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# Intermediates in Assisted-Aquation Reactions of Ligandopentaamminecobalt(III) Complexes

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Product ratios from competition reactions accompanying the assisted aquations of $[Co(NH_3)_5(OS(CH_3)_2)]^{3+}$ by $MnO_4^-$ and of $[Co(NH_3)_5N_3]^{2+}$ by nitrous acid show that different intermediates produce the final products in the two systems. Product ratios determined under different conditions in aqueous media, in ethanol–water media, in three-way competition studies, and in temperature-dependence studies are more consistent with the formation of the final products by interchange ($I_d$) processes, rather than by dissociation (D) processes, of the intermediates $[Co(NH_3)_5(O_2S(CH_3)_2)]^{3+}$ and $[Co(NH_3)_5N_4O]^{3+}$.

## Introduction

The evidence obtained from several studies[2,3] of base hydrolysis of $MX^{2+}$ ($M^{3+} = Co(NH_3)_5^{3+}$; $X^- = Cl^-, Br^-, I^-, NO_3^-, SCN^-, CH_3SO_3^-, NO_2C_6H_4SO_3^-$, and $CF_3SO_3^-$) in the presence of competing nucleophiles has led to a conclusion that a common five-coordinate intermediate, $[Co(NH_3)_4NH_2]^{2+}$, was formed in these reactions. However, a recent study[4] has shown that the postulate of a single five-coordinate intermediate was inadequate to explain the product ratios formed from different starting complexes and that an experimentally significant proportion of the base hydrolysis occurred through an intermediate which still retained a memory of the leaving group. Apparently the conjugate-base form of the starting complex gave products, partially if not entirely, through $I_d$,[5] rather than D,[5] reactions. In a $I_d$ reaction the leaving group must be present in the activated complex for product formation (since it is the entering group in the reverse reaction), and hence it can influence the product ratios of competition reactions by its presence there. In a D reaction, the leaving group will not be present in the activated complexes leading to the formation of competition-reaction products because the intermediate of a lower coordination number has existed sufficiently long to change the solvation shell or cage in which it was formed. The leaving group, if present in the reaction mixture only by virtue of its displacement from the original reactant, will be unable to influence the product ratios of competition reactions. If the five-coordinate intermediate is so reactive that it must react with components of its solvation shell before the leaving group has escaped from this shell, then the process is by definition[5] $I_d$, not D.

The evidence obtained from studies of the assisted aquations of[6,7] $MN_3^{2+}$ and of[7] $M(O_2CNH_2)^{2+}$ by nitrous acid and of[7] $MX^{2+}$ ($X^- = Cl^-, Br^-, I^-$) by Hg(II) has led to the conclusion that a common five-coordinate intermediate $M^{3+}$ was formed in all these reactions.[8,9] Thus, when the assisted aquations of these complexes were carried out in nitric and sulfuric acid media, the product ratios $[MNO_3^{2+}]/[MOH_2^{3+}]$ and $[MSO_4^+]/[MOH_2^{3+}]$, respectively, were very nearly equal for a given acid concentration as they should be for a common intermediate. However, it has been shown[10] that the assisted aquation of $MCl^{2+}$ by Hg(II) in sulfate media proceeded by paths involving $Hg^{2+}$, $HgSO_4$, and $Hg(SO_4)_2^{2-}$ with intermediates having approximately 0, 15, and 30% efficiencies, respectively, for conversion to $MSO_4^+$ independent of sulfate concentration. Since the efficiency of conversion of $M^{3+}$ (presumably) to $MSO_4^+$ in the nitrosation reactions was dependent on the sulfate concentration, the intermediates in the Hg(II)-assisted aquations could not have been $M^{3+}$. There is some uncertainty in this conclusion because the kinetic studies were not carried out at the same high concentrations as the competition reactions.

Similarly the Hg(II)-assisted aquation of $MCl^{2+}$ in nitrate media proceeded[11] by paths involving $Hg^{2+}$ and $HgNO_3^+$ with intermediates having approximately 2 and 98% efficiencies, respectively, for conversion to $MNO_3^{2+}$ independent of nitrate concentration. Consequently neither intermediate can be the same as the one in the nitrosation reactions.

