electron than acquiring the first. More specifically, we suspect that the radical, like the parent pyridine, is essentially aromatic in character, with all bonds within the ring nearly the same length, whereas in the transition state leading to the two-electron product, the distinction between single and double bonds ultimately appearing in the dihydro ring has begun to develop.

In summary, by considering the distortions in the kinetic curves obtained from catalyzed electron-transfer reactions, we have estimated specific rates for the individual processes resulting in deterioration of the catalysts. We have further found that N-methylation of dimethyl 2,4-pyridinedicarboxylate yields an extraordinarily active, although fragile, catalyst, whereas methylation of the parent dicarboxylic acid results in a catalyst unusually resistant to attrition without sacrifice of its reactivity. For a more detailed picture of the differences between the individual catalysts under reducing conditions, it is likely that electrochemical studies in cobalt-free systems will be informative. Continuing work is in this direction.[17,18]

Acknowledgment. We are indebted to Professors John Gordon and Milton Manes for valuable discussions.

Registry No. I, 499-80-9; II, 25658-36-0; III, 72121-35-8; IV, 75475-96-6; V, 65878-79-7; py$(NH_3)_5Co^{III}$, 31011-67-3; Eu^{II}, 16910-54-6.

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[17] A referee asks whether processes analogous to those described are present in biological electron-transport chains. Fanchiang[2b] has noted points of similarity and also has indicated[18] briefly where substantial areas of difference lie.

[18] Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1138 (1978).

Contribution from the Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania 15260

Coordination Rearrangement Controlled Electron Transfer. 5. Formation of V(III)-Ti(IV) and Ti(III)-Ti(IV) Binuclear Complexes in the Cross Reaction of Ti(hedta) and VO(hedta)⁻ [1]

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A twist mechanism or dissociative process involving rupture of a carboxylato–Ti^{III} bond in $Ti(hedta)(H_2O)$ limits the rate of oxidation of $Ti(hedta)(H_2O)$ by $VO(hedta)^-$ ($hedta^{3-}$ is the ligand *N*-(hydroxyethyl)ethylenediaminetriacetate). The electron-transfer step is outer sphere; a binuclear species containing Ti(IV) and V(III) appears by a substitution reaction after the electron-transfer step. The limiting redox process is first order in $[Ti(hedta)(H_2O)]$ alone with $k_{obsd} = 73.6 \pm 5.0\ s^{-1}$ ($\mu = 0.50$ (NaCl), pH 5.0, acetate buffer, $T = 25.2\ °C$). Relaxation studies reveal a ring opening of a glycinato fragment of the $hedta^{3-}$ ligand for $Ti(hedta)(H_2O)(OH)^-$ which proceeds by an inverse hydrogen ion pathway ($k_1 = 1.92 \times 10^{-4}\ M\ s^{-1}$) and reverse ring closure ($k_0 = 6.2\ s^{-1}$). A slower monomerization reaction involving a binuclear $Ti^{III}{}_2(hedta)_2$ complex is detectable. The monomerization of the binuclear complex saturates in $[H_3O^+]$. The magnitudes of the kinetic constants support a proton-scavenging mechanism involving a monohydroxy-bridged, strained intermediate with a rate-limiting bond-rupturing process of $0.33\ s^{-1}$. The formation of a new $Ti^{III}Ti^{IV}$ binuclear complex occurs with a second-order constant of $(3.12 \pm 0.42) \times 10^2\ M^{-1}\ s^{-1}$ in competition with the dominant outer-sphere cross reaction involving $Ti(hedta)(H_2O)$ and $VO(hedta)^-$. The species appears blue to the eye ($\lambda_{max} \simeq 800$ nm, $\epsilon = 47\ M^{-1}\ cm^{-1}$); the identical $Ti^{III}Ti^{IV}(hedta)_2$ complex may be prepared by autoxidation of $Ti(hedta)(H_2O)$. The $Ti^{III}Ti^{IV}$ ion is thermodynamically unstable at pH 4.0. Above pH 4.0 the dissociation of $Ti^{III}Ti^{IV}$ occurs by a first-order process ($k \simeq 0.14\ s^{-1}$) producing the redox-active isomer of $Ti(hedta)(H_2O)$. $Ti^{III}Ti^{IV}$, prepared by combination of thermally equilibrated samples of $Ti(hedta)(H_2O)$ and $TiO(hedta)^-$, forms by a different path dependent only on [Ti(IV)] ($k = 3.4 \pm 0.1\ s^{-1}$). The initial products of the $Ti(hedta)(H_2O)/VO(hedta)^-$ cross reaction are $TiO(hedta)^-$ and $V(hedta)(H_2O)$. These products combine at a rate of $23\ M^{-1}\ s^{-1}$ to form a third binuclear species $Ti^{IV}V^{III}(hedta)_2$ having a charge-transfer maximum at 453 nm ($\epsilon = (3.8 \pm 0.1) \times 10^2\ M^{-1}\ cm^{-1}$). The formation constant for this orange Ti(IV)–V(III) complex is $5.0 \times 10^2\ M^{-1}$ ($\mu = 0.50$ (NaCl), $T = 25.0\ °C$). A binuclear species which contains the reverse oxidation state assignment $Ti^{III}–V^{IV}$ is detected competitively early in the cross reaction with a rate of formation of $(1.23 \pm 0.14) \times 10^4\ M^{-1}\ s^{-1}$. However this species is not the precursor complex of the orange $Ti^{IV}V^{III}(hedta)_2$ complex; the $Ti^{III}–V^{IV}$ species is nonproductive for inner-sphere electron transfer.

Introduction

Recent reports have shown a chemistry for $Ti(edta)(H_2O)^-$ as a reducing agent parallel to the features of $Ti(H_2O)_6{}^{3+}$.[2] $Ti(H_2O)_6{}^{3+}$ is the most strongly reducing d^1 aquo ion; the $edta^{4-}$ complex of Ti(III) is even more powerful.[3] A diverse group of inorganic oxidants have been used to determine the mechanistic aspects of reductions with $Ti(H_2O)_6{}^{3+}$. These have included nonmetal acceptors (I_2, ClO_4^-),[4] simple aquo and oxo cationic oxidants (Hg^{2+}, Fe^{3+}, VO^{2+}, $VO_2{}^+$, $UO_2{}^{2+}$),[5,6] outer-sphere oxidants ($Co(NH_3)_6{}^{3+}$, $Co(bpy)_3{}^{3+}$, $Co(terpy)_2{}^{3+}$, $Ru(NH_3)_6{}^{3+}$, $Ru(NH_3)_5Cl^{2+}$),[7,8] and Co(III) oxidants which have a potential bridging ligand in $(NH_3)_5CoX^{3-n}$ ($X^{n-} = F^-$,

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[1] Parts of this paper were presented previously at the National Meeting of the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979.

[2] G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **18**, 2025 (1979).

[3] W. M. Latimer, "Oxidation Potentials", 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952.

[4] (a) D. M. Yost and S. Zabaro, *J. Am. Chem. Soc.*, **48**, 1181 (1926); (b) F. R. Duke and P. R. Quinney, *ibid.*, **76**, 3800 (1954).

[5] (a) R. Critchley and W. C. E. Higginson cited by A. G. Sykes, "Kinetics of Inorganic Reactions", Pergamon Press, New York, 1970, pp 208–209; (b) M. Matusek and A. Tockstein, *Collect. Czech. Chem. Commun.*, *34*, 316 (1969).

[6] (a) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537 (1973); (b) J. D. Ellis and A. G. Sykes, *ibid.*, 2553, (1973), and references therein; see also J. P. Birk and T. P. Logan, *Inorg. Chem.*, **12**, 580 (1973); (c) J. P. Birk and T. P. Logan, *ibid.*, **12**, 2464 (1973).

[7] A. Bakac, R. Marec, and M. Orkanovic, *Inorg. Chem.*, **16**, 3133 (1977).

[8] (a) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976); (b) K. M. Davies and J. E. Earley, *ibid.*, **17**, 3350 (1978); (c) A. Adejite, J. E. Earley, and J. F. Ojo, *ibid.*, **18**, 1535 (1979); (d) P. Chalilpoyil, K. M. Davies, and J. E. Earley, *ibid.*, **16**, 3344 (1977).

