not change from pH 4 up to at least pH 12, when observed by conventional or stopped-flow spectrophotometry. At pH 13 and higher the rate of basic decomposition of $NHCl_2$ is fast, and this interferes with the spectral measurements of the initial absorbance. If it is assumed that a 10% change in the concentration of $NHCl_2$ could be detected by a change in the initial absorbance, then the protonation constant for NCl_2^- must exceed 10^{13} M^{-1}. The protonation constant for NCl_2^- will not exceed that of $NHCl^-$, which is estimated[3,37] to be greater than 10^{18}.

Conclusion

It is not uncommon for traces of a species to catalyze a reaction, but it is less common for such traces to inhibit a reaction. This work shows that traces of ammonia inhibit the decomposition of dichloramine. This is because ammonia reacts with hypochlorous acid, which is responsible for the instability of dichloramine.

Solutions of dichloramine free of other nitrogen compounds can be prepared by cation-exchange chromatography. With use of these solutions, it has been shown that dichloramine is unstable in the presence of even trace concentrations of hypochlorous acid, a compound which is produced in the decomposition of dichloramine. Consequently, the decomposition is an autocatalytic process. Dichloramine produces trichloramine in a termolecular mechanism involving the simultaneous removal of the proton by a general base and chlorination by HOCl. Dichloramine also reacts with trichloramine to produce nitrogen gas and more hypochlorous acid. This latter reaction may cause trichloramine concentrations to increase when more hypochlorite is added to a system than is necessary to reach breakpoint stoichiometry. All of the dichloramine could be rapidly converted to trichloramine and be unavailable to participate in the subsequent production of N_2. The general-base catalysis observed suggests that the breakpoint chlorination reactions will be speeded by the presence of phosphate or other buffers in the solution.

Hypochlorite reacts more rapidly with ammonia than with dichloramine, so that dichloramine solutions are stabilized by the presence of ammonia. The slow decomposition of dichloramine in the presence of ammonia produces chloramine and other compounds.

The instability of dichloramine has implications for the analysis of chlorinated water for free and combined chlorine. Several of the standard methods for these analyses, namely the amperometric[31b] and syringaldazine[31c] protocols, require that the sample first be buffered at neutral pH. If the sample is initially at a lower pH and does not contain ammonia, then this step will cause some or all of the dichloramine to decompose before analysis. As a result, the values determined for total and combined chlorine will be low and the value for free chlorine may be high.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-7822456 and by a fellowship from the Phillips Petroleum Co. to V.C.H.

Registry No. $NHCl_2$, 3400-09-7; HOCl, 7790-92-3; NH_3, 7664-41-7; NCl_3, 10025-85-1; HPO_4^{2-}, 14066-19-4; OCl^-, 14380-61-1; CO_3^{2-}, 3812-32-6; OH^-, 14280-30-9.

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(37) Anbar, M.; Yagil, G. *J. Am. Chem. Soc.* **1962**, *84*, 1790–96.

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Kinetics of the Reduction of the Linkage Isomers of the Pentaamminecobalt(III) Complexes of 4-Cyanobenzoic Acid by Chromium(II)

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The chromium(II) reduction of the nitrile-bonded pentaamminecobalt(III) complexes with 3- and 4-cyanobenzoic acids has been studied. For the 4-cyanobenzoic acid complex, the rate law at 25 °C and $I = 1.0$ mol L^{-1} was $k_{obsd} = (k_H[H^+] + kK_a)/(K_a + [H^+])$. A nonlinear least-squares fit of the data to this equation gave $k_H = 0.290 \pm 0.005$ L mol^{-1} s^{-1}, $k = 0.99 \pm 0.12$ L mol^{-1} s^{-1}, and $K_a = 0.0031 \pm 0.0007$ mol L^{-1}. The reduction was shown to occur via remote attack of Cr(II) to produce a (carboxylato)chromium(III) product. At higher temperatures the inverse hydrogen ion term disappears, and the activation parameters for the k_H term were $\Delta H^* = 7.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^* = -37 \pm 3$ eu. The V(II) reduction of this complex followed the rate law $k_{obsd} = k_1 + k_2[H^+]^{-1}$ with $k_1 = 11.1 \pm 0.2$ L mol^{-1} s^{-1} and $k_2 = 0.21 \pm 0.04$ s^{-1} at 25 °C and $I = 1.0$ mol L^{-1}. The nitrile-bonded 3-cyanobenzoic acid complex is reduced by chromium(II) without ligand transfer and follows the simple rate law $-d \ln [Co(III)]/dt = k_2[Cr(II)]$. At 25 °C and $I = 1.0$ mol L^{-1}, $k_2 = (4.89 \pm 0.23) \times 10^{-2}$ L mol^{-1} s^{-1}, $\Delta H^* = 8.3 \pm 0.4$ kcal mol^{-1}, and $\Delta S^* = -37 \pm 2$ eu. The reductions are discussed in terms of the reducibilities of the ligands and the stabilities of possible precursor complexes.