Assisted-aquation studies of $M(Me_2SO)^{3+}$ ($Me_2SO$ = dimethyl sulfoxide) by $MnO_4^-$ have provided product ratios approximately equal to those from $MN_3^{2+}$ in chloride, bromide, and nitrate media[12] and led to the conclusion that $M^{3+}$ was also formed as an intermediate in this assisted aquation. However, this conclusion is now in doubt. Here we report further inquiries into the question of the occurrence and nature of common intermediates in assisted-aquation reactions.

## Experimental Section

**Reagents.** The substrates $[Co(NH_3)_5N_3](ClO_4)_2$,[13] $[Co(NH_3)_5(Me_2SO)](ClO_4)_3$,[14] and $[Co(NH_3)_5Cl](ClO_4)_2$[15] were prepared by literature methods. The bromo-,[16] nitrato-,[17] sulfato-,[18] phosphato-,[19] aquo-,[20] acetonitrile-,[12] and (*N,N*-dimethylformamide)pentaamminecobalt(III)[21] complexes were prepared by literature methods and converted to perchlorate salts by repeated recrystallization from aqueous perchlorate media. The observed $\lambda_{max}$ (nm) and molar extinction coefficients ($M^{-1}$ $cm^{-1}$) of the ten compounds respectively were 518 (266), 515 (62.3), 532 (50.4), 550 (57.7), 500 (57.4), 515 61.0), 519.5 (51.6), 490 (48.0), 465 (61.0), and 505 (80.0), all in very good agreement with literature values. In addition the value of 45.9 $M^{-1}$ $cm^{-1}$ was used for the aquo complex at 508.5 nm, the isosbestic point for the aquo and chloro complexes, to determine whether or not any aquo complex had been converted to the chloro complex during elution with 4 M HCl; no measureable conversion was ever detected.

All other chemicals were reagent grade and were used without further purification. Deionized water was used in all solutions.

**Competition Reaction Product Ratios.** A known amount, usually 0.1–0.15 mmol, of the substrate was placed in a reaction vessel, known volumes of stock solutions were added to give the desired reaction medium, and the solution was brought to the desire temperature within 15 min with stirring (in the absence of light in the case of the azido complex). To start the assisted aquations, we added a known amount (twofold excess) of solid $NaNO_2$ to the reaction mixture in the case of the azido substrate or known volumes of standard $KMnO_4$ or $Hg(ClO_4)_2$ solutions in the case of the $Me_2SO$ and chloro substrates, respectively. When the $M(Me_2SO)^{3+}$ reaction was complete, a small excess of $NaNO_2(s)$ was added to reduce excess $MnO_4^-$ to Mn(II). All final reaction mixtures were poured onto ice to quench all substitution reactions, diluted with ice water to reduce the ionic strength, and passed through a column of AG50W-X4, 200–400 mesh, resin. The column was thoroughly washed with water. The adsorbed products were eluted by using 1 M $HClO_4$ for 1+ complexes, 2 M $HClO_4$ to separate 2+ and 3+ complexes and then 3 M $HClO_4$ for the final stage, and 4 M HCl for $MOH_2^{3+}$. The acetonitrile and aquo complexes were separated by using 3 M $HClO_4$ to elute the former and 4 M HCl to elute the latter. The dimethylformamide and aquo complexes were separated by using 2 and 4 M HCl to elute the latter followed by 3 M $HClO_4$ to elute the former. The eluted products were collected in an ice bath, brought to room temperature, diluted to volume, and determined spectrophotometrically.

## Results

The products of the assisted aquations of $MN_3^{2+}$ and $M(Me_2SO)^{3+}$ in chloride, nitrate, sulfate, and phosphate media

