mol^{-1} dm^3 cm^{-1}) and the redetermined value for *cis*-$[(en)_2Co(NH_3)_2]^{3+}$ (ϵ_{469} = 79.1 mol^{-1} dm^3 cm^{-1}). For the determination of the cis/trans ratio in $[(en)_2NH_3CoOH]^{2+}$ by ^{13}C NMR, the NH_4Cl eluates were adsorbed once again on the resin, eluted with HCl (3 mol dm^{-3}), and evaporated to dryness at room temperature. Spectra were recorded on solutions of the dry residues in D_2O with a small amount of Na_2CO_3 for complete amine proton exchange.

Crystal Structure Determination. The space group was determined by using a Charles Supper Co. precession camera with Cu Kα radiation. Precise determination of the cell parameters and data collection were carried out on an automated CAD-4 (Enraf-Nonius) diffractometer at room temperature. The cobalt atoms were found in an initial Patterson synthesis, and the further non-hydrogen atoms in a subsequent Fourier synthesis. Refinement was made for all non-hydrogen atoms by the method of least squares with scattering factors from the literature.[43,44] Three positional and six thermal parameters were determined for each refined atom.

Acknowledgment. This work was supported by ETH funds administered through the Forschungskommission/Betriebsdirektion ETH. F.P.R. is grateful for his initiation to X-ray crystallography by Prof. J. D. Dunitz and Dr. E. Müller, ETH. Dr. Müller is also acknowledged for valuable discussion.

Registry No. $1(NO_3)_5 \cdot 2H_2O$, 87393-35-9; $[(en)_2Co]_2\{NH_2,Cl\}Cl_4$, 87420-78-8; $[(en)_2Co]_2\{NH_2,SO_4\}Br_3$, 87420-79-9; *trans*-$[Co(en)_2(NH_3)_2]Cl_3$, 36883-69-9; (±)-*cis*-$[Co(en)_2(NH_3)_2]Cl_3$, 52021-81-5; Λ-*cis*-$[(en)_2CoNH_3OH]^{2+}$, 45837-83-0; ΔΛ-*cis*-$[(en)_2CoNH_3OH]^{2+}$, 38246-61-6; *trans*-$[(en)_2CoNH_3OH]^{2+}$, 38246-62-7; Λ-*cis*-$[(en)_2CoNH_3N_3]^{2+}$, 46139-34-8; ΔΛ-*cis*-$[(en)_2CoNH_3N_3]^{2+}$, 36501-76-5; *trans*-$[(en)_2CoNH_3N_3]^{2+}$, 46139-36-0; $[(en)_2NH_3CoNH_2Co(OH)(en)_2]^{4+}$, 87372-44-9; (±)-*cis*,*cis*-$[(en)_2NH_3CoNH_2CoCl(en)_2]^{4+}$, 87372-45-0; (±)-(μ-amido)aquachlorotetrakis(1,2-ethanediamine)dicobalt tetranitrate, 87420-81-3; (±)-*cis*-dichlorobis(1,2-ethanediamine)cobalt chloride, 14040-32-5.

Supplementary Material Available: Listings of observed and calculated structure factors, temperature factors, and rate data in aqueous solution (Table VI) (17 pages). Ordering information is given on any current masthead page.

(43) Co: "International Tables for X-Ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1968; Vol. III.
(44) C, N, O: Cromer, D.; Mann, J. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.
(45) Dunitz, J. D.; Seiler, P. *Acta Crystallogr., Sect. B* **1972**, *B29*, 589.
(46) This short bond length coincides with a large thermal motion ellipsoid of C26 and one could suspect the presence of two disordered conformers. However, in a Fourier map at 0.1-Å resolution with C26 omitted, two maxima were not seen up to 1 Å around the idealized position of C26. Furthermore, the calculated N-C-C-N torsion angle in this chelate ring (47.2°) agrees reasonably with the experimental values of 50.3, -49.3, and -49.1°, respectively, for the other three en rings. Much larger deviations are expected if two disordered conformers were present. The carbon atoms of en chelate rings are basically quite mobile, but their motion is usually restricted by the proximity of other atoms in the lattice.
(47) Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 509.
(48) Rate law (2) is probably observed because of the more restricted range of $[OH^-]$.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, Department of Chemistry, University of Miami, Coral Gables, Florida 33124, Sandia National Laboratories, Albuquerque, New Mexico 87185, and Unidynamics Phoenix, Inc., Phoenix, Arizona 85062

Preparation, Characterization, and Chromium(II) Reduction Kinetics of Tetrazole Complexes of Pentaamminecobalt(III)

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The synthesis and characterization of several pentaamminecobalt(III) complexes of 5-substituted tetrazoles are reported: 5-cyanotetrazole, 5-methyltetrazole, 5-carbamoyltetrazole, and unsubstituted tetrazole. Characterization by proton, carbon-13, and nitrogen-15 NMR and by ultraviolet–visible spectroscopy established that bonding between cobalt(III) and the tetrazole ring occurs at the nitrogen at ring position 2 in agreement with previous crystal structure determinations on the 5-methyl and 5-cyanotetrazole complexes. Kinetics of the hexaaquachromium(II) reduction of these various cobalt(III) complexes is reported as well as the reduction kinetics for the N-1-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex, the linkage isomer of the N-2-bonded 5-methyl complex. All reductions proceed principally by an inner-sphere electron-transfer process with reduction pathways appearing for both the protonated (3+) and deprotonated (2+) complexes characterized by rate constants k_0 and k_1, respectively. A mechanistic scheme common to all five complexes is proposed that predicts the operation of two limiting forms of the rate law governed by the pK_a's of the five complexes. At 25 °C, k_0 values are 19 ± 2, 0.15 ± 0.08, and 2.4 ± 0.3 L mol^{-1} s^{-1} for the tetrazole, N-2-bonded 5-methyltetrazole, and N-1-bonded 5-methyltetrazole complexes, respectively. The k_1 values are 3.3 ± 0.3, 0.41 ± 0.02, and 0.83 ± 0.02 s^{-1} for these same three complexes at 25 °C. Separation of the observed rate constants into the two components was not possible for the 5-cyanotetrazole and 5-carbamoyltetrazole complexes.

