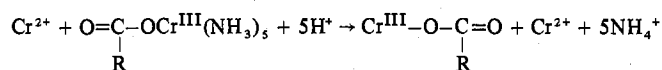# Electron Transfer. 35. Some Reactions of Carboxylatopentaamminechromium(III) Complexes with One-Electron Reductants[1]

C.-L. LIU, Y.-T. FANCHIANG, and EDWIN S. GOULD*

Pentaamminechromium(III) complexes, $RCOO(NH_3)_5Cr^{III}$, have been prepared from 2,3-pyridinedicarboxylic, 2,3-pyrazinedicarboxylic, 2-pyridinecarboxylic, and pyruvic acids. The pyridinecarboxylato and dicarboxylato derivatives, like the maleato complex in this group, undergo electron-transfer reactions with Cr^{2+} analogous to the reductions of the corresponding

$$Cr^{2+} + O{=}\underset{\underset{R}{|}}{C}{-}OCr^{III}(NH_3)_5 + 5H^+ \rightarrow Cr^{III}{-}O{-}\underset{\underset{R}{|}}{C}{=}O + Cr^{2+} + 5NH_4^+$$

cobalt(III) complexes, but much slower than the latter. The rate law for the reactions of the cobalt(III) and chromium(III) complexes is the same for the pyridinedicarboxylato derivatives (rate = $k(Cr^{2+})$(complex)$(H^+)^{-1}$, but this is not the case for the 2-pyridinecarboxylato and maleato derivatives. The rate constant (1.40 s^{-1}, 25 °C, μ = 1.0) for the pyridinedicarboxylatochromium(III) reaction, in combination with the observed pK_a, 2.76, leads to a bimolecular specific rate 8.2 $\times 10^2$ M s^{-1} for reaction of the deprotonated form of this complex. The latter value, unusually great for a reaction of this type, indicates that Cr(III) is coordinated to the 2-, rather than the 3-, carboxyl in this complex (I). Reaction of Cr^{2+} with the pyrazinedicarboxylato complex, II, yields a deep green species, similar to Cr(III)-bound pyrazine radicals observed in earlier studies, whereas reaction with the pyruvato complex, III, results in reduction of the ligand but preservation of the $(NH_3)_5Cr^{III}$ center. Reactions of each of the chromium(III) complexes with U^{3+} lead to rapid reduction of the ligand, rather than electron transfer between metal centers. The differences in behavior of the chromium(III) complexes toward Cr^{2+} and U^{3+} rule out the intervention of Cr(III)-bound radical intermediates common to both reaction series, an essential feature of the "chemical" or "radical-ion" mechanism for electron transfer. This mechanism, however, remains a reasonable one for the Cr^{2+} reduction of the pyruvatocobalt(III) complex.

The diverse roles that bound carboxyl groups assume as electron-transfer bridges have been explored almost exclusively through experiments dealing with the reductions of carboxylatocobalt(III) derivatives.[2,3] Although the ease with which such oxidants can be prepared, their structural integrity in aqueous solution, and the wide range of rates at which they react with a variety of reductants account for this direction of emphasis, it may be asked whether the several variations of the inner-sphere path observed extend to other oxidizing centers as well.

Prominent among metal centers forming substitution-inert complexes which undergo one-electron reductions at convenient rates is chromium(III). The latter is less strongly oxidizing than Co(III) by more than 2 V, but considerable thermodynamic driving force may contribute to the reduction of complexes derived from such basic ligands as ammonia and ethanediamine in acid media. Reductions of Cr(III) complexes are generally slower, by one to several orders of magnitude, than those of the corresponding Co(III) derivatives, with the differences between the two centers becoming least marked in cases where electron transfer to the bridging ligand constitutes an important aspect of the activation process.[3,4] It was therefore reasonable to anticipate that bridging action by those very powerful mediating groups which, in Co(III) reductions, result in specific rates measurable only with stop-flow techniques[5] would, in Cr(III) reductions, lead to rates that might be estimated using conventional methods.

