of the complex. Inasmuch as such transitions are usually from the highest occupied MO in the complex to an empty orbital of suitable symmetry on the ligand, they can in principle be related to the complete removal of the electron and hence to $E_{1/2}$. Although linear correlations between $E_{1/2}$ and the energy of the MLCT have been found to hold when limited to complexes containing related ligands,[4] they do not apply when ligands of widely varying types are considered as illustrated in Table VI. In the cases where the energy of the MLCT in the Ru(H_2edta) complexes can be compared to that of analogous tetraammine complexes, the electrons in the Ru(edta) center appear to be more firmly bound than in the $Ru(NH_3)_4$ moiety. This is in conflict with the relative ease of oxidation of some of the complexes as seen above.

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Registry No. [Ru(Hedta)Cl]K, 14741-19-6; Ru(H_2edta)$(C_5H_5N)_2$, 85661-97-8; Ru(H_2edta)$(C_6H_7N)_2$, 85661-98-9; Ru(H_2edta)$(C_{12}H_8N_2)$, 85661-99-0; Ru(H_2edta)$(C_{10}H_8N_2)$, 85662-00-6; [Ru(H_2edta)$(C_4H_7N_2O_2)$]K, 85662-01-7; Ru(H_2edta)$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]$, 85662-02-8; [Ru(Hedta)(NCS)]K_2, 85662-03-9; Ru(Me_2edta)$(C_5H_5N)_2$, 85662-04-0; [Ru(Meedta)CO]K, 85662-05-1; [Ru(Hedta)CO]K, 76095-15-3; [Ru(H_2edta)$(NCS)_2$]K, 85662-06-2; Ru(H_2edta)($CH_3COCHCOCH_3$), 85662-07-3; Ru(H_2edta)$(C_4H_7N_2O_2)$, 85662-08-4; Ru[(*p*-$CH_3C_6H_4NHCO)_2C_8O_4N_2H_{12}$](py)$_2$, 85662-09-5; [Ru(edta)(dtc)]Na_2, 85662-10-8; Ru(H_2edta)(NO)Cl, 76058-09-8; Ru(H_2edta)$(1,2\text{-}C_6H_4(CN)_2)_2$, 76058-11-2; Ru($H_2$edta)$(C_6H_5CN)_2$, 76068-58-1; Ru($H_2$edta)$(CH_3CN)_2$, 76058-10-1; Ru(edta)$(N_2)^{2-}$, 85717-53-9; (Ru(edta))$N_2^{4-}$, 85718-10-1; Ru($H_2$edta)(NCS)($H_2O$), 85662-11-9; Ru(Hedta)$H_2O$, 15282-93-6; Ru(Hedta)($N_3$), 85662-12-0.

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Assisted Aquation of Chloropentaamminecobalt(III) Ion in Different Media

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The product ratios from competition reactions accompanying the Hg^{2+}-assisted removal of Cl^- from $Co(NH_3)_5Cl^{2+}$ in aqueous solutions of $NaNO_3$, $NaHSO_4$, H_3PO_4 and CH_3CO_2H and in three water + nonaqueous solvent mixtures were determined at 0, 25, and 55 °C. The temperature dependence of these ratios was very small or undetectable outside of experimental error. An I_d interchange of leaving and incoming ligands was postulated which adequately explains the observed data. In mixtures of water with one of the nonaqueous solvents dimethyl sulfoxide, *N*,*N*-dimethylformamide, or acetonitrile the product ratios were equal for equal bulk mole fraction of nonaqueous solvent. This result was interpreted to mean that, at equal bulk mole fraction, the three nonaqueous solvents were equally available in the solvation shell of the encounter complex preceding the formation of products and that complete, preferential solvation by one solvent component did occur in some solvent mixtures but not in others.

