Kinetics of the Complexing of Cl^- and NCS^- to $[Mo(H_2O)_6]^{3+}$ and Assignment of an S_N2 Mechanism

By **Yoichi Sasaki** and **A. Geoffrey Sykes**,* Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

Details of the preparation and properties of hexa-aquomolybdenum(III) in aqueous *p*-toluene-sulphonic acid (HPTS) and HBF_4 are reported. The kinetics of the 1 : 1 reactions of $[Mo(H_2O)_6]^{3+}$ with Cl^- and NCS^- have been investigated spectrophotometrically in PTS media, $I = 1{\cdot}0$ M (LiPTS), and found to be independent of $[H^+]$ in the range 0·17—1·0M. The reaction with chloride was studied with $[Cl^-]$ in at least ten-fold excess of $[Mo(H_2O)_6]^{3+}$. Pseudo-first-order rate constants for the equilibration (i),

$$[Mo(H_2O)_6]^{3+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo(H_2O)_5Cl]^{2+} \qquad \text{(i)}$$

can be expressed as in (ii):

$$k_{eq} = k_1[Cl^-] + k_{-1} \qquad \text{(ii)}$$

At 25 °C $k_1 = 4{\cdot}6 \times 10^{-3}$ l mol^{-1} s^{-1}, $\Delta H_1^\ddagger = 23{\cdot}5 \pm 0{\cdot}6$ kcal mol^{-1}, $\Delta S_1^\ddagger = 9{\cdot}6 \pm 2{\cdot}1$ cal K^{-1} mol^{-1}, and $k_{-1} = 4{\cdot}26 \times 10^{-4}$ s^{-1}, $\Delta H_{-1}^\ddagger = 12{\cdot}9 \pm 0{\cdot}6$ kcal mol^{-1}, $\Delta S_{-1}^\ddagger = -30{\cdot}7 \pm 2{\cdot}1$ cal K^{-1} mol^{-1}. The formation constant $k_1/k_{-1} = 10{\cdot}8$ l mol^{-1} at 25 °C. The reaction with thiocyanate is thermodynamically much more favourable, formation constant *ca.* 10^5 l mol^{-1} at 25 °C. The reaction (iii) was followed with $[Mo(H_2O)_6]^{3+}$ in at least

$$[Mo(H_2O)_6]^{3+} + NCS^- \xrightarrow{k_2} [Mo(H_2O)_5(NCS)]^{3+} \qquad \text{(iii)}$$

ten-fold excess. At 25 °C, $k_2 = 0{\cdot}28$ l mol^{-1} s^{-1}, $\Delta H_2^\ddagger = 16{\cdot}3 \pm 0{\cdot}4$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -6{\cdot}4 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}. An S_N2 mechanism is suggested for these reactions. A comparison with aquation reactions of other trivalent aquo-metal ions is made.

THE preparation of the hexa-aquomolybdenum(III) ion in aqueous non-complexing *p*-toluene-sulphonic acid (HPTS) † and in trifluoromethylsulphonic acid has been described by Bowen and Taube.[1] Kustin and Toppen [2] have pointed out that the absorption spectrum obtained by Bowen and Taube is incorrect. However as indicated in a preliminary account of this work [3] we have been unable to reproduce the data given by Kustin and Toppen.[2] The spectrum which we report has now been obtained by Bowen and Taube.[4]

The paper by Bowen and Taube [1] prompted us into investigating substitution and redox properties of $[Mo(H_2O)_6]^{3+}$. A comparison of the substitution behaviour of $[Mo(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ (both d^3 ions), could be informative and help in the general understanding of the substitution behaviour of simple aquo-transition metal ions. Also in spite of the biological importance of molybdenum,[5] the reactivity of simple aquated molybdenum ions has not been investigated and could provide much relevant information.

Kinetic studies on the complexing of $[Mo(H_2O)_6]^{3+}$ with chloride and thiocyanate are reported in this paper, as well as the procedure for the preparation and general properties of solutions of $[Mo(H_2O)_6]^{3+}$.

Formation of $[Mo(H_2O)_6]^{3+}$.—Hexa-aquomolybdenum(III) was obtained by aquation of potassium hexachloromolybdate(III), in oxygen-free conditions in aqueous HPTS or HBF_4 media. To determine the optimum conditions for aquation u.v.–visible range spectra of solutions (*ca.* 20 °C) in 0·5, 2·0, and 5·5M-HBF_4 were monitored at suitable intervals. Spectrophotometric changes for all three solutions followed a similar pattern over the first 3 days. After 3 days a peak at *ca.* 350 nm appeared and the intensity slowly increased. The rate of increase was faster the lower the acidity. This band is attributed to the formation of green molybdenum(III)

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† Also known as toluene-*p*-sulphonic acid.