Introduction

Compared to the wealth of literature to be found for inner-sphere electron-transfer reactions involving bridging six-membered nitrogen heterocycles, relatively few studies utilizing five-membered heterocyclic bridges are available. This is indeed unfortunate considering the importance of five-membered nitrogen heterocycles in biological systems, e.g., imidazole, benzimidazole, the purines, proline, and tryptophan. The concentration of effort on the six-membered nitrogen heterocycles probably reflects expediency since numerous substituted pyridines, pyrazines, and pyrimidines are commercially available. The literature that does exist concerning the electron-transfer involvement of five-membered nitrogen heterocycles is somewhat confusing. Understandably, studies

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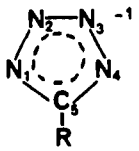
with imidazole dominate the field. Gould has documented very slow rates for hexaaquachromium(II) reduction of pentaammine(imidazolato)cobalt(III) in acidic solution.[1] Both the slow rate of chromium(II) reduction of this complex and rate ratio correlations with other reductants such as vanadium(II),[1b] hexaammineruthenium(II),[1c] europium(II),[2] and uranium(III)[3] have led Gould to assign an outer-sphere mechanism to the imidazole complex electron-transfer reaction with each of these various reductants. In contast to the apparently poor mediating ability of imidazole implied by Gould's studies, recent studies in other laboratories utilizing binuclear imidazolato-bridged Ru(II)–Co(III)[4] and Fe(II)–Co(III)[5] complexes indicate that the deprotonated imidazole ring system is an extremely efficient electron-transfer bridge. Studies of the Cr(II) reduction of pyrrole and pyrazole systems bound to Co(III) via carboxylato ring functions have been reported, but Cr(II) attack at the carbonyl oxygen of the carboxylato group[6a] or attack at the oxygen with chelation[1a] sheds little light on the electron mediating ability of these heterocyclic ring systems. The unsubstituted pyrazole complex of pentaamminecobalt(III), however, seems to react in an outer-sphere process with Cr(II) on the basis of a slow rate of electron transfer typical of outer-sphere processes.[6b]

A five-membered heterocyclic ring system that provides some flexibility for systematic variation of the bonding mode and ring substituents is the tetrazole ring system. Tetrazoles substituted at ring position 5 may be easily prepared in high yield from nitriles via the 1,3-dipolar cycloaddition of azide ion,[7] and the identity of the substituent at position 5 can lead to a significant variation in the pK_a of the tetrazole ring proton.[8] In this study we report the preparation and characterization of several pentaammine(tetrazolato)cobalt(III) complexes and their kinetics of reduction by hexaaquachromium(II).



tetrazolato ring and numbering scheme

Experimental Section

Reagents. Chromium(II) perchlorate solutions were prepared and standardized by methods described previously.[9,10] All chromium(II) solution transfers were made by using syringe techniques under an atmosphere of high-purity argon. Ionic strength was controlled with $NaClO_4$ and $HClO_4$ stock solutions prepared and standardized as described previously.[9,10]

Ligands. Tetrazole and 5-methyltetrazole were prepared as described in the literature.[11-13] 5-Cyanotetrazole was prepared by reaction of sodium azide with cyanogen in aqueous solution.[14-16] 5-Carbamoyltetrazole was prepared by hydrolysis of 5-cyanotetrazole in 15% hydrochloric acid at 70 °C. The melting points of these later two (102–103 and 235–237 °C, respectively) agree with the literature values.[14-17]

Cobalt(III) Complexes. *Warning*: The perchlorate salts of the complexes are explosive and should be handled with caution. The N-2-bonded complexes were prepared by anation of aquapentaamminecobalt(III) perchlorate in aqueous solution with the anion of the appropriate tetrazole. Generally the reaction was carried out at 85–90 °C for about 3 h. Cooling to 25 °C gave the desired product, which was collected and recrystallized from dilute perchloric acid. The perchlorate salts were converted to tetrafluoroborate salts with use of Dowex 1-X8 200–400 mesh strongly basic anion-exchange resin that had been converted to the tetrafluoroborate form. Complexes isolated after this procedure were routinely submitted to cation-exchange chromatography on CM-Sephadex C-25-120 resin to ascertain their purity. In all cases only one complex was eluted from the column with elution characteristics of a 2+ ion. Analytical data are given below (elemental analyses performed by Atlantic Microlabs, Inc., Atlanta, GA).

(5-Cyanotetrazolato)pentaamminecobalt(III) tetrafluoroborate, $[Co(NH_3)_5CN_4CN](BF_4)_2$: Anal. Calcd: C, 5.83; H, 3.67; N, 34.02. Found: C, 5.96; H, 3.70; N, 34.06. Electronic spectrum [λ_{max}, (ϵ_{max}), L mol^{-1} cm^{-1})]: 334 (63.1), 464 (65.4).

(5-Methyltetrazolato)pentaamminecobalt(III) tetrafluoroborate, $[Co(NH_3)_5CN_4CH_3](BF_4)_2$: Anal. Calcd: C, 5.99; H, 4.53; N, 31.46. Found: C, 6.07; H, 4.59; N, 31.43. Electronic spectrum [λ_{max}, nm (ϵ_{max})]: 334 (65.5), 464 (64.8).

(5-Carbamoyltetrazolato)pentaamminecobalt(III) tetrafluoroborate trihydrate, $[Co(NH_3)_5CN_4CONH_2](BF_4)_2 \cdot 3H_2O$: Anal. Calcd: C, 4.96; H, 4.79; N, 28.95. Found: C, 5.04; H, 4.79; N, 28.83. Electronic spectrum [λ_{max}, nm (ϵ_{max})]: 334 (67.5), 463 (66.8).

(Tetrazolato)pentammminecobalt(III) tetrafluoroborate, $[Co(NH_3)_5CN_4H](BF_4)_2$: Anal. Calcd: C, 3.11; H, 4.17; N, 32.60. Found: C, 3.24; H, 4.25; N, 32.72. Electronic spectrum [λ_{max}, nm (ϵ_{max})]: 335 (63.9), 464 (64.4).