Introduction

The question concerning the existence of the five-coordinate pentaamminecobalt(III) complex has been an intriguing one. If this complex exists, it is most likely formed in one or more of the so-called assisted aquations shown in reactions[1-4] 1–4

$$CoN_3^{2+} + HNO_2 + H^+ \rightarrow CoOH_2^{3+} + N_2 + N_2O \qquad (1)$$

$$CoX^{2+} + Hg^{2+} + H_2O \rightarrow CoOH_2^{3+} + HgX^+ \qquad X^- = Cl^-, Br^-, I^- \qquad (2)$$

$$Co(O_2CNH_2)^{2+} + HNO_2 + H^+ \rightarrow CoOH_2^{3+} + CO_2 + N_2 + H_2O \qquad (3)$$

$$Co(OS(CH_3)_2)^{3+} + MnO_4^- \rightarrow CoOH_2^{3+} + (CH_3)_2SO_2 + \text{other products} \qquad (4)$$

(Co represents the $Co(NH_3)_5$ group in these and subsequent equations) rather than in the unassisted substitution reactions.[5,6] These reactions are still being actively studied.[7-10] Attempts to detect the possible five-coordinate intermediate $Co(NH_3)_5^{3+}$ involve trapping it with nucleophilic competition reactions. If $Co(NH_3)_5^{3+}$ exists sufficiently long to qualify as an intermediate in these competition reactions, then it survives sufficiently long to experience loss of the leaving group from its solvation shell and a change in the composition of its solvation shell from diffusional processes. Hence, it can meet and react with nucleophiles not originally present in that solvation shell and the mechanism of ligand exchange is D. If $Co(NH_3)_5^{3+}$ does not exist sufficiently long to experience the change of composition in, or loss of leaving group from, the solvation shell, then it must react with a component in its solvation shell and the mechanism of ligand exchange is I_d. If loss of leaving ligand from the solvation shell and a change in the composition of the solvation shell occur on much different time scales, then, for example, the leaving ligand could be retained in the solvation shell to influence the product ratio while diffusional processes are bringing nucleophiles into the solvation shell for reaction with the vacant first-coordination-shell site. This might happen when the leaving ligand is so large and/or heavy as to be slow moving compared to the entering nucleophiles. In this case, the reaction mechanism would be borderline between D and I_d and would appear to be I_d because of the influence of leaving ligand on the product ratio.

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These assisted substitution reactions have recently been discussed[10] in terms of three different models. The models are presented below with reaction 2 and the competition between NO_3 and H_2O as an example. I_1 and I_2 are intermediates in the two paths; formation of I_1 does not require involvement of NO_3^- whereas formation of I_2 does. Although I_2 requires NO_3^- in the activated complex for its formation, I_2 may or may not contain NO_3^-; however, in either case, it must encounter NO_3^- in reaction 9 in order to form $CoNO_3^{2+}$.

Model 1

path 1

$$CoL^{2+} + Hg^{2+} \xrightarrow{k_1} I_1 \quad \text{(rate determining)} \tag{5}$$

$$I_1 + NO_3^- \xrightarrow{k_{1N}} CoNO_3^{2+} \quad \text{(fast)} \tag{6}$$

$$I_1 \xrightarrow{k_{1w}} CoOH_2^{3+} \quad \text{(fast)} \tag{7}$$

path 2

$$CoL^{2+} + Hg^{2+} + NO_3^- \xrightarrow{k_2} I_2 \quad \text{(rate determining)} \tag{8}$$

$$I_2 + NO_3 \xrightarrow{k_{2N}} CoNO_3^{2+} \quad \text{(fast)} \tag{9}$$

$$I_2 \xrightarrow{k_{2w}} CoOH_2^{3+} \quad \text{(fast)} \tag{10}$$

The fraction of the reactant CoL^{2+} converted to $CoNO_3^{2+}$ is given by eq 11 and the fraction to $CoOH_2^{3+}$ by eq 12. By

$$F_{CoNO_3} = \frac{k_1}{k_1 + k_2[NO_3^-]}\,\frac{k_{1N}[NO_3^-]}{k_{1w} + k_{1N}[NO_3^-]} + \frac{k_2[NO_3^-]}{k_1 + k_2[NO_3^-]}\,\frac{k_{2N}[NO_3^-]}{k_{2w} + k_{2N}[NO_3^-]} \tag{11}$$

$$F_{CoOH_2} = \frac{k_1}{k_1 + k_2[NO_3^-]}\,\frac{k_{1w}}{k_{1w} + k_{1N}[NO_3^-]} + \frac{k_2[NO_3^-]}{k_1 + k_2[NO_3^-]}\,\frac{k_{2w}}{k_{2w} + k_{2N}[NO_3^-]} \tag{12}$$