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Table I. Comparison of the Products Formed in the Assisted Aquations of $MN_3^{2+}$ and $M(Me_2SO)^{3+}$ in Aqueous Media at 25 °C and Constant Ionic Strength: Slopes and Intercepts of the Plots of the Product Ratio $[MX^{(3-n)+}]/[MOH_2^{3+}]$ against Acid Concentration

| complex | [HX]/M | [HX] range/M | $\mu^a$/M | slope | intercept |
|---|---|---|---|---|---|
| $MN_3^{2+}$ | $Cl^-$ | 0.2-1.0 | 1.0 | 0.246 ± 0.009 | −0.015 ± 0.005 |
| $M(Me_2SO)^{3+}$ | $Cl^-$ | 0.2-1.0 | 1.0 | 0.179 ± 0.005 | −0.026 ± 0.004 |
| $MN_3^{2+}$ | $NO_3^-$ | 0.4-1.0 | 1.0 | 0.477 ± 0.010 | +0.015 ± 0.008 |
| $M(Me_2SO)^{3+}$ | $NO_3^-$ | 0.4-1.0 | 1.0 | 0.517 ± 0.014 | −0.037 ± 0.011 |
| $MN_3^{2+}$ | $HSO_4^-$ | 0.8-2.0 | 2.0 | 0.251 ± 0.008 | −0.058 ± 0.011 |
| $M(Me_2SO)^{3+}$ | $HSO_4^-$ | 0.8-2.0 | 2.0 | 0.101 ± 0.009 | −0.026 ± 0.013 |
| $MN_3^{2+}$ | $H_3PO_4$ | 0.8-2.0 | 2.0 | 0.078 ± 0.009 | −0.044 ± 0.014 |
| $M(Me_2SO)^{3+}$ | $H_3PO_4$ | 1.2-2.0 | 2.0 | 0.037 ± 0.003 | −0.022 ± 0.006 |

[a] $HClO_4$ used to maintain constant $\mu$.

Table II. Comparison of the Products Formed in the Assisted Aquations of $MN_3^{2+}$ and $M(Me_2SO)^{3+}$ in Aqueous Media at 25 °C and Variable Ionic Strength: Slopes and Intercepts of the Plots of the Product Ratio against Acid Concentration

| complex | reacn medium$^a$ | slope | intercept |
|---|---|---|---|
| $MN_3^{2+}$ | 0.2-1.0 M HCl | 0.178 ± 0.005 | +0.051 ± 0.003 |
| $M(Me_2SO)^{3+}$ | 0.2-1.5 M HCl | 0.114 ± 0.017 | +0.043 ± 0.016 |
| $MN_3^{2+}$ | 0.2-1.0 M $HNO_3$ | 0.400 ± 0.011 | +0.092 ± 0.007 |
| $M(Me_2SO)^{3+}$ | 0.2-1.0 M $HNO_3$ | 0.413 ± 0.012 | +0.070 ± 0.006 |
| $MN_3^{2+}$ | 0.2-4.0 M $H_2SO_4$ | 0.194 ± 0.005 | +0.075 ± 0.010 |
| $M(Me_2SO)^{3+}$ | 0.5-2.0 M $H_2SO_4$ | 0.091 ± 0.005 | −0.002 ± 0.010 |
| $MN_3^{2+}$ | 1.0-2.0 M $H_3PO_4$ | 0.048 ± 0.002 | +0.024 ± 0.010 |
| $M(Me_2SO)^{3+}$ | 1.0-2.0 M $H_3PO_4$ | 0.017 ± 0.002 | +0.019 ± 0.010 |

[a] Ionic strength set by the acid and cobalt(III) complex; no electrolyte added to maintain constant ionic strength during variation of acid concentration.