Introduction

It is generally thought that the necessary criteria for remote attack in redox reactions between transition-metal complexes in solution are (1) a reducible ligand system and (2) a remote polar donor group capable of forming a precursor complex.[1-3] The relative importance of these requirements and the mechanism of electron transfer through the ligand are not fully understood. Complications in interpretation have arisen because the majority of studies have involved the reduction of (carboxylato)pentaamminecobalt(III) complexes by chromium(II) which can also proceed by adjacent attack of the reductant at the carbonyl oxygen of the coordinated carboxylate.[4,5] For example,[4] reduction of (terephthalato)penta-

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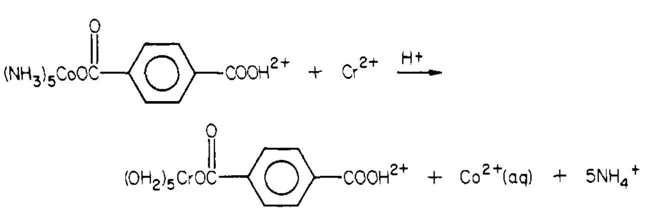
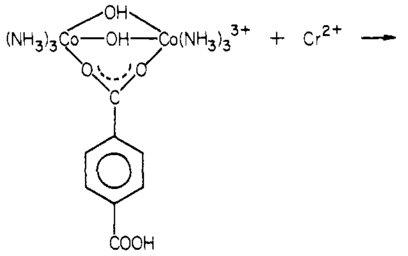
(1) Taube, H. *Pure Appl. Chem.* **1970**, *24*, 289.
(2) Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321.
(3) Taube, H. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 964.
(4) Gould, E. S. *J. Am. Chem. Soc.* **1965**, *87*, 4731.

amminecobalt(III) by chromium(II) occurs by adjacent attack:

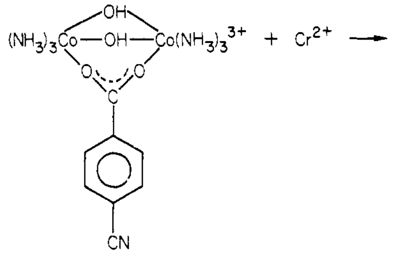


This mechanism has been assigned on the basis of rate comparisons with simple carboxylato systems where remote attack is not possible. The same Cr(III) product would result from either remote or adjacent attack and thus is not diagnostic. Furthermore, terephthalic acid is a relatively nonreducible ligand, and electron transmission through the ligand is energetically unfavorable.

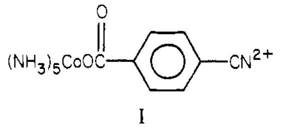
Wieghardt and Hery[6] have avoided this complication by coordinating both carboxylato oxygens, thus leaving only a remote attack path if the reaction is inner sphere:



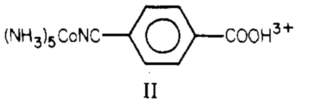
In this particular case, reduction of the first Co(III) is rate determining and occurs via an outer-sphere pathway. It was concluded that terephthalic acid does not mediate electrons efficiently from the remote carboxylic group to the oxidant presumably because it is not reduced by chromium(II). The same conclusion was drawn from a study of the following reaction, which again occurs by an outer-sphere path:



We have prepared the linkage isomers of the "nonreducible" ligand 4-cyanobenzoic acid, I and II,[8] and the analogous nitrile-bonded complex with 3-cyanobenzoic acid. In an attempt to obtain more information about the factors that determine whether a particular complexed ligand can participate in a remote attack pathway, we have studied the reduction of these complexes by chromium(II) and vanadium(II).



I



II

Experimental Section

Reagents were prepared and standardized as previously described.[9] All solutions were handled by using standard syringe techniques under an argon atmosphere.

Preparation of Complexes. The carboxylato-bonded isomer, I, was prepared by standard procedures.[10] The nitrile-bonded complex, II, was prepared from the 4-cyanobenzaldehyde complex[11] as described below.

$[(NH_3)_5Co(NCC_6H_4\text{-}4\text{-}CO_2H)](ClO_4)_3$. Two grams of the 4-cyanobenzaldehyde complex was dissolved in 300 mL of water and perchloric acid added to pH 2. The solution was cooled to 10–15 °C and chlorine gas passed through it for 5 h. Dissolved chlorine was subsequently removed under vacuum. To this solution were added 75 mL of concentrated perchloric acid and solid sodium perchlorate. Upon cooling, yellow crystals were obtained, separated by filtration, washed with 95% ethanol and diethyl ether, and air-dried. This product was then subjected to cation-exchange chromatography on SP-Sephadex C-25 resin. Elution was carried out with aqueous sodium chloride, starting with a 0.05 mol L^{-1} solution and gradually increasing the concentration to 0.20 mol L^{-1}. Two well-separated yellow-orange bands were obtained and physically separated from the column. The complexes were removed from the resin with a solution 3.0 mol L^{-1} in NaCl and 0.2 mol L^{-1} in HCl. The complexes were precipitated from solution by addition of solid $NaClO_4$ and were recrystalized from dilute perchloric acid. The slower moving band was the unreacted 4-cyanobenzaldehyde complex, whereas the faster moving band gave the desired nitrile-bonded 4-cyanobenzoic acid complex.

