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Synthesis, acid hydrolysis and formation of the $[(H_3N)_5CoOMoO_3]^+$ ion in aqueous solution

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The complex $[(H_3N)_5CoOMoO_3]ClO_4$ has been synthesised and characterised by elemental analysis, UV/VIS and infrared spectroscopy. The kinetics of its acid hydrolysis has been studied using the stopped-flow technique over the ranges $0.01 \leqslant [H^+] \leqslant 0.45$ mol dm^{-3}, $24.9 \leqslant \theta \leqslant 35.6$ °C, $0.04 \leqslant I \leqslant 1.0$ mol dm^{-3} ($NaClO_4$). The rate of reaction is inversely dependent on $[H^+]$ due to the expansion of the co-ordination of the molybdenum(VI) from four to six on protonation, along with resonance stabilisation. The rate constant (k_1) for the hydrolysis is 5.09 ± 0.02 s^{-1} at 24.9 °C for which $\Delta H^\ddagger = 82 \pm 1$ kJ mol^{-1} and $\Delta S^\ddagger = 43 \pm 5$ J K^{-1} mol^{-1}. The kinetics of formation of the complex from pentaammineaquacobalt(III) and molybdate(VI) ions has been studied using the stopped-flow method over the range pH 7.13–8.46 and at 25.0–35.9 °C, $I = 1.0$ mol dm^{-3}. Over this pH range both $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_5(OH)]^{2+}$ ion react with $HMoO_4^-$ to give $[(H_3N)_5CoOMoO_3]^+$, and the rate constants are $(2.03 \pm 0.05) \times 10^6$ and $(2.73 \pm 0.05) \times 10^5$ dm^3 mol^{-1} s^{-1}, respectively at 25.0 °C. Both acid hydrolysis and complexation are very rapid, suggesting a mechanism involving cleavage of the Mo^{VI}–O not the Co^{III}–O bond. Details of both mechanisms are discussed.

A significant feature of molybdenum chemistry is its wide range of stable and readily attainable oxidation states.[1] This more than any other factor is probably relevant in attempting to unravel the role of molybdenum in molybdoenzymes. The aim in the first instance is a better understanding of the co-ordination chemistry of molybdenum, while keeping very much in mind (and also attempting to understand) the remarkable properties and functions of molybdenum in enzymes.[2–5]

A series of novel cobalt(III) molybdato complexes were synthesised by Coomber and Griffith[6] in 1967. Since then there has been a resurgence of interest in the kinetic study of one of these complexes. The kinetics of the formation of the complex $[(H_3N)_5CoOMoO_3]^+$ was first reported by Taylor[7] in 1977 and more recently by Grace and Tregloan.[8] The rapid complexation was attributed[7,8] to a mechanism involving substitution at the molybdenum(VI) centre. A detailed mechanism of the formation of the complex was proposed by Grace and Tregloan,[8] and they concluded that the second-order term in $[MoO_4^{2-}]$ had arisen from $HMoO_4^-$ acting as a general acid catalyst.

We have, in recent years, been interested in the reactivity of co-ordinated oxoanions. We have reported previously[9,10] a detailed kinetic study on the formation and acid-catalysed hydrolysis of the $[(H_3N)_5CoOCrO_3]^+$ and have now extended this study to include the synthesis, acid hydrolysis and the effect of temperature on the formation of $[(H_3N)_5CoOMoO_3]^+$ ion in aqueous solution.

Experimental

Materials

All reagents were of analytical grade. Distilled water was used in the preparative work, while ultrapure water, obtained by deionising distilled water using a Milli-Q Reagent Grade water system (Millipore Co., Bedford, MA, U.S.A.), was used to make up solutions for all physical measurements.

Preparation of the complexes

The complex $[Co(NH_3)_5(OH_2)][ClO_4]_3$ was prepared by the standard method,[11,12] and its purity checked by UV/VIS spectrophotometry ($\varepsilon_{490} = 49.2$; lit.,[13] 49 dm^3 mol^{-1} cm^{-1}). The complex $[(H_3N)_5CoOMoO_3]ClO_4$ was prepared as by Grace and Tregloan[8] with the following modifications: $Na_2[MoO_4]\cdot 2H_2O$ (5.0 g, 0.0207 mol) was dissolved in deionised water (30 cm^3); then $[Co(NH_3)_5(OH_2)][ClO_4]_3$ (9.5 g, 0.0206 mol) was added in small portions with stirring. There was a rapid purple intensification of the mixture. The resultant mixture was cooled in an ice-bath for 30 min; then filtered, the residue was washed with cold water, 95% ethanol, and finally diethyl ether. The purple complex was then air dried. Yield: 6.66 g (80%). It was moderately soluble in water. The purity was checked by elemental analysis (Found: H, 3.65; Cl, 9.30; Co, 14.5; Mo, 23.8, N, 16.8. Calc. for $H_{15}ClCoMoN_5O_8$: H, 3.75; Cl, 8.80; Co, 14.6; Mo, 23.8; N, 17.4%). Visible spectrum: λ_{max}/nm (0.1 mol dm^{-3} Na_2MoO_4) 360 (61.3) and 526 (91.7). Infrared spectrum: (ε/dm^3 mol^{-1} cm^{-1}) bridging molybdate(VI), $\tilde{\nu}$(Mo–O)/cm^{-1} 848.5m (br).[6]

Instrumentation

All visible and ultraviolet spectra were recorded with either a Philips Scientific model PU 8800 or a Hewlett-Packard 8452A diode-array spectrophotometer and the infrared spectrum with a Perkin-Elmer 1600 series FT IR spectrophotometer employing KBr discs. Kinetic measurements were made using a Hi-Tech scientific SF-51 stopped-flow spectrophotometer interfaced with a computer. The spectrophotometer syringes were immersed in a water-bath linked to a thermostat system (Haake D8) capable of maintaining temperatures within ±0.02 °C.

For the acid hydrolysis, stock solutions of the complex and perchloric acid of known concentrations were prepared in volumetric flasks (10 cm^3). The ionic strength of each solution was adjusted to the required value with appropriate amounts of $NaClO_4$ and the flasks were thermostatted for 10 min before introducing the solutions into the syringes of the stopped-flow apparatus. The apparatus was equilibrated at the reaction temperature for at least 0.5 h prior to use and the solutions were kept in the thermostatted drive syringes for 5 min before each experiment.