at 25 °C and constant ionic strength, $\mu$, were determined as a function of the concentration of the nucleophile competing with $H_2O$ for the coordination site initially occupied by $N_3^-$ or $Me_2SO$. Plots of the product ratio, $P = [MX^{(3-n)+}]/[MOH_2^{3+}]$, against nucleophile concentration were linear over the ranges employed. The slope, intercept, and standard deviations obtained by a least-squares treatment of the data for each plot are given in Tables I and II for constant and variable $\mu$, respectively. For both 1.0 M HCl and 1.0 M $HNO_3$ at $\mu$ = 1.0 M, the results given in Tables I and II are in excellent agreement with the one-point values of the quotient $R$ $(=[MX^{2+}]/[MOH_2^{3+}][X^-])$ previously reported for the substrates $MN_3^{2+}$[7] and $M(Me_2SO)^{3+}$.[12] The nearly equal values for $R$ for the two substrates in the two named media have previously been considered[12] evidence that the same intermediate, namely, $M^{3+}$, was formed from both substrates. However, use of the linear relationships given in the tables shows that, except for 1.0 M $HNO_3$, the product ratios from $M(Me_2SO)^{3+}$ are smaller than those from $MN_3^{2+}$, especially for sulfuric and phosphoric acids. Therefore, we conclude that the two substrates do not form the same intermediate from which the products are produced. We propose that two intermediates $MN_3{\cdot}NO^{3+}$ and $M(O_2S(CH_3)_2)^{3+}$ are formed and react by dissociative interchange ($I_d$) processes with the incoming nucleophiles $H_2O$ and $X^{n-}$ to form the products as shown in reactions 1-3 and 4-6. The product ratio $P$ is given by $P = k_x[X^{n-}]/k_w$ for $MN_3{\cdot}NO^{3+}$ and by $P = k_w'[X^{n-}]/k_w'$ for $M(O_2S(CH_3)_2)^{3+}$, where the rate constants are for the interchange processes. The existence of $MN_3{\cdot}NO^{3+}$ has been postulated[6] previously. There is good evidence[22,23] to support the existence of $NON_3$ at temperatures of −50 °C and below; coordination of $N_3^-$ to cobalt(III) stabilizes the $NON_3$ electron configuration (A) as compared to uncoordinated $NON_3$ (B)

$$MN_3^{2+} + NO^+ \xrightarrow[\text{slow}]{\text{relatively}} MN_3{\cdot}NO^{3+} \quad (1)$$

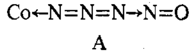
$$MN_3{\cdot}NO^{3+} + H_2O \xrightarrow{k_w} MOH_2^{3+} + N_2 + N_2O \quad (2)$$

$$MN_3{\cdot}NO^{3+} + X^{n-} \xrightarrow{k_x} MX^{(3-n)+} + N_2 + N_2O \quad (3)$$

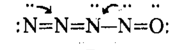
$$M(OS(CH_3)_2)^{3+} + MnO_4^- \xrightarrow[\text{slow}]{\text{relatively}} M(O_2S(CH_3)_2)^{3+} + Mn(V) \quad (4)$$

$$M(O_2S(CH_3)_2)^{3+} + H_2O \xrightarrow{k_w'} MOH_2^{3+} + (CH_3)_2SO_2 \quad (5)$$

$$M(O_2S(CH_3)_2)^{3+} + X^{n-} \xrightarrow{k_w'} MX^{(3-n)+} + (CH_3)_2SO_2 \quad (6)$$


$Co{\leftarrow}\ddot{N}{=}N{=}\ddot{N}{\rightarrow}\ddot{N}{=}\ddot{O}{:}$

A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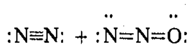
B

so far as a shift to product electron configuration (C) is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C

concerned. It is quite possible that $MN_4O^{3+}$ can survive sufficiently long to meet and react with different nucleophiles in an $I_d$ interchange of leaving and entering ligands.

The existence of the dimethyl sulfone complex in the $M(Me_2SO)^{3+}$ + $MnO_4^-$ reaction has also been postulated previously.[24] Although dimethyl sulfone is a very poor ligand, the complex may exist sufficiently long so as to react with nucleophiles in an $I_d$ interchange of leaving and entering ligands.

If the two proposed intermediates determine the product formation, the larger percentages of sulfato and phosphato complexes for $MN_4O^{3+}$ as compared to $M(O_2S(CH_3)_2)^{3+}$ can be explained in terms of hydrogen-bond formation between lone-pair electrons on N atoms and the incoming ligands $HSO_4^-$ and $H_2PO_4^-$ (or $H_3PO_4$) positioning the incoming ligand more favorably for competition for the site vacated in the interchange reaction.

The data in Table III show that the quotient $R^6$ is essentially independent of ionic strength. This result is in agreement with the linear free energy plot of Langford[25] which showed that the role of the anion in the activated complexes for $I_d$ unassisted aquation and anation of ligandopentaamminecobalt(III) complexes is very similar to its role in the bulk-solvent phase. If, likewise, the role of $NO_3^-$ in the activated complex of the $MN_4O^{3+}$ + $NO_3^-$ interchange ($I_d$) reaction is very similar to its role as a free ion, then the activity coefficients of both reactants in the activated complex can be essentially equal to those for the separated reactants because departure of the neutral grouping $N_3NO$ does not change the charge on the complex.