The synthesis and characterization of the N-1-bonded linkage isomer of (5-methyltetrazolato)pentaamminecobalt(III) were achieved as described previously[19] with the exception that $NaClO_4$ was used to precipitate the complex rather than NaI.

Product Studies. Equimolar mixtures of chromium(II) and cobalt(III) solutions were mixed under argon and allowed to react to completion. Product solutions were then submitted to ion-exchange chromatography on Dowex 50W-X200 cation-exchange resin in the lithium ion form. Chromium(III) products eluted from the column were determined spectrophotometrically as chromate[20] after being characterized in the visible region of the spectrum on a Cary Model 17 or Beckman Acta CIII ultraviolet–visible spectrophotometer.

Kinetic Measurements. For the N-2-bonded complexes the reduction reaction was monitored at 464 nm by using a Durrum stopped-flow spectrophotometer. Reaction progress for the N-1-bonded 5-methyltetrazolato complex was followed at 400 and 470 nm. Rate constants obtained at the two wavelengths agreed within experimental error. Kinetic runs on this system were performed on a stopped-flow temperature-jump apparatus[21] operating in the stopped-flow mode. All kinetic studies were performed under pseudo-first-order conditions using a tenfold or greater excess of Cr(II) reductant. Absorbance vs. time traces were analyzed as described previously.[9] For the N-1-bonded complex, acid was mixed with the freshly prepared Co(III) complex solution at the same time as the Cr(II) reductant in order to minimize linkage isomerization to the N-2-bonded complex. This precaution was necessary since the linkage isomerization reaction is acid catalyzed.[22] Such precautions were not necessary with the

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Table I. NMR Data for Pentaamminecobalt(III) Tetrazole Complexes

5-substituent on tetrazole	$\delta(^1H)^a$	$\delta(^{13}C)^a$	$\delta(^{15}N)^a$ cyn	$\delta(^{15}N)^a$ az
CN	3.50 (axial NH_3)	111.6 (-CN substituent)	246.9	278.0
	3.70 (equatorial NH_3)	141.1 (tetrazole ring C)	309.1	308.9
			326.8	377.1
$C(O)NH_2$	3.49 (axial NH_3)	159.7		
	3.63 (equatorial NH_3)	160.9		
	7.61 (amide)			
	7.90 (amide)			
CH_3	3.55 (axial, equatorial NH_3 unresolved)	161.9 (ring C)		
	2.45 ($-CH_3$ substituent)	10.98 ($-CH_3$)		
H	3.56 (axial, equatorial NH_3 unresolved)	153.4 (ring C)		
	8.76 (tetrazole ring proton)			

[a] ^1H and ^{13}C NMR with respect to Me_4Si; ^{15}N NMR with respect to $^{15}NH_4NO_3$.

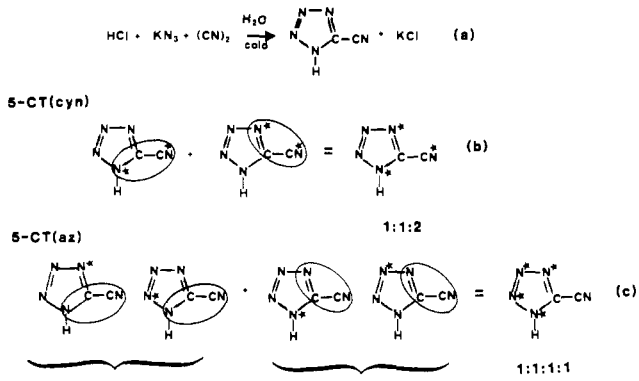

Figure 1. Synthesis of isotopically enriched 5-cyanotetrazoles.

N-2-bonded forms where isomerization does not occur.

Results

Cobalt(III) Complexes. Spectral data for the N-1-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex have already been reported.[19] The data given below refer to the complexes prepared by anation of aquopentaamminecobalt(III) by the various tetrazolate ligands.

The structures of the 5-cyanotetrazolato-, 5-carbamoyltetrazolato-, 5-methyltetrazolato-, and (tetrazolato)pentaamminecobalt(III) complexes have all been studied by using ^1H and ^{13}C NMR. For the 5-cyano derivative, ^{15}N NMR studies have also been carried out. Furthermore, for the 5-cyano and 5-methyl complexes, single-crystal X-ray studies are in accord with the NMR results. The NMR data for the complexes are presented in Table I. The ^1H resonances for the axial and equatorial NH_3 protons clearly indicate that the tetrazoles are bonded to the cobalt(III) via a nitrogen donor.[23] For the 5-$CONH_2$, 5-CH_3, and 5-H complexes the ^1H NMR spectra also show the expected peaks due to these substituents.

With the exception of the carbamoyl complex, the ^{13}C NMR assignments are relatively straightforward and indicative of the tetrazole ring and its substituents. For the carbamoyl complex the ^{13}C signals are well resolved but relatively close together making it difficult unambiguously to assign one to the tetrazole ring carbon and the other to the amide carbon.

^{15}N NMR data were obtained for the 5-cyanotetrazole complex prepared from ^{15}N-enriched ligand. The enriched complexes were prepared by synthesizing the 5-cyanotetrazole ligand from either ^{15}N-enriched cyanogen and KN_3 or from enriched and terminally labeled KN_3 and unlabeled cyanogen according to the reaction in Figure 1a. The first set of conditions yield 5-cyanotetrazole labeled according to Figure 1b, designated 5-CT(cyn), in a 50:50 ratio. The second set of conditions yield the ligand as shown in Figure 1c, designated 5-CT(az), in a 25:25:25:25 ratio. The two differently labeled 5-cyanotetrazole complexes were then prepared by anation of aquopentaamminecobalt(III) with the labeled organic ligand and are designed as CP(cyan) and CP(az).

