

Contribution from the Research School of Chemistry, The Australian National University, Canberra, ACT 2600, Australia, and Joint Science Department, Claremont Colleges, Claremont, California 91711

Outer-Sphere Electron-Transfer Reactions Involving Caged Cobalt Ions

I. I. CREASER, A. M. SARGESON,* and A. W. ZANELLA

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Complexes in which Co^{2+} (high spin) and Co^{3+} (low spin) were encapsulated by the ligands sep (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane) or sar (3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) and a number of their derivatives were used in studies of outer-sphere electron-transfer reactions (25 °C and $\mu = 0.5$ and 0.2 M). The self-exchange rate constants of the caged complexes were determined polarimetrically. Other electron-transfer rate constants were measured spectrophotometrically for reactions between different caged complexes in the Co(II) and Co(III) oxidation states and between some caged complexes and the $\text{Cr}_{\text{aq}}^{2+}$, $\text{Eu}_{\text{aq}}^{2+}$, $\text{V}_{\text{aq}}^{2+}$, $\text{U}_{\text{aq}}^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{bpy})_3]^{3+}$ ions (en = 1,2-ethanediamine, bpy = 2,2'-bipyridine). Rate constants agree with those calculated by using the Marcus-Hush theories especially for the reactions involving the cages, $[\text{Co}(\text{en})_3]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$ when the revised self-exchange rate for $[\text{Co}(\text{NH}_3)_6]^{3+}$ is employed. With use of known or estimated self-exchange rate constants for $\text{Eu}_{\text{aq}}^{2+}$, $\text{V}_{\text{aq}}^{2+}$, and $[\text{Co}(\text{bpy})_3]^{3+}$, the calculated cross-reaction rate constants agree reasonably with the observed values. Also an outer-sphere self-exchange rate constant for $\text{Cr}_{\text{aq}}^{2+/3+}$ of $\sim 10^{-10} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C is deduced, which is considerably less than the upper limit estimated experimentally. The influence of the stereochemistry on the electron-transfer rate constants for (+) and (-)- $[\text{Co}(\text{sep})]^{2+}$ with (-)- $[\text{Co}(\text{diamsarH}_2)]^{5+}$ (diamsar is the 1,8-diamine of sar) was found to be small (<10%) in aqueous solution. The results in general support adiabatic behavior for the systems studied when they are coupled with the self-exchange rates and Marcus-Hush correlations of the low-spin-low-spin $[\text{Co}(\text{azacapt})]^{2+/3+}$ system (azacapt = 8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo[6.6.6]eicosane).

Introduction

Several papers¹⁻⁵ have discussed redox reactions in relation to the Marcus-Hush theories^{6,7} for outer-sphere electron transfer. These theories predict a simple relationship between the rate constant k_{12} for the redox reaction, k_{11} and k_{22} , the self-exchange rate constants for the reactants, and K_{12} , the equilibrium constant for the reaction

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (1)$$

$$\log f_{12} = \frac{(\log K_{12})^2}{4 \log (k_{11}k_{22}/Z^2)}$$

where the collision frequency is $Z \approx 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. The theories are based on the assumptions that the reactions are adiabatic and that the work terms for the self-exchange and cross-reactions are essentially the same. Furthermore, the reagents are supposed to be spherical structureless reactants and the motions of the inner coordination shells are assumed to be harmonic. The theories are essentially the same, and the predictions of the outer-sphere electron-transfer rate constants between 3+ and 2+ charged reactants frequently agree within a factor of 25. However, k_{obsd} is usually smaller than k_{calcd} .⁴ Several possibilities for the origin of the observed disagreements with the theory have been suggested such as noncancellation of work terms, anharmonic effects,⁴ or differences in the nature of the oxidants,⁵ and more data are needed to assess the problem areas.

The caged cobalt complexes, Co(III) ions encapsulated by hexaaza cryptand ligands (Figure 1),^{8,9} offer a new set of cobalt reactants. They are unusual in cobalt amine chemistry in being inert to ligand dissociation in both the Co(II) and Co(III) states in aqueous solution at 25 °C. This ensures their electron-transfer reactions with each other to be outer sphere. Furthermore, the tight packing of the ligands around the cobalt ion makes them nearly spherical and the similarity between the structures and charges of the different caged complexes ensures that the work terms for the self-exchange and cross-reactions will be similar. The complexes are therefore especially well suited for testing electron-transfer theory in an area that has hitherto appeared anomalous. In practice, the inert nature of the caged complexes in both oxidation states makes

it possible to measure the self-exchange rates simply and accurately and the redox potentials of some of the complexes are sufficiently different to allow cross electron transfers to be studied. This paper describes some of these reactions together with electron exchange between the cages and hexaaqua metal ion reductants and makes comparisons with other values in the literature.¹⁰

Experimental Section

All chemicals were analytical grade. Cary 118 and 16K spectrophotometers were used for the absorption spectra and kinetic runs, and optical rotations were measured with a Perkin-Elmer P 22 spectropolarimeter. Standard electrochemical measurements were performed with a three-electrode *iR*-compensated system with a Pt auxiliary electrode and PAR Model 170 electrochemistry system together with a dropping Hg electrode or a Beckman Pt or Au electrode vs. a saturated calomel electrode (SCE). A Radiometer P101 Pt electrode was used with a Radiometer Model 26 pH meter and a SCE reference electrode in a salt bridge containing 1.6 M NH_4NO_3 and 0.2 M NaNO_3 at pH 7. All oxygen-sensitive experiments were performed under an atmosphere of pure nitrogen or argon after the gases had been scrubbed with solutions of $\text{Cr}_{\text{aq}}^{2+}$.

Oxidizing Agents. The syntheses of the cobalt(III) cage complexes (Figure 1) will be described elsewhere.^{8,9} $[\text{Co}(\text{en})_3]\text{Cl}_3$ was prepared according to a published procedure¹¹ except that activated charcoal was added to the reaction. It was converted to the perchlorate salt by treating it with AgClO_4 . $[\text{Co}(\text{bpy})_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ¹² and $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ ¹³ were synthesized as previously described. All compounds were analyzed by standard microanalytical methods for Co, N, H, and C where appropriate to an accuracy $\leq 1\%$ of the theoretical values.

- Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545.
- Jacks, C. A.; Bennett, L. E. *Inorg. Chem.* **1974**, *13*, 2035.
- Linck, R. G. *Surv. Prog. Chem.* **1976**, *7*, 89.
- Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.
- Lavallee, C.; Lavallee, D. K.; Deutsch, E. A. *Inorg. Chem.* **1978**, *17*, 2217.
- Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21.
- Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- Creaser, I. I.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181; **1982**, *104*, 6016.
- Harrowfield, J. M.; Sargeson, A. M., to be submitted for publication. For a synopsis of this chemistry, see: Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23.
- First presented at the ACS/CSJ Chemical Congress: "Abstracts of Papers", 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979; American Chemical Society: Washington, DC, 1979; INOR 39.
- Work, J. B. *Inorg. Synth.* **1946**, *2*, 221.
- Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.
- Bjerrum, J.; McReynolds, J. P. *Inorg. Synth.* **1946**, *2*, 216.

* To whom correspondence should be addressed at The Australian National University.

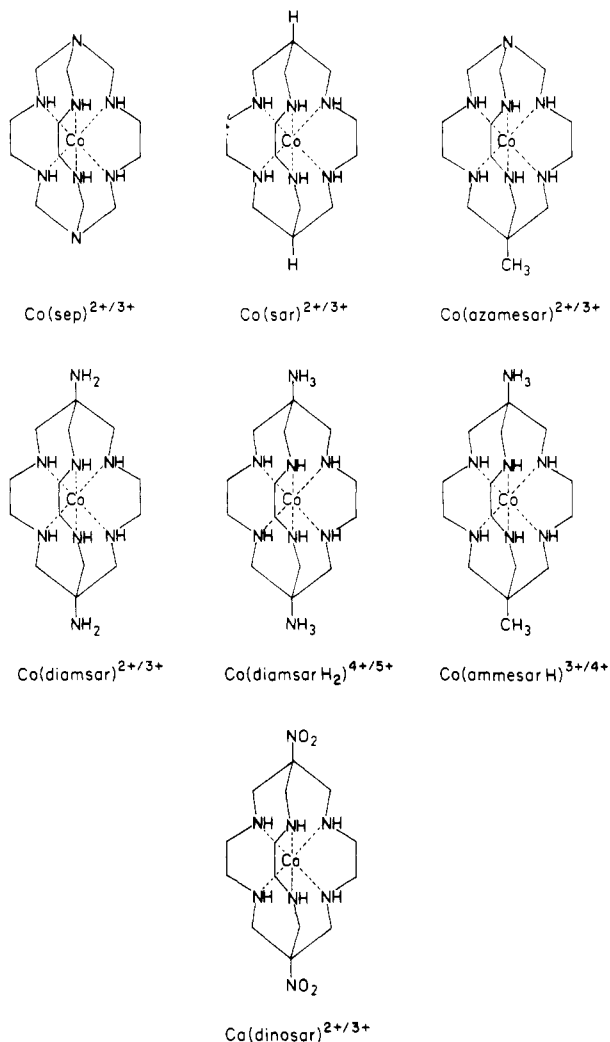


Figure 1. Structures of caged cobalt complexes: sep, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; sar, 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; azamesar, 1-methyl-3,6,8,10,13,16,19-heptaazabicyclo[6.6.6]eicosane; diamsar, 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; ammesar, 1-amino-8-methyl-1,3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; dinosar, 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane.