Experimental Section

Materials. Aquopentaamminechromium(III) perchlorate was prepared from the corresponding nitrate[6] by the method of Davies et al.[7] Lithium perchlorate[8] and solutions of chromium(II) perchlorate[9] and uranium(III) perchlorate[10] were prepared as described. Carboxylic acids (Aldrich products) were used as received. 2,3-Pyridinecarboxylic anhydride[11] and 2,3-pyrazinedicarboxylic anhydride[12] were prepared from the parent diacids by literature procedures.

Preparation of the Complexes. Acetato-, maleato-, 2,3-pyridinedicarboxylato-, and 2,3-pyrazinedicaroboxylatochromium(III) perchlorates were prepared from the aquo perchlorate and the ap-

propriate anhydride by a modification of the method of Davies.[7] To a solution of 1.0 g of the aquo complex in 15 mL of dimethylformamide was added 4.8 mmol of the anhydride and 0.6 g of N,N-dimethylbenzylamine. The mixture was stirred for 45 min in the dark, and the crude product was precipitated by addition of 200 mL of sec-butyl alcohol. The complex was crystallized three times by dissolving in a minimum volume of water at room temperature, making the solution 1 M in $HClO_4$, and then keeping it at 0 °C for 30 min. The usual products from the pyridine and pyrazine preparations were mixtures of nonprotonated and protonated (tris(perchlorate)) complexes. Pure tris(perchlorates) of these complexes could be obtained (in low yield) by recrystallization from a larger volume of dilute $HClO_4$.

Pyruvatopentaamminechromium(III) perchlorate was prepared in aqueous solution by heating a solution of 2 g of the aquo complex and 4.0 mL of pyruvic acid in 15 mL of water at 55 °C for 25 min. An orange precipitate separated from the deep red solution. The mixture was cooled, treated with 1 mL of 70% $HClO_4$, and allowed to stand at 0 °C for 30 min. The product was filtered off and recrystallized twice from dilute $HClO_4$ in the usual way. The 2-pyridinecarboxylato complex was prepared similarly by heating 11 mmol of picolinic acid and 1.0 g of the aquo complex in 14 mL of water for 25 min at 70 °C and then recovering the product in the usual way. Attempts were made to use this method, and several variations of it, to prepare the complexes of 2,6-pyridinedicarboxylic acid, glycolic acid, salicylic acid, and S-benzylthioglycolic acid, but these were unsuccessful.

All carboxylatopentaamminechromium(III) complexes were stored in the dark at 0 °C.

Elemental analyses and spectral characteristics of new complexes are listed in Table I.

Kinetic Experiments. Rates of reaction of Cr^{2+} with the carboxylatochromium(III) complexes were followed spectrophotometrically by observing the decreases in absorbance at the low-energy carboxylatopentaamminechromium(III) maximum near 488 nm. Reactions were carried out under N_2 at 25.0 ± 0.2 °C. Reactions with the 2,3-pyridinedicarboxylato and 2-pyridinecarboxylato complexes were first order each in Cr(III) and Cr^{2+} but were generally run under pseudo-first-order conditions with at least a tenfold excess of Cr^{2+}. Ionic strength was maintained at 1.0 M (LiClO$_4$ + HClO$_4$). Reactions were followed for at least 5 half-lives. Specific rates, obtained from the slopes of logarithmic plots of absorbance differences against reaction time, checked to within 6% for replicate runs.

Table I. Carboxylatopentaamminechromium(III) Perchlorates, $RCr(NH_3)_5(ClO_4)_2$

R	% C[e]	% H[e]	% Cr[b,e]	% ClO$_4$[c,e]	ϵ_1	λ_{max}, nm	ϵ_2	λ_{max}, nm
2,3-Pyridinedicarboxylato (I)[a,d]	13.77 (13.97)	3.47 (3.32)	8.7 (8.6)	47.6 (49.5)	50.3	486	39.5	359
2,3-Pyrazinedicarboxylato (II)[a]	11.72 (11.93)	3.40 (3.15)	8.8 (8.6)	48.7 (49.5)	65.1	487		
Pyruvato (III)	8.28 (8.21)	4.30 (4.26)	12.3 (12.0)	47.5 (47.0)	58.9	488	44.3	357
2-Pyridinecarboxylato (IV)	16.24 (17.52)	3.73 (4.15)	11.3 (11.4)	43.7 (47.5)	53.6	483	84.1	353