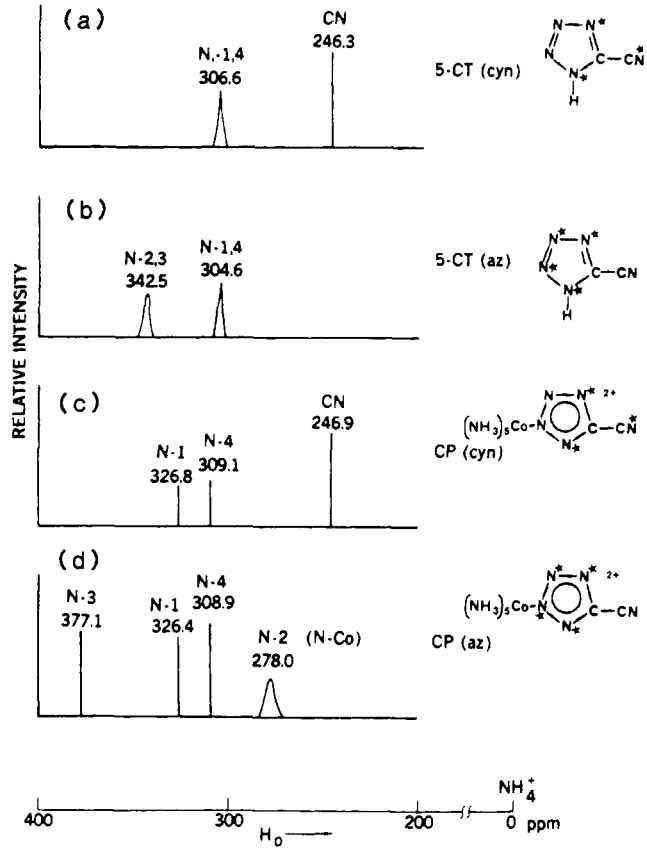

Figure 2. ^{15}N NMR spectra of enriched 5-cyanotetrazole and (5-cyanotetrazolato)pentaamminecobalt(III). Starred nitrogens are enriched in ^{15}N.

Schematics of the ^{15}N NMR spectra obtained for 5-CT and -CP are shown in Figure 2. For the free ligands (Figure 2a,b), the ring nitrogens 1,4 and 2,3 are equivalent, and their signals are broadened by the presence of the proton at its four tautomeric positions. Coordination of the ligand to the cobalt(III) has the effects shown in Figure 2c,d. For the case of CP(cyn), the 1- and 4-nitrogens are no longer equivalent, but their resonances are much sharper, indicating that the proton is no longer residing there, nor is anything else. When the spectrum of CP(az) is obtained, one sees the nonequivalence of all four ring nitrogens and, furthermore, one also sees a strong upfield shift of the 2-nitrogen accompanied by broadening that is not present for the other nitrogens. It is reasonable that coordination to cobalt(III) is responable for both the shift and,

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Table II. Spectral Characteristics of Cr(III) Products from the Reduction of (5-Substituted tetrazolato)pentaamminecobalt(III) Complexes by Cr(II)

5-substituent on tetrazole	tetrazole bonding mode to Co(III)	$[HClO_4]$, mol L^{-1}	Cr(III) product λ_{max}, (ϵ_{max}, L mol^{-1} cm^{-1})	% recovery of Cr(III)
CH_3	N-1	0.25	549 (16.6), 398 (19.8)	75, 76
CH_3	N-2	0.10	556 (17.0), 399 (19.1)	86
CH_3	N-2	1.0	556 (16.1), 400 (18.6)	89
H	N-2	0.10	549 (16.8), 397 (19.7)	91, 95
H	N-2	1.0	549 (17.0), 397 (19.4)	93, 88
$C(O)NH_2$	N-2	0.10	536 (23.1), 397 (23.9)	86, 96
$C(O)NH_2$	N-2	1.0	544 (22.4), 397 (25.8)	82, 68
CN	N-2	0.10	543 (20.0), 397 (20.0)	93, 83
CN	N-2	1.0	550 (19.5), 397 (22.5)	92

because of the ^{59}Co quadrupole moment, the broadening of the N-2 signal.

The X-ray crystal structures of the 5-cyanotetrazolato- and (5-methyltetrazolato)pentaamminecobalt(III) complexes have also been determined.[24,25] In both cases the cobalt(III) atom is coordinated to N-2 of the tetrazole ring, implying (vide supra) that N-2 bonding is favored for all of the complexes prepared by anation, both in the solid state and in solution.

Kinetics. The spectral characteristics and percent recovery of Cr(III) products obtained from the Cr(II)/Co(III) complex reaction mixtures are summarized in Table II. Only one Cr(III) product was observed on the ion-exchange column in each case.

Repetitive scans of stoichiometric mixtures of Cr(II) and the Co(III) complexes of N-2-bonded 5-cyano-, 5-methyl-, and 5-carbamoyltetrazolato ligand systems in the visible–near-ultraviolet spectral region showed isosbestic behavior. However, under these conditions reaction spectra of the N-2-bonded tetrazolato and the N-1-bonded 5-methyltetrazolato complexes of pentaamminecobalt(III) were nonisosbestic.

Each of the five systems studied obeyed one of two experimentally derived rate laws. The N-2-bonded 5-cyanotetrazolato and 5-carbamoyltetrazolato complexes of pentaamminecobalt(III) obey a rate law of the form

$$-\frac{d[\text{Co(III) complex}]}{dt} = k[\text{Co(III)complex}][\text{Cr(II)}] \quad (1)$$

No dependence of the rate on H^+ concentration was detected in the range 0.1–0.5 mol L^{-1} $HClO_4$. Values obtained for the rate constant k are 2.14 ± 0.15 and 13.88 ± 0.02 L mol^{-1} s^{-1} for the 5-cyano and 5-carbamoyl derivatives, respectively, at 25.0 ± 0.1 °C and ionic strength 1.0 mol L^{-1} ($LiClO_4/HClO_4$). The experimental data are given in Table III.

