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An Investigation of the Rapid Complexation of Aquopentaamminecobalt(III) with Molybdate in Weakly Basic Solution

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The kinetics of equilibration of aquopentaamminecobalt(III) with molybdate(VI)

$$Co(NH_3)_5OH_2^{3+} + MoO_4^{2-} \overset{k_f}{\rightleftharpoons} Co(NH_3)_5MoO_4^{+} + H_2O \tag{i}$$

have been studied at 25 °C and $I = 1.0$ M ($NaClO_4$) with $7.1 \leq pH \leq 8.0$ by the stopped-flow method. The spectrophotometric equilibrium constant for (i), $K_1 = k_f/k_r$, is 475 ± 15 M^{-1}. The kinetics show a greater than first-order dependence on $[MoO_4^{2-}]$ and the second-order formation rate constant, k_f, can be expressed as in

$$k_f = k_a + k_b[H^+] + k_c[MoO_4^{2-}] + k_d[H^+][MoO_4^{2-}] \tag{ii}$$

Values of $k_a = 96 \pm 7\ M^{-1}\ s^{-1}$, $k_b = (1.1 \pm 0.2) \times 10^9\ M^{-2}\ s^{-1}$, $k_c = (2.2 \pm 0.2) \times 10^3\ M^{-2}\ s^{-1}$, and $k_d = (1.02 \pm 0.05) \times 10^{11}\ M^{-3}\ s^{-1}$ are consistent with substitution at the Mo(VI) and not the Co(III) center. The paths k_a and k_b most probably correspond to the reaction of $HMoO_4^-$ with $Co(NH_3)_5OH^{2+}$ ($k_1 = 6.6 \times 10^4\ M^{-1}\ s^{-1}$) and $Co(NH_3)_5OH_2^{3+}$ ($k_2 = 3.2 \times 10^5\ M^{-1}\ s^{-1}$), respectively. These rate constants are much lower than those observed for addition of ligands to tetrahedral molybdate(VI) to give products of increased coordination number. The pathways involving two molybdate ions, k_c and k_d, correspond to reactions of dimolybdate(VI), a species which has not previously been detected in aqueous solution.

The extreme inertness of the metal–oxygen bond in aquopentaamminecobalt(III) results in very slow complex formation. With oxy anions which exhibit rapid oxygen exchange, complexation may be extremely rapid since the cobalt(III)–oxygen bond does not need to be broken. Studies on such reactions[1,2] and those of other inert trivalent transition metal–aquo complexes[3] have yielded valuable information on the nature of substitution mechanisms at oxy anion centers.

Molybdate(VI) forms a series of stable octahedral complexes in weakly basic solution with bidentate ligands such as catechol,[4] oxine,[5] and oxinesulfonic acid,[6] and kinetic studies of complex formation have been carried out. It is also known that molybdate(VI) complexes with $Co(NH_3)_5OH_2^{3+}$ and that the product $Co(NH_3)_5MoO_4^+$ contains tetrahedrally coordinated molybdate(VI).[7] The fact that there is retention of tetrahedral geometry is of particular interest in this reaction. Conditions, $[Mo(VI)] \leq 0.1$ M and pH >7, were chosen so that isopolymolybdate species were not present.[8]

Experimental Section

Conditions. All measurements were carried out at 25 °C and $I = 1.0$ M ($NaClO_4$ or $LiClO_4$) in the presence of at least 0.1 M triethanolamine (TEA) buffer, unless otherwise stated.

Materials. $LiClO_4$ was prepared and purified as described previously.[9] $NaClO_4$ (Analar, Hopkin and Williams), triethanolamine (reagent grade, BDH), and $Na_2MoO_4H_2O$ (Analar, BDH) were not further purified. $[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared by the standard method.[10,11]

Measurement of pH. A Radiometer pHM4 meter fitted with G202C glass and K401 calomel (containing saturated NaCl instead of KCl) electrodes was used for pH measurement. The meter was calibrated at 1.0 M ionic strength with perchloric acid solutions (0.001–0.100 M) so that the measured pH corresponds to $-\log[H^+]$, and pH used in this paper refers to such a quantity. Experiments in lithium perchlorate media contain up to 0.20 M Na^+ from sodium molybdate. It was demonstrated that this does not affect the measured pH in $NaClO_4$–$LiClO_4$ mixtures.

Spectrophotometric Studies. K_H and K_1 were determined by spectrophotometric titration of solutions initially at pH ≥7.0 with 1.0 M NaOH. Sufficient buffer was present so that pH remained stable during absorbance measurements on a Unicam SP500 spectrophotometer, while changes in $[MoO_4^{2-}]$ during the titration could be neglected. Absorbance measurements however were corrected for the small (<5%) dilution effects which were introduced.

The spectrum of $Co(NH_3)_5OH_2^{3+}$ was recorded in $HClO_4$ (0.2 M), $Co(NH_3)_5OH^{2+}$ in triethanolamine buffer (0.1 M), $NaClO_4$ (0.1 M) at pH 8.50, and $Co(NH_3)_5MoO_4^+$ in sodium molybdate solution (0.1 M) at pH 6.63, conditions where complex formation is estimated to be complete while isopolymolybdates are not present in significant concentration, the lower ionic strength favoring both of these factors.