Reducing Agents. The Co(II) solutions were generated by reduction of the corresponding Co(III) complexes in water with zinc amalgam. A solution of the Co(III) salt of the appropriate concentration and the desired ionic strength was deoxygenated in a gas-scrubbing bottle for 30 min with Cr^{2+} -scrubbed nitrogen. Zinc amalgam was added, and reduction was carried out under the N_2 atmosphere until the complex was fully reduced and virtually colorless (at least 1 h). $\text{Cr}_{\text{aq}}^{2+}$ solutions were prepared from primary standard potassium dichromate by reducing it to $\text{Cr}_{\text{aq}}^{3+}$ with hydrogen peroxide in a known amount of perchloric acid¹⁴ followed by further reduction with zinc amalgam. The chromium concentration was determined by atomic absorption analysis. $\text{Eu}_{\text{aq}}^{2+}$ solutions were prepared by reducing dried Eu_2O_3 with zinc amalgam in perchloric acid. Its reducing capacity was determined by reaction with excess bromopentaamminecobalt(III)¹⁵ followed by ion-exchange separation of the generated $\text{Co}_{\text{aq}}^{2+}$, which was eluted and analyzed by atomic absorption. $\text{V}_{\text{aq}}^{2+}$ perchlorate solutions were prepared by reduction of vanadyl perchlorate¹⁶ (0.163 M VO^{2+} , 0.205 M H^+) with zinc amalgam. Solutions were used within 2 h of preparation to minimize oxidation of $\text{V}_{\text{aq}}^{2+}$ by perchloric acid. The total vanadium concentration was determined by atomic absorption, and total perchlorate concentration was determined from the vanadyl and perchlorate values. $\text{U}_{\text{aq}}^{3+}$ perchlorate solutions were

prepared by dissolving a known amount of $\text{K}_2\text{U}_2\text{O}_7$ in perchloric acid and reducing it with liquid zinc amalgam. It was analyzed by its reaction with bromopentaamminecobalt(III).¹⁷

Kinetic Measurements. The rates of self-exchange were measured with a Perkin-Elmer P22 spectropolarimeter as described earlier.⁸ The rate for the $[\text{Co}(\text{sar})]^{2+/3+}$ self-exchange was recorded in neutral aqueous solution while that of $[\text{Co}(\text{diamsar})]^{2+/3+}$ was measured in a *N*-ethylmorpholine/ HClO_4 buffer (pH 7.5, 0.05 M) to ensure complete deprotonation of the amine groups. The self-exchange rate for $[\text{Co}(\text{diamsarH}_2)]^{4+/5+}$ was measured in 0.1 M HClO_4 to ensure complete protonation of the complex ($\text{p}K_a \approx 3$ for $[\text{Co}(\text{diamsarH}_2)]^{5+}$).¹⁸ The wavelengths used were as follows: $[\text{Co}(\text{sar})]^{2+/3+}$, 500 nm; $[\text{Co}(\text{diamsar})]^{2+/3+}$ and $[\text{Co}(\text{diamsarH}_2)]^{4+/5+}$, 520 nm. The electron-exchange cross-reaction rates were measured spectrophotometrically with use of one reactant in ≥ 10 -fold excess to ensure pseudo-first-order conditions. After thorough deoxygenation of solutions and apparatus the reactants were mixed in a stopped-flow apparatus or by a syringe technique and the change in absorbance vs. time was recorded at the following wavelengths: $[\text{Co}(\text{sep})]^{3+}$ - $[\text{Co}(\text{sar})]^{2+}$, 280 nm; $[\text{Co}(\text{diamsarH}_2)]^{5+}$ - $[\text{Co}(\text{sep})]^{2+}$, 270 nm; $[\text{Co}(\text{azamesar})]^{3+}$ - $[\text{Co}(\text{sar})]^{2+}$, 280 nm; $[\text{Co}(\text{en})_3]^{3+}$ - $[\text{Co}(\text{sar})]^{2+}$, 290 nm; $[\text{Co}(\text{bpy})_3]^{3+}$ - $[\text{Co}(\text{diamsarH}_2)]^{4+}$, 325–335 nm; $[\text{Co}(\text{sep})]^{3+}$ - $\text{U}_{\text{aq}}^{3+}$, 350 nm; $\text{Eu}_{\text{aq}}^{2+}$, $\text{Cr}_{\text{aq}}^{2+}$, and $\text{V}_{\text{aq}}^{2+}$ reactions at 470–475 nm; $[\text{Co}(\text{NH}_3)_6]^{3+}$ - $[\text{Co}(\text{sar})]^{2+}$, 275 nm. All cross-reactions were measured in slightly acid solutions to avoid hydrolysis of reactants or precipitation of zinc hydroxide.

Results

The Co(II) states of the caged complexes were obtained quantitatively with amalgamated zinc in neutral aqueous solution. The solutions of the Co(II) ions were stable for at least 3 days under a N_2 atmosphere. The exception was $[\text{Co}(\text{dinosar})]^{3+}$, where prolonged treatment with Zn led to reduction of the nitro groups and the production of $[\text{Co}(\text{diamsar})]^{2+}$. The aza-capped Co(II) cages decompose in acid solution at a rate that is first order in $[\text{H}^+]$ concentration,⁸ but the other Co(II) cages are stable in acid for at least 24 h.

Reduction potentials were obtained from a variety of methods including dc¹⁹ and ac polarography, cyclic voltammetry using a growing Hg drop, a stationary Au electrode, or a rotating Pt electrode, and potentiometry using a Pt-spade electrode (Table I). For the same technique, the measured potentials were the same in 0.1 and 0.2 M NaClO_4 but became slightly more negative in 0.2 M NaCl. The addition of 10^{-3} M HClO_4 to the $[\text{Co}(\text{sep})]^{2+/3+}$ couple in 0.2 M NaClO_4 did not alter the potential from that obtained in neutral solution. However, different techniques gave some variation in reduction potentials. Adsorption on the Hg surface and difficulties in obtaining completely clean Pt and Au electrodes probably contribute to these differences. The cyclic voltammetry confirms that the electron transfers between the Co(II) and Co(III) cages are close to being reversible with the peak to peak separations varying from 70 to 90 mV for sweep rates of 100–200 mV/s. The $[\text{Co}(\text{en})_3]^{2+/3+}$ couple showed quasi-reversible behavior on Hg (90 mV peak separation) and Au (120 mV peak separation) in 0.1–0.2 M NaClO_4 , but it was irreversible on Pt. Although the redox potentials differed with different techniques (≤ 50 mV), the differences in potentials for any two complexes remained essentially constant when measured by the same technique. For example, the potential differences for $[\text{Co}(\text{sar})]^{2+/3+}$ and $[\text{Co}(\text{en})_3]^{2+/3+}$ in 0.1–0.2 M NaClO_4 were 0.25 V by ac polarography, 0.27 V by the dc methods, and 0.25 V by cyclic voltammetry on Au. In the two instances where the thermodynamic values have been measured, $[\text{Co}(\text{sep})]^{3+}$ and $[\text{Co}(\text{diamsarH}_2)]^{5+}$, agreement between the equilibrium potentials and ac polarography and cyclic voltammetry on Hg was observed but the other methods did not differ by more than ± 25 mV.

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

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

(16) Rossotti, F. J. C.; Rossotti, H. S. *Acta Chem. Scand.* **1955**, *9*, 1177.