The same procedure was repeated for the formation studies, except that both complex and sodium molybdate were buffered with tris(hydroxymethyl)aminomethane (Tris) at ionic strength 1.0 mol dm^{-3} with $NaClO_4$ as supporting electrolyte. The $NaClO_4$ solution was standardised by an ion-exchange method using Dowex 50 W-X8 (50 mesh, H^+ form) resin. Kinetic runs were made at 524 nm, where there is an appreciable change in absorbance between the pentaammineaquacobalt(III) ion (ε_{524} = 37.9 dm^3 mol^{-1} cm^{-1}) and $[(H_3N)_5CoOMoO_3]^+$ ion (ε_{524} = 87.5 dm^3 mol^{-1} cm^{-1}). All measurements were done under pseudo-first-order conditions. For the acid hydrolysis the acid was in excess, while in the formation study molybdate(VI) was in excess.

The equilibrium constants for the formation of $[(H_3N)_5CoOMoO_3]^+$ were determined spectrophotometrically over the range $7.06 \leqslant pH \leqslant 7.90$ at $I = 0.9$ mol dm^{-3} ($NaClO_4$) at 524 nm with the Tris buffer.

The kinetic data were collected and processed with the Hi-Tech Scientific IS-1 software suite V 1.0a. The pseudo-first-order rate constants (k_{obs}) were determined by a non-linear least-squares regression fit to the curve of the photomultiplier voltage *versus* time. The reported rate constants are averages of at least seven kinetic runs. The standard deviation for each k_{obs} is ±5%.

Results and Discussion

(*a*) Formation studies

Addition of rose-red pentaammineaquacobalt(III) perchlorate solution to an excess of molybdate solution resulted in a rapid intensification in colour to give a purple solution. The final spectrum obtained was identical to that of the complex $[(H_3N)_5CoOMoO_3]^+$. The equilibrium constant for this reaction represented by equations (1) and (2) was determined

$$[Co(NH_3)_5(OH)]^{2+} + H^+ \xrightleftharpoons{K_H} [Co(NH_3)_5(OH_2)]^{3+} \quad (1)$$

$$[Co(NH_3)_5(OH_2)]^{3+} + MoO_4^{2-} \xrightleftharpoons{K_1} [(H_3N)_5CoOMoO_3]^+ + H_2O \quad (2)$$

using the Benesi–Hildebrand method[14] over the range pH 7.06–7.90. The apparent absorption coefficient, ε_{obs}, can be expressed as in equation (3) where ε_{OH}, ε_A and ε_C represent the

$$\varepsilon_{obs} = \frac{\varepsilon_{OH} + \varepsilon_A K_H[H^+] + \varepsilon_C K_1 K_H[H^+][MoO_4^{2-}]}{1 + K_H[H^+] + K_1 K_H[H^+][MoO_4^{2-}]} \quad (3)$$

molar absorption coefficients of $[Co(NH_3)_5(OH)]^{2+}$, $[Co(NH_3)_5(OH_2)]^{3+}$ and $[(H_3N)_5CoOMoO_3]^+$, respectively. The values of ε_A and ε_{OH} were determined from the spectra of the pentaammineaquacobalt(III) ion in 0.1 mol dm^{-3} $HClO_4$ and Tris buffer in the range pH 7.36–7.89. At 524 nm the value of ε_{OH} was 61 dm^3 mol^{-1} cm^{-1}. Equation (3) can be rearranged to (4), where $\Delta\varepsilon = (\varepsilon_A - \varepsilon_{OH}) + (\varepsilon_C - \varepsilon_{OH})K_1[MoO_4^{2-}]$. Plots

$$(\varepsilon_{obs} - \varepsilon_{OH})^{-1} = \Delta\varepsilon^{-1}(1 + K_1[MoO_4^{2-}] + K_H^{-1}[H^+]^{-1}) \quad (4)$$

of $(\varepsilon_{obs} - \varepsilon_{OH})^{-1}$ *versus* $[H^+]^{-1}$ at various molybdate concentrations are shown in Fig. 1. Since the value of K_H has been[7] previously determined as 2.44 x 10^6 dm^3 mol^{-1} the values of K_1 at the three different temperatures were calculated from the ratios of slope to intercept of Fig. 1, *i.e.* 459 ± 19, 539 ± 40 and 588 ± 24 dm^3 mol^{-1} at 25.0, 30.2 and 35.0 °C, respectively. The values of ΔH° and ΔS° were then determined as 19 ± 3 kJ mol^{-1} and 115 ± 9 J K^{-1} mol^{-1}, respectively.

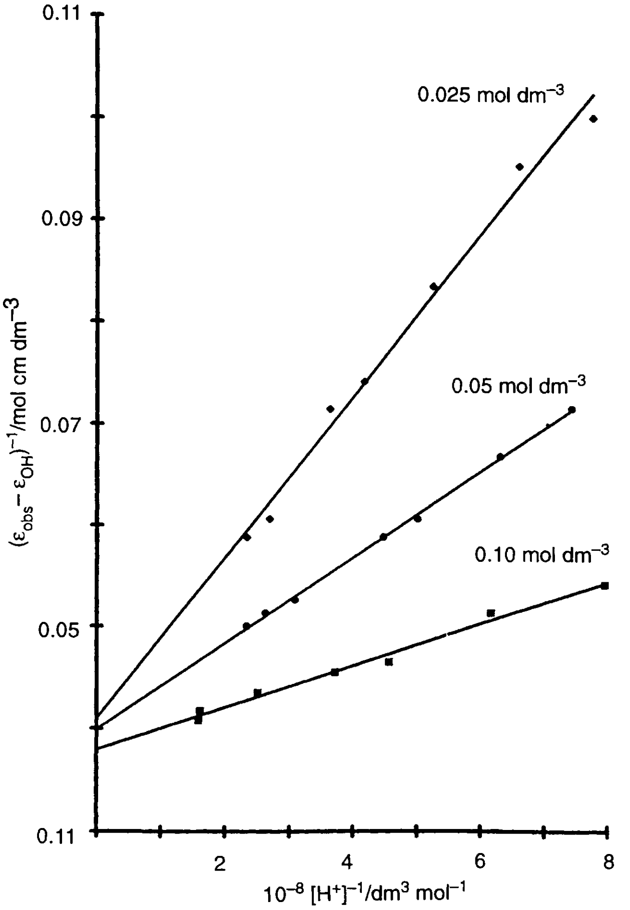
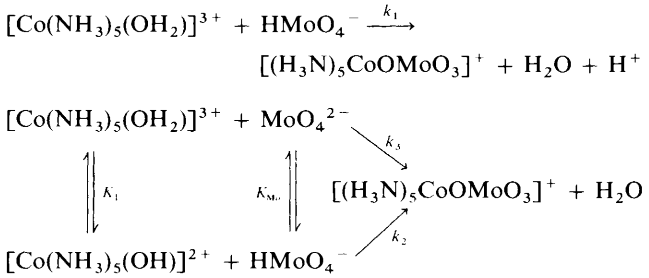


