimethyltriethylenetetramine (one of the optically active derivatives of triethylenetetramine) in the place of unsubstituted triethylenetetramine.[3] On the other hand, L,L-2,9-dimethyltriethylenetetramine, also an optically active derivative of triethylenetetramine, was revealed to give the *cis*-α form in the similar preparative conditions.[4] It is considered that in L,L-3,8-dimethyltriethylenetetramine coordinated in the form of *cis*-α (and *cis*-β), there are repulsive interactions among the methyl groups substituted on the carbon atoms adjacent to secondary nitrogen atoms and hydrogen atoms of the central ethylene bridge of triethylenetetramine. The influence of such interactions may be one of the reasons for obtaining only the *trans* isomer in the case of this ligand.

An N-methylamino acid coordinated to a metal ion can be regarded as a simple model system of a chelate ring which contains such an alkyl-substituted carbon atom adjacent to a coordinated secondary nitrogen. Therefore, investigation of the steric interaction between the N and C substituents in the five-membered chelate ring would aid in understanding the mode of wrapping with a ligand chain such as L,L-3,8-dimethyltriethylenetetramine.

Sargeson and his coworkers showed the possibility of resolving a secondary amine coordinated to a metal ion using the $Co(NH_3)_4sar^{2+}$ ion (sarH = sarcosine, N-methylglycine) and reported the RD and CD curves of the optically active form.[5] Shimura and his coworkers pointed out that the L-proline complex shows a considerably different CD curve from the other L-amino acid complexes.[6,7] It was thought that the anomalous CD curve of the L-proline complex is probably due to the

(1) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).
(2) F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).
(3) S. Yoshikawa, T. Sekihara, and M. Goto, *Inorg. Chem.*, **6**, 169 (1967).
(4) R. G. Asperger and C. F. Liu, *ibid.*, **4**, 1395 (1965).
(5) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **88**, 4630 (1966).
(6) (a) T. Yasui, J. Hidaka, and Y. Shimura, *ibid.*, **87**, 2762 (1965); (b) T. Yasui, *Bull. Chem. Soc. Japan*, **38**, 1746 (1965).
(7) T. Yasui, J. Hidaka, and Y. Shimura, *ibid.*, **39**, 2417 (1966).

additional asymmetric character of the coordinated secondary nitrogen in this ligand.

The cobalt(III) complex containing optically active N-methyl-L-alanine, $Co(NH_3)_4$-N-Meala^{2+} (N-MealaH = N-methyl-L-alanine), and related compounds have been prepared in the present study. The asymmetric character of the coordinated secondary nitrogen in these complexes was investigated by means of RD and CD measurements, and it was concluded that the secondary nitrogen of N-methyl-L-alanine is coordinated stereospecifically to the cobalt(III) ion. Furthermore, the contribution to the optical activity from the asymmetric secondary nitrogen is found to be qualitatively additive to that from the asymmetric carbon in this complex.

Experimental Section

N-Methyl-L-alanine and **N-methyl-L-leucine** were synthesized according to the method of Quitt, Hellerbach, and Vogler.[8]

D(+)-Pipecolic Acid.[9]—Racemic pipecolic acid, obtained by passing an aqueous solution of its hydrochloride through a column of Amberlite IRA-410 (OH form), was dissolved in hot ethanol, mixed with an equimolar amount of *d*-tartaric acid in hot ethanol, and cooled to room temperature; after 48 hr the precipitated crystals were filtered off. The diastereoisomeric salt (20.3 g), which had an optical rotation $[\alpha]^{25}D$ +17.1°, was recrystallized from ethanol seven times, and 9 g of a diastereoisomeric salt of $[\alpha]^{25}D$ +20.4° was obtained. The aqueous solution of this salt was passed through a column of Amberlite IR-45 (OH form) and 3 g of D(+)-pipecolic acid was recovered from the eluent, $[\alpha]^{25}D$ +28.3° (lit.[9] +35.7°).

N-Methyl-L-alaninatotetraamminecobalt(III) Nitrate Monohydrate, $[Co(NH_3)_4$-N-Meala$](NO_3)_2 \cdot H_2O$.—This complex was prepared by a method similar to that for the sarcosine complex described by Sargeson and his coworkers.[5] N-Methyl-L-alanine (4.1 g) was dissolved in 35 ml of 1 *N* NaOH, 11.1 g of $[Co(NH_3)_4Cl \cdot H_2O]SO_4$ was added, followed by 3 ml of 2 *N* ammonia, and the solution was stirred and heated at 70°. After 90 min, the solution was filtered, 10 g of NH_4NO_3 and a small volume of ethanol were added, and the precipitate was filtered off. More ethanol was added carefully and the filtrate was cooled to 5°. The red crystals which separated were filtered off and washed with ethanol. This product was recrystallized from warm water with NH_4NO_3. *Anal.* Calcd for $[Co(NH_3)_4$-N-Meala$](NO_3)_2 \cdot H_2O$: C, 12.94; H, 5.97; N, 26.42. Found: C, 12.70; H, 6.00; N, 26.48.