(17) Wang, R. T.; Espenson, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 380.

(18) Lawson, P. J., unpublished result.

(19) Lay, P. A. Ph.D. Thesis, The Australian National University, 1981.

Table I. Redox Potentials, E (V vs. NHE), Obtained by Different Techniques in Different Media at 25 °C

complex	medium	technique ^a	E
[Co(sep)] ^{2+/3+}	0.1–0.2 M NaClO ₄	pol, ac	–0.28
		pol, dc	–0.26 ¹⁹
		CV, Au	–0.30
		CV, Pt	–0.30
		CV, Hg	–0.29
	pnt	–0.28	
	0.2 M NaCl	pol, ac	–0.32
		CV, Pt	–0.32
		CV, Hg	–0.33
		pnt	–0.31
[Co(sar)] ^{2+/3+}	0.1–0.2 M NaClO ₄	pol, ac	–0.43
		pol, dc	–0.40 ¹⁹
		CV, Au	–0.43
		CV, Pt	–0.45
		CV, Pt	–0.45
0.2 M NaCl	pol, ac	–0.44	
	CV, Au	–0.45	
	CV, Pt	–0.46	
[Co(en) ₃] ^{2+/3+}	0.1–0.2 M NaClO ₄	pol, ac	–0.18
		pol, dc	–0.13 ¹⁹
		CV, Au	–0.18
		CV, Hg	–0.16
		CV, Hg	–0.16
0.2 M NaCl	pol, ac	–0.19	
	pol, ac	–0.19	
[Co(diamsarH ₂)] ^{4+/5+}	0.1 M NaClO ₄ + 0.1 M HClO ₄	pol, ac	+0.02
		pol, dc	+0.06 ¹⁹
		CV, Pt	+0.03
		CV, Hg	+0.02
		pnt	+0.04
0.1 M NaCl + 0.1 M HCl	CV, Pt	–0.01	
	pnt	0.00	
[Co(azamesar)] ^{2+/3+}	0.1 M NaClO ₄	pol, dc	–0.34 ¹⁹
		CV, Pt	–0.36
[Co(ammesarH)] ^{3+/4+}	0.05 M HClO ₄ + 0.05 M NaClO ₄	pol, dc	–0.19 ¹⁹
[Co(diamsar)] ^{2+/3+}	0.1 M NaClO ₄	pol, dc	–0.30 ¹⁹
		CV, Pt	–0.32

^a Abbreviations: pol, polarography; CV, cyclic voltammetry; pnt, potentiometry.

For the [Co(dinosar)]³⁺ complex the substituent nitro groups were reduced irreversibly to the NH₂ groups at potentials close to that of the Co(II)/Co(III) couple.

The self-exchange rates of the caged complexes were determined by measuring the change of rotation of solutions containing the chiral isomers Λ -[Co(cage)]³⁺ and Δ -[Co(cage)]²⁺ or vice versa as described for [Co(sep)]^{2+/3+}.⁸ The experimental data are shown in Table II, and the second-order rate constants are summarized in Table III, together with self-exchange rate constants and redox potentials of the other reagents where relevant. Reactions were studied in perchlorate media, solubilities permitting. The Co(II) cage complexes were unusually much less soluble as the perchlorate salts compared to the Co(III) complexes. In the instances where perchlorate

could not be used, sodium chloride was substituted to provide the desired ionic strength. The self-exchange rate for [Co(sep)]^{2+/3+} was studied in both media, giving the same rate.⁸ These results indicate that the chloride ion has no catalyzing effect on the self-exchange rates of the [Co(cage)]^{2+/3+} system at least in the ionic strength range employed. The common rate law for the self-exchange reactions was

$$\frac{-d \ln(\alpha - \alpha_0)}{dt} = k_{et}[\text{Co}]_{\text{total}} = k_{\text{obsd}}$$

Because of the difficulty in preparing a solution of [Co(dinosar)]²⁺ without reducing the nitro groups, the self-exchange rate of this couple was not measured. The rate constants for the cages with the same charge are the same within 1 order of magnitude while the protonated complex [Co(diamsarH₂)]^{4+/5+} shows a somewhat smaller rate constant.

The variation in the redox potentials for the caged cobalt complexes made it possible to study redox reactions involving the reduced form of one cage with an oxidized form of another. These reactions were followed spectrophotometrically in the UV region for those instances where the spectral differences were favorable. The absorption spectra of the hexamine cage complexes are very similar, the only significant differences being in the intense charge-transfer bands. The observed changes in absorbance (A) during the reactions were comparatively small (0.1 A) for a relatively high total absorbance ((0.5–1.5) A). Because of the large absorbances, low concentrations of the reactants (10^{–4}–10^{–5} M) were necessary and this made the Co(II) concentration very sensitive to traces of oxygen (k for [Co(sep)]²⁺ + O₂ is 43 M^{–1} s^{–1} at 25 °C⁸). Although every attempt was made to exclude oxygen from the solutions as well as from the apparatus, in some cases an initial fast reaction was observed, which was attributed to traces of oxygen, and only the latter part (>90% of the total absorbance change) of the curve was used in calculating the rate constant (Table IV).

Various other reagents were used as oxidants or reductants for the cage complexes, including [Co(NH₃)₆]³⁺, [Co(bpy)₃]³⁺, Cr_{aq}²⁺, Eu_{aq}²⁺, V_{aq}²⁺, and U_{aq}³⁺. While most reactions were studied at an ionic strength (μ) of 0.2 M, the Cr_{aq}²⁺ reductions were performed at $\mu = 0.5$ to enable the use of higher concentrations of Cr_{aq}²⁺ in order to give reasonably rapid rates. The solubility problems were dealt with in the same way as for the self-exchange studies. The reaction between [Co(diamsarH₂)]⁵⁺ and [Co(sep)]²⁺ was studied in both perchlorate and chloride media and showed a slight enhancement (~2-fold) in the presence of chloride ions. Ion pairing between the 5+ cage and chloride ion may account for the difference, but it is clearly not important at this ionic strength in a relative sense.

For all the net oxidation–reduction reactions studied the rate law observed was

$$\frac{-d[\text{ox}]}{dt} = k_{12}[\text{ox}][\text{red}]$$

Table II. Self-Exchange Rates for Co(II)–Co(III) Cages ($\mu = 0.2$ M, 25 °C)

reacn	medium	10 ³ × [Co(III)], M	10 ³ × [Co(II)], M	k_{obsd} , s ^{–1} ^b	k_{ex} , M ^{–1} s ^{–1}
[Co(sar)] ^{2+/3+}	NaCl	2.25	2.50	5.50 × 10 ^{–3} (2)	1.9
		2.94	2.99	5.63 × 10 ^{–3} (3)	2.3
		1.65	2.08	4.03 × 10 ^{–3} (4)	2.2
[Co(diamsar)] ^{2+/3+}	LiClO ₄ , pH 7.5 ^a	2.29	1.59	0.976 × 10 ^{–3} (2)	0.50
		2.31	2.17	1.13 × 10 ^{–3} (2)	0.50
[Co(diamsarH ₂)] ^{4+/5+}	LiClO ₄ , pH 1.0	2.18	1.44	4.81 × 10 ^{–5} (1)	0.026
		2.29	1.93	4.28 × 10 ^{–5} (1)	0.020
		2.31	2.28	5.78 × 10 ^{–5} (1)	0.025

^a *N*-ethylmorpholine-HClO₄ buffer, 0.05 M. ^b Numbers in parentheses indicate numbers of determinations.