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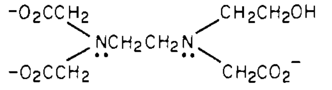
Cl^-, Br^-, I^-, H_2O, SO_4^{2-}, NCS^-, N_3^-, dicarboxylic acids, substituted pyridines, and substituted benzoic acids).[9,10] Two important factors are found for $Ti(H_2O)_6^{3+}$ as a reductant: (1) $Ti(H_2O)_5OH^{2+}$ is the more reactive species for both inner-sphere and outer-sphere reductions and (2) Ti(III) prefers hard bridging ligands (F^-, N_3^-, O donors with chelation) to promote a favorable inner-sphere redox process. The closer resemblance of $Ti(H_2O)_5OH^{2+}$ to the Ti(IV) product is considered to be the source of the greater reactivity of the hydroxy form as compared to the aquo species. The Ti(IV) product is formulated as TiO^{2+}, but it may be further hydrolyzed or polymeric depending upon the acidity.

The requirement for hard bridging ligands to promote an inner-sphere path for $Ti(H_2O)_6^{3+}$ is also found for $Ti(edta)(H_2O)^-$ with the $(NH_3)_5CoX^{3-n}$ series.[2] We have completed several studies which have been aimed at the effect of chelating ligands in controlling the reactivities of reductants and oxidants through elimination of hydrolysis problems that often dominate the observations of the simple aquo ion reagents.[11-14] *N*-(Hydroxyethyl)ethylenediaminetriacetate (I) has



I

proven to be an important ligand for many of these studies. The commonly accepted abbreviation for I is $hedta^{3-}$.[38] This notation is used throughout this paper. The ligand abbreviation $hedta^{3-}$ should not be confused with the monoprotonated ethylenediaminetetraacetate species, $Hedta^{3-}$. These studies have revealed that chelate rearrangements about the metal center and ring openings at the metal center can be rate limiting for electron-transfer reactions. Chelate rearrangements are rate controlling in the inner-sphere cross reaction of $VO(hedta)^-$ and $V(hedta)(H_2O)^-$,[11,12] in the proton-promoted intramolecular electron transfer with the $(NH_3)_5RuOV(hedta)^+$ complex,[13] and in the outer-sphere oxidation of $VO(hedta)^-$ by $Mn(edta)(H_2O)^-$.[14] We wish to report on the cross reaction between $Ti(hedta)(H_2O)$ and $VO(hedta)^-$. This reaction occurs by an outer-sphere path which appears to be limited by an isomerism of $Ti(hedta)(H_2O)$ into a form structurally compatible with the $TiO(hedta)^-$ product. Two new binuclear ions, having a charge-transfer interaction due to mixed oxidation states, have been detected at two steps during the overall reaction. These are $Ti^{III}Ti^{IV}(hedta)_2$ and $Ti^{IV}V^{III}(hedta)_2$. The affinity of Ti(III) for other metal centers, either as a kinetically active intermediate species or in binuclear products, appears to be related to the hardness of the bridging ligands, which is in concert with trends found for $Ti(H_2O)_6^{3+}$ and $Ti(edta)(H_2O)^-$.

Experimental Section

Kinetic Measurements. Data were collected on a Durrum D-110 stopped-flow spectrophotometer under anaerobic conditions as described previously.[15] Data analysis was carried out either in an on-line fashion with a DEC-1103 interfaced computer or by a point-by-point data reduction of the absorbance–time curves from photographs of a Tektronics storage oscilloscope. The photographic method was particularly important for determination of the time range of the sequential reactions involving $Ti(hedta)(H_2O)$ and $VO(hedta)^-$, as well as the binuclear species formed during this reaction. Data reduction was achieved with use of appropriate first- and second-order kinetic programs on floppy magnetic disks or by hand with use of the familiar rate laws.

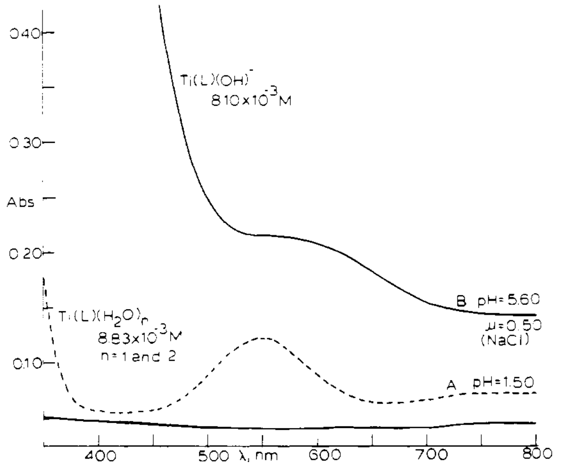


Figure 1. Electronic solution spectra of Ti(hedta) solutions: (A) pH 1.50, $[Ti(III)]_{tot} = 8.83 \times 10^{-3}$ M, L = $hedta^{3-}$, $\mu = 0.50$ (NaCl), $T = 25$ °C; (B) pH 5.60, $[Ti(hedta)(OH)^-] = 8.10 \times 10^{-3}$ M, $\mu = 0.50$ (NaCl), $T = 25$ °C.

UV–Visible Spectra. Spectra were obtained on a Varian-Cary 118C spectrophotometer with a thermostated sample compartment. Spectra were obtained in cells that were purged with N_2 or Ar gas, which had been scrubbed through Cr(II) solutions. Cells were sealed by rubber septa, and solution transferals were achieved by standard procedures using gastight, preflushed syringes.[16]

Solutions. A weighed sample of $TiCl_3$ (Alfa) was dissolved in 0.60 M HCl. Insoluble materials were removed by filtration, and the total titanium was converted to Ti(III) by reduction of residual Ti(IV) over Zn/Hg for at least 3 h.[17] The analysis for $Ti(H_2O)_6^{3+}$ was made at 502 nm ($\epsilon = 3.97$ M^{-1} cm^{-1}). Ti(IV) may be analyzed according to the procedure of Sykes.[18] The $Ti(H_2O)_6^{3+}$ stock solution was prepared at 0.3 M and stored over Zn/Hg. $Ti(hedta)(H_2O)$ solutions were prepared immediately prior to use in order to prevent loss of Ti(III) titer. Appropriate aliquots of $Ti(H_2O)_6^{3+}$ were combined with H_3hedta of a mass equal to ca. 2 times the amount of Ti(III) in order to ensure chelation of both Ti(III) and Zn^{2+}.

The $VO(hedta)^-$ solutions were prepared as described previously.[11,13] The solutions of $TiO(hedta)^-$ were prepared by oxidation of $Ti(hedta)(H_2O)$ by bubbling the solution with a rapid stream of O_2. No peroxo species, $Ti(O_2)(hedta)^-$, was detected as a product in contrast to the $Ti(O_2)(edta)^{2-}$ complex which is formed in the autoxidation of $Ti(edta)(H_2O)^-$.[19]

$TiO(hedta)^-$-Catalyzed Appearance of $Ti^{III}Ti^{IV}(hedta)_2$. The appearance of a transient species during the cross reaction of $Ti(hedta)(H_2O)$ and $VO(hedta)^-$ was followed as a function of $[TiO(hedta)^-]$. The changing concentration of $TiO(hedta)^-$ brought about by the net redox reaction required a method to calculate the average concentration of $TiO(hedta)^-$ during the time interval corresponding to the aborbance changes due to the transient species. Addition of $TiO(hedta)^-$ caused an enhancement in the rate over the time interval shown by letter b in Figure 4. The enhancement in rate was easier to follow at 375 nm since the A_∞ value at 375 nm was more readily determined at the minimum between the decay curve and the onset of the development of a Ti^{III}–V^{IV} binuclear complex in the final, slow reaction. The Ti(IV)-dependent process at 750 nm was more difficult to analyze because of deviations due to the earlier first decay interfering with the early points in the growth part of the absorbance–time curve and

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(9) J. E. Earley and M. Orkanovic, *Inorg. Chem.*, **14**, 1478 (1975); (b) J. P. Birk, *ibid.*, **14**, 1724 (1975); (c) A. G. Sykes and G. A. K. Thompson, *ibid.*, **15**, 638 (1976); (d) A. Adejite and J. F. Ojo, *ibid.*, **16**, 477 (1977).

(10) E. S. Gould and A. H. Martin, *Inorg. Chem.*, **14**, 873 (1975).

(11) F. J. Kristine and R. E. Shepherd, *J. Am. Chem. Soc.*, **100**, 4398 (1978).

(12) F. J. Kristine, D. R. Gard, and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 994 (1976).

