°C and then recovered by adding aqueous NaClO$_4$ and quickly cooling.

(15) This conversion in the 2,3 series proceeded easily with equivalent quantities of the carboxamido complex and NOClO$_4$ in trimethyl phosphate at 0 °C. The less soluble 4- and 5-CONH$_2$ complexes required a 50% excess of NOClO$_4$ and reaction periods of several hours. Deaminated complexes were recovered from the reaction mixtures by dilution with water, extraction of the Me$_3$PO$_4$ with ether, and addition of NaClO$_4$ to the aqueous phase.

(16) (a) C. Norris and F. Nordmeyer, *J. Am. Chem. Soc.*, **93**, 4044 (1971); (b) J. R. Barber, Jr., and E. S. Gould, *ibid.*, **93**, 4045 (1971); (c) E. R. Dockal and E. S. Gould, *ibid.*, **94**, 6673 (1972); (d) J. C. Chen and E. S. Gould, *ibid.*, **95**, 5539 (1973).

(17) Reduction of the 2-COOMe-3-COOCo^{III} complex was so slow that the intervention of secondary reactions (possibly associated with reduction of the heterocyclic ring) led to extremely erratic values for the apparent absorbances of the product obtained from this derivative.

(18) We estimate the pK_A values for the protonated forms of the blocked cobalt(III) complexes in the present study to be ~2.5, i.e., 2 pK units below[19] that for the monofunctional 2-COOCo complex, for which a pK_A of 4.49 has been reported.[2a] The limited solubilities of these complexes in water at room temperature appear to rule out experimental determinations of pK_A's by partial titration. The visible and near-UV spectra of the protonated and nonprotonated forms are not sufficiently different to allow spectrophotometric determinations.

(19) See, for example, R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

(20) The comparison is complicated by the high values of λ_{max} observed for the 2,6 Cr(III) products (Table IV), which are doubtless chelated. No convincing rationale for the position or intensity of the low-energy maxima for such complexes has yet appeared. It is likely, however, that the normally octahedral bond angles about Cr(III) are substantially distorted in such derivatives, reflecting the severe steric requirements of the 2,6 ligands, and partially relaxing Laporte restrictions. A reviewer suggests the possibility of tridentate chelation in these 2,6 Cr(III) products. Although such chelation by ligands closely related to the present systems is known (see, for example, J. D. Curry and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 592 (1964)), examination of molecular models of such chelates shows them to be severely strained. We do not favor such structures in this study, since the spectrum of the 2,6-(COOH)$_2$ product is found to undergo no substantial alteration when one of the carboxyl groups is blocked off by conversion to an ester or amide function.

(21) The present results also appear to rule out the possibility, once seriously considered,[2a] that reduction of carboxyl-bound Co(III) in pyridinedicarboxylato complexes is initiated by attack at an uncoordinated COOH, COOMe, or CONH$_2$ group. If such a mechanism were important, the 2,5 complexes, in which the carboxyl groups are in conjugation with each other, would be expected to react much more rapidly than the 2,4, whereas the reverse is observed.

(22) It is assumed that proton transfers and substitutions at Cr(II) centers are very rapid in comparison to the other steps.

(23) It has been reported, for example (E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6797 (1970)), that the rates at which 4-substituted benzoatopentaammine derivatives of (NH$_3$)$_5$Co^{III} are reduced by Cr^{2+} are very nearly independent of the net charge on the oxidant.

(24) See, for example, U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).

(25) A. Zanella and H. Taube, *J. Am. Chem. Soc.*, **94**, 6403 (1972).

(26) J. K. Hurst and H. Taube, *J. Am. Chem. Soc.*, **90**, 1178 (1968).

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Electron Transfer through Organic Structures. 38. Blocked Pyridinedicarboxylato Groups as Mediators in the Reactions of Copper(I) with Bound Cobalt(III)[1]

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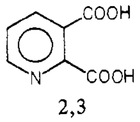
Received March 24, 1978

