difficult to advance a case for one of the possible mechanisms, A or B, over the other. Indeed the oxidation of $CrCH_2OH^{2+}$ and other (α-hydroxyalkyl)chromium complexes with Cu^{2+} and Fe^{3+} shows a pronounced k_0 term although in these instances $k_{-1}[H^+] \gg k_2$. On this basis mechanism A certainly seems reasonable. On the other hand the $k_4[H^+]$ term of mechanism B is also plausible in view of the different degree of hydrolysis of the initial (VO^{2+}) and final (V^{3+}) oxidation states of the vanadium.

The rate laws of eq 12 and 13 imply that the electron-transfer step (k_2 or $k_3 + k_4[H^+]$) and dissociation of the binuclear complex into reactants ($k_{-1}[H^+]$) take place at comparable rates; i.e., electron transfer is not the sole rate-determining step. This is different from our findings on the oxidation of $CrCH_2OH^{2+}$ by Cu^{2+} and Fe^{3+}. The reason for this is not quite clear. One might expect that VO^{2+} would utilize the very labile axial position[15-17] to bind to $CrCH_2OH^{2+}$ in the transition state, in which case a dissociation of the intermediate is expected to be a very favorable process too. However it was pointed out before that substitutions on VO^{2+} most likely occur at one of the four equatorial positions.[12] If this is the case, the stability of the intermediate toward dissociation could be greatly enhanced, making the electron-transfer rate comparable to the dissociation.

Our arguments about the detailed mechanism of the inner-sphere oxidation of $CrCH_2OH^{2+}$ by VO^{2+} are based mainly on the acidity dependence of the reaction rates. This approach, although very useful, has limitation, especially for the reactions of metal ions in higher oxidation states where the hydrolysis of the reactants and/or products may obscure the mechanistic picture. However even with that limitation the results of this work support the idea that $CrCH_2OH^{2+}$ (and other (α-hydroxyalkyl)chromium complexes) preferably react with oxidants in inner-sphere reactions, most likely by forming bridged activated complexes through the alcoholic OH group.

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Registry No. $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; VO^{2+}, 20644-97-7.

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Multidentate Ligand Kinetics: Exchange of Aminocarboxylate Ions with (Tetraethylenepentamine)nickel(II)

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The nickel polyamine formation and dissociation reactions have been thoroughly studied in the past.[1,2] The dissociation of nickel polyamine complexes has been shown to involve the following two steps repeated sequentially:[2] nickel–nitrogen bond breakage followed by nickel–solvent bond formation. This sequence continues until the polyamine completely dissociates from the nickel ion. Excluding strongly acidic conditions the rate-determining step is the last nickel–nitrogen bond rupture.

Table I. Resolved Rate Constants and Activation Parameters for the Substitution Reaction of Nickel(II) Polyamine by Aminocarboxylates

(I) $NiTet^{2+}$–TMDTA Reaction System	
$k_L = 18.2\ M^{-1}\ s^{-1}$	$E_a = 5.47$ kcal
$k_{HL} = 8.9\ M^{-1}\ s^{-1}$	$\Delta H^{\ddagger} = 4.88$ kcal
$k_{H_2L} = 142\ M^{-1}\ s^{-1}$	$\Delta S^{\ddagger} = -34.11$ eu
	$pZ = 2.06 \times 10^5\ cm^{-1}$
(II) $NiTet^{2+}$–HEEDTA Reaction System	
$k_L = 8.10\ M^{-1}\ s^{-1}$	$E_a = 11.90$ kcal
$k_{HL} = 12.6\ M^{-1}\ s^{-1}$	$\Delta H^{\ddagger} = 11.31$ kcal
$k_{H_2L} = 6.3 \times 10^3\ M^{-1}\ s^{-1}$	$\Delta S^{\ddagger} = -15.66$ eu
	$pZ = 2.22 \times 10^9\ cm^{-1}$

The reaction reported in this note (shown without protonation) is

$$NiTet^{2+} + L^{n-} \rightarrow NiL^{2-n} + Tet \qquad (1)$$

where Tet is tetraethylenepentamine and L is TMDTA (trimethylenediaminetetraacetic acid) or HEEDTA (hydroxyethylethylenediaminetriacetic acid).

