

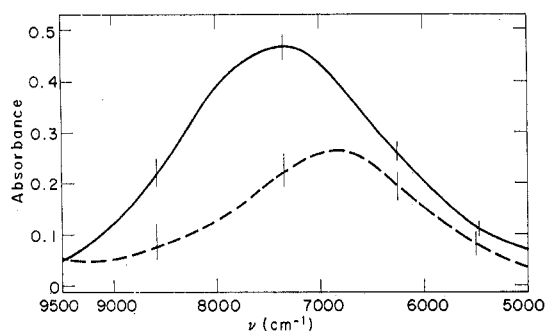


Figure 3.—Intervalence electron-transfer absorption bands of $(\text{tfd})_2\text{Co}-(\text{L-L})-\text{Co}(\text{tfd})_2^-$ in dichloromethane: —, $(\text{L-L}) = \text{DPPE}$; ---, $(\text{L-L}) = \text{DPPA}$. Spectra refer to $5 \times 10^{-4} M$ solutions initially equimolar in $z = 2-$ and 0 complexes in 2-cm cells and were obtained by difference. The vertical lines indicate the approximate uncertainty in absorbance.

difference spectrum consists of a well-defined band at $\sim 7350 \text{ cm}^{-1}$ which is within the energy range expected for intervalence electron-transfer absorptions.^{16, 34-36} At higher energies the difference spectrum contained weaker bands ($\lesssim 20\%$ deviation from additivity), which are attributed to concentration-dependent dis-

sociation and shifts in band maxima for the $z = 1-$ complex relative for the $z = 2-, 0$ species. The above spectral interpretations are provisional, since the spectral bands of the $z = 2-, 0$ species have not been assigned. Similar results were obtained for the DPPA system, but no analogous absorption band could be detected in the DPPB system. The two electron-transfer bands are shown in Figure 3. Additional spectral studies showed that these bands are not due to mononuclear adducts or $[\text{Co}(\text{tfd})_2]_2$. Following previously published arguments,^{34b, 36} the energies (E_{op}) of these bands may be used to estimate the intramolecular electron-transfer rate constants: $(\text{tfd})_2\text{Co}-\text{DPPA}-\text{Co}(\text{tfd})_2^-$, $E_{\text{op}} = 6850 \text{ cm}^{-1}$, $k = 2 \times 10^9 \text{ sec}^{-1}$; $(\text{tfd})_2\text{Co}-\text{DPPE}-\text{Co}(\text{tfd})_2^-$, $E_{\text{op}} = 7350 \text{ cm}^{-1}$, $k = 9 \times 10^8 \text{ sec}^{-1}$. These values are consistent with the expectation that interaction between the two metal centers would be larger with the shorter DPPA bridge and are similar in magnitude to other cases^{16, 36} where two metal centers in the same ion are separated by *ca.* 4–7 Å. However, any attempt to account quantitatively for differences in the preceding quantities must await preparation of a more extensive series of complexes exhibiting intervalence electron-transfer processes.

Acknowledgment.—This research was supported by the National Science Foundation under Grant GP-7576X.

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Mixed-Ligand Complexes of Cobalt(III). $\text{trans-Bis}(\text{amino acid})(\text{tetramine})\text{cobalt(III)}$ Complexes

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The syntheses and some properties of cobalt(III) complexes with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) and the amino acids glycine and alanine are reported. Comparison of the properties of these complexes with those of the corresponding acetate derivatives indicates that the amino acid residues are bonded to mutually *trans* sites through the carboxyl groups.

Introduction

Complexes of cobalt(III) with the flexible tetramine ligands 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and 4,7-diaza-1,10-decanediamine (3,2,3-tet) show a marked preference for the *trans* topology.¹⁻³ In contrast, complexes with triethylenetetramine (trien or 2,2,2-tet) most commonly adopt a *cis* geometry.^{4,5} Similarly, the sulfur-containing ligands 3,7-dithia-1,9-nonanedi-

amine (ete) and 4,7-dithia-1,10-decanediamine (tet) readily adopt the *trans* geometry⁶ which is not found for complexes with 3,6-dithia-1,8-octanediamine (eee).⁷ As a part of our continuing study of the steric course of some reactions of mixed-ligand cobalt(III) complexes, we have utilized the demonstrated preference of long-chain flexible tetradentate ligands for the *trans* topology in the synthesis of some novel *trans-bis*(amino acid)-(tetramine)cobalt(III) complexes.