Fig. 1 Benesi–Hildebrand plots for the determination of the apparent binding constants, *k*, at various molybdate(VI) concentrations for the reaction of $[Co(NH_3)_5(OH_2)]^{3+}$ with MoO_4^{2-} at 25.0 °C and I = 0.9 mol dm^{-3} ($NaClO_4$)



Scheme 1

The kinetics of the formation of $[(H_3N)_5CoOMoO_3]^+$ was studied over the ranges $7.13 \leqslant pH \leqslant 8.46$, $0.01 \leqslant [MoO_4^{2-}] \leqslant 0.10$ mol dm^{-3} and $25.0 \leqslant \theta \leqslant 35.9$ °C. Tables 1, 2 and 3 summarise the results obtained for k_{obs} at various pH, molybdate concentrations, $[NaH_2PO_4]$ and temperatures. The values show a dependence on $[H^+]$ and $[NaH_2PO_4]$ (see Tables 2 and 3). A change in supporting electrolyte, for example from $NaClO_4$ to $NaNO_3$ (1.0 mol dm^{-3}), results in no change in k_{obs} (0.76 and 0.71 s^{-1} at pH 8.46, 25.0 °C and [Tris] = 0.1 mol dm^{-3}, for $NaClO_4$ to $NaNO_3$, respectively). A change in the cations results in a change in k_{obs}, that is k_{obs} (K^+) > k_{obs} (Na^+) > k_{obs} (Li^+) as shown in Table 3.

Over this pH range the main molybdate species are the $HMoO_4^-$ and MoO_4^{2-} ions. The pentaammineaquacobalt(III) ion is present as an equilibrium mixture of $[Co(NH_3)_5(OH_2)]^{3+}$ and $[Co(NH_3)_5(OH)]^{2+}$ ions. The observed decrease in rate constant with increasing pH is interpreted in terms of Scheme 1.

Table 1 Pseudo-first-order rate constants for the formation of $[(H_3N)_5CoOMoO_3]^+$; variation in $[MoO_4^{2-}]$, $\lambda = 524$ nm, [complex] = 2×10^{-3} mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$), $\theta = 25.0$ °C, [Tris] = 0.1 mol dm^{-3}, buffer = Tris–$HClO_4$

	k_{obs}/s^{-1}		
$[MoO_4^{2-}]$/mol dm^{-3}	pH 7.12	pH 7.45	pH 8.03
0.01	1.07	0.55	0.29
0.02	1.74	0.85	0.38
0.03	2.56	1.21	0.47
0.04	3.50	1.64	0.54
0.05	4.82	2.13	0.64
0.06	5.93	2.68	0.73
0.07	7.43	3.32	0.84
0.08	9.71	3.93	0.97
0.09	10.9	4.70	1.06
0.10	12.1	5.54	1.19

Table 2 Pseudo-first-order rate constants for the formation of $[(H_3N)_5CoOMoO_3]^+$; variation in pH and temperature, $\lambda = 524$ nm, [complex] = 2×10^{-3} mol dm^{-3}, $I = 1.0$ mol dm^{-3} ($NaClO_4$), $[MoO_4^{2-}] = 0.07$ mol dm^{-3}, [Tris] = 0.1 mol dm^{-3}, buffer = Tris–$HClO_4$

θ = 25.0 °C*		θ = 30.9 °C		θ = 35.9 °C	
pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}	pH	k_{obs}/s^{-1}
7.18	8.06	7.14	16.5	7.13	30.0
7.28	5.93	7.24	11.5	7.23	20.2
7.36	4.64	7.34	8.42	7.33	14.9
7.46	3.32	7.44	6.01	7.43	10.8
7.58	2.39	7.54	4.42	7.53	8.36
7.69	1.72	7.64	3.41	7.65	5.73
7.78	1.31	7.74	2.41	7.75	4.25
7.86	1.09	7.83	1.93	7.85	3.52
7.96	0.89	7.94	1.55	7.95	2.75
8.03	0.84	8.05	1.23	8.03	2.31
8.08	0.82	—	—	—	—

* [complex] = 3×10^{-3} mol dm^{-3}, pH 7.23, $k_{obs} = 7.17$ s^{-1}; [complex] = 4×10^{-3} mol dm^{-3}, pH 7.23, $k_{obs} = 7.72$ s^{-1}, [complex] = 1×10^{-3} mol dm^{-3}, pH 7.28, $k_{obs} = 5.78$ s^{-1}.

Table 3 Pseudo-first-order rate constants for the formation of $[(H_3N)_5CoOMoO_3]^+$;* effect of cations and NaH_2PO_4, $\lambda = 524$ nm, [complex] = 2×10^{-3} mol dm^{-3}, $[MoO_4^{2-}] = 0.04$ mol dm^{-3}, [Tris] = 0.2 mol dm^{-3}, $\theta = 25.0$ °C, pH 7.36, $I = 1.0$ mol dm^{-3} ($NaNO_3$), buffer = Tris–HNO_3

10^3 $[H_2PO_4^-]$/mol dm^{-3}	k_{obs}/s^{-1}
0.5	7.42
1.0	11.4
2.0	19.3
3.0	28.2
4.0	39.4

* $I = 1.0$ mol dm^{-3} ($LiNO_3$), $k_{obs} = 2.62$ s^{-1}; $I = 1.0$ mol dm^{-3} ($NaNO_3$), $k_{obs} = 3.34$ s^{-1}; $I = 1.0$ mol dm^{-3} (KNO_3), pH 7.54, $k_{obs} = 3.54$ s^{-1}.

The possibility of the $[Co(NH_3)_5(OH)]^{2+}$ ion reacting with MoO_4^{2-} was discarded on the basis that this would result in an increase in k_{obs} with increasing pH since the concentration of both these species increases with increasing pH. The k_2 and k_3 paths are mechanistically identical and are therefore indistinguishable.

