Experimental Section

Reagents. $(NH_4)_2B_{10}H_{10}$[7] and $[(C_6H_5)_3P]_3CuCl$[5] were prepared according to the literature. $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ was prepared by the method of Gill and Lippard[1] from the above reactants. Preparation of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$[4] has been described previously. Anal. Calcd for 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$: C, 66.5; H, 5.85; B, 8.30; P, 9.55; Cu, 9.80. Found: C, 66.95; H, 6.00; B, 7.95; P, 9.30; Cu, 9.70. Calcd for $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}\cdot CHCl_3$ (Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.): C, 62.06; H, 5.06; B, 7.65; P, 8.76. Found: C, 61.82; H, 5.41; B, 7.63; P, 9.02.

Spectra. The ^1H NMR spectra were obtained at 90 MHz with a Bruker HX-90 NMR spectrometer. Proton chemical shifts are relative to $Si(CH_3)_4$, τ 10.00 ($CHCl_3$, τ 2.75). Infrared spectra were obtained with a Perkin-Elmer 457 infrared spectrometer. The solution infrared spectrum of 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$ was recorded using a cell path length of 0.1 mm. The solution infrared spectrum of $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$ was recorded using custom-built matched cells with a path length of 8 mm. The cells are sufficiently matched that $CHCl_3$ absorptions are canceled out. The cells are of stainless steel with KBr windows.

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Registry No. 2,3-μ-$[(C_6H_5)_3P]_2CuB_5H_8$, 32491-36-4; $\{[(C_6H_5)_3P]_2Cu\}_2B_{10}H_{10}$, 54020-26-7.

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Effect of Solvent on the Energy of Intervalence-Transfer Bands

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Mixed-valence compounds often have unusual absorption bands in their electronic spectra.[1] In systems where metal–metal interactions are sufficiently strong, the metal sites are equivalent and the absorption bands have their origin in transitions involving delocalized molecular orbitals over the various metal centers.[1-3] If metal–metal interactions are relatively weak, the metal sites are nonequivalent and localized valences are present. In this latter class of compounds, there commonly appear low-energy absorption bands which can be assigned to intervalence-transfer (IT) transitions.[4,5] In IT transitions, light-induced electron transfer occurs between different valence state sites (eq 1).

$$[\mathrm{M(III)\text{-}M(II)}] \xrightarrow{h\nu} [\mathrm{M(II)\text{-}M(III)}]^* \qquad (1)$$

Hush has developed a treatment which predicts the properties of IT bands in cases where delocalization is not extensive. One of the predictions made is that the energies of IT bands should depend on solvent dielectric properties. This prediction has been borne out for the symmetrical mixed-valence ions $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$ [6] (4,4'-bpy is 4,4'-bipyridine) and $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ [7] (bpy is 2,2'-bipyridine; pyr is pyrazine). In contrast, the energy of the IT band in the Creutz and Taube ion $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{5+}$ does not vary with solvent,[8] apparently because of extensive delocalization.[7]

In earlier papers the mixed-valence properties of a series of unsymmetrical dimers were reported.[9] In the ion $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+}$, there is an oxidation-state asymmetry induced by the difference in coordination environments, and the Ru(III) site is localized on the pentaammine end.[9] The IT solvent dependence is more difficult to test experimentally for unsymmetrical cases and insufficient data were available in the earlier work to make a searching test. Because of the importance of establishing the validity and limitations of the Hush treatment, of relating IT processes to thermal electron-transfer processes in solution, and of probing the effects of electronic delocalization on mixed-valence properties, we have carried out a detailed study of the variation of IT band with solvent for the ion $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+}$.

Experimental Section

Measurements. Ultraviolet–visible and near-infrared spectra were recorded using Cary Models 14 and 17 and Bausch and Lomb 210 spectrophotometers. Electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2 °C and are uncorrected for junction potentials. The measurements were made using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetric experiments.

Materials. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques.[9] Acetonitrile (MCB Spectrograde) was dried over Davidson 4-Å molecular sieves for electrochemical measurements and used without drying for spectral measurements. Water was deionized and then distilled from alkaline permanganate. Propylene carbonate was vacuum distilled with the middle 60% collected. Dimethyformamide (reagent grade) was stirred over molecular sieves (type 3A pellets) for 24 h and then vacuum distilled from phosphorus pentoxide. All other solvents (reagent grade) were used without further purification. The preparations of the complexes $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{4+/3+}$ [9] and $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+/2+}$ [7] have been reported elsewhere.