Table III. Rate Constants for Self-Exchange Reactions at 25 °C and Redox Potentials

reagents	conditions for k_{ex}	$k_{ex}, M^{-1} s^{-1}$	E, V	conditions for E
[Co(sar)] ^{2+/3+}	0.2 M NaCl	2.1 ± 0.2	<i>a</i>	
[Co(diarnsar)] ^{2+/3+}	0.2 M LiClO ₄ , pH 7.5	0.50 ± 0.01	<i>a</i>	
[Co(diarnsarH ₂)] ^{4+/5+}	0.2 M LiClO ₄ , pH 1.0	0.024 ± 0.003	<i>a</i>	
[Co(sep)] ^{2+/3+}	0.2 M NaCl or NaClO ₄	5.1 ± 0.3 ^b	<i>a</i>	
	0.5 M NaCl	11.5 ^b		
[Co(azamesar)] ^{2+/3+}	0.2 M NaCl	2.9 ^b	<i>a</i>	
[Co(en) ₃] ^{2+/3+}	0.2 M KCl	3.4 × 10 ^{-5 c}	<i>a</i>	
[Co(NH ₃) ₆] ^{2+/3+}		~10 ^{-7 d}	+0.058 ^e	1 M NH ₄ NO ₃
[Co(bpy) ₃] ^{2+/3+}	0.1 M KNO ₃	~17 ^f	+0.37 ^g	satd KClO ₄
[Co(phen) ₃] ^{2+/3+}	0.1 M KNO ₃	40 ^f	+0.42 ^g	satd KClO ₄
Cr _{aq} ^{2+/3+}	1 M HClO ₄	<2 × 10 ^{-5 h}	-0.41 ^h	μ = 0
Eu _{aq} ^{2+/3+}	2 M NaClO ₄ -HClO ₄	<1 × 10 ^{-4 i}	-0.38 ⁱ	1 M NaClO ₄
V _{aq} ^{2+/3+}	2 M NaClO ₄ -HClO ₄	1.0 × 10 ^{-2 j}	-0.255 ^k	μ = 0
U _{aq} ^{3+/4+}			-0.63 ^k	μ = 0

^a See Table I. ^b Reference 8. ^c Reference 23a. ^d Reference 22. ^e Reference 26. ^f Neumann, H. M., quoted in: Farina, R.; Wilkins, R. *G. Inorg. Chem.* 1968, 7, 514. ^g Paglia, E.; Sironi, C. *Gazz. Chim. Ital.* 1957, 87, 1125. ^h Anderson, A.; Bonner, H. A. *J. Am. Chem. Soc.* 1954, 76, 3826. ⁱ Meier, D. J.; Garner, L. S. *J. Phys. Chem.* 1952, 56, 853. ^j Krishnamurty, K. V.; Wahl, A. C. *J. Am. Chem. Soc.* 1958, 80, 5921. ^k Latimer, W. M. "Oxidation Potentials"; Prentice-Hall: Englewood Cliffs, NJ, 1952. ^l Yee, E. L.; Care, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* 1979, 101, 1131.

Table IV. Rate Constants for Some Outer-Sphere Electron-Transfer Reactions (25 °C, μ = 0.2 M Unless Otherwise Stated)

reactants	medium ^e	$k_{12}, M^{-1} s^{-1}$	$k_{12}^{calcd}, M^{-1} s^{-1}$ ^a	$k_{12}^{calcd}, M^{-1} s^{-1}$ ^b
[Co(sar)] ²⁺ -[Co(sep)] ³⁺	NaCl, [H ⁺] = 10 ⁻³	20 ± 1	32-46	32-46
[Co(sep)] ²⁺ -[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , [H ⁺] = 0.1	145 ± 12	88-148	180-300
	NaCl, [H ⁺] = 0.1	262 ± 12		
[Co(sar)] ²⁺ -[Co(azamesar)] ³⁺	NaClO ₄ , [H ⁺] = 10 ⁻³	10 ± 1	8-14	8-14
[Co(sar)] ²⁺ -[Co(en) ₃] ³⁺	NaClO ₄ , [H ⁺] = 10 ⁻³ -10 ⁻¹	1.1 ± 0.2	0.9-1.3	0.9-1.3
[Co(sar)] ²⁺ -[Co(NH ₃) ₆] ³⁺	NaCl, [H ⁺] = 0.1	2.3 ± 0.1	~1	4.8
[Co(diarnsarH ₂)] ⁴⁺ -[Co(bpy) ₃] ³⁺	NaClO ₄ , [H ⁺] = 0.1	33 ± 0.1	~200	10 ³
Cr _{aq} ²⁺ -[Co(sep)] ³⁺	NaClO ₄ , μ = 0.5, [H ⁺] = 0.05-0.1	(8.7 ± 0.1) × 10 ⁻⁴	≤0.2	≤0.16
Cr _{aq} ²⁺ -[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , μ = 0.5, [H ⁺] = 0.05-0.1	(8.1 ± 0.2) × 10 ⁻³	≤4	≤6.0
Cr _{aq} ²⁺ -[Co(ammesarH)] ⁴⁺	NaClO ₄ , μ = 0.5, [H ⁺] = 0.05-0.1	(4.9 ± 0.3) × 10 ⁻⁴	≤0.09 ^c	≤0.12
Cr _{aq} ²⁺ -[Co(azamesar)] ³⁺	NaClO ₄ , μ = 0.5, [H ⁺] = 0.05-0.1	1.4 × 10 ⁻⁴	≤0.03	≤0.027
Eu _{aq} ²⁺ -[Co(sep)] ³⁺	NaClO ₄ , [H ⁺] = 0.1-0.16	0.12 ± 0.04	≤0.2	≤0.075
Eu _{aq} ²⁺ -[Co(azamesar)] ³⁺	NaClO ₄ , [H ⁺] = 0.1	0.015 ± 0.002	≤0.04	≤0.015
Eu _{aq} ²⁺ -[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , [H ⁺] = 0.02-0.1	0.13 ± 0.01	≤5	≤2.3
Eu _{aq} ²⁺ -[Co(ammesarH)] ⁴⁺	NaClO ₄ , [H ⁺] = 0.1	0.03	≤0.1 ^c	≤0.06
V _{aq} ²⁺ -[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , [H ⁺] = 0.05-0.1	0.40 ± 0.1	5	2.4
V _{aq} ²⁺ -[Co(NH ₃) ₆] ³⁺	NaClO ₄ , [H ⁺] = 0.1, μ = 1.0	1 × 10 ^{-2 d}	~10 ⁻²	4.7 × 10 ⁻³ , 2.0 × 10 ⁻³ (μ = 2.0)
U _{aq} ³⁺ -[Co(sep)] ³⁺	LiClO ₄ , [H ⁺] = 0.05-0.1	15.8 ± 0.6		
(+)-[Co(sep)] ²⁺ -(-)-[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , [H ⁺] = 0.1	140 ± 1		
(-)-[Co(sep)] ²⁺ -(-)-[Co(diarnsarH ₂)] ⁵⁺	NaClO ₄ , [H ⁺] = 0.1	156 ± 3		

^a Calculated from eq 1 with self-exchange data and potentials obtained from identical techniques in Table I. ^b Calculated from eq 2. ^c Self-exchange rate for [Co(ammesarH)]^{3+/4+} is estimated to be 0.1 M⁻¹ s⁻¹. ^d Reference 1. ^e All concentrations given in M.

No dependence of rate on hydrogen ion concentration was observed in any of the reactions except for the protonated and unprotonated amine systems. Where all self-exchange rates were known, the cross-electron-exchange rates were measured and calculated by using the Marcus-Hush correlation, and these data are shown in Table IV, where the rate constants are summarized.

The present study shows that although different electrochemical techniques give slightly different redox potentials (Table I) for a couple, the differences between the different couples are essentially constant for a single technique. As the equilibrium constant K_{12} in the Marcus-Hush relation is calculated from potential differences between two couples, it becomes independent of the absolute redox potentials as long as they are measured with use of the same technique and medium. Variations in technique and media can lead to fairly substantial differences in the calculated rate constants of the cross-reactions or self-exchange.

Some problems were encountered in measuring the rate of the reaction between [Co(sar)]²⁺ and [Co(NH₃)₆]³⁺. In the NaCl-HCl media the kinetics were not reproducible on occasion unless a small amount of disodium ethylenediamine-

tetraacetate (Na₂edta) was added. Attempts were made to measure the rates in the HSO₃CF₃-CF₃SO₃Na media in order to investigate the effect of different anions on the redox potentials of [Co(NH₃)₆]^{2+/3+}. These were also frustrated by irreproducible results even after the addition of edta. Presumably, the reaction is catalyzed by some metal ion impurity in the reaction mixture present in very small concentrations but extensive purification of all reagents did not improve the results.

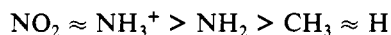
A study of the [Co(sep)]²⁺-[Co(NH₃)₆]³⁺ reaction revealed a similar problem, but this reaction was further complicated by the decomposition of [Co(sep)]²⁺ in the acid solution, and in these respects our studies presumably differ from those reported by Endicott et al.²⁰

Discussion

The cobalt(III) hexaamine type cage complexes exhibit a range of reversible reduction potentials (+0.06 to -0.40 V)

- (20) Kumar, K.; Durham, B.; Endicott, J. F. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, DC, 1981; INOR 84; *Inorg. Chem.* 1982, 21, 2437.