[a] Tris(perchlorates). [b] G. W. Haupt, *J. Res. Natl. Bur. Stand.*, 48, 414 (1952). [c] See ref 9. [d] $pK_a = 2.76$ (25 °C, 1.0 M LiClO$_4$). [e] Calculated values are given in parentheses.

Absorbance changes occurring when the acetato complex was treated for 1 h with 0.1 M Cr(ClO$_4$)$_2$ were slight and corresponded to those observed in the absence of Cr(II).

The reaction of Cr^{2+} with the pyruvato and pyrazinedicarboxylato complexes resulted in increases in absorbance at 488 nm, rather than decreases. The effect was particularly intense for the pyrazine derivative, which yielded a deep green species similar in appearance to the chromium(III)-bound pyrazine radicals formed by the reaction of Cr^{2+} on uncoordinated pyrazines.[13] The rate of formation of the green material was too great to be measured, even under stop–flow conditions. The less marked increase in the pyruvato reaction, to which a bimolecular specific rate about 3×10^2 M^{-1} s^{-1} (25 °C, 0.12 M HClO$_4$, $\mu = 1.2$) could be assigned, appeared to reflect the formation of Cr(H$_2$O)$_6$$^{3+}$ with no attendant drop in the carboxylatopentaamminechromium(III) absorbance.

Reactions of the carboxylato complexes with uranium(III) were rapid and were followed, using the Durrum-Gibson stop–flow spectrophotometer, at 420 nm. These reactions were run in 0.24 M HClO$_4$ with Cr(III) in excess. Reproducible bimolecular rate constants could be obtained for reactions of the maleato (4×10^3 M^{-1} s^{-1}) and pyruvato (6×10^3 M^{-1} s^{-1}) derivatives, but the remaining complexes exhibited less straightforward kinetic behavior.[14] Since it could be shown (see below) that all U^{3+} reductions were occurring at the ligand, rather than at the Cr(III) center, these reactions were not studied further. Reaction of the 2,3-pyrazinedicarboxylato complex with Eu^{2+} yielded a strongly absorbing yellow species, but here again the kinetic picture was not simple.

Additional Experiments. Addition of Cr^{2+} to solutions of the 2-pyridinecarboxylato and 2,3-pyridinedicarboxylato complex resulted in absorbance decreases at the carboxylatopentaamminechromium(III) maxima near 488 and 355 nm and increases at carboxylatopentaaquochromium(III) maxima near 570 and 410 nm. Isosbestic points were observed near 387, 440, and 520 nm. In contrast, addition of Cr^{2+} to an equivalent quantity of the pyruvato complex yielded a solution having a spectrum corresponding to superposition of equal parts of carboxylatopentaammine absorbance and Cr(H$_2$O)$_6$$^{3+}$ absorbance.[15] The latter solution did not reduce added (NH$_3$)$_5$CoCl^{2+} to Co^{2+}, thus indicating that Cr^{2+} was no longer present. Addition of U^{3+} to the maleato, pyruvato, and 2-pyridinecarboxylato complexes yielded, in each case, spectra corresponding to superposition of carboxylatopentaamminechromium(III) and U^{4+}.[16] Such solutions likewise did not reduce (NH$_3$)$_5$CoCl^{2+}, demonstrating the absence of both Cr^{2+} and U^{3+}. The strongly absorbing solution resulting from action of U^{3+} on the 2,3-pyridinedicarboxylato derivative was similarly shown to be devoid of reducing power.[9,13b]

Results and Discussion

Since the carboxylato derivatives of (NH$_3$)$_5$Cr^{III} are hydrolyzed much more rapidly than the analogous complexes of Co(III) but undergo electron transfer much more slowly, difficulty resulting from competition between the two processes would be expected, and has been reported,[3a] in studying electron-transfer reactions of such slowly reacting complexes as (NH$_3$)$_5$CrOAc^{2+}. In the present work, such complications have been minimized by utilizing complexes with very effectively mediating carboxylato groups. At the same time, however, such ligands are oxidants in their own right,[2a,17] and the possibility of irreversible reduction of the organic substituent must thus be considered.

