Inorg. Chem. **1981**, *20*, 1739-1742 **1739**

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Thiocyanate Ion as a Bridging Ligand in Reduction of Ruthenium(III) by Titanium(III) and by (*N*-(Hydroxyethyl)ethylenediaminetriacetato)titanium(III)

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Received August 6, 1980

Ti^{3+} reduces $Ru(NH_3)_5NCS^{2+}$ with a second-order rate constant of 840 M^{-1} s^{-1} at 25 °C (2 M LiCl). The corresponding activation parameters are $\Delta H^* = 35$ kJ/mol and $\Delta S^* = 70$ J/mol. The Ti(HEDTA) complex (HEDTA = anion of *N*-(hydroxyethyl)ethylenediaminetriacetic acid) reduces the same oxidant with a second-order rate constant of 2.8×10^4 M^{-1} s^{-1} (25 °C, 2 M LiCl). Comparison of these results with previously available data leads to the conclusions that both reactions involve inner-sphere electron transfer, that thiocyanate ion is more efficient as a bridging ligand in these redox processes than in Co^{III}–Cr^{II} systems, and that Ti(III) is less sensitive to labilization by amino acid ligands than are Ru(III) and Cr(III).

Previous papers[1,2] showed that both outer-sphere and inner-sphere mechanisms operate in Ru(III)–Ti(III) electron-transfer (ET) reactions, but that patterns of effectiveness of bridging ligands differ from those found for other pairs of redox agents.[3] We now report kinetic studies of the reduction of $Ru(NH_3)_5NCS^{2+}$ (and related species) by Ti^{3+} and by the Ti(III) complex of *N*-(hydroxyethyl)ethylenediaminetriacetic acid (hereafter denoted HEDTA). The results are interpreted in terms of the influence of orbital symmetry-match on ET bridge efficacy.

Experimental Section

(Thiocyanato)pentaammineruthenium(III) Perchlorate. The procedure of Schreiner and Lin[4] (hereafter method A) was followed. Only the most soluble fraction of the solid product was taken for the final precipitation with $NaClO_4$. The less-soluble fraction contains polymeric substances.[5] An alternate preparation (method B) given by Lim, Barclay, and Anson[6a] was also used. Each of these methods gave two types of products, denoted I and II. Either product (I or II) could be obtained by either method (A or B), but it was not found possible to predict which would be obtained in a given experiment. (*Caution*: *explosive*.)[6b]

Compounds I and II differed slightly in UV–visible spectra. λ, nm (ε, M^{-1} cm^{-1}): I, 495 (3300), 327 (460), 205 (12300); II, 505 (3500), 327 (590), 205 (13 100). Compound I appeared more reddish than compound II, which had a deeper, more purplish color. Anal. Calcd for $[Ru(NH_3)_5(SCN)](ClO_4)_2$: Ru,[7] 22.8; N,[8] 18.9; C,[8] 2.7; S,[9] 7.2. Found for I: Ru, 21 ± 1; N, 18.5; C, 3.2; S, 4.2. Found for II: Ru, 21 ± 1; N, 19.6; C, 3.0; S, 4.6. Weighed samples of II dissolved in dilute HCl were adsorbed on Dowex 50 and the total acidity of the effluent determined by titration with base. The amount of acid corresponded to a charge of 2.1 per ruthenium. The red band on the column moved with 2.5 M $HClO_4$ but not with 2.0 M $HClO_4$. This is consistent with a charge of 2+ per cation.[9] Solutions of II were analyzed for SCN^- by polarography, using the anodic wave of SCN^- (after the complex had been destroyed by heating with OH^-). These experiments indicated 0.99 ± 0.16 SCN^- ions per Ru in II. IR spectra for I and II were similar but not identical. Both spectra closely resembled previously reported spectra.[4,6] The X-ray powder pattern of I indicated a face-centered cubic structure, while that of II showed peaks split into triplets, indicating an orthorhombic structure. I and II appear, on this basis, to be distinct crystalline forms, not mixtures.[12] X-ray data are included in the supplementary material.