Pentaamminecobalt(III) derivatives of 2,3-, 2,4-, and 2,5-pyridinedicarboxylic acids, in which Co^{III} is attached specifically to the 2 position and, alternatively, to the position more distant from ring nitrogen, have been reduced with Cu$^+$. Under comparable conditions, rates for the 2-COOCo complexes are 10^1–10^3 times those for the remotely coordinated complexes, with the latter reacting about as rapidly as ordinary straight-chain and aromatic carboxylato derivatives of (NH$_3$)$_5$Co^{III}. As with reductions by Cr^{2+}, the greater rates for the 2-COOCo oxidants are attributed to chelation in the Co^{III}–Cu^I precursor complexes. However, we find no evidence for operation of a radical–ion mechanism in reduction of the 4- and 5-COOCo derivatives, a path which has been suggested to account for rate enhancements observed when these remotely coordinated oxidants react with the more strongly reducing Cr^{2+}. The acidity patterns observed for the 2-COOCo reductions are consistent with two mechanisms. In the first, a two-step path, a chelated precursor complex is formed (k_1) from the two metal centers with loss of H$^+$, after which nonproductive dissociation of the precursor (k_{-1}) competes with internal electron transfer (k_2). Values of k_1, which reflect substitution at two of the available positions at the Cu^I center, fall in the range 1–7 M^{-1} s^{-1}, i.e., several powers of 10 less than rates for substitution of nonchelating ligands. The alternate mechanism, a three-step process, involves reversible deprotonation of the oxidant, formation of a chelated precursor (k_1'), and proton-induced internal electron transfer (k_2'). The latter mechanism leads to more credible values for the rate constants for substitution at Cu^I, but the proton-induced electron-transfer step is without precedent for systems of this sort. Choice between the two kinetically equivalent mechanisms is not yet possible.

In 1971 it was reported that the 2,3-, 2,4-, and 2,5-pyridinedicarboxylato derivatives of (NH$_3$)$_5$Co^{III} were reduced with Cu$^+$ much more rapidly than were ordinary aliphatic and aromatic carboxylato complexes.[2] It was proposed at that time that cobalt(III) in these more rapid oxidants was coordinated at the 2-carboxyl, rather than at the position more remote from nitrogen, and that the high rates simply reflected the intervention of a chelated intermediate, I. Although the picture presented was internally consistent, it lacked certainty.

The recent availability[3] of pyridinedicarboxylato derivatives, in which coordination by cobalt(III) is directed specifically by chemical blocking to the 2 or to the more remote position, has enabled us to examine the question more critically. The present results confirm, in a general way, earlier interpretations but, at the same time, disclose some new facets.



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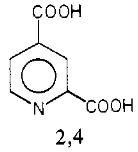

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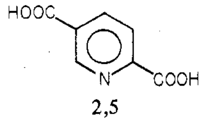

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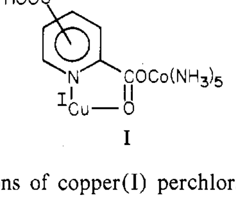


I

Experimental Section

Materials. Cobalt(III) complexes were available from a previous study[3] or were prepared by published procedures.[2,4] Lithium perchlorate and solutions of copper(I) perchlorate were prepared as described.[2]

Rate Measurements. Reactions were followed by measuring absorbance differences on a Cary spectrophotometer as described.[2,5] Measurements were carried out under pseudo-first-order conditions using a 5- to 20-fold excess of Cu(I). Initial concentrations of Co(III) were 0.0001–0.001 M. For most runs, ionic strength was kept near 1.1 M by addition of $LiClO_4$. Reaction temperatures were 25.0 ± 0.2 °C.

Table I. Kinetic Data for Copper(I) Reductions of Pentaamminecobalt(II) Complexes of Dicarboxylatopyridines[a]

substituents	(H^+), M	k
2-$COOCo(NH_3)_5$-3-$COOCH_3$	0.02	8.3
	0.10	7.1
	0.25	3.0
	0.50	2.7
	0.75	1.96
	1.00	1.71
2-$COOCo(NH_3)_5$-3-$CONH_2$	0.02	1.40
	0.10	1.33
	0.25	1.08
	0.50	0.89
	0.75	0.67
	1.00	0.57
2-$COOCo(NH_3)_5$-4-$CONH_2$	0.02	1.27
	0.10	1.15
	0.25	1.03
	0.50	0.86
	0.75	0.63
	1.00	0.53
2-$COOCo(NH_3)_5$-5-$COOCH_3$	0.02	1.44
	0.10	1.25
	0.50	1.05
	0.75	0.75
	1.00	0.72
2-$COOCo(NH_3)_5$-5-$CONH_2$	0.02	1.33
	0.10	1.20
	0.25	1.10
	0.75	0.62
	1.00	0.53
2-$COOCo(NH_3)_5$-6-$COOCH_3$	0.10	9.0
	1.00	9.0
2-$COOCo(NH_3)_5$-6-$CONH_2$	0.10	40
	1.00	41
2-$COOCH_3$-3-$COOCo(NH_3)_5$	0.10	0.02
2-$COOCH_3$-4-$COOCo(NH_3)_5$	0.10	0.08
2-$COOCH_3$-5-$COOCo(NH_3)_5$	0.10	0.05
2-$COOCo(NH_3)_5$-3-COOH	0.10	1.95[b]
	0.10	1.95[c]
2-$COOCo(NH_3)_5$-5-COOH	0.10	1.69[b]
	0.10	1.78[d]
formato	1.00	0.03[e]
acetylenecarboxylato	0.25	0.01[e]
acetato	1.00	<0.004[e]