The proposed mechanism leads to expression (5) where

$$\frac{k_{obs}}{[MoO_4^{2-}]_T} = \frac{k_1[H^+]^2 + k_2K_1[H^+] + k_3K_{Mo}[H^+]}{(K_1 + [H^+])(K_{Mo} + [H^+])} \quad (5)$$

$[MoO_4^{2-}]_T$ represents the total molybdate concentration. Since the k_2 and k_3 paths are indistinguishable, the expression can be simplified to (6) which can be rearranged to give (7).

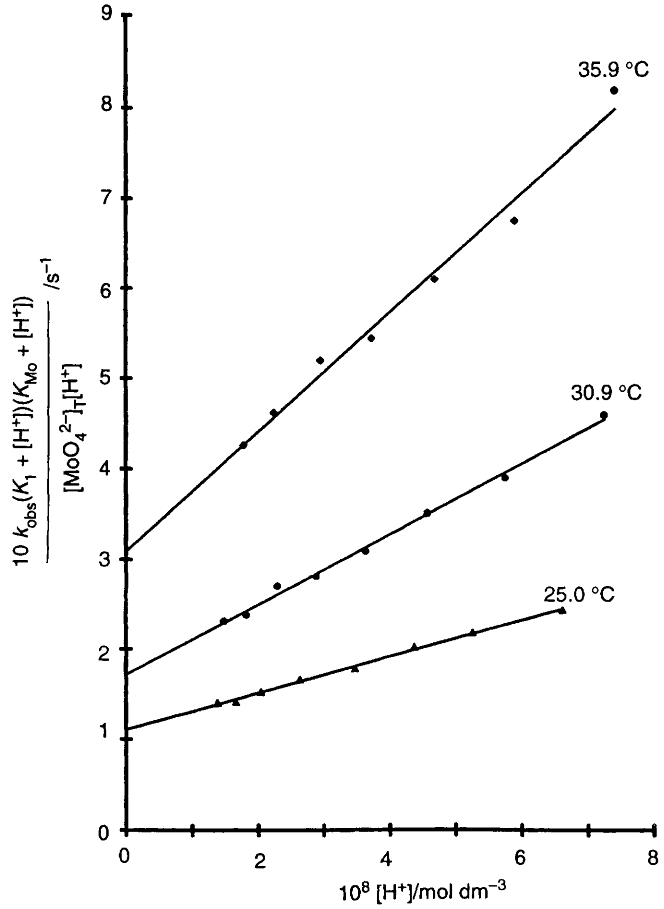


Fig. 2 Plots of the left-hand side of equation (7) *versus* $[H^+]$ for the formation of $[(H_3N)_5CoOMoO_3]^+$ at various temperatures

$$\frac{k_{obs}}{[MoO_4^{2-}]_T} = \frac{k_1[H^+]^2 + k_2K_1[H^+]}{(K_1 + [H^+])(K_{Mo} + [H^+])} \quad (6)$$

$$\frac{k_{obs}(K_1 + [H^+])(K_{Mo} + [H^+])}{[MoO_4^{2-}]_T[H^+]} = k_1[H^+] + k_2K_1 \quad (7)$$

Here, $pK_1 = 6.39$ and $pK_{Mo} = 3.53$.[7] Plots of the left-hand side of equation (7) *versus* $[H^+]$ was linear in the range $7.13 \leqslant pH \leqslant 7.86$, with slope k_1 and intercept k_2K_1, over the temperature range shown in Fig. 2. The values of k_1 and k_2 obtained were used as initial fitting parameters for a non-linear regression analysis of equation (6) in the range $7.13 \leqslant pH \leqslant 7.86$ by a computer iterative process. The final values of k_1 and k_2 are shown in Table 4, along with the corresponding enthalpy and entropy of activation calculated using Eyring's equation.[15]

The rapid formation rate constants observed [at 25.0 °C, $k_1 = (2.03 \pm 0.05) \times 10^6$ dm^3 mol^{-1} s^{-1} and $k_2 = (2.73 \pm 0.05) \times 10^5$ dm^3 mol^{-1} s^{-1}] are consistent with a mechanism involving substitution at the Mo^{VI} and not the Co^{III} since values for reactions involving Co^{III}–O bond cleavage[16–19] are of the order of 10^{-5}–10^{-7} s^{-1}. It is interesting that the exchange of $[Co(NH_3)_5(OH_2)]^{3+}$ with $^{18}OH_2$ occurs[16] at a rate of 5.9×10^{-6} s^{-1} as compared[17] with 5.4×10^{-2} s^{-1} for MoO_4^{2-}.

Taylor[7] studied the formation of $[(H_3N)_5CoOMoO_3]^+$ in the range pH 7.1–8.0. He noted that the complexation showed a greater than first-order dependence upon $[MoO_4^{2-}]$ and that the rate of reaction was consistent with substitution at Mo^{VI} rather than at Co^{III}. The values of the rate constants, k_1 and k_2, obtained by him of $(3.2 \pm 0.6) \times 10^5$ and $(6.6 \pm 0.5) \times 10^4$ dm^3 mol^{-1} s^{-1}, respectively, differ significantly from our values

Table 4 Rate parameters * for the formation of $[(H_3N)_5CoOMoO_3]^+$

θ/°C	$10^{-6}\ k_1$/dm^3 mol^{-1} s^{-1}	$10^{-5}\ k_2$/dm^3 mol^{-1} s^{-1}
25.0	2.03 ± 0.05	2.73 ± 0.05
30.9	3.91 ± 0.10	4.20 ± 0.10
35.9	6.62 ± 0.32	7.59 ± 0.39

$\Delta H_1^\ddagger = 81 \pm 1$ kJ mol^{-1}, $\Delta H_2^\ddagger = 69 \pm 9$ kJ mol^{-1}, $\Delta S_1^\ddagger = 146 \pm 1$ J K^{-1} mol^{-1}, $\Delta S_2^\ddagger = 89 \pm 35$ J K^{-1} mol^{-1}

* The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values should be considered as approximate due to the limitation of the temperature range to 10 °C.