Ti(III),[1] Cr(II),[10] and other solutions were prepared by standard methods. Initially a Durrum-Gibson stopped-flow kinetic spectrometer was used, but lack of reproducibility, ascribed to interaction of thiocyanate with metal parts of the instrument, was encountered. Most of the kinetic data was taken by using an Aminco-Morrow instrument in which the solution does not contact metal.

Under favorable conditions, good pseudo-first-order rate plots linear within 2% for 3 half-times and reproducible to ±5% were obtained. For reduction of electronic noise, damping circuits were generally employed and the initial portions of the data disgarded. This reduced the precision of the results. Kinetic measurements were made at the wavelength of maximum visible absorption of the oxidant, generally, 505 nm. Polarographic and spectral measurements were made by standard techniques.

Results

When a solution containing Hg^{2+} is added to acidified solutions of either I or II, the wavelength of maximum absorbance shifts (to near 490 nm). Subsequent addition of a solution containing bromide ion restores the original spectrum. Cyclical voltammetry (0.33 M Na_2SO_4, pH 2) gives formal potentials for Ru(III) reduction of 0.124, 0.132, and 0.053 V vs. NHE for I, II, and $Ru(NH_3)_6^{3+}$. Reduction of I by a less-than-equivalent quantity of Cr^{2+}, at 5 °C in 0.1 M HCl–0.9 M LiCl gives a Cr(III) product which, on separation by Dowex 50 at 5 °C, showed absorbance peaks characteristic of both $CrSCN^{2+}$ and $CrNCS^{2+}$.[13]

Ion-exchange experiments show that the cation of II is dipositive and contains one thiocyanate ion. Reaction with Hg^{2+} shows that I has a sulfur atom available for coordination. The IR and UV–visible spectra and reduction potential show that II is the same species to which Anson assigned the structure $Ru(NH_3)_5NCS^{2+}$, on the basis of electrochemical studies.[6] In view of the ease of conversion of $CrSCN^{2+}$ to the more stable $CrNCS^{2+}$ the result of the Cr^{2+} reduction is also consistent with the assignment of II as $Ru(NH_3)_5NCS^{2+}$, which is adopted.

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(1) K. M. Davies and J. E. Earley, *Inorg. Chem.*, **17**, 3350 (1978).

(2) A. Adegite, J. E. Earley, and J. F. Ojo, *Inorg. Chem.*, **18**, 1535 (1979).

(3) R. N. Bose and J. E. Earley, *Inorg. Chem.*, in press.

(4) S. W. Lin and A. F. Schreiner, *Inorg. Chim. Acta*, **5**, 290 (1971).

(5) R. Parashad and U. Agarwala, private communication.

(6) (a) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1977). (b) Safety note: a reviewer reports that potentially serious explosions have occurred during preparations of $Ru(NH_3)_5NCS(ClO_4)_2$. Extreme care should be used in this preparation.

(7) J. Woodhead and J. Fletcher, *J. Chem. Soc.*, 5039 (1961). This method gave results averaging 1% higher than stoichiometry for $[Ru(NH_3)_5Cl]Cl_2$. It seems likely that complete oxidation of ruthenium was not attained in analysis of $[Ru(NH_3)_5(SCN)]ClO_4$. The calculated value was used to calculate concentrations.

(8) Galbraith Laboratories, Knoxville, Tenn. Thiocyanate is the only source of either C or S in this compound. Carbon analyses are systematically high and S analyses systematically low. Values reported are averages of duplicates.

(9) D. A. Buckinghan, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(10) K. M. Davies and J. E. Earley, *Inorg. Chem.*, **15**, 1074 (1976).

(11) D. I. Bustin and J. E. Earley, *Inorg. Chem.*, **7**, 1238 (1968).

(12) We are grateful for Dr. Judith Stalich of the National Bureau of Standards and to Professor Jacek Grochowski for help on the X-ray work. Crystal and molecular structure determinations on both crystal forms are in progress.

