Other factors may also be important since both acid dissociation and metal complex stability constant measurements for amines in aqueous solution are known[24] to be complicated by solvation terms, ion-pair association, and entropy effects. The acid dissociation constants reported for udmen[11] and en, sdmen, and tetmen[12] are a net reflection of these effects and give the following order of increasing basicity: $R_2NH > RNH_2 > R_3N > NH_3$. Similarly the formation constants measured for Cu(II) and Ni(II) diamine complexes[9-12] are influenced by these competitive reactions as well as by the steric effects of increasing N-methyl substitution. It has further been shown[24] that, although primary aliphatic amine complexes of Ni(II) dissociate readily in water, the amines occupy a higher position than water in the spectrochemical series. Accordingly, the instability of these complexes in water cannot be attributed to the relative strength of the metal ion–ligand interaction of water and the amines.

However, any factor that increases metal–nitrogen bond strength would be expected to influence both ν(Rh–N) and the nephelauxetic series, the latter of which is considered[5,22] to represent closely the tendency toward covalent bonding and as a result is primarily dependent on inductive and polarization factors. It is also known[25] that the nephelauxetic series often more closely resembles the order of thermodynamic stability constants than does the spectrochemical series, and a correlation has previously been found[26] between the metal–nitrogen stretching frequencies and stability constants of a number of en complexes. The agreement in the order of the ligands in the ν(Rh–N) series and the nephelauxetic series is therefore consistent with previously observed trends and is a good indication that the thermodynamic stabilities would follow the same order. The data, therefore, provide evidence that the complexes are examples of systems containing tertiary amino groups more stable thermodynamically than those with primary or secondary amines.

Acknowledgment. This work was supported by the U. S. Atomic Energy Commission and the Robert A. Welch Foundation.

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Complexes of Chromium(III) with Some N-Substituted Ethylenediaminetriacetic Acids[1]

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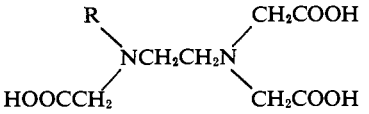
Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. 20007. *Received November 4, 1966*

Abstract: A potentiometric, polarographic, and spectrophotometric study of the complexes of Cr(III) with N-(2-hydroxyethyl)ethylenediaminetriacetic acid, N-(2-hydroxycyclohexyl)ethylenediaminetriacetic acid, and N-phenethylethylenediaminetriacetic acid has been carried out. Several equilibrium and kinetic parameters of these systems have been determined. The mechanisms of the electrode reductions are discussed.

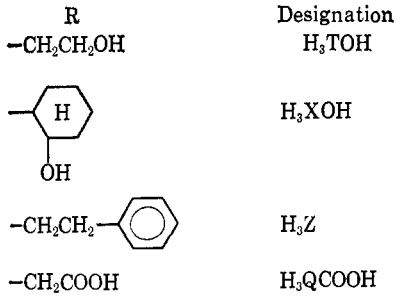
We have studied complexes of Cr(III) with ligands of the type



We will use the designations in Chart I for these ligands to emphasize the number of replaceable hydrogens. The Cr(III) complex of H_3QCOOH (more commonly known as EDTA) has been studied previously by several authors.[2-4] We have performed some additional experiments on this system to compare it with the triacetic acid systems.

Previous work on this Cr(III) complex of EDTA has shown that one coordination position is occupied by a water molecule and that the complex has interesting acid–base and redox chemistry.

Chart I



Experimental Section

Analytical grade reagents and water triple-distilled from quartz were employed. The ligands were received in purified form, most having been used in a previous study.[5] Chromium(III)–ligand

(1) Supported in part by the U. S. Air Force Office of Scientific Research under Research Grant AF 133-65.