A mechanism for the exchange reaction is proposed which involves the formation of a series of mixed-ligand complex intermediates where in each succeeding step the nickel ion increases its coordination to the incoming aminocarboxylate and decreases the number of coordinate bonds to the leaving polyamine. The final conclusion is the same as that arrived upon by previous workers.[3,4]

Experimental Section

The purification of Tetren and the preparation and standardization of NiTet solutions were carried out by methods previously reported.[2] TMDTA was prepared and recrystallized by a method described in the literature.[5a] HEEDTA was obtained from K & K Labs. The ionic strength was maintained at 0.1 M with $NaClO_4$. All absorption measurements were made with a Toshniwal Model RL-02 (Beckman DU type) spectrophotometer which was equipped with a thermostated cell compartment. The reaction was followed by a cyanide quenching method described in literature.[4]

Results and Discussion

Both the reactions have been carried out at a pH of 11.0 ± 0.1. The rate constants have been determined by the initial rate method. The orders with respect to NiTet and aminocarboxylate are found to be one in each reactant. The rate expression can be written as

$$Re = -\frac{d[NiTet]_T}{dt} = k_{L_T}^{NiTet}[NiTet]_T[L]_T \qquad (2)$$

The rate constants for the two reactions are 19.88 ± 1.41 and 8.87 ± 1.10 $M^{-1}\ s^{-1}$ for TMDTA and HEEDTA reactions, respectively. Activation parameters have been calculated and are given in Table I. It was also found that reaction rates are strongly dependent on pH in the pH range 5–11. The observed dependence can be attributed to the formation of various protonated and unprotonated forms of reactants present at the working pH values.[6] On the basis of acid protonation

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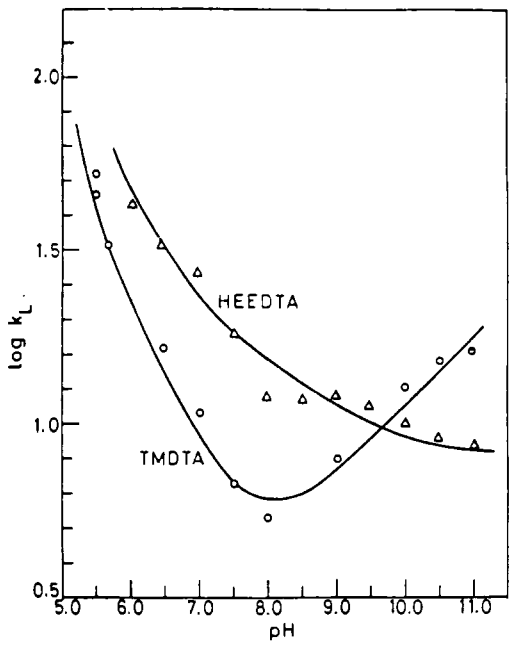

Figure 1. Fit of theoretical curves and the observed rate constants for exchange of aminocarboxylate with $NiTet^{2+}$.

constants of aminocarboxylates and NiTet the rate equation (3) is proposed. This can be transformed by algebraic ma-

$$\mathrm{Re} = \{k_L[L^{n-}] + k_{HL}[HL^{1-n}] + k_{H_2L}[H_2L^{2-n}] + \text{—}\}\{[\mathrm{NiTet}] + [\mathrm{NiHTet}]\} \quad (3)$$

nipulation to eq 4 and 5, where k_0, k_1, etc. are a collection of

$$\mathrm{Re} = \{k_L + (k_{HL}K_1 + k_LK_{NiHTet})[H^+] + (k_{H_2L}K_1K_2 + k_{HL}K_1K_{NiHTet})[H^+]^2 + k_{H_2L}K_1K_2K_{NiHTet}[H^+]^3\}[NiTet^{2+}][L^{n-}] \quad (4)$$

$$\mathrm{Re} = \{k_0 + k_1[H^+] + k_2[H^+]^2 + k_3[H^+]^3\}[\mathrm{NiTet}][L^{n-}] \quad (5)$$

appropriate rate constants and protonation constants. Comparing eq 2 and 5 gives eq 6, where $[L]_T/[L^{n-}] = 1 + K_1[H^+]$

$$k_{L_T}\frac{[L]_T[\mathrm{NiTet}]_T}{[L^{n-}][\mathrm{NiTet}]} = k_0 + k_1[H^+] + k_2[H^+]^2 + k_3[H^+]^3 \quad (6)$$

$+ K_1K_2[H^+]^2 + K_1K_2K_3[H^+]^3$, K_1K_2 and K_3 are protonation constants of ligands, and $[\mathrm{NiTet}]_T/[\mathrm{NiTet}] = 1 + K^{NiTet}_{NiHTet}[H^+]$. The plot of log k_{L_T} vs. pH is shown in Figure 1. In the pH range 8.5–11.0 the terms containing higher powers of $[H^+]$ can be ignored, and eq 6 takes the form of eq 7. From a plot of the left-hand side of eq 7 vs. $[H^+]$ the rate

$$k_{L_T}\frac{[\mathrm{NiTet}]_T[L]_T}{[\mathrm{NiTet}][L^{n-}]} = k_L + k_{HL}K_1[H^+] \quad (7)$$

constants k_L and k_{HL} can be obtained.