The N-2-bonded tetrazolato and 5-methyltetrazolato complexes and the N-1-bonded 5-methyltetrazolato complex all follow a more complex rate law of the form

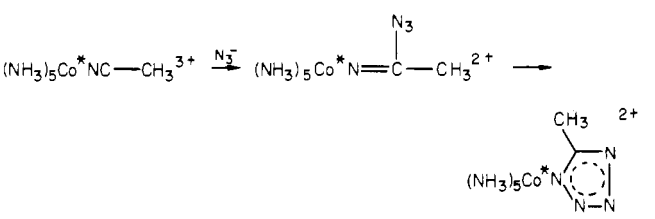
$$-\frac{d[\text{Co(III) complex}]}{dt} = (k_0 + k_1[H^+]^{-1})[\text{Co(III)}][\text{Cr(II)}] \quad (2)$$

The data are presented as supplementary material. Experimental values obtained for the rate constants k_0 and k_1 are summarized in Table IV.

Discussion

Characterization of Complexes. Since it is known that the anions of 5-substituted tetrazoles possess two bonding modes (N-1 and N-2) that are energetically equivalent,[26] it is necessary to establish unambiguously the bonding position of cobalt(III) in order to interpret the kinetic results. A further complication results from 5-substituents that contain potential coordinating atoms (5-CN, 5-$CONH_2$). In theory, the synthesis involving anation of aquopentaamminecobalt(III) by the tetrazole ligands could produce N-1-, N-2-, or substituent-bonded complexes exclusively or any combination of these isomers. The ^1H NMR data indicate that the tetrazoles are all bonded exclusively through a tetrazole ring nitrogen. Furthermore, the enriched ^{15}N NMR data for the 5-cyanotetrazolato complex prove N-2 bonding. This was subsequently confirmed by X-ray structure determinations on the 5-cyanotetrazolato complex as well as the 5-methyltetrazolato complex prepared by the anation procedure.[24,25]

A different synthetic strategy was adopted in order to synthesize the N-1-bonded 5-methyltetrazolato complex. This method uses the reaction of a coordinated nitrile with azide anion and can only result in an N-1-bonded complex.



The characterization of this complex has already been described.[19]

Table III. Kinetic Data for the Reduction of N-2-Bonded (5-Carbamoyltetrazolato)- and (5-Cyanotetrazolato)pentaamminecobalt(III) by Cr(II)[a]

$(NH_3)_5Co^{III}$ complex	$10^3 \times$ [Co(III)], mol L^{-1}	$10^2 \times$ [Cr(II)], mol L^{-1}	$[H^+]$, mol L^{-1}	k_{obsd}/[Cr(II)], L mol^{-1} s^{-1}
5-carbamoyl-tetrazolato	2.34	4.01	0.100	13.9
	2.33	4.01	0.153	13.8
	2.35	4.01	0.199	13.9
	2.33	1.30	0.199	13.9
	2.34	4.01	0.299	13.9
	2.40	4.01	0.507	13.9
5-cyano-tetrazolato	3.18	5.18	0.102	2.18
	3.43	5.18	0.148	2.37
	3.43	5.18	0.202	2.18
	3.43	2.01	0.202	2.14
	3.38	5.18	0.348	2.13
	3.10	5.18	0.502	1.96
	3.13	5.18	0.748	2.01

[a] T = 25 °C; I = 1.0 mol L^{-1} ($LiClO_4$); λ = 464 nm.

Table IV. Kinetic Parameters for the Reduction of (Tetrazolato)pentaamminecobalt(III) Complexes by Cr(II)[a]

5-substituent on tetrazole (bonding mode)	T, °C	k_0, L mol^{-1} s^{-1}	k_1, s^{-1}
H (N-2)	25.1	19 ± 2	3.3 ± 0.3
CH_3 (N-2)	25.0	0.15 ± 0.08	0.41 ± 0.02
CH_3 (N-2)	30.0	0.10 ± 0.02	0.485 ± 0.003
CH_3 (N-2)	35.0	0.22 ± 0.07	0.626 ± 0.008
CH_3 (N-1)	14.4	1.8 ± 0.3	0.65 ± 0.03
CH_3 (N-1)	23.9	2.4 ± 0.3	0.83 ± 0.02
CH_3 (N-1)	33.4	3.1 ± 0.8	1.2 ± 0.1
CN (N-2)	25.0	2.1 ± 0.1[b]	
$C(O)NH_2$ (N-2)	25.0	13.9 ± 0.1[b]	

[a] I = 1.0 mol L^{-1} ($LiClO_4$). [b] Rate constant given is $k_0 + k_1'$ (inseparable—see text).

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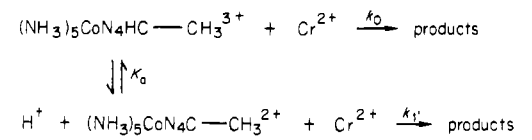
Kinetics. Inner-sphere mechanisms for the Cr(II) reductions of all five Co(III) complexes are indicated by several experimental observations. First, inverse acid-dependent terms appear in the rate laws of three of the five systems studied (see Results) indicative of a ligand deprotonation process prior to rate-limiting electron transfer. Second, several of the experimental rate constants (see Results) are too large to be associated with the normally slow outer-sphere Cr(II)–Co(III) electron-transfer reactions. Finally, the spectra of the Cr(III) products isolated from reaction mixtures (see Table I) are consistent with the spectra of nitrogen donors coordinated to the pentaaquachromium(III) moiety,[27] while hexaaquachromium(III), the product expected from an outer-sphere electron-transfer reaction, was not detected in any of the separated product mixtures.

Each Co(III)-coordinated tetrazolato ligand possesses three uncoordinated nitrogen atoms from the tetrazole ring, and a single-crystal X-ray diffraction study of N-2-bonded (5-cyanotetrazolato)pentaamminecobalt(III) perchlorate[24] shows a planar tetrazole ring with π-electron delocalization required to account for the observed bond lengths. Thus, any of these three uncoordinated nitrogens would be a suitable attack site for the incoming Cr(II) reductant. The ring substituents of the 5-cyano- and 5-carbamoyltetrazolato systems provide additional potential bridging sites, namely the cyano group nitrogen and the oxygen of the carbamoyl group. Since the electron-transfer reactions are strictly inner sphere, the fundamental mechanistic detail that requires our attention is the site of reductant attack on each of the 5-tetrazolato complexes studied here.