setting $R_1 = k_{1N}/k_{1w}$ and $R_2 = k_{2N}/k_{2w}$, one can express the product ratio by eq 13. The experimental data[10] fit eq 13 for

$$\frac{[CoNO_3^{2+}]}{[CoOH_2^{3+}]} = \frac{F_{CoNO_3}}{F_{CoOH_2}} = [NO_3^-] \times \left\{\frac{k_1R_1(1 + R_2[NO_3^-]) + k_2R_2[NO_3^-](1 + R_1[NO_3^-])}{k_1(1 + R_2[NO_3^-]) + k_2[NO_3^-](1 + R_1[NO_3^-])}\right\} \tag{13}$$

reaction 1 with $R_1 = R_2 = 0.40_5$ and for reaction 2 with $R_1 = 1.06$ and $R_2 = 0.59$.

The comments made concerning I_1 in Model 1 apply for Model 2 as well. The intermediate I_2 collapses to form $CoNO_3^{2+}$ and $CoOH_2^{3+}$ in simultaneous, parallel reactions. The overall product ratio is given by eq 15. The experimental

$$\frac{[CoNO_3^{2+}]}{[CoOH_2^{3+}]} = [NO_3^-]\left\{\frac{k_1R_1(1 + R_2) + k_2R_2(1 + R_1[NO_3^-])}{k_1(1 + R_2) + k_2[NO_3^-](1 + R_1[NO_3^-])}\right\} \tag{15}$$

data fit eq 15 with[10] $R_1 = 0$ and $R_2 = 4.0$ for reaction 1 and with $R_1 = 0.46$ and $R_2 = 1.6$ for reaction 2.

Model 2

path 1

same three reactions as given in Model 1, path 1

path 2

$$CoL^{2+} + Hg^{2+} + NO_3^- \xrightarrow{k_2} I_2 \quad \text{(rate determining)} \tag{8}$$

$$I_2 \xrightarrow{k_{2N}} CoNO_3^{2+} \quad \text{(fast)} \tag{14}$$

$$I_2 \xrightarrow{k_{2w}} CoOH_2^{3+} \quad \text{(fast)} \tag{10}$$

In Model 3 intermediate I_1 can collapse to form $CoOH_2^{3+}$ as in Models 1 and 2. It can also form $CoNO_3^{2+}$ in two or more steps at a rate that is independent of NO_3^- concentration and that is characterized by k_{1N}. I_1 (which does not contain NO_3^-) cannot form $CoNO_3^{2+}$ in one elementary step at a rate independent of NO_3^- concentration.

Model 3

path 1

$$CoL^{2+} + Hg^{2+} \xrightarrow{k_1} I_1 \quad \text{(rate determining)} \tag{5}$$

$$I_1 \xrightarrow{k_{1N}} CoNO_3^{2+} \quad \text{(fast)} \tag{16}$$

$$I_1 \xrightarrow{k_{1w}} CoOH_2^{3+} \quad \text{(fast)} \tag{7}$$

path 2

same three reactions as given in Model 2, path 2

Intermediate I_2, as in Model 2, can contain NO_3^- and can collapse to either $CoNO_3^{2+}$ or $CoOH_2^{3+}$.

The overall product ratio for Model 3 is given by eq 17.

$$\frac{[CoNO_3^{2+}]}{[CoOH_2^{3+}]} = \frac{k_1R_1(1 + R_2) + k_2R_2(1 + R_1)[NO_3^-]}{k_1(1 + R_2) + k_2(1 + R_1)[NO_3^-]} \tag{17}$$

The experimental data fit[10] eq 17 with $R_1 = 0$ and $R_2 = 4.0$ for reaction 1 and with $R_1 = 0.02$ and $R_2 = 45.0$ for reaction 2.