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complexes were prepared by heating $Cr(H_2O)_6(ClO_4)_3$ with slightly less than an equivalent amount of ligand in acidic aqueous solution or by the same reaction catalyzed by Cr(II).[6] No difference was observed between the complexes prepared by these methods. The product was separated from unreacted Cr(III) and polymeric products using a Dowex 50W-X8 cation-exchange column and distilled water as eluent. Measurements were made on freshly prepared solutions. Although a concentration of uncomplexed Cr^{3+} less than 1% of that of the complex would have been readily detectable polarographically, none was found in these solutions.

All measurements were made in borax–boric acid, borax–sodium hydroxide, or ligand–sodium hydroxide buffers with ionic strength adjusted to 0.2 *M* with $NaClO_4$. Spectrophotometric and polarographic properties were the same in various buffers at the same pH. The polarographic properties of the H_3QCOOH complexes in buffered solutions were the same, within experimental error, as those previously reported[4] for solutions of the same pH but without added buffer. Experiments in which excess ligand was added gave the same results as those in the absence of added ligand.

Spectrophotometric measurements were made using the Cary 14 spectrophotometer using 1- and 5-cm cells. A Sargent XV polarograph was used for recording current–voltage curves. The Kalousek commutator[7] at 50 cps was used to demonstrate the reversibility of the electrode reaction. Solutions measured were 10^{-3} *M* in Cr.

The capillary used had a drop time of 3.4 sec and flow rate of 2.05 mg/sec^{-1} (in short circuit with sce and 64-cm Hg column). A modified Kalousek polarographic cell[8] was used for measurement. All measurements were made at 22 ± 1°. Potentials are listed in volts *vs.* the saturated calomel electrode.

Potentiometric titrations of 0.02 *M* Cr complexes were made using the Sargent combination glass–calomel electrode and the Fisher Expandometric pH meter.

Results and Discussion

Determination of Acidity Constants. Equilibrium constants for a number of reactions of the type $HA \rightleftarrows A^- + H^+$, $K_a = [H^+][A^-]/[HA]$, where HA is a Cr(III) complex, were measured by potentiometric titrations (Table I). Independent measurements of these

Table I. Values of p*K* for the Reaction $HA \rightleftarrows A^- + H^+$ Determined by Potentiometric Titration of Cr(III) Complexes at 22° in Aqueous 0.2 *M* $NaClO_4$ Solutions

HA	A	p*K*
$[Cr(H_2O)TOH]^0$	$[Cr(OH)TOH]^-$	6.44
$[Cr(OH)TOH]^-$	$[Cr(OH)TO]^{-2}$	9.80
$[Cr(H_2O)XOH]^0$	$[Cr(OH)XOH]^-$	4.0
$[Cr(OH)XOH]^-$	$[Cr(OH)XO]^{-2}$	8.95
$[Cr(H_2O)Z]^0$	$[Cr(OH)Z]^-$	6.5
$[Cr(H_2O)QCOOH]^0$	$[Cr(H_2O)QCOO]^-$	3.1[a]
$[Cr(H_2O)QCOO]^-$	$[Cr(OH)QCOO]^{-2}$	7.5[a]

[a] The values are taken from G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948); R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).

and other acid–base reactions were obtained by measurement of the variation of the visible spectra of the complexes with pH (Table II).

Polarographic Measurements. The presence of any of the ligands causes a decrease of the polarographic wave of $Cr(H_2O)_6^{+3}$ and the formation of a second, more negative wave. The sum of the heights of both waves is equal to the height of the initial one, which corresponds to a one-electron reduction. The ratio of the wave heights depends on the ratio of the concentrations of $Cr(H_2O)_6^{+3}$ and ligand, and on the pH of the solution. The second wave is identical with that obtained when the Cr(III) complex of the ligand is reduced in the absence of $Cr(H_2O)_6^{+3}$. This effect has been described by Tanaka[3] for the reduction of $Cr(H_2O)_6^{+3}$ in the presence of H_3QCOOH according to the mechanism

$$Cr(H_2O)_6^{+3} + e^- \overset{E_1}{\Longrightarrow\!\rangle} Cr^{+2}$$

$$Cr^{+2} + H_2QCOO^{-2} + H_2O \rightleftarrows [Cr^{II}(H_2O)QCOO]^{-2} + 2H^+ \quad (1)$$

$$[Cr^{III}(H_2O)QCOO]^- + e^- \langle\!\Longrightarrow [Cr^{II}(H_2O)QCOO]^{-2}$$