Kinetic Studies. Stopped-flow studies were performed on a Durrum-Gibson spectrophotometer under conditions of at least 10-fold excess $[MoO_4^{2-}]$ at λ 530–550 nm and pH 7.1–8.0. Tabulated rate constants are the averages of several determinations (usually ≥3). With [TEA] = 0.1 M, the pH changes on reaction by ≤0.02 unit. At pH 7.1 the buffering capacity of TEA is least and so [Co(III)] was kept as low as possible for measurements where [TEA] was not >0.1 M.

Analysis of Data. Least-squares analyses were performed using a standard nonlinear program.[12] Weighting (y^{-2}), to give constant percent error on the dependent variable, y, was used.

Results

Spectrophotometric Studies and Equilibrium Constants. On mixing $Co(NH_3)_5OH_2^{3+}/Co(NH_3)_5OH^{2+}$ with molybdate(VI) at pH 7 there is a rapid intensification of the purple color of the cobalt complex. The spectra of the complexes $Co(NH_3)_5OH_2^{3+}$, $Co(NH_3)_5OH^{2+}$, and $Co(NH_3)_5MoO_4^+$ are shown in Figure 1.

Spectrophotometric changes at λ 550 nm for the reaction sequence

$$Co(NH_3)_5OH^{2+} + H^+ \overset{K_H}{\rightleftharpoons} Co(NH_3)_5OH_2^{3+} \tag{1}$$

$$Co(NH_3)_5OH_2^{3+} + MoO_4^{2-} \overset{K_1}{\rightleftharpoons} Co(NH_3)_5MoO_4^{+} + H_2O \tag{2}$$

were analyzed by the Benesi–Hildebrand[13] method for spectrophotometric titration of a solution of complex containing excess molybdate(VI) initially at pH 7, with base. The apparent absorption coefficient ϵ_{obsd} can be expressed by (3),

$$\epsilon_{obsd} = \frac{\epsilon_{OH} + \epsilon_A K_H[H^+] + \epsilon_C K_1 K_H[H^+][MoO_4^{2-}]}{1 + K_H[H^+] + K_1 K_H[H^+][MoO_4^{2-}]} \tag{3}$$

where ϵ_{OH}, ϵ_A, and ϵ_C are the molar absorption coefficients of $Co(NH_3)_5OH^{2+}$, $Co(NH_3)_5OH_2^{3+}$, and $Co(NH_3)_5MoO_4^+$, respectively. Equation 3 can be arranged to give (4), where

$$(\epsilon_{obsd} - \epsilon_{OH})^{-1} = \Delta\epsilon^{-1}(1 + K_1[MoO_4^{2-}] + K_H^{-1}[H^+]^{-1}) \tag{4}$$

$\Delta\epsilon = \epsilon_A - \epsilon_{OH} + (\epsilon_C - \epsilon_{OH})K_1[MoO_4^{2-}]$. Plots of $(\epsilon_{obsd} - \epsilon_{OH})^{-1}$ against $[H^+]^{-1}$, at constant $[MoO_4^{2-}]$, are shown in

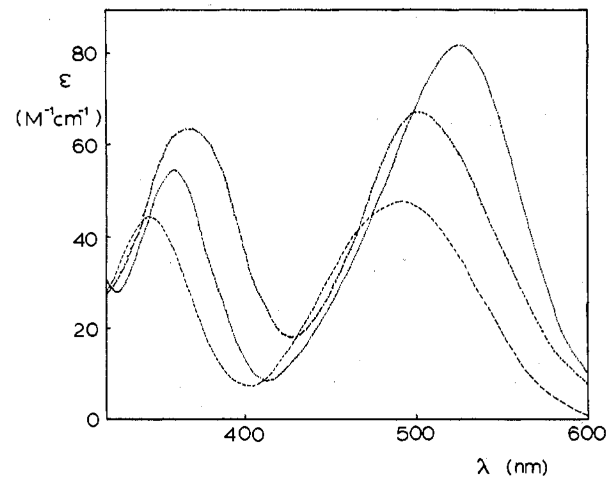

Figure 1. Spectra of $Co(NH_3)_5H_2O^{3+}$ (- - -), $Co(NH_3)_5OH^{2+}$ (· - · -), and $Co(NH_3)_5MoO_4^{+}$ (· · · ·) at 25 °C.