[a] Specific rates at 25 °C; $\mu = 1.1$; supporting electrolyte was $LiClO_4$-$HClO_4$. $(Co^{III}) = 0.00015$–0.0015 M and $(Cu^I)/(Co^{III}) =$ 10–20. Values are averages of two to five replicate runs. Agreement between runs was better than 6% for the 2-COOCo complexes, less precise for the more slowly reacting complexes (see Experimental Section). [b] Oxidant prepared by deamination of the the corresponding $CONH_2$-substituted complex.[3,6] Observed decrease in absorbance corresponded to 70 ϵ units per Co(III) at 502 nm. [c] Oxidant prepared by action of the unblocked acid on the aquo complex.[4] Observed decrease in absorbance corresponded to 45 ϵ units per Co(III) at 502 nm. [d] Oxidant prepared by action of the unblocked acid on the aquo complex. Observed decrease in absorbance corresponded to 50 ϵ units per Co(III) at 502 nm. [e] Reference 2.

Reactions were first order in both Cu(I) and Co(III) and were not affected by changes in the concentration of Cu^{2+}, which was present in all mixtures in order to minimize difficulties associated with disproportionation of Cu(I).[2,5] Provided precipitation of copper did not occur, reactions were followed for at least 5 half-lives, and rate constants obtained from successive half-life values within a single run agreed to within 4%. In such cases, no trends indicative of systematic errors were noted, and average values checked well with those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs checked to within 6%. For the slower runs, in which copper precipitated after partial reduction of Co(III), specific rates were estimated from initial slopes and are reliable only to a single significant figure.

When kinetic curves from the reductions of the complexes prepared directly from the action of 2,3- and 2,5-pyridinedicarboxylic acids on aquopentaamminecobalt(III) perchlorate in water[4] were compared to curves from reductions of the complexes obtained from deamination, using $NOClO_4$,[3,6] of the 2-COOH-3-$CONH_2$- and 2-COOH-5-$CONH_2$-substituted derivatives, good agreement between specific rates was obtained, but absorbance differences observed for the aquo preparations were significantly less than those for the deamination preparations, indicating that the former were a mixture of rapidly and very slowly reacting isomers.

Results and Discussion

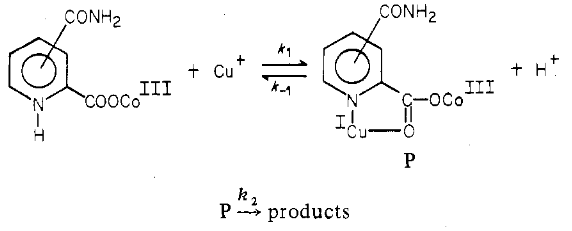
Kinetic data are summarized in Table I. Specific rates for reduction of the 2-COOCo complexes are found to be 10^1–10^3 as great as those for the remotely coordinated isomers under comparable conditions and are similar to those for the unblocked dicarboxylato complexes prepared by direct ligation of the dicarboxylic acids. Moreover, the rates for the 2-COOCo-3-COOH and 2-COOCo-5-COOH oxidants, prepared unambiguously by deamination of the respective $CONH_2$-substituted complexes, agree closely with those of the complexes prepared from the diacids.