(13) F. J. Kristine and R. E. Shepherd, *Inorg. Chem.*, **17**, 3145 (1978).

(14) J. Nelson and R. E. Shepherd, *Inorg. Chem.*, **17**, 1030 (1978).

(15) J. Guardalabene, S. Gulnac, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, **18**, 22 (1979); see also ref 13.

(16) D. Shriver, "Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, 1969, pp 139–205; see also ref 8b, 2, and 25.

(17) Usually the time period for reduction was overnight, ca. 12 h.

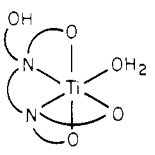
(18) Reference 6a.

(19) F. J. Kristine and R. E. Shepherd, *J. Chem. Soc., Chem. Commun.*, 132 (1980).

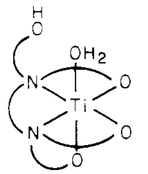
the bleaching process which altered the A_∞ for data in the latter points for the growth process. The data in Table III for 375-nm evaluation showed a linear dependence on the [TiO(hedta)$^-$] present in solution. The [TiO(hedta)$^-$] was taken to be the amount of Ti(IV) added for each study plus 20% of the initial Ti(III) (consumed in the first decay process forming Ti(IV) plus half of the remaining Ti(III), which is ultimately oxidized during the growth and subsequent decay interval). Therefore $[TiO(hedta)^-]_{av}$ throughout any run was estimated as the added concentration plus 60% of the initial Ti(III) concentration.

Results and Discussion

Ti(hedta)(H_2O) Complex. An equimolar mixture of $Ti(H_2O)_6^{3+}$ and H_3hedta, adjusted to pH 3.5, produces a solution of Ti(hedta)(H_2O). The electronic spectrum of Ti(hedta)(H_2O) with only one band, centered at 550 nm (ϵ = 8.6 M^{-1} cm^{-1}), is shown in Figure 1A. The formulation of the Ti^{III}–hedta complex as to the number of coordinated molecules of water has the uncertainties associated with all of the labile transition-metal complexes of the edta family of ligands. It is likely that all the carboxylate–Ti^{III} bonds are labile. Therefore more highly aquated species such as Ti(hedta)$(H_2O)_2$ may exist at low concentrations at equilibrium with Ti(hedta)(H_2O) and serve as kinetically active species. The formulation Ti(hedta)(H_2O) has been assumed for several reasons: (a) the analogous Ti(Hedta)(H_2O) complex is reputed to be quinquidentate;[2,37] (b) all neighboring first-transition series (M = V, Cr, Mn) have hedta^{3-} and edta^{4-} complexes containing a coordinated water position with pendant CH_2CH_2OH or $CH_2CO_2^-$ fragments;[20] (c) the coordinated H_2O in Ti(hedta)(H_2O) may be titrated, altering the visible spectrum above pH 3.5; (d) redox experiments with Ti(hedta)(H_2O) reported in this work imply rates limited by achieving a specific structural isomer for Ti(hedta)(H_2O).[39] It is reasonable to assume that the CH_2CH_2OH group of Ti(hedta)(H_2O) is pendant just as the protonated carboxylate group of Ti(Hedta)(H_2O) is described as being pendant.[37] With the remaining three carboxylates of hedta^{3-} coordinated to Ti(III), there are two reasonable isomeric structures of Ti(hedta)(H_2O) as shown by A and B. Studies with Co(III) complexes of edta-family ligands have shown that chelate ring strain is greater for the "in-plane" rings (two in isomer B) as opposed to the case of the "axial" rings (two in isomer A).[41] Therefore isomer A is anticipated as being more abundant in solutions at equilibrium between isomers A and B.



A



B

It is most likely that the proper formulation of the hydroxy complex is Ti(hedta)(H_2O)(OH)$^-$. The titration data provide no way to unambiguously discern Ti(hedta)(H_2O)(OH)$^-$ from Ti(hedta)(OH)$^-$.[40] Evidence presented later in the discussion of relaxation processes observed upon dilution and pH-jump experiments shows that the Ti(hedta)(H_2O)(OH)$^-$ complex is required to be present in solution to equilibrate monomeric Ti^{III}–hedta complexes with a binuclear Ti(III) species in solution. The equilibrium shown in eq 1 is intended to represent the proper acid dissociation equilibrium whether Ti(hedta)(H_2O)(OH)$^-$ or the ring-closed form, Ti(hedta)(OH)$^-$, is the correct formulation. If both species are present at equilibrium, the measured pK_a for eq 1 is the conditional pK_a defined by

$$-\log \{([Ti(hedta)(H_2O)(OH)^-] + [Ti(hedta)(OH)^-]) \times [H_3O^+]/[Ti(hedta)(H_2O)]\}$$

Table I. pK_a's of Coordinated Water Molecules in M(III) Aquo and hedta^{3-} Complexes

M(III)	pK_a-($M(H_2O)_6{}^{3+}$)	ref	pK_a-(M(hedta)(H_2O))	ref
Ti	2.7	21	4.1	this work
V	2.9	22	6.5	25
Cr	4.0	23	6.1	26
Fe	2.1	24	4.1	27

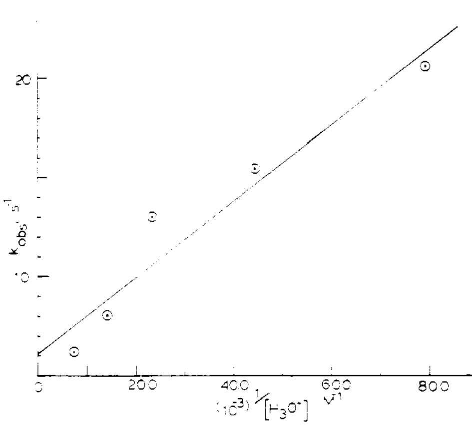


Figure 2. Hydroxide-catalyzed glycinato ring opening on Ti(hedta)(OH)$^-$ ($[Ti(III)]_i$ = 3.65 × 10^{-3} M, $[NaC_2H_3O_2]_{tot}$ = 0.10 M, [NaCl] = 0.40 M, buffer ratios adjusted with $HC_2H_3O_2$, T = 25 °C).

The formation of Ti(hedta)(H_2O)(OH)$^-$ occurs with the appearance of a charge-transfer band which shifts toward the original 550-nm maximum over the range of pH from 3.5 to 6.0. The solution appears dark yellow in this region (Figure 1B). Precipitation begins to occur above pH 6.0; no isosbestic point is observed during titration, which suggests that several species including Ti(hedta)(H_2O)(OH)$^-$ and, perhaps, $[Ti(hedta)(OH)]_2{}^{2-}$ are present. The presence of a binuclear complex is confirmed by pH-jump experiments discussed below. Difficulties due to adsorption of Ti(hedta)(H_2O) on the glass electrode and the competitive equilibria involving the binuclear species made it difficult to determine the pK_a with high precision (eq 1). The value obtained from a titration

$$H_2O + Ti(hedta)(H_2O) \rightleftharpoons \underset{C}{Ti(hedta)(H_2O)(OH)^-} + H_3O^+ \quad (1)$$

curve was 4.1 ± 0.1, which is in reasonable agreement with the spectrophotometric results of 4.4 ± 0.2. Complexation of M(III) ions by hedta^{3-} will generally cause a 2–3 pK_a unit increase above the value for the aquo ion as shown in Table I. The pK_a of $Ti(H_2O)_6{}^{3+}$ is estimated at 2.7;[21] the value of 4.1 for Ti(hedta)(H_2O) is consistent with the usual effect of the presence of the hedta^{3-} ligand.

pH-Dependent Relaxations of Ti(hedta) Solutions. Dilution experiments at nearly constant pH were performed by stop-

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(20) (a) Reference 25; (b) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975); (c) R. E. Hamm and M. A. Suwyn, *ibid.*, **6**, 139 (1967); (d) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed., Wiley-Interscience, New York, 1978, pp 311–317.

(21) C. L. Gregoire and M. R. Paris, *Anal. Chim. Acta*, **42**, 439 (1968); (b) F. Brito and H. Krentzien, *Chem. Abstr.*, **73**, 78656 (1970); (c) ref 8d.

(22) K. B. Yatsimirskir and V. P. Vail'ev, "Instability Constants of Complex Compounds", Pergamon Press, Elmsford, N.Y., 1960; see also ref 24.