Anal. Calcd for $[Co(NH_3)_5(NCC_6H_4CO_2H)](ClO_4)_3$: C, 16.30; H, 3.43; N, 14.26. Found: C, 16.52; H, 3.61; N, 14.60. Infrared spectrum: C≡N stretch, 2300 cm^{-1} (complex), 2230 cm^{-1} (uncomplexed 4-cyanobenzoic acid); C=O stretch, 1705 cm^{-1} (complex), 1700 cm^{-1} (uncomplexed 4-cyanobenzoic acid). Proton magnetic resonance spectrum: trans NH_3, 3.46 ppm; cis NH_3, 3.87 ppm; aromatic protons, 8.17 ppm (center of quartet). Visible spectrum: λ_{max} 468 nm (ϵ_{max} 80.0 L mol^{-1} cm^{-1}).

$[(NH_3)_5Co(NCC_6H_4\text{-}3\text{-}CO_2H)](ClO_4)_3$. This complex was prepared and purified in a manner analogous to that for the 4-cyanobenzoic acid complex described above.

Anal. Calcd for $[Co(NH_3)_5(NCC_6H_4CO_2H)](ClO_4)_3$: C, 16.30; H, 3.43; N, 14.26. Found: C, 16.60; H, 3.75; N, 14.49. Infrared spectrum: C≡N stretch, 2294 cm^{-1} (complex), 2230 cm^{-1} (uncomplexed 3-cyanobenzoic acid); C=O stretch, 1714 cm^{-1} (complex), 1705 cm^{-1} (uncomplexed 3-cyanobenzoic acid). Proton magnetic resonance spectrum: trans NH_3, 3.53 ppm; cis NH_3, 3.93 ppm; aromatic protons, 8.25 ppm (center of multiplet). Visible spectrum: λ_{max} 468 nm (ϵ_{max} 86.0 L mol^{-1} cm^{-1}).

Kinetic Measurements. The reduction of the complexes was studied by observing the change in absorbance at 468 nm. Kinetic runs were performed on a Beckman Acta CIII spectrophotometer equipped with temperature control equipment. All runs were carried out under pseudo-first-order conditions using an excess of chromium(II). The rate constants were obtained from the slope of a plot of log $(A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances at time t and after the reaction is complete.

Ion-Exchange Separation of Reaction Mixtures. Chromatographic separations were carried out by using Dowex 50W-X2 cation-exchange resin in the lithium ion form at 5 °C in a cold room. Elution was carried out with a solution of sodium perchlorate and perchloric acid of gradually increasing concentrations. Chromium concentrations of products were determined spectrophotometrically as chromate, ϵ 4815 L mol^{-1} cm^{-1} at 372 nm. In cases where cobalt(II) was eluted along with the chromium products, the solutions were filtered to remove cobalt oxide formed in the conversion of chromium(III) to chromate.

Results

Preparation and Characterization of Complexes. The (carboxylato)pentaamminecobalt(III) complexes of 3- and 4-cyanobenzoic acids can be obtained from aquopentaamminecobalt(III) and mixtures of the corresponding acid and its sodium salt. This method does not yield the nitrile-bonded complex. In order to prepare the nitrile-bonded complex, a

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(5) Balahura, R. J.; Purcell, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 4457.

(6) Hery, M.; Wieghardt, K. *Inorg. Chem.* **1976**, *15*, 2315.

(7) Von Wharton, R. K.; Weighardt, K. *Z. Anorg. Allg. Chem.* **1976**, *425*, 145.

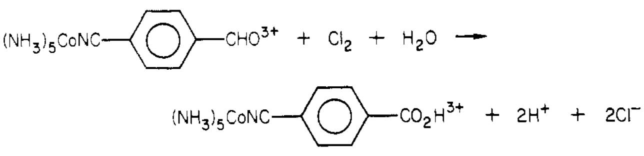
(8) By definition, the linkage isomers are I and the conjugate base of II

(9) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1533.

(10) Barrett, M.; Swinehart, J.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983.

(11) Balahura, R. J. *Can. J. Chem.* **1974**, *52*, 1762.

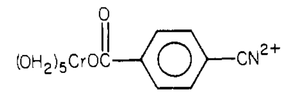
strategy developed by Fraser and Taube[12] was used. These authors found that a 2e-oxidizing agent cleanly oxidized the aldehydo function in (4-formylbenzoato)pentaamminecobalt(III) to a carboxylato group. Thus, we have prepared the nitrile-coordinated 3- and 4-cyanobenzoic acid complexes by the reaction



The method used conveniently requires that the nitrile remain coordinated, and this was confirmed by the physical measurements given in the Experimental Section. In addition, both nitrile-bonded complexes undergo hydrolysis to the coordinated carboxamides in dilute base.[11]

Stoichiometry and Product Analysis. The products of the reaction of Cr(II) with the nitrile-coordinated 3- and 4-cyanobenzoic acid complexes were isolated by cation-exchange chromatography on Dowex 50W-X2 in the lithium ion form at 5 °C. For the 3-cyanobenzoic acid complex only free 3-cyanobenzoic acid and $Cr(OH_2)_6^{3+}$ were isolated. For several experiments with [Co(III) complex] = 9.00×10^{-3} mol L^{-1}, [Cr(II)] = $(1.00–6.25) \times 10^{-2}$ mol L^{-1}, and $[H^+]$ = 0.0625–0.100 mol L^{-1}, 97.9 ± 1.5% $Cr(OH_2)_6^{3+}$ was isolated. The percent $Cr(OH_2)_6^{3+}$ was calculated on the basis of the total number of moles of cobalt(III) complex initially used. In addition to the above analysis, the complete spectrum was scanned during reduction. For [Cr(II)] = 0.0127 mol L^{-1}, [Co(III)] = 0.00181 mol L^{-1}, and $[H^+]$ = 0.081 mol L^{-1}, isosbestic points were observed at 641, 533, 403, and 384 nm. The final spectrum obtained corresponded to $Cr(OH_2)_6^{3+}$. There was no evidence to indicate the formation of any (carboxylato)chromium(III) intermediates.