The data in Table III also show that the quotient $R$ is independent of $NaNO_3$ concentration up to at least 3.0 M. It is concluded that the 3+ intermediate (whether $M^{3+}$ or $MN_4O^{3+}$) does not survive sufficiently long in solution to establish equilibrium with respect to ion-pair formation; if it did, one would expect saturation effects to be apparent because anation reactions between 3+ cations and 1− anions show marked saturation effects with respect to ion-pair formation

**Table III.** Dependence of *R* for $NO_3^-$ on Ionic Strength and $NaNO_3$ Concentration in the $MN_3^{2+}$-Assisted Aquation (0.050 M $HClO_4$, 25 °C)

| $[NaNO_3]$/M | $\mu^a$/M | % $MNO_3^{2+}$ | *R* |
|---|---|---|---|
| 0.500 | 1.0 | 14.2 | 0.33 |
| 1.00 | 1.05 | 26.8 | 0.37 |
| 0.500 | 2.0 | 15.1 | 0.36 |
| 1.00 | 2.0 | 24.9 | 0.33 |
| 2.00 | 2.05 | 43.3 | 0.38 |
| 0.500 | 3.0 | 14.8 | 0.35 |
| 1.00 | 3.0 | 24.2 | 0.32 |
| 3.00 | 3.05 | 53.3 | 0.37 |
| 0.500 | 4.0 | 14.4 | 0.34 |
| 1.00 | 4.0 | 25.8 | 0.35 |
| 2.00 | 4.0 | 40.2 | 0.33 |
| 3.00 | 4.0 | 50.4 | 0.34 |

[a] $NaClO_4$ used to maintain constant ionic strength.

at anion concentrations[26,27] of 0.3–0.5 M. Further, if formation of $MNO_3^{2+}$ occurred through an equilibrium concentration of such ion pairs, the large value of the percentage $MNO_3^{2+}$ being formed at 3.00 M $NaNO_3$ (50–53%) would require that the same percentage of the intermediate be ion paired if every ion pair resulted in one $MNO_3^{2+}$ being formed. However, it is unlikely that every ion pair would do so; some ion pairs would form $MOH_2^{3+}$ instead. Hence a much larger percentage of ion pairing would be required to account for the observed production of $MNO_3^{2+}$, and saturation effects would most certainly be apparent at the larger $NaNO_3$ concentrations used. Indeed, if the competition ratio for $NO_3^-$ and $H_2O$ within the ion pair was as improbably large as 1:1, the intermediate would have to be 100% ion paired. And if the competition ratio was smaller than this (i.e., $NO_3^-$ entering once for every two $H_2O$ groups entering), the intermediate would have to be more than 100% ion paired. Langford and Muir[26] have shown that the competition ratio for anions and water molecules in the solvent cage surrounding the $Co(NH_3)_5^{3+}$ moiety in an ion-paired activated complex is much smaller than 1:1.