The experimental data for reactions 1 and 2 do not simultaneously fit any one model with the same values of R_1 ($=k_{1N}/k_{1w}$) and R_2 ($=k_{2N}/k_{2w}$). Hence, the two reactions cannot be forming the same intermediates in paths 1 and 2 in any one of the three cases. For example, the intermediate I_1 in Model 1 for reaction 1 has the ratio $k_{1N}/k_{1w} = 0.40$ whereas for reaction 2 it has $k_{1N}/k_{1w} = 1.06$. The same intermediate, for example, $Co(NH_3)_5^{3+}$, existing sufficiently long to change its solvent cage and admit NO_3^- via diffusional processes as in reaction 6 cannot exist in both reaction 1 and reaction 2. (It is most unlikely that the two I_1's differ because $Co(NH_3)_5^{3+}$ is square pyramidal in one reaction and trigonal bipyramidal in the other since there is retention of configuration in both reactions.[11]) The most probable reason for the different I_1's is that the leaving groups are still present near the vacated first-coordination-shell site with either weak partial bonds or no bonds to Co(III) when the products in reactions 6 and 7 are formed. The experimental evidence[8] strongly indicates that there is no detectable partial bond formed between Co(III) and a variety of entering ligands for reaction 1. Hence, $Co(NH_3)_5^{3+}$ is a distinct possibility for intermediates I_1 and I_2 in that reaction. It remained to be seen whether reaction 2 had any such detectable Co(III)–entering ligand weak partial bond formation distinguishing its intermediates from those of reaction 1. Here we report on efforts to detect

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Table I. Product Ratios as a Function of Temperature, Concentration, and Ionic Strength, $\mu(NaClO_4)$

compd	[compd]/ M	μ/M	t/°C	%[a] $CoL^{(3-1)+}$	$[CoL^{(3-1)+}]$/ $[CoOH_2{}^{3+}]$[a]
$NaNO_3$	0.500	2.00	0	13.5 ± 0.3	0.157 ± 0.005
			25	13.9 ± 0.3	0.161 ± 0.004
			55	14.2 ± 0.3	0.166 ± 0.005
	1.00	2.00	0	26.9 ± 0.4	0.370 ± 0.009
			25	26.6 ± 0.9	0.363 ± 0.017
			55	27.1 ± 0.5	0.374 ± 0.008
	2.00	3.00	0	42.9 ± 0.2	0.751 ± 0.006
			25	41.7 ± 0.7	0.721 ± 0.029
			55	41.1 ± 0.5	0.701 ± 0.017
	3.00	4.00	0	50.0 ± 0.5	1.00 ± 0.02
			25	50.9 ± 0.7	1.05 ± 0.03
			55	51.8 ± 0.7	1.08 ± 0.03
$NaHSO_4$	0.500	2.00	0	19.1 ± 0.4	0.237 ± 0.006
			25	18.1 ± 0.4	0.221 ± 0.006
			55	18.4 ± 0.4	0.226 ± 0.006
	1.00	2.00	0	22.4 ± 0.4	0.289 ± 0.007
			25	23.0 ± 0.5	0.299 ± 0.010
			55	23.5 ± 0.5	0.299 ± 0.010
	2.00	3.00	0	28.6 ± 0.5	0.404 ± 0.011
			25	29.0 ± 0.7	0.410 ± 0.015
			55	29.3 ± 0.8	0.416 ± 0.016
	3.00	4.00	0	38.9 ± 0.7	0.641 ± 0.018
			25	37.6 ± 0.7	0.606 ± 0.014
			55	37.3 ± 0.7	0.601 ± 0.014
H_3PO_4	1.00	2.00	0	4.34 ± 0.16	0.046 ± 0.002
			25	4.92 ± 0.18	0.052 ± 0.002
			55	5.18 ± 0.21	0.055 ± 0.002
	2.00	2.00	0	6.21 ± 0.12	0.067 ± 0.002
			25	6.97 ± 0.17	0.076 ± 0.003
			55	7.78 ± 0.22	0.085 ± 0.004
CH_3CO_2H	1.00	2.00	0	4.19 ± 0.13	0.044 ± 0.002
			25	4.56 ± 0.20	0.048 ± 0.002
			55	5.26 ± 0.30	0.055 ± 0.003
	2.00	2.00	0	5.21 ± 0.21	0.055 ± 0.003
			25	5.80 ± 0.17	0.062 ± 0.002
			55	6.82 ± 0.28	0.074 ± 0.003

[a] Standard deviation for a single measurement from four measurements.

such interactions in the intermediates of reaction 2.