[1] A. R. Bowen and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 3287.

[2] K. Kustin and D. Toppen, *Inorg. Chem.*, 1972, **11**, 2851.

[3] Y. Sasaki and A. G. Sykes, *J.C.S. Chem. Comm.*, 1973, 767.

[4] A. R. Bowen and H. Taube *Inorg. Chem.*, 1974, **13**, 2245 and personal communication from Professor Taube.

[5] See for example, J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

species.[*] The peak at 350 nm appeared after 2 h when the aquation was carried out in neutral solution, but further changes followed, probably due to polymer formation. It is concluded that the aquation of chloride ligands is independent of [H$^+$], but that dimerization is faster at lower [H$^+$] values. Over the 2 days required for aquation there was at least 95% retention of molybdenum(III) as shown by cerium(IV) titration. Aquation of ammonium aquopentachloromolybdate(III), $[NH_4]_2[MoCl_5(H_2O)]$, also gives $[Mo(H_2O)_6]^{3+}$. The full procedure including ion-exchange separation of $[Mo(H_2O)_6]^{3+}$ is given in the Experimental section. Solutions obtained were (3—8) × 10^{-3}M and the yield >60% of the initial chloro-complex.[†] Other bands were observed on the column. The first, a yellow band, which was eluted with 0·5M-HPTS was found to contain Cl$^-$ ions on addition of $AgNO_3$ to the air-oxidized solution. The second was a more strongly held red-brown band which was eluted with 2M-HPTS. The component has an absorption peak at *ca.* 505 nm, ε = 126 l mol^{-1} cm^{-1}, *i.e.* per dimer, and is the molybdenum(IV) dimer.[9] It was noted that $[Mo(H_2O)_6]^{3+}$ on the ion-exchange column was light sensitive and was slowly converted into a green compound, probably molybdenum(III) dimer.

Stability of Solutions.—Stock solutions of $[Mo(H_2O)_6]^{3+}$ in 1M-HPTS could be stored at 0 °C in a refrigerator for at least a week without serious deterioration. Solutions more dilute in acid, *e.g.* 0·1M-HPTS, were stable over at least a day, but at lower [H$^+$] values formation of the green complex was observed. No photochemical reaction similar to that occurring on the ion-exchange column was observed in solution. Hexa-aquomolybdenum(III) is very reactive to oxygen and an immediate increase in absorbance below 350 nm is observed on exposure to air. The oxidation of $[MoCl_6]^{3-}$ and $[MoCl_5(H_2O)]^{2-}$ is much slower. Solutions containing $[Mo(H_2O)_6]^{3+}$ react with perchlorate to give the molybdenum(V) dimer, $[Mo_2O_4(H_2O)_6]^{2+}$.[10] Recent observations of the reaction at high concentrations of ClO_4^- showed fairly complicated kinetic behaviour, and earlier conclusions, with $[Mo(H_2O)_6]^{3+}$ in excess,[3] that this ion reacts with ClO_4^- much faster than other metal ions may need reconsideration. Under conditions [ClO_4^-] = 0·2—0·5M, [$Mo(H_2O)_6^{3+}$] *ca.* 4 × 10^{-3}M, absorbance changes at 330 nm of <10% of the total changes are observed over the first hour at 25 °C. Subsequently, more rapid changes are observed.[8] With $[Mo(H_2O)_6]^{3+}$ in excess of perchlorate it is concluded that the molybdenum(V) dimer reacts further with chlorate and other oxidation states of chlorine to give molybdenum(VI).