Table I of the supplementary material shows the effect of ethanol addition. The modest increase in the $MNO_3^{2+}$ production in the $MN_3^{2+} + HNO_2$ system could be due to decreased water content or to an increased equilibrium concentration of ion pairs; however, the arguments given immediately above militate against formation of products through an equilibrium population of ion pairs. The larger increases in $MNO_3^{2+}$ production in the $MCl^{2+}$ + Hg(II) system can be ascribed to increased $HgNO_3^+$ formation bringing $NO_3^-$ to the reaction site since $HgNO_3^+$ converts $MCl^{2+}$ to $MNO_3^{2+}$ with ca. 98% efficiency.[11] Increase of Hg(II) concentration at certain $NaNO_3$ and Hg(II) concentrations listed in the table decreased the percentage of $MNO_3^{2+}$ formed in the $MN_3^{2+} + HNO_2$ system by complexing $NO_3^-$ and in the $MCl^{2+}$ + Hg(II) system by increasing the fraction of the reaction proceeding through the intermediate $MClHg^{4+}$ which produces only ca. 2%[11] of $MNO_3^{2+}$. Addition of ethanol also increased the percentage of $MCl^{2+}$ formed in the $MN_3^{2+} + HNO_2$ system, and this increase was the same whether $HClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, or $Al(ClO_4)_3$ was used to maintain constant ionic strength. Since variation of $ClO_4^-$ concentration did not measurably affect the product ratio, competition by $ClO_4^-$ with subsequent high-efficiency aquation[28] of $MOClO_3^{2+}$ to $MOH_2^{3+}$ was not important in these media. However, the negative intercepts reported in Table I can be due to $ClO_4^-$ competition. At constant ionic strength and small $X^{n-}$ concentration the $ClO_4^-$ concentration is greater than at large $X^{n-}$ concentration. Consequently competition by $ClO_4^-$ to form $MOClO_4^{2+}$ followed by high-efficiency conversion to $MOH_2^{3+}$ results in smaller product ratios at smaller $X^{n-}$ concentrations than would be formed in the absence of $ClO_4^-$ and negative intercepts for plots of product ratio vs. $X^{n-}$ concentration. In Table II the intercepts are slightly positive or zero within experimental error in the absence of $ClO_4^-$.

The results given in Table II of the supplementary material for three-way competition between water, $NO_3^-$, and $SO_4^{2-}$ in the $MN_3^{2+} + HNO_2$ system, shown in reactions 7–9, show

$$MN_3{\cdot}NO^{3+} + H_2O \xrightarrow{k_w} MOH_2^{3+} + N_2 + N_2O \quad (7)$$

$$MN_3{\cdot}NO^{3+} + NO_3^- \xrightarrow{k_{NO_3^-}} MNO_3^{2+} + N_2 + N_2O \quad (8)$$

$$MN_3{\cdot}NO^{3+} + SO_4^{2-} \xrightarrow{k_{SO_4^{2-}}} MSO_4^+ + N_2 + N_2O \quad (9)$$

that at constant ionic strength and $NaNO_3$ concentration the value of $R_{SO_4^{2-}}$ $(=[MSO_4^+]/[MOH_2^{3+}][SO_4^{2-}])$ is independent of $SO_4^{2-}$ concentration; for the same conditions, the value of $R_{NO_3^-}$ $(=[MNO_3^{2+}]/[MOH_2^{3+}][NO_3^-])$ remains constant or, at most, decreases only very slightly. The results also show that at constant ionic strength and constant $SO_4^{2-}$ concentration $R_{NO_3^-}$ is independent of $NO_3^-$ concentration as is $R_{SO_4^{2-}}$ within experimental error. Hence, the results once again suggest that the products are not formed from an equilibrium concentration of ion pairs or increasing $SO_4^{2-}$ could displace $NO_3^-$ from ion pairs and vice versa. The intermediate forming the products reacts with $NO_3^-$ and $SO_4^{2-}$ ions in proportion to their relative populations in the solution. Similar results were obtained for the $M(Me_2SO)^{3+} + MnO_4^-$ system where the intermediate is different from the $M^{3+}$ intermediate presumed to exist in the $MN_3^{2+} + HNO_2$ system. In both systems the amounts of $MNO_3^{2+}$ formed were equal within expeimental error for equal $NO_3^-$ concentrations, but the amount of $MSO_4^+$ formed from $M(Me_2SO)^{3+}$ was always markedly smaller than was formed from $MN_3^{2+}$. Thus, the intermediate for which $H_2O$, $NO_3^-$, and $SO_4^{2-}$ simultaneously competed in the $MN_3^{2+} + HNO_2$ system gave the same percentage of $MNO_3^{2+}$ as, but a different percentage of $MSO_4^+$ than, the intermediate for which the same three nucleophiles competed in the $M(Me_2SO)^{3+} + MnO_4^-$ system. This is strong evidence against the argument that both substrates yield equal amounts of $MNO_3^{2+}$ in nitrate media because in these media alone both form $M^{3+}$. The parallel sets of results from both substrates (with equal $MNO_3^{2+}$ percentages but unequal $MSO_4^+$ percentages) suggest similar competition reactions in both systems; these could be the nucleophiles reacting with the intermediates $MN_4O^{3+}$ and $M(O_2S(CH_3)_2)^{3+}$ by interchange of leaving neutral groups and incoming nucleophile.