The reduction of the nitrile-bonded 4-cyanobenzoic acid complex, II, yielded a blue Cr(III) complex, which eluted as a 2+ ion. The visible spectrum of this complex had λ_{max} (ϵ_{max}) at 570 (24.2) and 409 nm (23.6 L mol^{-1} cm^{-1}). This product is formulated as the carboxylato complex III. The spectrum



III

obtained above is identical with that found for reduction of the carboxylato-bound pentaamminecobalt(III) complex by chromium(II).[13] Experiments were also carried out to determine the percent ligand transfer for the reaction of II with chromium(II). For five experiments at $[H^+]$ = 0.0615 mol L^{-1}, [Co(III)] = 8.58×10^{-3} mol L^{-1}, and [Cr(II)] = 1.12×10^{-2} mol L^{-1}, 70 ± 5% of product III was isolated from the cation-exchange column. Also, for four runs at $[H^+]$ = 0.321 mol L^{-1}, [Co(III)] = 9.20×10^{-3} mol L^{-1}, and [Cr(II)] = 1.11×10^{-2} mol L^{-1}, 71 ± 5% of product III was obtained. It should be noted that a good separation of the Cr(III) carboxylato complex from $Cr(OH_2)_6^{3+}$ was not possible since the bands diffused together on the column. This difficulty may have resulted in some loss of complex III in the isolation procedure. An attempt was also made to determine the amount of free 4-cyanobenzoic acid produced in the reduction. By collection of the first eluent upon addition of reaction mixtures to an ion-exchange column, the amount of free ligand could be estimated spectrophotometrically at 237 nm where ϵ = 1.51×10^4 L mol^{-1} cm^{-1} in H_2O. The average of all experiments gave 20 ± 10% free ligand formed. The stoichiometry of the reaction was determined to involve one Cr(II) per cobalt(III) complex by collecting the total chromium(III) products from reactions with several different initial molar ratios.

Table I. Kinetic Data for the Reduction of the Nitrile-Bonded Complex $(NH_3)_5Co(3\text{-cyanobenzoic acid})^{3+}$ by Chromium(II)

T, °C	10^4[Co(III)], mol L^{-1}	10^2[Cr(II)], mol L^{-1}	$[H^+]$, mol L^{-1}	10^2k_2, L mol^{-1} s^{-1}
25.0[a]	10.5	2.00	0.389	3.04
	9.5	4.15	0.284	3.18
	8.7	4.15	0.284	3.11
	9.5	4.20	0.202	3.17
	9.5	4.20	0.100	3.21
	8.7	2.02	0.100	3.49
	8.7	4.15	0.049	3.35
	9.5	4.20	0.020	3.48
	9.5	4.20	0.020	3.02
	8.7	2.97	0.018	3.47
25.1[b]	9.6	3.00	0.841	5.03
	8.7	4.15	0.784	4.53
	9.3	4.04	0.299	5.10
	9.5	2.02	0.300	4.95
	9.3	3.03	0.299	5.25
	9.3	3.02	0.102	4.74
	9.6	3.03	0.100	4.72
	9.6	3.00	0.100	4.77
	9.6	3.00	0.020	5.10
	8.7	4.15	0.018	4.53
35.1[b]	9.3	2.92	0.845	8.18
	9.3	2.92	0.845	7.74
	9.3	2.92	0.300	8.12
	9.3	2.92	0.300	7.84
	9.3	2.92	0.102	8.36
	9.3	2.92	0.020	8.36
45.0[b]	9.2	2.99	0.842	12.9
	9.3	2.92	0.845	11.7
	9.4	3.00	0.851	12.2
	9.2	2.99	0.300	11.9
	9.4	3.00	0.102	12.3
	9.4	2.99	0.102	11.6
	9.4	3.00	0.020	13.4
	9.5	2.99	0.020	13.9

[a] I = 0.50 mol L^{-1} maintained with $LiClO_4$. [b] I = 1.0 mol L^{-1} maintained with $LiClO_4$.

Kinetic Studies

Nitrile-Bonded 3-Cyanobenzoic Acid. The reaction of the 3-cyanobenzoic acid complex with chromium(II) was first order in both chromium(II) and cobalt(III) complex. The rate was independent of the hydrogen ion concentration and followed the simple rate law

$$-\frac{d \ln [\text{cobalt(III)}]}{dt} = k_2[Cr^{2+}]$$

At 25 °C, rate data were obtained at ionic strengths 0.50 and 1.0 mol L^{-1}, yielding values of k_2 = (3.25 ± 0.18) × 10^{-2} L mol^{-1} s^{-1} and (4.89 ± 0.23) × 10^{-2} L mol^{-1} s^{-1}, respectively. The kinetic data are summarized in Table I. For the I = 1.0 mol L^{-1} data, ΔH^* = 8.3 ± 0.4 kcal mol^{-1} and ΔS^* = −37 ± 2 eu.