Experimental Section

Reagents. The aquo-,[14] chloro-,[15] (nitrato)-,[16] (sulfato)-,[17] (phosphato)-,[18] (acetato)-,[19] (*N,N*-dimethylformamide)-,[20] (dimethyl sulfoxide)-,[21] and (acetonitrile)pentaamminecobalt(III)[4] perchlorates were prepared by literature methods. The observed λ_{max} (nm) values and molar extinction coefficients (ϵ_{max}, M^{-1} cm^{-1}) of these compounds respectively were 490 (48.0), 532 (50.6), 500 (57.2), 515 (61.0), 519.5 (51.6) for $Co(NH_3)_5OPO_3H_3{}^{3+}$, 505 (74.0), 505 (79.8), 516 (62.3), and 465 (60.8), which are all in good agreement with literature values and were used in the quantitative determination of these compounds. All other chemicals were reagent grade and were used without further purification.

Competition Reaction Product Ratios. A known amount of the chloro complex (usually 0.150 mmol) was dissolved in a predetermined volume of the competition reaction medium thermostated at the desired temperature. A twofold excess of $Hg(ClO_4)_2$ solution at the same temperature was added quickly by syringe and the assisted aquation reaction allowed to go to completion. The reaction mixture was quenched by pouring onto crushed ice, diluted, and passed onto a column of AG50W-X4, 200–400 mesh resin cooled by circulating ice water. The adsorbed products were eluted with 1 M $HClO_4$ for 1+ complexes and 2 M $HClO_4$ for separation of 2+ and 3+ complexes and then 3 M $HClO_4$ for the quick elution of the 2+ species. The aquo and acetonitrile complexes were separated with use of 2.5 M H_2SO_4 for the former and 4 M H_2SO_4 for the latter; the aquo and dimethyl sulfoxide complexes were separated in the same way. The aquo and dimethylformamide complexes were separated with 2 M HCl and then 4 M HCl to elute the former and 3 M $HClO_4$ to elute the latter. The eluted products were collected in an ice bath, brought to room temperature, diluted to volume, and determined spectrophotometrically. The absorbance of the eluted aquo complex was measured at 508.5 nm (45.9 M^{-1} cm^{-1}), the isosbestic point of the aquo and chloro complexes, as well as 490 nm so as to determine whether any anation by Cl^- had occurred on elution with HCl; none was detected.

Table II. Percentage $Co(NH_3)_5S^{3+}$ Formed in Water + Nonaqueous Solvent Mixtures as a Function of Temperature and Mole Fraction of Nonaqueous Solvent

nonaqueous solvent, S	X_S[a]	t/°C	%[b] $Co(NH_3)_5S^{3+}$
DMF	0.10	0	10.1 ± 0.8
		25	10.4 ± 0.3
		55	10.0 ± 0.3
	0.20	0	15.4 ± 0.4
		25	14.8 ± 0.3
		55	15.2 ± 0.2
	0.30	0	18.3 ± 0.3
		25	18.2 ± 0.5
		55	19.6 ± 0.5
Me_2SO	0.10	0	9.4 ± 0.4
		25	9.2 ± 0.2
		55	10.0 ± 0.4
	0.20	0	14.7 ± 0.6
		25	15.1 ± 0.5
		55	14.6 ± 0.5
	0.30	0	19.0 ± 0.5
		25	18.8 ± 0.6
		55	19.5 ± 0.9
CH_3CN	0.10	0	10.9 ± 0.3
		25	11.2 ± 0.3
		55	10.3 ± 0.5
	0.20	0	15.0 ± 0.3
		25	14.8 ± 0.3
		55	14.9 ± 0.3
	0.30	0	19.6 ± 0.5
		25	18.2 ± 0.3
		55	20.0 ± 0.4

[a] Mole fraction. [b] Standard deviation for a single measurement from four measurements.

Ionic strength was varied by addition of $NaClO_4$. Since the exact extent of ionization of HSO_4^-, H_3PO_4, and CH_3CO_2H in these solutions is not known, the ionic strength of the solutions cannot be calculated exactly. However, the concentrations of the products of the ionizations are small and will not contribute importantly.

