Nd. An observed $\Delta H_1°$ value, also $\Delta S_1°$, for the formation of the monochloro complex thus changes depending on the equilibrium constant between the eight- and nine-coordination species. As both $\Delta H°$ and $\Delta S°$ values for eq 6 are negative,[35] the chloro complexation of $[Ln(DMF)_9]^{3+}$ is more endothermic than that of $[Ln(DMF)_8]^{3+}$. A systematic decrease in the $\Delta H_1°$ and $\Delta S_1°$ values in the sequence La > Ce > Pr > Nd thus implies that the equilibrium in eq 6 is shifted to the right to a greater extent in the same order. This conclusion is consistent with that obtained by the ^1H NMR study.[33,34] Consequently, it is plausible that, in DMF, the La^{3+} ion prefers $[La(DMF)_9]^{3+}$ to $[La(DMF)_8]^{3+}$, while the Nd^{3+} ion prefers $[Nd(DMF)_8]^{3+}$.

Also according to Merbach, the sole eight-coordinated species $[Ln(DMF)_8]^{3+}$ occurs for Sm^{III}–Lu^{III}. That the $\Delta S_1°$ values of Sm^{III}–Ho^{III} ions are practically the same in the range 103–110 J K^{-1} mol^{-1} is consistent with the unvarying geometries of these solvate ions. The $\Delta H_1°$ value increases gradually with Z, which suggests that the metal–DMF bonds within $[Ln(DMF)_8]^{3+}$ are enhanced monotonically as ionic radii of Ln^{III} ions decrease.

The $\Delta H_1°$ and $\Delta S_1°$ values of Tm^{III}, Yb^{III}, and Lu^{III} systems are particularly large compared to those of the Tb^{III}, Dy^{III}, and Ho^{III} systems. Interestingly, the drastic change in the $\Delta H_1°$ and $\Delta S_1°$ values seems parallel to that for the solvent-exchange mechanism. Indeed, the solvent-exchange mechanism of $[Ln(DMF)_8]^{3+}$ in DMF is shown as an interchange mechanism for Tb^{III}, Dy^{III}, and Ho^{III} and as a dissociative one for Tm^{III} and Yb^{III}.[34] Thus a mechanistic crossover occurs at Er^{III}. It is also noteworthy that the solvent-exchange rate of Tm^{III} and Yb^{III} increases remarkably compared to that of Tb^{III}–Ho^{III}. This implies that the $[Ln(DMF)_8]^{3+}$ (Ln = Tm, Yb, Lu) solvates involve Ln^{3+}–DMF bonds that are extremely weak and labile. On the other hand, the large and positive $\Delta H_1°$ and $\Delta S_1°$ values show that the $[Ln(DMF)_8]^{3+}$ solvates involve also Ln^{3+}–DMF bonds of normal strength. These facts thus suggest that there exist two kinds of solvents, one bonded strongly and the other weakly, within $[Ln(DMF)_8]^{3+}$ (Ln = Tm, Yb, Lu). A largely distorted geometry is thus plausible for $[Ln(DMF)_8]^{3+}$ (Ln = Tm, Yb, Lu). It is also plausible that a simultaneous rupture of both strong and weak Ln^{3+}–DMF bonds accompanies the chloro complexation of Tm^{III}, Yb^{III}, and Lu^{III} ions.

Although the $\Delta H_2°$ and $\Delta S_2°$ values involve large uncertainties, the values evidently depend on the lanthanide ion. Also, the $\Delta S_{\beta_4}°$ values provide evidence of extensive desolvation of Ln^{3+} ions at higher stages of complexation. These facts suggest that a coordination geometry change occurs upon the chloro complexation of Ln^{III} ions.

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[35] With Nd^{III}, the values of $\Delta H° = -14.9$ kJ mol^{-1} and $\Delta S° = -69$ J K^{-1} mol^{-1} have been obtained in DMF.[32]

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Pressure Effects on the Self-Exchange Rates of Cobalt(III/II) Couples: Evidence for Adiabatic Electron Transfer in the Bis(1,4,7-trithiacyclononane) and Sepulchrate Complexes

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The pressure dependences of the logarithms of the self-exchange rate constants k for the title complexes in aqueous solution at 25 °C are linear within experimental uncertainty and are characterized by the following parameters: for low-spin/low-spin $Co([9]aneS_3)_2^{3+/2+}$ at ionic strength $I = 0.1$ mol L^{-1} (CF_3SO_3K), $k = 9.5 \times 10^4$ L mol^{-1} s^{-1} at 0.1 MPa, and $\Delta V^* = -4.8 \pm 0.2$ cm^3 mol^{-1}; for low-spin/high-spin $Co(sep)^{3+/2+}$ at $I = 0.2$ mol L^{-1} (NaCl), $k = 5.0$ L mol^{-1} s^{-1} at 0.1 MPa, and $\Delta V^* = -6.4 \pm 0.2$ cm^3 mol^{-1}. The pressure dependence of k is accounted for in both cases by an adaptation of the Marcus–Hush theory if internal reorganization makes the usual small contribution (ca. +1 cm^3 mol^{-1}) to ΔV^*. The implication is that the title reactions are essentially fully adiabatic, despite the difference in spin type, and that the low-spin/high-spin $Co(en)_3^{3+/2+}$ exchange, for which the pressure-dependent ΔV^* is some 13 cm^3 mol^{-1} more negative than predicted on the above basis (Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385), is nonadiabatic.