Table II. Specific Rates for Reactions of Chromium(II) with Pyridinecarboxylatopentaamminechromium(III) Complexes, $R(NH_3)_5Cr^{III}$ (eq 1)[a]

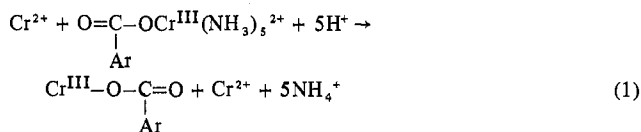| R	(H$^+$), M	k
2,3-Pyridinedicarboxylato (I)	0.25	5.6
	0.50	2.7
	0.75	2.0
	1.00	1.56
2-Pyridinecarboxylato (IV)	0.20	0.0039
	0.45	0.0034
	0.75	0.0030
	1.00	0.0030

[a] Specific rates are in M^{-1} s^{-1}. Reactions were carried out at 25 °C; $\mu = 1.0$ (LiClO$_4$). (Cr^{III})$_0$ = 7×10^{-4} to 1×10^{-2} M; (Cr^{2+})/(Cr^{III}) = 10. Values are averages of two to five replicate runs. Agreement between runs was better than 6%.

Of the complexes in the present series, the 2-pyridinecarboxylato (IV) and 2,3-pyridinedicarboxylato (I) derivatives
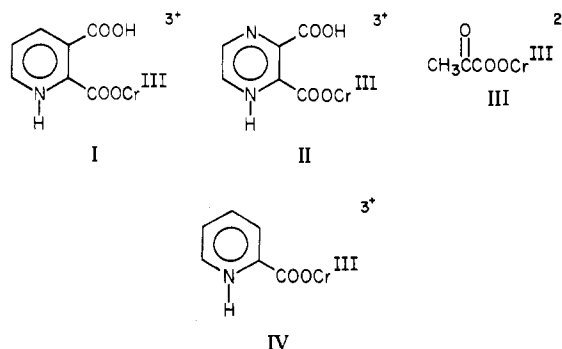
react with Cr^{2+}, undergoing electron transfer to the chromium(III) center, with the net result the detachment of ammonia from Cr(III):

$$\text{Cr}^{2+} + \underset{\underset{\text{Ar}}{|}}{\text{O=C-OCr}^{III}(\text{NH}_3)_5}{}^{2+} + 5\text{H}^+ \rightarrow$$

$$\underset{\underset{\text{Ar}}{|}}{\text{Cr}^{III}-\text{O-C=O}} + \text{Cr}^{2+} + 5\text{NH}_4{}^+ \qquad (1)$$

There is no net consumption of Cr^{2+} in the primary reaction, although slow reduction of the pyridine ring undoubtedly occurs. Results of rate measurements dealing with these pyridine systems are summarized in Table II.

Kinetic data for the 2,3-pyridine derivative support the assignment of structure I, with coordination at the 2-position, rather than the isomeric 3-coordinated structure. The high rate of reduction and (less compellingly) the inverse-H$^+$ dependence are taken to be characteristic of pyridinedicarboxylato complexes in which the oxidizing center is situated close enough to the ring nitrogen to allow chelation prior to the act of electron transfer.[5b,8,18] Within the range of acidity studied, reaction of this complex closely adheres to the monomial rate law $k_{obsd} = 1.40/(\text{H}^+)$ M^{-1} s^{-1}, indicating that

Table III. Specific Rates for the Reactions of Chromium(II) with Carboxylatopentaamminechromium(III) Complexes, $R(NH_3)_5Cr^{III}$, and with the Analogous Cobalt(III) Complexes[a]