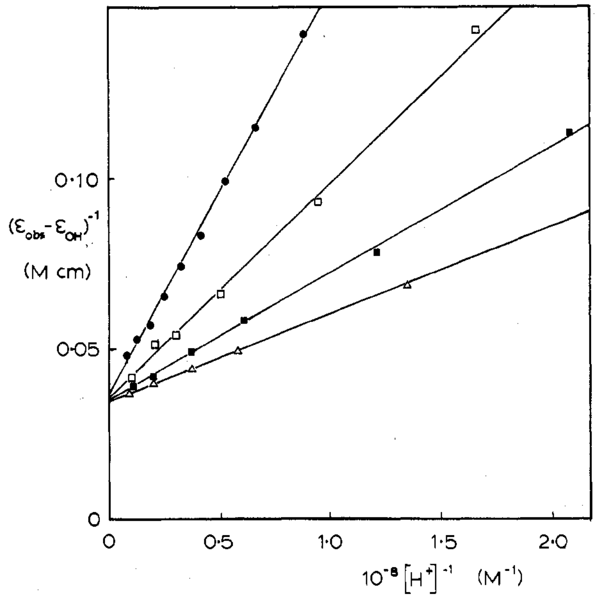

Figure 2. Benesi–Hildebrand plots for the determination of apparent binding constants, K, for the reaction of $Co(NH_3)_5H_2O^{3+}$ with MoO_4^{2-} at 25 °C and $I = 1.0$ M ($NaClO_4$); $[MoO_4^{2-}] = 0.025$ M (●), 0.050 M (□), 0.075 M (■) and 0.10 M (△); $[Co(III)]_0 = 2.0 \times 10^{-3}$ M.

Table I. Apparent Equilibrium Constants, K (M^{-1}), for the Reaction of Aquopentaamminecobalt(III) with Molybdate(VI) at 25 °C and 1.0 M Ionic Strength, in $NaClO_4$ (K_{Na}) and $LiClO_4$ (K_{Li})

$[MoO_4^{2-}]$, M	$10^{-7}K_{Na}$[a]	$10^{-7}K_{Li}$[b]
0.000	0.245 ± 0.01	0.245 ± 0.01
0.025	2.95 ± 0.18	2.74 ± 0.41
0.050	5.78 ± 0.52	4.84 ± 0.39
0.075	9.29 ± 0.33	8.30 ± 0.16
0.100	13.06 ± 0.52	10.21 ± 0.46

[a] Least-squares analysis gives $K_H = (2.44 \pm 0.13) \times 10^6$ M^{-1} and $K_1 = 475 \pm 30$ M^{-1}. [b] Least-squares analysis gives $K_H = (2.45 \pm 0.12) \times 10^6$ M^{-1} and $K_1 = 400 \pm 30$ M^{-1}.

Figure 2 and the ratio of intercept to slope yields a value for an apparent stability constant, K, defined by (5), and these

$$K = (1 + K_1[MoO_4^{2-}])K_H \qquad (5)$$

values are given in Table I. In the absence of molybdate(VI) K is simply equal to K_H, and this quantity has been determined with some precision at λ 390 nm where $(\epsilon_A - \epsilon_{OH})$ is large. At 1.0 M ionic strength log K_H is found to be 6.39 in both $LiClO_4$ and $NaClO_4$ media. A least-squares fit of K_1 values to eq 5 also gives a value of log $K_H = 6.39 \pm 0.02$ in both media while K_1 is 475 ± 30 M^{-1} ($NaClO_4$) and 400 ± 30 M^{-1} ($LiClO_4$).

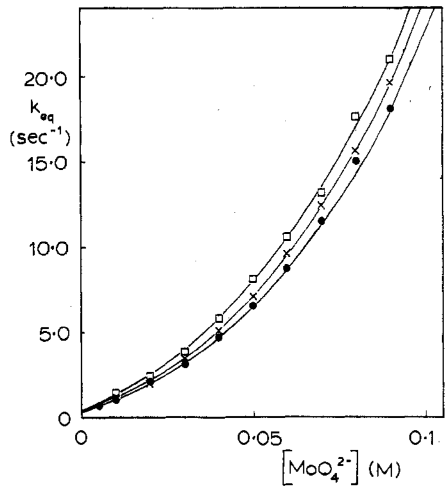

Figure 3. Dependence of pseudo-first-order rate constants, k_{eq}, for the reaction of $Co(NH_3)_5H_2O^{3+}$ with MoO_4^{2-} on $[MoO_4^{2-}]$ at pH 7.11, 25 °C, and $I = 1.0$ M ($NaClO_4$) with [buffer] = 0.1 M (●), 0.2 M (X), and 0.3 M (□); $[Co(III)]_0 = 8.7 \times 10^{-4}$M.