Introduction

As Endicott and Ramasami[1] have remarked, there is growing evidence that, of the various outer-sphere electron-transfer (ET) reactions of metal complexes that have been studied in aqueous solution, the self-exchange reactions are relatively adiabatic. In the case of redox reactions involving the $Fe(H_2O)_6^{3+/2+}$ couple, for example, it appears that the self-exchange reaction is essentially adiabatic even though its "cross-reactions" may not be.[2-4] However, ET reactions of the numerous cobalt(III/II) couples for which the ground states of the Co^{III} and Co^{II} complexes are low- and high-spin (^1A and ^4T), respectively, are spin-forbidden in the sense that they are three-electron processes. It may therefore be anticipated either that ET will involve the ground states of both the Co^{III} and the Co^{II} complexes and be nonadiabatic or that ET occurs adiabatically from a low-spin ^2E excited state of Co^{II} in (usually unfavorable) equilibrium with the ^4T ground state. In either case, the result should be slower ET and a much stronger acceleratory effect of pressure P on ET than are predicted from the adiabatic Marcus–Hush theory.[5-7]

These expectations appear to be realized for the $Co(en)_3^{3+/2+}$ self-exchange (en = 1,2-diaminoethane), for which the rate constant k is small (8×10^{-4} L mol^{-1} s^{-1} at 65 °C, 0.1 MPa, and ionic strength $I = 0.5$ mol L^{-1}) and the pressure effect much larger than predicted from the Marcus–Hush theory for adiabatic ET between the ground states (limiting zero-pressure volume of activation $\Delta V_0^* = -20$ cm^3 mol^{-1}, vs. −7 cm^3 mol^{-1} predicted).[6] The

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(1) Endicott, J. F.; Ramasami, T. *J. Phys. Chem.* **1986**, *90*, 3740 and references cited.

(2) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

(3) (a) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374. (b) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615. (c) Macartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530. (d) Fürholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 3091.

(4) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948.

(5) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979; **1957**, *26*, 867; *Discuss. Faraday Soc.* **1960**, *29*, 21; *Faraday Discuss. Chem. Soc.* **1982**, *74*, 7. (b) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557. (c) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.

(6) Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385.

(7) Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 5017.

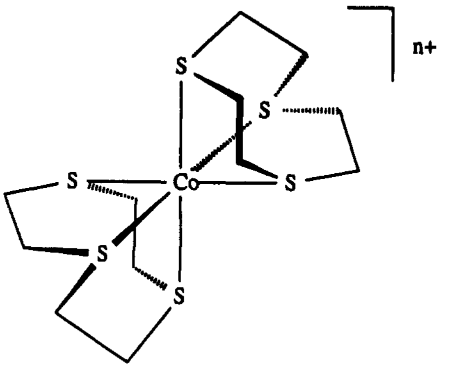

Figure 1. $\mathrm{Co([9]aneS_3)_2}^{n+}$ (schematic).

pressure effect is consistent with nonadiabatic ET with a distance scaling factor α of 16 or 19 $\mathrm{nm^{-1}}$ (depending on whether an ion-pairing correction is or is not applied), although adiabatic ET following a *very* unfavorable spin preequilibrium cannot be ruled out.

The main purposes of this paper are (i) to place the $\mathrm{Co(en)_3}^{3+/2+}$ result in the context of the pressure effect on a self-exchange reaction in which *both* $\mathrm{Co^{II}}$ and $\mathrm{Co^{III}}$ are known to be low-spin in their ground states, viz., $\mathrm{Co([9]aneS_3)_2}^{3+/2+}$ (Figure 1),[8-12] and (ii) to seek some further insights into why the $\mathrm{Co(sep)}^{3+/2+}$ self-exchange[13-19] proceeds some 5×10^4 times faster than the $\mathrm{Co(en)_3}^{3+/2+}$ reaction despite some structural resemblances—the predominant current view[11] is that the effect may be ascribed largely to the smaller Co–N elongation Δd on reduction in $\mathrm{Co(sep)}^{3+/2+}$ ($\Delta d \simeq 17$ pm) as compared with $\mathrm{Co(en)_3}^{3+/2+}$ ($\Delta d \simeq 21$ pm). Finally, there are at present too few published data to establish beyond reasonable doubt our contention that an adaptation of the Marcus–Hush theory can account essentially quantitatively for the effects of pressure on adiabatic self-exchange reaction rates in *aqueous* solution (*nonaqueous* systems are better served with data but conform poorly to predictions);[7] the results presented here will help fill this need.

Experimental Section

Materials. Both optical isomers of $\mathrm{[Co(sep)]Cl_3{\cdot}H_2O}$ were prepared, in better than 95% optical purity, from optically resolved $\mathrm{[Co(en)_3]Cl_3}$[20] by the method of Sargeson, Harrowfield, and co-workers,[14-16,21] and the integrity of the compounds was confirmed by spectrophotometry and by CHN microanalyses. Solutions of optical isomers of $\mathrm{Co(sep)^{2+}}$ were obtained by reduction of the relevant $\mathrm{[Co(sep)]Cl_3}$ isomers with mossy zinc in slightly acidic (pH $\simeq$ 3, HCl) aqueous solution. Kinetic experiments could not be carried out in nonaqueous solvents such as acetonitrile or *N*,*N*-dimethylformamide because the complexes were insufficiently soluble. For the same reason, ionic strength adjustments in aqueous solution were made with NaCl rather than (e.g.) $\mathrm{NaClO_4}$.