(23) (a) Reference 22; (b) ref 3.

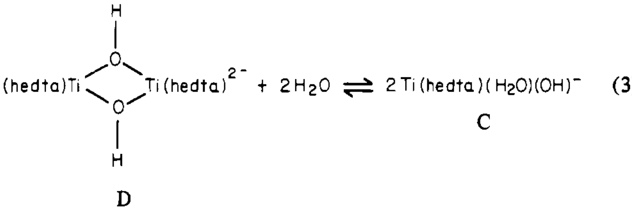
(24) J. Bjerrum, G. Schwartzenbach, and L. G. Sillen, Eds., "Stability Constants of Metal-Ion Complexes", The Chemical Society, London, 1958, Part II, pp 53–54.

ped-flow mixing the Ti(hedta)(H_2O) solution, adjusted to a given pH in the range 4.0–5.0, into a nearly identical acetate buffer, such that $\Delta pH \leq 0.5$. The rapid dilution into a nearly identical buffer produced two relaxation reactions. The first process increases the total absorbance; the second decreases the absorbance. The initial change occurs with an apparent first-order relaxation of ca. 25 s^{-1} (pH 5.0) and the second with 0.23 s^{-1}. The first relaxation process was found to be dependent on $1/[H_3O^+]$ while the second saturates in $[H_3O^+]$. The inverse hydrogen-ion-dependent step is consistent with formation of a monoaquo–monohydroxy Ti(hedta) species as in eq 2. A simple relaxation between Ti(hedta)(H_2O) and

$$\mathrm{Ti(hedta)(H_2O) + OH^- \rightleftharpoons Ti(hedta)(H_2O)(OH)^-} \quad (2)$$

Ti(hedta)$(OH)^-$ would be diffusion limited and too fast for stopped-flow detection. The relaxation data for reaction 2 in the pH range 4.0–5.0 are given in Figure 2. The origin of the catalysis by OH^- for loss of one of the coordinated acetato groups of $hedta^{3-}$ is probably due to the labilization effect of OH^- in the M(hedta)$(OH)^-$ complex compared to that in M(hedta)(H_2O).[28] The observed rate law $k_0 + k_1/[H_3O^+]$, with $k_0 = 6.2 \pm 0.3$ s^{-1} and $k_1 = 1.92 \times 10^4$ M s^{-1}, suggests an approach to equilibrium formation of Ti(hedta)(H_2O)$(OH)^-$. The k_0 term is most likely associated with the reverse of eq 2, the ring closure step of a pendant carboxylate of $hedta^{3-}$ in the Ti(hedta)(H_2O)$(OH)^-$ species, followed by rapid protonation of the coordinated hydroxide by a solvent molecule. The k_1 term is associated with the forward reaction of eq 2. Hydrolysis forming initially Ti(hedta)$(OH)^-$ followed by titanium(III) carboxylate ring opening and aquation are indicated for the k_1 pathway. The ratio k_1/K_wk_0 is the equilibrium constant for eq 2. The value calculated from the kinetically determined constants is 3.1×10^9 M^{-1}. If eq 2 is combined with the autoprotolysis equilibrium of water, eq 1 is obtained. Therefore k_1/k_0 yields a kinetically determined K_a for Ti(hedta)(H_2O) of 3.1×10^{-5} or pK_a of 4.5. This value is in excellent agreement with the direct titration value of 4.1 ± 0.1 or the spectrophotometric titration of 4.4 ± 0.2. These results support the formulation of Ti(hedta)(H_2O)$(OH)^-$ as being the proper one for the main Ti^{III}(hedta)–hydroxy monomer species in solution.

The slower relaxation process ($k \approx 0.23$ s^{-1}) is appropriate for the monomerization process of a $Ti^{III}Ti^{III}(hedta)_2$ binuclear complex by an acid-catalyzed pathway (eq 3). A similar



$$\mathrm{(hedta)Ti(\mu\text{-}OH)_2Ti(hedta)^{2-} + 2H_2O \rightleftharpoons 2Ti(hedta)(H_2O)(OH)^-} \quad (3)$$

D C

monomerization path is known for the analogous V(III) binuclear ion and for $(Fe(hedta))_2O^{2-}$.[25,27] The observed rate constant for the slower process saturates in $[H_3O^+]$ as shown by the double-reciprocal plot in Figure 3; the dependence of $1/k_{obsd}$ vs. $1/[H_3O^+]$ is linear. There are two schemes which have previously been suggested for the acid-catalyzed monomerization reactions. These are the preequilibrium protonation (Mechanism I) and the proton-assisted rupture of a strained chemical structure (Mechanism II). Both of these mechanisms provide identical mathematical rate forms.[25] (In the mechanisms shown here D is the binuclear complex and D* is a strained structure of D.)

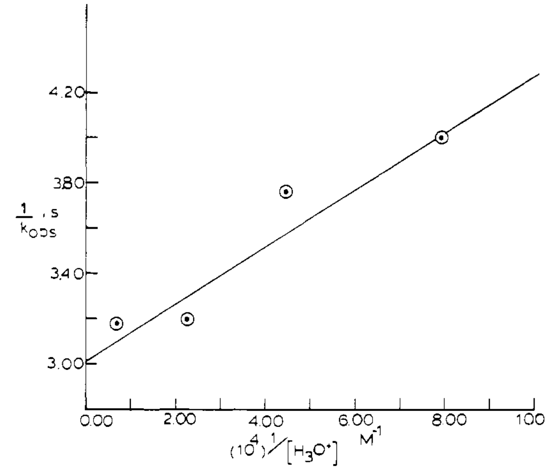


Figure 3. Acid-dependent monomerization of $(Ti(hedta)(OH))_2^{2-}$ (concentration conditions identical with those for Figure 2).

Mechanism I

$$\mathrm{D + H_3O^+ \overset{K}{\rightleftharpoons} DH^+ + H_2O} \quad \text{(i)}$$

$$\mathrm{D \xrightarrow{k_{ii}} monomers} \quad \text{(ii)}$$

$$\mathrm{DH^+ \xrightarrow{k_{iii}} monomers} \quad \text{(iii)}$$

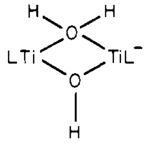
Mechanism II

$$\mathrm{D \overset{K'}{\rightleftharpoons} D^*} \quad \text{(iv)}$$

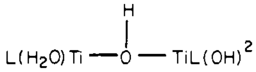
$$\mathrm{D^* \xrightarrow{k_v} monomers} \quad \text{(v)}$$

$$\mathrm{H_3O^+ + D^* \xrightarrow{k_{vi}} monomers} \quad \text{(vi)}$$

The reciprocal of the slope of Figure 3 corresponds to a second-order rate constant of a



species undergoing a Mechanism I monomerization process of 8.0×10^4 M^{-1} s^{-1} compared with 2.5×10^3 M^{-1} s^{-1} for the analogous V(III) system. However the value determined for a preequilibrium association constant (based on the intercept of Figure 3) is calculated as 2.4×10^5 M^{-1}. This value appears to be much too large to be reasonable for a preequilibrium protonation path. Values of 7.8 M^{-1} for the V(III) analogue[25] and 43 M^{-1} for a related Co(III) complex have been determined. On these grounds the monomerization process seems to be best described by proton scavenging of a strained or partially broken structure of the Mechanism II variety, with a bond-rupturing process of 0.33 s^{-1} at saturation. Therefore a better description of the $[Ti(hedta)(OH)]_2^{2-}$ intermediate involved in the step which saturates in $[H_3O^+]$ appears to be a partially bond-broken form in which the distorted dihydroxy structure is virtually equivalent to a monohydroxy-bridged aquo species, e.g.



$$\mathrm{L(H_2O)Ti{-}O(H){-}TiL(OH)^{2-}}$$

Martell has proposed a similar species in the monomerization of the Fe(III) analogue.[31]

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[25] F. J. Kristine and R. E. Shepherd, *J. Am. Chem. Soc.*, **99**, 6562 (1977).

[26] Reference 20b.

[27] (a) H. J. Schugar, A. T. Hubbard, F. C. Anson, and H. B. Gray, *J. Am. Chem. Soc.*, **91**, 71 (1969); (b) R. L. Gustafson and A. E. Martell, *J. Phys. Chem.*, **67**, 576 (1963).