Table IV shows the results of the study of the temperature dependence of the products formed for a number of charged and uncharged nucleophiles competing with water in the assisted substitution reactions of $MN_3^{2+}$ and $M(Me_2SO)^{3+}$. Temperatures as high as 60–65 °C frequently caused significant decomposition of the cobalt(III) complexes so the temperature range was limited to 45 °C and below. Except for $NO_3^-$, no temperature dependence was found within the experimental errors. Hence, the reactions forming the products (except $MNO_3^{2+}$) from the intermediate for a given substrate all have the same activation enthalpy. If there is appreciable interaction between the cobalt(III) center and the incoming ligands in the activated complexes, it is improbable that this interaction would be the same throughout the range of ligands used; it is more probable that there is very little interaction. Furthermore, because all ligands (except $NO_3^-$) listed in Table IV for a given substrate have the same activation enthalpy but very different solvation energies for the bulk phase, it is very probable that little desolvation of the ligand occurs during formation of the activated complex. This result is in agreement with the lack of significant ionic strength effect on the per-

**Table IV.** Temperature Dependence of Product Percentage

| substrate | $X^{n-}$ | $[X^{n-}]$/M | $\mu$/M | $t$/°C | % $MX^{(3-n)+}$ [a] |
|---|---|---|---|---|---|
| $MN_3^{2+}$ | $Cl^-$ | 0.2 | 0.2 | 0.0 | 7.5 ± 0.35 |
| | $Cl^-$ | 0.2 | 0.2 | 25.0 | 7.6 ± 0.71 |
| | $Cl^-$ | 0.2 | 0.2 | 45.0 | 7.4 ± 0.28 |
| $M(Me_2SO)^{3+}$ | $Cl^-$ | 1.0 | 1.0 | 0.0 | 13.0 ± 0.30 |
| | $Cl^-$ | 1.0 | 1.0 | 25.0 | 13.3 ± 0.21 |
| | $Cl^-$ | 1.0 | 1.0 | 45.0 | 13.1 ± 0.42 |
| $MN_3^{2+}$ | $Br^-$ | 0.2 | 0.2 | 0.0 | 6.3 ± 0.99 |
| | $Br^-$ | 0.2 | 0.2 | 25.0 | 6.5 ± 0.30 |
| | $Br^-$ | 0.2 | 0.2 | 45.0 | 5.9 ± 0.20 |
| $MN_3^{2+}$ | $NO_3^-$ | 0.2 | 0.2 | 0.0 | 17.2 ± 0.57 |
| | $NO_3^-$ | 0.2 | 0.2 | 25.0 | 14.5 ± 0.17 |
| | $NO_3^-$ | 0.2 | 0.2 | 45.0 | 11.4 ± 0.19 |
| $M(Me_2SO)^{3+}$ | $NO_3^-$ | 1.0 | 1.0 | 0.0 | 41.2 ± 2.10 |
| | $NO_3^-$ | 1.0 | 1.0 | 25.0 | 32.6 ± 0.70 |
| | $NO_3^-$ | 1.0 | 1.0 | 45.0 | 23.0 ± 1.50 |
| $MN_3^{2+}$ | $HSO_4^-$ | 2.0 | 2.0 | 0.0 | 30.3 ± 0.60 |
| | $HSO_4^-$ | 2.0 | 2.0 | 25.0 | 31.0 ± 0.60 |
| | $HSO_4^-$ | 2.0 | 2.0 | 45.0 | 29.0 ± 0.58 |
| $M(Me_2SO)^{3+}$ | $HSO_4^-$ | 1.0 | 1.0 | 0.0 | 10.1 ± 0.14 |
| | $HSO_4^-$ | 1.0 | 1.0 | 25.0 | 10.3 ± 0.15 |
| | $HSO_4^-$ | 1.0 | 1.0 | 45.0 | 11.4 ± 0.28 |
| $M(Me_2SO)^{3+}$ | $N_3^-$ | 1.0 | 1.0 | 0.0 | 22.4 ± 1.4 |
| | | 1.0 | 1.0 | 25.0 | 19.7 ± 1.4 |
| | | 1.0 | 1.0 | 45.0 | 17.4 ± 1.0 |
| $MN_3^{2+}$ | $H_3PO_4$ | 2.0 | 1.0 | 0.0 | 11.3 ± 0.34 |
| | | 2.0 | 1.0 | 25.0 | 10.7 ± 0.30 |
| | | 2.0 | 1.0 | 45.0 | 11.2 ± 0.35 |
| $M(Me_2SO)^{3+}$ | $H_3PO_4$ | 2.0 | 1.0 | 0.0 | 4.6 ± 0.07 |
| | | 2.0 | 1.0 | 25.0 | 5.1 ± 0.28 |
| | | 2.0 | 1.0 | 45.0 | 5.7 ± 0.36 |
| $MN_3^{2+}$ | $CH_3CN$ | 0.125 [b] | 0.1 | 0.0 | 28.8 ± 0.91 |
| | | 0.125 [b] | 0.1 | 25.0 | 23.9 ± 1.00 |
| | | 0.125 [b] | 0.1 | 45.0 | 25.6 ± 1.13 |
| $MN_3^{2+}$ | $Me_2Fam$ | 0.13 [b] | 0.1 | 0.0 | 24.4 ± 0.57 |
| | | 0.13 [b] | 0.1 | 25.0 | 23.8 ± 0.55 |
| | | 0.13 [b] | 0.1 | 45.0 | 20.5 ± 0.57 |