Table I. Rate Constants for the Self-Exchange of $\mathrm{Co(sep)}^{3+/2+}$ in Aqueous Solution at Variable Temperature and Ionic Strength[a]

T^b/°C	I^c/ mol $\mathrm{L^{-1}}$	I^c/ mol $\mathrm{kg^{-1}}$	k^d/L $\mathrm{mol^{-1}\ s^{-1}}$	k^d/kg $\mathrm{mol^{-1}\ s^{-1}}$
11.8	0.199	0.201	2.40	2.39
17.8			3.12	3.11
20.0			3.27	3.26
25.0			5.10	5.08
34.0			8.74	8.71
24.8	0.100	0.101	3.49	3.48
	0.501	0.517	9.00	8.92
	1.00	1.063	13.0	12.8

[a] P = 0.1 MPa. [b] ±0.2 °C. [c] NaCl. [d] ±5%.

Table II. Rate Constants for the Self-Exchange of $\mathrm{Co(sep)}^{3+/2+}$ in Aqueous Solution at Variable Pressure[a]

P/MPa	k^b/kg $\mathrm{mol^{-1}\ s^{-1}}$	P/MPa	k^b/kg $\mathrm{mol^{-1}\ s^{-1}}$
0.1	4.95, 5.20	104.0	6.51
27.0	5.37	129.8	7.11
47.2	5.86	152.7	7.50
52.7	5.73	178.1	8.20
77.2	6.26	203.2	8.52

[a] 25.0 °C, I = 0.2 mol $\mathrm{kg^{-1}}$. [b] ±5%. Data are from two independent series of experiments.

$\mathrm{[Co([9]aneS_3)_2](ClO_4)_3}$, $\mathrm{[Co([9]aneS_3)_2](CF_3SO_3)_3}$, and $\mathrm{[Co([9]aneS_3)_2](CF_3SO_3)_2}$ were made by published methods.[9,11] [*Warning! The perchlorate salt is potentially explosive.*] The purity of the $\mathrm{Co^{III}}$ triflate was established spectrophotometrically, and that of the $\mathrm{Co^{II}}$ complex by CHN microanalyses. The 400-MHz proton NMR spectrum of fresh $\mathrm{[Co([9]aneS_3)_2](ClO_4)_3}$ in $\mathrm{D_2O}$ showed the expected multiplet at 3.6 ppm, but the minor feature seen at 3.1 ppm in Figure 6 of ref 10 appeared only in solutions made from old samples of the solid (which also developed an odor) and presumably represents a decomposition product. The freshly made solid complexes were therefore stored at 0 °C in the dark, although it was demonstrated that the presence of the decomposition product had no effect on the kinetic results described below. The multiplet was unresolved at 90 MHz in the high-pressure probehead.

Kinetic Measurements. The $\mathrm{Co(sep)}^{3+/2+}$ self-exchange rate is too fast to measure by conventional methods at high pressure and too slow for NMR line-broadening techniques. The thermostated, pressurizable rapid-mixing assembly of a Hi-Tech HPSF-56 stopped-flow spectrophotometer system was therefore adapted to be used with a Jasco J-500A spectropolarimeter, and the self-exchange rate was measured through the change of the circular dichroism (CD) after mixing of pressurized solutions of Λ-$\mathrm{Co(sep)^{2+}}$ and Δ-$\mathrm{Co(sep)^{3+}}$, recorded at 450–470 nm as a function of time.[16,22] Careful alignment of the observation tube of the rapid-mixing system with the light beam of the spectropolarimeter was necessary; otherwise, the CD spectrum, instead of being a smooth curve, would cycle repeatedly from positive to negative absorption and back within the true CD envelope as the wavelength was scanned. This spectacular phenomenon was evidently caused by phase changes when the misaligned light beam reflected off the inside wall of the tube, but was time-independent, and any residual effect after proper alignment could not have affected the kinetic measurements. The concentrations of the $\mathrm{Co^{II}}$ and $\mathrm{Co^{III}}$ optical isomers were chosen so that, at the end of the reaction, no net optical activity remained. The solutions were handled under nitrogen at all times. The pH of the solutions after reaction was 3.6–6.4. The temperature of the sample solutions, monitored with a platinum resistance sensor, was always within 0.2 °C of the set value.