Nitrile-Bonded 4-Cyanobenzoic Acid. The reduction of the 4-cyanobenzoic acid complex was first order in chromium(II) and cobalt(III), and at 25 °C also varied with the hydrogen ion concentration:

$$k_{obsd} = \frac{k_H[H^+] + kK_a}{K_a + [H^+]} \qquad (1)$$

At the higher temperatures studied, this hydrogen ion dependence was not discernible. The data are summarized in Table II. A nonlinear least-squares fit of the data at 25 °C to the equation above gave k_H = 0.290 ± 0.005 L mol^{-1} s^{-1},

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[12] Fraser, R. T. M.; Taube, H. *J. Am. Chem. Soc.* **1960**, *82*, 4152.
[13] Balahura, R. J. Ph.D. Thesis, University of Alberta, 1970, p 121.

Table II. Kinetic Data for the Reduction of the Nitrile-Bonded Complex $(NH_3)_5Co(4\text{-cyanobenzoic acid})^{3+}$ by Chromium(II)

T, °C	$10^4 \times$ [Co(III)], mol L^{-1}	$10^2 \times$ [Cr(II)], mol L^{-1}	[H^+], mol L^{-1}	k_{obsd}, L mol^{-1} s^{-1}	k_{calcd},[a] L mol^{-1} s^{-1}
25.0[b]	20.0	2.00	0.400	0.273	0.292
	19.0	2.00	0.353	0.291	0.292
	20.0	4.00	0.300	0.294	0.293
	20.0	2.00	0.100	0.298	0.299
	20.0	2.00	0.050	0.318	0.309
	20.0	4.00	0.050	0.315	0.309
	9.60	1.01	0.051	0.292	0.308
	19.0	4.05	0.035	0.343	0.316
	19.0	2.00	0.025	0.333	0.325
	19.0	2.00	0.025	0.330	0.325
	19.0	2.00	0.024	0.338	0.326
	10.1	1.01	0.020	0.325	0.333
	9.60	1.01	0.018	0.332	0.336
	9.60	1.01	0.013	0.331	0.349
25.0[c]	4.4	1.98	0.896	0.299	0.292
	9.3	1.99	0.892	0.281	0.292
	9.6	2.04	0.890	0.300	0.292
	9.4	2.04	0.890	0.296	0.292
	9.4	1.99	0.890	0.303	0.292
	4.7	2.01	0.500	0.289	0.294
	9.3	2.00	0.499	0.309	0.294
	9.3	1.99	0.499	0.290	0.294
	9.6	1.99	0.201	0.311	0.301
	9.3	2.04	0.201	0.294	0.301
	9.3	3.01	0.200	0.288	0.301
	9.3	1.99	0.299	0.295	0.301
	9.3	1.99	0.101	0.314	0.311
	4.7	2.01	0.100	0.316	0.311
	9.4	1.99	0.100	0.311	0.311
	9.4	2.04	0.100	0.303	0.311
	9.8	1.97	0.101	0.311	0.311
	9.4	1.99	0.083	0.306	0.315
	9.3	2.00	0.083	0.304	0.315
	9.4	1.99	0.050	0.335	0.331
	9.4	1.99	0.050	0.341	0.331
	9.3	2.04	0.030	0.354	0.356
	9.3	1.99	0.023	0.372	0.374
	9.3	2.04	0.020	0.386	0.385
	0.3	2.00	0.020	0.385	0.385
	4.6	1.99	0.015	0.422	0.411
	4.6	1.99	0.012	0.432	0.435
	4.6	1.99	0.010	0.459	0.457
	4.6	1.99	0.010	0.459	0.457
	9.3	2.04	0.010	0.444	0.457
	4.7	1.94	0.010	0.464	0.457
35.0[c]	9.3	1.98	0.890	0.461	
	9.6	2.05	0.201	0.451	
	9.3	1.98	0.201	0.440	
	9.3	1.98	0.201	0.440	
	9.3	1.98	0.102	0.461	
	6.5	2.09	0.045	0.465	
	9.3	1.98	0.020	0.452	
	9.3	1.98	0.020	0.460	
45.0[c]	9.1	1.10	0.938	0.624	
	9.5	1.10	0.201	0.673	
	9.5	1.10	0.051	0.656	
	9.1	1.10	0.020	0.673	

[a] Rate constant calculated according to eq 1 with use of the best fit parameters given in the text. [b] $I = 0.50$ mol L^{-1}. [c] $I = 1.0$ mol L^{-1}.