Experimental Section

Physical Measurements. Electronic and Circular Dichroism

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Spectra and Optical Rotatory Dispersion Curves.—Electronic absorption spectra were measured on a Beckman Model DBG spectrophotometer equipped with a Beckman Model 1005 10-in. potentiometric recorder using matched 1-cm silica cells. ORD curves were recorded with a Cary Model 60 spectropolarimeter. CD curves were recorded with a Cary Model 6002 circular dichroism accessory. For both the CD and ORD spectra, the solutions were approximately 10^{-3} M, and the cell path length was 1, 2, 5, or 10 cm as dictated by the optical density and the rotation. A solvent blank was used to determine the base lines for these spectra; the solvent was water unless otherwise noted. Optical isomers are denoted by (+) or (−), the sign of the rotation at the Na D line; if another wavelength was used, the wavelength appears as a subscript.

Elemental Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and by Micro-Tech Laboratories, Skokie, Ill.

Syntheses. **Preparation of 3,7-Diaza-1,9-nonanediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, 2,3,2-tet.**—The procedure reported by Hamilton and Alexander¹ was modified as follows. To a solution of 500 g of ethylenediamine in 500 ml of ethanol was added 240 g of 1,3-dibromopropane in 10-ml portions every 20 min. This slow addition was used because of the highly exothermic nature of the reaction. The temperature should remain about 50° throughout the addition after which 400 g of potassium hydroxide was added and the solution was stirred for 1 hr. After filtration, ethylenediamine and ethanol were removed by distillation. The product was then collected by vacuum distillation at 140–145 (8 mm).

Preparation of 4,7-Diaza-1,10-decanediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 3,2,3-tet.—The procedure used here was similar to that given above for 3,7-diaza-1,9-nonanediamine using 240 g of 1,2-dibromoethane and 500 g of 1,3-diaminopropane in place of 1,3-dibromopropane and ethylenediamine. The product was collected at 150–160° (5 mm).

Preparation of *trans*-Dichloro(3,7-diaza-1,9-nonanediamine)cobalt(III) Chloride, *trans*-[Co(2,3,2-tet)Cl₂]Cl.—This was prepared according to the directions of Hamilton and Alexander.¹

Preparation of *trans*-Dichloro(4,7-diaza-1,10-decanediamine)cobalt(III) Chloride, *trans*-[Co(3,2,3-tet)Cl₂]Cl.—4,7-Diaza-1,10-decanediamine (17 g, 0.1 mol) was added to a solution of CoCl₂·6H₂O (24 g, 0.1 mol) in 200 ml of water. A stream of air previously passed through a KOH solution to remove CO₂ was bubbled through the solution for 16 hr. To the red solution was added 25 ml of concentrated HCl and it was evaporated to near dryness on a steam bath. The solution was cooled and the crude green product was removed by filtration, washed with ethanol, recrystallized from hot water, and dried at 110° for 24 hr. *Anal.* Calcd for CoC₈H₂₂N₄Cl₃: C, 28.29; H, 6.48; N, 16.50. Found: C, 28.12; H, 6.68; N, 16.45.

Preparation of *trans*-Bis(acetato)(4,7-diaza-1,10-decanediamine)cobalt(III) Perchlorate, *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄).—A solution containing 2 g of *trans*-[Co(2,3,2-tet)Cl₂]Cl and 4 g of sodium acetate was warmed on a steam bath for 2 hr after which excess LiClO₄ was added and the solution cooled. The large red-violet needles were removed by filtration, washed with acetone, and air dried. *Anal.* Calcd for CoC₁₂H₂₈N₄ClO₈: C, 32.00; H, 6.22; N, 12.44. Found: C, 31.71; H, 6.08; N, 12.22.

Preparation of *trans*-Bis(acetato)(3,7-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄).—This was prepared in a manner analogous to the preparation of *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄) using 2 g of *trans*-[Co(2,3,2-tet)Cl₂]Cl in place of *trans*-[Co(3,2,3-tet)Cl₂]Cl. *Anal.* Calcd for CoC₁₁H₂₆N₄ClO₈: N, 12.84. Found: N, 12.45.