(13) M. Orhanovic, H. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968).

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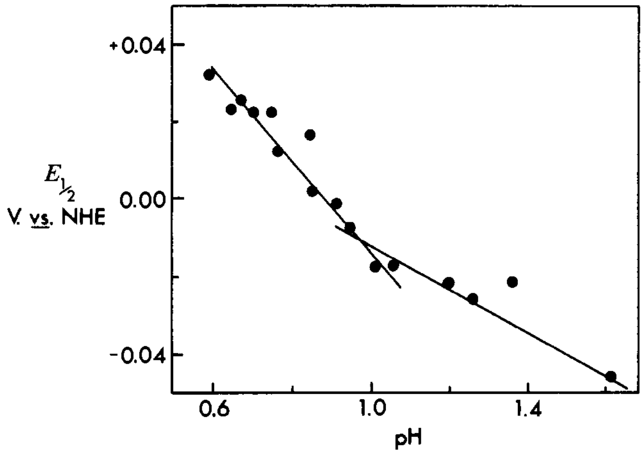

Figure 1. Dependence of half-wave potential on acidity for oxidation of Ti^{3+} in 1.0 M LiCl at 25 °C. Lines correspond to eq 1.

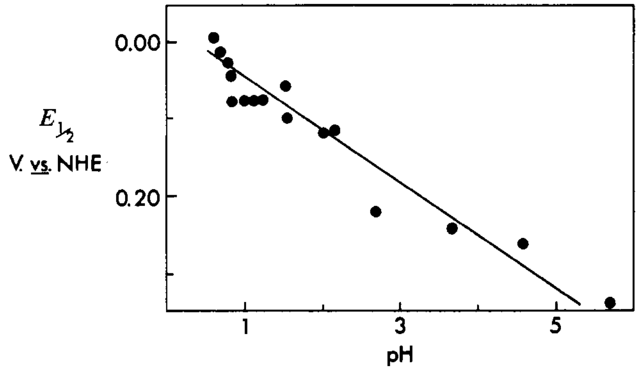

Figure 2. Dependence of the half-wave potential on pH for the $Ti(HEDTA)^{4+/3+}$ couple at 25 °C in 2.0 M LiCl-HCl medium.

Figure 1 shows the variation in half-wave potential with pH for the quasi-reversible anodic (oxidation) wave of Ti^{3+} in 1 M LiCl media. The data do not fall on a single straight line, but they are adequately fitted by two lines[14a] (see Figure 1) given by eq 1.

$$\begin{aligned} E_{1/2} &= 0.100 - 0.12\text{pH} \quad (\text{V vs. NHE}) \\ E_{1/2} &= 0.46 - 0.06\text{pH} \quad (\text{V vs. NHE}) \end{aligned} \tag{1}$$

In 2 M LiCl, the data do not show two separate segments, but scatter about the line given by eq 2. These results are

$$E_{1/2} = 0.08 - 0.09\text{pH} \quad (\text{V vs. NHE}) \tag{2}$$

consistent with prior reports[15] that increase of ionic strength favors deprotonation of Ti(IV). Figure 2 shows variation of half-wave potential with pH for the reversible anodic wave of Ti(III), in the presence of a slight excess of HEDTA. The data follow eq 3.

$$E_{1/2} = 0.01 - 0.06\text{pH} \quad (\text{V vs. NHE}) \tag{3}$$

Titration indicate that three protons are released when Ti^{3+} coordinates with HEDTA. Solutions of Ti(HEDTA) are blue, with an absorbance maximum at 555 nm for 0.10 M > $[H^+]$ > 0.0010 M. As $[H^+]$ is increased above 0.1 M, the absorbance shifts to shorter wavelengths. At pH values above 4, the absorbance maximum occurs at longer wavelengths (at 565 nm for 6 < pH < 10), and the solutions are yellow-green. The anodic polarographic wave is quasi-reversible in the range 1 < pH < 5. The half-wave potential follows the eq 4.[16a]