Table III. Kinetic Data for the Reduction of the Nitrile-Bonded Complex $(NH_3)_5Co(4\text{-cyanobenzoic acid})^{3+}$ by Vanadium(II)[a]

10^4[Co(III)], mol L^{-1}	10^2[V(II)], mol L^{-1}	[H^+], mol L^{-1}	k_{obsd}, L mol^{-1} s^{-1}
9.00	1.91	0.0500	16.1
8.57	1.98	0.0757	13.2
8.57	1.98	0.0757	13.7
9.50	1.98	0.106	12.7
9.50	1.98	0.106	13.1
8.48	1.98	0.197	12.5
8.48	1.98	0.197	12.8
8.40	1.91	0.775	11.8
8.74	1.98	0.830	11.0
8.74	1.98	0.830	11.2
5.30	1.00	0.775	11.6

[a] 25 °C; $I = 1.0$ mol L^{-1} maintained with $LiClO_4$.

$k = 0.99 \pm 0.12$ L mol^{-1} s^{-1}, and $K_a = 0.0031 \pm 0.0007$ mol L^{-1} at $I = 1.0$ mol L^{-1}. At $I = 0.50$ mol L^{-1}, the best fit gave $k_H = 0.289 \pm 0.007$ L mol^{-1} s^{-1}, $k = 0.51 \pm 0.13$ L mol^{-1} s^{-1}, and $K_a = 0.0040 \pm 0.0039$ mol L^{-1}. Also included in Table II is the rate constant calculated according to eq 1 by using the best fit parameters given. The behavior observed is consistent with a mechanism where both the protonated (k_H) and deprotonated (k) forms of the complex are reduced by Cr(II). K_a is the acid dissociation constant of the complex. The K_a value obtained from the kinetic data at $I = 1.0$ mol L^{-1} agrees remarkably well with an independent spectrophotometric determination that gave $K_a = 0.0026$ mol L^{-1}. The activation parameters for the k_H term were $\Delta H^\ddagger = 7.1 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -37 \pm 3$ eu.

For comparative purposes the V(II) reduction of the 4-cyanobenzoic acid complex was also studied. The rate showed a very slight dependence on acid at 25 °C and obeyed the rate law

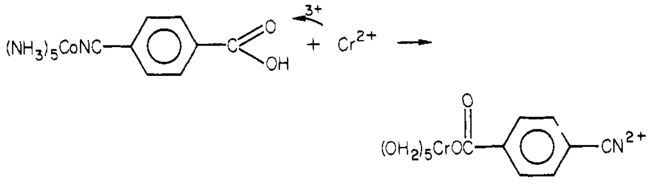
$$k_{obsd} = k_1 + k_2[H^+]^{-1} \quad (2)$$

with $k_1 = 11.1 \pm 0.2$ L mol^{-1} s^{-1}, $k_2 = 0.21 \pm 0.04$ s^{-1}, and $I = 1.0$ mol L^{-1} maintained with $LiClO_4$. The rate law is consistent with the same mechanism suggested above for the Cr(II) reduction. However in this case, the lack of curvature of a plot of k_{obsd} vs. $[H^+]^{-1}$ indicates $[H^+] \gg K_a$ (Table III).

Discussion

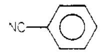
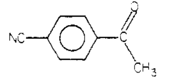
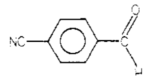
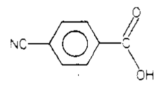
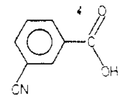
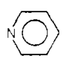
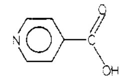
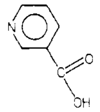
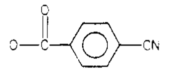
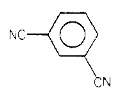
The data for the 3-cyanobenzoic acid complex indicate that the reduction proceeds via an outer-sphere process. The observed rate constant of 4.89×10^{-2} L mol^{-1} s^{-1} at 25 °C is consistent with values obtained for other nitrile-bonded cobalt(III) complexes that have been demonstrated to proceed by outer-sphere mechanisms.[5] Also, the only chromium(III) product of the reaction was $Cr(OH_2)_6^{3+}$. Since a chromium(III) carboxylate would be expected to be stable to aquation, it would appear that $Cr(OH_2)_6^{3+}$ is formed directly in the reduction reaction.

In contrast, the results obtained for reduction of the 4-cyanobenzoic acid complex are all indicative of an inner-sphere process where the reductant attacks at the remote carboxylate group.



The most compelling evidence for this mechanism is the isolation of the carboxylato-coordinated complex (4-cyanobenzoato)pentaaquochromium(III) as the major chromium-containing product. This complex could not have been formed by substitution of free 4-cyanobenzoic acid on $Cr(OH_2)_6^{3+}$ (both species generated by an outer-sphere reaction) because this substitution would be some 6 orders of magnitude slower than the observed rate of reduction. The relatively large rate constant observed when compared (Table IV) to those obtained for outer-sphere reductions of nitrile-bonded complexes also points to an inner-sphere pathway. Furthermore, the fact that the rate does not change with a change in ionic strength is interesting and suggests that the reductant attacks at a remote site away from the influence of the charge on the complex. For the 3-cyanobenzoic acid complex, which is reduced by an

Table IV. Data for Reduction of $Co^{III}(NH_3)_5L$ Complexes by Cr(II)

L	$k^{25\,°C}$, L mol^{-1} s^{-1}	mechanism^a	ref
	0.043	os	24
	6×10^3	is, r	25
	2.5×10^5	is, r	5
	0.290	is, r	this work
	0.0489	os	this work
	0.0040	os	26
	10.0	is, r	27
	0.0113	os	27
	0.162	is, a	13, 28
	0.059	os	5

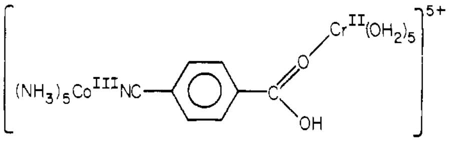
^{a} os = outer sphere; is = inner sphere; r = remote; a = adjacent.

outer-sphere process, a change from an ionic strength of 1.0 to 0.50 mol L^{-1} results in a 30% decrease in the rate constant.