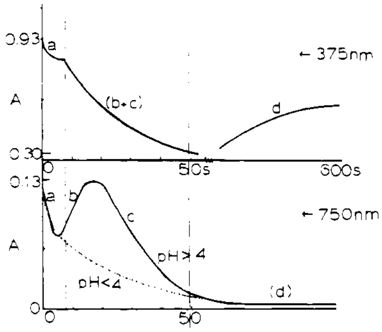


Figure 4. Appearance of stopped-flow absorbance–time data for the Ti(hedta)(H_2O)/VO(hedta)$^-$ cross reaction: (a) initial decrease region; (b) growth region for forming $Ti^{III}Ti^{IV}$; (c) oxidation region for $Ti^{III}Ti^{IV}$; (d) formation region of $Ti^{IV}V^{III}$ ($[Ti(III)]_i = [V(IV)]_i = 1.97 \times 10^{-3}$ M, $\mu = 0.50$ (NaCl), $T = 25.2$ °C).

Table II. Kinetics of the Fast Absorbance Change in the Ti(hedta)(H_2O)/VO(hedta)$^-$ Reaction^a

$10^3[Ti(III)]_i$, M	$10^2[V(IV)]_i$, M	10^2k_{obsd}, s^{-1}
1.99	1.04	2.00
1.97	1.72	3.01
1.99	1.96	3.19
1.77	2.11	3.27

^{a} $\mu = 0.50$ (NaCl), $T = 25.2$ °C.

Cross Reaction of Ti(hedta)(H_2O) and VO(hedta)$^-$. Examination of the spectra of the reactants and the products at various pH values revealed that at pH ≥4.5 the rate could be successfully monitored by the changes in the charge-transfer feature of Ti(hedta)(H_2O)(OH)$^-$ at 375 nm. Three distinct absorbance changes are observed when Ti(hedta) and VO(hedta)$^-$ are combined in a stopped-flow cuvette under these conditions. When $[VO(hedta)^-] \simeq 10^{-2}$ M and $[Ti(hedta)]_{tot} \simeq 10^{-3}$ M, the first two chemical processes are complete in 30 s. The final absorbance change proceeds at a much lower rate with a detectable increase. The approximate appearance of the sequential absorbance–time curves as monitored at 375 and 750 nm is shown in Figure 4. The appearance of these curves under different pH conditions, and at different wavelengths in the same time domain, is essential in establishing the various events described in the following sections. The results are summarized in Scheme I (discussed later). The final slow growth is detectable beginning about 1 min after mixing and continues to completion in about 10 min. The final reaction is the formation of the orange binuclear Ti(IV)–V(III) ion at equilibrium with its monomer complexes V(hedta)(H_2O) and TiO(hedta)$^-$; this is discussed in a later section.

The initial process that occurs after mixing exhibits a rapid decrease in absorbance at 375 nm. The observed decrease depends on $[VO(hedta)^-]_i$ as shown in Table II. The first reaction amounts to about 20% of the total decrease in absorbance for the two initial reactants as detected at 375 nm. The data in Table II show a linear relationship (eq 4) between

$$k_{obsd} = k_0' + k_1'[VO(hedta)^-]_i \qquad (4)$$

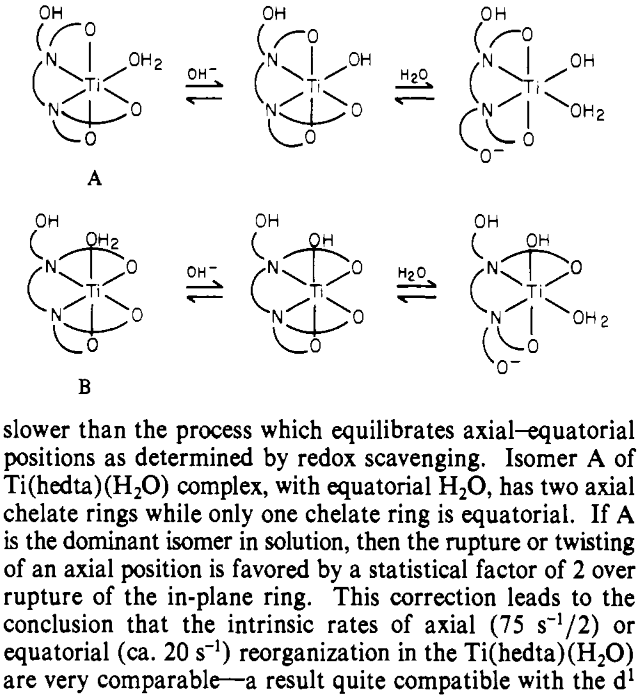
k_{obsd} and $[VO(hedta)^-]_i$ with V(IV) in excess. The value of k_0' is found to be 77 ± 25 s^{-1} and $k_1' = (1.23 \pm 0.14) \times 10^4$ M^{-1} s^{-1}. The same time interval was monitored at 750 nm where a decrease in absorbance due to consumption of V(IV), stoichiometrically equal to the consumption of Ti(III), is observed. At 750 nm, even under conditions where $[VO(hedta)^-]_i = [Ti(hedta)(H_2O)]_i$, the absorbance loss showed a first-order rate decrease with $k_{obsd} = 73.6 \pm 5.0$ s^{-1} ($\mu = 0.50$, $T = 25.2$ °C). When these results are considered together with the dependence of eq 4, one must conclude that the k_0' term detected at 375 nm and the value of k_{obsd} at 750 nm reflect the same chemical process, i.e., one solely dependent upon the [Ti(hedta)(H_2O)]. Hence a step that limits the rate of electron transfer between Ti(hedta)(H_2O) and VO(hedta)$^-$ is controlled by a chemical change at the Ti(III) center alone. These observations are accountable by the redox scavenging of one solution isomer but not the other as shown in eq 5 and 6. The

$$\underset{\text{isomer A}}{Ti(hedta)(H_2O)} \overset{k_{lim}}{\rightleftharpoons} \underset{\text{isomer B}}{Ti(hedta)(H_2O)} \qquad (5)$$

$$\underset{\text{isomer B}}{Ti(hedta)(H_2O)} + VO(hedta)^- \xrightarrow{\text{fast}} TiO(hedta)^- + V(hedta)(H_2O) \qquad (6)$$

isomerism process most likely involves the axial chelate ring rupture or a twist mechanism which converts isomer A into isomer B. It is likely that TiO(hedta)$^-$ has the oxo ligand in the "axial" position similar to the arrangement in isomer B or the VO(hedta)$^-$ complex, which possesses the pseudo-square-pyramidal structure.[29,30] And it follows that the pH-dependent ring opening found by the relaxation method must involve a process other than the axial–equatorial interchange which equilibrates isomers A and B.

We wish to suggest that the relaxation process which involves monomeric Ti(hedta)(H_2O) should be assigned to the equatorial chelate ring rupture as shown here for isomers A and B. The first-order process at pH 5.0 is about 3 times



slower than the process which equilibrates axial–equatorial positions as determined by redox scavenging. Isomer A of Ti(hedta)(H_2O) complex, with equatorial H_2O, has two axial chelate rings while only one chelate ring is equatorial. If A is the dominant isomer in solution, then the rupture or twisting of an axial position is favored by a statistical factor of 2 over rupture of the in-plane ring. This correction leads to the conclusion that the intrinsic rates of axial (75 s^{-1}/2) or equatorial (ca. 20 s^{-1}) reorganization in the Ti(hedta)(H_2O) are very comparable—a result quite compatible with the d^1 configuration of Ti(III).

The unproductive pathway which involves both Ti(III) and V(IV), without a change in oxidation states, may be accounted for due to the substitution lability of Ti(III). The rate of solvent exchange in Ti(edta)(H_2O)$^-$ is estimated at ca. 10^7 s^{-1}, which converts to a second-order rate of ca. 10^4 when the substituting ion has an outer-sphere association constant, K_{os}, of about 10^{-2}–10^{-3}. The magnitude of the required K_{os} constant is compatible with an overall 0/2− pair for Ti(hed-

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(28) References 13 and 8b.

(29) NMR experiments have failed to unambiguously identify the solution structure of TiO(hedta)$^-$ or TiO(edta)$^{2-}$; a solid-state structure of TiO(H_2edta) is in progress. If the preferred structure of TiO(hedta)$^-$ has the oxo ligand trans to the N donor, the roles suggested here for the A and B isomers may be reversed.

(30) J. D. Ellis, G. A. K. Thompson, and A. G. Sykes, *Inorg. Chem.*, **15**, 3172 (1976).