Results

Electrochemical data and IT absorption band maxima are given in Table I. The $E_{1/2}$ values are from voltammetry and cyclic voltammetry. The slopes of plots of E vs. log $[i/(i_1 - i)]$ from voltammetry and the difference between anodic and cathodic peak potentials (ΔE_p) gave values between 60 and 100 mV. The cyclic voltammograms were essentially invariant to changes in the sweep rate in the range 50–500 mV/s, and the higher than theoretically predicted ΔE_p values apparently arise from uncompensated solution resistance.

Except for the usually small correction term for differences in diffusion coefficients, the $E_{1/2}$ values are reduction potentials for the couples

$$\begin{aligned}&[(bpy)_2ClRu^{III}(pyr)Ru^{III}C(bpy)_2]^{4+} + e^-\\&\quad\rightarrow [(bpy)_2ClRu^{III}(pyr)Ru^{II}Cl(bpy)_2]^{3+} \quad (E_{1/2}(2))\end{aligned} \qquad (2)$$

$$\begin{aligned}&[(bpy)_2ClRu^{III}(pyr)Ru^{II}Cl(bpy)_2]^{3+} + e^-\\&\quad\rightarrow [(bpy)_2ClRu^{II}(pyr)Ru^{II}Cl(bpy)_2]^{2+} \quad (E_{1/2}(1))\end{aligned} \qquad (3)$$

and

$$\begin{aligned}&[(NH_3)_5Ru^{III}(pyr)Ru^{III}Cl(bpy)_2]^{5+} + e^-\\&\quad\rightarrow [(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+} \quad (E_{1/2}(2))\end{aligned} \qquad (4)$$

$$\begin{aligned}&[(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+} + e^-\\&\quad\xrightarrow[\mathcal{E}_1^{\circ\prime}]{} [(NH_3)_5Ru^{II}(pyr)Ru^{II}Cl(bpy)_2]^{3+} \quad (E_{1/2}(1))\end{aligned} \qquad (5)$$

Table I. $E_{1/2}$[a] and Intervalence-Transfer Data

Ion	Medium	$E_{1/2}$-(1), V	$E_{1/2}$-(2), V	IT $\bar{\nu}_{max}$, kK[b]	$\Delta G^{\circ\prime}$, kK[c]
$[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{2+}$	Acetonitrile[d]	0.89	1.01		
	Nitrobenzene[e]	0.70	0.82		
	DMF[e]	0.89	1.01		
	DMSO[e]	0.90	1.02		
	Propylene carbonate[e]	0.84	0.96		
	Water[f]	0.55	0.67		
$[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{3+}$	Acetonitrile[d]	0.61	1.03	10.4	2.3
	Nitrobenzene[e]	0.63	0.95	8.3	0.6
	DMF[e]	0.36	1.05	12.4	4.3
	DMSO[e]	0.29	1.03	12.6[g]	4.9
	Propylene carbonate[e]	0.48	0.95	11.5	2.9
	Water[f]	0.30	0.81	11.1[h]	2.0

[a] ±0.01 V vs. the SSCE at 22 ± 2 °C. [b] ±0.2 kK; the IT bands were measured for the 4+ ion in pure solvents without added electrolytes. [c] See text. [d] 0.1 M $[N(n\text{-}Bu)_4](PF_6)$. [e] 0.2 M $[N(n\text{-}Bu)_4](PF_6)$. [f] 0.1 M $HClO_4$. [g] The IT band appears as a shoulder on the intense, visible charge-transfer band. E_{op} was resolved using SPECSOLVE, a local variation of the BIGAUS program for deconvolution of electronic spectra, written by H. Gold, The University of North Carolina, Chapel Hill, N. C. [h] D_2O.

For the Ru(II)–Ru(II) dimeric ions, there are two anodic waves in the potential region 0–1.5 V (vs. the SSCE), and they are labeled $E_{1/2}(1)$ and $E_{1/2}(2)$ in the order of their appearance in sweeping from 0 to 1.5 V. For the symmetrical dimer, the difference between the two waves ($\Delta E_{1/2}$) is essentially invariant with solvent because $E_{1/2}(1)$ and $E_{1/2}(2)$ are affected equally. For the unsymmetrical dimer, $\Delta E_{1/2}$ varies noticeably with solvent which is consistent with different sites of oxidation for the two processes.