(Table I) that depend upon the substituents on the macrocyclic ligand. The ion $[\text{Co}(\text{diansarH}_2)]^{5+}$, which is protonated on both pendant amine groups, is the most readily reduced complex. It has a reduction potential similar to that of $[\text{Co}(\text{dinosar})]^{3+}$ ($E = +0.04$ V),¹⁹ which is not inconsistent with the similar inductive effects that NO_2^- and NH_3^+ exert in organic chemistry. The $[\text{Co}(\text{sep})]^{3+}$ ion is more easily reduced than the structurally similar $[\text{Co}(\text{sar})]^{3+}$ ion. Presumably the more electronegative aza caps as compared to the CH caps on the sar complex favor reduction of the sepulchrate complex. The order of the reduction potentials indicates the following trend for carbon substituents in enhancing reduction:



which parallels the electron-withdrawing capabilities of these groups.²¹

The rate constants (Table III) for the self-exchange reaction between the +2 and +3 oxidation states of the cage complexes measured in this work are similar to those measured for $[\text{Co}(\text{sep})]^{2+/3+}$.⁸ The somewhat lower rate measured for the $[\text{Co}(\text{diansarH}_2)]^{4+/5+}$ couple could be ascribed to differences in the work terms in bringing the ions together, but the effect is not large. The self-exchange rates are extremely rapid compared to those determined for $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ ($\sim 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$, 40 °C, $\mu = 2.5$)²² and $[\text{Co}(\text{en})_3]^{2+/3+}$ ($3.4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, 25 °C, $\mu = 0.23^a$ or $7.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, 25 °C, $\mu = 1.0^{23b}$), despite the insulating saturated organic cage and despite the electronic similarities between the cage species and the simpler hexamine complexes. These similarities extend over bond lengths, ligand field spectra, and magnetic properties and have been detailed in an earlier publication.⁸ They will not be reiterated here other than to state the conclusion that the spin states in relation to the ligand fields in the systems were nearly identical and differences in this factor therefore could not account for the rate differences.

Explanations for the discrepancies in rate for such similar complexes have been sought, but no simple explanation has been found yet. Some of the possible explanations for the rate differences are now discussed. One of the possible reasons for the unusually rapid self-exchange rate of the $[\text{Co}(\text{sep})]^{2+/3+}$ system was that the accessible unshared electron pairs on the tertiary N atoms of the caps allowed the ions to communicate more directly. However, it can be seen now that the C-H cap in the $[\text{Co}(\text{sar})]^{2+/3+}$ system does not seriously impede the exchange and of course the ligand does not contain unshared electron pairs other than those in the nonbonding d orbitals of the metal ion. Clearly, the rapid self-exchange rate appears to be a property of this type of cage.

Another explanation was sought in the differences in hydration of the complexes and the activated complex. The larger cage complexes exchange more rapidly than the smaller $[\text{Co}(\text{en})_3]^{2+/3+}$ and $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ ions (in that order). This could reflect the more extensive hydration of the smaller ions and a correspondingly larger reorganization of their hydration spheres in the activated complexes. It could be argued that the effect should then be important in the self-exchange rates for the very bulky $[\text{tris}(\text{trans-1,2-cyclohexanediamine})\text{cobalt(III)}]^{2+/3+}$ system. Although the self-exchange rate for this system has not been measured directly, it has been shown that the rates of reduction of the $[\text{Co}(\text{chxn})_3]^{3+}$ and

$[\text{Co}(\text{en})_3]^{3+}$ ions by $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^+$, $[\text{Cr}(\text{bpy})_3]^{2+}$, or $\text{V}_{\text{aq}}^{2+}$ indicate that their self-exchange rate constants are not significantly different.²⁴ Beattie et al.²⁴ have asserted that this could arise through communication along the C_3 axes for the two partners in each system. The distance of closest approach along this axis would be similar for the pairs of ions. At present, we are testing this explanation by synthesizing the cyclohexanediamine cages.²⁵

A further possibility was that the cages were anomalous and $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ and $[\text{Co}(\text{en})_3]^{2+/3+}$ behaved normally or vice versa. In order to look at this aspect, the cross-reactions with various cages and other ions were examined and it is now considered in some detail.

Cross-Reactions between Cobalt Cages and Other Cobalt Complexes. The cross-electron-transfer rate constants measured for three sets of cage complexes span approximately a factor of 20. They showed excellent agreement with rate constants calculated from the Marcus-Hush relation (Table IV). The agreement is within a factor of 2-3 and is better than has been found previously in such cross correlations. One advantage of the present system is the fact that redox potentials, self-exchange rates, and cross-electron-exchange rates have all been measured under similar or identical conditions. For many other systems these data have often been obtained at quite different ionic strengths and/or acidities. Some, if not all, are dependent upon both. For example, the reduction potential for $[\text{Co}(\text{en})_3]^{2+/3+}$ in 0.1 M NaClO_4 has been found to be -0.13 V (25 °C)¹⁹ by the polarographic dc method while it is -0.26 V in 1.0 M KCl-en^{26} (30 °C) measured by potentiometric titrations; the temperature dependence of the couple is $<0.01 \text{ V}/10^\circ \text{C}$. The difference corresponds to a variation in calculated k_{12} of a factor of 10 and for k_{11} a factor of 100. Relatively few self-exchange rates are known with accuracy. Often they are given as upper limits because of the difficulties in measuring them. The method used for the present systems is accurate, and more reliability can therefore be placed on the data used for calculating the rate constants. However, the largest contributing factor to the agreement may lie in the nature of the complexes themselves. There cannot be any doubt that the reactions are outer sphere. The inertness of both the Co(II) and Co(III) complexes to substitution arises, especially for Co(II), from the close packing of the cage atoms. This packing appears to resist any change in coordination number for the cages. Also the complexes approach the spherical structureless nature required by the theory and the similarity between the complexes means that the work terms for the self-exchange and cross-reactions should be similar. Usually, the Marcus-Hush theory has been tested with reactions between 2+ and 3+ ions. In one instance of the present series, an ion $[\text{Co}(\text{diansarH}_2)]^{5+}$ has a 5+ charge and the measured rate is still largely in agreement with that predicted by the theory. The influence of work terms on the calculated rate constants were determined by using the extended equation²⁷

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \quad (2)$$

where

- (21) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1. Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Anderson, K. K.; Davis, G. T. *J. Am. Chem. Soc.* **1963**, *85*, 709.
 (22) Geselowitz, D. A.; Hammershoi, A.; Taube, H. *Inorg. Chem.*, in press.
 (23) (a) Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* **1961**, *65*, 1892. (b) Lewis, W. B.; Coryell, C. D.; Irvine, J. W. *J. Chem. Soc.* **1949**, 386 (Supplementary Issue 2).

- (24) Beattie, J. K.; Binstead, R. A.; Broccardo, M. *Inorg. Chem.* **1978**, *17*, 1822.
 (25) Geue, R. J.; McCarthy, M. G.; Sargeson, A. M., to be submitted for publication.
 (26) Bjerrum, J. "Metal Ammine Formation in Aqueous Solution"; P. Haase & Son: Copenhagen, 1941; p 230.
 (27) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 467.

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4 \left[\ln \frac{k_{11}k_{22}}{A_{11}A_{22}} + \frac{(w_{11} + w_{22})}{RT} \right]}$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT]$$

$$A_{11} = (4\pi N r^2 \nu_n \delta_r / 1000)_{11}$$

$$A_{22} = (4\pi N r^2 \nu_n \delta_r / 1000)_{22}$$

$$w(r) = \frac{z_1 z_2 e^2}{D_s r (1 + \beta r \mu^{1/2})}$$

Here, $\beta = (8\pi N e^2 / 1000 D_s k T)^{1/2}$, z_1 and z_2 are the charges on the two reactants, r is the sum of the radii of the two reactants, D_s is the static dielectric constant for the medium, and μ is the ionic strength. The data are summarized in the last column of Table IV. The details of the calculations are given in the supplementary material. The implication in these results, coupled with the relatively small variation in the self-exchange rates of the cages, is that the noncancellation of work terms, arising from bringing the highly charged ions together, is not a large factor in aqueous solution at $\mu = 0.2$ M. The work terms may be much more significant in much lower ionic strengths but such a study would require very dilute solutions of the complexes and presumably the use of ^{60}Co tracer methods.