(where $\langle\!\Longrightarrow$ refers to a reversible electrode reaction and $\Longrightarrow\!\rangle$ refers to an irreversible electrode reaction). Cr^{+2}, formed by reduction of $Cr(H_2O)_6^{+3}$, is in rapid equilibrium with the Cr(II) complex of the ligand, which is stable in solutions that are not strongly acidic. Since E_2 is more negative than E_1, the Cr^{+2} complex is oxidized between E_1 and E_2. The oxidation current exactly cancels the reduction current of $Cr(H_2O)_6^{+3}$. When E_2 is reached, the reduction wave of $[Cr^{III}(H_2O)QCOO]^-$ is observed.

The reduction curves of the Cr(III) complexes of each of these ligands were measured between pH 2 and 12.5. Between pH 4 and 9 totally reversible waves corresponding to a one-electron change were obtained. This was demonstrated by logarithmic analysis of the waves and by the use of the Kalousek commutator.

Figures 1–3 show the variation of $E_{1/2}$ with pH for the several members of the series studied. In basic solution, the limiting current decreased with increasing pH, as shown in Figures 4–6. In this region of pH, the limiting currents for complexes of H_3TOH and H_3XOH, if small in comparison with that corresponding to one-electron reduction, do not depend on the head of mercury, indicating that the reduction is kinetically controlled. For complexes of H_3Z and H_3QCOOH in this pH region, and for all complexes in other pH regions, reductions were diffusion controlled.

N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid Complexes. Below pH 4.5 this reduction is complicated by dissociation of the product of the electrode reaction and discharge of H^+. Between pH 4.5 and pH 6.0 $E_{1/2}$ is independent of pH at −1.22 v.

Table II. Spectral Properties of Chromium(III) Complexes[a]

Cr(III) complex	$\tilde{\nu}_{max} \times 10^{-3}$, cm^{-1}	ϵ	$\tilde{\nu}_{max} \times 10^{-3}$, cm^{-1}	ϵ	pK_a
$[Cr(H_2O)TOH]^0$	18.4	106.6	26.0	88.4	6.5
$[Cr(OH)TOH]^-$	17.5	87.0	25.0	65.6	9.8
$[Cr(OH)TO]^{-2}$	17.6	83.4	24.4	81.6	
$[Cr(H_2O)XOH]^0$	18.6	127	26.0	57.8	4.4
$[Cr(OH)XOH]^-$	18.0	166	25.2	107.5	8.8
$[Cr(H_2O)XO]^{-2}$	17.9	105	24.4	111	
$[Cr(H_2O)Z]^0$	18.3	134	25.9	105	5.6
$[Cr(OH)Z]^-$	17.1	100	25.4[b]	69.4	11.7
$[Cr(OH)_2Z]^{-2}$	17.2	70	24.8	71	12.3
$[Cr(OH)_3Z]^{-3}$	17.5	50	24.5	79	
$[Cr(H_2O)QCOOH]^0$ [c]	18.4	16.8	25.6	113	2.27
$[Cr(H_2O)QCOO]^-$ [c]	18.4	202	25.5	117	7.41
$[Cr(OH)QCOO]^{-2}$ [c]	17.2	124	25.6	86	12.25
$[Cr(OH)_2QCOO]^{-3}$ [c]	17.5	56	24.5	91	

[a] Ionic strength of aqueous solutions kept at 0.2, 22°. [b] Split band. [c] The values are taken from C. Furlani, G. Morpurzo, and G. Sartori, *Z. Anorg. Allgem. Chem.*, **303**, 1 (1960).