In the pH range 5.5–8.0, however, the terms including one and two protons on the ligand are important, and the protonated form of the NiTet complex is also expected to play an important role in the reaction. Therefore, eq 6 takes the form of eq 8, where A is the left-hand side of eq 6. k_2 and

$$\{A - (k_0 + k_1[H^+])\}/[H^+]^2 = k_2 + k_3[H^+] \quad (8)$$

k_3 and therefore k_{HL} and k_{H_2L} can be obtained from a plot of the left-hand side of eq 8 against $[H^+]$. The rate constants resolved from eq 7 and 8 are given in Table I.

In an earlier work[2] it has been shown that the rate of dissociation of NiTet is much slower than the exchange rate of EDTA with this complex. Therefore, the presence of aminocarboxylate facilitates the dissociation of $NiTet^{2+}$, showing that both the processes take place through a succession of bond formation and bond rupture steps. The same appears to hold good in the reactions under investigation. It is proposed, as was done by Rorabacher and Margerum,[4] that the entering aminocarboxylate forms an increasing number of coordinate bonds with Ni^{2+} prior to complete dissociation of the nickel polyamine complex. In this way the aminocarboxylates, viz., TMDTA and HEEDTA, block the reformation of the nickel–polyamine bond much in the same manner as the protons in the dissociation reactions. A series of mixed-ligand complexes is formed in the intervening steps such that the coordination of the nickel ion decreases with the polyamine and successively increases with the aminocarboxylates in each following step. The formation of such mixed-ligand complexes is not unusual and has, in fact, been demonstrated[7,8] in many reactions involving displacement of polydentate ligands from their complexes.

A consideration of the peculiar structural features of EDTA and structurally similar aminocarboxylates would show that during formation of the first bond a carboxylate donor group is highly favored over a nitrogen due to their steric configuration and the difficulty that the nitrogen atom experiences in approaching the coordination sites. The electrostatic attraction between Ni^{2+} and COO^- should increase this preference further. When one considers the formation of second and subsequent bonds, the factors like steric difficulties and rotational barriers to be encountered for approaching the coordination sites on Ni^{2+} exclude the possibility that an aminocarboxylate atom can approach the nickel at the same time as the nickel–polyamine bond is broken. On the other hand the solvent molecules, in this case water, can rapidly coordinate at this site vacated by a polyamine segment. It is, therefore, proposed that the mechanisms of displacement of a polyamine by an aminocarboxylate consists of two alternating steps: a cleavage of a nickel–polyamine bond attended by rapid coordination by water molecules at the vacated site followed by rupture of the nickel–water bond and rapid coordination of an aminocarboxylate donor atom, which must rotate to assume a position favorable for bonding. These features of the mechanism proposed above (for nonprotonated reactants) can be considered the same as in the case of NiTrien and EDTA reaction.[4]

The pinpointing of the rate-determining step poses a difficult problem, but this should be one of the following processes: (a) loss of water[9] or (b) rupture of the metal–polyamine bond. It should thus depend upon either the rate constant for water loss (similar to metal chelate formation) or the rate constant for breakage of the nickel–polyamine bond (similar to metal chelate dissociation).

The rate-determining step can be identified by methods given in the literature.[4,10,11] In the present investigation we have made use of a method used by Rorabacher and Margerum.[4] The basic idea is that the experimental rate constants can be equated to the relative stability of the intermediate immediately preceding the rate-determining step by the relationship

$$k(\mathrm{exptl}) = \frac{K(n\text{th intermediate})}{K(\mathrm{reactants})}k_n \quad (9)$$

where $K(n\text{th intermediate}) = K(\text{polyamine segment})K(\text{ami-}$

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nocarboxylate segment)/K(electrostatic) and k_n is the rate constant for the nickel–nitrogen or nickel–water bond-breaking process corrected for rotation barrier involved in the particular case.[4] By using eq 9 for calculation of k and comparing it with k(exptl), we could reach the conclusion arrived at by Rorabacher and Margerum[4] that, in all probability, the rate-determining step is where four nitrogens of Tetren and one acetate of aminocarboxylate is coordinated to Ni^{2+}. The rate-determining step thus appears to be the loss of a water molecule followed by coordination of the first nitrogen of TMDTA or HEEDTA.