The rate of exchange of the $\mathrm{Co([9]aneS_3)_2}^{3+/2+}$ triflates in $\mathrm{N_2}$-purged 99.996% $\mathrm{D_2O}$ (Sigma; ionic strength adjusted to 0.1 mol $\mathrm{kg^{-1}}$ with $\mathrm{CF_3SO_3K}$) was followed by ^{1}H NMR spectroscopy at 90 MHz on a Bruker WH-90 spectrometer, through broadening of the $\mathrm{Co([9]aneS_3)_2}^{3+}$ methylene band at 3.6 ppm.[10] The standard Bruker WH-90 probehead with a 5-mm sample tube was used for measurements at variable temperature T, and the high-pressure study was carried out with the home-built probe described elsewhere.[23] Because it was possible that the shim settings could have been affected by pressurizing the probehead, the line width ν^0 in the absence of exchange was derived from that of an internal standard in the solution, sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS; MSD Isotopes), for which eq 1 had been established at 25.8 °C.

$$\nu^0 = 0.826\nu_{\mathrm{DSS}} + 3.18 \qquad (1)$$

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(8) $\mathrm{[9]aneS_3}$ = 1,4,7-trithiacyclononane.

(9) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(10) Küppers, H.-J.; Wieghardt, K.; Steenken, S.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1989**, *573*, 43.

(11) Küppers, H.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.

(12) Wieghardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.

(13) sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane.

(14) Creaser, I. I.; Harrowfield, J.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181.

(15) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23.

(16) Creaser, I. I.; Geue, R.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

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

(18) Creaser, I. I.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1983**, *22*, 4022.

(19) Bernhard, P.; Sargeson, A. M. *Inorg. Chem.* **1987**, *26*, 4122.

(20) Broomhead, J. A.; Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1960**, *6*, 183.

(21) Harrowfield, J. M. Personal communication.

(22) Im, Y. A.; Busch, D. H. *J. Am. Chem. Soc.* **1961**, *83*, 3357.

(23) Doine, H.; Swaddle, T. W. *Inorg. Chem.* **1988**, *27*, 665.

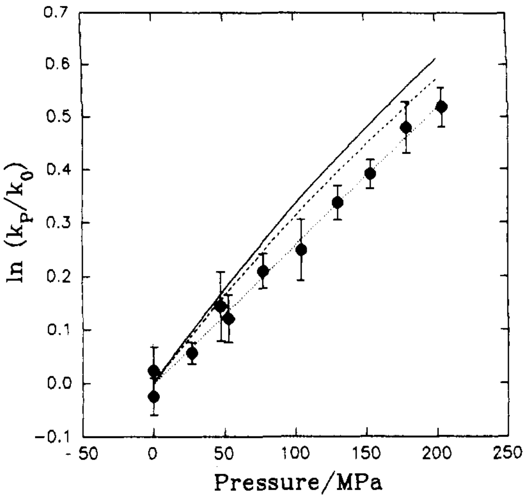

Figure 2. Pressure dependence of ln k relative to zero pressure for $Co(sep)^{3+/2+}$ at 25.0 °C and $I = 0.2$ mol L^{-1}. Theoretical curves represent adiabatic ET without allowance for the effect of pressure on the internal reorganization of the complexes: solid curve, Debye–Hückel parameter a set at 600 pm with Fuoss ion pairing; dashed curve, a estimated from experiment with no allowance for ion pairing; dotted line, linear regression of experimental data.

Limited solubility and redox stability precluded line-broadening measurements in nonaqueous solvents.

Results

The $Co(sep)^{3+/2+}$ Exchange. The recorded change of CD with time t gave a good fit to eq 2, yielding rate constants k_{obsd} with

$$-\ln [(CD_t - CD_\infty)/(CD_0 - CD_\infty)] = k_{obsd}t = kt[Co]_{tot} \quad (2)$$

an estimated experimental uncertainty of ±5%. Thus, for $[Co]_{tot} = 2.01$, 3.92, and 6.33 mmol L^{-1}, $k_{obsd} = 0.0172$, 0.0353, and 0.0560 s^{-1}, respectively, at 25.0 °C and $I = 0.5$ mol L^{-1} (NaCl), so that $k = 9.0$ L mol^{-1} s^{-1}.

Values of k as functions of temperature T, pressure P, and ionic strength I are summarized in Tables I and II. Concentrations in Table I are given in both mol L^{-1} (25 °C, 0.1 MPa) and mol kg^{-1}, to make the point that the difference between the scales is not significant for these aqueous solutions in the context of the experimental uncertainty in k.[24] The linear dependence of ln (k/T) on $1/T$ at 0.1 MPa and $I = 0.2$ mol L^{-1} gives ΔH^* and ΔS^* values (Table IV) in excellent agreement with those of Sargeson and co-workers,[16] who found that Cl^- gave the same k as ClO_4^- at a given T and I. We find that the data at variable I are well represented ($r^2 = 0.9988$) by the Brønsted–Bjerrum–Christiansen function

$$\ln k = \ln k^0 + 2z_1z_2CI^{1/2}/(1 + BaI^{1/2}) \quad (3)$$

if k^0 and the anion–cation closest approach parameter a are treated as adjustable parameters; z_1 and z_2 are the reactant ion charge numbers, and B and C are calculated from theory (3.286×10^9 $L^{1/2}$ $mol^{-1/2}$ m^{-1} and 1.175 $L^{1/2}$ $mol^{-1/2}$, respectively, at 25.0 °C). Nonlinear least-squares regression gave $k^0 = 0.326 \pm 0.013$ L mol^{-1} s^{-1} and $a = 863 \pm 18$ pm.