Table II. Values of k_{eq} and k_{calcd}[a] (s^{-1}) for the Equilibration of Aquopentaamminecobalt(III)[b] with Molybdate(VI) as a Function of pH and $[MoO_4^{2-}]$ at 25 °C, $I = 1.0$ M ($NaClO_4$), and [TEA] = 0.1 M

$[MoO_4^{2-}]$, M	pH			
	7.11	7.40	7.70	8.00
0.005	0.66 (0.68)	0.47 (0.44)	0.31 (0.33)	
0.010	1.08 (1.06)	0.61 (0.61)	0.40 (0.41)	0.32 (0.33)
0.020	2.05 (2.05)	1.20 (1.04)	0.62 (0.62)	0.51 (0.45)
0.030	3.35 (3.37)	1.69 (1.57)	0.81 (0.86)	0.61 (0.58)
0.040	4.70 (5.01)	2.29 (2.22)	1.16 (1.15)	0.68 (0.73)
0.050	6.65 (6.98)	3.35 (2.98)	1.46 (1.47)	0.82 (0.89)
0.060	8.90 (9.27)	4.06 (3.86)	1.85 (1.83)	1.11 (1.07)
0.070	11.5 (11.9)	5.06 (4.84)	2.17 (2.24)	1.28 (1.26)
0.080	15.0 (14.8)	5.60 (5.94)	2.59 (2.68)	1.70 (1.47)
0.090	18.1 (18.1)	7.10 (7.15)	3.18 (3.16)	1.67 (1.70)
0.100	23.3 (21.7)	9.25 (8.47)	3.48 (3.68)	1.85 (1.94)

[a] k_{calcd} in parentheses. [b] $[Co(III)] = (1.0–2.5) \times 10^{-3}$ M.

Kinetic Studies. Pseudo-firsts-order plots with excess $[MoO_4^{2-}]$ are linear for at least 3 half-lives, and pseudo-first-order rate constants, k_{eq}, are independent of [Co(III)] in the range (0.88–4.4) × 10^{-3} M. The values of k_{eq} show a greater than first-order dependence on $[MoO_4^{2-}]$ as well as a dependence on $[H^+]$ (Table II, Figure 3). Since the reaction was carried out in the presence of a relatively high (0.1 M) buffer concentration, it was necessary to demonstrate that k_{eq} showed not great dependence on the concentration of buffer. Over the range of [TEA] = 0.10–0.30 M there is a small but significant increase in k_{eq} under the same conditions (Figure 3). However changing the medium from $NaClO_4$ to $LiClO_4$ causes a marked decrease in k_{eq} (Figure 4), and it seems reasonable to assign the [TEA] dependence similarly to a medium effect.

For the reaction mechanism in eq 1 and 2, k_{eq} is given by (6), where k_f is the formation rate constant and k_r the aquation

$$k_{eq} = \frac{k_f K_H [H^+][MoO_4^{2-}]}{1 + K_H[H^+]} + k_r \qquad (6)$$

rate constant of molybdatopentaamminecobalt(III). Both of

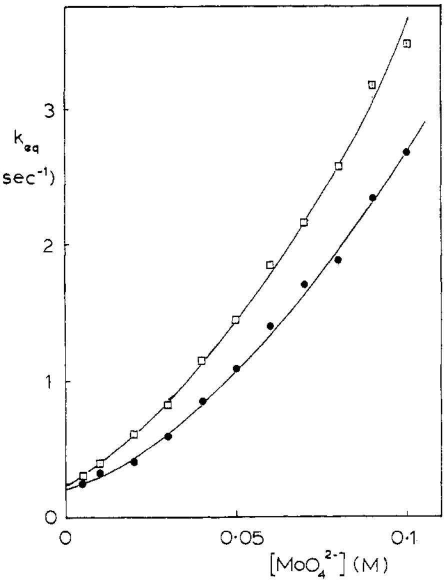

Figure 4. Dependence of k_{eq} for the reaction of $Co(NH_3)_5H_2O^{3+}$ with MoO_4^{2-} on $[MoO_4^{2-}]$ in the presence of 0.1 M buffer at 25 °C and $I = 1.0$ M, made up with $NaClO_4$ at pH 7.70 (○) and with $LiClO_4$ at pH 7.66 (●).

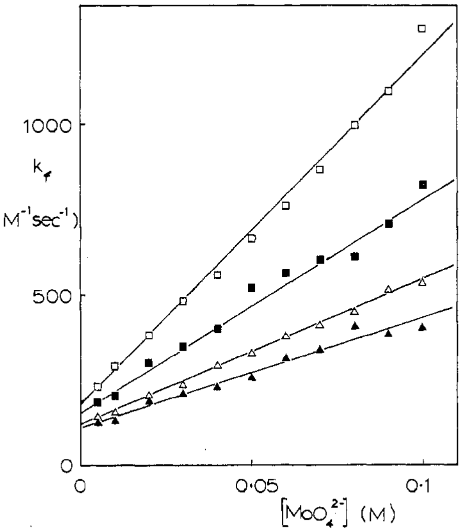

Figure 5. Dependence of second-order rate constants, k_f, for the formation of $Co(NH_3)_5MoO_4^+$ on $[MoO_4^{2-}]$ at 25 °C, $I = 1.0$ M ($NaClO_4$), and [TEA] = 0.1 M, with pH 7.11 (□), 7.40 (■), 7.70 (△), and 8.00 (▲).

these constants are dependent on $[MoO_4^{2-}]$ as well as $[H^+]$ as discussed below.