Preparation of *trans*-Bis(amino acid)(4,7-diaza-1,10-decanediamine)cobalt(III) Perchlorate *trans*-[Co(3,2,3-tet)(aaH)₂](ClO₄).—The method was the same for the diglycine and dialanine complexes. One gram of *trans*-[Co(3,2,3-tet)Cl₂]Cl and 1.5 g of the amino acid were dissolved in 15 ml of water. The

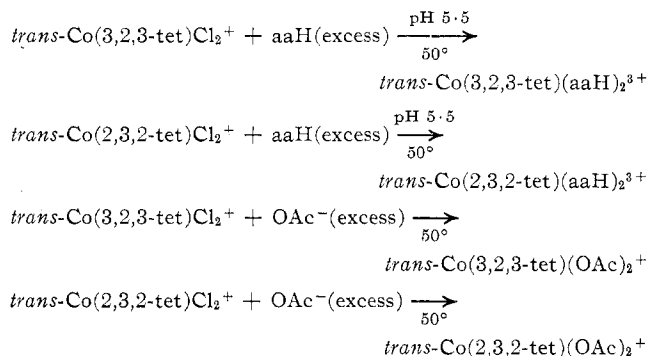
solution was adjusted to pH 5.5 with 5 M NaOH and warmed at 40° for 16 hr. On adding LiClO₄ and cooling, red-violet crystals formed and were removed by filtration. *Anal.* Calcd for the glycine complex, *trans*-[Co(3,2,3-tet)(glyH)₂](ClO₄)₃, CoC₁₂H₃₂N₆Cl₃O₁₆: C, 21.11; H, 4.69; N, 12.32. Found: C, 21.37; H, 5.14; N, 11.95. Calcd for the alanine complex *trans*-[Co(3,2,3-tet)((S)-ala)](ClO₄)₃, CoC₁₄H₃₆N₆Cl₃O₁₆: C, 23.66; H, 5.07; N, 11.83. Found: C, 24.26; H, 5.22; N, 11.67.

Preparation of *trans*-Bis(amino acid)(3,7-diaza-1,9-nonanediamine)cobalt(III) Perchlorate, *trans*-[Co(2,3,2-tet)(aaH)₂](ClO₄)₃.—The method was the same as for the preparation of *trans*-[Co(3,2,3-tet)(aaH)₂](ClO₄)₃ using *trans*-[Co(2,3,2-tet)Cl₂]Cl in place of *trans*-[Co(3,2,3-tet)Cl₂]Cl. *Anal.* Calcd for the glycine complex, *trans*-[Co(2,3,2-tet)(glyH)₂](ClO₄)₃, CoC₁₁H₃₀N₆Cl₃O₁₆: C, 19.76; H, 4.49; N, 12.57. Found: C, 19.98; H, 5.11; N, 12.80. Calcd for the alanine complex, *trans*-[Co(2,3,2-tet)((S)-alaH)₂](ClO₄)₃, CoC₁₃H₃₄N₆Cl₃O₁₆: C, 22.41; H, 4.88; N, 12.07. Found: C, 22.60; H, 5.29; N, 11.88.

(−)-*trans*-(RR)-Co(3,2,3-tet)Cl₂⁺ → *trans*-(RR)-Co(3,2,3-tet)(glyH)₂³⁺. —(−)-*trans*-(RR)-[Co(3,2,3-tet)Cl₂]ClO₄⁸ (0.02500 g) and 1 g of glycine were dissolved in 10 ml of water and warmed at 40° for 2 hr. At this time the solution was spectrophotometrically identical with a solution containing *trans*-[Co(3,2,3-tet)(glyH)₂](ClO₄)₃ and excess glycine. The circular dichroism curve of the solution was then measured. Δε₅₆₅ = 0.16.

Results and Discussion

Synthesis and Characterization.—During the course of this study, several 2,3,2-tet and 3,2,3-tet complexes containing monodentate amino acids were prepared along with the bis-acetato complexes of (3,2,3-tet)-Co^{II} and (2,3,2-tet)Co^{II}. These reactions are summarized below (where aaH is amino acid and OAc is the acetate anion).