Table III. Rate Constants for the Self-Exchange of $Co([9]aneS_3)_2^{3+/2+}$ at Variable Temperature and Pressure[a]

T^b/°C	$[Co^{II}]^c$/ mmol kg^{-1}	$[Co^{III}]^d$/ mmol kg^{-1}	P^e/MPa	$k/10^5$ kg mol^{-1} s^{-1}
14.7	0.516	4.25	0.1	0.707
19.3				0.823
26.4				1.043
32.0				1.35
37.5				1.52
37.5				1.56
19.3	0.545			0.733
26.4				0.958
32.0				1.222
37.4				1.611
25.8	0.385	4.20	0.1	0.976, 0.983
			25.6	1.05
			50.3	1.05
			57.0	1.13
			73.3	1.16
			97.3	1.21
			125.0	1.26
			152.0	1.39
			174.2	1.39
			199.7	1.45
			207.7	1.44

[a] $I = 0.1$ mol kg^{-1}. [b] ±0.2 °C. [c] As triflate. [d] As perchlorate. [e] ±0.1 MPa.

Table IV. Activation Parameters for Self-Exchange[a]

	$Co(sep)^{3+/2+}$	$Co([9]aneS)_2^{3+/2+}$
I/mol L^{-1}	0.20	0.10
k^b/L mol^{-1} s^{-1}	5.0	9.5×10^4
ΔH^*/kJ mol^{-1}	41.4 ± 1.2	25.4 ± 1.7
ΔS^*/J K^{-1} mol^{-1}	−93 ± 4	−64 ± 6
ΔV^{*c}/cm^3 mol^{-1}	−6.4 ± 0.2	−4.8 ± 0.2

[a] Standard state of concentration 1 mol L^{-1} at 25.0 °C and 0.1 MPa. [b] 25 °C, 0.1 MPa. [c] Mean for range 0–200 MPa.

The pressure dependence of ln k (Table II) is linear within the experimental uncertainties (Figure 2) and gives a volume of activation ΔV^* of -6.4 ± 0.2 cm^3 mol^{-1} at 25.0 °C and $I = 0.2$ mol L^{-1}. As pointed out elsehwere,[7] a nonlinear dependence is predicted by theory and may be obscured by the experimental uncertainty; this value of ΔV^* should therefore be regarded as a *mean* for this pressure range (0–200 MPa).

The $Co([9]aneS_3)_2^{3+/2+}$ Exchange. The broadening $\delta\nu_{1/2}$ of the $Co([9]aneS_3)_2^{3+}$ band at 3.6 ppm was proportional to the concentration of added Co^{II} complex at given T and P, so that k was given by $\pi\delta\nu_{1/2}/[Co^{II}]$ to better than ±5% for the variable-temperature experiments and around ±5% for measurements at elevated pressures. The results are summarized in Table III. It was not possible to vary the ionic strength significantly. The linear dependence of ln (k/T) on $1/T$ gave the ΔH^* and ΔS^* values of Table IV, which may be compared with $\Delta H^* = 28.0 \pm 1.7$ kJ mol^{-1} and $\Delta S^* = -54 \pm 6$ J K^{-1} mol^{-1} obtained by Macartney[25] at $I = 0.1$ mol L^{-1}. Wieghardt and co-workers[10] reported $\Delta H^* = 35 \pm 10$ kJ mol^{-1} and $\Delta S^* = -29 \pm 17$ J K^{-1} mol^{-1} at $I = 0.2$ mol L^{-1}, from data obtained over a narrower temperature range; a possibly spurious factor of $\sqrt{3}$ in k,[10] together with the difference in I, accounts in large part for the discrepancy between their data and those reported here.

As Figure 3 shows, the pressure dependence of ln k is linear, within experimental uncertainty, although again theory would predict a curved plot. The value of ΔV^* calculated for the linear plot (-4.8 ± 0.2 cm^3 mol^{-1}) is therefore better taken as a mean for the range 0–200 MPa.

Discussion

The adaptation of the Marcus–Hush theory for the prediction of pressure effects on the rate of self-exchange reactions of metal complexes in solution has been considered in detail elsewhere.[7] The tentative conclusion that the theory is effective for simple ET processes in aqueous solution[7] receives support from the present

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(24) Although chemical kinetics are appropriately discussed in terms of molecules per unit volume, the effect of pressure or temperature on k must necessarily be expressed with reference to a pressure- and temperature-independent concentration unit such as mol kg^{-1} or, if a reference temperature and pressure (in this paper, 25 °C and 0.1 MPa) are defined, mol L^{-1}. For the NMR studies, the small solution samples were made up by mass for optimal accuracy and economy, and the basic kinetic data are therefore presented on the mol kg^{-1} basis. For $Co(sep)^{3+/2+}$, ΔS^* was a mere 0.1 J K^{-1} mol^{-1} more negative on conversion from the mol kg^{-1} to the mol L^{-1} (25 °C, 0.1 MPa) standard state, and no correction was necessary, in the context of the experimental uncertainty, for the other parameters of Table IV.

(25) Macartney, D. H. Personal communication.