Discussion

For a symmetrical mixed-valence dimer in which there are discrete valences, the energy of the IT band in solution is given by[4]

$$E_{op} \geq 4E_{th} = \chi \tag{6}$$

where E_{th} is the activation energy for the related thermal intramolecular electon-transfer process and χ is the reorganizational energy term. If metal–metal interactions are weak

$$E_{op} = 4E_{th} = \chi \tag{7}$$

For the unsymmetrical ion the difference in internal energy (E_0) between the valence-state isomers $[(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+}$ and $[(NH_3)_5Ru^{II}(pyr)Ru^{III}Cl(bpy)_2]^{4+}$ (eq 8) must be taken into account giving eq 9,[4] where now E_{th} is

$$[(NH_3)_5Ru^{III}(pyr)Ru^{II}Cl(bpy)_2]^{4+} \xrightarrow[E_0,\ \Delta G^{\circ\prime}]{} [(NH_3)_5Ru^{II}(pyr)Ru^{III}Cl(bpy)_2]^{4+} \tag{8}$$

$$E_{op} = \chi + E_0 \tag{9}$$

given by[4] eq 10. χ includes contributions from both inner-

$$E_{th} = (E_{op})^2/4(E_{op} - E_0) \tag{10}$$

sphere (χ_{inner}) and outer-sphere (χ_{outer}) rearrangement energies,[4] and

$$E_{op} - E_0 = \chi_{outer} + \chi_{inner} \tag{11}$$

Using a dielectric continuum model, χ_{outer} is predicted to vary directly with $(1/n^2) - (1/D_s)$ where n^2 and D_s are the optical and static dielectric constants of the solvent. From eq 11, $E_{op} - E_0$ is predicted to vary with $(1/n^2) - (1/D_s)$ for the unsymmetrical ion in a series of solvents.

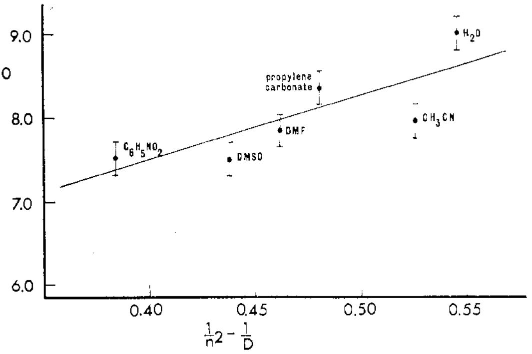

Figure 1. Solvent dependence for the IT band of $[(NH_3)_5Ru(pyr)RuCl(bpy)_2](PF_6)_4$. The line shown is a linear least-squares fit of the data; the vertical error bars represent the estimated uncertainties in $\bar{\nu}_{max}$ for the IT band.

From the difference in reduction potentials for the couples in eq 5 and 12, the free energy change for reaction 8, $\Delta G^{\circ\prime}$,

$$[(NH_3)_5Ru^{II}(pyr)Ru^{III}Cl(bpy)_2]^{4+} + e^- \xrightarrow[\mathcal{E}_2^{\circ\prime}]{} [(NH_3)_5Ru^{II}(pyr)Ru^{II}Cl(bpy)_2]^{4+} \tag{12}$$

$$\Delta G^{\circ\prime}\ (\text{in kK}) = 8.067(\mathcal{E}_2^{\circ\prime} - \mathcal{E}_1^{\circ\prime}) \tag{13}$$

can be calculated (eq 13). $\mathcal{E}_1^{\circ\prime}$ values are given in Table I, but $\mathcal{E}_2^{\circ\prime}$ must be estimated. To a first approximation, $\mathcal{E}_2^{\circ\prime}$ could be taken from $E_{1/2}(2)$ for the unsymmetrical dimer (eq 4). However, a better approximation would appear to be $E_{1/2}(1)$ for the 2,2'-bipyridine dimer (eq 3) which measures the reduction potential of a Ru(III) site adjacent to a Ru(II) site.[13] This is a better choice because there is some delocalization between Ru(II) and Ru(III) in $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$.[7] Assuming that $T\Delta S^{\circ\prime} \approx 0$ for eq 8 gives[10]

$$E_0 = \Delta G^{\circ\prime} \tag{14}$$

$E_{op} - E_0$ is plotted against $(1/n^2) - (1/D_s)$ in Figure 1.[12] The predicted linear relationship appears to hold. For the linear least-squares line in Figure 1 the correlation coefficient is 0.79 (slope 7.58) which probably represents a reasonable agreement given the assumptions used and the approximations needed to obtain E_0. The uncertainty in E_0 values is probably the major source of error in the experiment.