U.v.-visible Spectrum.—Absorption spectra of $[Mo(H_2O)_6]^{3+}$ in 1·0M-HPTS and 1·5M-HBF_4 are shown alongside that of $[MoCl_6]^{3-}$ in 12M-HCl (Figure 1). Similar general features to the spectrum of $[MoCl_6]^{3-}$ are to be noted, and support an octahedral structure for the aquo-ion, where chloride gives a small ligand field splitting as compared to H_2O. Strong absorption by HPTS is observed below 290 nm. The spectrum reported by Bowen and Taube [1] is similar to that of the strongly absorbing molybdenum(V) dimer, $[Mo_2O_4(H_2O)_6]^{2+}$,[10] and suggests *ca.* 35% of the species as impurity. Hexa-aquomolybdenum(III) gives peaks at 310 nm (ε 25·8 ± 1·2 l mol^{-1} cm^{-1}) and at 380 nm (ε 15·4 ± 0·3 l mol^{-1} cm^{-1}). Bowen and Taube have repeated their preparation and obtained spectra with peaks at 308 nm (ε 28·8 ± 1·4 l mol^{-1} cm^{-1}) and 370 nm (16·4 ± 0·8 l mol^{-1} cm^{-1}), in good agreement with our values.[4] Kustin and Toppen [2] do not give full details of their spectrum, but report an absorption coefficient of 370 l mol^{-1} cm^{-1} at 293 nm, which compares with a value 22 l mol^{-1} cm^{-1} obtained in this work. The peaks (Figure 1) at 310 and 380 nm can be assigned to *d–d* transitions, $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ respectively, of the octahedrally co-ordinated d^3 ion. From these assignments, the crystal-field splitting, 10 *Dq*, is 26,300 cm^{-1} for $[Mo(H_2O)_6]^{3+}$.

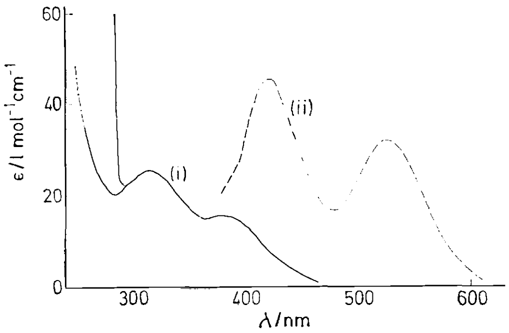

FIGURE 1 A comparison of the u.v.-visible spectra of (i) $[Mo(H_2O)_6$-$^{3+}$ in 1·0M-HPTS(——) and 1·5M] HBF_4 (— · —) and (ii)$[MoCl_6]^{3-}$ in 12M-HCl. The absorption below 300 nm in (i) is due to the medium

Reaction of $[Mo(H_2O)_6]^{3+}$ *with* Cl$^-$.—On addition of sodium chloride, concentrations up to 0·1M, to *ca.* 5 × 10^{-3}M [$Mo(H_2O)_6^{3+}$], [H$^+$] = 0·5 and 1·0M, absorption changes were observed with an isosbestic point at 308 nm. With HBF_4 for HPTS an additional isosbestic point was observed at 273 nm. The two *d–d* bands shifted to longer wavelengths on complexing with chloride. The final spectrum was dependent on the concentration of chloride which indicated an equilibration reaction (1):

$$[Mo(H_2O)_6]^{3+} + Cl^- \rightleftharpoons [Mo(H_2O)_5Cl]^{2+} + H_2O \quad (1)$$

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[*] As already indicated [1] an earlier assignment [6] of $[Mo(H_2O)_6]^{3+}$ to these green solutions is incorrect. Recent studies on the green species suggests a dimeric structure of 4+ charge.[7]

[†] More concentrated $[Mo(H_2O)_6]^{3+}$ solutions have now been prepared [8] by carrying out a further separation using a Dowex 50 W-X2 cation exchange resin. Solutions of up to 1·2 × 10^{-2}M in $[Mo(H_2O)_6]^{3+}$ have been obtained in this way by eluting with 1M-HPTS.

[6] H. Hartmann and H. J. Schmidt, *Z. phys. Chem. N.F.*, 1957, **11**, 234.

[7] M. Ardon and A. Pernick, *Inorg. Chem.*, 1974, **13**, 2274.

[8] A. B. Soares, A. T. Thornton, and A. G. Sykes, unpublished observations.

[9] M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871; see also, M. Lamache-Duhameaux, *Rev. Chim. minérale*, 1968, 459; *J. Less Common Metals*, 1975, **39**, 179.

[10] M. Ardon and A. Pernick, *Inorg. Chem.*, 1973, **12**, 2484; Y. Sasaki and A. G. Sykes, *J.C.S Dalton*, 1974, 1468.

At [Cl$^-$] > 0·1M isosbestic points were not maintained and further absorption changes were observed consistent with co-ordination of a second chloride. Attempts to isolate $[Mo(H_2O)_5Cl]^{2+}$ using ion-exchange separation techniques did not yield solutions of sufficiently high concentration. Using the kinetically determined equilibrium constant it is possible to calculate the absorption spectrum of $[Mo(H_2O)_5Cl]^{2+}$ which gives a peak *ca.* 410 nm with ε = *ca.* 19 l mol^{-1} cm^{-1}.