R	k_{CrIII}	k_{CoIII}
2,3-Pyridinedicarboxylato (I)	1.40/(H⁺)	950/(H⁺)[b]
2-Pyridinecarboxylato (IV)	0.0033	36/(H⁺)[c]
Pyruvato (III)	3×10^2 [d]	1×10^4 [e]
Maleato	0.018 + 0.0015/ (H⁺)[f]	2×10^2 [g]
Acetato	$<10^{-4}$	0.35[h]

[a] Specific rates are in M^{-1} s^{-1}; reactions at 25 °C, $\mu = 1.0$. [b] From data in ref 5b. [c] Reference 8. [d] Approximate specific rate for reduction of the ligand; (H⁺) = 0.12 M (see text). [e] Reference 5a. [f] Reference 3a. [g] Reference 21. [h] Limiting specific rate at low acidities. See M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, 10, 1983 (1971).

virtually all is reacting at the deprotonated (dipositive) level, which, like the corresponding cobalt(III) derivative,[5b] is expected to feature partition into an inactive (VII) and active (VIII) species. The bimolecular rate constant for this path,
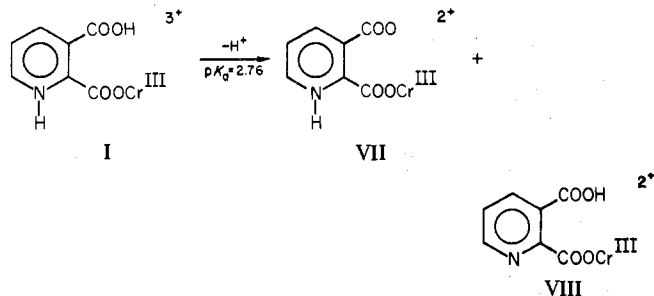
obtained by dividing by K_a for the oxidant, $(1.7 \times 10^{-3}$ M^{-1} in 1.0 M LiClO₄) is 8.2×10^2 M s^{-1}. Although the latter value is not the highest reported for electron transfer to Cr(III),[19] it may be considered to be unusually great for a $(NH_3)_5Cr^{III}$–Cr^{2+} reaction.[20]

Specific rates for the reactions of Cr^{2+} with chromium(III) complexes are assembled and compared with values for the corresponding reductions of $(NH_3)_5Co^{III}$ derivatives in Table III. As expected, the cobalt(III) reactions are considerably more rapid in each case, but comparison is complicated by dissimilarities in the kinetic acidity patterns. In particular, with the maleato complexes, the inverse-acid path is observed for chromium(III), but not for cobalt(III);[21] in contrast, with the 2-pyridinecarboxylato oxidants, the inverse-acid path is predominant for cobalt(III) but marginal for chromium(III) within the range of acidities examined here. In principle, both an acid-independent path and an inverse-acid path should exist for all oxidants having an acidic proton. It has been shown, however, that distribution between available paths varies greatly as the reducing center is altered,[22] although such variation, except perhaps in the case of V^{2+} reductions,[22a] has not yet been satisfactorily accounted for. The present work indicates that such a distribution is comparably sensitive to changes in the oxidizing center, but too few cases have been examined to allow a generalization.

Loss of Cr^{2+} in a process other than the primary electron transfer has been reported for the maleatochromium(III) derivatives by Davies and Jordan,[3a] and we observe a similar consumption in the pyruvatochromium(III) reaction. In the maleato case, however, reduction of the ligand has been shown to follow electron transfer between chromium centers, whereas in the pyruvato reaction, we find that virtually all of the characteristic RCOO(NH₃)₅Cr^{III} absorption peak remains. If it is assumed that the position and intensity of this peak are very nearly independent of the nature of the carboxylato group

(see, for example, Table I), we must infer that reduction of the ligand has consumed Cr^{2+} *before* electron transfer with bound Cr(III) could occur. A similar description applies to reactions of the pyruvato, maleato, and 2-pyridinecarboxylato complexes with the more powerful reductant U^{3+}, for in these instances also, the reactant is quickly consumed without detachment of chromium from the ammonia molecules bound to it.[23-25]