The analytical values of the complexes prepared clearly indicate that the amino acids coordinate with the cobalt(III) ion as unidentate ligands. Since these complexes are obtained from an acidic solution, the amino acid retains an acidic proton and is coordinated as a neutral ligand, in agreement with the analytical results.

The amino acid may be bound to the cobalt(III) ion as a monodentate ligand with an oxygen atom of the carboxyl group or with the nitrogen of the amino group. Previous syntheses of monodentate bis(amino acid)-tetraamminecobalt(III) complexes under conditions similar to the ones used in this study; that is, reaction of the diaquotetraamminecobalt(III) ion, Co(NH₃)₄(H₂O)₂³⁺, with excess amino acid, resulted in the formation of the oxygen-bonded amino acid complex.⁹

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Similarly, reaction of excess glycine with the hydroxy-aquotriethylenetetraminecobalt(III) ion at pH 5 produces the monodentate, oxygen-bonded glycine complex.¹⁰ We therefore expect that the monodentate amino acid complexes of 3,2,3-tet and 2,3,2-tet we have prepared contain the oxygen-bonded amino acid ligand. Of course, the acetato ligand must coordinate *via* a carboxyl oxygen.

In accord with the postulate of oxygen-bonded amino acid residues, the infrared spectra show a strong absorption at 1655 cm^{-1} assignable to the OCO symmetrical stretch of the coordinated carboxyl group. The corresponding vibration for the *trans*-bis-acetato complexes occurs at about 1645 cm^{-1} .

Our attempts to prepare N-bonded monodentate amino acid complexes, either directly from the amino acid at pH 8 or indirectly from the amino acid ester,¹⁰ produced only the chelated amino acid complex.

Electronic Spectra—Electronic spectra of *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄)₃, *trans*-[Co(3,2,3-tet)(glyH)₂](ClO₄)₃, *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄)₃, and *trans*-[Co(2,3,2-tet)(glyH)₂](ClO₄)₃ are shown in Figure 1.

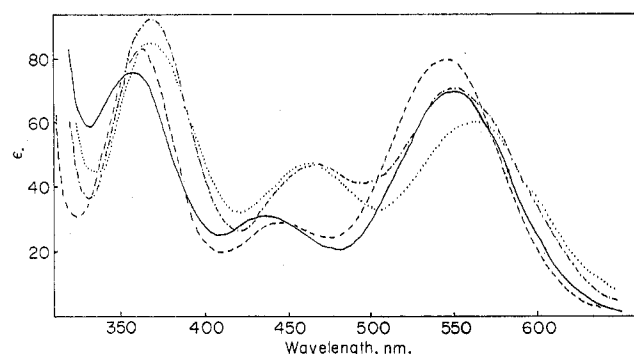


Figure 1.—Electronic absorption spectra: *trans*-[Co(2,3,2-tet)(glyH)₂](ClO₄)₃, —; *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄)₃, ----; *trans*-[Co(3,2,3-tet)(glyH)₂](ClO₄)₃,; *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄)₃, -.-.-.-.-.

TABLE I
ELECTRONIC ABSORPTION SPECTRA FOR SOME
CoN₄O₂⁺ COMPLEXES

	λ_{max} , nm (e)		
	Band I	Band Ia	Band II
<i>trans</i> -[Co(NH ₃) ₄ (OAc) ₂](ClO ₄)	552 (58)		367 (58)
<i>cis</i> -[Co(NH ₃) ₄ (OAc) ₂](ClO ₄)	523 (102)		366 (59)
<i>cis</i> -[Co(NH ₃) ₄ (glyH) ₂](ClO ₄) ₃	516 (96)		362 (58)
<i>trans</i> -[Co(en) ₂ (OAc) ₂](ClO ₄)	540 (51)		360 (68)
<i>cis</i> -[Co(en) ₂ (OAc) ₂](ClO ₄)	505 (115)		360 (98)
<i>cis</i> - α -[Co(trien)(glyH) ₂](ClO ₄) ₃	512 (221)		
<i>cis</i> - β -[Co(trien)(glyH) ₂](ClO ₄) ₃	493 (173)		360 (114)
<i>trans</i> -[Co(2,3,2-tet)(glyH) ₂](ClO ₄) ₃			
	550 (69)	437 (31)	358 (76)
<i>trans</i> -[Co(2,3,2-tet)(OAc) ₂](ClO ₄)	543 (79)	443 (29)	361 (82)
<i>trans</i> -[Co(3,2,3-tet)(glyH) ₂](ClO ₄) ₃			
	560 (60)	460 (47)	367 (63)
<i>trans</i> -[Co(3,2,3-tet)(OAc) ₂](ClO ₄)	550 (70)	465 (46)	368 (93)

