In order to eliminate confusion,[34] it should be pointed out that a recent complete matrix least-squares anisotropic temperature factor refinement of trimethylindum[35] gave In–C distances of In–C_1, –C_2, –C_3 of 2.24 ± 0.06, 2.25 ± 0.06, and 2.16 ± 0.04 A and C–In–C angles of C_3–In–C_1 120.5 ± 1.8°, C_2–In–C_3 117.3 ± 1.3°, and C_2–In–C_1 122.2 ± 1.8°. These distances and angles are not statistically different from the earlier results,[7] but the estimates of error are probably more realistic. It is to be noted that $In(CH_3)_3$ is still planar well within statistical error, and the "pseudotetramer" should be viewed as very weakly bonded together, if at all. Where weak chemical bonds begin and end is by no means a clear-cut, unambiguous decision.

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[35] G. G. Messmer and E. L. Amma, unpublished research.

Steric Effects in Fast Metal Complex Substitution Reactions. II[1]

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Abstract: The rate constants for the formation and dissociation of nickel(II) and cobalt(II) complexes with α- and β-aminobutyric acids have been determined by the temperature-jump method. Although rate constants for formation of higher order as well as monosubstituted complexes were measured, the most significant results with respect to a comparison between the two different metal ions concern the rate constants (k_1) for the first substitution. It was determined that substitution for both nickel(II) and cobalt(II) is faster with α-aminobutyric acid than with the β acid. That is, at 20° an ionic strength = 0.1 M for nickel(II) with α-aminobutyrate, $k_1 = 1.0 \times 10^4$ M^{-1} sec^{-1}; with β-aminobutyrate, $k_1 = 4.0 \times 10^3$ M^{-1} sec^{-1}. Under the same conditions, for cobalt(II) with α-aminobutyrate, $k_1 = 2.5 \times 10^5$ M^{-1} sec^{-1}; with β-aminobutyrate, $k_1 = 2.0 \times 10^4$ M^{-1} sec^{-1}. The relative error for these rate constants is ±20%. The rate constants determined for α-aminobutyric acid are consistent with a mechanism in which release of a water molecule from the metal ion's inner coordination sphere is rate determining. In reaching this conclusion, it is shown that an empirical factor of $^1/_2$, to account for the partial absence of spherical symmetry in these chelating agents, must be used when comparing these (and the β) values with rate constants previously determined for other ligands. The slower reactions with β-aminobutyric acid are explained by the kinetic chelate effect, in which chelate ring closure is the rate-determining step. The steric effect is appreciably greater for cobalt(II) than for nickel(II) because of the inherently greater lability of the former ion.

Studies of fast metal complex substitution reactions can be explained by a previously proposed mechanism for the formation of complexes between divalent ions and simple anionic ligands.[3-6] The initial process is the diffusion-controlled, ion-pair formation between the aquated metal ion and ligand. For most monodentate and certain polydentate ligands, the rate-determining step is the loss of a water molecule with concomitant substitution of the reactant ligand into the inner coordination shell. Since the rate-determining step is controlled by the rate of release of a water molecule from the inner coordination sphere, it is therefore a characteristic of the metal ion.

For metal complexes with multidentate ligands, the stability of the metal chelate is, in part, governed by the chelate structure.[7] The thermodynamic data for divalent metal ions with amino acids show that a five-membered ring is more stable, unless a linear complex is formed. For example, the stability constants for α- and β-aminobutyric acids differ by over a factor of 10 (see Table I).

Recently, evidence has been reported that there is also a kinetic chelate effect.[6] Studies of divalent metal chelates with α- and β-alanine show that there is a decrease in rate when changing the ligand from α-alanine to β-alanine. This decrease in rate is explained by the difficulty in forming a six-membered, as opposed to a five-membered, ring with an aminocarboxylic acid ligand. The mechanism is the same as that originally proposed, but the rate-determining step is believed to be closing of the chelate ring rather than the release of a water molecule from the inner coordination sphere of the metal ion.

The kinetics for the formation of nickel(II) and cobalt(II) chelates with α- and β-aminobutyric acid (α-

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[3] (a) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960); (b) M. Eigen and K. Tamm, *ibid.*, **66**, 93 (1962); (c) *ibid.*, **66**, 107 (1962).