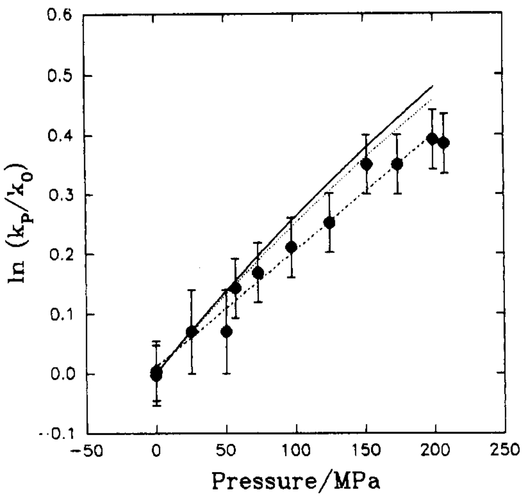

Figure 3. Pressure dependence of ln *k* relative to zero pressure for $Co([9]aneS_3)_2^{3+/2+}$ at 25.8 °C and $I = 0.1$ mol L^{-1}. Theoretical curves represent adiabatic ET without allowance for the effect of pressure on the internal reorganization of the complexes: Debye–Hückel parameter *a* set at 1100 pm (solid curve) or 1000 pm (dotted curve) with no allowance for ion pairing; linear regression of experimental data (dashed line).

results. This may be seen from Figures 2 and 3, in which the contributions ΔV_{IR}^* of internal reorganization (which are in general small, $\simeq 1$ cm^3 mol^{-1} [5c,7]) have been omitted for want of firm data to build on. The reactant radii are taken to be 420 pm for $Co(sep)^{n+}$ and 500 pm for $Co([9]aneS_3)^{n+}$—the latter value is an arbitrary compromise because of the diabolo-like (i.e., double-headed top-like) shape of the complexes (Figure 1). The theoretical plots of ln *k* (relative to its zero-pressure value) against *P* come acceptably close to the experimental data, although their distinct curvature seems not to be echoed by the measurements, for which ln *k* appears to be a linear function of *P* within the error limits. However, the theoretical ΔV^* values at midrange of pressure (−7.0 cm^3 mol^{-1} for $Co(sep)^{3+/2+}$ and −5.9 cm^3 mol^{-1} for $Co([9]aneS_3)^{3+/2+}$, from the closer fitting curves of Figures 2 and 3) are only about 1 cm^3 mol^{-1} more negative than the experimental values derived from the linear regressions; this small difference could be accounted for entirely by the omitted contribution ΔV_{IR}^*.

The treatment of ionic medium effects is one of the weaker points of the theory, as the effect of pressure on ionic activity coefficients is poorly understood and is not readily predictable from first principles.[26] We have previously used a combination of extended Debye–Hückel theory (eq 3) and Fuoss ion pairing to address this issue.[7] For $Co(sep)^{3+}/^{2+}$, however, we have been able to obtain an "experimental" value of the anion–cation closest approach parameter *a* such that eq 3 fits the measurements well over the relevant range of *I* without invoking additional electrolyte effects. Since the pressure dependences of the other parameters in eq 3 can be calculated from the Debye–Hückel theory, this equation can presumably be used with this *a* value without reference to possible ion pairing. Both approaches are applied in Figure 2, for comparison; the latter fits the data a little better. The "experimental" value of *a* is some 260 pm larger than the sum of the crystallographic radii of a Cl^- and a Co sepulchrate ion. With this and the diabolo-like shape of $Co([9]aneS_3)^{n+}$ in mind, the value of *a* was arbitrarily set to 1.0 nm for the $[9]aneS_3$ complexes in triflate media, and the pressure dependence of ln *k* was calculated without invoking ion pairing; Figure 3 shows that a 100-pm error in *a* would be immaterial.

Figures 2 and 3, then, represent successes for our adaptation of the Marcus–Hush theory—or, conversely, they imply that the $Co(sep)^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ exchanges are essentially fully adiabatic and "well-behaved" in the Marcus–Hush sense. The similarity in the moderately negative mean ΔV^* values for the low-spin/high-spin $Co(sep)^{3+/2+}$ and low-spin/low-spin $Co([9]aneS_3)_2^{3+/2+}$ reactions and the sharp contrast between these and the much more negative value found for the low-spin/high-spin $Co(en)_3^{3+/2+}$ self-exchange (Figure 4; note that the vertical scale is compressed relative to Figures 2 and 3)[6] suggest that the $Co(sep)^{3+/2+}$ exchange is essentially fully adiabatic, as Sargeson et al.[17-19] have maintained, but that the $Co(en)_3^{3+/2+}$ case is not. An alternative explanation previously advanced[6] to explain the anomalously strong acceleration of the $Co(en)_3^{3+/2+}$ exchange, viz., that ET occurred efficiently (i.e., adiabatically) only via a doublet excited state of Co^{II} produced in an unfavorable $Co^{II}(^4T)$–$Co^{II}(^2E)$ pre-equilibrium, now seems less credible, since any such spin-state preequilibrium would be very unfavorable in the $Co(sep)^{3+/2+}$ case, too, and would contribute a further −10 cm^3 mol^{-1}, approximately, to ΔV^*.[27]