[a] Indicated error is the standard deviation of a single measurement. [b] Mole fraction.

centages of products formed. The small temperature dependence for $NO_3^-$ as a ligand shows that there is a smaller (2–3 kcal $mol^{-1}$) activation enthalpy for $MNO_3^{2+}$ than for $MOH_2^{3+}$ formation, in line with the observation[8] that $NO_3^-$ seems to be more "extractable" from water than other nucleophiles examined. Since the other nucleophiles apparently undergo little change of solvation in forming the activated complex, the lower activation enthalpy for $NO_3^-$ cannot arise from a smaller desolvation enthalpy contribution but can arise from interaction with the cobalt(III) center; that is, the interchange reaction for $NO_3^-$ has a small $Co^{III}$–$ONO_2^-$ bonding energy in the activated complex.

The data of Table IV also provide evidence against the existence of $M^{3+}$ in the assisted substitution reactions examined. Suppose that $M^{3+}$ is formed from $MN_3^{2+}$ but not from $MCl^{2+}$ or $M(Me_2SO)^{3+}$ because the $N_4O$ grouping is a much poorer ligand than $ClHg^+$ or than dimethyl sulfone; $N_4O$ needs no assistance to leave its coordination site but $ClHg^+$ and dimethyl sulfone do. Interaction between cobalt(III) and the incoming nucleophile can assist the latter two ligands to leave via interchage reactions; such interaction means partial bond formation. For the range of ligands given in Table IV for $M(Me_2SO)^{3+}$, it is doubtful that each ligand (except $NO_3^-$) would form a bond of exactly the same strength as that formed by $H_2O$ so that the product ratio would be independent of temperature. We conclude that it is more likely that the assisted-substitution reactions studied differ in their product ratios because unstable intermediates with different leaving groups form the competition products via $I_d$ reactions rather than via D reactions producing the five-coordinate $Co(NH_3)_5^{3+}$ intermediate.

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**Registry No.** $MN_3^{2+}$, 14403-83-9; $M(Me_2SO)^{3+}$, 44915-85-7; $MOH_2^{3+}$, 14403-82-8; $MCl^{2+}$, 14970-14-0; $MBr^{2+}$, 14970-15-1; $MNO_3^{2+}$, 15077-47-1; $MHSO_4^{2+}$, 15156-26-0; $MH_3PO_4^{3+}$, 71277-76-4; $MCH_3CN^{3+}$, 44819-13-8; $MMe_2Fam^{3+}$, 31125-61-8; Hg(II), 14302-87-5; $HNO_2$, 7782-77-6; $MnO_4^-$, 14333-13-2.

**Supplementary Material Available:** Tables showing the results of the ethanol–water and three-way competition studies (2 pages). Ordering inforamtion is given on any current masthead page.

## References and Notes

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