Kinetics of the Equilibration of Cl$^-$ *with* $[Mo(H_2O)_6]^{3+}$.—The rate of equilibration (1) was studied at 435 nm with chloride in at least 10-fold excess of $[Mo(H_2O)_6]^{3+}$. Plots of absorbance changes log (O.D.$_\infty$ — O.D.$_t$) against time, *t*, were linear to at least 80—90% of reaction. First-order rate constants, k_{eq}, obtained are listed in Table 1. The extent (and degree) of complex formation limited the variation in [Cl$^-$] to the range (3·3—9·6) × 10^{-2}M. The stock solution of $[Mo(H_2O)_6]^{3+}$ was in 1M-HPTS and to maintain the concentration of molybdenum at a sufficiently high value it was required that [H$^+$] > 0·17M. When the ionic strength was adjusted to 1·0M with LiPTS no dependence on [H$^+$] in the range 0·17—1·00M was observed. A dependence on [H$^+$] which was obtained when NaPTS was used instead of LiPTS had no obvious mechanistic implications, and was attributed to medium (activity) effects. Runs using NaPTS were not included in the subsequent computation of data.

TABLE 1

First-order rate constants for the equilibration of $[Mo(H_2O)_6]^{3+}$ and Cl$^-$, equation (1), I = 1·0M(LiTPS)

t/°C	[H$^+$]/M	$10^3[Mo(H_2O)_6{}^{3+}]$/M	10^2[Cl$^-$]/M	10^4k_{eq}/s^{-1}
25·0	0·50	2·42	4·23	5·60 [a]
	0·50	2·42	6·35	6·13 [a]
	0·50	2·42	8·46	6·75 [a]
	0·50	2·40	5·53	6·79
	0·50	2·87	8·60	8·11
	1·0	2·02	3·33	5·90
	1·0	3·36	4·21	6·14
	1·0	2·85	4·31	6·42
	1·0	2·57	6·47	6·90
	1·0	2·85	8·62	8·40
30·0	0·50	2·00	4·65	10·2
	0·50	2·40	7·74	13·2
	1·0	2·57	4·31	10·4
	1·0	1·71	6·56	12·3
	1·0	2·85	8·62	13·8
35·0	0·17	1·23	8·27	23·0
	0·33	2·45	8·27	22·6
	0·50	2·42	4·28	14·8 [a]
	0·50	2·42	8·56	20·3 [a]
	0·50	1·71	7·59	21·9
	0·50	1·71	8·68	24·3
	0·67	2·28	4·34	16·4
	0·75	2·57	6·51	19·9
	1·0	2·42	4·37	16·9
	1·0	2·42	6·56	20·3
	1·0	2·42	8·56	23·4
40·5	0·50	2·00	4·65	28·4
	0·50	1·60	7·29	37·4
	1·0	2·40	3·49	24·9
	1·0	2·88	6·09	33·4
	1·0	4·00	6·98	36·8
	1·0	2·48	9·59	46·7

[a] Ionic strength adjusted with NaPTS. Not included in computation of activation parameters.

The dependence of rate constants k_{eq} on [Cl$^-$] (Figure 2) can be summarized by equation (2)

$$k_{eq} = k_1[Cl^-] + k_{-1} \qquad (2)$$

where k_1 and k_{-1} correspond to forward and back reactions in (1). From this data activation parameters $\Delta H_1^\ddagger$ = 23·5 ± 0·6 kcal mol^{-1}, $\Delta S_1^\ddagger$ = 9·6 ± 2·1 cal K^{-1} mol^{-1}, $\Delta H_{-1}^\ddagger$ = 12·9 ± 0·6 kcal mol^{-1}, and $\Delta S_{-1}^\ddagger$ = —30·7 ± 2·1 cal K^{-1} mol^{-1} were obtained. Values of k_1 and k_{-1} and the equilibrium constant k_1/k_{-1} at each temperature are given in Table 2.

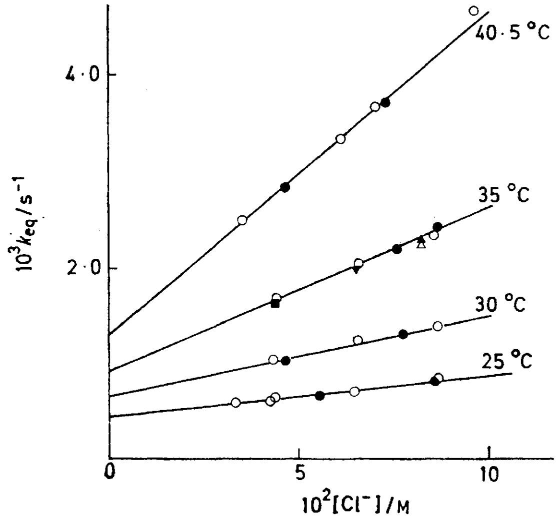

FIGURE 2 The dependence of equilibration rate constants k_{eq} on [Cl$^-$] for the reaction of $[Mo(H_2O)_6]^{3+}$ and Cl$^-$, equation (1), I = 1·0M(LiPTS); [H$^+$] ▲ = 0·17, △ = 0·33, ● = 0·50, ■ = 0·67, ▼ = 0·75, ○ = 1·00