[4] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

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Table I. Stoichiometric Equilibrium Constants[a] at 20° and Ionic Strength 0.1 *M*

Ligand	Metal ion	K_{HL}, *M*	K_{H_2L}, *M*	K_1, M^{-1}	K_2, M^{-1}	K_3, M^{-1}
α-Aminobutyric acid	Ni^{2+}	6.57×10^{-11}	2.25×10^{-3}	3.16×10^{5}	3.02×10^{4}	1.55×10^{3}
	Co^{2+}	6.57×10^{-11}	2.25×10^{-3}	2.27×10^{4}	2.79×10^{3}	2.63×10^{2}
β-Aminobutyric acid	Ni^{2+}	2.39×10^{-11}	3.01×10^{-4}	5.72×10^{4}	4.86×10^{3}	5.36×10^{2}
	Co^{2+}	2.39×10^{-11}	3.01×10^{-4}	7.63×10^{3}	6.8×10^{2}	2.6×10^{2}
Indicator		K_{In}, *M*				
Phenolphthalein		2.51×10^{-10} [b]				
Phenol red		1.26×10^{-8} [c]				

[a] $K_{H_2L} = [H][HL]/[H_2L]$; $K_{HL} = [H][L]/[HL]$; $K_n = [ML_n]/[ML_{n-1}][L]$, $n = 1, 2, 3$; $K_{In} = [H]/[In]/[HIn]$. [b] A. Thiel and G. Coch., *Z. Anorg. Allgem. Chem.*, **217**, 353 (1934). [c] I. M. Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930).

Table II.[a] Results for Nickel(II) with α- and β-Aminobutyric Acids

$[Ni]_0$	$[Abu]_0$	$[HIn]_0$	pH	$\tau_{exptl} \times 10^2$	$\tau_{calcd} \times 10^2$
		A. Nickel (II) with α-Aminobutyric Acid			
1.00×10^{-3}	4.04×10^{-3}	1.00×10^{-5} [b]	8.5	$\tau_1 = 11$	$\tau_1 = 15$
				$\tau_{2}, = 2.5$	$\tau_2 = 2.3$
1.01×10^{-3}	8.08×10^{-4}	1.00×10^{-5} [b]	8.5	18	12
1.01×10^{-3}	2.02×10^{-3}	1.00×10^{-5} [b]	8.5	10	10
2.00×10^{-3}	4.04×10^{-3}	1.00×10^{-5} [b]	8.5	8.6	6.1
2.00×10^{-3}	6.07×10^{-3}	1.00×10^{-5} [b]	8.5	$\tau_1 = 8.9$	$\tau_1 = 8.6$
				$\tau_2 = 1.7$	$\tau_2 = 1.7$
2.00×10^{-3}	8.08×10^{-3}	1.00×10^{-5} [b]	8.6	$\tau_1 = 12$	$\tau_1 = 12$
				$\tau_2 = 1.3$	$\tau_2 = 1.6$
1.00×10^{-3}	2.50×10^{-3}	8.00×10^{-5} [c]	9.0	19	16
		B. Nickel(II) with β-Aminobutyric Acid			
2.00×10^{-4}	4.00×10^{-3}	4.00×10^{-5} [a]	9.2	14	16
2.00×10^{-4}	1.30×10^{-2}	1.00×10^{-5} [b]	8.4	31	26
2.00×10^{-3}	4.00×10^{-3}	4.00×10^{-5} [c]	9.0	8	12
2.00×10^{-3}	2.00×10^{-3}	9.80×10^{-6} [b]	8.5	10	16
1.00×10^{-3}	2.00×10^{-3}	9.80×10^{-6} [b]	8.5	17	16

[a] The subscript zero refers to total stoichiometric concentration. All concentrations are molar and at all times are in seconds. [b] HIn = phenol red. [c] HIn = phenolphthalein.

Abu and β-Abu, respectively) have been examined to investigate further the possibility of a kinetic chelate effect. The stability constants for all the aminobutyric acid–metal complex systems have not been previously reported. The stability constants that have been used were measured in this laboratory by a potentiometric method. The details for the determination of these constants will be published separately.[8] The results of this thermodynamic investigation, as well as other pertinent equilibrium constants, are given in Table I.

Experimental Section

Fisher reagent grade KNO_3, $Ni(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were used without further purification, as were all other reagents. The α-aminobutyric acid and β-aminobutyric acid were Nutritional Biochemical Co. products. Phenolphthalein (Baker reagent grade) and phenol red (Aldrich reagent grade) were used as indicators.