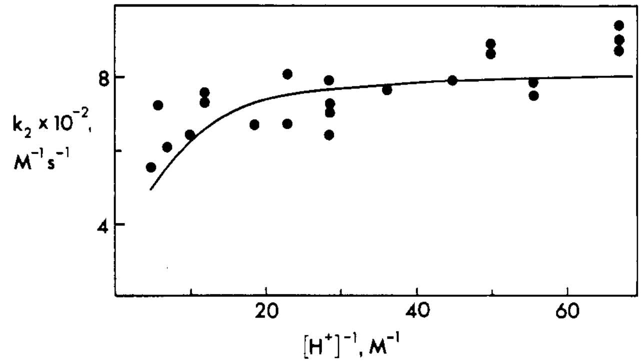

Figure 3. Dependence of k_2 on $[H^+]^{-1}$ for the reaction between $Ru(NH_3)_5NCS^{2+}$ and Ti^{3+} at 25.0 °C in 2.0 M LiCl-HCl medium.

$$E_{1/2} = 0.008 - 0.058\text{pH} \quad (\text{V vs. NHE}) \tag{4}$$

At pH >6 the anodic wave which follows eq 4 decreases in height,[16b] a second anodic wave, at −0.158 V vs. NHE, is observed, and the sample appears cloudy. In acid solutions, one of the chelate rings opens, with protonation of the ligand: in neutral solutions, the coordinated water molecule is deprotonated and then other reactions, leading to polymeric products, ensue. Estimates of p*K* for these two protonations are 1 and 4.5, respectively.

From eq 1 and 2, we conclude that the potential for eq 5

$$\epsilon^- + H^+ + TiOH^{3+} \Leftrightarrow Ti(H_2O)_6^{3+} \tag{5}$$

(in 2 M LiCl at 25 °C) is 0.06 ± 0.01 V vs. NHE. In eq 5, the formula $TiOH^{3+}$ represents the deprotonated quadrivalent titanium species which is initially formed at the dropping-mercury electrode. The reversible shape of the Ti(III) oxidation wave and the drawn-out shape of the Ti(IV) reduction wave indicate that polymerization of that species occurs on a time scale at least somewhat slower than reoxidation on the electrode surface.[14b] A likely formulation of this species is $TiOH^{3+}$, but somewhat higher aggregation is not ruled out by present data.

For the Ti(HEDTA) case eq 3 leads to the conclusion that (in 2 M LiCl at 25 °C) $\mathcal{E}°$ is 0.010 V vs. NHE for reaction 6. In this case the reversibility of both polarographic waves

$$\epsilon^- + H^+ + Ti^{IV}(EDTA)H_2O^+ \Leftrightarrow Ti(HEDTA)H_2O \tag{6}$$

indicates that the species which is produced at the electrode also predominates in solution.

Experiments carried out under second-order conditions showed that reaction of I and II with Ti^{3+} and with Ti(HEDTA) followed 1/1 stoichiometry (within 10%) in the range 0.020 M < $[H^+]$ < 0.20 M. Rates of reduction were linear in [Ti(III)] (within 2%) up to a total Ti(III) concentration of 15 mM.

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(14) J. Heyrovsky and J. Kuta, "Principles of Polarography", Czechoslovakian Academy of Science, Prague, 1965: (a) p 163; (b) Chapter 14.

(15) B. Brunschweig and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968). The present results are consistent with previously reported indications that $TiOH^{3+}$ has a lower acidity at lower ionic strength than at higher ionic strength.

(16) (a) R. Pecsok and N. Sutin, *Inorg. Chem.*, **18**, 1731 (1979); (b) D. I. Bustin and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 1818 (1967).