TABLE 2

The temperature dependence of rate constants k_1 and k_{-1},[a] equation (2), for the equilibration $[Mo(H_2O)_6]^{3+}$ and Cl$^-$, I = 1·0M(LiPTS)

t/°C	10^3k_1/l mol^{-1} s^{-1}	10^4k_{-1}/s^{-1}	k_1/k_{-1}/l mol^{-1}
25·0	4·60 ± 0·23	4·26 ± 0·12	10·8
30·0	8·69 ± 0·63	6·42 ± 0·42	13·5
35·0	16·2 ± 2·0	9·17 ± 1·41	17·6
40·5	35·7 ± 1·0	11·9 ± 0·7	29·9

[a] From the difference in activation parameters for k_1 and k_{-1}, ΔH = 10·6 ± 1·2 kcal mol^{-1} and ΔS = 40·3 ± 4·2 cal K^{-1} mol^{-1}.

The Reaction of NCS$^-$ *with* $[Mo(H_2O)_6]^{3+}$.—On addition of NCS$^-$ to $[Mo(H_2O)_6]^{3+}$ the absorption at *ca.* 300 nm increased, and there were no isosbestic points. With $[Mo(H_2O)_6{}^{3+}]$ = *ca.* 5 × 10^{-3}M and [NCS$^-$] < 5 × 10^{-4}M the peak position was at 303 nm, and the absorbance was proportional to the concentration of NCS$^-$ added. The peak position appeared at longer wavelengths with [NCS$^-$] > 5 × 10^{-4}M or at lower molybdenum concentrations with [NCS$^-$] > $[Mo(H_2O)_6{}^{3+}]$. It is concluded that with [NCS$^-$] < *ca.* 5 × 10^{-4}M the 1 : 1 complex $[Mo(H_2O)_5(NCS)]^{2+}$ is predominant. This complex was isolated by ion-exchange technique (details in Experimental section), and the spectrum $\lambda_{max.}$ 303 nm, ε 2170 l mol^{-1} cm^{-1} is shown in Figure 3.

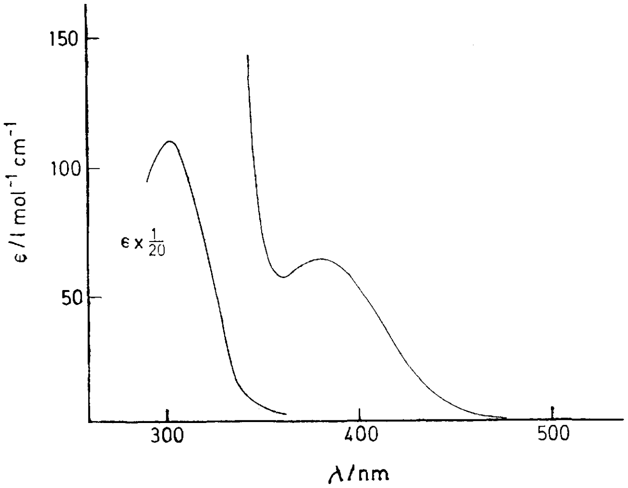

FIGURE 3 U.v. visible spectrum of $[Mo(H_2O)_5(NCS)]^{2+}$ in 0·3M-HPTS

A solution of 2×10^{-3}M-$[Mo(H_2O)_5(NCS)]^{2+}$ in 0·3M-HPTS gave no spectrophotometric changes during 1 day. On dilution to 2×10^{-4}M-$[Mo(H_2O)_5(NCS)]^{2+}$ a slow decrease (*ca.* 6 h) in absorption was observed at 303 nm without any change in peak shape. The decrease was attributed to the partial dissociation of $[Mo(H_2O)_5(NCS)]^{2+}$; from the changes observed the formation constant for $[Mo(H_2O)_5(NCS)]^{2+}$ was estimated to be greater than 10^5 l mol^{-1} at 25 °C.