Stock solutions of the metal nitrate, acid ligand, and indicator were prepared. The solutions to be studied were made up by mixing the desired amounts of stock solutions into 100-ml volumetric flasks and diluting to the mark. The pH was adjusted by dropwise addition of solutions of NaOH and/or HNO_3. The final pH value was measured by a pH meter (Radiometer, Copenhagen), within 0.01 pH unit.

The ionic strength of all solutions was 0.1 *M*. The temperature of this study was 20 ± 1° for all experiments. The details of the temperature-jump instrumentation have been described elsewhere.[9] Blank experiments with solutions containing only the metal and indicator, or the acid ligand and the indicator (both solutions at ionic strength 0.1 *M*), did not show any relaxation effect in the time range of the instrument.

Results

The relaxation times for the various solutions were computed and averaged from at least three (generally, five) photographs of the oscilloscopic traces. The averages of the relaxation times are reported in Tables II and III together with the pH and total concentrations of metal and ligand. The relaxation times thus evaluated have errors of ±20% with respect to the reported averages. It should also be noted that the pH range of this study is from pH 8.0 to 9.2. The calculated relaxation times in Tables II and III were obtained (*vide infra*) by use of the best set of rate constants without the introduction of any pH-dependent terms.

A pH dependence of the rate constant would result from side reactions involving the neutral ligand, HL, or any hypothetical species MOH^+, where M = Ni^{2+} or Co^{2+}. The lack of a dependence of the rate constants on pH makes these steps insignificant under the conditions of this investigation. A more extensive variation of pH was precluded at the upper end by the precipitation of the metal (as metal hydroxide, presumably) and, at the lower end, by diminution of the amplitude of the relaxation effect. Indeed, by lowering the pH, the free L^- concentration decreases with respect

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(8) K. Kustin and R. Davidow, submitted for publication. *Cf.* L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964, Table 249, in which the first- and second-step stability constants for cobalt(II) and α-aminobutyric acid are given as $K_1 = 1.9 \times 10^4$, $K_2 = 2.1 \times 10^3$ M^{-1} at ionic strength 0.1 *M* and 30°.

(9) P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

Table III.[a] Results for Cobalt(II) with α- and β-Aminobutyric Acids

$[\mathrm{Co}]_0$	$[\mathrm{Abu}]_0$	$[\mathrm{HIn}]_0$	pH	$\tau_{\mathrm{exptl}} \times 10^3$	$\tau_{\mathrm{calcd}} \times 10^3$
A. Cobalt(II) with α-Aminobutyric Acid					
1.00×10^{-3}	2.00×10^{-3}	1.00×10^{-5}[b]	8.5	0.74	0.66
1.00×10^{-3}	2.50×10^{-3}	1.00×10^{-5}[b]	8.5	0.64	0.61
1.00×10^{-3}	2.50×10^{-3}	4.00×10^{-5}[c]	9.0	0.71	0.79
1.00×10^{-3}	6.00×10^{-3}	4.00×10^{-5}[c]	9.0	0.60	0.69
1.00×10^{-3}	8.00×10^{-3}	4.00×10^{-5}[c]	9.1	0.56	0.64
B. Cobalt(II) with β-Aminobutyric Acid					
2.00×10^{-3}	4.00×10^{-3}	1.00×10^{-5}[b]	8.5	4.5	6.7
1.00×10^{-3}	5.00×10^{-3}	9.8×10^{-6}[b]	8.6	10	7.9
1.00×10^{-3}	10.0×10^{-3}	9.8×10^{-6}[b]	8.6	7.7	7.3
1.00×10^{-3}	20.0×10^{-3}	1.00×10^{-5}[b]	8.6	8.0	6.6
1.00×10^{-3}	15.0×10^{-3}	1.00×10^{-5}[b]	8.6	7.2	6.7
1.00×10^{-3}	10.0×10^{-3}	4.00×10^{-5}[c]	8.9	6.4	6.6
1.00×10^{-3}	10.0×10^{-3}	1.00×10^{-5}[b]	8.0	7.3	8.7
2.00×10^{-3}	1.00×10^{-3}	2.00×10^{-5}[b]	8.5	7.0	9.1

[a] The subscript zero refers to total stoichiometric concentration. All concentrations are molar and all times are in seconds. [b] HIn = phenol red. [c] HIn = phenolphthalein.