N-Methyl-L-leucinatotetraamminecobalt(III) Nitrate, $[Co(NH_3)_4$-N-Meleu$](NO_3)_2$.—A 1.6-g sample of N-methyl-L-leucine was dissolved in 9 ml of 1 *N* NaOH, 2.8 g of $[Co(NH_3)_4Cl \cdot H_2O]SO_4$, 0.8 ml of ammonia (2 *N*), and 10 ml of water were added, and the mixture was stirred and heated at 70° for 90 min. The resultant solution was filtered, 2.5 g of NH_4NO_3 was added, and the precipitated impurity was filtered off. The filtrate was concentrated to half its volume on a steam bath, 10 ml of methanol was added, and the solution was filtered. To the filtrate 150 ml of methanol was added, and the precipitate was filtered and washed with methanol. The pink residue was dissolved in a minimum volume of warm water; NH_4NO_3 was added and cooled to 5°. Fine needle orange-pink crystals were filtered off, washed with methanol and acetone, and air dried. *Anal.* Calcd for $[Co(NH_3)_4$-N-Meleu$](NO_3)_2$: C, 21.27; H, 6.63; N, 24.81. Found: C, 21.09; H, 6.49; N, 24.64.

D-Pipecolinatotetraamminecobalt(III) Nitrate, $[Co(NH_3)_4$-D-pipec$](NO_3)_2$.—A 1.74-g sample of D-pipecolic acid was dissolved in 11.7 ml of 1 *N* NaOH, 3.7 g of $[Co(NH_3)_4Cl \cdot H_2O]SO_4$ and 1 ml of ammonia (2 *N*) were added, and the mixture was stirred and heated at 70° for 90 min. The solution was filtered hot, 3.3 g of NH_4NO_3 was added, and the solution was filtered again. The filtrate was cooled to 5°. After 24 hr, the crystals were filtered off, washed with aqueous methanol (1:1) and methanol, and air dried. The crude product was recrystallized from warm water containing NH_4NO_3 giving orange-pink fine needle crystals. *Anal.* Calcd for $[Co(NH_3)_4$-D-pipec$](NO_3)_2$: C, 19.00; H, 5.86; N, 25.85. Found: C, 19.20; H, 5.73; N, 25.74.

Measurements.—Rotatory dispersion curves were measured in a 1-cm cell using a Model ORD/UV-5 spectrophotometer from Japan Spectroscopic Co. The circular dichroism curves were measured in a 1-cm cell using 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 reference.

Results and Discussion

RD and CD curves for $Co(NH_3)_4aa^{2+}$ (aaH = L-amino acid) have been examined by Shimura and his coworkers,[7] and RD and CD curves for optically active $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ have been reported recently by Sargeson, *et al.*[5] In the former case the optical activity of the complexes was attributed to the so-called vicinal effect of an asymmetric carbon of coordinated L-amino acids on a cobalt(III) ion but in the latter to the vicinal effect of the asymmetric secondary nitrogen of sarcosine coordinated to cobalt(III) ion. RD and CD curves for $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} are shown in Figures 1 and 2, respectively, along with the corresponding curves for $Co(NH_3)_4ala^{2+}$ (alaH = L-alanine) and $(-)_{436}$-$Co(NH_3)_4sar^{2+}$. It is noteworthy that the RD curve for $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} is remarkably different from the corresponding curve for $Co(NH_3)_4ala^{2+}$; rather it resembles that for $(-)_{436}$-$Co(NH_3)_4sar^{2+}$. Such resemblance in RD curves suggests that the chelate ring of sarcosine in $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ and that of N-methyl-L-alanine in $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} possess an asymmetric center of similar structure. The asymmetric secondary nitrogen may correspond to such an asymmetric center, since the NCH_3 group is common to sarcosine and N-methyl-L-alanine.