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Preparative High-Pressure Liquid Chromatographic Separation of Cobalt(III) Coordination Complexes

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We have previously reported[1] a versatile solvent system that has proven extremely useful for the analytical and preparative thin-layer chromatographic (TLC) separations of a variety of cobalt(III) complexes and azodye ligands.[1,2] By extending the previous results to include high-pressure liquid chromatographic techniques (HPLC), it was assumed that *any* type of separation problem could be approached in a systematic way by using a combination of TLC and HPLC methods. Analytical TLC would be used to rapidly define reaction conditions favorable to product formation. The TLC results could then be directly applied to preparative isolation procedures, since all of the chromatography would be performed on the same type of stationary phase with the same solvent system. This is in direct contrast to the way most complexes have been isolated in our laboratory. Even when a suitable TLC separation can be performed on a reaction mixture, preparative TLC has not always provided sufficient material for subsequent manipulations. In most cases ion exchange chromatography on polystyrene or dextran stationary phases must be performed. In these separations the elution order of the various compounds, and the resolution exhibited, does not necessarily follow the TLC results. The colors of the metal complexes on different stationary phases are not always comparable, complicating the isolation procedure. Furthermore, for complexes with a charge greater than 1, or for the case where aromatic groups are present in the ligands, high salt concentrations (>1 M) are required for elution. The use of these high ionic strengths often degrades resolution and lengthens the isolation procedure due to the desalting that is required.

Though cobalt(III) complexes have been separated by HPLC,[3,4] a general preparative method that would be useful to synthetic inorganic chemists has not appeared. This may be due in part to the theoretical nature of the publications dealing with the preparative separations of nonpolar comounds that appear in the chromatography literature or to the chromatographer's preoccupation with expensive, complicated equipment.[5,6]

This study describes a "bare bones" liquid chromatograph and a "new" sample introduction method. The results of three distinctly different types of separations are presented: different comounds, geometrical isomers, and diastereomers with and without aromatic functionality. From these data some conclusions can be drawn concerning the present method's speed, resolution, and capacity.

Experimental Section

Reagents. All reagents used in this study were at least of reagent grade. The preparation of the 70/30 isopropyl alcohol–2 M pH 9 triethylammonium bicarbonate buffer system (abbreviated 70/30 IS–TEA) has been described previously.[1]

Separations. The majority of the separations were first performed on a programmable gradient liquid chromatograph described elsewhere.[7] A 1 × 100 cm column was constructed from 0.500-in. o.d. × 0.049-in. wall, 304 stainless steel hydraulic tubing (purchased locally), and Swagelok SS-810-6-1-SR-15 $^1/_{16}$–$^1/_2$ in. reducing unions which come fitted with 10-μ frits. A 500-mL packing reservoir (a Whitey gas sampling cylinder, part number 304-HDF4-500) was adapted to the column and filled with a slurry consisting of 200 g of Whatman LP-1, 10–20 μ of silica, and 500 mL of 70/30 IS–TEA. This slurry was packed at approximately 20 mL/min (3500–4500 psi) for 30 min. After the reservoir was removed, the column was connected to an ISCO UA-5 monitor fitted with filters for operation at 510 nm.

Samples from 1–3 mL (solute concentration 50–100 mg/mL) were applied to the column by placing the sample loop of the sample injection valve in the solvent flow stream with the pump's flow rate control set to 0. The flow rate was then gradually increased to the final value, usually 4–8 mL/min, over a 10–20-min period with use of a flow program.[7]

Strongly retained compounds ($R_f \approx 0$ on TLC) were removed from samples prior to introduction to the liquid chromatograph by prechromatography on 60–200 mesh silica (Baker) packed in 30-mL disposable syringe bodies with the use of 70/30 IS–TEA as eluant. Eluant was pulled across the precolumn by vacuum into a filter flask. Samples were then concentrated on a rotovap at 30–40 °C. Prior to injection all samples were filtered to 0.45 μ with a Millipore inline filter unit, as previously described.

A considerably simpler, less expensive, liquid-chromatography system capable of reproducing the separations developed above, but on a larger scale, was also constructed. It consisted of a Milton Roy instrument minipump connected with a 0.0625-in. o.d. Teflon tubing and miniature tubing fittings (both Altex and Unimetrics brands have been used) to a Merk 4 × 40 cm "Lo-Bar" column body (similar to Michel-Miller glass columns manufactured by Ace Glass, Vineland, NJ).

The column was slurry packed with Whatmen LP-1 silica and 70/30 IS–TEA (100 g silica plus 100 mL eluant) at approximately 8 mL/min (200–250 psi). Since a packing reservoir was not available for this column, packing was accomplished in two or three steps, stopping where the column body began to taper to its upper flow adapter. Although contrary to normal packing procedure, excellent results were obtained, with no discontinuities in the bed observed, as compounds were eluted across regions where the packing had been interrupted. (Packing reservoirs are available for the Michel-Miller type columns allowing them to be packed in a single step.)

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