(17) The rate constant corresponding to *k* is 100 M^{-1} s^{-1} for compound I. This lower redox rate constant is the most striking difference between I and $Ru(NH_3)_5NCS^{2+}$. Presently available evidence indicates that I contains a cation which is quite closely related to $Ru(NH_3)_5NCS^{2+}$ but differs in some way which reduces its redox reactivity such as by having a bent rather than linear $RuNCS^{2+}$ grouping: J. Lewis, R. S. Nyholm, and P. Smith, *J. Chem. Soc.*, 4590 (1961).

(18) A. Chemlnich and D. Fiat, *J. Chem. Phys.*, **51**, 4238 (1969); D. Fiat and R. Connick, *J. Am. Chem. Soc.*, **90**, 608 (1968).

The absorbance peak of $Ru(NH_3)_5NCS^{2+}$ remains at 505 nm from pH 1.7 to 8.9 but shifts to longer wavelength in more acidic solution (513 nm at $[H^+] = 0.50$ M). This is consistent with the existence of equilibrium 7. No high-acid limit was

$$Ru(NH_3)_5NCSH^+ \rightleftharpoons Ru(NH_3)_5NCS^{2+} + H^+ \qquad (7)$$

approached so that only a lower limit $K_r > 0.2$ M can be assigned for the acidity constant of the conjugate acid of the thiocyanato complex.

Variation of the second-order rate constant for the redox reaction with acid concentration is given in Figure 3. On the basis of spectral evidence which indicates that the equilibrium shown in eq 7 obtains, it is expected that a rate law of the form of eq 8 would be observed. The data scatter around $k_2 = 800$

$$k_2 = kK/([H^+] + K) \qquad (8)$$

$M^{-1}\,s^{-1}$, but there is a tendency to higher values at lower acidities and some tendency to decreased values in the high-acid range, where protonation occurs. The solid line in the figure is drawn with use of eq 8 and the values $K = 0.3$ M (consistent with the spectral experiments) and $k = 840\ M^{-1}\,s^{-1}$.

The variation of k_2 at $[H^+] = 0.029$ M with temperature is consistent with a ΔH^* of 35 ± 5 kJ/mol and ΔS^* of 70 ± 20 J/mol (10^2k_2 ($M^{-1}\,s^{-1}$) is 3.6 at 12.0 °C and 10.6 at 30.4 °C).

Both the acid dependence and the temperature dependence of the reaction of present interest are quite similar to the corresponding properties of the reaction of $Ru(NH_3)_5OOCCH_3^{2+}$ but quite different from those of the reaction with Ti(III) of oxidants (such as $Ru(NH_3)_6^{3+}$) that lack a lead-in group. In the case of the $Ru(NH_3)_6^{3+}$–Ti(III) reaction, the kinetics are best interpreted as an outer-sphere electron-transfer reaction involving $TiOH^{2+}$ as reductant. A relatively low value of K (eq 7) and a high value of ΔH^*, for these reactions, is consistent with this interpretation. Relatively low values of K (eq 7), consistent with pK_a's of the conjugate acids of the Ru(III) oxidants, and relatively low values of ΔH^* for the reactions in which good lead-in groups are present indicate a different mechanism. The results on the present systems are consistent with inner-sphere electron transfer involving a bridged binuclear intermediate (eq 9 and 10).

$$Ru(NH_3)_5NCS^{2+} + Ti^{3+} \underset{k''}{\overset{k'}{\rightleftharpoons}} Ru(NH_5)_5{\cdot}NCS{\cdot}Ti^{5+} \qquad (9)$$

$$Ru(NH_5)_5{\cdot}NCS{\cdot}Ti^{5+} \xrightarrow{k_\epsilon} \text{products} \qquad (10)$$

Application of the steady-state approximation to the concentration of the intermediate leads to the relationship

$$k = k'k_\epsilon/(k'' + k_\epsilon + k'[Ti(III)]) \qquad (11)$$

if the steady-state concentration of the intermediate is significant with respect to that of the oxidant. Experiments designed to detect the spectrum of an intermediate during the reaction gave negative results. Also, the dependence of rate on [Ti(III)] was linear within 2% up to [Ti(III)] = 0.015 M: this requires that $k'' + k_\epsilon > 49(0.015\ M)k'$. Both of these considerations lead to the conclusion that the steady-state concentrations of intermediate is small with respect to the concentration of the oxidant, so that eq 11 simplifies to eq 12.