(31) G. McLendon, R. J. Motekaitis, and A. E. Martell, *Inorg. Chem.*, **15**, 2306 (1976).

Table III. Ti(IV)-Accelerated Absorbance Changes at 375 and 750 nm[a]

$10^3[\mathrm{TiO(hedta)^-}]_{\mathrm{av}}$, M	λ, nm	k_{obsd}, s^{-1}
1.18	375	0.322
2.19	375	0.456
3.14	375	0.825
3.15	375	0.700
4.90	375	1.46
1.07	750	0.680
1.09	750	0.710
2.18	750	1.09
2.79	750	1.47
2.95	750	1.53
3.13	750	1.78
4.89	750	2.55

[a] $\mu = 0.50$ (NaCl), $T = 25.2$ °C, $[\mathrm{Ti(III)}]_i = [\mathrm{VI(IV)}]_i = 1.97 \times 10^{-3}$ M, $[\mathrm{TiO(hedta)^-}]_{\mathrm{av}} = [\mathrm{TiO(hedta)^-}]_{\mathrm{added}} + 0.6[\mathrm{Ti(hedta)(H_2O)}]$.

ta)(H_2O)/VO(hedta)$^-$. Substitution to form an oxo-bridged ion having the $\mathrm{Ti^{III}}$–O–$\mathrm{V^{IV}}$ composition, but with the wrong chelate structures favorable for electron transfer, would account for the non-redox-dependent V(IV) path detected by the absorbance decrease at 375 nm. This reaction is given in eq 7. Species wherein bridging occurs between two dissimilar

$$\mathrm{Ti(hedta)(H_2O)} + \mathrm{VO(hedta)^-} \overset{k_1'}{\rightleftharpoons} \underset{\mathrm{E}}{\mathrm{(hedta)TiOV(hedta)^-}} + \mathrm{H_2O} \quad (7)$$

metal ion sites but which do not provide an appropriate electron-transfer pathway are known. The best known example is the cross reaction of $\mathrm{Co(edta)^{2-}}$ with $\mathrm{Fe(CN)_6{}^{3-}}$ studied by Haim et al.[32] and earlier by Wilkins and Huchital.[33] The unusually long lifetime of the $\mathrm{V^{II}V^{IV}}$ binuclear analogue, (hedta)VOV(hedta)$^{4-}$, has been attributed to the ligand reorganizational barrier.[11,12] The accumulation of the bridged species in eq 7 should not cause substantial deviation from first-order kinetics as long as the reverse reaction is $\gtrsim 100$ s^{-1} such that the dissociation is more rapid than the isomerism step (~77 s^{-1}). If a value of 10^2 s^{-1} is taken for the reverse reaction in eq 7, an association constant of about 1.2×10^2 M^{-1} is calculated. The magnitude of association constant of the non-redox-reactive binuclear complex is smaller by at least 10^2 than for the $\mathrm{V^{II}V^{IV}}$ analogue and 50-fold smaller than for the $\mathrm{V^{III}}_2$ complex.[11] This feature is in agreement with the anticipated lower affinity of Ti(hedta)(H_2O) for soft ligands. The vanadyl oxygens of VO(hedta)$^-$ and even $\mathrm{VO(H_2O)_5{}^{2+}}$ are surprisingly soft as shown by their affinity for $\mathrm{Ru(NH_3)_5{}^{2+}}$ and the resultant charge-transfer spectra for the $\mathrm{(NH_3)_5RuOVL^{4-n}}$ series.[13] Also the dominant redox pathway (eq 6) is outer sphere in harmony with requirement for a hard bridging ligand system to promote inner-sphere reactivity.

Second Observable Process during the Cross Reaction. The second absorbance change for the Ti(hedta)(H_2O)/VO(hedta)$^-$ system is shown by a more rapid decay at 375 nm but a growth in absorbance at 750 nm. The process was found to be independent of $[\mathrm{VO(hedta)^-}]_i$ throughout the range of [Ti(III)]:[V(IV)] of 1:1 to 1:10. The rate of decay at 375 nm or growth at 750 nm is accelerated by the addition of TiO(hedta)$^-$ to the system (cf. Table III). Independent spectral studies showed that no change in absorbance occurred when TiO(hedta)$^-$ was mixed with VO(hedta)$^-$. Therefore TiO(hedta)$^-$, present to study the acceleration of the second spectral change, was added together with the VO(hedta)$^-$. Uncertainties in rate constants in Table III are estimated to be within ±12% (cf. Experimental Section).[47]

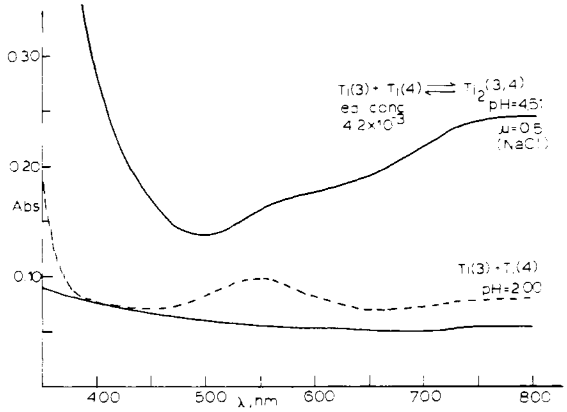

Figure 5. Equilibrium spectra for Ti(hedta)(H_2O) and TiO(hedta)$^-$ ($[\mathrm{Ti(III)}]_i = [\mathrm{Ti(IV)}]_i = 4.2 \times 10^{-3}$ M, $\mu = 0.50$ (NaCl), $T = 25$ °C).

The data at 375 nm conform to eq 8 with an intercept a

$$k_{\mathrm{obsd}} = a + b[\mathrm{TiO(hedta)^-}]_{\mathrm{av}} \quad (8)$$

nearly equal to 0 (−0.15 ± 0.13) and first-order dependence on [TiO(hedta)$^-$]. The overall second-order term exhibits a rate constant $b = (3.12 \pm 0.42) \times 10^2$ M^{-1} s^{-1}.[47] The data obtained at 750 nm also conform to eq 8 with $a = 0.13 \pm 0.70$ s^{-1}, $b = (4.93 \pm 0.24) \times 10^2$ M^{-1} s^{-1}. Considering the experimental problems in the 750-nm region, the agreement in kinetic constants is quite reasonable, within a factor of 1.6. The growth in absorbance at 750 nm, accelerated by Ti(IV) and followed by a slower bleaching, suggested to us the likelihood of the formation of another binuclear species containing both Ti(III) and Ti(IV). This view was supported by the absence of the growing absorbance at 750 nm if the pH was less than 4.0. In separate experiments authentic samples of TiO(hedta)$^-$ and Ti(hedta)(H_2O) were combined and examined as a function of pH. Below pH 4 the spectrum was found to be equivalent to the separate sum of the individual spectra. Above pH 4 a new species of blue color is formed. These spectra are shown in Figure 5. Since we are at present uncertain as to the type of bridging between the Ti(III) and Ti(IV) centers, the binuclear formation reaction (eq 9) is

$$\mathrm{Ti(hedta)(H_2O)} + \mathrm{TiO(hedta)^-} \rightleftharpoons \mathrm{Ti_2(hedta)_2} \equiv \underset{\mathrm{F}}{\mathrm{Ti^{III}Ti^{IV}}} \quad (9)$$

purposefully left unassigned as to charge and bridging groups. A separate kinetic study was made on the formation rate of $\mathrm{Ti^{III}Ti^{IV}}$ by monitoring its appearance at 750 nm in the stopped-flow spectra. The rate of appearance was found to be limited by a first-order event dependent only on Ti(IV) with $k_{\mathrm{obsd}} = 3.4 \pm 0.1$ s^{-1}. The difference in this value from ca. 0.13 s^{-1} found in competition with the Ti(hedta)(H_2O) electron-transfer reaction suggests that the direct combination of Ti(III) and Ti(IV) forming $\mathrm{Ti^{III}Ti^{IV}}$ may be utilizing a different pathway to produce the binuclear ion than is the dominant path during the competitive process to the redox reaction of Ti(III) and V(IV). One possibility is that the formation of $\mathrm{Ti^{III}Ti^{IV}}$ from the authentic samples of Ti(III) and Ti(IV) solutions is largely due to a substitution process while the appearance during the redox system sequence occurs via outer-sphere electron transfer, perhaps between $\mathrm{Ti^{III}}_2$ and Ti(IV),[48] when the available pool of monomeric Ti(III) is being rapidly depleted by several competitive pathways. Another possibility is that the authentic Ti(III) and Ti(IV) samples are mixed at an equilibrium distribution of isomers and various aquo and diaquo forms having different substitution rates while during the redox reaction of Ti(III) and V(IV) a nonequi-