The agreement found is significant since it reinforces the validity of the Hush treatment for weakly interacting systems. The Hush treatment can also be used to obtain fundamental information about the related thermal electron-transfer process. The energy of activation for the thermal process can be calculated from eq 10.[4] In acetonitrile using E_{op} = 10.4 kK and E_0 = 2.4 kK gives E_{th} = 3.4 kK (9.7 kcal/mol). The reorganizational energy term can also be partitioned into inner- and outer-sphere contributions. From eq 11, the intercept of the plot in Figure 1 gives χ_{inner} = 4.5 kK. χ_{outer} can then be calculated for each solvent using eq 11. In acetonitrile χ_{outer} = 3.5 kK.

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Registry No. $[(NH_3)_5Ru(pyr)RuCl(bpy)_2]^{3+}$, 54713-81-4; $[(bpy)_2ClR_4(pyr)RuCl(bpy)_2]^{2+}$, 47896-81-1; $[(NH_3)_5Ru(pyr)RuCl(bpy)_2](PF_6)_4$, 58561-03-8.

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(10) The assumption that $T\Delta S°' \approx 0$ is probably resonable. The standard entropy differences between 2+ and 3+ ions in water for the couples $\mathrm{Ru(bpy)_3^{3+}}$–$\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{Ru(NH_3)_6^{3+}}$–$\mathrm{Ru(NH_3)_6^{2+}}$ are +0.4 ± 2.0 and +4.1 ± 1.9 eu, respectively.[11]
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(12) The IT and $\Delta G°'$ data are in different media, but E_{op} is apparently relatively insensitive to medium effects. E_{op} is the same within experimental error in 0.1 M $(n\text{-Bu})_4\mathrm{NPF_6}$–$\mathrm{CH_3CN}$ and in pure acetonitrile.
(13) $E_{1/2}(1)$ for the symmetrical dimer, $\mathrm{[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+/2+}}$ (Table I), is disfavored by a statistical factor of 2, since there are two equivalent sites for redox. Thus $\mathcal{E}_2°' = E_{1/2}(1)_{\mathrm{sym}} + 0.059 \log 2 \simeq E_{1/2}(1)_{\mathrm{sym}} + 0.02$ V.

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Catalysis of "Franck–Condon Forbidden" Electron-Transfer Reactions by Macrocyclic Cobalt(II) Complexes[1]

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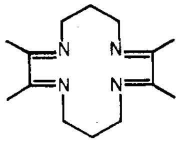
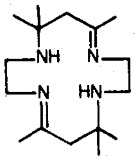
In an earlier study[2] we observed that the $\mathrm{Cr^{2+}}$ reduction of $\mathrm{Co([14]tetraeneN_4)(NH_3)_2^{3+}}$ [3] was autocatalytic. We were able to demonstrate in this system that the significance of the catalytic pathway increased with $\mathrm{[Co([14]tetraeneN_4)(OH_2)_2^{2+}]}$ and we suspected the reactive intermediate to be a cobalt(I) complex. The small rates for outer-sphere $\mathrm{Cr^{2+}}$ reductions of cobalt(III) complexes may be attributed to relatively large inner-sphere reorganizational barriers.[2] The observation of a catalytic pathway suggests the existence of a reaction channel in which the apparent Franck–Condon constraints may be somewhat relaxed. This possibility and the novel possibility of finding a convenient means for generating and studying reactive cobalt(I) species in aqueous solution have led us to investigate these effects further. For these investigations we have selected the $\mathrm{Co([14]tetraeneN_4)(OH_2)_2^{2+}}$-catalyzed $\mathrm{Cr^{2+}}$ reduction of $\mathrm{Co([14]dieneN_4)(NH_3)_2^{3+}}$ because (1) the net reaction is not autocatalytic and thus relatively convenient to investigate quantitatively and (2) the $\mathrm{Cr^{2+}}$–$\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}$ reaction has a larger apparent reorganizational barrier[2] than the one we originally discovered, so it could be more susceptible to catalytic effects. This report of our studies has been prompted by the recent elucidation of the chemistry of $\mathrm{Co^{I}([14]tetraeneN_4)}$ and $\mathrm{Co^{I}([14]dieneN_4)}$ using pulse radiolytic techniques.[4]