Spectral data for these ions and some related tetramine complexes are tabulated in Table I. Note, from Figure 1, that in the visible region the spectra of the bis-acetato complexes of 3,2,3-tet and 2,3,2-tet are very similar to

those of the bis-(amino acid) complexes of 3,2,3-tet and 2,3,2-tet, confirming the assignment of oxygen-bonded amino acids. If the amino acid were nitrogen bonded, we would expect an electronic spectrum more typical of a CoN₆ complex, with the bands at higher energy consistent with the relative positions of nitrogen and oxygen donors in the spectrochemical series, or, in the unlikely case that one amino acid was oxygen bonded and one was nitrogen bonded, the spectra should be typical of a CoN₅O complex but inconsistent with the observed spectra.

Comparison of the spectra of *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄) and *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄) with those of the isomers of Co(en)₂(OAc)₂ and Co(NH₃)₄(OAc)₂ confirms the *trans* configuration. The first band of the bis(acetato)tetraamminecobalt(III) complex shows a distinct splitting in the *trans* isomer but no splitting in the *cis* isomer¹¹ as do the corresponding Co(en)₂(OAc)₂¹² isomers. The *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄) and *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄) complexes show splitting of the first band. The spectra of the *cis* isomers should be more intense than those of the *trans* isomers.

The electronic spectra are in accord with the behavior expected for complex ions of the type CoA₄B₂ as predicted from crystal field theory.¹³ In the *D*_{4h} complex Co(NH₃)₄(OAc)₂⁺ and pseudo-*D*_{4h} Co(en)₂(OAc)₂⁺, the ¹T_{1g}(O_h) excited state is split into ¹E_g and ¹A_{2g} components. Due to the nature of the ligands, the in-plane field (the plane containing the four nitrogen atoms, the *xy* plane) is greater than the axial (*z* axis) field, and the more intense low-energy band may be attributed to the ¹A_{1g} → ¹E_g transition while the band next higher in energy is assigned to the ¹A_{1g} → ¹A_{2g} transition. Although *trans*-Co(3,2,3-tet)(OAc)₂⁺ and *trans*-Co(2,3,2-tet)(OAc)₂⁺ are not of *D*_{4h} symmetry, their spectra closely approximate this model. Thus, for *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄) and *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄) the long-wavelength band is assigned to the transition approximating the ¹A_{1g} → ¹E_g and the next shorter wavelength band assigned to that approximating the ¹A_{1g} → ¹A₂ transition. The monodentate amino acid complexes of 3,2,3-tet and 2,3,2-tet, structurally similar to the acetato complexes, are assigned the *trans* configuration under the same criteria.

Under the alkaline conditions used for the preparation of *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄) and *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄), the secondary amine protons exchange rapidly, and we expect that the thermodynamically more stable configuration of the donor atoms will be obtained. Thus the *trans*-[Co(2,3,2-tet)(OAc)₂](ClO₄) complex should have the *RS* (meso) configuration shown to be more stable for *trans*-Co(2,3,2-tet)Cl₂⁺.¹⁴ *trans*-[Co(3,2,3-tet)(OAc)₂](ClO₄) is assigned the more

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stable *RR,SS* configuration of *trans*-Co(3,2,3-tet)Cl₂⁺. With these assumptions the *trans*-Co(3,2,3-tet)(OAc)₂⁺ ion is of C₂ symmetry and *trans*-Co(2,3,2-tet)(OAc)₂⁺ is of C_s symmetry. The amino acid complexes are prepared in acid solution, and the configuration of the secondary nitrogen atoms should be the same as that of the starting *trans*-dichlorotetramine complex. In both cases three components resulting from the splitting of the ¹T_{1g} state make it impossible to distinguish C₂ from C_s symmetry by the number of spectral components.