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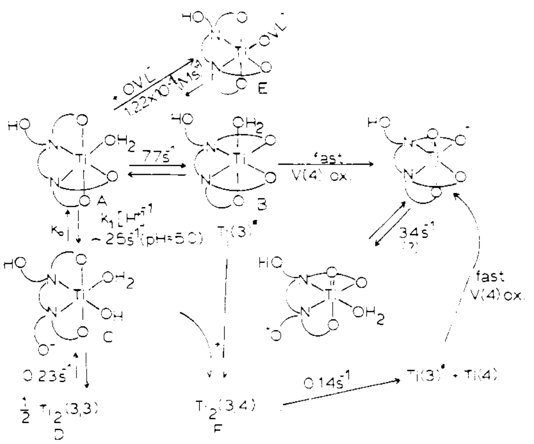
(32) L. Rosenhein, D. Speiser, and A. Haim, *Inorg. Chem.*, **13**, 1571 (1974).

(33) (a) D. Huchital and R. J. Hodges, *Inorg. Chem.*, **12**, 998 (1973); (b) B. Huchital and R. G. Wilkins, *ibid.*, **6**, 1022 (1967).

Scheme I



librium distribution is generated. This could account for the observed ≳30-fold faster rate for the equilibrium mixed forms.

The $Ti^{III}Ti^{IV}$ complex may be prepared in situ by the autoxidation of $Ti(hedta)(H_2O)$ as in eq 10. The binuclear

$$2Ti(hedta)(H_2O) \xrightarrow{O_2} Ti^{III}Ti^{IV} \qquad (10)$$

$Ti^{III}Ti^{IV}$ species is surprisingly inert to further oxidation by O_2; complete conversion to $TiO(hedta)^-$ by prolonged exposure of $Ti^{III}Ti^{IV}$ is observed, but the process requires ca. 12 h. These results are striking in view of the formation of $Ti(O_2)(edta)^{2-}$ and $TiO(edta)^{2-}$ in 1:1 amounts when $Ti(edta)(H_2O)^-$ is autoxidized. The differences in the reactivities of various Ti(III) complexes toward O_2 and H_2O_2 are a subject of a future report.[47]

The decay at 750 nm must involve the redox elimination of $Ti^{III}Ti^{IV}$ since the A_∞ value matches the A_∞ absorbance when the cross reaction of Ti(III) and V(IV) is carried out with the pH <4. The value obtained for the redox loss of $Ti^{III}Ti^{IV}$ was found to be a first-order decay with rate constant 0.14 s^{-1}. This step is most probably related to the *a* term in eq 8. The value is comparable to the noncatalyzed dissociation rate of the V^{III}(hedta) and Fe^{III}(hedta) binuclear complexes. The result is compatible with the dissociation of $Ti^{III}Ti^{IV}$ into an activated Ti(III) complex and Ti(IV). The Ti(III) species is rapidly scavenged by $VO(hedta)^-$ to form Ti(IV) and V(III). Therefore the product of dissociation of $Ti^{III}Ti^{IV}$ is most likely the same as isomer B for the Ti(III) center.

The second term in eq 8 may be then associated with the process which causes the growth in absorbance at 750 nm. This event is not readily studied at 750 nm because of the competitive sequence of reactions which create and destroy absorbing species, in both the initial and the final parts of the growth phase. The growth phase at 750 nm reaches a maximum value at about 20 s. The rate constant, 3.1×10^2 M^{-1} s^{-1}, of the *b* term is reasonable for either a substitution-limited step or an electron-transfer-limited step, forming $Ti^{III}Ti^{IV}(hedta)_2$.[48] The chemical processes for the series of observed absorbance changes occurring during the first 50 s in the $Ti(hedta)(H_2O)/VO(hedta)^-$ reaction are shown in Scheme I.

$Ti^{IV}V^{III}(hedta)_2$ Binuclear Ion. The ultimate products of the cross reaction between $Ti(hedta)(H_2O)$ and $VO(hedta)^-$ vary depending on the pH of the medium. Below pH 2.5 the only products appear to be $V(hedta)(H_2O)$ and $TiO(hedta)^-$ as characterized by the visible spectrum.[25] Above pH 7.5 the final V(III) product is the $(V(hedta\text{-}H))_2^{2-}$ binuclear complex.[25,34,44] The Ti(IV) products were not identified as these are transparent in the visible region. In the intermediate range 2.5 ≤ pH ≤ 7.5, the presence of an orange species is observed. The same species may be generated by the combination of authentic samples of $V(hedta)(H_2O)$ and $TiO(hedta)^-$. The maximum concentration of the orange ion occurs between pH 4.9 and 5.2 for 1:1 Ti(IV)–V(III) mixtures. The visible spectrum is shown in Figure 6. The binuclear species has a charge-transfer maximum at 453 nm.

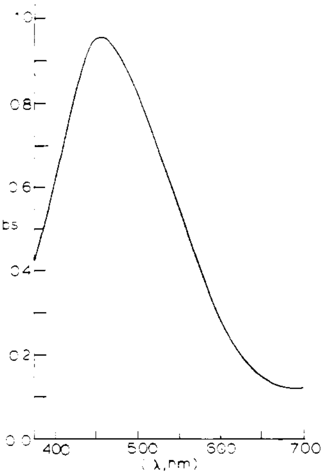


Figure 6. Equilibrium spectrum showing the presence of the $Ti^{IV}V^{III}(hedta)_2$ binuclear ion ($[Ti(IV)]_i = 4.7 \times 10^{-3}$ M, $[V(III)]_i = 5.1 \times 10^{-3}$ M, $\mu = 0.50$ (NaCl), $T = 25$ °C, pH 5.10).

The orange species may be shown to be at equilibrium with the monomeric components (eq 11). The species has been

$$TiO(hedta)^- + V(hedta)(H_2O) \rightleftharpoons (hedta)Ti(OH)_2V(hedta)^- \equiv \underset{G}{Ti^{IV}V^{III}(hedta)} \qquad (11)$$

written as the dihydroxy-bridged form similar to the solid-state structure of the V^{III}_2 analogue.[34] However, the proper formulation may be $(hedta)TiOV(hedta)^-$ on the basis of the affinity of Ti(IV) for the oxo ligand in numerous complexes.

Several binuclear complexes in which the metal centers are bound by members of the edta-chelate family of ligands and bridged by oxo, dihydroxy, or dialcoxy units have recently been characterized by X-ray diffraction. These include the $V^{IV}V^{V}$–nta complex $(NH_4)_3[V_2O_3(nta)_2]\cdot3H_2O$,[42] the Cr^{III}_2–edda complex $[Cr(edda)(OH)]_2\cdot4H_2O$,[43] the V^{III}_2–hedta

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[34] Magnetic measurements support a dialcoxy structure: F. J. Kristine, W. E. Hatfield, and R. E. Shepherd, to be submitted for publication.

(35) H. Schugar, C. Walling, R. B. Jones, and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3712 (1967); (b) ref 27b.

(36) R. E. Shepherd, F. J. Kristine, I. Gosh, D. Stout, and W. E. Hatfield, to be submitted for publication.

(37) J. Podlahova and J. Podlaka, *J. Inorg. Nucl. Chem.*, **28**, 2267 (1966).

(38) J. E. Huheey, "Inorganic Chemistry", 2nd ed., Harper and Row: New York, 1978, p 834.

(39) This feature argues against appreciable amounts of $Ti(hedta)(H_2O)_2$ being present in solution. The redox-restricted pathways would not have obtained unless $Ti(hedta)(H_2O)_2$ had both water molecules in the same approximate plane as defined by trans N donors to water. Since the free energies of complexes with one water trans to the in-plane N donor and one water out-of-the plane containing the N donors vs. two waters in-plane are likely to be very comparable, it is considered very unlikely that a substantial energy barrier exists between two diaquo forms. Furthermore, the IR data in ref 37 argue against the existence of $Ti(hedta)(H_2O)_2$ and in favor of $Ti(hedta)(H_2O)$ only.