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(7) J. Heyrovsky and J. Kuta, "Principles of Polarography," Publishing House of Czechoslovak Academy of Sciences, Prague, 1965, p 477 (English edition).
(8) A. Rusina, *Chem. Listy*, **57**, 1070 (1963).

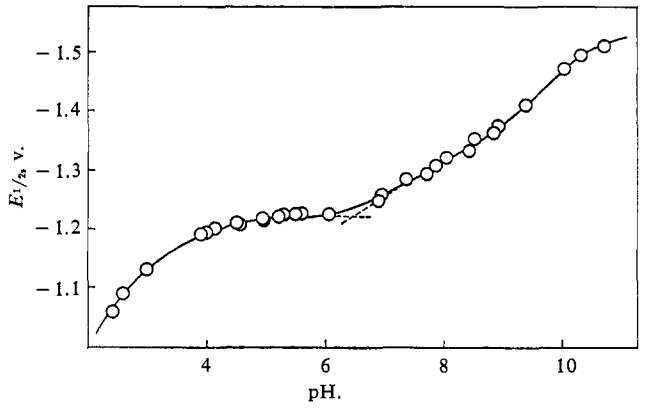

Figure 1. pH dependence of $E_{1/2}$ for the reduction of the Cr(III) complex of N-(2-hydroxyethyl)ethylenediaminetriacetic acid: borate and acetate buffers, 22°, ionic strength 0.2 M ($NaClO_4$).

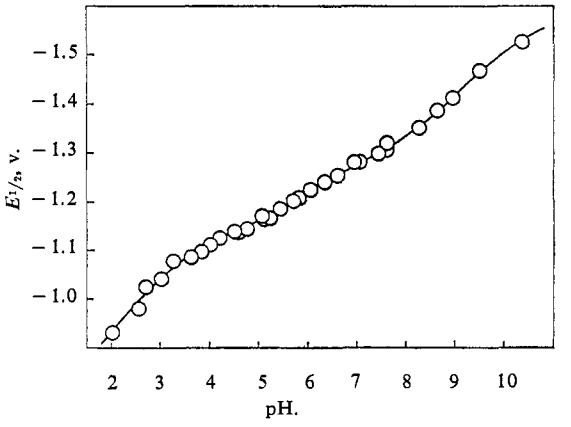

Figure 2. pH dependence of $E_{1/2}$ for the reduction of the Cr(III) complexes of N-(2-hydroxycyclohexyl)ethylenediaminetriacetic acid (conditions as in Figure 1).

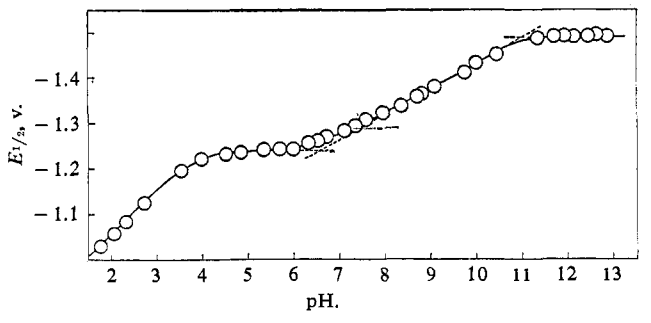

Figure 3. pH dependence of $E_{1/2}$ for the reduction of the Cr(III) complex of N-phenethylethylenediaminetriacetic acid (conditions as in Figure 1).