Comparisons between reactions of chromium(III) and cobalt(III) acceptor systems have in the past[3,4a] been used to differentiate between a "radical-ion" or "chemical" mechanism for inner-sphere reduction, in which one-electron reduction of a ligand precedes acceptance by the oxidizing center, and a "resonance transfer" mechanism, in which interaction between the participating metal centers is more direct. Considerable indirect evidence for the radical-ion mechanism exists in specific cases,[3,4,17] but the intervening radical has not yet been observed in any inner-sphere reaction mediated by a substituted pyridine or by an acyclic ligand.[26] Although the ligands used in this study are among those that might be expected to accommodate this mechanism most readily, our results appear to weigh against such a path for the chromium(III) reactions. An essential feature of the chemical mechanism is that internal electron transfer from the radical intermediate to the acceptor center must not depend upon the nature of the reducing species used to generate the radical. Hence, participation of the maleato, 2-pyridinecarboxylato, and 2,3-pyridinedicarboxylato complexes in metal-to-metal electron transfer when the reducing center is Cr^{2+}, but not when it is U^{3+}, may be taken to be inconsistent with the intervention of an intermediate common to the two reductants. Some interaction between the metal centers in the electron-transfer reaction is evidently essential.

A chemical mechanism remains reasonable for the very rapid reduction, using Cr^{2+}, of the pyruvatocobalt(III) complex, with one-electron reduction of the ligand being the initial step both in this reaction and in the reaction with the analogous chromium(III) derivative. Because of the weak oxidizing potential of bound Cr(III), however, subsequent internal electron transfer from ligand to acceptor is much slower with the latter complex and consequently does not compete successfully with those secondary reactions that modify the ligand but preserve the $(NH_3)_5Cr^{III}$ center.[27-29]

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) See, for example: (a) H. Taube and E. S. Gould, *Acc. Chem. Res.*, 2, 321 (1969); (b) P. K. Thamburaj, M. K. Loar, and E. S. Gould, *Inorg. Chem.*, 16, 1946 (1977).
(3) Just two studies of electron transfer in carboxyl-bridged systems not involving Co(III) appear to have been reported: (a) R. Davies and R. B. Jordan, *Inorg. Chem.*, 10, 2432 (1971); (b) H. Diaz and H. Taube, *ibid.*, 9, 1304 (1970).
(4) See, for example: (a) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, 90, 1162 (1968); (b) M. M. Itzkowitz and F. Nordmeyer, *ibid.*, 96, 2124 (1974).
(5) (a) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968); (b) E. S. Gould, *J. Am. Chem. Soc.*, 96, 2673 (1974).
(6) G. G. Schlessinger, "Inorganic Laboratory Preparations", Chemical Publishing Co., New York, N.Y., 1962, pp 198–200.
(7) R. Davies, G. B. Evans, and R. B. Jordan, *Inorg. Chem.*, 8, 2025 (1969).
(8) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, 93, 5661 (1971).
(9) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, 86, 1318 (1964).
(10) R. T. Wang and J. H. Espenson, *J. Am. Chem. Soc.*, 93, 380 (1971).
(11) A. W. Dox, *J. Am. Chem. Soc.*, 37, 1958 (1915).
(12) I. A. Solomons and P. E. Spoerri, *J. Am. Chem. Soc.*, 75, 679 (1953).
(13) (a) H. Speicker and K. Wieghardt, *Inorg. Chem.*, 16, 1290 (1977); (b) M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *ibid.*, 17, 326 (1978).
(14) Reaction of the 2-pyridinecarboxylato complex with U(III) appeared to be autocatalytic with an initial specific rate near 10² M^{-1} s^{-1}. The

kinetic curve for the 2,3-pyridinedicarboxylato complex indicated the formation and decay of an intermediate species; with (Cr^{III}) = 0.004 M and (U^{III}) = 0.0025 M, this intermediate attained its maximum concentration about 8 ms after mixing. Action of U(III) on the 2,3-pyrazinedicarboxylato complex yielded a strongly absorbing yellow-green species, the rate of formation of which was too great to be measured by our methods.