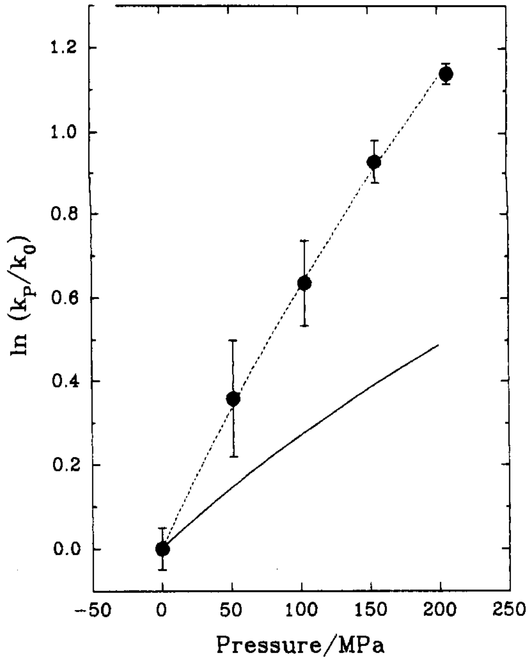

Figure 4. Pressure dependence of ln *k* relative to zero pressure for $Co(en)_3^{3+/2+}$ at 65.0 °C and $I = 0.5$ mol L^{-1}: solid curve, adiabatic ET with inclusion of the effect of pressure on the internal reorganization of the complexes,[5c] *a* set at 686 pm, and Fuoss ion pairing included; dashed curve, nonadiabatic ET with distance scaling factor $\alpha = 16$ nm^{-1} and other conditions as for solid curve (data taken from ref 6).

It should be stressed that the occurrence of direct adiabatic ET between the ground states of reactants in both the $Co(sep)^{3+/2+}$ and the $Co([9]aneS_3)_2^{3+/2+}$ exchanges does *not* imply that the rates of these reactions be comparable, since the Co–N bond distances differ markedly between Co^{III} and Co^{II} in the sepulchrate complexes (199 vs 216 pm)[16] whereas the Co–S lengths in the $Co([9]aneS_3)_2^{3+/2+}$ pair are less disparate (225 pm for Co^{III}–S and 236, 224, and 237 pm for the tetragonally distorted Co^{II} complex).[9,11] Thus, the $Co(sep)^{3+/2+}$ couple will be more susceptible than $Co([9]aneS_3)_2^{3+/2+}$ to Franck–Condon (internal reorganizational)[2] effects on the ET rate, and indeed *k* is some 2×10^4 times larger for the latter exchange reaction. No such significant difference shows up in ΔV^* for the $Co(sep)^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ exchanges, however, because the effect of pressure on the internal reorganizational contribution to *k* is too small.[5c,28]

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(26) Hamann, S. D. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2541.

(27) Binstead, R. A.; Beattie, J. K. *Inorg. Chem.* **1986**, *25*, 1481.

(28) A reviewer has pointed out that the marked tetragonal distortion of the Co–S unit in solid $[Co([9]aneS_3)_2](BF_4)_2 \cdot 2CH_3NO_2$[9] and the 3.3 ● 0.9 pm range in Co–N bond lengths in $[Co(sep)]S_2O_6 \cdot H_2O$[11] may imply higher polarizabilities for these Co^{II} complexes and hence larger ΔV_{IR}^* values for the corresponding $Co^{III/II}$ exchange reactions than are predicted by Stranks' calculations.[5c] These irregularities, however, may well reflect the presence of strong, highly directional lattice forces such as hydrogen bonding in the solids and are not necessarily relevant to the isotropic effects of hydrostatic pressure in solution. In any event, our point is that the experimental results for the $Co(sep)^{3+/2+}$ and $Co([9]aneS_3)_2^{3+/2+}$ self-exchange reactions are fully consistent with Marcus–Hush behavior if ΔV_{IR}^* is small ($\simeq 1$ cm^3 mol^{-1}).

It seems, then, that the Co(sep)$^{3+/2+}$ and Co([9]aneS$_3$)$_2{}^{3+/2+}$ self-exchange reactions can be taken to represent the adiabatic "norm" for Co$^{III/II}$ couples and that Co(en)$_3{}^{3+/2+}$ is distinctly nonadiabatic. Endicott and co-workers[29,30] have considered the problem of the relative reactivities of Co(sep)$^{3+/2+}$ and Co(en)$_3{}^{3+/2+}$ in detail and calculate a difference of 15 kJ mol^{-1} in the contributions of internal reorganization to the free energies of activation for the two exchange reactions, taking into account the small but significant difference in Δd (17 vs 21 pm, respectively) and the greater relaxation of nonbonded repulsions in the former reaction. This would account for a factor of about 400 in k and so suggests an electronic transmission coefficient of perhaps 10^{-2} in the latter couple, since the complexes are otherwise similar in size and charge type.

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(29) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.* **1983**, *30*, 141.

(30) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754.