Buckingham and his coworkers indicated that sarcosine is coordinated stereospecifically in $Co(en)_2sar^{2+}$.[10] Furthermore, it was pointed out by these authors that the RD curve for $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ is nearly equal to the composite curve arising from the superposition of those for $(+)_{589}$-$Co(en)_2sar^{2+}$ and $(-)_{589}$-$Co(en)_2gly^{2+}$; consequently, the absolute configuration of the secondary nitrogen in $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ is identical with that in $(+)_{589}$-$Co(en)_2sar^{2+}$. More recently, the X-ray analysis of $(-)_{589}$-$Co(en)_2sar^{2+}$ was reported,[11] indicating that the structure of sarcosine in $(+)_{589}$-$Co(en)_2sar^{2+}$, and, therefore, $(-)_{436}$-$Co(NH_3)_4sar^{2+}$, is the one shown in Figure 3(a). Applying the *R* and *S* terminology,[12] the absolute configuration of the asymmetric secondary nitrogen atom in $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ may be denoted as *R*.

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

(9) R. S. Schweet, J. T. Holden, and P. H. Lowy, *J. Biol. Chem.*, **211**, 517 (1954).

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

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

(12) C. K. Ingold, V. Prelog, and R. S. Cahn, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

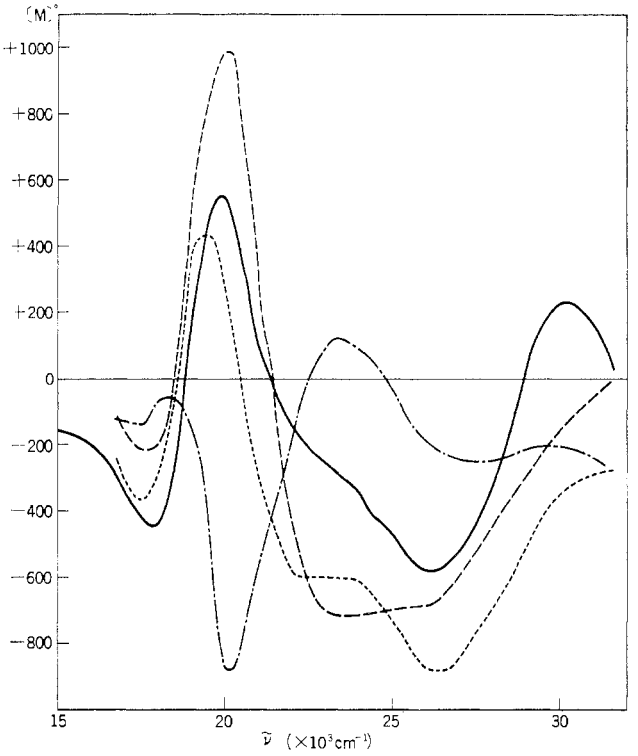

Figure 1.—Rotatory dispersion curves for $Co(NH_3)_4$-N-Meala^{2+} (———), (−)-$Co(NH_3)_4sar^{2+}$ (– – – –), and $Co(NH_3)_4ala^{2+}$ (— – —) and the composite curve for (−)-$Co(NH_3)_4sar^{2+}$ + $Co(NH_3)_4ala^{2+}$ (- - - - - -).

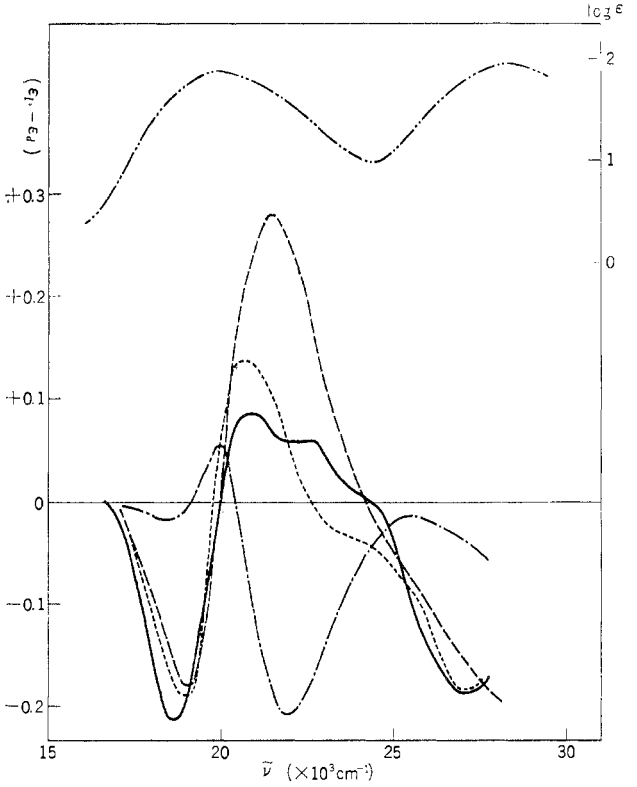

Figure 2.—Visible absorption curve for $Co(NH_3)_4$-N-Meala^{2+} (- - — - -), circular dichroism curves for $Co(NH_3)_4$-N-Meala^{2+} (———), (−)-$Co(NH_3)_4sar^{2+}$ (– – – –), and $Co(NH_3)_4ala^{2+}$ (— - —), and the composite curve for (−)-$Co(NH_3)_4sar^{2+}$ + $Co(NH_3)_4ala^{2+}$ (- - - - - -).