Although these experiments thus confirm the view that the more rapid copper(I) reductions in those systems described by Dockal et al.[2] involved cobalt(III) coordinated to the 2 position, we find the absorbance changes observed for oxidants prepared directly from the diacids to be 25–35% less than those for oxidants prepared by deamination. The implication here is that ligation of the unblocked diacids yields a mixture of isomers with the 2-COOCo species predominating in each case. Under conditions used for measuring the rate of the more active isomer, reduction of the less active is negligibly slow.[7,8]

As with Cr^{2+} reductions, the high specific rates exhibited by the 2-COOCo complexes may be attributed principally[9] to increases, resulting from chelation, in the association constants of the binuclear precursor complexes. In the Cr(II) series, however, the nonchelating 4- and 5-COOCo complexes, although less active than the 2-COOCo, are found to be reduced several powers of 10 more rapidly than ordinary straight-chain and aromatic carboxylato derivatives of $(NH_3)_5Co^{III}$,[3] whereas with Cu^+, this enhancement is, at most, marginal. This difference is in accord with the proposal[3,4] that Cr^{2+} reductions of the remotely coordinated oxidants of this type occur mainly by a radical–ion mechanism, featuring preliminary one-electron reduction of the pyridine ligand, for it is expected that this mechanism should be very much less favored with Cu^+, which is 0.56 V less strongly reducing than Cr^{2+}.

Although reductions of the 2-COOCo complexes in the 2,3, 2,4, and 2,5 series have been found to be retarded at high acidities, we are not dealing with simple $(H^+)^{-1}$ proportionalities, analogous to those observed for Cr^{2+} reductions of these complexes,[3] for specific rates with Cu^+ are seen generally to approach limiting values near 0.02–0.10 M H^+.[10] The patterns perceived typify systems in which one of the reactants exists in both an inactive acidic and a kinetically active basic form, with the two forms at comparable concentrations in 0.2–0.7 M H^+. Note, however, that both the oxidants, for which pK_A values lie above 2,[11,12] and the reductant, for which pK_A exceeds 8,[13,14] are very nearly completely protonated in this acidity range.

The kinetic picture here is consistent with two mechanisms. The first, a two-step mechanism, is analogous to that proposed for reduction of a number of chelating salicylato complexes of $(NH_3)_5Co^{III}$ by Ti(III).[15] This features internal electron transfer within a precursor complex, represented as P, formed from the two metal centers with loss of H^+

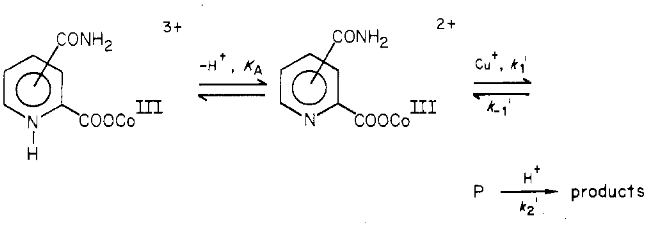


Application of the steady-state approximation to precursor P in this sequence leads to rate law 1. Although kinetic measurements under steady-state conditions do not allow us to evaluate individual values of k_1, k_{-1}, and k_2, plots of $1/k_{\text{obsd}}$ vs. (H^+), which are very nearly linear (see, for example, Figure 1) give k_{-1}/k_1k_2 as slope and $1/k_1$ as intercept, thus allowing estimates of k_1 and the ratio k_2/k_{-1}. These calculated parameters are assembled in Table II.

$$\text{rate} = \frac{(\mathrm{Cu^I})(\mathrm{Co^{III}})k_1k_2}{k_{-1}(\mathrm{H^+}) + k_2} \qquad (1)$$

The most questionable aspect of the two-step mechanism shown is certainly the set of relatively low values for k_1, the specific rate for formation of the precursor, a process requiring loss of a proton and chelation at the $\mathrm{Cu^I}$ center. Although we have been able to find no descriptions of kinetic studies of substitution reactions on $\mathrm{Cu^I}$ in aqueous media, reported[5] specific rates greater than 10^5 M^{-1} s^{-1} for the Cu^+ reductions of halogen-substituted cobalt(III) complexes (doubtless by inner-sphere routes) indicate that such substitutions may, in favorable cases, be very rapid. This is in accord with the general view[16] that substitution reactions at metal centers in aqueous solutions are measurable by conventional mixing techniques only when activation entails a substantial loss in ligand field stabilization. At the same time, however, there are an increasing number of reports of measurably slow substitution reactions at metal centers such as Ti(III)[15,17] Al(III),[18] and Zn(II),[19] which are conventionally taken to be substitution labile. Although too few cases have been examined to allow one to generalize with confidence, it seems clear that such reactions are quite sensitive to charge type[20] and may be sluggish when the creation or breakage of a ring is involved. In our systems, formation of the precursors requires the electrostatically unfavorable association of two positive species, as well as chelation. Moreover, considering the known variability of the coordination number of $\mathrm{Cu^I}$,[21] a reorganization of the coordination polyhedron about this metal center during chelation may be regarded as a reasonable possibility.