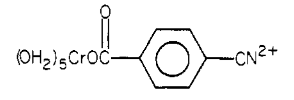
The data for reduction of the nitrile-bonded 4-cyanobenzoic acid complex by V(II) are also consistent with a remote-attack inner-sphere process. The rate constants for reduction of the protonated (11.1 L mol^{-1} s^{-1}) and unprotonated (80.8 L mol^{-1} s^{-1}) forms of the complex are consistent with the predominance of inner-sphere processes with rates limited by ligand substitution on V(II)[14] but do not demand such a conclusion. The values obtained are reasonable for the substitution of a neutral –COOH group and its deprotonated form, –COO$^-$, by V(II). Also, the slight inverse hydrogen ion dependence suggests an inner-sphere process.

It should be pointed out that the magnitude of the ratio of rate constants for reduction of the 4-cyanobenzoic acid complex by Cr(II) and V(II), 0.026, has been used as being diagnostic of an outer-sphere process operating for both reductants.[6,7,15,16] However, with the evidence presented above, the case for an inner-sphere process is strong. Furthermore, as will be discussed later, this may be a reflection of a change in detailed mechanism for the two reductants. Also, there are many other examples where rate comparisons should be used with caution.[17]

An unusual feature of the reduction of the nitrile-bonded 4-cyanobenzoic acid complex by chromium(II) is the fact that the major path for reduction involves the protonated form of the complex. At [H$^+$] = 0.10 mol L^{-1} approximately 93% of the reaction involves the protonated form of the complex. This requires that Cr(II) attack the carbonyl oxygen of the remote carboxylic acid group, forming the precursor complex

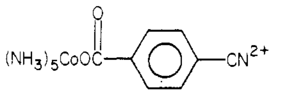


After electron transfer, deprotonation in the initial Cr(III) complex occurs, giving the final stable (4-cyanobenzoato)pentaaquochromium(III) complex



The ligand 4-cyanobenzoic acid is not reducible by chromium(II) and has a polarographic half-wave potential of –2.53 V in DMF.[13] Thus, the mechanism postulated can be understood in terms of the relative reducibilities of the protonated vs. deprotonated ligand. A lower energy path for electron transmission through the ligand involves the protonated form. Similar arguments have been used to explain the first-order hydrogen ion term in the rate law for reduction of (4-formylbenzoato)pentaamminecobalt(III) by chromium(II).[18] In this case, the ligand is deprotonated by virtue of complexing to cobalt(III), and a proton must be added to the adjacent carbonyl in order to produce a readily reducible ligand.

The reduction of the "linkage isomer" (4-cyanobenzoato)pentaamminecobalt(III)



by chromium(II) proceeds by attack at the adjacent carbonyl oxygen. In this case the low-energy path bypasses the cyanobenzene group and for nonreducible ligands is the dominant pathway. Also mitigating against attack at the remote nitrile nitrogen in the 2+ form of the complex above or in a protonated form is the fact that the nitrile nitrogen does not provide a sufficiently stable precursor complex. A reasonably stable precursor complex is likely necessary to balance the "nonreducible" nature of the ligand, and this can only be accomplished by the carboxyl group. The only known cases of Cr(II) attack at nitrile nitrogen are for 4-cyanopyridine[19] and terephthalonitrile,[20] both "reducible" ligands. Furthermore, the Cr(III) nitrile-bonded complexes formed are extremely labile.

In Table IV are collected some relevant data. The 4-carboxypyridine complex is reduced about 30 times faster than the 4-cyanobenzoic acid complex presumably because the substituted pyridine is more "reducible" than the analogous 4-cyanobenzoic acid, the precursor complex stability being approximately the same. This is further evidenced by comparing the rates of the 4-formylbenzonitrile, 4-acetylbenzonitrile, and 4-cyanobenzoic acid complexes. If the precursor complex stability is considered to be roughly constant, the difference in rates reflects a decrease in "reducibility" of the ligands. Thus there are two factors mitigating against an inner-sphere reduction for

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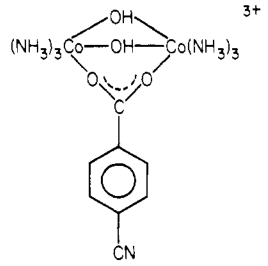
(20) See ref 16 in: Balahura, R.; Purcell, W. *J. Am. Chem. Soc.* **1976**, *98*, 4457.

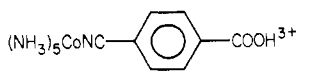


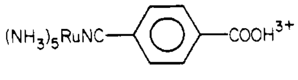
(1) the "nonreducible" nature of the ligand (deprotonated) and (2) relatively unstable precursor complex formation at the nitrile nitrogen.