When an excess of NCS^- (1×10^{-3}M) was added to $[Mo(H_2O)_5(NCS)]^{2+}$ (8×10^{-5}M) slow absorbance changes were again noted. The peak at 303 nm shifted to longer wavelengths and there was an increase in intensity. These changes correspond to further co-ordination of one or more NCS^- to $[Mo(H_2O)_5(NCS)]^{2+}$.

The position of the *d–d* band for $[Mo(H_2O)_5(NCS)]^{2+}$ (380 nm) is more similar to that for $[Mo(H_2O)_6]^{3+}$ (380 nm) than for $[Mo(H_2O)_5Cl]^{2+}$ (410 nm). It is concluded that the thiocyanate is *N*-bonded to the molybdenum, since NCS^- is near to Cl^- in the spectrochemical series when it is *S*-bonded.[11] The NCS^- ligands in $[Mo(NCS)_6]^{3-}$ are known to be nitrogen-bonded.[11,12]

Kinetics of the Reaction of NCS^- *with* $[Mo(H_2O)_6]^{3+}$.—The rate of the 1 : 1 complex formation, (3), was monitored at fixed wavelengths 303—330 nm with concentrations of $[Mo(H_2O)_6]^{3+}$ ($4·4 \times 10^{-4}$—$4·4 \times 10^{-3}$M) in at least ten-fold excess. Absorbance changes corresponded to completion of (3) ($K = ca.\ 10^5$ l mol^{-1}), and unlike the reaction with chloride it was only necessary to consider the forward reaction. For most of the runs O.D.$_\infty$ was not well defined, owing to subsequent slow reactions (see above), and the Guggenheim procedure [13] was used to evaluate rate constants. The Guggenheim treatment gives linear plots for 1·5 half-lives. Plots of log(O.D.$_\infty$ — O.D.$_t$) against time when O.D.$_\infty$ was well defined gave straight lines for more than 80% reaction. First-order rate constants (k_{obs}) evaluated by the two methods were in satisfactory agreement, and were independent of $[H^+] = 0·17 - 1·0$M (see Table 3).

$$[Mo(H_2O)_6]^{3+} + NCS^- \longrightarrow [Mo(H_2O)_5(NCS)]^{2+} \qquad (3)$$

TABLE 3

Rate constants for the formation of $[Mo(H_2O)_5(NCS)]^{2+}$ from $[Mo(H_2O)]^{3+}$ and NCS^-, $I = 1·0$M(LiPTS). First-order rate constants obtained by Guggenheim method except where stated

$\frac{t}{°C}$	$\frac{[H^+]}{M}$	$\frac{10^3[Mo(H_2O)_6{}^{3+}]}{M}$	$\frac{10^5[NCS^-]}{M}$	$\frac{10^4 k_{obs}}{s^{-1}}$
25·0	0·50	0·518	5·00	1·51
	0·50	1·54	5·00	4·83
	0·50	2·43	4·01	6·90
	0·50	3·64	4·82	9·97
	0·50	3·64	33·7	9·89
	1·00	1·54	5·00	4·03
30·0	0·50	0·518	5·00	2·22
	0·50	1·23	4·01	5·06
	0·50	2·45	4·01	9·90
	0·50	3·68	4·0	15·7 [a]
35·0	0·17	1·23	4·01	8·43
	0·50	0·439	4·01	3·45
	0·50	1·23	4·01	8·81
	0·50	2·45	4·01	17·1 [a]
	0·50	3·68	4·01	26·0 [a]
	0·75	1·23	4·01	8·24
	1·00	1·23	4·01	8·43
40·5	0·50	0·518	5·00	6·59
	0·50	1·23	4·01	14·2
	0·50	2·19	8·02	24·2 [a]
	0·50	3·37	7·50	37·2 [a]
	0·50	4·39	4·01	47·0 [a]

[a] First-order rate constant evaluated from plot of log (O.D.$_\infty$ — O.D.$_t$) against time.