An alternative mechanism,[22] the three-step sequence



leads, under conditions where the oxidant is present predominantly in its tripositive protonated form, to rate law 2,

$$\text{rate} = \frac{(\mathrm{Cu^I})(\mathrm{Co^{III}})K_Ak_1'k_2'}{k_{-1}' + k_2'(\mathrm{H^+})} \qquad (2)$$

which is algebraically of the same form as (1). When interpreted in terms of this three-step mechanism, plots of $1/k_{\text{obsd}}$ vs. (H^+) give $1/K_Ak_1'$ as slope and $k_{-1}'/K_Ak_1'k_2'$ as intercept, thus allowing calculation of K_Ak_1' and k_2'/k_{-1}'. These parameters are also summarized in Table II.

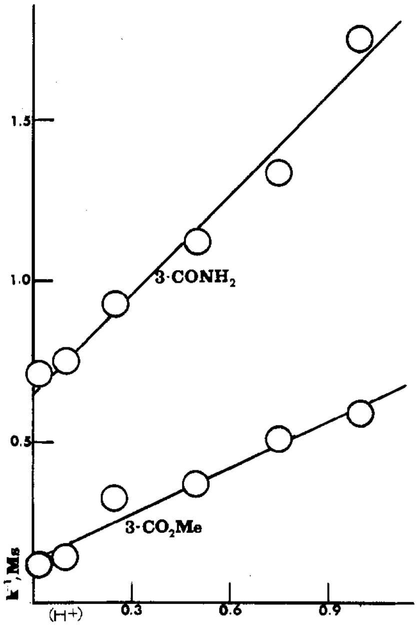


Figure 1. Rate data for the Cu^+ reductions of the 2-COOCo$(NH_3)_5$-3-$COOCH_3$- and the 2-COOCo$(NH_3)_5$-3-$CONH_2$-substituted pentaamminecobalt(III) complexes of 2,3-pyridinedicarboxylic acid at 25 °C, μ = 1.1 ($HClO_4$–$LiClO_4$). Values of k_{obsd}^{-1} are plotted against (H^+). Slopes and intercepts of the regression lines shown are used to calculate kinetic parameters, listed in Table II, associated with the two proposed mechanisms (see text).

Table II. Calculated Kinetic Parameters for Copper(I) Reduction of Pentaamminecobalt(III) Complexes of Dicarboxylatopyridines[a]

	for the two-step mechanism		for the three-step mechanism	
substituents	k_1,[b] M^{-1} s^{-1}	k_2/k_{-1},[b] M	K_Ak_1',[c] s^{-1}	k_2'/k_{-1}',[c] M^{-1}
2-COOCo$(NH_3)_5$-3-$COOCH_3$	6.7	0.29	1.95	3.4
2-COOCo$(NH_3)_5$-3-$CONH_2$	1.6	0.61	0.95	1.7
2-COOCo$(NH_3)_5$-4-$CONH_2$	1.4	0.64	0.89	1.6
2-COOCo$(NH_3)_5$-5-$COOCH_3$	1.5	0.94	1.37	1.06
2-COOCo$(NH_3)_5$-5-$CONH_2$	1.5	0.57	0.83	1.08

[a] Reactions at 25 °C, μ = 1.1; supporting electrolyte was $HClO_4$–$LiClO_4$. [b] k_1, k_{-1}, and k_2 are specific rates in eq 1. Values were calculated from plots of $(\text{rate}/(Cu^+)(Co^{III}))^{-1}$ vs. (H^+) (see text). [c] k_1', k_{-1}', and k_2' are specific rates in eq 2. K_A is the acidity constant for the oxidant. Parameters were calculated from plots of $(\text{rate}/(Cu^+)(Co^{III}))^{-1}$ vs. (H^+) (see text).