The possible structures for N-methyl-L-alanine coordinated as a bidentate ligand are given in Figure 3(b) and (c). These two forms differ in the stereochemical relationship of the N-substituted methyl group to the C-methyl group. In (b), the two methyl groups are located *gauche* relative to the C–N bond, whereas in (c) they are eclipsed. From the stereochemical viewpoint, the structure shown in Figure 3(b) is considered to be preferable to that in Figure 3(c). Moreover, the absolute configuration of the secondary nitrogen in this structure (Figure 3(b)) is apparently identical, *i.e.*, *R*, with that of sarcosine in $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ (Figure 3(a)). Therefore, it is supposed that the similarity in RD curves between $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} and $(-)_{436}$-$Co(NH_3)_4sar^{2+}$ is due to the coincidence of the absolute configuration of the coordinated secondary nitrogen, suggesting that N-methyl-L-alanine is coordinated stereospecifically in the form shown in Figure 3(b).

An aqueous solution of $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} shows no evidence for mutarotation or change in optical rotation after standing for 3 hr. This is in contrast to the optically active $Co(NH_3)_4sar^{2+}$ which is found to be racemized in neutral solution. The racemization of an active sarcosine complex was considered to be caused by the abstraction of the N–H proton by OH^-. The abstraction of the N–H proton would also take place on N-methyl-L-alanine complexes. No change in optical rotation was observed for an aqueous solution of $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+}, suggesting either of the following two possibilities: (1) N-methyl-L-alanine is coordinated stereospecifically to the cobalt(III) ion or (2) the obtained product of $(-)_{436}$-$[Co(NH_3)_4$-N-Meala$](NO_3)_2$ is an equilibrium mixture of diastereomeric isomers shown in Figure 3(b) and (c). However, the latter possibility is excluded by the pmr measurements.

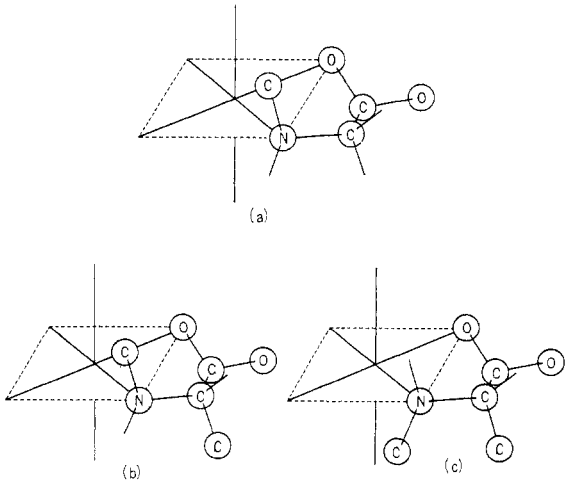

Figure 3.—The structure of the sarcosinate ion in (−)-$Co(NH_3)_4sar^{2+}$ (a) and the probable structures of the N-methyl-L-alaninate ion in $Co(NH_3)_4$-N-Meala^{2+} (b and c).

The pmr spectra for $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+} ion in 0.1 *N* D_2SO_4 and D_2O solutions are shown in Figure 4(a) and (b), respectively. In these spectra, the doublet at 1.50 ppm is assigned to the C-substituted methyl