Using the relationship $k_r = k_f/K_1$ for (2), we can rewrite (6) as (7), and values of k_f can be determined by using the

$$k_{eq} = k_f\left(\frac{K_H[H^+][MoO_4^{2-}]}{1 + K_H[H^+]} + \frac{1}{K_1}\right) \tag{7}$$

known spectrophotometric equilibrium constants K_1 and K_H. The dependence of k_f on $[MoO_4^{2-}]$ at different pH values illustrated in Figure 5 implies a four-term equation for k_f as in (8).

$$k_f = k_a + k_b[H^+] + k_c[MoO_4^{2-}] + k_d[H^+][MoO_4^{2-}] \tag{8}$$

Table III. Values of Kinetic Parameters for the Reaction of Aquopentaamminecobalt(III) with Molybdate(VI) at 25 °C and $I = 1.0$ M ($NaClO_4$)

Formation		Aquation[a]	
Constant	Value	Constant	Value
k_a, M^{-1} s^{-1}	96 ± 6	k_{-a}, s^{-1}	0.20
k_b, M^{-2} s^{-1}	(1.12 ± 0.19) × 10^9	k_{-b}, M^{-1} s^{-1}	2.3 × 10^6
k_c, M^{-2} s^{-1}	(2.21 ± 0.17) × 10^3	k_{-c}, M^{-1} s^{-1}	4.6
k_d, M^{-3} s^{-1}	(1.02 ± 0.05) × 10^{11}	k_{-d}, M^{-2} s^{-1}	2.1 × 10^8

[a] $k_{-n} = k_n/K_1$; $K_1 = 475$ M^{-1}.

$$k_{eq} = (k_a + k_b[H^+] + k_c[MoO_4^{2-}] + k_d[H^+][MoO_4^{2-}])\left(\frac{K_H[H^+][MoO_4^{2-}]}{1 + K_H[H^+]} + \frac{1}{K_1}\right) \tag{9}$$

This dependence is borne out by a least-squares analysis of all data in terms of the full expression for k_{eq}, eq 9, and values of the constants k_a to k_d have been determined using a value of $K_1 = 475$ M^{-1}. It is possible to obtain an independent set of values, $k_a = 57 \pm 21$ s^{-1}, $k_b = (0.75 \pm 0.31) \times 10^9$ M^{-2} s^{-1}, $k_c = (1.64 \pm 0.46) \times 10^3$ M^{-2} s^{-1}, and $k_d = (1.09 \pm 0.05) \times 10^{11}$ M^{-3} s^{-1}, if the value of K_1 is also allowed to float in the computational procedure. A value of $K_1 = 305 \pm 95$ M^{-1} is in reasonable agreement with the spectrophotometric value. Since K_{calcd} values from the two sets of parameters differ by ≥2% for only 2 out of 44 data points, the data analysis does not discriminate between the different K_1 values involved, and all further discussion is in terms of the parameters obtained using the spectrophotometric value of K_1.

Discussion

Equilibrium Constants. The value of K_H is in reasonable agreement with others in the literature at 25 °C: 6.55 (1 M $NaNO_3$),[14] 6.22 (0.3 M $NaClO_4$),[15] and 6.24 (0.145 M $NaClO_4$).[11] The spectrophotometric values of K_1 in both $LiClO_4$ and $NaClO_4$ are similar and the kinetic value in $NaClO_4$ (Table III) is in reasonable agreement considering the complexity of the rate law.

Kinetic Studies. The rapid formation reaction observed in this study is consistent with a mechanism involving substitution at Mo(VI) but not Co(III), and a molybdate(VI) oxygen is replaced by the cobalt(III) coordinated oxygen. The reverse rate constants (Table III) are also high suggesting that molybdenum(VI)–oxygen and not cobalt(III)–oxygen bond cleavage is occurring in the aquation reaction.

No allowance has been made in this study for the presence of significant amounts of ion-paired complex. The apparent ion-pairing constant, K_O, is probably small (<1 M^{-1}) at this ionic strength, since under our conditions $Co(NH_3)_5OH^{2+}$ is the predominant cobalt(III) species. Moreover a low value of K_O for molybdate might be expected from the results of studies on ion pairing of the related complex $Co(NH_3)_6^{3+}$ with molybdate(VI)[16] and sulfate,[17] where $K_O(SO_4^{2-})$ is reported to be 6 times $K_O(MoO_4^{2-})$.[16] It is unlikely then that, even at the highest $[MoO_4^{2-}]$ and lowest pH, the concentration of ion pair is much greater than 5% of the total aquo complex.

The complex formed is $Co(NH_3)_5MoO_4^+$ and a particularly interesting feature is the retention of tetrahedral geometry around the molybdenum. Since this is the first kinetic study of such a reaction for molybdate, a comparison with reactions which give rise to six-coordinate products is of interest.

Pathways Involving a Single Molybdate(VI). The data for pathways k_a and k_b can usefully be compared with the results of several other kinetic studies of molybdate(VI) complexation in weakly basic solution.[4-6,8] Since these studies all involve reaction with weakly basic ligands, proton ambiguities in the rate law preclude the indentification of the molybdate(VI) species, which is actually taking part in the reaction. A reasonable approach has been to discuss kinetic data in terms of only one molybdate(VI) species, and this has most usually been $HMoO_4^-$.