The pK values of the first acid–base change found spectrophotometrically and potentiometrically are in good agreement with each other and with the value found as the intersection of linear portions of the pH dependence of $E_{1/2}$ (pH 6.45). By comparison of spectra with the similar change of the EDTA complex, we assign the change as

$$[Cr^{III}(H_2O)TOH]^0 \rightleftharpoons [Cr^{III}(OH)TOH]^- + H^+ \quad pK_a = 6.45 \quad (2)$$

The pK value of similar change for Cr(II) complexes is expected to be higher, so that $[Cr^{II}(H_2O)TOH]^-$ is

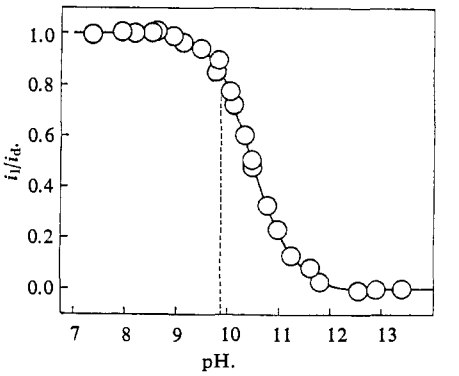

Figure 4. pH dependence of the reduction current of the Cr(III) complex of N-(2-hydroxyethyl)ethylenediaminetriacetic acid: dashed line is pK_a value found by potentiometric and spectrophotometric titration (conditions as in Figure 1).

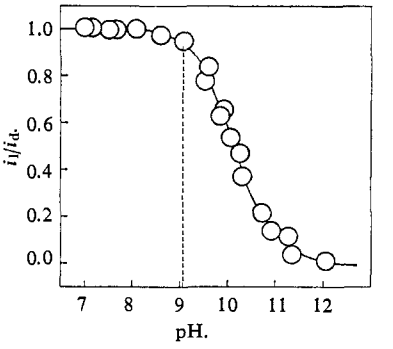

Figure 5. pH dependence of the reduction current of the Cr(III) complex of N-(2-hydroxycyclohexyl)ethylenediaminetriacetic acid: dashed line is pK_a value found by potentiometric and spectrophotometric titration (conditions as in Figure 1).

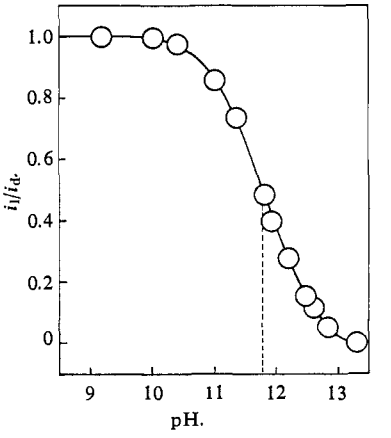

Figure 6. pH dependence of the reduction current of the Cr(III) complex of N-(2-phenethyl)ethylenediaminetriacetic acid: dashed line is pK_a value found by spectrophotometric titration (conditions as in Figure 1).

taken as the prevailing form over the pH range studied. For the electrode reduction in the pH range under pH 6.5, we can write the equation

$$[Cr^{III}(H_2O)TOH]^0 + e^- \rightleftharpoons [Cr^{II}(H_2O)TOH]^- \quad E_{1/2} = -1.22 \text{ v} \quad (3)$$

In solutions of pH above 6.5, the stable Cr(III) form is deprotonated, but the Cr(II) form is not, so that reduction is followed (eq 4) or preceded (eq 5) by a fast pro-

tonation, which is responsible for the pH dependence of $E_{1/2}$. This dependence corresponds to a gain of a single proton.

$$[Cr^{III}(OH)TOH]^- + e^- \rightleftarrows [Cr^{II}(OH)TOH]^{-2}$$
$$[Cr^{II}(OH)TOH]^{-2} + H^+ \rightleftarrows [Cr^{II}(H_2O)TOH]^- \quad (4)$$

$$[Cr^{III}(OH)TOH]^- + H^+ \rightleftarrows [Cr^{III}(H_2O)TOH]^0$$
$$[Cr^{III}(H_2O)TOH] + e^- \rightleftarrows [Cr^{II}(H_2O)TOH]^- \quad (5)$$