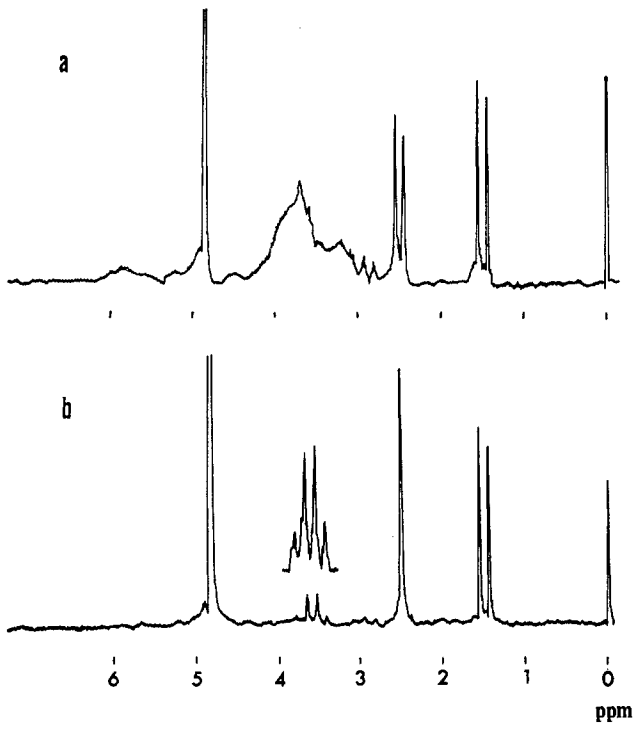

Figure 4.—Pmr spectra (60 Mc) of $Co(NH_3)_4$-N-Meala^{2+} in (a) 0.1 *N* D_2SO_4 and (b) D_2O.

group split by the methyne proton which is observed as the quartet at 3.60 ppm in D_2O solution. The doublet at 2.50 ppm observed in D_2SO_4 solution is converted to the singlet in D_2O. This signal is assigned to the protons of the N-methyl group. In acidic solution, an N–H proton is not deuterated (corresponding signal is observed as a broad peak in the region 5.5–6.0 ppm) and, therefore, the signal for the N-methyl protons is observed as the doublet split by the N–H proton. In D_2O solution, however, the N–H proton is deuterated completely (3 hr after dissolution) and the corresponding signal is observed as the singlet. There is no indication that the signals for two methyl groups are split into more peaks in either D_2O or D_2SO_4 solution, supporting the existence of single C- and N-methyl groups. This suggests that only one species exists in the solution of $(-)_{436}$-$Co(NH_3)_4$-N-Meala^{2+}. Thus, the results of RD, CD, and pmr measurements suggest that the N-methyl-L-alanine is coordinated stereospecifically to the cobalt(III) ion at the secondary nitrogen.

It is interesting to examine in detail the CD or RD curve for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+} and other complexes of this type. Both CD curves for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+} and $(-)_{436}$-*R*-$Co(NH_3)_4$sar^{2+} (Figure 2) give a negative band of nearly equal magnitude at about 19,000 cm^{-1}, whereas the latter shows a greater positive Cotton effect than the former in the region 20,000–25,000 cm^{-1}. Moreover, the CD band for the N-methyl-L-alanine complex seems to split into two components in this region. The difference in the CD curves is ascribed to the influence of the asymmetric carbon in N-methyl-L-alanine, since there is no asymmetric carbon in sarcosine. The contributions to the CD curve from the asymmetric carbon may be assumed to be equal in $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+} and $Co(NH_3)_4$ala^{2+}, because the composite CD curve arising from the superposition of those for $Co(NH_3)_4$-ala^{2+} and $(-)_{436}$-*R*-$Co(NH_3)_4$sar^{2+} (Figure 2) has a greater resemblance to the CD curve for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+} than that for $(-)_{436}$-*R*-$Co(NH_3)_4$-sar^{2+} alone. A similar trend is observed in the corresponding RD curves shown in Figure 1. These results suggest that the contributions to the optical activity from the vicinal effect of asymmetric carbon and from that of asymmetric secondary nitrogen are additive qualitatively. Douglas and coworkers were the first to recognize, in the study of L-aminoacidobis(ethylenediamine)cobalt(III) complexes, that the contributions to RD and CD from the configuration of the complex and from the vicinal effect are almost quantitatively additive.[13] However it is reasonable to expect that the additive relation of the contributions from the vicinal effects of asymmetric carbon and secondary nitrogen centers, observed for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+} in the present study, is merely qualitative. The two asymmetric centers in $Co(NH_3)_4$-N-Meala^{2+} being close to one another are considered to be in slightly different circumstances from where each asymmetric center exists independently and, therefore, their contributions to RD and CD may be varied.

It was pointed out by Shimura, *et al.*,[7] that the RD and CD curves for $Co(NH_3)_4$leu^{2+} (leuH = L-leucine) are similar to those for $Co(NH_3)_4$ala^{2+}. If N-methyl-L-leucine is coordinated stereospecifically in the same manner as N-methyl-L-alanine, it may be expected that the CD and RD curves for $Co(NH_3)_4$-N-Meleu^{2+} (N-MeleuH = N-methyl-L-leucine) will be similar to the corresponding curves for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+}. The RD and CD curves for $(-)_{436}$-$Co(NH_3)_4$-N-Meleu^{2+} are shown in Figures 5 and 6, respectively, and resemble those for $(-)_{436}$-*R*-$Co(NH_3)_4$-N-Meala^{2+}. This means that there is no fundamental difference in the environments of the two asymmetric centers of the N-methyl-L-leucine complex from those of the N-methyl-L-alanine complex and that N-methyl-L-leucine is coordinated stereospecifically in a form similar to N-methyl-L-alanine (Figure 3(b)).