Table IV. Rate Constants of Metal Complexation at 20° and $\mu = 0.1\ M$

Metal	n	α-Abu	β-Abu
		k_n, M^{-1} sec^{-1}	
Co^{2+}	1	2.5×10^5	2.0×10^4
	2	1.9×10^6	7.0×10^4
	3	...	...
Ni^{2+}	1	1.0×10^4	4.0×10^3
	2	1.5×10^4	8.0×10^3
	3	3.0×10^4	3.0×10^3
		k_{-n}, sec^{-1}	
Co^{2+}	1	11.0	2.6
	2	6.8×10^2	1.0×10^2
	3	...	...
Ni^{2+}	1	3.2×10^{-2}	7.0×10^{-2}
	2	0.5×10^{-1}	1.6
	3	19	5.6

to the relatively inert HL, thus depriving the solution of reacting ligand.

The equilibrium concentrations for the species M, ML, ML_2, ML_3, L, HL, and H_2L for the various solutions were calculated using the constants in Table I, with the help of a computer program run on an IBM 1620.

The relaxation processes observed were interpreted in terms of reactions of the type

$$ML_{n-1} + L \underset{k_{-n}}{\overset{k_n}{\rightleftharpoons}} ML_n \qquad K_n = k_n/k_{-n} \tag{1}$$

where $n = 1$, 2, or 3. The symbol L refers to the anionic form of the ligand, which is responsible for complexation of the metal ion. (Charges have been neglected in this and all other equations.) The general treatment given by Hammes and Steinfeld[4] for a system of two coupled reactions has been used in calculating the relaxation times. The relation

$$\tau^{-2} - \tau^{-1}(a_{11} + a_{22}) + (a_{11}a_{22} - a_{12}a_{21}) = 0 \tag{2}$$

derived from the solution of the secular determinant

$$\begin{vmatrix} a_{11} - 1/\tau & a_{12} \\ a_{21} & a_{22} - 1/\tau \end{vmatrix} = 0 \tag{3}$$

where $1/\tau$ is the eigenvalue, was used to find the rate constants when two reactions of type 1 were present. In (3), the a_{ij}'s are related to (1) the concentrations of the appropriate reactants, (2) the rate constants, and (3) the equilibrium constants for the coupled fast (relative to the metal complexation) reactions

$$H + L \rightleftharpoons HL$$

$$H + In \rightleftharpoons HIn$$

where the symbol In represents the indicator anion form.[4]

Calculation of τ by trial-and-error methods employing appropriately varying values of the k_n for the two processes where $n = 1$ and 2 were performed. In some cases the concentration of ML_3 was sufficiently high to enable the determination of all three rate constants, *via* solutions of (2) in which $n = 2$ and 3. The rate constants used to calculate the relaxation times reported in Tables II and III are given in Table IV.

Discussion

General Mechanism. The mechanism for metal chelate substitution reactions may be written as shown in eq a–c, where W_1 and W_2 represent the two water

$$M_{aq} + A\text{-}B_{aq} \underset{\text{rapid}}{\overset{\text{very}}{\rightleftharpoons}} W_2MW_1,A\text{-}B \qquad K_a = \frac{[W_2MW_1,A\text{-}B]}{[M][A\text{-}B]} \tag{a}$$

$$W_2MW_1,A\text{-}B \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} W_2M\text{-}A\text{-}B + H_2O \qquad K_b = \frac{[W_2M\text{-}A\text{-}B]}{[W_2MW_1,A\text{-}B]} \tag{b}$$

$$W_2M\text{-}A\text{-}B \underset{k_{-0}'}{\overset{k_0'}{\rightleftharpoons}} M\Big<\begin{matrix}A\\B\end{matrix}\Big)_{aq} + H_2O \qquad K_c = \frac{\left[M\Big<\begin{matrix}A\\B\end{matrix}\Big)\right]}{[W_2M\text{-}A\text{-}B]} \tag{c}$$

molecules in the inner coordination sphere which are eventually replaced by the bidentate ligand. The two binding sites of the ligand are represented as A and B. Reaction a is the formation of the ion pair, W_2MW_1, A–B with K_a the ion-pair formation constant.