Values of k_2/k_{-1} (or k_2'/k_{-1}') do not allow a choice between mechanisms, for this ratio is not greatly different from unity in either case. If K_A for the oxidants is taken to be near 0.003 M,[11] the three-step mechanism leads to k_1' values near 300 and, on that basis, is preferable to the two-step. On the other hand, the final step is an act of electron transfer which is triggered by protonation. Such a process appears to be without precedent for systems of this type, although protonation is known to favor inner-sphere reductions of a number of carboxylatocobalt(III) complexes having a carbonyl group in conjugation with the coordinated carboxyl.[8,23]

Thus, serious, although not necessarily preclusive, objections apply to both mechanisms. We await further evidence before choosing.

References and Notes

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 5661 (1971).

(3) J. C.-K. Heh and E. S. Gould, *Inorg. Chem.*, preceding paper in this issue. This report describes the preparations of such selectively blocked complexes, their characterization, and their reductions by Cr^{2+}.

(4) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(5) O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 1968 (1969).

(6) C. Norris and F. Nordmeyer, *Inorg. Chem.*, **10**, 1235 (1971).

(7) A similar conclusion may be drawn from the drifts in the infinity readings observed when the complexes prepared from ligation of the diacids are reduced with Cr^{2+}.[3,8]

(8) E. S. Gould, *J. Am. Chem. Soc.*, **96**, 2373 (1974).

(9) P. K. Thamburaj, M. K. Loar, and E. S. Gould, *Inorg. Chem.*, **16**, 1946 (1977).

(10) The observed variations of rate are too marked to be attributed reasonably to medium effects associated with substitution of H^+ for Li^+ in the supporting electrolyte. See, for example, D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

(11) The limited solubilities of these complexes, as perchlorates, in water near room temperature, in conjunction with the relatively low pK_A values, has thus far ruled out determinations of pK_A's by partial titration, whereas the visible and near-UV spectra of the protonated and nonprotonated forms do not appear to be sufficiently different to allow reliable spectrophotometric determinations. The stated lower limit reflects the finding[3] that the Cr(II) reductions of these complexes, which in most instances involve only the nonprotonated forms, adhere closely to a single-term inverse-H^+ rate law in the range 0.1–1.2 M H^+, whereas with pK_A values ≤ 2, indications of kinetic saturation would appear near the lower end of the range. The structures of the oxidants suggest pK_A's near 2.5, i.e., 2 pK units below[12] that for monofunctional 2-COOCo complex, for which a value of 4.5 has been reported.[4]

(12) See, for example, R. W. Green and H. K. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956).

(13) Although pK_A for Cu^+_{aq} does not appear to have been recorded, it may be assumed, as a singly charged d^{10} ion, to have a value somewhat greater than that for Zn^{2+}_{aq} ($pK_A = 8.7$).[14]

(14) L. G. Sillen and A. G. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, Sect. 1, 62 (1964).

(15) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **15**, 1934 (1976).

(16) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, N.Y., 1968, Chapter 3. These authors not only summarize this view but also voice specific warnings concerning its misapplication.

(17) (a) J. P. Birk, *Inorg. Chem.*, **14**, 1724 (1975); (b) G. A. K. Thompson and A. G. Sykes, *ibid.*, **15**, 638 (1976).

(18) A. C. Dash and R. K. Nanda, *Inorg. Chem.*, **12**, 2024 (1973).

(19) G. Paquette and M. Zador, *Inorg. Chim. Acta*, **26**, L23 (1978).

(20) See, for example, D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1973).

(21) A. G. Massey, N. R. Thompson, B. F. G. Johnson, and R. Davis, "The Chemistry of Copper, Silver and Gold", Pergamon Press, Oxford, 1973, p 20.

(22) We thank a reviewer for suggesting this mechanism.

(23) A. Zanella and H. Taube, *J. Am. Chem. Soc.*, **94**, 6403 (1972).

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pH-Jump-Induced Intramolecular Electron Transfer within the $(NH_3)_5RuOV(HEDTA)^+$ Binuclear Ion