The carbamoyl oxygen can be eliminated as the Cr(II) attack site on the 5-carbamoyltetrazolato complex since product studies indicate a nitrogen bound to the Cr(III) product. The cyano group nitrogen can also be eliminated as the reductant attack point on the 5-cyanotetrazolato complex since a stable Cr(III) product is isolated from the chromatography column, and nitriles bound to Cr(III) have been shown to be labile leading to final formation of hexaaquachromium(III) as product.[28] Initial Cr(II) attack at the amide oxygen or cyano nitrogen, followed by a second redox reaction with excess Cr(II) in solution leading to a stable Cr(III) nitrogen-bound product, does not appear likely here since isosbestic behavior is observed in the visible–near-ultraviolet scans of each of these systems.

The above considerations indicate that one or more of the three available tetrazole ring nitrogens serve as the Cr(II) attack site for the electron-transfer reactions of all five systems studied here. The spectral characteristics of the Cr(III) products are of little value in indicating which ring nitrogen is utilized in this regard since visible spectral parameters of both N-1- and N-2-bonded tetrazole complexes are quite similar in peak position and extinction coefficient.[19] The steric environments of the uncoordinated ring nitrogens are, however, sufficiently different so that certain nitrogens become much more available for external Cr(II) attack than others. An examination of molecular models constructed by utilizing the bond lengths of Graeber and Morosin[24] for the N-2-bonded 5-cyanotetrazolato complex indicates that N-1-bonded tetrazolato complexes have two nitrogens, N-3 and N-4, situated in a virtually steric-free, solvent-exposed environment while N-2 is shielded somewhat from the solvent (and potential Cr(II) approach) by the four cis ammines of the pentammminecobalt(III) complex. Should one of these two nitrogens, either N-3 or N-4, serve as the protonation site in the 3+ complex, then one site will still remain open for Cr(II) attack. Deprotonation to the 2+ complex opens the second site for attack. Such a situation is envisaged for the N-1-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex since we observe a rather sizable acid-independent k_0 term for this complex as well as an inverse acid-dependent k_1 term. Thus, for this complex we suggest a mechanism as indicated in Scheme I to account for the experimental rate law. Such a mechanism requires a rate constant of the form given in eq 3. In the limit where $K_a[H^+]^{-1} << 1$, eq 3 reduces to the form

Scheme I



$$k_{obsd} = k_0 + \frac{k_1'K_a[H^+]^{-1}}{1 + K_a[H^+]^{-1}} \quad (3)$$

observed for this complex, eq 2, with $k_1 = k_1'K_a$. The lack of isosbestic behavior for Cr(II)–Co(III) mixtures of this complex implies a multistep process within a similar time interval and suggests to us that different sites are attacked by Cr(II) in the k_0 and k_1 steps. Attack at N-3 in one case and N-4 in the other case would lead to a mixture of (5-methyltetrazolato)pentaaquachromium(III) linkage isomers, which would be expected to isomerize exclusively to the N-2-bonded form as has already been shown to occur for the Co(III) linkage isomers.[19,22] Should such linkage isomerization occur on the same time scale as the electron-transfer reaction, then the observed nonisosbestic behavior would be expected.

Activation parameters for the k_0 process determined from Eyring plots are $\Delta H_0^{\ddagger} = 4.2 \pm 0.2$ kcal mol^{-1} and $\Delta S_0^{\ddagger} = -43 \pm 1$ cal deg^{-1} mol^{-1}. Similarly for the k_1 process, $\Delta H_1^{\ddagger} = 5.7 \pm 1.1$ kcal mol^{-1} and $\Delta S_1^{\ddagger} = -40 \pm 4$ cal deg^{-1} mol^{-1}. Note that for the k_1 activation parameters our mechanism requires $\Delta H_1^{\ddagger} = \Delta H_1'^{\ddagger} + \Delta H_a$ and $\Delta S_1^{\ddagger} = \Delta S_1'^{\ddagger} + \Delta S_a$, where ΔH_a and ΔS_a are the thermodynamic parameters for proton ionization of the tetrazole complexes.

For N-2-bound tetrazolato ligands molecular models indicate that only one nitrogen, N-4, is fully exposed to the solvent while N-1 and N-3 are shielded from external Cr(II) approach somewhat by the cis ammines on Co(III). The experimental rate law for the N-2-bonded 5-methyltetrazolato complex suggests that a mechanism as outlined in Scheme I operates for this complex. However, the structural differences that exist between N-1- and N-2-bonded complexes require an extension of the Cr(II) attack process to that described above. We note that the k_0 values for the N-2 linkage isomer are about 1 order of magnitude smaller than those for the N-1 isomer. Such differences might be expected if the electron-transfer pathways for these protonated complexes were sufficiently different. Such differences are shown in the following Scheme II, which is a detailed accounting of the general Scheme I mechanism. Attack at N-4 by Cr(II) on the protonated N-2 linkage isomer leads to a Cr(III) N-1-bonded tetrazole complex which isomerizes to the N-2-bonded form. However, since the k_0 path is utilized by at most only 20% of the reactants-to-products conversion process under the acid concentrations utilized here, reasonable isosbestic behavior would be anticipated for spectral scans of the reaction. On the other hand, the N-1-bonded protonated isomer makes considerable use of the k_0 path (under the acid concentrations used here, approximately 50% of the reaction proceeds by the k_0 path), forming, by Scheme II, relatively larger proportions of N-1-bonded Cr(III) tetrazole complex, which subsequently isomerizes to the stable N-2-bonded form, demonstrating in the process nonisosbestic behavior. Note also from Scheme II that the conjugated path-