Optical Activity.—Whereas the visible spectra of the *trans*-Co(3,2,3-tet)(aaH)₂³⁺ and *trans*-Co(2,3,2-tet)(aaH)₂³⁺ ions are in accord with a D₄ crystal field model, the circular dichroism spectrum of *trans*-(*RR*)-Co(3,2,3-tet)(glyH)₂³⁺ (Figure 2) distinctly shows the lower sym-

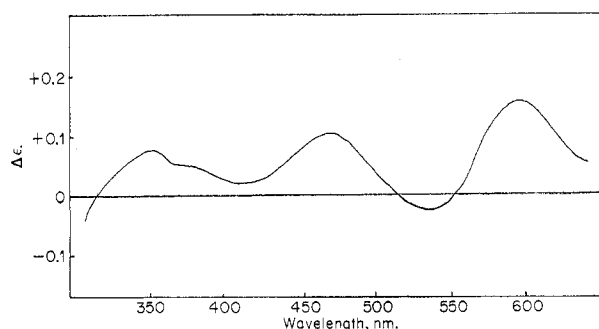


Figure 2.—Circular dichroism curve for (–)-*trans*-(*RR*)-Co(3,2,3-tet)(glyH)₂³⁺.

metry of the molecule. *trans*-Co(3,2,3-tet)(glyH)₂³⁺ was not isolated but was prepared by warming (–)-*trans*-(*RR*)-[Co(3,2,3-tet)Cl₂]ClO₄ in a solution saturated with glycine and was detected in solution by comparing the electronic spectrum with that of *trans*-[Co(3,2,3-tet)(glyH₂)](ClO₄)₃ in a saturated glycine solution. There are three transitions apparent in the circular dichroism spectrum, as the degenerate ¹E_g(D₄) state has split into the two components expected in C₂ symmetry. The great similarity in shape between the CD curves of *trans*-(*RR*)-Co(3,2,3-tet)(glyH)₂³⁺ and *trans*-(*RR*)-[Co(3,2,3-tet)Cl₂]ClO₄¹⁵ is obvious on comparison, both showing the same order (+, –, +) and same magnitude for the ¹T_{1g} components. Those of the *trans*-bis-glycine complex occur at higher energy, reflecting the relative positions of the glycine and chloro ligands in the spectrochemical series.

In warm basic solutions, one of the amino acid residues is displaced by hydroxide. In a subsequent step, the remaining amino acid molecule undergoes intramolecular chelate ring closure with a concomitant topological shift. A detailed study of the steric course of these reactions is now in progress.

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A Nuclear Magnetic Resonance Study of Ligand-Exchange Kinetics of Cobalt(II)- and Nickel(II)-Dimethyl Sulfoxide Complexes in Mixed Solvents

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The ligand-exchange kinetics of ML₆ (M = Co or Ni, L = dimethyl sulfoxide (DMSO)) in DMSO and the mixed solvents DMSO–nitromethane and DMSO–methylene chloride are independent of the composition of the solvent. The following kinetic parameters have been obtained: NiL₆²⁺, *k*(25°) = 3.2 × 10³ sec^{−1}, Δ*H*^{*} = 13.0 kcal/mol, Δ*S*^{*} = 1.4 eu; CoL₆²⁺, *k*(25°) = 3.1 × 10⁵ sec^{−1}, Δ*H*^{*} = 12.2 kcal/mol, Δ*S*^{*} = 9.8 eu. The independence of the exchange parameters on the composition of the solution is consistent with a dissociative mechanism.

Many nmr studies have been reported on the ligand-exchange kinetics of octahedral paramagnetic transition metal complexes in a neat solution of the ligand.² Under these conditions, pseudo-first-order kinetics, the role of the ligand as a stoichiometric component of the reaction cannot be definitively studied. Mixed solvents can be utilized to elucidate the dependence of the ligand-exchange rate on the ligand concentration. Experiments of this type should aid in elucidating a reac-

tion mechanism. We report data on the ligand-exchange kinetics of M(DMSO)₆²⁺, M = Co(II) or Ni(II), in dimethyl sulfoxide (DMSO) and in admixtures with nitromethane and methylene chloride.³ The latter two solvents are inert in the sense that they are noncoordinating.

Experimental Section

The metal complexes of DMSO were prepared as described previously except dehydration with triethyl orthoformate of M-

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