(Table 4). The exact reasons for these differences seem to be due to the difference in mechanistic interpretation. Taylor's rate expression contains[7] more rate parameters than ours, which made the fitting of raw data relatively much easier by non-linear regressional analysis, but the error limits for each individual rate constant became bigger. We did not find any reason to make our mechanism more complicated than what we proposed. Our value for the equilibrium constant of 459 ± 19 dm^3 mol^{-1} at 25.0 °C compares well with Taylor's value.[7] A marked decrease in k_{obs} has been observed on changing the medium from $NaClO_4$ to $LiClO_4$ (see Table 3). Similar observations were made by Taylor.[7] We think that this is entirely due to the variation of hydration number of the alkali-metal ions. The ionic radius of Group 1 cations increases as one goes down the group, but the approximate hydrated radius and approximate hydration numbers decrease.[20] Of the three cations studied, Li^+ has the smallest ionic radius (0.86 Å) and the largest hydrated radius (3.40 Å), while K^+ has the largest crystal radius (1.44 Å) and the smallest hydrated radius (2.32 Å). Owing to the large hydrated radius of Li^+, the rate of nucleophilic attack of $[Co(NH_3)_5(OH_2)]^{3+}/[Co(NH_3)_5(OH)]^{2+}$ on $HMoO_4^-$ would be lower than that of a medium containing Na^+ or K^+ ion, which has a smaller hydrated radius and hence $k_{obs}(K^+) > k_{obs}(Na^+) > k_{obs}(Li^+)$.

Grace and Tregloan[8] also studied the formation of $[(H_3N)_5CoOMoO_3]^+$ in the range pH 7.1–8.0. They suggested that the observed second-order rate dependence upon $[MoO_4^{2-}]$ may be explained by $HMoO_4^-$ acting as a proton-donating catalyst. An increase in rate upon the addition of other protonated anions (HCO_3^- and $H_2PO_4^-$) to the reaction solution, which supported the contention of a general proton-assisted mechanism, has also been noted. A similar increase in the reaction rate was also noted when $H_2PO_4^-$ was added, and as a result it is concluded that the second-order dependence upon $[MoO_4^{2-}]$ is due to $HMoO_4^-$ acting as a proton-donating catalyst in the course of complexation. The values of the rate constants determined by Grace and Tregloan[8] are $k_1 = (6.6 \pm 0.9) \times 10^4$ and $k_2 = (1.3 \pm 0.2) \times 10^6$ dm^3 mol^{-1} s^{-1}, both different from our values (Table 4), perhaps because of the same reasons as previously discussed.

The mechanism of complex formation probably involves nucleophilic attack by the oxygen of the aqua or hydroxo ligand of the cobalt(III) complex at the molybdenum(VI) centre. This will result in a hydrogen-bonded activated complex in which the Mo^{VI} assumes a five-co-ordinate geometry, possibly distorted trigonal bipyramidal (molybdenum can expand its co-ordination sphere), with the loss of water resulting in Mo^{VI}–O bond cleavage. This process can be classified as an associative interchange (I_a) mechanism, with comparable activation parameters. Molybdenum(VI) with a d^0 configuration has available d orbitals for attack by an entering ligand, making this mechanism quite feasible. The transition states for this mechanism are shown in Fig. 3 for the k_1 and k_2 paths. The presence of the additional proton in the transition state labilises the system and accelerates the various bond adjustments required to release the water molecule, resulting in the k_1 path being faster than the k_2 path.

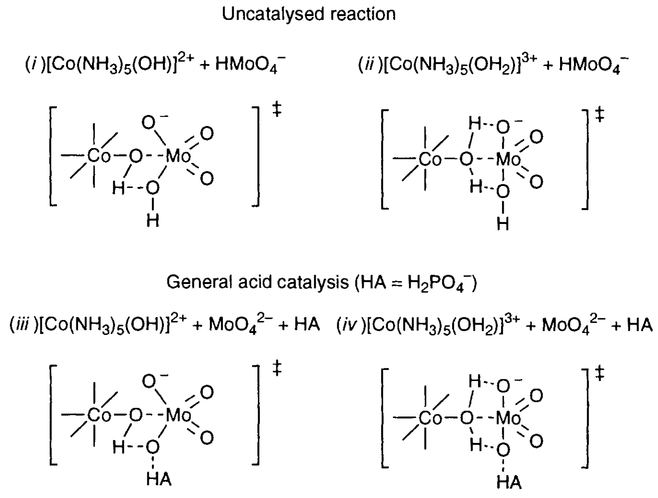


Fig. 3 Possible transition states for the formation of $[(H_3N)_5CoOMoO_3]^+$

The enthalpies of activation for the formation of $[(H_3N)_5CoOMoO_3]^+$ from the aqua- and hydroxo-cobalt(III) moieties are 81 ± 1 and 69 ± 9 kJ mol^{-1}, respectively. These values are in contrast to those of the order 100–130 kJ mol^{-1} usually observed for reactions based on Co^{III}–O bond fission, for example solvent water exchange with the $[Co(NH_3)_5(OH_2)]^{3+}$ ion[16] shows $\Delta H_{ex} = 118$ kJ mol^{-1}. The activation energy for solvent exchange of the molybdate anion[17] is 62.8 kJ mol^{-1} (k_a path) at pH > 11, where only the MoO_4^{2-} exists. For the k_b path the value is 70.3 kJ mol^{-1}. The values show a remarkable similarity with our values for the k_1 and k_2 paths, and this could suggest a similarity in the mechanisms of the reactions. The smaller value for $\Delta S_2^\ddagger$ (89 ± 35 J K^{-1} mol^{-1}) suggests that the transition state for the k_2 path is more organised than that for the k_1 path.

The possibility of a dissociative mechanism occurring for the formation reactions should also be considered. Over the pH range employed the transfer of a proton from $[Co(NH_3)_5(OH_2)]^{3+}$ ($pK_1 = 6.39$) to $HMoO_4^-$ ($pK_{Mo} = 3.53$) is expected to be less likely.[7] Previously, a dissociative mechanism has been proposed by Haim[21] for the reactions of chromate(VI) with ions such as hydrogenthiosulfate, hydrogenthiocyanate, and hydrogenchromate in acidic media. We have worked under weakly basic conditions, so we would expect the reaction to be associatively activated. Associative mechanisms have been proposed for reactions with chromate, arsenate, iodate, and selenate which proceed without cleavage of the Co^{III}–O bond.[9]

The positive $\Delta S^\ddagger$ values would seem consistent with a dissociative mechanism, but a conclusive mechanism cannot be drawn from the activation parameters obtained here due to the errors associated with the narrow temperature range since in our case the $\Delta H^\ddagger$ values and $\Delta S^\ddagger$ values compensate each other. As a result of the high $\Delta H^\ddagger$ values the $\Delta S^\ddagger$ values would compensate by being very positive. The positive $\Delta S^\ddagger$ values might be due to the proton involved in the transition state. One would expect a large contribution of solvation entropy which makes the I_a mechanism quite feasible.