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4- and 3-Cyanopyridine-Bridged Binuclear Complexes of Pentacyanoferrate and Pentaammineruthenium

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The binuclear complexes (CN)$_5$Fe(PyCN)Ru(NH$_3$)$_5{}^-$ (III) (4- and 3-isomers) were prepared by the substitution reactions of Ru(NH$_3$)$_5$NCPy^{2+} on Fe(CN)$_5$OH$_2{}^{3-}$. Complexes III undergo nitrile hydrolysis to give mixed-valence species of the form (CN)$_5$Fe(PyCONH)Ru(NH$_3$)$_5{}^-$ (IV) (4- and 3-isomers) when they are subjected to chemical oxidations of 1 equiv of peroxydisulfate. The results of UV-vis, IR, and electrochemical data suggest that complexes IV belong to a valence-trapped formulation containing the localized oxidation states Fe(II) and Ru(III). Rate constants of formation and dissociation of III and IV were measured, and the values of k_f ($\sim 10^3$ M^{-1} s^{-1}) and k_d ($\sim 10^{-3}$ s^{-1}) were consistent with kinetic results expected for the substitution of Fe(CN)$_5$OH$_2{}^{3-}$ with the divalent ligands. The kinetics of the nitrile hydrolysis were investigated, and it was found that the oxidized binuclear complexes III hydrolyze at a faster rate than the corresponding mononuclear Ru(III) complexes. Cyclic voltammetry of IV shows that the oxidation proceeds in two one-electron steps corresponding to [III,L,III] + e $\rightleftharpoons$ [II,L,III] and [II,L,III] + e $\rightleftharpoons$ [II,L,II]. The 4-isomer-bridged binuclear complex IV exhibits an intervalence band at 645 nm with molar absorbance 5.70 × 10^2 M^{-1} cm^{-1} and a half-width of 5100 cm^{-1}. The properties of the IT band are discussed on the basis of Hush's theory.

Since the preparation of the Creutz-Taube ion,[1] [(NH$_3$)$_5$RuPzRu(NH$_3$)$_5$]$^{5+}$ (I), the binuclear compounds based on the [Ru(NH$_3$)$_5{}^{3+/2+}$] couple have played a central role in the study of mixed-valence chemistry.[2,3] Series of both localized[4-8] and delocalized[9-11] systems have been prepared and examined spectroscopically and electrochemically. The electronic structure of the Creutz-Taube ion is still a matter of controversy.[12-18] Taking advantage of the similarity between the Ru(NH$_3$)$_5{}^{2+/3+}$ and Fe(CN)$_5{}^{3-/2-}$ moieties, we have prepared and characterized the heterobinuclear complexes [(CN)$_5$FePzRu(NH$_3$)$_5$]^n (n = -1, 0) (II).[19] The mixed-valence state of II contains valence-trapped Fe(II)/Ru(III) oxidation states. Recently, we have carried out some studies on binuclear complexes analogous to II, but using 4- and 3-cyanopyridines as bridging ligands, [(CN)$_5$FePyCNRu(NH$_3$)$_5$]^n (n = -1, 0) (III). The mixed-valence states of III for both bridge ligands are unstable with respect to ligand hydrolysis, which gives the final species in the form [(CN)$_5$Fe^{II}PyCONHRu^{III}(NH$_3$)$_5$] (4- and 3-isomers) (IV). We wish to report herein our studies of the spectroscopic, kinetic, and electrochemical properties of the binuclear complexes III and IV, with emphasis on the characterization of the mixed-valence species IV. A study of the binuclear complex III with the 4-cyanopyridine bridge ligand has recently been reported briefly.[20] However, the results are restricted to the solid-state form, and nothing has been reported concerning the mixed-valence species.

Experimental Section

Materials. Chloropentaammineruthenium(III) chloride[21] and sodium amminepentacyanoferrate(II) trihydrate[22,23] were prepared according to the cited literature methods. 4- and 3-cyanopyridines were purchased from Fluka and were recrystallized from ethanol before use. 4-Cyano-N-methylpyridinium iodide ((4-NCPyCH$_3$)I) was prepared by adding 3 g of 4-cyanopyridine to a solution containing 10 mL of neat methyl iodide and 50 mL of anhydrous diethyl ether. The resulting solution was mixed well and stored in the dark for 1 week to allow the reaction to proceed to completion. The orange-yellow precipitate thus formed was filtered out, washed with ethanol, and dried in a vacuum desiccator overnight. Yield: 5.9 g. Anal. Calcd for C$_7$H$_7$N$_2$I: C, 34.2; N, 11.4; H, 2.87.

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(1) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(2) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(3) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.

(4) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(5) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(6) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.

(7) Tanner, M.; Ludi, A. *Inorg. Chem.* **1981**, *20*, 2348.

(8) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(9) Tom, G. M.; Taube, H. *Inorg. Chem.* **1975**, *97*, 5310.

(10) Krentzien, K.; Taube, H. *Inorg. Chem.* **1982**, *21*, 4001.

(11) Richardson, D. E.; Sen, J.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136.

(12) Furholz, U.; Burgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.

(13) Stebler, A.; Ammeter, J. H.; Furholz, U.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 2764.

(14) Krausz, E.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 939.

(15) Joss, S.; Burgi, H. B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 949.

(16) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179.

(17) Krausz, E. R.; Man, A. W. H. *Inorg. Chem.* **1986**, *25*, 1484.

(18) Zhang, L. T.; Ko, J.; Ordrechen, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 1666.

(19) Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *107*, 369.

(20) Cutin, E. H.; Katz, N. E. *Polyhedron* **1987**, *6*, 159.

(21) Vogt, L. H.; Katz, J. L.; Wiberly, S. E. *Inorg. Chem.* **1965**, *4*, 1158.

(22) Brauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic Press: New York, 1965,; Vol. II, p 1511.

(23) Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.

0020-1669/91/1330-1862$02.50/0