If we restrict our attention to the first substitution only, and use the assumptions made in part I,[6] we can relate the observed rate constants to the above mechanism by eq 4a and b. This mechanism shows two limit-

$$k_1 = k_0K_a\left(\frac{k_0'}{k_{-0} + k_0'}\right) \tag{4a}$$

$$k_{-1} = k_{-0}\left(\frac{k_{-0}'}{k_{-0} + k_0'}\right) \tag{4b}$$

ing types of behavior, depending upon the relative magnitudes of the two rate constants k_{-0} and k_0'. These cases are summarized below as normal substitution, $k_0' \gg k_{-0}$, $k_1 = k_0K_a$ (M^{-1} sec^{-1}), $k_{-1} = k_{-0}/K_c$ (sec^{-1}); and sterically controlled substitution, $k_{-0} \gg k_0'$, $k_1 = k_0'K_aK_b$ (M^{-1} sec^{-1}), $k_{-1} = k_{-0}'$ (sec^{-1}).

If the complex formation is a "normal" substitution, then by using a calculated value for the ion-pair constant, K_a, one obtains a value for k_0, the rate constant for the elimination of water from the first coordination sphere. Swift and Connick[10] have determined k_0 by the use of nmr line-broadening measurements. Their values are 3×10^4 and 1×10^6 sec^{-1} for nickel-

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(10) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962); **41**, 2553 (1964).

(II) and cobalt(II), respectively. The results for glycine[4] and α-alanine[6] are in good agreement with the above values. The results for k_1 ($=k_0K_a$) reported here for Ni^{2+} and Co^{2+} with α-aminobutyric acid are 1.0×10^4 and 2.5×10^5 M^{-1} sec^{-1}, respectively, which also agree qualitatively with the nmr data, and with the data obtained with other ligands.

As more evidence on the nature of metal complex substitution reactions accumulates, resort is being made to investigations with increasingly larger and more complex ligands. It would be worthwhile to reexamine the applicability of ion-pair formation constant calculations in this regard. The constant for ion-pair formation between two ions leading to a solvated species MW,L can be calculated with the function derived independently by Fuoss[11] on statistical and by Eigen[12] on kinetic grounds, namely

$$K_a = \frac{4\pi N a^3}{3000}\exp(b)\exp[-b\kappa a/(1+\kappa a)]\,M^{-1} \qquad (5)$$

In the above expression, N is Avogadro's number; $\exp[-b\kappa a/(1+\kappa a)] = \gamma_{\pm}^2$, which is the square of the Debye–Hückel mean activity coefficient; a is the minimum approach distance between the charged particles; b is the Bjerrum ratio between potential and kinetic energy ($b = |Z_MZ_L|e_0^2/aD\mathbf{k}T$) where Z_M and Z_L are the ionic charges, e_0 is the elementary charge, $\mathbf{k}$ is the Boltzmann constant, D is the dielectric constant, and T is the absolute temperature); the parameter κ is the reciprocal of the distance between the central ion and the ionic atmosphere at the maximum of its charge density according to the Debye–Hückel theory.

Equation 5 has been based on models in which the solvent is assumed to be a continuum and the ions are considered to be rigid spheres of radii $a/2$. It is evident that for the anions discussed in this study this model does not fit, even to a first approximation, the molecular structures of these amino acids. The expression is, moreover, strongly dependent on the distance a. Choosing $a = 5$ A, as has been done,[4] leads to a value of $K_a = 2$ M^{-1}. While this procedure yields reasonable results, in some cases, we feel that to expect good agreement with the theory for ligands of different geometry is impractical. On the other hand, attempts to adapt the model—and, hence, the theory—to the present situation, would involve efforts out of keeping with a kinetic study. We are mainly interested in a *relative* comparison of the observed k_1 between α- and β-aminobutyric acid complexes with cobalt(II) and nickel(II). Therefore, even if the absolute value of K_a is unknown, some of its characteristics with respect to the two ligands may be inferred, and we may draw some valid conclusions about the mechanism.