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 dm^3 mol^{-1}) at this ionic strength ($I = 1.0$ mol dm^{-3}, $NaClO_4$), since under our conditions $[Co(NH_3)_5(OH)]^{2+}$ is the predominant cobalt(III) species. Moreover a low value of K_o for molybdate might be expected from the results of studies on the ion pair of the related complex $[Co(NH_3)_6]^{3+}$ with[19] molybdate(VI) and sulfate,[22] where $K_o(SO_4^{2-})$ is reported to be six (6) times $K_o(MoO_4^{2-})$.[19] It is unlikely that, even at the highest $[MoO_4^{2-}]$ and lowest pH, the concentration of the ion pair is greater than 5% that of the total aqua complex.

The rate of formation of the $[(H_3N)_5CoOMoO_3]^+$ compared with that of the analogous chromate ion, which is formed by a similar mechanism as shown[9] in equations (8) and (9), with $k_1 = 16.4$ and $k_2 = 8.03$ dm^3 mol^{-1} s^{-1} at 25 °C. These

$$[Co(NH_3)_5(OH_2)]^{3+} + HCrO_4^- \xrightarrow{k_1} [(H_3N)_5CoOCrO_3]^+ + H_2O + H^+ \quad (8)$$

$$[Co(NH_3)_5(OH)]^{2+} + HCrO_4^- \xrightarrow{k_2} [(H_3N)_5CoOCrO_3]^+ + H_2O \quad (9)$$

formation rate constants are lower in comparison with those of $[(H_3N)_5CoOMoO_3]^+$. This suggests that the Mo^{VI}–O bond is more labile than the Cr^{VI}–O bond towards substitution, which is borne out by the rapid water exchange rate of MoO_4^{2-}, $k_{ex} = 5.4 \times 10^2$ s^{-1} at 5 °C,[17] whereas k_{ex} for CrO_4^{2-} is 3.2×10^{-7} s^{-1} at 25 °C.[9] The greater ability of the MoO_4^{2-} to expand its co-ordination sphere can facilitate the formation of the five-co-ordinate geometry required in the transition state more easily than can the chromate ion. This can also contribute to the enhanced rates observed. The reaction between the aquacobalt(III) moiety and $HCrO_4^-$ is faster than that of the hydroxo moiety, an observation also made in our studies with the molybdate ion.

(*b*) Acid hydrolysis

On mixing $[(H_3N)_5CoOMoO_3]ClO_4$ with $HClO_4$ there was a rapid change from purple to rose red, the colour of $[Co(NH_3)_5(OH_2)]^{3+}$. This product was confirmed by comparing the final spectrum after hydrolysis with that of an acidic synthetic mixture of $[Co(NH_3)_5(OH_2)]^{3+}$ and Na_2MoO_4 in the same stoichiometric proportion.

The kinetics of acid hydrolysis of $[(H_3N)_5CoOMoO_3]^+$ was studied by the stopped-flow technique over the acidity range $0.01 \leqslant [H^+] \leqslant 0.45$ mol dm^{-3}, $24.9 \leqslant \theta \leqslant 35.6$ °C, $0.04 \leqslant I \leqslant 1.0$ mol dm^{-3} and at ionic strength 1.0 mol dm^{-3} ($NaClO_4$). Table 5 summarises the results obtained for k_{obs} at the various hydrogen-ion concentrations. Table 6 shows the variation of k_{obs} with ionic strength. One can see that k_{obs} remains unchanged with changing ionic strength in the range $0.04 \leqslant I \leqslant 0.11$ mol dm^{-3}. This is consistent with a charged species and a neutral species reacting in the rate-determining step.

Table 5 Pseudo-first-order rate constants for the hydrolysis of $[(H_3N)_5CoOMoO_3]^+$; variation in $[H^+]$, λ = 524 nm, [complex] = 1×10^{-3} mol dm^{-3}, I = 1.0 mol dm^{-3} ($NaClO_4$)

	k_{obs}/s^{-1}		
$[H^+]$/mol dm^{-3}	θ = 24.9 °C	θ = 30.6 °C	θ = 35.6 °C
0.01	23.8	42.4	61.8
0.02	11.6	20.9	36.6
0.03	7.46	11.9	22.9
0.04	6.35	8.97	15.9
0.05	4.47	7.40	12.3
0.06	3.42	5.56	10.5
0.07	3.26	5.27	8.32
0.08	3.23	5.03	8.02
0.09	3.11	4.79	7.43
0.10	3.03	4.55	7.13
0.11	2.94	—	6.86
0.12	2.86	4.15	6.35
0.13	2.74	4.03	6.29
0.14	2.67	3.89	5.94
0.15	2.56	3.75	5.71
0.20	2.27	3.19	4.72
0.25	2.02	2.75	—
0.30	1.91	2.76	—
0.35	1.90	2.87	—
0.40	1.86	2.78	—
0.45	1.82	2.77	—

The observed rate constants are high, indicating that the reaction proceeds without cleavage of the cobalt(III) bond but with molybdenum(VI) bond cleavage.[16,17] It is also clear that there is an inverse dependence on $[H^+]$, *i.e.* a decrease in k_{obs} with increasing $[H^+]$ (Table 5). Such a dependency can be explained satisfactorily by the mechanism proposed shown in Scheme 2. This mechanism leads to expression (10). Assuming

$$k_{obs} = \frac{k_1K_1[H^+]}{1 + K_1[H^+] + K_1K_2[H^+]^2} \quad (10)$$

in the range $0.06 \leqslant [H^+] \leqslant 0.30$ mol dm^{-3} that $(K_1K_2[H^+]^2 + K_1[H^+]) \gg 1$, this expression can be simplified to (11)

$$k_{obs} = \frac{k_1K_1[H^+]}{K_1[H^+] + K_1K_2[H^+]^2} \quad (11)$$

which rearranges to (12). A plot of the left-hand side *versus*

$$1/k_{obs} = (1/k_1) + (K_2[H^+]/k_1) \quad (12)$$

$[H^+]$ is linear in the range $0.06 \leqslant [H^+] \leqslant 0.30$ mol dm^{-3}. This treatment is illustrated in Fig. 4 at the three temperatures, and the values of k_1 and K_2 obtained from these plots were used as

$$\underset{\textbf{A}}{[(H_3N)_5CoOMoO_3]^+} + H^+ \overset{K_1}{\rightleftharpoons} \underset{\textbf{B}\ \ \text{c.n.} = 4}{[(H_3N)_5CoOMoO_2(OH)]^{2+}}$$

$$[(H_3N)_5CoOMoO_2(OH)]^{2+} \xrightarrow[H_2O]{k_1} [Co(NH_3)_5(OH_2)]^{3+} + HMoO_4^-$$