$$k = k'k_\epsilon/(k'' + k) \qquad (12)$$

The activation energy for water exchange between the first coordination sphere of $Ti(H_2O)_6^{3+}$ and solvent water is unusually low (when compared to the corresponding quantity for other tripositive aquo ions). Rates of formation of Ti(III) complexes are more sensitive to the charge (and other properties) of the entering group than can be explained on the basis of outer-sphere complex formation constants. Both these considerations have led Diebler[19] to the conclusion that substitution reactions of Ti(III) have a substantial associative component. The activation energy reported here as being associated with k, the redox rate constant, is similar to that found for water exchange on $Ti(H_2O)_6^{3+}$ and for Ti(III) reduction of $Ru(NH_3)_5OOCH_3^{2+}$. The value of the rate constant for reduction of monopositive complexes by Ti(III) is about 2 orders of magnitude larger than those for the dipositive oxidants. All of these suggest that the rate of the redox reaction is determined, in large part at least, by k', the rate constant for displacement of coordinated water from the reductant.

Armor and Haim[20] report that the formation constant of $Hg{\cdot}SCN{\cdot}Cr^{4+}$ is $10^4\ M^{-1}$: our data indicate that the formation constant of $Ru(NH_3)_5{\cdot}NCS{\cdot}H^+$ is $\sim 10^{-1}\ M^{-1}$. If the redox reaction is in fact substitution limited, as we have concluded above, then $k \cong k'$ which entails eq 13, which reduces to k_ϵ

$$0.1k'M + k_\epsilon > 0.735k'M \qquad (13)$$

$> 0.6k'M$. Since $k' = 840\ M^{-1}\,s^{-1}$, the lower limit for the rate constant for the intramolecular electron transfer is then

$$k_\epsilon > 500\ s^{-1} \qquad (14)$$

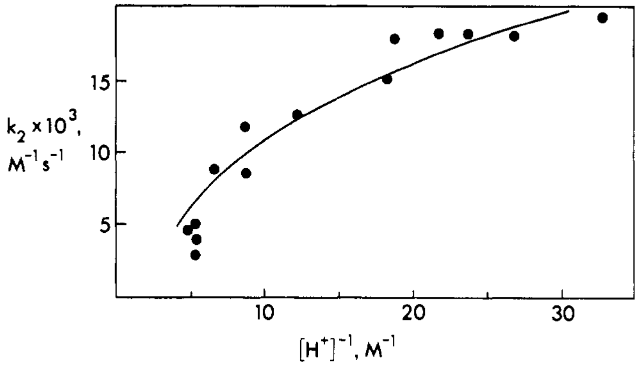

Figure 4. Dependence of the second-order rate constant, k_2, on $[H^+]^{-1}$ for the reaction of $Ru(NH_3)_5NCS^{2+}$ and Ti(HEDTA) at 25 °C in 2.0 M LiCl–HCl medium.

Figure 4 gives the variation of second-order rate constant for reduction of $Ru(NH_3)_5NCS^{2+}$ by Ti(HEDTA) as a function of $[H^+]$. Spectral changes with pH indicate that both oxidant and reductant are partially protonated in the range of acidities covered by Figure 4, so that the data is fitted by eq 15, where K is 0.3 M and K' is taken as 0.1 M. The

$$k_2 = kKK'/([H^+] + K)([H^+] + K') \qquad (15)$$

low-acid limit, k, is $2.8 \times 10^4\ M^{-1}\,s^{-1}$. The corresponding value for $Ti(EDTA)^-$ was found to be $k > 10^5\ M^{-1}\,s^{-1}$.