The second acid–base change of the Cr(III) complex has been found spectrophotometrically and potentiometrically to take place with $pK = 9.85$. Two reactions could be assigned to this change

$$[Cr^{III}(OH)TOH]^- + H_2O \rightleftarrows [Cr^{III}(OH)_2TOH]^{-2} + H^+ \quad (6)$$

$$[Cr^{III}(OH)TOH]^- \rightleftarrows [Cr^{III}(OH)TO]^{-2} + H^+ \quad (7)$$

The decrease of polarographic limiting current with increasing pH in this region of pH is connected with this change in such a way that the deprotonated species is not reducible in the potential range available polarographically. This decrease has the form of a titration curve. There is a difference between the pK value, found from spectrophotometry and potentiometric titration, and the apparent polarographic pK (pH value at which the observed limiting current is one-half of the current corresponding to a one-electron reduction). This fact, together with the partly reaction-rate-controlled current in the case of small waves, indicates that a relatively slow protonation reaction causing formation of an electroactive species takes place. There are thus four possible mechanisms for the over-all reaction: reaction 6 or 7 followed by either couple 4 or couple 5.

Koutecky[9] has derived an equation for the reduction current of an acid limited by its rate of formation through protonation of an inactive anion. For the case of a single proton gained in the course of reaction, the dependence

$$\log \frac{i_l}{i_d - i_l} = f(\mathrm{pH})$$

(where i_l is the current at the given pH and i_d is the current in the pH region where the acid is the only form present) is linear with slope -1. If the rate-limiting protonation is followed by another fast protonation before the electrode reaction proper, the slope should have the value -2 if the pH is greater than the pK_a corresponding to the rate-determining protonation. Analysis of the curves of Figures 4 and 5 shows that a single proton is gained. This eliminates mechanisms involving reaction couple 5.

The rate constant k_p for this relatively slow protonation may be computed[9] from the value of the pK_a determined potentiometrically and $[H^+]$ where the observed limiting current is one-half of the current corresponding to one-electron reduction

$$k_p = 1.27\frac{K_a}{[H^+]^2 t_l}$$

where t_l is the drop time. The rate constant for dissociation k_d is K_a/k_p.

(9) J. Koutecky, quoted in ref 7, pp 360–365; *Collection Czech. Chem. Commun.*, 18, 597 (1953).

In the H_3TOH case, the rate constants for dissociation and recombination are, respectively, $k_d \approx 3\ \mathrm{sec}^{-1}$ and $k_p = 2 \pm 1 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$.

As will be discussed below, comparison of the properties of complexes of ligands with and without the alcohol functional group indicate that this acid–base change involves loss of the proton from this group. For this reason, we postulate that the mechanism of the over-all reduction is

$$[Cr^{III}(OH)TOH]^- \underset{k_p\ \text{slow}}{\overset{k_d}{\rightleftarrows}} [Cr^{III}(OH)TO]^{-2} + H^+ \quad pK_a = 9.85 \quad (7)$$

$$[Cr^{III}(OH)TOH]^- + e^- \langle\!=\!\rangle [Cr^{II}(OH)TOH]^{-2}$$
$$[Cr^{II}(OH)TOH]^{-2} + H^+ \underset{\text{fast}}{\rightleftarrows} [Cr^{II}(H_2O)TOH]^- \quad (4)$$

N-(2-Hydroxycyclohexyl)ethylenediaminetriacetic Acid Complexes. The pK of the first deprotonation of $[Cr^{III}(H_2O)XOH]^0$ is 4.0. This is already in the region where reduction is influenced by hydrogen evolution and decomposition of the Cr(II) complex. There is a suggestion of a trend to independency of $E_{1/2}$ of pH around pH 4, and it is possible to extrapolate from the analogy with the N-(2-hydroxyethyl)ethylenediaminetriacetic acid complex the value for the reversible $E_{1/2}$ for the reduction

$$[Cr^{III}(H_2O)XOH]^0 + e^- \langle\!=\!\rangle [Cr^{II}(H_2O)XOH]^- \quad E_{1/2} = -1.1\ \mathrm{v} \quad (8)$$