$$[(H_3N)_5CoOMoO_2(OH)]^{2+} + H^+ + 2H_2O \overset{K_2}{\rightleftharpoons} \underset{\text{c.n.} = 6}{[(H_3N)_5CoOMoO(OH)_2(H_2O)_2]^{3+}}$$

$$HMoO_4^- + 2H_2O + 3H^+ \overset{K_3}{\rightleftharpoons} [Mo(OH)_4(H_2O)_2]^{2+}$$

$$[Mo(OH)_4(H_2O)_2]^{2+} \xrightarrow{\text{fast}} \text{polymolybdates}$$

Scheme 2 c.n. = Co-ordination number; $K_3 = 10^{3.7}$ dm^9 mol^{-3}

Table 6 Variation in ionic strength for the hydrolysis of $[(H_3N)_5CoOMoO_3]^+$; λ = 524 nm, [complex] = 1×10^{-3} mol dm^{-3}, θ = 28.3 °C, $[H^+]$ = 0.01 mol dm^{-3}, supporting electrolyte = $NaClO_4$

I/mol dm^{-3}	k_{obs}/s^{-1}
0.04	82.3
0.05	84.4
0.06	81.3
0.07	80.1
0.08	81.6
0.09	82.4
0.10	80.4
0.11	82.8

Table 7 Rate and equilibrium constants and activation parameters for the hydrolysis of $[(H_3N)_5CoOMoO_3]^+$

θ/°C	k_1/s^{-1}	K_1/dm^3 mol^{-1}	10^2K_2/dm^3 mol^{-1}
24.9	5.09 ± 0.02	119 ± 1	4.98 ± 0.05
30.6	9.47 ± 0.02	132 ± 1	7.50 ± 0.04
35.6	16.6 ± 0.02	119 ± 1	10.4 ± 0.07

$\Delta H^\ddagger = 82 \pm 1$ kJ mol^{-1}, $\Delta S^\ddagger = 43 \pm 5$ J K^{-1} mol^{-1}

Table 8 Rate constants for the hydrolysis of pentaamminecobalt(III) complexes with oxoanions as ligands. I = 1.0 mol dm^{-3}

Complex ion	k/s^{-1}	θ/°C	Ref.
$[Co(NH_3)_5(PO_4)]$	2.0×10^{-6}	60	31
$[Co(NH_3)_5(HPO_4)]^+$	1.1×10^{-6}	60	31
$[Co(NH_3)_5(H_2PO_4)]^{2+}$	1.6×10^{-5}	60	31
$[Co(NH_3)_5(HAsO_4)]^+$	2.9×10^{-5}	22	32
$[Co(NH_3)_5(H_2AsO_4)]^{2+}$	4.1×10^{-4}	22	32
$[Co(NH_3)_5(H_3AsO_4)]^{3+}$	6.7×10^{-1}	22	32
$[Co(NH_3)_5(CrO_4)]^+$	$3.7 \times 10^{-7\,a}$	25	33
$[Co(NH_3)_5(HCrO_4)]^{2+}$	8.3×10^{-1}	25	10
	$2.2 \times 10^{-3\,a}$	25	33
$[Co(NH_3)_5(H_2CrO_4)]^{3+}$	1.6×10^{4}	25	10
$[Co(NH_3)_5(HCrO_4)]^{2+} + H^+$	$1.5 \times 10^{2\,a}$	25	33
$[Co(NH_3)_5(HC_2O_4)]^{2+}$	2.4×10^{-8}	25	34
$[Co(NH_3)_5(H_2C_2O_4)]^{3+}$	2.1×10^{-5}	25	34
$[Co(NH_3)_5(O_2CMe)]^{2+}$	3.15×10^{-8}	25	35
$[Co(NH_3)_5(OSO_2Me)]^{2+}$	2.0×10^{-4}	25	13
$[Co(NH_3)_5(NO_2)]^{2+}$	1.15×10^{-4}	25	36
$[Co(NH_3)_5\{OP(OMe)_3\}]^{3+}$	2.0×10^{-4}	25	37
$[Co(NH_3)_5(HMoO_4)]^{2+}$	5.09	24.9	*b*

[a] I = 0.01 mol dm^{-3}. [b] This work.

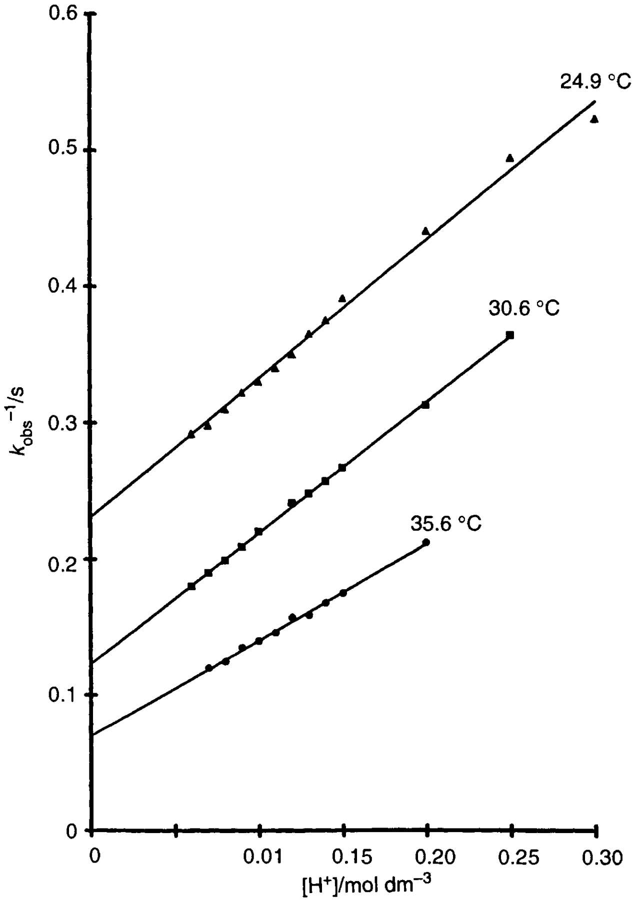
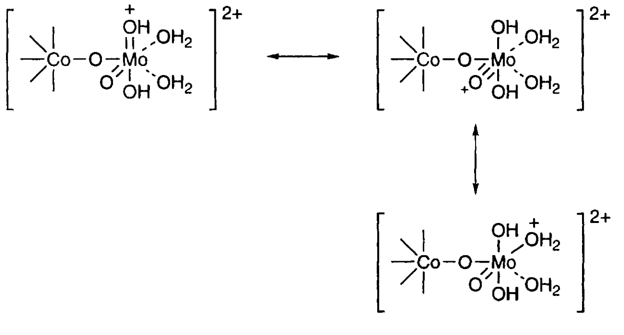


Fig. 4 Plots of $1/k_{obs}$ *versus* $[H^+]$ for the acid hydrolysis of $[(H_3N)_5CoOMoO_3]^+$ at various temperatures

initial fitting parameters for a non-linear regressional analysis of equation (10) in the range $0.06 \leq [H^+] \leq 0.30$ mol dm^{-3} by computer iteration. The final values of k_1, K_1 and K_2 along with the activation parameters are displayed in Table 7.