Another example of the stereospecific coordination of an N-substituted amino acid is presented by the complex with optically active pipecolic acid (2-piperidinecarboxylic acid). The most probable structure for the coordinated L-pipecolic acid, from a stereochemical point of view, is given in Figure 7. This indicates that the piperidine ring, adopting a chair form, is extended coplanar with the chelate ring in order to minimize the steric interaction with axial ligands. The structure having a boat-formed piperidine ring is excluded thermodynamically, since the energy difference between the chair and boat forms of cyclohexane has been estimated at about 5.5 kcal. The structure proposed above has the same absolute configuration at the secondary nitrogen as that of sarcosine in $(-)_{436}$-$Co(NH_3)_4$sar^{2+}, that

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

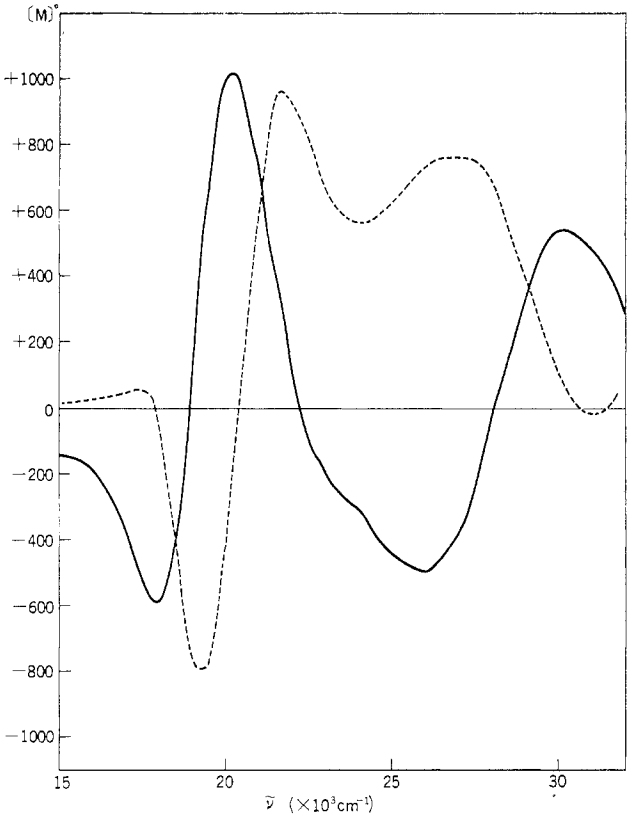

Figure 5.—Rotatory dispersion curves for $Co(NH_3)_4$-N-Meleu^{2+} (———) and $Co(NH_3)_4$-D-pipec^{2+} (– – – –).

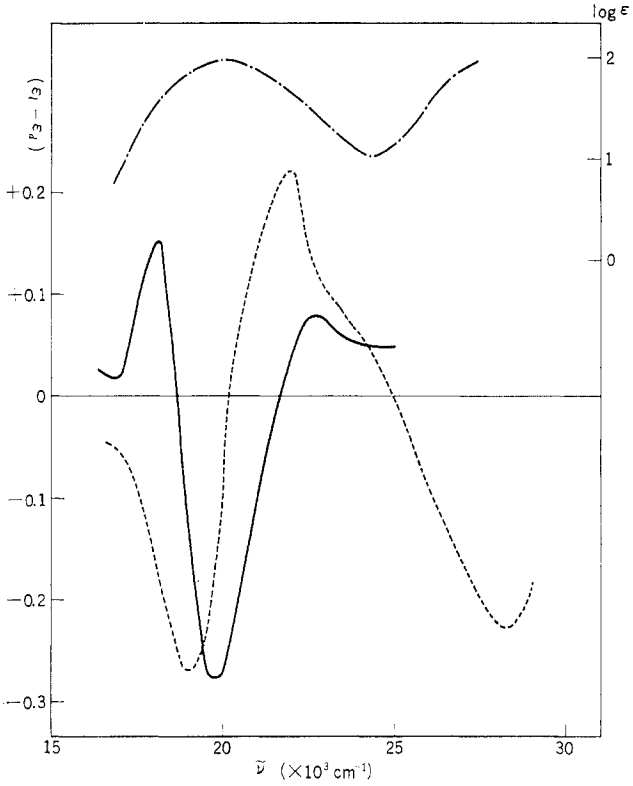

Figure 6.—Visible absorption curve for $Co(NH_3)_4$-D-pipec^{2+} (— · —) and circular dichroism curves for $Co(NH_3)_4$-N-Meleu^{2+} (———) and $Co(NH_3)_4$-D-pipec^{2+} (– – – –).