The polarographic behavior of the complex in the region of second deprotonation is similar to that of N-(2-hydroxyethyl)ethylenediaminetriacetic acid and the discussion of the probable mechanism is also similar.

$$Cr^{III}(OH)XOH]^- \underset{k_p}{\overset{k_d}{\rightleftarrows}} [Cr^{III}(OH)XO]^{-2} + H^+ \quad pK = 9.05 \quad (9)$$

$$[Cr^{III}(OH)XOH]^- + e^- \langle\!=\!\rangle [Cr^{II}(OH)XOH]^{-2} \quad (10)$$

The values found are $k_p = 5 \times 10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_d = 4 \times 10\ \mathrm{sec}^{-1}$.

Ethylenediaminetetraacetic Acid Complexes. Above pH 11, the reduction wave of the Cr(III) complex of this ligand collapses in a manner qualitatively similar to that shown in Figures 4 and 5; however, with the important difference that the limiting current is diffusion controlled throughout. The pH at which the wave has collapsed to half its original height is the same (12.25) as the value of a pK_a determined spectrophotometrically by Furlani.[10] On the basis of a consideration of the spectra, Furlani proposes that this acidity corresponds to insertion of an OH^- ion into the coordination sphere of Cr(III). If, as would be expected, this change were slow with respect to diffusion, agreement of polarographic and spectrophotometric determinations of pK_a should follow; also the wave should be diffusion controlled at all pH values.

N-Phenethylethylenediaminetriacetic Acid Complexes. The dependence of $E_{1/2}$ on pH in very acidic solutions corresponds approximately to a gain of two protons per electron exchanged

$$[Cr^{III}(H_2O)Z]^0 + e^- + 2H^+ \rightleftarrows Cr^{+2} + H_2Z^- + H_2O \quad (11)$$

Spectrophotometric and potentiometric titrations indicate that the first deprotonation takes place with a pK

(10) See footnote *c*, Table II.

of 6.5, which is in good agreement with the pH value of the intersection of linear portions of a $E_{1/2}$ *vs.* pH plot. In the pH region 4–6, a simple reduction

$$[Cr^{III}(H_2O)Z]^0 + e^- \rightleftharpoons [Cr^{II}(H_2O)Z]^- \quad E_{1/2} = -1.24 \text{ v} \quad (12)$$

takes place. Above pH 7, the reaction is the reduction of the deprotonated species with protonation

$$[Cr^{III}(OH)Z]^- + e^- + H^+ \rightleftharpoons [Cr^{II}(H_2O)Z]^- \quad (13)$$

The extinction coefficient of the first band of the Cr(III) complex of H_3Z decreases markedly over the pH range 11.5–12.5. The extinction coefficient of the second band decreases over the pH range 10.5–12, but remains constant from 12 to 12.5. Above pH 10, the height of the reduction wave decreases with increasing pH, and the limiting current is diffusion controlled like that of the H_3QCOOH complex and not kinetically controlled like the complexes of H_3TOH or H_3XOH. The half-wave potential remains constant above pH 11.5. The following scheme provides a consistent explanation for these observations

$$[Cr^{III}(HO)Z]^0 \langle\!=\!\!=\!\rangle [Cr^{II}(OH)Z]^- \quad E_{1/2} = -1.49 \text{ v} \quad (14)$$

$$[Cr^{III}(OH)Z]^0 + H_2O \rightleftharpoons [Cr^{III}(OH)_2Z]^- + H^+ \quad pK_a = 11.7 \quad (15)$$

$$[Cr^{III}(OH)_2Z]^- \rightleftharpoons [Cr^{III}(OH)_3Z]^{-2} \quad pK_a = 12.2 \quad (16)$$

$$[Cr^{II}(H_2O)Z]^- \rightleftharpoons [Cr^{II}(OH)Z]^{-2} + H^+ \quad pK_a = 11.0 \quad (17)$$