It is obvious from Scheme 2 that the cleavage of the Mo^{VI}–O bond in species C has not been considered because extension of the co-ordination sphere of the molybdenum(VI) by two H_2O molecules opens up the possibility of enhanced stabilisation by resonance. In the six-co-ordinated species the most basic O atoms (those bearing a negative charge, namely the terminal ones) become protonated. The resonance scheme is as shown.



It is seen in Table 7 that K_1, the protonation constant for the formation of $[(H_3N)_5CoOMoO_2(OH)]^{2+}$, is independent of temperature, having an average value of 123 dm^3 mol^{-1}. The acid-dissociation constant which can be expressed as K_1' ($= 1/K_1$) is 8.11×10^{-3} mol dm^{-3}, that is, pK_1' = 2.09. This result shows that there is a change of 1.44 pK units on going from the[7] 'free' $HMoO_4^-$ (pK_a = 3.53) to the co-ordinated monodentate $HMoO_4^-$ species, $[(H_3N)_5CoOMoO_2(OH)]^{2+}$. The p$K_a$ of the equilibrium involving $Mo(OH)_6$ [or more correctly $Mo_2(OH)_2(H_2O)_2$] is 3.7, which[23,24] is more basic than that of $[(H_3N)_5CoOMoO_2(OH)]^{2+}$. A similar study on $[(H_3N)_5CoOCrO_3]^+$ reported by Sadler and Dasgupta[10] revealed that the pK_1 of the protonated complex, $[(H_3N)_5CoOCrO_2(OH)]^{2+}$, was 3.6. It is obvious that the acidity of the complex changes with the metal centre; by changing the metal centre from Cr to Mo the acid-dissociation constant changes by about an order of magnitude.

The co-ordinated MoO_4^{2-} resembles the 'free' MoO_4^{2-} closely in chemistry on protonation. For the 'free' molybdate(VI) the protonation scheme in equations (13)–(16) was proposed,[25] where $K_a = 10^{3.5}$ and $K_b = K_c = K_d = 10^{3.7}$ dm^3 mol^{-1}.

$$[MoO_4]^{2-} + H^+ \underset{}{\overset{K_a}{\rightleftharpoons}} [MoO_3(OH)]^- \tag{13}$$

$$[MoO_3(OH)]^- + H^+ + 2H_2O \overset{K_b}{\rightleftharpoons} [MoO_2(OH)_2(H_2O)_2] \tag{14}$$

$$[MoO_2(OH)_2(H_2O)_2] + H^+ \overset{K_c}{\rightleftharpoons} [MoO(OH)_3(H_2O)_2]^+ \tag{15}$$

$$[MoO(OH)_3(H_2O)_2]^+ + H^+ \overset{K_d}{\rightleftharpoons} [Mo(OH)_4(H_2O)_2]^{2+} \tag{16}$$

There is a tendency for molybdate(VI) to increase its co-ordination number on protonation.[26–28] Spectrophotometric studies by Rohwer and Cruywagen[29] suggest that six-co-ordinate molybdate(VI) species are detected only in the presence of a second proton. As seen above in equation (14), the increase in the co-ordination number of molybdenum(VI) takes place in the second protonation step. The values for the successive protonation constants[23,30] of molybdate(VI) are very similar, *i.e.* $K_a = 10^{3.5}$ and $K_b = 10^{3.7}$ dm^3 mol^{-1}.

It is useful to compare the acid hydrolysis of $[(H_3N)_5CoOMoO_3]^+$ with those of other cobalt(III) complexes containing oxoanions. The data along with those from our work are compiled in Table 8. Complexes containing the oxoanions of the transition metals namely chromate(VI) and molybdate(VI) are the most reactive of the complexes listed. The rate of water exchange of the 'free' oxoanions follows the same reactivity pattern. With chromate, molybdate, and arsenate the hydrolysis mechanism is similar and hydrolysis takes place without any Co^{III}–O bond cleavage. For the other oxoanions listed Co^{III}–O bond cleavage is involved and the rates are distinctly less.

Successive protonation does not increase the lability of the oxoanion in $[(H_3N)_5CoOMoO_3]^+$ in contrast to that of the cobalt(III) complex containing chromate(VI) as oxoanion, even though Cr and Mo are both Group 6 elements. This anomalous behaviour of Mo^{VI} can be explained partly in terms of its ability to expand its co-ordination number on protonation.

It can be concluded that molybdenum(VI) with a co-ordination number of four is [*cf.* chromium(VI)] more labile than that of molybdenum(VI) with a co-ordination number of six; so $[(H_3N)_5CoOMoO_2(OH)]^{2+}$, $[(H_3N)_5CoOCrO_2(OH)]^{2+}$, and $[(H_3N)_5CoOCrO(OH)_2]^{3+}$ are the reactive species undergoing Mo^{VI}–O or Cr^{VI}–O bond cleavage during acid hydrolysis.[10]

The activation parameters fall in the same range as those obtained in the formation studies, and it is quite interesting that the formation of $[(H_3N)_5CoOMoO_3]^+$ from $[Co(NH_3)_5(OH_2)]^{3+}$ and $HMoO_4^-$ has almost identical $\Delta S^‡$ and $\Delta H^‡$ values as those of the k_1 path corresponding to hydrolysis of the $[(H_3N)_5CoOMoO_2(OH)]^{2+}$ ion. This indicates that both reactions share a similar transition state which is expected based on the principle of microscopic reversibility.[38]

Acknowledgements

Funding for this work was provided by the Department of Chemistry, and a Postgraduate Award by the Board of Graduate Studies, University of the West Indies, Mona Campus (to A. A. H.) is gratefully acknowledged.

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Received 30*th October* 1995; *Paper* 5/07156I