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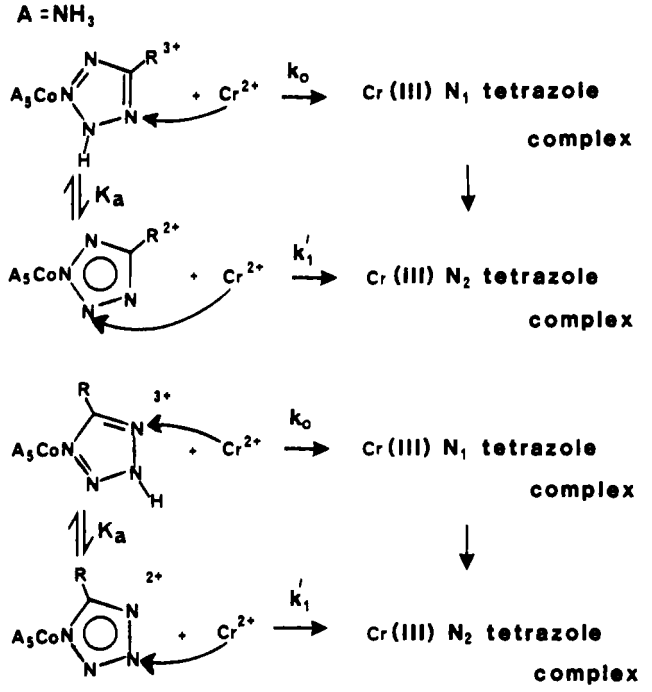
Scheme II



ways from reductant center to oxidant center for the k_0 paths are different, being N–N–N in the case of the N-2-bonded Co(III) complex vs. N–C–N for the N-1-bonded linkage isomer. Thus, k_0 values of similar magnitude would not be expected for the two complexes.

Scheme II also accounts for several observations regarding the k_1' pathways for electron transfer of the linkage isomers. The arguments in favor of different Cr(II) attack points for the N-1-bonded 5-methyltetrazolato complex were presented above. Thus, we visualize Cr(II) attack at the exposed N-3 nitrogen for this complex. For the N-2-bonded linkage isomer, the dominant k_1' path requires Cr(II) attack at a site which will yield a stable N-2-bonded Cr(III) tetrazole complex since isosbestic behavior is observed in the spectral scans. Thus, Scheme II shows Cr(II) attack at N-3. An alternative scheme with Cr(II) attack at N-4 during the k_1 process and very rapid linkage isomerization would also lead to isosbestic behavior but would not be compatible with the observations of the N-1 system that require that this same linkage isomerization reaction occur on a time scale comparable with electron transfer.

It should be noted that the k_0 value for the N-2-bonded 5-methyltetrazole complex measured at 25 °C will not justify its inclusion in the experimental rate law. However, the 30 and 35 °C data require its inclusion for a reasonable fit. Nevertheless, due to the relative uncertainty in the k_0 values for this complex, calculation of activation parameters is not justified. For the k_1 process, however, we obtain $\Delta H_1^* = 7.2 \pm 1.0$ kcal mol^{-1} and $\Delta S_1^* = -36 \pm 3$ cal deg^{-1} mol^{-1}.

When the methyl group is replaced by H, the N-2-bonded (tetrazolato)pentaamminecobalt(III) complex also obeys the rate law in eq 2 and, hence, conforms to the mechanism of Scheme I. Both k_0 and k_1 are larger with this complex than in the methyl systems discussed above. The large k_0 term can be rationalized on the basis of Scheme II by Cr(II) attack on N-4 as with the N-2-bonded 5-methyltetrazolato complex. Since R = H rather than CH_3, Cr(II) approach should be less inhibited resulting in a larger k_0. The k_1' path again involves attack of Cr(II) at N-3. Since the k_0 path makes a sizable contribution to the overall electron-transfer process, a considerable proportion of N-1-bonded Cr(III) tetrazole complex would be formed and nonisosbestic behavior predicted due to the N-1 to N-2 linkage isomerization reaction of this product. Such nonisosbestic behavior is indeed observed for this system.

The final two systems, the 5-cyano- and 5-carbamoyltetrazolato complexes, are both N-2 bonded and follow the simple second-order rate law given in eq 1. No acid dependency is observed for either of these two complexes in their reaction with Cr(II). Such behavior can be accommodated into the mechanism of Scheme I if $K_a[H^+]^{-1} >> 1$, whereupon the experimental rate constant $k = k_0 + k_1'$.

Each of the five systems studied here has been adapted to the mechanism of Scheme I by applying only limiting forms to eq 3. We now examine the validity of the $K_a[H^+]^{-1} << 1$ limit for the N-1- and N-2-bonded 5-methyltetrazolato complexes. The K_a values for all five systems have not yet been measured, but K_a values of 0.030 and 0.020 have been determined for the N-1- and N-2-bonded (5-methyltetrazolato)pentaamminecobalt(III) complexes, respectively, at 25 °C and ionic strength 1.0 M.[29] The K_a of uncoordinated 5-methyltetrazole at 25 °C in water is 2.3×10^{-6}.[8] Thus, the pK_a of this ligand is lowered by 3.9–4.1 units upon coordination to the pentaamminecobalt(III) moiety. If we assume that the pK_a's of all tetrazoles will be lowered by approximately 4 units when coordinated and that the site of coordination, N-1 or N-2, will have a minimal effect on the complex pK_a, then the data of Hansen et al.[8] may be utilized to estimate the pK_a's of the other complexes studied here. It should be noted that ref 8 does not record pK_a's for 5-cyano- or 5-carbamoyltetrazole. However, we find that a plot of the author's pK_a's vs. Hammett σ_m values[30,31] is linear with a correlation coefficient for six points of −0.989, which permits an estimate of these two ligand pK_a values using their appropriate σ_m parameters.[30] These assumptions and estimates yield pentaamminecobalt(III) complex pK_a's of 0.9 for the tetrazole system, −1.0 for the 5-carbamoyltetrazole system, and −3 for the 5-cyanotetrazole system. Considering the range of $HClO_4$ concentrations employed in our studies, $K_a[H^+]^{-1}$ never exceeds 0.3 for either of the 5-methyltetrazole complexes, thus satisfying the $K_a[H^+]^{-1} << 1$ limit required by our mechanistic interpretation. For the tetrazole complex, our estimate of pK_a has the $K_a[H^+]^{-1}$ term comparable to 1 for many kinetic runs, but if our estimate is off by only 0.5 pK_a unit, then the limit required by our mechanistic scheme is satisfied. Also, our pK_a estimates and acid conditions find $K_a[H^+]^{-1}$ always exceeding 10 (usually considerably so) for the 5-cyano- and 5-carbamoyltetrazole complexes while our mechanism requires $K_a[H^+]^{-1} >> 1$. It is impossible to estimate the contributions of k_0 and k_1' to the observed rate constants of the 5-cyano- and 5-carbamoyltetrazole systems from our data. However, the isosbestic behavior of these systems when mixed with Cr(II) indicates that the k_1' path of Schemes I and II dominates. For the N-1- and N-2-bonded 5-methyltetrazolato complexes and the tetrazolato complex, our K_a estimates indicate that k_1' values are approximately 28, 20, and 26 L mol^{-1} s^{-1} at 25 °C, respectively. The similarity in values of these rate constants is somewhat surprising, but considering the questionable accuracy of the estimated K_a value for the tetrazole complex, the latter value must be considered a very rough estimate.