(15) J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).
(16) D. C. Stewart, Argonne National Laboratory Report No. ANL-4812, 1952, p 14.
(17) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965); **88**, 2983 (1966).
(18) Confirmatory evidence on this point arises from recent measurements by J. C.-K. Heh (Kent State University, 1977). The specific rate of reduction (25 °C, μ = 1.2), using Cr^{2+}, of the 2-coordinated monoester complex V has been found to be 500/(H$^+$) M^{-1} s^{-1}, whereas the corresponding (almost acid-independent) specific rate for its 3-coordinated isomer, VI, is 0.5 M^{-1} s^{-1}. Note that the chromium(III) derivative of

$k_{Cr} = 5 \times 10^2/(H^+)$ M^{-1} s^{-1}

$k_{Cr} = 0.5$ M^{-1} s^{-1}
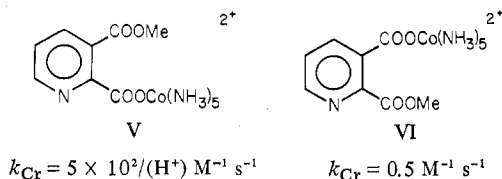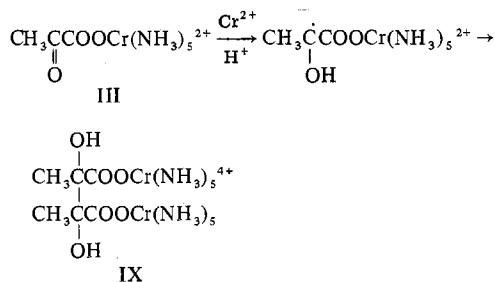
2,3-pyridinedicarboxylic acid in the present series reacts considerably more rapidly with Cr^{2+} than does the 3-coordinated cobalt(III) complex, VI.

(19) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966), report a specific rate greater than 2 × 10^4 M^{-1} s^{-1} for the reaction Cr(SCN)OH$^+$ + Cr^{2+} → Cr^{2+} + Cr(NCS)OH$^+$.
(20) In view of evidence that pyridinecarboxylic acids exist predominantly in their zwitterionic forms in aqueous solution (see, for example, R. W. Green and K. H. Tong, *J. Am. Chem. Soc.*, **78**, 4896 (1956)), a large fraction of the deprotonated form of I would be expected to be microspecies VII. Since the observed specific rate for reduction of two rapidly equilibrating species is the weighted average of the individual specific rates, the specific rate associated with VIII alone would be considerably greater than 10^3 M^{-1} s^{-1}.
(21) In their study of the Cr^{2+} reduction of the maleato derivative of (NH$_3$)$_5$Co^{III}, M. V. Olson and H. Taube, *Inorg. Chem.*, **9** 2072 (1970), extend their measurements to (H$^+$) = 0.004 M, at which acidity about 30% of the maleato complex (K_a = 0.00182) is converted to its conjugate base. Since k_{Cr} for this complex neither increases nor decreases with

acidity in the range 0.004–1.0 M, it must be inferred that, in this one case, the protonated and nonprotonated forms of the oxidant are reduced at very nearly the same specific rate.

(22) (a) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973); (b) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974); (c) A. H. Martin and E. S. Gould, *ibid.*, **14**, 873 (1975).
(23) Although we have not attempted to identify the products formed from reductions of the ligands, analogy with a related system^{24} suggests formation of the bimolecular reduction product IX in the pyruvato reactions