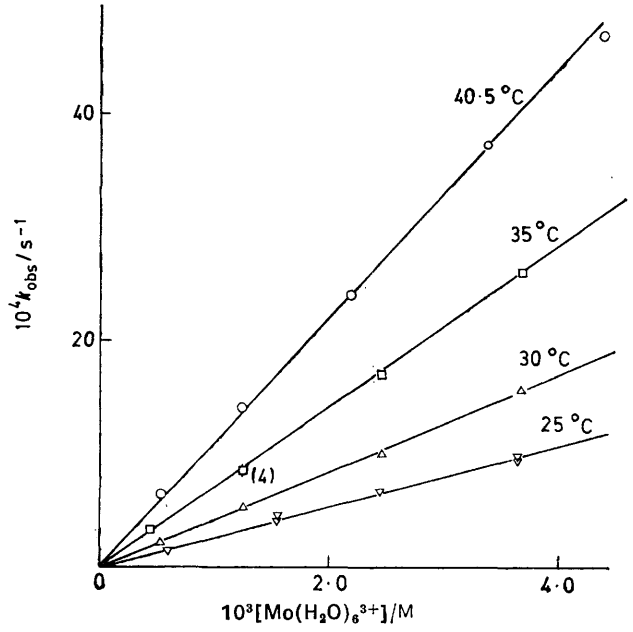

FIGURE 4 The dependence of first-order rate constants k_{obs} for the anation of $[Mo(H_2O)_6]^{3+}$ with NCS^-, on $[Mo(H_2O)_6]^{3+}$, $I = 1·0$M (LiPTS)

The linear dependence of k_{obs} on $[Mo(H_2O)_6{}^{3+}]$, (4), is illustrated in Figure 4. Values of k_2

$$k_{obs} = k_2[Mo(H_2O)_6{}^{3+}] \qquad (4)$$

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[11] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

[12] J. K. Knox and K. Eriks, *Inorg. Chem.*, 1968, **7**, 84.

[13] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' J. Wiley, New York, 1961, 2nd edn., p. 49.

(1 mol^{-1} s^{-1}) obtained by a least-squares treatment with weighting unity are $0{\cdot}268 \pm 0{\cdot}013$ (25 °C), $0{\cdot}424 \pm 0{\cdot}012$ (30 °C), $0{\cdot}70 \pm 0{\cdot}01$ (35 °C), $1{\cdot}05 \pm 0{\cdot}01$ (40·5 °C). Activation parameters for k_2 are $\Delta H_2^\ddagger = 16{\cdot}3 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S_2^\ddagger = -6{\cdot}4 \pm 1{\cdot}3$ cal K^{-1} mol^{-1}.

Other Reactions.—Attempts were made to study the bromide and azide anation reactions. With bromide, $[\mathrm{Mo(H_2O)_6}^{3+}] = 5 \times 10^{-3}$M and $[\mathrm{Br^-}] = 8 \times 10^{-2}$M, absorption changes were small and the reactions difficult to follow. Complex formation with azide[8] was also difficult to study in detail since the reaction is slow and takes several days at $[\mathrm{H^+}] > 0{\cdot}015$M. During this time redox reactions are also effective.

TABLE 4

Activation parameters for anation (Cl$^-$ and NCS$^-$) and water exchange reactions of hexa-aquo-metal ions

Metal ion	Reactant	$\Delta H^\ddagger$ / kcal mol^{-1}	$\Delta S^\ddagger$ / cal K^{-1} mol^{-1}	Ref.
$\mathrm{Ti^{3+}}$	H_2O	6·1	−15	14
$\mathrm{V^{3+}}$	Cl$^-$	>11·2		15
	NCS$^-$	7·6	−23·8	16
	H_2O	9	−15	17
$\mathrm{Cr^{3+}}$	Cl$^-$ [a]	30·3	8·6	18*a*
	NCS$^-$ [a]	25·1	0·7	18*a*
	H_2O	27·6	10·0	18*b*
$\mathrm{Mo^{3+}}$	Cl$^-$	23·5	9·6	This work
	NCS$^-$	16·3	−6·4	This work
$\mathrm{Fe^{3+}}$	Cl$^-$ [a]	16·6	2·0	*b*
	NCS$^-$ [a]	13·0	−15·0	*c*

[a] Data for [H$^+$]-independent path. [b] R. E. Connick and C. P. Coppel, *J. Amer. Chem. Soc.*, 1959, **81**, 6389. [c] J. F. Below and R. E. Connick, *J. Amer. Chem. Soc.*, 1958, **80**, 2961.

DISCUSSION

As is to be expected for a d^3 electronic configuration, molybdenum(III) exhibits substitution inert behaviour. Results presented in this paper for the 1 : 1 complexing of $[\mathrm{Mo(H_2O)_6}]^{3+}$ with Cl$^-$ and NCS$^-$ provide strong evidence for a mechanism exhibiting S_N2 character.