[14]tetraeneN$_4$



[14]dieneN$_4$

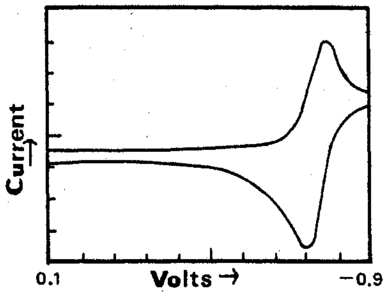


Figure 1. Cyclic voltammogram for the ([14]tetraeneN$_4$)Co$^{\mathrm{II}}$–([14]tetraeneN$_4$)Co$^{\mathrm{I}}$ couple in water; sweep time 1 division/s; 1 μA/division; voltage range +0.1 to −0.9 V vs. SCE.

Experimental Section

The complexes $\mathrm{[Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2](ClO_4)_3{\cdot}2H_2O}$[2] and $\mathrm{[Co([14]tetraeneN_4)(ClO_4)_2]{\cdot}2H_2O}$[5] were prepared as described elsewhere.

Preparation of $\mathrm{Cr^{2+}}$ solutions, sample-handling techniques, most kinetic procedures, and electrochemical techniques were similar to those described previously.[2,5–7] $\mathrm{Cd(NO_3)_2}$ was used to calibrate the potential output of the Chemtrix SSP-2; for the present study we equipped the instrument with an external voltmeter to improve the precision of voltage measurements.

Solutions of $\mathrm{Cr^{2+}}$, $\mathrm{Co^{II}([14]tetraeneN_4)}$, and $\mathrm{Cr^{3+}}$ were mixed in a 1-cm cell prior to the addition of a solution of $\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}$. The ionic strength was 0.82 M in $\mathrm{HClO_4}$ and $\mathrm{NaClO_4}$. The reaction was followed at the 330 nm (ϵ 2.4 × 10^3) charge-transfer absorption maximum[6a,7] of the $\mathrm{Co^{II}([14]\text{-}4,11\text{-}dieneN_4)}$ product.

Similar procedures were used in studies with $\mathrm{B_{12}}$ complexes, except that aquocobalamin (Sigma Chemical, St. Louis, Mo.) was mixed directly with $\mathrm{Cr^{2+}}$ to obtain vitamin $\mathrm{B_{12r}}$ in solution.

Results and Discussion

Kinetic data are collected in Table I for the reaction of $\mathrm{Co([14]dieneN_4)(NH_3)_2^{3+}}$ with mixtures of $\mathrm{Cr^{2+}}$ and $\mathrm{Co^{II}([14]tetraeneN_4)}$. The experimental rate law may be expressed as in (1) with $k' = 0.12 \pm 0.04\ \mathrm{M^{-1}\,s^{-1}}$. The

$$-\frac{d[\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}]}{dt} = k'[\mathrm{Cr^{2+}}][\mathrm{Co^{II}([14]tetraeneN_4)}] \tag{1}$$

reaction system may be plausibly described by reactions 2–5.

$$\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+} + Cr^{2+} \xrightarrow[H_3O^+]{k_2} Co([14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2^{2+} + 2NH_4^+ + Cr^{3+}} \tag{2}$$

$$\mathrm{Co([14]tetraeneN_4)(OH_2)_2^{2+} + Cr^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co^{I}([14]tetraeneN_4) + Cr^{3+}} \tag{3}$$

$$\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+} + Co^{I}([14]tetraeneN_4) \xrightarrow[H_3O^+]{k_4} Co([14]\text{-}4,11\text{-}dieneN_4)(OH_2)_2^{2+} + 2NH_4^+ + Co([14]tetraene)(OH_2)_2^{2+}} \tag{4}$$

$$\mathrm{Co^{I}([14]tetraeneN_4) + H^+ \xrightarrow{k_5} HCo([14]tetraeneN_4)^{2+}} \tag{5}$$

This reaction scheme, assuming a stationary state in $\mathrm{Co^{I}([14]tetraeneN_4)}$, leads to the rate expression in eq 6, provided

$$-\frac{d[\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}]}{dt} = \frac{k_3k_4[\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}][\mathrm{Cr^{2+}}] \times [\mathrm{Co([14]tetraeneN_4)(OH_2)_2^{2+}}]}{k_{-3}[\mathrm{Cr^{3+}}] + k_4[\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}] + k_5[\mathrm{H^+}]} \tag{6}$$

$k_2[\mathrm{Cr^{2+}}][\mathrm{Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}}] \ll$ rate as given