The rates of reaction of $TiOH^{2+}$ and Ti(HEDTA) with $Ru(NH_3)_5pyr^{3+}$ (pyr = pyrazine) were found to be similar, as would be expected for outer-sphere reactions involving oxidants of similar potential. In contrast, there is a large difference in rate between reductions of $Ru(NH_3)_5NCS^{2+}$ by Ti(III) and by Ti(HEDTA), indicating inner-sphere redox reactions involving reductants of differing substitution lability. Assuming (conservatively) a formation constant of 10^2 for $Ru(NH_3)_5NCSTi(HEDTA)^{3+}$, we have $0.01k'\ M + k_\epsilon > 0.735k'M$. Since k' is $3 \times 10^4\ M^{-1}\,s^{-1}$, this leads to 2×10^4

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[19] H. Diebler, *Z. Phys. Chem. (Frankfurt/Main)*, **68**, 64 (1969).

[20] J. Armor and A. Haim, *J. Am. Chem. Soc.*, **93**, 867 (1971).

s^{-1} as a lower limit for the intramolecular ET rate constant k_ϵ.

Discussion

Matsubara and Creutz[21] have reviewed the influence of EDTA-like ligands on replacement rates for water molecules also coordinated to various metal ions. They have pointed out that metal ions with partially vacant t_{2g} orbitals (their first class; Cr(III), Ru(III), Os(III)) demonstrate very large (10^5–10^{10}) increases in rate when EDTA and similar ligands replace water, but the metals with filled t_{2g} shells (their second class; Co(III), Rh(III), Ru(II)) demonstrate more modest increases, up to 10^2. For Ti(III), the data presented here show that rates of substitution for H_2O, HEDTA, and EDTA[22] complexes are in the ratios $1/360/10^4$. Ti(III), though it has unfilled t_{2g} orbitals and hence falls into Matsubara and Creutz's first class, is not as sensitive to labilization as other cations of this class. The substitution reactions of the other aquo ions of the first class are primarily dissociative, but the reactions of the EDTA complexes have associative character. The substitution reaction of the Ti(III) aquo ion appears to have a large associative component so mechanism does not change on complex formation, perhaps explaining lower rate differences.

The reduction of $Ru(NH_3)_5SCN^{2+}$ by Ti^{3+} is much faster than the corresponding reaction[23] of $Co(NH_3)_5NCS^{2+}$. This indicates that the latter reaction is not substitution limited but that the factors which retard ET reactions of Co(III) also are important.[24]

The rate constant for reaction of $Ru(NH_3)_5NCS^{2+}$ with Ti^{3+}, 840 $M^{-1}\ s^{-1}$, is similar to the rate constant for reduction of $Ru(NH_3)_5OOCCH_3^{2+}$ by the same reductant (700 $M^{-1}\ s^{-1}$, $\mu = 1$ M).[1] Both of these values are in the range of rate to be expected for substitution of a dipositive ion onto Ti^{3+}. The linear free energy relationship for outer-sphere Ru(III)–Ti(III) ET predicts a rate of $10^2\ M^{-1}\ s^{-1}$ for an outer-sphere process of similar driving force. Sutin[25] has calculated values in the range of 10^{-4}–$10^{-2}\ M^{-1}$ for the formation constants of precursor complexes for reactions involving highly charged cations. Other calculations[26] suggest that these estimates may be somewhat low for high ionic strength media. Taking $10^{-2}\ M^{-1}$ as a conservative estimate for the stability constant of the outer-sphere (or encounter) complex which would correspond to the Ru(III)–Ti(III) reaction which would fall on the measured linear free energy relationship (at the potential corresponding to the same driving force) leads to an estimate of 100 s^{-1} for the first-order rate constant for outer-sphere Ru(III)–Ti(III) ET. Comparison of this value with the values of k_ϵ previously calculated (500 s^{-1} for Ti^{3+} and $2 \times 10^4\ s^{-1}$ for Ti(HEDTA)) indicates that SCN^- as an inner-sphere bridging ligand greatly facilitates Ru(III)–Ti(III) ET.