Results and Discussion

The product ratios obtained under various conditions for solutions of $NaNO_3$, $NaHSO_4$, H_3PO_4, and CH_3CO_2H are given in Table I; those for mixtures of dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (DMF), and acetonitrile (CH_3CN) with water are given in Table II. The degrees of ionization of HSO_4^-, H_3PO_4, and CH_3CO_2H change somewhat with temperature. For example, $\Delta H° = -5200$ cal/mol and $\Delta S° = -26.6$ cal/K mol for the acid ionization of HSO_4^- at zero ionic strength so that $K_a = 2.34 \times 10^{-2}$ M at 0 °C and 4.69×10^{-3} M at 55 °C. Hence, in a solution containing 0.0500 M $HClO_4$ and 0.500 M $NaHSO_4$ the equilibrium concentrations of SO_4^{2-} and HSO_4^- are 0.08 and 0.42 M, respectively, at 0 °C and 0.03 and 0.47 M, respectively, at 55 °C. In more concentrated solutions containing 1.00, 2.00, and 3.00 M $NaHSO_4$ the percentage ionization is, of course, much less. For H_3PO_4 and CH_3CO_2H, which have smaller ionization constants than HSO_4^-, the ionization percentages are much smaller. Therefore, there is relatively little change in the concentrations of the major species present due to changing temperature at a given total concentration.

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From Tables I and II it is seen that the product ratios are essentially independent of temperature for each nucleophile listed. This temperature independence means that the following statements apply.

1. k_{1L}/k_{1w} for the intermediate I in path 1 is temperature independent for all nucleophiles L so that the product ratio coming out of path 1 remains unchanged by T changes.

2. k_{2L}/k_{2w} for the intermediate I_2 in path 2 is temperature independent for all nucleophiles L so that the product ratio coming out of path 2 remains unchanged by T changes.

3. Either the product ratios as given in eq 13, 15, and 17 do not depend upon the ratio k_1/k_2 or this ratio is temperature independent so that the relative contributions of paths 1 and 2 to the product ratio do not change with temperature. (It is possible but unlikely that all three rate constant ratios change considerably but change in such a way as to cancel completely.) The ratio k_1/k_2 affects only the ratio of path 1 to path 2; it does not affect the reactions between intermediates I_1 and I_2 and incoming ligands and will not be discussed further here.

The temperature independence of k_{1L}/k_{1w} means that $\Delta H^\ddagger_{1L} = \Delta H^\ddagger_{1w}$; likewise the temperature independence of k_{2L}/k_{2w} means that $\Delta H^\ddagger_{2L} = \Delta H^\ddagger_{2w}$. This very important result means that the activation enthalpy for forming $CoL^{2+(3+)}$ is equal to the activation enthalpy for forming $CoOH_2^{3+}$ in path 1 and also in path 2. We believe that $\Delta H^\ddagger_{1L} = \Delta H^\ddagger_{1w}$ and $\Delta H^\ddagger_{2L} = \Delta H^\ddagger_{2w}$ as a result of zero bonding between Co(III) and incoming L and between Co(III) and incoming H_2O in the activated complexes from which the products are formed for the following reason. Reaction 7 forming $CoOH_2^{3+}$ from intermediate I_1 does not involve L either as a part of I_1 or as a reactant. Hence $\Delta H^\ddagger_{1w}$ will not depend on the L present in solution. However, $\Delta H^\ddagger_{1w} = \Delta H^\ddagger_{1L}$ for every L used. Thus it is likely that there is no partial bonding between Co(III) and L contributing to $\Delta H^\ddagger_{1L}$.