In the present study, for k_b, the proton must be associated with molybdate(VI) since there is no free protonation site on

Table IV. Values of Second-Order Rate Constants, k, for Reaction of $HMoO_4^-$ with Different Ligands (25 °C)

Ligand (L_n)	k, M^{-1} s^{-1}	Product[a]	Conditions	Ref
$Co(NH_3)_5OH^{2+}$	$\leq 6.6 \times 10^4$	MoO_3L^+	1.0 M ($NaClO_4$)	This work
$Co(NH_3)_5OH_2^{3+}$	3.2×10^5	MoO_3L^+	1.0 M ($NaClO_4$)	This work
MoO_3EDTA^{4-}	$\leq 3.3 \times 10^4$	$MoO_3L_3^{4-}$	0.1 M ($NaNO_3$)	*b*
H_2EDTA^{2-}	2.3×10^5	$MoO_3L_3^{2-}$	0.1 M ($NaNO_3$)	*b*
$H(oxine)SO_3^-$ [f]	3.9×10^6	$MoO_2(OH)_2L_2^{2-}$	0.2 M ($NH_4^+/NaNO_3$)	*c*
$H(oxine)$[g]	4.5×10^6	$MoO_2(OH)_2L_2^-$	0.2 M ($NH_4^+/NaNO_3$)	*d*
$(oxine)SO_3^{2-}$	4.0×10^7	$MoO_2(OH)_2L_2^{2-}$	0.2 M ($NH_4^+/NaNO_3$)	*c*
$oxine^-$	1.5×10^8	$MoO_2(OH)_2L_2^-$	0.2 M ($NH_4^+/NaNO_3$)	*d*
$H(catechol)^-$ [h]	1.9×10^8	$MoO_2(OH)_2L_2^{2-}$	0.1 M (KNO_3)	*e*

[a] L represents one coordinating group on ligand. [b] Reference 18. [c] Reference 6. [d] Reference 5. [e] Reference 4. [f] 8-Hydroxyquinoline-5-sulfonate. [g] 8-Hydroxyquinoline. [h] Product of the first acid dissociation of 1,2-dihydroxybenzene.

the cobalt complex, and it seems most reasonable therefore to discuss both paths in terms of reactive $HMoO_4^-$; see (10) and (11). The rate constant k_1 is related to k_a and k_2 to k_b

$$Co(NH_3)_5OH^{2+} + HMoO_4^- \xrightarrow{k_1} Co(NH_3)_5MoO_4^+ + H_2O \qquad (10)$$

$$Co(NH_3)_5OH_2^{3+} + HMoO_4^- \xrightarrow{k_2} Co(NH_3)_5MoO_4^+ + H_2O + H^+ \qquad (11)$$

as in (12) and (13), where a value of $\log K_{HM} = 3.53$ (25 °C,

$$k_1 = k_a K_H / K_{HM} = 6.6 \times 10^4\ M^{-1}\ s^{-1} \qquad (12)$$

$$k_2 = k_b / K_{HM} = 3.2 \times 10^5\ M^{-1}\ s^{-1} \qquad (13)$$

1 M (NaCl))[19] referring to molybdate protonation has been used. The possibility that k_b corresponds to reaction between $Co(NH_3)_5OH^{2+}$ and H_2MoO_4 has been considered. The rate constant for this path, 1.4×10^8 M^{-1} s^{-1}, calculated using K_H and the protonation constant for $HMoO_4^-$,[19] seems too high for such a process and this possibility will not be discussed further.

All available kinetic data for molybdate(VI) complexation reactions with $HMoO_4^-$ as reactant are shown in Table IV. Consideration of literature data together with results from the present study reveals an interesting correlation. The fastest reactions with catechol,[4] oxine,[5] and oxinesulfonate[6] ($k = (0.4–2.0) \times 10^8$ M^{-1} s^{-1}, which are only about a factor of 10 slower than diffusion-controlled processes) probably involve simple addition to molybdate(VI) with no necessity for any of the four Mo–O bonds to be broken. The reactions with protonated oxine and oxinesulfonate ($k \approx 4 \times 10^6$ M^{-1} s^{-1}) are similar in that they also involve retention of all four molybdate(VI) oxygens in the product. The low rates here are probably due to chelate-ring closure as opposed to first-bond formation being rate determining. Similar slow rates for reaction of protonated oxine have been observed with the very labile ions Mg^{2+} [20] and Cu^{2+}.[21] With Ni^{2+},[21] however, which is much more inert, first-bond formation becomes the rate-determining step, and the rate constant is normal for a neutral ligand.