(40) An IR method to examine solutions for the presence of pendant $CH_2CO_2^-$ functionalities, required for the $Ti(hedta)(H_2O)(OH)^-$ formulation, fails because the concentration required to achieve a desirable absorbance change exceeds the solubility of the complexes present in the required pH range.

(41) (a) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1988 (1966); (b) C. Chang, Ph.D. Thesis, University of Pittsburgh, 1978; University Microfilms, Ann Arbor, Mich.; (c) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(42) M. Nishizauwa, K. Hirotsu, S. Ooi, and K. Saito, *J. Chem. Soc., Chem. Commun.*, 707 (1979).

(43) G. Srdanov, R. Herak, D. J. Radanovic, and D. S. Veselinovic, *Inorg. Chim. Acta*, **38**, 37 (1980).

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complex $[enH_2][V(hedta\text{-}H)]_2\cdot 2H_2O$,[44] and the Fe^{III}_2–hedta complex $[enH_2][Fe_2O(hedta)_2]$.[45] $((NH_3)_5RuOV(hedta))^+$ has also been identified in solution by EPR.[13] That $Ti^{III}Ti^{IV}(hedta)_2$ and $Ti^{IV}V^{III}(hedta)_2$ complexes are blue and orange is not surprising in light of the blue and green colors imparted to corundum by Ti^{IV}–O–Fe^{III} and Fe^{III}–O–Fe^{II} impurities.[46]

Equilibrium studies of eq 11 are hindered by the competitive dimerization of $V(hedta)(OH)^-$ in the pH range 4.9–5.2 (eq 12) and by the precipitation problems of $TiO(hedta)^-$ solutions

$$2V(hedta)(OH)^- \rightleftharpoons (V(hedta\text{-}H))_2^{2-} \qquad (12)$$

in this range. Studies at pH ~5 were carried out as a perturbation of equilibrium 11 by the reaction in eq 12. The $Ti^{IV}V^{III}$ binuclear ion is fully formed when [Ti(IV)]:[V(III)] is 1:50. Under these conditions $\epsilon_{453} = (3.8 \pm 0.1) \times 10^2$ M^{-1} cm^{-1}. By varying the ratio of reactants, we found an equilibrium constant for eq 11 to be 5.0×10^2 M^{-1} ($\mu = 0.50$ (NaCl), $T = 25.0$ °C). The forward rate of formation (eq 11) was easily followed at 453 nm in the stopped-flow studies after 50 s. The formation rate followed second-order kinetics under equal initial concentrations of Ti(III) and V(IV), or Ti(IV) and V(III), after 50 s. The measured rate constant is 23.1 M^{-1} s^{-1} ($\mu = 0.50$ (NaCl), $T = 25.0$ °C). Combination of this value with the measured association constant of 500 M^{-1} yields a rate constant for dissociation of 4.6×10^{-2} s^{-1}. This result is within a factor of 10 of the breakup of the V^{III}_2 and Fe^{III}_2 species; it is therefore quite reasonable for either the dihydroxy- or oxo-bridged structures. The overall stability constant for $Ti^{IV}V^{III}$ of 5.0×10^2 M^{-1} is comparable to that for the Fe^{III}_2 complex (2.4×10^2)[35] and 10-fold smaller than the V^{III}_2 value (5.5×10^3 M^{-1}).[25] The rate of formation (23 M^{-1} s^{-1}) is 15 times slower than the forward dimerization reaction in eq 12, suggesting that more reorganization is required at the $TiO(hedta)^-$ center than for $V(hedta)(OH)^-$.

The fact that the $Ti^{IV}V^{III}$ species is not formed in the initial steps of the cross reaction of $Ti(hedta)(H_2O)$ and $VO(hedta)^-$ is definitive in showing that the dominant electron-transfer process between these complexes is outer sphere in nature. Such a process should be first order in each of the Ti(III) and V(IV) species unless the redox process is limited by a slow step as described in eq 5.

The orange color of the Ti^{IV}–V^{III} binuclear species is similar to the orange color of the peroxo complex of $Ti(edta)(O_2)^{2-}$. Since $TiO(hedta)^-$ is colorless in the visible region, the presence of an electron-rich chromophore coordinated to Ti(IV) is required for the appearance of the charge-transfer band. This is similar to the ligand to metal CT in the peroxo complex. Coordination of V(III) to an oxo ligand makes the Ti–O–V chromophore appropriately electron rich for a similar MLCT transition.[46]

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Registry No. $Ti(hedta)(H_2O)$, 75431-40-2; $VO(hedta)^-$, 62560-22-9; $(hedta)TiOV(hedta)^-$, 75716-19-7; $TiO(hedta)^-$, 75431-41-3; $V(hedta)(H_2O)$, 75431-42-4.

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(47) If only $[TiO(hedta)^-]_{added}$ is used to evaluate rate constants instead of $[TiO(hedta)^-]_{av}$ in eq 8, the following constants are obtained (375 nm): $a = 0.23 \pm 0.08$ s^{-1}, $b = (3.17 \pm 0.37) \times 10^2$ M^{-1} s^{-1}. Hence the *b* path values are unchanged within experimental error. A reviewer has asked why a reiterative type of fit, utilizing the instantaneous amount of $[TiO(hedta)^-]$, was not attempted for eq 8. This would require a knowledge of rate constants for all parallel redox pathways that generate $TiO(hedta)^-$ to a greater accuracy than seem valid from this study. In addition, there may be other species that exist at equilibrium in this pH range with the dominant form $TiO(hedta)^-$ such as $TiO(hedta)(H_2O)^-$ and $TiO(Hhedta)(H_2O)$. Each of these may differ kinetically or may be produced at different rates via the redox reactions producing Ti(IV). For example, the reactions of H_2O_2 with $TiO(edta)^{2-}$, $TiO(edta)^{2-}$, and $TiO(Hedta)(H_2O)^-$ have widely different reactivities toward H_2O_2 (F. Kristine and R. E. Shepherd, submitted for publication in *Inorg. Chem.*). Since the distribution of fully and partially chelated species for $TiO(hedta)^-$ is not certain, a reiterative approach would not produce additional meaningful results, relatable to a single molecular species.

(48) The *b* path proceeds at least a factor of 3 times faster than any *a* path. Using $[TiO(hedta)^-]_{av}$ the magnitude of *a* approaches zero within experimental error. However if $[TiO(hedta)^-]_{added}$ is used in evaluating eq 8, the value of *a* obtained at 375 nm (0.23 ± 0.08 s^{-1}) agrees quite well with the value obtained from relaxation methods for the monomerization of $Ti^{III}_2(hedta)_2$: 0.23 ± 0.01 s^{-1}. A convenient interpretation of all of these results would be shown with absorbance changes first order in $Ti^{III}_2(hedta)_2$:

$$Ti^{III}_2 + Ti^{IV} \xrightarrow{b} Ti^{III}Ti^{IV} + Ti^{III}$$

$$Ti^{III}_2 \overset{a}{\rightleftharpoons} 2Ti^{III}$$

$$Ti^{III} + Ti^{IV} \xrightarrow{fast} Ti^{III}Ti^{IV}$$

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Valency of Chromium in the Equilibrium Ternary Phase Belonging to the Noncondensed System $CaO-Cr_2O_3-O_2$

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In the title system the three equilibrium phases—the ternary compound, calcium chromate, and monocalcium chromite—were synthesized. The solid-state IR, diffuse-reflectance, and ESR spectra of the ternary phase were compared with those of the two other phases to reveal the valency of chromium in this phase *in solid state*. The different spectral results were communicated and interpreted. The absence of Cr^{III} was confirmed and the presence of $Cr^VO_4^{3-}$ tetraoxoanion was strongly suggested in the composition of the solid ternary phase. Hence, the ternary phase has *in the solid state* the tricalcium orthochromate formula $Ca_3(Cr^VO_4)_2$ rather than the chromate chromite formula $Ca_9(Cr^{VI}_4Cr^{III}_2)O_{24}$, which describes the composition of the ternary phase in acid solutions.

Introduction

The study of solid-state chemistry of the equilibrium phases based on the noncondensed $CaO-Cr_2O_3-O_2$ system has definite importance in the chemistry of transition-metal ions involving oxo ligands as well as the manufacture and service of basic refractories.

Three equilibrium phases—monocalcium chromite ($CaCr^{III}_2O_4$), calcium chromate ($CaCr^{VI}O_4$), and a ternary

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