The k_1 value for nickel with α-aminobutyric acid is somewhat lower than the corresponding value for related ligands (*e.g.*, glycine, α-alanine, diglycine). Indeed, the same is true for the cobalt values, and, as shall later be shown, the rate constants for β-aminobutyric acid, as well. To find the reason for this decrease, we start by examining eq 5. This expression consists of two parts. The preexponential factor is entropic in nature. It increases with increasing ionic radius, reflecting the enhanced probability of pairing as the reaction cross section increases. The exponential factor is the energy part and is controlled mainly by the electrostatic interaction. This factor decreases with increasing ionic size. Calculations indicate that, at this temperature and ionic strength, the function is at this minimum point, being almost insensitive to size for $3 < a < 8$ (A). Moreover, the electrostatic (exponential) term begins to show inappreciable change with ionic size as a increases beyond 5 or 6 A. It would thus appear that, in this range, larger ligand size makes the electrostatic interactions less significant, while increasing K_a, which would also increase the observed rate constants, rather than decrease them.

However, an increase in ligand size has been achieved in this case at the expense of spherical symmetry. This effect would be directly manifested in the rate constant for formation of the ion pair (as shown by Eigen, *et al.*,[13]), thereby reducing K_a in magnitude. Essentially then, we assume that the important effect on K_a is given by the diminished accessibility of ion-pairing sites on the ligand. To adjust for this reduction in the solid angle corresponding to reactive encounters, we shall introduce an empirical factor of approximately $^1/_2$ into eq 5.[14] The basis for introducing this factor will be explained more fully as we discuss each ion in detail.

Nickel(II). The observed value of k_1 for Ni^{2+} and α-aminobutyrate is 1.0×10^4 M^{-1} sec^{-1}. The value for α-alanine, also determined in this laboratory, is 2.0×10^4 M^{-1} sec^{-1}, from which the previously discussed empirical factor of $^1/_2$ has been obtained by taking the ratio of these rate constants. The increased rates of formation of the higher order complexes is explained by a loosening in the binding between the metal ion and the remaining coordinated waters.[4] The results for the α-aminobutyric acid, in comparison to α-alanine, lead to the conclusion that the mechanism of substitution is "normal"; that is, the rate-determining step is given by reaction b.

The value of k_1 for Ni^{2+} and β-aminobutyrate is less than that reported for the α complex, *viz.*, 4×10^3 M^{-1} sec^{-1} as compared to 1×10^4 M^{-1} sec^{-1}. This difference is most interesting when one considers that a similar result was observed for α- and β-alanine, the value of the latter being one-half as large as the α-Ala k_1 (where Ala = alanine). If the reduction in the β-aminobutyric acid rate constant is assumed to indicate partial steric control, then one-half the k_1 for α-aminobutyric acid (where $^1/_2 = k_1(\beta\text{-Ala})/k_1(\alpha\text{-Ala})$), or 5×10^3 M^{-1} sec^{-1}, should be the approximate value for k_1 when β-aminobutyric acid is the ligand. The measured value of 4×10^3 M^{-1} sec^{-1} is in good agreement with this hypothesis.

Cobalt(II). The rate constants for formation of the first and second α complexes, as given in Table IV, are $k_1 = 2.5 \times 10^5$ and $k_2 = 1.9 \times 10^6$ M^{-1} sec^{-1}, while k_3 could not be determined. The fact that k_2 is larger than k_1 corresponds to the loosening of the waters in the first coordination sphere, as in the nickel case. This effect is larger than for nickel(II), however, and may reflect the greater crystal-field stabilization of a d^8 ion. As noted before, the value of k_1 is somewhat less

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[11] R. M. Fuoss, *J. Am. Chem. Soc.*, 80, 5059 (1958).

[12] M. Eigen, *Z. Physik. Chem.* (Frankfurt), 1, 176 (1954).

[13] M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, 2, 287 (1964).

[14] R. A. Alberty and G. G. Hammes, *J. Phys. Chem.*, 62, 154 (1958).

than anticipated for normal substitution. The empirical factor can be calculated from the ratio of rate constants as $k_1(\alpha\text{-Abu})/k_1(\alpha\text{-Ala}) = 2.5/6 = 0.42$ and $k_1(\alpha\text{-Abu})/k_1$ (Gly) = 0.54 (Gly = glycine). The average value is, again, approximately $^1/_2$. This result compares favorably with the procedure adopted for the Ni^{2+} complexes. Thus, this relatively small difference in the value of k_1 can be explained, and the substitution classified as normal.