The redox rate constants found for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Co}(\text{sar})]^{2+}$ and for $[\text{Co}(\text{bpy})_3]^{3+}$ and $[\text{Co}(\text{diamsarH}_2)]^{4+}$ also agree with the values calculated from the theory within the accepted limits. The agreement for the $[\text{Co}(\text{NH}_3)_6]^{3+}$ - $[\text{Co}(\text{sar})]^{2+}$ system is also good. Independently, Geselowitz and Taube²² and the present authors had come to recognize that the rate constant for the $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ self-exchange obtained by the radio tracer technique ($<10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ at 65 °C, $\mu = 1.0 \text{ M}$)²⁸ was not correct, and using the data from the present study, $E = 0.058 \text{ V}$,²⁹ and the Marcus-Hush correlations, we had concluded that the rate constant should be $\sim 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. Geselowitz, Hammershøi, and Taube have remeasured the self-exchange rate for $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ using an elegant ^{15}N NMR method. They conclude the rate constant is $\sim 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C.²² There may be some difficulty with E for $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ also since the equilibrium constant K_6 for $[\text{Co}(\text{NH}_3)_6]^{2+}$ is not well-defined³⁰ and was determined under very different conditions from those used in the cross-exchange reactions. Attempts to determine the redox potential for $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ in 0.1 M NaClO_4 by rapid cyclic voltammetry with a dropping mercury electrode revealed irreversible electrochemical behavior on a seconds to subseconds time scale.¹⁹ An irreversible reduction was observed at $E = -0.02 \text{ V}$ (vs. NHE)¹⁹ by dc polarography. Both this value and the value of $E = +0.058 \text{ V}$ ²⁹ were used in our Marcus-Hush correlations to give values of 2×10^{-6} and $1 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ for the self-exchange reaction of $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$. From the reaction between $\text{V}_{\text{aq}}^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ values of 1×10^{-6} and $9 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ are respectively deduced. Which E value is the more accurate to use in the present instance is difficult to assess, and we are led to conclude that k_{22} for $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ is in the range of 10^{-8} - $10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $\mu = 0.2$, consistent with the new value measured.²² Given a value of $10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C for the $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ self-exchange rate constant, the calculated and observed rates for $[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{sar})]^{2+}$ are in good agreement (Table IV).

The results in Table IV appear to indicate, after the anomalous data are accounted for, that the cages, $[\text{Co}(\text{en})_3]^{2+/3+}$, and $[\text{Co}(\text{NH}_3)_6]^{2+/3+}$ fit the Marcus-Hush theoretical framework. In other words, the cobalt(II)/cobalt(III) hexaamine chemistry is not exceptional and the electron transfers are adiabatic in the systems we have examined or the degree of nonadiabaticity in the self-exchange rates is carried over into the Marcus-Hush correlations.

Reductions with $\text{Cr}_{\text{aq}}^{2+}$ Ion. The rates for electron transfer between the Co(III) cage complexes and $\text{Cr}_{\text{aq}}^{2+}$ ion (Table IV) are all slow and resemble the rates measured for other saturated hexaamine complexes which react by an outer-sphere mechanism. Although unshared electron pairs are available to coordinate the reductant on the sep and azamesar complexes, the magnitudes of the rate constants for the two complexes with these ligands are much smaller than expected for an inner-sphere mechanism.³ The product spectra were also characteristic of the Co(II) cage complexes rather than a $\text{Cr}_{\text{aq}}^{3+}$ -Co(cage)²⁺ binuclear species, and the rates showed no dependence upon acid concentration from 0.05 to 0.10 M H^+ , which might be the case if $\text{Cr}_{\text{aq}}^{2+}$ had to compete with a proton for an unshared pair of electrons. Furthermore, the ratios of rate constants for the $\text{Cr}_{\text{aq}}^{2+}$ and $\text{Eu}_{\text{aq}}^{2+}$ reductions are consistent with an outer-sphere mechanism for the cage complexes.³ In Table IV the observed rate constants for the $\text{Cr}_{\text{aq}}^{2+}$ reductions are compared to the theoretical values calculated from the Marcus-Hush relation. The calculated rate constants are much larger than the experimental values, even if one allows for the higher ionic strength used in estimating the upper limit for the $\text{Cr}_{\text{aq}}^{2+/3+}$ exchange rate.³¹ If the Marcus-Hush relation is used to calculate the self-exchange rate constant from the reactions with the cages, a value of 10^{-10} - $10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C is obtained (Table V), which is considerably less than the experimental upper limit,³¹ $\leq 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. The fairly constant value spans a set of log K_{12} values from ~ 1 to 8. If, however, the self-exchange rate is calculated from the reaction with $[\text{Co}(\text{en})_3]^{3+}$,¹ a larger value of $8 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ is obtained. log K_{12} for this reaction is 4.8, well within the above-mentioned range. From the reaction with $[\text{Co}(\text{phen})_3]^{3+}$ a value of $5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$ arises with a value of log $K_{12} = 13.2$. This unusually low value may be ascribed to the large driving force as previously suggested,⁴ but the value of $8 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ does not fit either set of data. The implication is that either the Marcus-Hush relation does not adequately describe the $\text{Cr}_{\text{aq}}^{2+}$ reactions or that the measured self-exchange rate for $\text{Cr}_{\text{aq}}^{2+/3+}$ is overestimated. The possibility that the theory does not fit the experimental data for the $\text{Cr}_{\text{aq}}^{2+/3+}$ exchange rate has been alluded to previously⁴ and discussed in terms of nonadiabaticity or anharmonic effects. However, the fairly consistent values in the present calculations suggest that the theory holds up for the $\text{Cr}_{\text{aq}}^{2+/3+}$ reactions as long as the driving force is not too large and that the estimated upper limit for self-exchange rate is much greater than the real outer-sphere rate.

Reductions with $\text{Eu}_{\text{aq}}^{2+}$ Ion. The similarity of the rate constants for reduction of the cage complexes by $\text{Eu}_{\text{aq}}^{2+}$, the similarity to the $\text{Cr}_{\text{aq}}^{2+}$ reductions, and the absence of suitable binding sites on some of the cage complexes all imply outer-sphere electron-transfer reactions. Also, if the ratios of rates for reduction by $\text{Cr}_{\text{aq}}^{2+}$ and $\text{Eu}_{\text{aq}}^{2+}$ ion are considered, the cages show values similar to those for well-defined outer-sphere reactions involving Co(III) amine complexes.³ As Gould³² has pointed out, these similarities do not establish the mechanism but, along with the structural considerations, the inertness of the ligand-exchange reaction, and the lack of metal ion binding sites, they do imply outer-sphere electron-transfer chemistry.

(28) Stranks, D. R. *Discuss. Faraday Soc.* **1960**, *29*, 73.

(29) Reference 26, p 250.

(30) Reference 26, p 188.

(31) Anderson, A.; Bonner, N. A. *J. Am. Chem. Soc.* **1954**, *76*, 3826.

(32) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

Table V. Calculated Self-Exchange Rates for $\text{Cr}_{\text{aq}}^{2+/3+}$ at 25 °C

reactant	$k_{22},^a \text{ M}^{-1} \text{ s}^{-1}$	$\mu, \text{ M}$	$k_{12}, \text{ M}^{-1} \text{ s}^{-1}$	$k_{11}^{\text{calcd } a} \text{ M}^{-1} \text{ s}^{-1}$	$\log K_{12}$
$[\text{Co}(\text{sep})]^{3+}$	$11.5^b (\mu = 0.5)$	0.5	8.7×10^{-4}	2×10^{-10}	2.5
$[\text{Co}(\text{azamesar})]^{3+}$	$2.9^b (\mu = 0.2), 6.5^c (\mu = 0.5)$	0.5	1.4×10^{-4}	2×10^{-10}	1.2
$[\text{Co}(\text{diamsarH}_2)]^{5+}$	$0.024 (\mu = 0.2), 0.06^c (\mu = 0.5)$	0.5	8.1×10^{-3}	4×10^{-11}	8.0
$[\text{Co}(\text{phen})_3]^{3+}$	$40^d (\mu = 0.1)$	1.0	30^e	5×10^{-12}	13.2
$[\text{Co}(\text{en})_3]^{3+}$	$7.1 \times 10^{-5} f (\mu = 1.0)$	1.0	$3.4 \times 10^{-4} e$	8×10^{-8}	4.8

^a k_{11} and k_{22} are the self-exchange rate constants for the reductant and oxidant, respectively. ^b Reference 8. ^c Estimated at $\mu = 0.5$. ^d Neumann, H. M., quoted in: Farina, R.; Wilkins, R. G. *Inorg. Chem.* 1968, 7, 514. ^e Reference 1. ^f Reference 23b.