The four other reactions, those in the present study and two involved in the MoO_4^{2-}–EDTA system,[18] all have k values $<4 \times 10^5$ M^{-1} s^{-1} despite the electrostatically favorable outer-sphere complexation with the cobalt complex. These slower reactions all have one thing in common: one of the oxygens has to be lost from the molybdate(VI) coordination sphere. It must be remembered however that the EDTA complexes formed are six- and not four-coordinate.[18]

It has been suggested that very rapid reactions of $HMoO_4^-$ are due to a tendency of molybdate(VI) to increase its coordination number on protonation.[8,19,22] Recent spectrophotometric studies by Cruywagen and Rohwer[23] however suggest that only in the presence of a second proton are six-coordinate molybdate species detected. This observation is not in conflict with the results of kinetic studies in which only a single proton is required in the rate-determining step, since the first proton may promote the increase in coordination number while the second stabilizes the six-coordinate species which is formed. Most of the reaction products, e.g., $MoO_2(OH)_2(catechol)^{2-}$, do in fact contain two protons, the second being added after the rate-determining step. The implication for the reactions with catechol,[4] oxine,[5] and oxinesulfonate[6] seems to be that the reaction must involve addition to $HMoO_4^-$ rather than substitution of labile water ligands as has been suggested elsewhere.[4]

While for reactions involving no molybdenum–oxygen bond breakage an associative addition process is likely, the mechanism for processes involving substitution at molybdenum(VI) is not clear. For the latter category of reactions in which an oxo ligand is lost the situation is complicated and further worthwhile comment as to mechanism is not possible at this stage.

Pathways Involving Two Molybdate(VI) Species. The most remarkable feature of this study is the presence of two paths (k_c and k_d) which involve not one but two molybdate(VI) anions. One possible explanation is that a second molybdate(VI) is reacting with the aquopentaammine complex which is already ion paired to a molybdate(VI), although the concentration of ion pair may be small. Such a reactive pathway would give rise to a second-order $[MoO_4^{2-}]$ dependence but it requires that the ion pair is much more reactive than the non-ion-paired starting complex, with molybdate(VI). On both electrostatic and steric grounds such a possibility seems unlikely.

The most reasonable suggestion that would be consistent with the effectiveness of a second molybdate(VI) in catalyzing complex formation in this system is that rapidly formed discrete reactive dimolybdate(VI) species are present, albeit at low steady-state concentration. Reactions involving the formation of dimolybdate(VI) species would be expected to be fast since kinetic studies of the rapid molybdate(VI) polymerization[8] in weakly acidic solution provided no evidence for condensed species intermediate between monomer and heptamer. Reaction of molybdate(VI) with dimolybdate(VI) must therefore also be rapid, and fast complexation of $Co(NH_3)_5OH_2^{3+}$ with dimolybdate(VI) and hence catalysis of $Co(NH_3)_5MoO_4^+$ formation by a second molybdate(VI) are not unreasonable.

The form of the rate law (9) provides certain information regarding the degree of protonation of the dimolybdate(VI) species, and reactions of $Co(NH_3)_5OH_2^{3+}$ with $Mo_2O_8^{4-}$ (k_c) and $HMo_2O_8^{3-}$ (k_d) and of $Co(NH_3)_5OH^{2+}$ with $HMo_2O_8^{3-}$ (k_c) and $H_2Mo_2O_8^{2-}$ (k_d) are the only possibilities. Since dimolybdate(VI) anions in aqueous solution were previously unknown,[24] it is not possible to comment on these species any further, and the formulas above simply represent the number of protons and monomeric molybdate(VI) species involved and imply nothing regarding coordination number or degree of hydration. Comparisions with dichromate(VI) should be avoided since of the species above only $H_2Mo_2O_8$,$^{2-}$ i.e., $Mo_2O_7^{2-}$, can conceivably be tetrahedral.

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Registry No. $Co(NH_3)_5OH_2^{3+}$, 14403-82-8; $Co(NH_3)_5OH^{2+}$, 16632-75-0; $Co(NH_3)_5MoO_4^{+}$, 60464-07-5; $HMoO_4^{-}$, 14259-84-8.

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Nuclear Magnetic Resonance Investigation of Cobalt(II) Aminocarboxylates: Evidence for Pentadentate Coordination by EDTA