For β-aminobutyric acid, values of $k_1 = 2 \times 10^4$ and $k_2 = 7 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ were found. Although k_2 is larger than k_1, the effect is not nearly as pronounced as for α-aminobutyric acid. Moreover, the value of k_1 is significantly lower than the corresponding value for α-aminobutyric acid or glycine, being reduced, primarily, by the factor $(1 + k_{-0}/k_0')^{-1}$. Here, a steric effect due to the difficulty of closing the six-membered ring in the chelate complex can be postulated, as in the case of β-alanine,[6] where it was also indicated that the limiting case ($k_{-0} \gg k_0'$) was not reached. It is thus possible to predict the value of k_1 for the β complex by a semiempirical calculation as follows.

Let us assume that the steric effect appearing in Co^{2+}–β-alanine reactions is roughly equal to the steric effect with β-aminobutyric acid. Then the rate constant for Co^{2+} + β-aminobutyrate is $k_1(\beta\text{-Abu}) = k_1(\alpha\text{-Abu})\cdot[k_1(\beta\text{-Ala})/k_1(\alpha\text{-Ala})] = 2.5 \times 10^5(7.5/60) = 3.1 \times 10^4\ M^{-1}\ \text{sec}^{-1}$. The same calculation can be performed in an alternate way. Suppose that the ratio (7.5/60) expresses the steric control contribution to the closing of the six-membered ring with respect to the five-membered ring. Then, the β rate constant can be calculated from k_1(Gly) by the introduction of the statistical collision factor $P = {}^1/_2$, to adjust for the decreased active "surface of reaction." Therefore, $k_1(\beta\text{-Abu}) = Pk_1(\text{Gly})[k_1(\beta\text{-Ala})/k_1(\alpha\text{-Ala})] = {}^1/_2(4.6 \times 10^5)(7.5/60) = 2.9 \times 10^4\ M^{-1}\ \text{sec}^{-1}$, while the experimental value is $k_1 = 2.0 \times 10^4\ M^{-1}\ \text{sec}^{-1}$.

Nucleophilic Reactivity in Substitution Reactions of Square-Planar Metal Complexes. II. A Comparison of the Kinetic Behavior of Platinum(II) and Gold(III) Complexes

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Abstract: The kinetics of the displacement of chloride from the $[AuCl_4]^-$ anion by pyridine, NO_2^-, N_3^-, Br^-, I^-, and SCN^- in methanol have been studied over a range of temperature and reagent concentration. The usual two-term rate law is observed, and the rate constants and Arrhenius parameters are reported and compared with the data for the analogous $[PtCl_4]^{2-}$ anion. The discriminating power of the Au(III) reaction center is found to be very much greater than that of Pt(II) in a similar ligand environment, and an explanation is offered in terms of the extent to which the mechanism moves from an associative toward a synchronous bimolecular process.

Although kinetic studies of nucleophilic displacement of ligands from square complexes of d^8 transition metal ions have, in the past, been limited mainly to those of platinum(II),[1] sufficient information about the behavior of corresponding gold(III) complexes has now become available for it to be possible to attempt to make a preliminary general comparison of the kinetic behavior of Pt(II) and Au(III) substrates.

In part I,[2] the factors which determine the reactivity of nucleophiles toward Pt(II) complexes were discussed. It was shown that, apart from biphilic reagents, such as NO_2^-, $SeCN^-$ and thiourea, the sequence of relative reactivity followed a linear free-energy relationship with the index, n_{Pt},[3] defined by $n_{Pt} = \log (k_2/k_s)$, where k_2 and k_s are the second-order rate constant for the entry of the nucleophile in question and the first-order rate constant for the solvolysis by methanol, respectively, of the reference substrate *trans*-$[Pt(py)_2Cl_2]$. This was taken to be a measure of the "softness" or micropolarizability of the entering nucleophile since its basicity appeared to have only a minor effect upon its reactivity.

In order to make the comparison between Pt(II) and Au(III) complexes, it was necessary to augment the available data relative to nucleophilic displacement reactions of the gold(III) derivatives. Apart from the isotopic exchange[4] of chloride ion with $[AuCl_4]^-$ and from the reactions[5] of some nucleophiles on the cationic complex $[Au(\text{dien-H})Cl]^+$, the processes studied until now were mainly limited to the use of pyridine derivatives, either as entering[6,7] or leaving[8,9] groups. We have therefore studied the reactions of $[AuCl_4]^-$ with

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