In comparison to the $\text{Cr}_{\text{aq}}^{2+}$ reaction and to the other Eu^{2+} reductions, the reduction of $[\text{Co}(\text{diamsarH}_2)]^{5+}$ by $\text{Eu}_{\text{aq}}^{2+}$ appears to be 1 order of magnitude too slow. It is not clear why this occurs, although the relatively larger size of the $\text{Eu}_{\text{aq}}^{2+}$ ion coupled with the 5+ charge on the cage may be significant here.

The experimental rate constants in three cases are in relatively good agreement with those predicted by the Marcus-Hush theory (Table IV), and k_{11} for $\text{Eu}_{\text{aq}}^{2+/3+} \leq 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. The observed values tend to be somewhat lower than the calculated rate constants. Chou, Creutz, and Sutin⁴ have calculated the self-exchange rate for $\text{Eu}_{\text{aq}}^{2+/3+}$ from several reactions where $\text{Eu}_{\text{aq}}^{2+}$ has been used as the reducing agent and found that the calculated self-exchange rates at 25 °C and $\mu = 1.0$ vary from 10^{-3} to $10^{-10} \text{ M}^{-1} \text{ s}^{-1}$. Their estimate of the rate constant from these data and from comparison with the measured rate constant at $\mu = 2.0$ is 10^{-5} – $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. The calculated rate constants for the $\text{Eu}_{\text{aq}}^{2+/3+}$ exchange from the reactions with $[\text{Co}(\text{sep})]^{3+}$, $\log K_{12} = 2.0$, and with $[\text{Co}(\text{azamesar})]^{3+}$, $\log K_{12} = 0.68$, are 3×10^{-5} and $2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 0.2$, which is in reasonable agreement with the above estimate. The $\text{Eu}_{\text{aq}}^{2+/3+}$ self-exchange rate calculated from the reaction with $[\text{Co}(\text{diamsarH}_2)]^{5+}$ is substantially smaller.

Reductions with $\text{V}_{\text{aq}}^{2+}$ and $\text{U}_{\text{aq}}^{3+}$. Only one cage complex, $[\text{Co}(\text{diamsarH}_2)]^{5+}$, had a redox potential that made it suitable for reduction by $\text{V}_{\text{aq}}^{2+}$. The observed rate constant (Table IV) was 10 times smaller than that calculated by the Marcus-Hush relation. Since there are no available sites to attack the reductant ion, the reaction is assumed to proceed by an outer-sphere mechanism. Furthermore, the rate ratio for the reductions by $\text{Cr}_{\text{aq}}^{2+}$ and $\text{V}_{\text{aq}}^{2+}$ is 0.02, which is the value stipulated by Linck³ for an outer-sphere mechanism.

The strong reductant $\text{U}_{\text{aq}}^{3+}$ was used in the reaction with $[\text{Co}(\text{sep})]^{3+}$ (Table IV). The reaction between $[\text{Co}(\text{en})_3]^{3+}$ and $\text{U}_{\text{aq}}^{3+}$ has been studied,¹⁷ and the rate ratio for these two reactions is ~ 100 , the same as with all the reducing agents used. This implies that an outer-sphere mechanism also obtains here. The self-exchange rate for $\text{U}_{\text{aq}}^{3+/4+}$ has not been measured, but calculations using the Marcus-Hush equations and the observed rate constant yield a value of $6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. Data from the $\text{U}_{\text{aq}}^{3+}$ – $[\text{Co}(\text{en})_3]^{3+}$ reaction ($k_{12} = 0.13 \text{ M}^{-1} \text{ s}^{-1}$, 25 °C, $\mu = 0.2$)¹⁷ give the value $6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. The reaction $[\text{Ru}(\text{NH}_3)_6]^{3+}$ – $\text{U}_{\text{aq}}^{3+}$ has been studied at 25 °C, $\mu = 1.0$, giving a rate constant of $1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.⁵ The self-exchange rate for $\text{U}_{\text{aq}}^{3+/4+}$ calculated from these data and k_{22} for $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ at $2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ was $6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. These data are in reasonable agreement with each other and indicate that the self-exchange rate for $\text{U}_{\text{aq}}^{3+/4+}$ at 25 °C is 10^{-4} – $10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

Stereoselective Electron Transfer. There have been several studies³³ of electron transfer between sets of different optical isomers to establish whether there is a rate difference for the reaction of enantiomers with a chiral reagent. Until recently

any claimed stereoselectivity has been refuted.^{33c} This could however be due to racemization of any chiral product by electron transfer with its reduced form.³⁴ Thus, if the rate of oxidation is less than the rate of racemization of the reductant any optically active product will be racemized as quickly as it is being formed. By selecting systems where this is not the case, Geselowitz and Taube³⁴ were able to observe stereoselectivity in some systems, although small. For example, the reaction between Δ - $[\text{Os}(\text{bpy})_3]^{3+}$ and $[\text{Co}(\text{edta})]^{2-}$, produced an enantiomeric excess of 5% of Δ - $[\text{Co}(\text{edta})]^-$ in aqueous solution. The 5% induction corresponds to a rate ratio of 1:11 between the Δ and Λ forms of the reductant. In another example, the oxidation of $[\text{Mo}^{\text{V}}\text{O}_4(\text{R},\text{S-pdta})]^{2-}$ with Δ , Δ - $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^{(-)})\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ (pdta = 1,2-propanediaminetetraacetic acid) was claimed to exhibit stereoselectivity leading to 0.15–0.25% in favor of either the (R)-pdta or the (S)-pdta complex depending on ionic strength.³⁵ Quenching of the phosphorescence at Δ - $[\text{Ru}(\text{bpy})_3]^{2+}$ by racemic $[\text{Co}(\text{acac})_3]$ led to the production of 4% of Δ - $[\text{Co}(\text{acac})_3]$.³⁶

The cage complexes constitute another system that is suitable for testing stereoselectivity because of the inertness to substitution and racemization. Slightly different rate constants were observed for the reactions between the two optical isomers of $[\text{Co}(\text{sep})]^{2+}$ and $(-)$ - $[\text{Co}(\text{diamsarH}_2)]^{5+}$ (Table III), but they are not large enough to make any strong claim for selective electron transfer based only on these data. Although the precision for each set of reactions was quite good, it is not unlikely that some systematic error could have caused the approximately 10% difference, especially when oxygen-sensitive reagents are involved. If, however, the difference is real, then the stereoselectivity is of the same order of magnitude as that observed for the $[\text{Os}(\text{bpy})_3]^{3+}$ – $[\text{Co}(\text{edta})]^{2-}$ systems.³⁵ These effects may be much more substantial in nonaqueous media, and the Geselowitz and Taube experiments³⁴ point that way.

Apart from doubtful aspects of the reaction of $[\text{Co}(\text{NH}_3)_6]^{3+}$ with reductants, the results on the whole point to well-behaved Co(II)–Co(III) electron-transfer systems that fit the Marcus-Hush theoretical framework despite the difference in the type of spin state for the two oxidation states. The results are complementary to those observed for the $[\text{Co}^{\text{II/III}}(\text{azacapt})]^{2+/3+}$ ions³⁷ (azacapt = 8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo[6.6.6]eicosane), where both oxidation states are in the low-spin condition and the Marcus-Hush correlations hold for electron-transfer reactions with the other cage complexes containing the two oxidation states in high- and low-spin conditions. For the azacapt ions, the rate constant for self-exchange is much greater ($\sim 10^3$) than those of the hexamine cage systems and the internal reorganizational energy correspondingly less. Despite the different spin conditions, there is no discontinuity in the

(33) (a) Grossman, B.; Wilkins, R. G. *J. Am. Chem. Soc.* 1967, 89, 4230. (b) Sutter, J. H.; Hunt, J. B. *Ibid.* 1969, 91, 3107. (c) Kane-Maguire, N. A. P.; Tollison, R. M.; Richardson, D. E. *Inorg. Chem.* 1976, 15, 499.

(34) Geselowitz, D. A.; Taube, H. *J. Am. Chem. Soc.* 1980, 102, 4525.

(35) Kondo, S.; Sasaki, Y.; Saito, K. *Inorg. Chem.* 1981, 20, 429.