The rate of the reverse reaction 15 is slow with respect to diffusion, and therefore the limiting current is diffusion controlled throughout, and $E_{1/2}$ can be evaluated. The existence of reaction 16 makes it difficult to compare polarographic and spectrophotometric values for the pK of reaction 15, but both sets of data are consistent with the value of 11.8. A species analogous to the product of reaction 16 has been reported in the Fe(III)–EDTA system.[11]

The acid–base changes near pH 12 for the H_3Z and H_3QCOOH complexes cannot be associated with dissociation of a ligand proton, since all of these are lost in acid solution for these two complexes. Addition of an OH^-, either by increase of coordination number of Cr(III) or by opening a chelate ring with or without rupture of a Cr–O bond, must be invoked.

The complexes of the ligands, H_3TOH and H_3XOH, which have an –OH functional group, lose a proton with K_a two orders of magnitude larger than those of ligands without a fourth replaceable proton. The rates of the associated protonations are of the order of magnitude ($\sim 10^{10}$ M^{-1} sec^{-1}) accessible to polarographic measurement. The rate constants for dissociation referred from these are less than 10^2 sec^{-1}.

These considerations leads us to postulate that, for the H_3TOH and H_3XOH complexes, the proton lost near pH 10 is that of the OH group. It is possible but not necessary that these reactions involve closure of an additional chelate ring. The observation that the rates of protonation associated with these changes are too slow to measure polarographically is consistent with this interpretation, as are the spectra.

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(11) R. Skockdople and S. Chaberek, *J. Inorg. Nucl. Chem.*, **11**, 222 (1960).

An Inorganic Analog of Nitrogen Reductase

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Abstract: The platinum hydride $(Et_3P)_2PtHCl$ reacts with a diazonium salt in much the same way that a reducing enzyme is thought to react with a metal complex of N_2 in a biological system. The initial adduct, $[ArN{=}NHPtCl(PEt_3)_2]^+$, is reduced by $Na_2S_2O_4$ or H_2 to give $[ArNHNH_2PtCl(PEt_3)_2]^+$, $ArN_2H_4^+ + (Et_3P)_2PtHCl$, and $ArNH_2 + NH_4^+$ in successive steps. The close analogy between this reduction and that occurring in nitrogen-fixing bacteria is consistent with the presence of a metal hydride in the biological system. A spectroscopic comparison of the two known classes of arylazometal complexes, $ArN{=}NPtCl(PEt_3)_2$ and $ArN{=}NMo(CO)_2C_5H_5$, suggests a higher N=N bond order in the molybdenum complexes.

Recent studies of biological nitrogen fixation have provided strong evidence for the involvement of transition metal ions. A protein fraction in cell-free extracts of *Azotobacter vinelandii* has the ability to reduce molecular nitrogen to ammonia.[1,2] This enzyme system, which contains both molybdenum and iron, has at least two forms of activity. When supplied with adenosine triphosphate (ATP) and reducing potential (as $Na_2S_2O_4$ or reduced ferredoxin), the enzyme solutions evolve hydrogen. If N_2 is added to the solution, hydrogen evolution slows and ammonia forms. Metal ion involvement in these distinct hydrogenase and nitrogenase functions has been shown by inhibition experiments. Strong-field monodentate ligands, such as CO, inhibit nitrogen reduction but not hydrogen evolution.

(1) W. A. Bulen, R. C. Burns, and J. R. Lecomte, *Proc. Natl. Acad. Sci. U. S.*, **53**, 532 (1965).
(2) R. W. F. Hardy and E. Knight, Jr., *Biochim. Biophys. Acta*, **122**, 520 (1966).