A similar argument based on $\Delta H^\ddagger_{2w} = \Delta H^\ddagger_{2L}$ leads to the conclusion that there is also no partial bonding between Co(III) and L contributing to $\Delta H^\ddagger_{2L}$ if L is not present in I_2. (The fact that L is present in the activated complex from which I_2 is formed does not mean that L is present in I_2.) If L is present in I_2, it is still unlikely that all incoming L groups contribute the same to $\Delta H^\ddagger_{2L}$ as H_2O does to $\Delta H^\ddagger_{2w}$ so that $\Delta H^\ddagger_{2L} = \Delta H^\ddagger_{2w}$ for every L. A reasonable interpretation of the experimental results is that there is zero bonding between Co(III) and incoming L or H_2O in reaction 2 just as is the case for reaction 1.[8] Hence the two assisted substitution reactions (1) and (2) do not have different R_1 ($=k_{1L}/k_{1w}$) and R_2 ($=k_{2L}/k_{2w}$) values by virtue of zero bonding in reaction 1 and some partial bonding in reaction 2. The rate constant ratio R_1 is different in reactions 1 and 2, as is R_2, for another reason. Both reaction 1 and reaction 2 are the same in that one ligand of the starting complex is being released to leave behind a $Co(NH_3)_5^{3+}$ moiety which has no detectable bonding to incoming ligands appearing in the products. The most reasonable, and likely, manner in which reactions 1 and 2 can differ is that the leaving group in one or both reactions remains in the solvation shell of $Co(NH_3)_5^{3+}$ to influence the product ratio $[CoL^{2+(3+)}]/[CoOH_2^{3+}]$ formed. Because $R_1 = R_2$ in reaction 1, it is possible that $I_1 = I_2 = Co(NH_3)_5^{3+}$ in that reaction. In reaction 2 $I_1 \neq I_2 \neq Co(NH_3)_5^{3+}$ because $R_1 \neq R_2$ and neither R value is equal to the two equal R values of reaction 1. In reaction 2 it is probably the heavy $ClHg^+$ leaving group that remains in the solvation shell of $Co(NH_3)_5^{3+}$ in I_1 and I_2 to influence the product ratios. In this sense the mechanism of the substitution of leaving group for an entering group appears to be I_d. However, I_1 must live sufficiently long to acquire an L (NO_3^- in reaction 6 of Models 1 and 2) by diffusional processes so that $CoL^{2+(3+)}$ may be formed. In this sense the mechanism of the substitution appears to be D. The leaving group $ClHg^+$ (which is certainly solvated to a certain extent) is heavy compared to most entering nucleophiles and may retain its place in the solvation shell of the $Co(NH_3)_5^{3+}$ moiety while allowing some diffusional processes to change parts of the solvation shell. In this sense reaction 2 involves an overlapping I_d and D mechanism.

The data of Table II give a second very interesting result for water + nonaqueous solvent mixtures. They show that, at a given mole fraction of nonaqueous solvent S, the product ratio $[CoS^{3+}]/[CoOH_2^{3+}]$ is the same for all three nonaqueous solvents. The substitution of Cl^- by S and by H_2O probably occurs through the formation of a dinuclear complex in equilibrium 18 followed by rate-determining steps 19 and 20.

$$CoCl^{2+} + Hg^{2+} \underset{}{\overset{K_{dc}}{\rightleftharpoons}} CoClHg^{4+} \tag{18}$$

$$CoClHg^{4+} + S \xrightarrow{k_s} CoS^{3+} + HgCl^+ \tag{19}$$

$$CoClHg^{4+} + H_2O \xrightarrow{k_w} CoOH_2^{3+} + HgCl^+ \tag{20}$$

In reactions 19 and 20 the solvated $CoClHg^{4+}$ is the encounter complex and S and H_2O are derived from the solvation shell around $CoClHg^{4+}$ in the transition state as deactivation to products occurs. Whether or not the exchange is I_d, D, or borderline between the two, the three nonaqueous solvents are approximately equally available in this solvation shell. This is strong evidence that the solvation shell around the complex, be it $(NH_3)_5CoClHg^{2+}$ or $Co(NH_3)_5^{3+}$ from which the products are formed, contains *both* solvent components in a ratio determined by the bulk solvent composition. The mole fraction of S in the solvation shell is approximately the same for all three S groups at any one bulk mole fraction of S although the mole fraction of S in the solvation shell need not be the same as the bulk mole fraction of S. This is an important result. Glavaš, Seif El-Nasr, and Reynolds[13] have reasoned that the experimental evidence from solvent interchange reactions shows that the $Co(NH_3)_5^{3+}$ group does not rotate within its solvation shell provided preferential solvation does not lead to exclusive occupancy of all solvation shell sites by one solvent component. The facts that the product ratios for Me_2SO, DMF, and CH_3CN are equal for each bulk mole fraction of S suggest strongly that the three S groups are equally available in the solvation shell of the encounter complex preceding CoS^{3+} and $CoOH_2^{3+}$ formation and that the occupancy of the solvation shell by S increases with increasing bulk mole fraction of S. These facts are consistent with the interpretation[13] that both water and S share the solvation shell sites and that S occupies an increasing fraction of these sites as the bulk mole fraction of S increases.

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