In the Ru(III)–Ti(III) reaction, chloride is not an effective bridging ligand although thiocyanate is. In the case of Co(III)–Cr(II) ET both Cl^- and SCN^- are effective bridging ligands.[26] In the case of Ru(III)–Ti(III) reactions both electron-donor and electron-acceptor orbitals are t_{2g} orbitals, and their mutual interaction is greatly facilitated by low-lying antibonding π orbitals on thiocyanate. In the Co(III)–Cr(II) case e_g orbitals are involved, and outer-sphere paths are unfavorable. Coordination of both oxidant and reductant to a common ligand provides a path for reaction, but there is no special advantage for thiocyanate.[27]

Acknowledgment. This research was begun under support by a National Science Foundation Grant, for which we are grateful.

Registry No. $[Ru(NH_3)_5(SCN)](ClO_4)_2$, 38139-15-0; $Ti(H_2O)_6^{3+}$, 17524-20-8; $Ti(HEDTA)(H_2O)$, 75431-40-2.

Supplementary Material Available: Tables of angles of maximum reflectance and assigned Miller indices, half-wave potentials for the Ti(IV)/Ti(III) couple and the $Ti(HEDTA)^{4+/3+}$ couple, and rate constants (8 pages). Ordering information is given on any current masthead page.

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(22) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **18**, 1731 (1979).

(23) J. Birk, *Inorg. Chem.*, **14**, 1724 (1975).

(24) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

(25) (a) M. Chow, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **99**, 5615 (1979). (b) N. Sutin, *Inorg. Biochem.*, **2**, 623 (1973).

(26) J. L. Walsh, J. A. Bauman, and T. J. Meyer, *Inorg. Chem.*, **19**, 2149 (1980).

(27) T. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973).

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Proton-Transfer Reactions of Copper(II)–Tetraglycine Complexes

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Received September 2, 1980

The triply, doubly, and singly deprotonated tetraglycine complexes $Cu^{II}(H_{-3}G_4)^{2-}$, $Cu(H_{-2}G_4)^-$, and $Cu(H_{-1}G_4)$ all show general-acid catalysis in their reactions with acids, indicating that direct protonation of the peptide nitrogen is rate determining. The H_3O^+ rate constants ($M^{-1}\ s^{-1}$ at 25.0 °C) decrease in a stepwise manner with values of 1.6×10^8, 1.6×10^6, and 2.1×10^5, respectively. The reactions of $Cu(H_{-2}G_4)^-$ with base provide evidence for the $[Cu(H_{-2}G_4)OH]^{2-}$ species, and it is proposed that the hydroxide ion is coordinated in an equatorial position. The $[Cu(H_{-2}G_4)OH]^{2-}$ and the $Cu(H_{-3}G_4)^{2-}$ species, which are in equilibrium, account for 11% and 89% of the triply deprotonated copper(II)–tetraglycine species in solution.

Introduction

Copper(II) reacts with tetraglycine (G_4) in aqueous solution to form the complex CuG_4^+, which may ionize up to three peptide hydrogens depending on the solution pH. Deprotonation of CuG_4^+ occurs stepwise to form $Cu(H_{-1}G_4)$, $Cu(H_{-2}G_4)^-$, and $Cu(H_{-3}G_4)^{2-}$ with successive dissociation constants of $10^{-5.6}$, $10^{-6.96}$, and $10^{-9.14}$ (25 °C, $\mu = 1.0$ M).[1] The crystal structure of $Na_2Cu(H_{-3}G_4)\cdot 10H_2O$ has been determined, and all four nitrogens (one amine and three deprotonated peptide nitrogens) are bound to copper with approximately square-planar geometry.[2] Spectral[3,4] and potentio-

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(1) Smith, R. M.; Martell, A. E., Eds., "Critical Stability Constants"; Plenum Press: New York, 1974; Vol. 1.

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