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Received April 17, 1978

A series of Ru(II)–V(IV) oxo-bridged binuclear complexes, $(NH_3)_5RuOVL^{4-n}$ (L = EDTA, $n = 4$; L = HEDTA, $n = 3$; L = EDDA, $n = 2$), have been formed in solution from $(NH_3)_5RuOH_2^{2+}$ and the corresponding VOL^{2-n} complex. The formation rate constant, k_1, for $(NH_3)_5RuOV(HEDTA)^+$ (I) is 2.83 ± 0.37 M^{-1} s^{-1} (25.0 °C, $\mu = 0.10$ NaCl, pH 6.86), indicative of substitution of the monovalent anion complex $VO(HEDTA)^-$ on Ru(II). The $(NH_3)_5RuOVL^{4-n}$ complexes exhibit a MLCT band near 605 nm which gives their characteristic dark green color. This band is assigned to the Ru(II) $d_{xy}(B_2) \rightarrow VO^{2+}$ $\pi^*(E)$ transition similar to the MLCT spectra observed for $(NH_3)_5Ru(II)$–X complexes (X = an aromatic N heterocyclic ligand, N_2, nitriles, etc.). The $(NH_3)_5RuOVL^{4-n}$ complexes exhibit an eight-line ESR spectrum characteristic of a localized V(IV) oxidation state ($A_{iso} = 100.9$ G for I compared to 102.1 G for $VO(HEDTA)^-$ in 50:50 vol % propylene glycol–water). The MLCT bands and ESR spectra are bleached under proton-jump conditions; the products are observed to be Ru(III) and V(III) monomer complexes. The rate law for this process is given by $-d(I)/dt = (k_2 + k_3[H_3O^+]^2)[I]$ with $k_2 = 0.11 \pm 0.04$ s^{-1}, $k_3 = (3.55 \pm 0.04) \times 10^3$ M^{-2} s^{-1} (25.2 °C, $\mu = 0.10$ NaCl/HCl). The activation parameters for the k_3 path of intramolecular electron transfer are $\Delta H_3^{\ddagger} = 6.86 \pm 0.24$ kcal/mol and $\Delta S_3^{\ddagger} = -19.2 \pm 0.8$ eu. Regeneration of the Ru(II)–V(IV) binuclear complexes can be achieved under pH-jump conditions by recombination of Ru(III) and V(III) monomers, $(NH_3)_5RuOH^{2+}$ and $VL(OH)^{2-n}$. The regeneration reaction proceeds by the inner-sphere path. The second-order rate constant for regeneration of I, k_4, is 1.32×10^6 M^{-1} s^{-1} (25.3 °C, $\mu = 0.10$) and exhibits activation parameters of $\Delta H_4^{\ddagger} = 12.1 \pm 0.5$ kcal/mol and $\Delta S_4^{\ddagger} = 9.4 \pm 1.6$ eu. The $(NH_3)_5RuOV(EDDA)^{2+}$ complex undergoes competitive intramolecular electron transfer and H_3O^+ catalyzed loss of EDDA. At pH 2.4 the ligand dissociation pathway consumes 57% of the initial Ru(II), forming $(NH_3)_5RuOV(H_2O)_4^{4+}$ which does not undergo proton-promoted intramolecular electron transfer for $[H_3O^+] \leq 0.35$ M. Mechanisms are proposed which involve cis OH^-, H_2O coordination positions at the V(IV) center for the $[H_3O^+]^2$ promoted bleaching process of I. A related cis OH^-, OH^- orientation is proposed for the recombination of Ru(III) and V(III) monomers in the pH-jump-induced regeneration of I. Regeneration rates are modestly sensitive to specific interactions between phosphate, Tris, and 2,6-lutidine buffer species and $(NH_3)_5RuOH^{2+}$. This effect is described in terms of unstructured and structured ion pairs or ion-dipole pairs between $(NH_3)_5RuOH^{2+}$ and the buffers.

Introduction

The redox chemistry of transition-metal centers is often modified dramatically by a chelating environment relative to the simple aquo species. These effects are usually due to ligand field factors which restrict the labilities, or spin state of the central ion, or due to the existence of low-lying unfilled ligand orbitals which are available to promote the electron-transfer process. Much less attention has been given to the effect of concerted structural changes which may be coupled to redox events. Recently coordination-controlled electron-transfer processes have been detected in the cross reactions of $VO(HEDTA)^-/V(HEDTA)^-$ [1,2] and $VO(HEDTA)^-/Mn(EDTA)(H_2O)^-$.[3] The rearrangement factor is transmitted to the observed rate constant in terms of an additional activation entropy, $\Delta S_{CR}^{\ddagger}$.[2,3] Rate-limiting rearrangements are slow enough to allow the detection of the $V^{II}V^{IV}O(HEDTA)_2^{2-}$

0020-1669/78/1317-3145$01.00/0 © 1978 American Chemical Society