is, *R*. Since both complexes have the same absolute configuration at the secondary nitrogen atom, it is expected that $Co(NH_3)_4$-L-pipec^{2+} (pipecH = pipecolic acid) will show RD and CD curves similar to those for $(-)_{436}$-$Co(NH_3)_4$sar^{2+}. The RD and CD curves for $(+)_{436}$-$Co(NH_3)_4$-D-pipec^{2+} shown in Figures 5 and 6, respectively, are similar to those for $(+)_{436}$-*S*-$Co(NH_3)_4$-sar^{2+} (the enantiomorph of the $(-)_{436}$ isomer), though the CD peaks of the former complex are slightly shifted to the lower wave number side and an additional peak is observed at about 22,700 cm^{-1}. The additional CD peak is attributed to the influence of the asymmetric carbon of D-pipecolic acid. The resemblance between RD and CD curves of $(+)_{436}$-$Co(NH_3)_4$-D-pipec^{2+} and $(+)_{436}$-*S*-$Co(NH_3)_4$sar^{2-}, or their enantiomorphs, $(-)_{436}$-$Co(NH_3)_4$-L-pipec^{2+} and $(-)_{436}$-*R*-$Co(NH_3)_4$sar^{2+}, may be attributed to having the same absolute configuration at the secondary nitrogen atom. This suggests that L-pipecolic acid is coordinated in a manner shown in Figure 7.

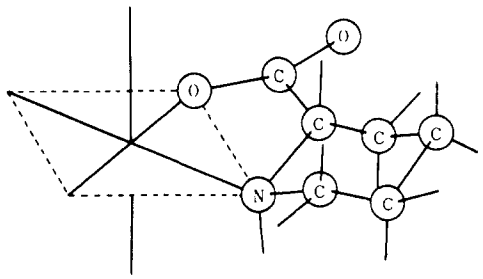

Figure 7.—The probable structure of L-pipecolinato ion in $Co(NH_3)_4$-L-pipec^{2+}.

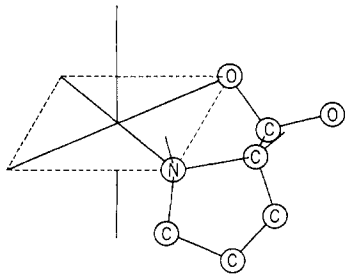

Figure 8.—The structure of L-prolinato ion in $Co(NH_3)_4$prol^{2+}.

However, the stereoselective coordination of pipecolic acid is considered to be rather intrinsic, because this ligand is restricted from adopting any form other than that shown in Figure 7, owing to its cyclic structure. It has been pointed out that L-proline complexes show a remarkably different CD or RD curve in comparison to the complexes of the other L-amino acids.[6,7] L-Proline is a cyclic amino acid including the five-membered pyrolidine ring instead of the six-membered piperidine ring. The proposed structure for the coordinated L-proline is shown in Figure 8, indicating that the coordinated secondary nitrogen of L-proline is asymmetric. It is interesting to note that the absolute configuration of the secondary nitrogen in coordinated L-proline (*S*) is apparently different from that in L-pipecolic acid (*R*). The CD curve for $Co(NH_3)_4$prol^{2+} (prolH = L-proline) reported by Shimura, *et al.*,[7] and that for $Co(NH_3)_4$-D-pipec^{2+}, which is considered to adopt the same absolute

configuration of R at the secondary nitrogen, exhibit three Cotton effects in the first absorption band region; their signs are (−), (+), and (−). However, the peak heights of the corresponding CD bands are markedly different from one another. A similar disagreement is recognized in the RD curves. These results may be attributed to the antipodal character of the asymmetric carbon of these ligands. Moreover, it is difficult to consider that the CD or RD curve for $Co(NH_3)_4prol^{2+}$ is a composite curve of $Co(NH_3)_4ala^{2+}$ and $(+)_{436}$-S-$Co(NH_3)_4sar^{2+}$. This means that the environments of the asymmetric carbon and the secondary nitrogen in the L-proline complex differ somewhat from those of the other complexes owing to the five-membered structure, since the CD or RD curve is considered to reflect clearly the slight difference of the circumstances of cobalt(III) ion. The additive nature of two (or more) vicinal effects in the same chelate ligand will be restricted in similar cases.