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The nuclear magnetic resonance temperature dependence of the complexes $Co^{II}[EDTA]^{2-}$, $Co^{II}[1,2\text{-}PDTA]^{2-}$, $Co^{II}[EDDA]$, $Co^{II}[(EDTA)(CN)]^{3-}$, $Co^{II}[ED3A]^{-}$, $Co^{II}[CyDTA]^{2-}$, $Co^{II}[1,3\text{-}PDTA]^{2-}$, $Co^{II}[(EDTA)(OH)]^{3-}$, $Co^{II}[IDA]$, and $Co^{II}(IDA)_2^{2-}$ are reported. Racemization is rapid for $Co^{II}[EDTA]^{2-}$, $Co^{II}[(EDTA)(CN)]^{3-}$, $Co^{II}[(EDTA)(OH)]^{3-}$, and $Co^{II}[1,3\text{-}PDTA]^{2-}$ at 34 °C; racemization of $Co^{II}[ED3A]^{-}$ is intermediate at 34 °C and rapid by 50 °C. $Co^{II}[EDTA]^{2-}$, $Co^{II}[1,2\text{-}PDTA]^{2-}$, and $Co^{II}[1,3\text{-}PDTA]^{2-}$ exist in solution predominantly as pentacoordinate species. The spectrum of $Co^{II}[EDTA]^{2-}$ is essentially pD independent in the pD range 2.7–11.6; pD dependence above pD 12 results from the formation of a mixed hydroxy complex. Deuteration of $Co^{II}[CyDTA]^{2-}$ is stereospecific; both in-plane and out-of-plane acetate arms experience first-order base-catalyzed deuteration. First-order rate constants for deuteration of $Co^{II}[CyDTA]$ are reported. Cis $\rightleftharpoons$ trans equilibration is rapid in $Co^{II}(IDA)_2^{2-}$ at room temperature. The reaction $Co^{II}(IDA) + Co^{II}(IDA)_2 \rightleftharpoons Co^{II}(IDA)_2 + Co^{II}(IDA)$ is rapid at elevated temperature with retention of IDA configuration. An S_N2 type mechanism is proposed for this reaction. The following abbreviations are used: $EDTA^{4-}$, $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$; $1,2\text{-}PDTA^{4-}$, $(^-O_2CCH_2)_2NCH(CH_3)CH_2N(CH_2CO_2^-)_2$; $EDDA^{2-}$, $(^-O_2CCH_2)NHCH_2CH_2NH(CH_2CO_2^-)$; $ED3A^{3-}$, $(^-O_2CCH_2)NHCH_2CH_2N(CH_2CO_2^-)_2$; $CyDTA^{4-}$, *trans*-$1,2\text{-}(^-O_2CCH_2)_2N(c\text{-}Hx)N(CH_2CO_2^-)_2$; $1,3\text{-}PDTA^{4-}$, $(^-O_2CCH_2)_2NCH_2CH_2CH_2N(CH_2CO_2^-)_2$; IDA^{2-}, $(^-O_2CCH_2)_2NH$.

Introduction

The solution structure of bivalent and trivalent transition metal complexes of EDTA and related ligands has long been investigated. The results of these investigations are conflicting and no one has succeeded to date in unambiguously determining the number of coordination sites actually utilized by EDTA type ligands to coordinate labile metal ions. The early works of Schwarzenbach[1] concluded that transition metal–EDTA complexes assume a pentacoordinate structure with a molecule of H_2O, OH^-, or some other unidentate ligand occupying the sixth position. Jorgensen,[2] on the basis of electronic spectroscopy data, also assigned pentacoordination to such complexes. Higginson[3] compared acid dissociation constants of various metal–EDTA complexes and concluded that for most bivalent transition metal–EDTA complexes only five of the possible six sites available are utilized by the EDTA chelate. More recently, Higginson spectrophotometrically determined stability constants for mixed-complex formation of EDTA and various unidentate ligands and concluded that aqueous solutions of metal complexes containing EDTA and other related ligands, PDTA and CyDTA, exist as hexacoordinate species approximately 70% of the time [76% for Co(II)].[4] Charles[5] concluded from the viscosities of aqueous solutions containing bivalent metal–EDTA complexes that, with the exception of Pb, a hexacoordinated structure is favored. Later, on the basis of large differences found between the Jones–Dale viscosity coefficients for Co^{II}EDTA and Co^{III}EDTA, Yasuda[6] proposed that Co^{II}EDTA is present as a pentadentate complex or possibly as a mixture of the penta- and hexacoordinated species. The x-ray studies of Hoard[7,8] have clearly shown that an uncoordinated acetate exists in solid Co^{II}EDTA but did not allow for the assignment of a coordination number to the solution structure of this complex. The spectrophotometric studies of EDTA complexes mixed with OH^- and NH_3 led Bhat[9] to assume hexacoordination for Co^{II}EDTA and Cu^{II}EDTA and pentacoordination for Ni^{II}EDTA. Burnett[10] interpreted the free energy and enthalpy changes which accompanied the protonation of divalent metal–EDTA complexes as a hexacoordinate geometry existing in the original species. Margerum and Rosen[11] utilized kinetic behavior of Ni^{II}EDTA to assign pentacoordination while Wilkins and Yelin[12] interpreted their kinetic scheme to indicate at least 80% hexacoordination for Co^{II}EDTA. Later, Wilkins and Yelin[13] rapidly oxidized the labile Co^{II}EDTA and examined the resultant inert Co^{III}EDTA complexes; the results of these experiments were in agreement with their previous conclusions. ^{13}C and ^{17}O NMR spectroscopy led Matwiyoff[14] to conclude hexacoordination for Ni^{II}EDTA in a pH range of 4–10 and, at pH <4, an equilibrium between hexa- and pentacoordination. In his work Matwiyoff stated that if Co^{II}EDTA is hexacoordinate, it is stereochemically nonrigid.

It has been well established[15] for Ni(II) complexes of EDTA and related ligands that the conformationally different protons of the ethylene backbone and acetate arms experience large chemical shifts resulting from the delocalization of the unpaired d electrons toward the ligand. It has also been