(36) Porter, G. B.; Sparks, R. H. *J. Chem. Soc., Chem. Commun.* 1979, 1094.

(37) Dubs, R. V.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* 1983, 22, 2523.

Marcus-Hush correlations and the implication is that both systems are essentially adiabatic. The probability that the electron-tunneling and nuclear-tunneling factors cancel to the same degree in each system seems too remote to contemplate. The argument regarding adiabatic behavior would not be secure, however, if the partner ions in the activated complex could be considered to reach the transition-state energy essentially by independent activation.³⁸

(38) Ratner, M. A.; Levine, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 4898.

Registry No. [Co(sep)]³⁺, 72496-77-6; [Co(sar)]³⁺, 85664-13-7; [Co(en)₃]³⁺, 14878-41-2; [Co(diarsarH₂)]⁵⁺, 85663-73-6; [Co(azamesar)]³⁺, 85664-08-0; [Co(ammesarH)]⁴⁺, 85663-85-0; [Co(diarsar)]³⁺, 85663-96-3; [Co(NH₃)₆]³⁺, 14695-95-5; [Co(bpy)]³⁺, 19052-39-2; [Co(phen)₃]³⁺, 18581-79-8; Cr²⁺, 22541-79-3; Eu²⁺, 16910-54-6; V²⁺, 15121-26-3; U³⁺, 22578-81-0.

Supplementary Material Available: Tables containing the experimental kinetic data and data for calculation of k_{12}^{calcd} including work terms (12 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratorium für anorganische Chemie der Eidgenössischen Technischen Hochschule, CH-8092 Zürich, Switzerland, Research School of Chemistry, The Australian National University, Canberra, ACT 2600, Australia, and Department of Chemistry, The Royal Veterinary and Agricultural University, DK-1871 Copenhagen, Denmark

Acid Cleavage of Nickel(II) Complexes Containing *cis,cis*-1,3,5-Cyclohexanetriamine (tach), Crystal Structure of [Ni(tach)(H₂O)₃](NO₃)₂, and a Correlation between Structure and Reactivity of Nickel-Polyamine Complexes

GEROLD SCHWARZENBACH,^{1,2} HANS-BEAT BÜRGI,^{*1,3} WILLIAM P. JENSEN,^{1,4} GEOFFREY A. LAWRENCE,⁵ LENE MØNSTED,⁶ and ALAN M. SARGESON^{*5}

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The cleavage of Ni(tach)₂²⁺ (tach = *cis,cis*-1,3,5-cyclohexanetriamine) to give Ni(tach)(H₂O)₃²⁺ is strictly first order in complex, and no intermediate species has been detected. The observed rate constant is strongly acid dependent, and for HCl and HBF₄ the rate law is $k_{\text{obsd}} = k_1 / \{1 + (b + c[\text{H}^+])^{-1} + (e + f[\text{H}^+])^{-1}\}$ with a limiting rate constant $k_1 = 0.78 \pm 0.02 \text{ s}^{-1}$, $\Delta H^\ddagger = 72 \pm 2 \text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -6 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ (25 °C, $\mu = 1.0 \text{ M}$). The limiting rate is ascribed to the first Ni-N bond rupture, apparently not involving the chair-boat (skew boat) conformational change of the ligand in the rate-determining step; the acid dependence is traced to a competition between protonation and rechelation of partly dissociated amine ligand. Cleavage in acetate/acetic acid buffers shows that the reaction is catalyzed by acetate and/or acetic acid and that the acid dependence has to be more complex than that indicated above. Cleavage of the Ni-N bonds in acid for Ni(tach)(H₂O)₃²⁺ is markedly slower than for Ni(tach)₂²⁺ at the same acid concentrations and has a rate law of the form $k_{\text{obsd}} = k_0 + k_{\text{HX}}[\text{HX}]$ (25 °C, $\mu = 3.0 \text{ M}$, $k_0 \approx 6 \times 10^{-5} \text{ s}^{-1}$, HX = HClO₄, HCOOH, Cl₂CHCOOH, CH₃COOH, and H₂PO₄⁻). The behavior is accommodated by a mechanism similar to that proposed for the bis complex. An X-ray crystallographic analysis of [Ni(tach)(H₂O)₃](NO₃)₂ (space group *Pnma*, *Z* = 4, *a* = 14.142 (2) Å, *b* = 12.637 (2) Å, and *c* = 8.000 (1) Å) showed the amine coordinated tridentate to the Ni²⁺ ion with Ni-N distances (2.07 Å) ~0.06 Å shorter than those in [Ni(tach)₂](NO₃)₂; conversely Ni-O distances (2.10 Å) are ~0.05 Å longer than in Ni(H₂O)₆²⁺. An analogous trend is observed for the Ni-N and Ni-O distances of Ni(en)_{*n*}²⁺ (*n* = 1-3); Ni-N and Ni-O bond distances decrease with increasing number of water oxygen atoms in the first coordination sphere. Within each family of complexes the rates of Ni-N or Ni-O bond rupture correlate with bond lengths: short bonds are cleaved more slowly than long bonds.

Introduction

The complex ion Ni(tach)(H₂O)₃²⁺ (tach = *cis,cis*-1,3,5-triaminocyclohexane) is strikingly inert to substitution of the ligand by water. It is cleaved by strong acids with a reaction half-life $t_{1/2} \approx 3600 \text{ s}$ (0.7 M HClO₄, 25 °C).⁷ By comparison, Ni(dien)(H₂O)₃²⁺ (dien = 3-azapentane-1,5-diamine) decomposes much more rapidly in acid;⁸ it has a reaction half-life $t_{1/2} \approx 0.05 \text{ s}$. Ni(tach)₂²⁺ with six nitrogens as ligand atoms is somewhat less labile ($t_{1/2} \approx 1 \text{ s}$). Acid catalysis of the decomposition of Ni(tach)₂²⁺ to Ni(tach)(H₂O)₃²⁺ and of the latter to Ni(H₂O)₆²⁺ and H₃tach³⁺ requires proton concentrations at which the rate constants for cleavage of related nickel amine complexes appear to be pH independent.⁹

It is therefore difficult to compare observed rate constants for hydrolysis of different nickel amine complexes directly.

The constitution and conformational flexibility of the coordinating amine ligand might be one of the factors determining the rate constant of the cleavage reaction. Specifically, the activation energy for chair-boat interconversion of the cyclohexane ring in tach or of a six-membered chelate ring might be coupled with the activation energy for Ni-N rupture.

Such observations and ideas prompted us to investigate in some detail the kinetics of the cleavage of tach from Ni(tach)₂²⁺ and Ni(tach)(H₂O)₃²⁺ in acid solution. X-ray crystallographic investigations of both ions have been carried out^{10,11} in order to define the denticity of the ligand and the precise geometry of the complex cations. Structural data have been compared to kinetic data to see whether correlations exist between the two classes of experimental results.

Experimental Section

Syntheses. The complexes [Ni(tach)₂]Cl₂ and [Ni(tach)(H₂O)₃]Cl₂ were synthesized as previously described.¹² Ni(tach)(en)(H₂O)²⁺

- (1) ETH Zürich.
- (2) Deceased.
- (3) Present address: Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, 3012 Bern, Switzerland.
- (4) Present address: Chemistry Department, South Dakota State University, Brookings, SD 57006.
- (5) The Australian National University.
- (6) The Royal Veterinary and Agricultural University.
- (7) Childers, R. F.; Wentworth, R. A. D. *Inorg. Chem.* **1969**, *8*, 2218-2220.
- (8) Melson, G. A.; Wilkins, R. G. *J. Chem. Soc.* **1963**, 2662-2672.
- (9) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974. See also: Wilkins, R. G. *Acc. Chem. Res.* **1970**, *3*, 408-416.

(10) [Ni(tach)₂](NO₃)₂: Ammeter, J. H.; Bürgi, H. B.; Gamp, E.; Meyer-Sandrin, V.; Jensen, W. P. *Inorg. Chem.* **1979**, *18*, 733-750.

(11) [Ni(tach)(H₂O)₃](NO₃)₂: Huffmann, J. C.; Wentworth, R. A. D.; Tsai, C. C.; Huffmann, C. J.; Streib, W. E. *Cryst. Struct. Commun.* **1981**, *10*, 1493 (*R* = 0.036).

(12) Egli, H. Doctoral Dissertation 5535, ETH Zürich, 1975.