Although Buckingham, *et al.*,[10] have pointed out that the sarcosinate chelate is coordinated stereoselectively in $Co(en)_2sar^{2+}$, the analogous complexes with other N-substituted amino acids have not been reported. Bis(ethylenediamine) complexes with optically active N-substituted amino acids should be restricted in the configuration about the cobalt(III) ion, and the $\Delta(C_2)$ or $\Lambda(C_2)$ isomer will be formed stereospecifically according to the absolute configuration of the asymmetric secondary nitrogen atom, R or S, respectively. An attempt to prepare the L-prolinatobis(ethylenediamine)-cobalt(III) ion was reported to be unsuccessful.[14] However, the bis(ethylenediamine) complexes containing N-methyl-L-alanine and D-pipecolic acid are now isolated, and evidence supporting the stereoselective formation of the $\Delta(C_2)$ or the $\Lambda(C_2)$ isomer, respectively, has been obtained; this will be reported in subsequent papers.

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

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY,[1] UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA 46556

Mössbauer Spectra of Some Complexes of Tin(IV) Chloride and Tin(IV) Bromide with Organic Ligands

BY JOSE PHILIP, M. ANGELA MULLINS, AND COLUMBA CURRAN

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Mössbauer data are reported for 25 complexes of tin(IV) halides with organic ligands. The effectiveness of the donor atom in the six-coordinate complexes in reducing the electron density at the tin nucleus follows the order O > N > S > P. Quadrupole splittings have been observed for nine complexes having oxygen or phosphorus as the donor atom. The largest splitting, 1.0 mm/sec, was observed for $[(n\text{-}C_4H_9)_3P]_2SnCl_4$, for which dielectric data suggest a *trans* configuration.

Previous reports[2,3] of Mössbauer spectra of complexes of tin(IV) halides with organic ligands, using tin(IV) oxide as a source, have failed to reveal quadrupole splittings in these complexes and no correlations have been found between isomer shifts and the donor atoms of the ligands. In the present investigation a palladium–tin alloy source was used having a narrower line width than tin(IV) oxide, and complexes having a variety of donor ligands were studied.

Experimental Section

Preparation and Purification of Compounds.—Hexamethylphosphoramide $\{[(CH_3)_2N]_3PO\}$, pyrrolidine (C_4H_8N), tetrahydrothiophene (C_4H_8S), tetramethylammonium chloride $[(CH_3)_4NCl]$, tetraethylammonium bromide $[(C_2H_5)_4NBr]$, and 1,2-dimethoxyethane $[CH_3O(CH_2)_2OCH_3]$ were obtained from Eastman Organic Chemicals; the 1,2-dimethoxyethane was dried by shaking with potassium carbonate. Pyridine (C_5H_5N), stannic chloride, N,N,N′,N′-tetramethylethylenediamine $[(CH_3)_2N(CH_2)_2N(CH_3)_2]$, and 1,4-dioxane were J. T. Baker products; the tetramethylethylenediamine was purified by distilling over sodium and the dioxane was purified according to Fieser.[4] Tetramethylurea $\{[(CH_3)_2N]_2CO\}$ and α,α-dipyridyl ($C_{10}H_8N_2$) were obtained from Matheson Coleman and Bell. Tetramethylthiourea $\{[(CH_3)_2N]_2CS\}$ and triphenylphosphine $[(C_6H_5)_3P]$ were products of Chemical Intermediates and Research Corp. Tri-*n*-butylphosphine $[(C_4H_9)_3P]$ and thiophosphoryl chloride ($PSCl_3$) were from K & K Laboratories. Stannic bromide was obtained from City Chemical Corp. Piperidine ($C_5H_{10}N$) was obtained from Fisher Scientific Co. Triphenylphosphine oxide $[(C_6H_5)_3PO]$ was purchased from Aldrich Chemical Co. The 1,2-di(methylthio)ethane was synthesized in this laboratory by the method of Morgan and Ledbury.[5] Carbon tetrachloride was reagent grade and was dried over phosphorus pentoxide. All solvents were CP grade or better.

Tripiperidinophosphine sulfide $[(C_5H_{10}N)_3PS]$ and tripyrrolidinophosphine sulfide $[(C_4H_8N)_3PS]$ were prepared by the general

(1) The Radiation Laboratory is operated by the University of Notre Dame under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-419.

(2) V. I. Goldanski, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Krapov, *Dokl. Akad. Nauk SSSR*, **156**, 400 (1964).

(3) N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc., A*, 1679 (1967).

(4) L. F. Fieser, "Experiments in Organic Chemistry, 2nd ed, D. C. Heath and Co., New York, N. Y., 1941.

(5) G. T. Morgan and W. Ledbury, *J. Chem. Soc.*, **121**, 2882 (1922)