Since inner-sphere electron-transfer pathways operate for each of the five tetrazole complexes reported here, it is in retrospect rather unexpected that the isoelectronic pyrazole and imidazole complexes of pentaamminecobalt(III) do not show inner-sphere pathways in their reductions by chromium(II).[1c,6b] However, it must be considered that the 3+ forms of these complexes have a proton on the only available nitrogen

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for reductant attack, thus blocking a k_0 path similar to that observed here for tetrazole complexes. Additionally, the pK_a's of these complexes are considerably higher (10 for the imidazole complex[32]) than those of our tetrazole complexes, thus suppressing the k_1 path at low pH where the chromium(II) reductions were followed, i.e., 0.10 M $HClO_4$ for the imidazole system[1c] and 1.2 M $HClO_4$ for the pyrazole system.[6b] The present study, however, points to the efficient operation of a tetrazole ring as an electron-transfer mediator, and, perhaps, if higher pHs are employed with the imidazole and pyrazole systems, evidence for inner-sphere electron transfer will become apparent in those systems as well.

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Registry No. $[Co(NH_3)_5CN_4CN](BF_4)_2$, 87371-39-9; *N*-2-$[Co(NH_3)_5CN_4CH_3](BF_4)_2$, 87371-40-2; *N*-1-$[Co(NH_3)_5CN_4CH_3](ClO_4)_2$, 84927-29-7; $[Co(NH_3)_5CN_4CONH_2](BF_4)_2$, 87371-41-3; $[Co(NH_3)_5CN_4H](BF_4)_2$, 87371-43-5; hexaaquachromium(II), 20574-26-9; aquapentaamminecobalt(III) perchlorate, 13820-81-0.

Supplementary Material Available: A table of kinetic data (3 pages). Ordering information is given on any current masthead page.

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Magnetic Circular Dichroism Studies on [5,10,15,20-Tetrakis(1-methylpyridinium-4-yl)porphinato]iron and Some of Its Derivatives

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Magnetic circular dichroism (MCD) spectra are reported for [5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphinato]iron(III) and -iron(II), Fe^{III}TMP and Fe^{II}TMP, and some of their derivatives in the near-UV to near-IR regions. Two proton equilibria existed between the three Fe^{III}TMP monomers with pK_a values of ca. 5.7 and 12.3 while, after electrochemical reduction, an equilibrium was observed between the two Fe^{II}TMP monomers with a pK_a of ca. 11.2. The species were in high-spin states except Fe^{III}TMP at pH >13 and Fe^{II}TMP at pH >12 (low spin). Porphyrin electronic structures of the coordination spheres on these species and their bis(imidazole) and bis(cyanide) derivatives are discussed in comparison with information on iron porphyrins and hemes previously studied.

Introduction

Since its introduction in 1970,[1] 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphine, TMP, and its metal complexes have been of particular interest among porphyrin researchers because of its stability and high solubility in water over a wide range of pH. In addition to several spectroscopic studies,[2-8] recent studies[9-13] have demonstrated in particular that the iron complex of this porphyrin, FeTMP, is an eminent catalyst for the electroreduction of oxygen. Irrespective of such an attractiveness, however, its mechanisms are not completely elucidated owing to simultaneous acid-dissociation and dimerization equilibria depending on pH and/or concentration.

Recently two papers[7,8] appeared on the electrochemical and spectral speciation of this porphyrin in water, in which emphasis was placed on acid-dissociation and monomer-dimer equilibria. In this study, therefore, we present the results of MCD on $Fe^{III/II}$TMP species in water. MCD spectroscopy has proven to be a powerful technique to verify the oxidation, spin and ligand states of chromophores.[14,15] Accordingly, by the use of MCD spectroscopy, it is expected that not only the information on proton equilibria is obtainable but also the porphyrin electronic structures of the coordination spheres can be discussed in comparison with information on iron porphyrins and hemes previously studied.

Experimental Section

(i) Materials. Chemicals were commercially available guaranteed reagents and were used without further purification. Fe^{III}TMP(Cl) was prepared by the method of Fleischer.[1] The ratio of C:N:Fe was experimentally determined to be 44:7.9:0.98 as compared to theoretical values of 44:8:1. To generate Fe^{II}TMP from Fe^{III}TMP in an optically transparent thin-layer electrode (OTTLE), a potential of -0.7 V[9] vs. a saturated calomel electrode (SCE) was supplied by a potentiostat that was built according to the literature.[16] For pH variation experiments, Fe^{III}TMP was dissolved in a 0.05 mol dm^{-3} Na_2SO_4 solution, and concentrated H_2SO_4 or NaOH solutions were added with stirring, except for the highly acidic (pH <2) and basic (pH ≅12) solutions. To prepare basic solutions of pH 12-13.4, the NaOH solution of Fe^{III}TMP was first prepared and then Na_2SO_4 was added to produce

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