(24) E. S. Gould, N. A. Johnson, and R. B. Morland, *Inorg. Chem.*, **15**, 1929 (1976).
(25) See, for example: (a) H. Cohen and D. Meyerstein, *Isr. J. Chem.*, **12**, 1049 (1974); (b) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969); (c) E. Hayon, T. Ibata, N. Lichtin, and M. Simic, *ibid.*, **76**, 2072 (1972).
(26) For descriptions of radical intermediates in related systems, see: (a) M. Z. Hoffmann and M. Simic, *J. Am. Chem. Soc.*, **94**, 1757 (1972); (b) E. S. Gould, *ibid.*, **94**, 4360 (1972).
(27) A reviewer has asked whether it is reasonable to attribute the observed differences in the behavior of Cr^{2+} and U^{3+} to the action of the latter as a two- rather than a one-electron reductant. In view of the marked instability of the two-electron oxidation product, U(V), under our reaction conditions^{28} and in view of the difficulty in carrying out one-electron oxidations of U(IV) in oxidizing media similar to ours,^{29} we consider this alternative as relatively unlikely.
(28) L. B. Asprey and B. B. Cunningham, *Prog. Inorg. Chem.*, **2**, 290 (1960).
(29) See, for example, R. T. Wang and J. H. Espenson, *J. Am. Chem. Soc.*, **93**, 380 (1971).

Moreover, in view of the very rapid dimerization reported for a large number of related one-electron reduction products in aqueous media,^{25} it seems likely that bimolecular chromium(III) products are formed also in the reductions by U^{3+} in the present study.

Magnetic Exchange Interactions in Transition-Metal Dimers. 14. Binuclear Copper(II) Schiff Base Compounds of Salicylaldehyde with Aromatic Polyamines[1]

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The variable-temperature (4.2–290 K) magnetic susceptibility characteristics of three binuclear copper(II) complexes, two binuclear nickel(II) complexes, and one binuclear cobalt(II) complex are reported. Each binuclear complex has an iminobenzene moiety bridging between the two metal ions. Condensation of salicylaldehyde with either *m*- or *p*-phenylenediamine gives ligands which react with cupric ion to give the complexes Cu$_2$(sal-*m*-pda)$_2$ and Cu(sal-*p*-pda)$_2$, respectively. The magnetism of the former is found to be as reported previously. An improved glass EPR spectrum is reported which shows *intra*dimer zero-field splitting. The compound Cu$_2$(sal-*p*-pda)$_2$ has an antiferromagnetic interaction ($J \simeq -1.9$ cm^{-1}) of essentially comparable strength to Cu$_2$(sal-*m*-pda)$_2$. The compound Ni$_2$(sal-*m*-pda)$_2$·3H$_2$O also shows an antiferromagnetic interaction with $J = -1.6$ cm^{-1}. Condensation of 2,2′,6,6′-tetraaminobiphenyl with salicylaldehyde gives a binucleating ligand which is used to prepare Cu$_2$(sal-tabp), Ni$_2$(sal-tabp)·H$_2$O, and Co$_2$(sal-tabp)·^{1}/$_2$H$_2$O. The copper(II) compound shows very little sign of an interaction in the susceptibility data taken down to 4.2 K. The room temperature CHCl$_3$ solution EPR spectrum, however, shows that there is an interaction. The liquid nitrogen temperature CHCl$_3$ glass EPR spectrum is well resolved for Cu$_2$(sal-tabp). Some comments and data are presented bearing on the electrochemistry of binuclear copper(II) complexes. Both Ni$_2$(sal-tabp)·H$_2$O and Co$_2$(sal-tabp)·^{1}/$_2$H$_2$O show weak antiferromagnetic exchange interactions in their susceptibility curves to 4.2 K, which are fit to give $J = -0.49$ and $J = -0.60$ cm^{-1}, respectively.

Introduction

In previous work[4] the magnetic exchange interactions present in the binucleated copper(II) complexes Cu$_2$A^4(B^3)$_2$ and Cu$_2$A^3(B^3)$_2$ were determined. An *intra*molecular an-

tiferromagnetic exchange interaction was found to be present in Cu$_2$A^4(B^3)$_2$ where $J = -12$ cm^{-1} (Hamiltonian = $-2J\hat{S}_1 \cdot \hat{S}_2$). The interaction between the two copper(II) ions, which are separated by ca. 7.5 Å, is propagated by the 1,2,4,5-tetra-