An intramolecular rate of electron transfer with the 4-cyanobenzoic acid complex can be estimated. A value of approximately 10 Lmol^{-1} is available for the complexing of Cr(II) with carboxylates,[21] but in this case a somewhat lower value would be appropriate. If we use this value, an intramolecular rate constant for electron transfer <0.028 s^{-1} is obtained for 4-cyanobenzoic acid coordinated to cobalt(III).

One other possibility should be mentioned—a bridged outer-sphere mechanism where the bridging ligand serves only to hold the reductant in close proximity to the oxidant and thus facilitate outer-sphere electron transfer. Examples of this pathway involve oxidants with flexible saturated groups in the bridging ligands.[16,22] In the present case, the separation between Cr(II) and Co(III) is large with a rigid bridging ligand maintaining this separation, and this pathway does not appear likely.

The question of detailed mechanism for the reaction of with Cr(II) can only be partly answered. Generally, reactions with Co(III) complexes involving remote attack have been assigned a radical-ion mechanism.[2,3] In terms of orbital symmetry, the donor–mediator–acceptor interaction, σ–π–σ, involves a mismatch in orbital symmetry and makes a resonance mechanism unfavorable. Analogous Ru(III) complexes are reduced by Cr(II) about 10^5 times faster than their Co(III) counterparts, and this is explained in terms of a change in mechanism to resonance transfer for Ru(III). In the latter case, resonance transfer is expected to provide a lower energy path than radical ion since the acceptor–mediator match is now π–π.[23] We have also studied the reaction of the complex with Cr(II) and determined a rate constant of 2.8×10^4 L mol^{-1} s^{-1}. Thus, it appears that despite the "nonreducibility" of 4-cyanobenzoic acid it may react by a radical-ion mechanism when coordinated to cobalt(III) via the nitrile nitrogen. Similar arguments favor a resonance-transfer mechanism for the vanadium(II) reduction of the 4-cyanobenzoic acid complex. In this case the donor–mediator–acceptor interaction is π–π–σ, and the V(II) reduction proceeds more rapidly than the Cr(II) reduction even though V(II) is a weaker reductant. This change in detailed mechanism, resonance transfer for V(II) and radical ion for Cr(II), may explain the "anomalous" rate ratio referred to earlier.





Acknowledgment. The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

Registry No. Cr, 7440-47-3; $[(NH_3)_5Co(NCC_6H_4\text{-}4\text{-}CO_2H)]^{3+}$, 41759-02-8; $[(NH_3)_5Co(NCC_6H_4\text{-}3\text{-}CO_2H)]^{3+}$, 85135-60-0; V, 7440-62-2; $[(NH_3)_5Co(O_2CC_6H_4\text{-}4\text{-}CN)]^{2+}$, 40544-46-5; $[(NH_3)_5Cr(O_2CC_6H_4\text{-}4\text{-}CN)]^{2+}$, 85135-61-1.

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Kinetics and Mechanisms of Ligand Exchange, Substitution, and Isomerization of Me$_2$SO–Amino Acid Complexes of Platinum(II): Evidence for a Pseudorotation Mechanism

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Kinetic data are reported for the reversible, second-order substitution of Cl$^-$ of Pt(amino acid)(Me$_2$SO)Cl (amino acid = glycine, sarcosine, *N,N*-dimethylglycine, proline) by Me$_2$SO in aqueous solution at 35 °C to form *cis*(*N,S*)- and *trans*(*N,S*)-Pt(amino acid)(Me$_2$SO)Cl and for the reversible, second-order chloride- and Me$_2$SO-catalyzed isomerization of these isomers. In addition, second-order rate constants are reported for chloride and Me$_2$SO exchange of cis and trans isomers in D$_2$O and of Me$_2$SO-catalyzed isomerization of Pt(*N,N*-Me$_2$gly)(Me$_2$SO)Cl in D$_2$O, methanol-*d*$_3$, and CDCl$_3$. The rate data, derived from NMR and radioisotope techniques, show clearly that a pseudorotation (turnstile) mechanism (presumably involving five-coordinate Pt(amino acid)(Me$_2$SO)Cl$_2^-$) predominates by a factor of 4–20 over the consecutive displacement mechanism for chloride-catalyzed isomerization. By contrast, the effect of solvent composition on the Me$_2$SO-catalyzed isomerization and the rate of reaction of chloride ion with Pt(gly)(Me$_2$SO)$_2^+$ suggest that the Me$_2$SO-catalyzed isomerization occurs via a consecutive displacement reaction mechanism, with intermediate formation of Pt(amino acid)(Me$_2$SO)$_2^+$. A general mechanism involving Pt(amino acid)Cl$_2^-$, cis and trans isomers of Pt(amino acid)(Me$_2$SO)Cl, Pt(amino acid)(Me$_2$SO)$_2^+$, and eight distinct trigonal-bipyramidal, five-coordinate intermediates is proposed to account for the data.

In 1976 we reported that dimethyl sulfoxide (Me$_2$SO) reacts with anionic amino acid complexes of platinum(II) of general formula Pt(amino acid)Cl$_2^-$ to form both *trans*(*N,S*)- and *cis*(*N,S*)-Pt(amino acid)(Me$_2$SO)Cl, with the Me$_2$SO coor-