TABLE 5

A comparison of [H$^+$]-independent k_a values (25 °C) for chloride and thiocyanate anation of hexa-aquo-metal ions: rate constants for water exchange are also given

Metal ion	k_{Cl} / l mol^{-1} s^{-1}	k_{NCS} / l mol^{-1} s^{-1}	$k_{\mathrm{H_2O}}$ / s^{-1}	$k_{\mathrm{NCS}}/k_{\mathrm{Cl}}$	Ref.
$\mathrm{Ti^{3+}}$	Not studied	8×10^3 (8—9 °C)	10^5		14, 19
$\mathrm{V^{3+}}$	$\leqslant 3$	110	$1{\cdot}6 \times 10^3$	$\geqslant 36$	15—17
$\mathrm{Cr^{3+}}$	$2{\cdot}9 \times 10^{-8}$	$1{\cdot}8 \times 10^{-6}$	$3{\cdot}5 \times 10^{-6}$ (27 °C)	62	18
$\mathrm{Mo^{3+}}$	$4{\cdot}6 \times 10^{-3}$	0·27	Not studied	59	This work
$\mathrm{Fe^{3+}}$	9·4	127	$8{\cdot}2 \times 10^3$	13·5	20
$\mathrm{Ru^{3+}}$	*ca.* 10^{-6}	Not studied	Not studied		21
$\mathrm{Co^{3+}}$	$\leqslant 2{\cdot}0$	86·5	Not studied	$\geqslant 43$	22—24
$\mathrm{Rh^{3+}}$	$5{\cdot}5 \times 10^{-6}$ (75 °C)	Not studied	$2{\cdot}2 \times 10^{-5}$ (64 °C)		25 [a]

[a] W. Plumb and G. M. Harris, *Inorg. Chem.*, 1964, **3**, 542.

Rate constants and activation parameters are listed in Table 4 together with data for other hexa-aquo 3+ ions in the first transition series. The basis for our assignment is firstly the ratio of rate constants $k_{\mathrm{NCS}}/k_{\mathrm{Cl}} = 59$ (Table 5), and secondly variations in activation parameters for $k_1(\mathrm{Cl^-})$ and $k_2(\mathrm{NCS^-})$, Table 4. By analogy with reactions of $[\mathrm{Ti(H_2O)_6}]^{3+}$ [19] and $[\mathrm{V(H_2O)_6}]^{3+}$ [15] the absence of $[\mathrm{H^+}]^{-1}$ terms in the rate law $[\mathrm{H^+}] = 0{\cdot}17$—$1{\cdot}00$M might also support this assignment. Alternatively the acid constant for $[\mathrm{Mo(H_2O)_6}]^{3+}$, which has not been determined, may be considerably smaller than for other 3+ transition-metal ions, and may explain this effect.

The assignment of mechanism to substitution reactions of oxidation state III transition-metal ions is by no means as clearcut and straightforward as for the II-state ions.[26] It has been suggested that III-state ions with low *d*-electron populations exhibit associative character in their substitution reactions. Probably the most compelling evidence for an associative mechanism for $[\mathrm{Ti(H_2O)_6}]^{3+}$ (d^1),[14] and $[\mathrm{V(H_2O)_6}]^{3+}$ (d^2),[17] is the magnitude of the activation parameter for water exchange. High $\Delta H^\ddagger$ values generally reflect energy requirements for bond breaking, and positive $\Delta S^\ddagger$ values an increase in number of particles in the transition state. For the water exchange of $[\mathrm{Ti(H_2O)_6}]^{3+}$ and $[\mathrm{V(H_2O)_6}]^{3+}$, $\Delta H^\ddagger$ is small and $\Delta S^\ddagger$ significantly negative. For the anation of $[\mathrm{V(H_2O)_6}]^{3+}$ a wide range of rate constants *ca.* 10^3 is observed for complexing with 1− reactants Cl$^-$, Br$^-$, $\mathrm{HC_2O_4}^-$, and NCS$^-$,[15] and in the one case where activation parameters have been measured, Table 4, $\Delta S^\ddagger$ is a large negative quantity.

A feature of anation reactions of $[\mathrm{Ti(H_2O)_6}]^{3+}$ and $[\mathrm{V(H_2O)_6}]^{3+}$ is the absence of an $[\mathrm{H^+}]^{-1}$ dependence. The [H$^+$] dependence of second-order rate constants, k_{obs}, for other transition-metal ions, notably $[\mathrm{Cr(H_2O)_6}]^{3+}$,[18]

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[25] T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

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$[Fe(H_2O)_6]^{3+}$,[20] and $[Co(H_2O)_6]^{3+}$ [22,23] can be expressed as in equation (5), and k_b makes a significant contribution

$$k_{obs} = k_a + k_b[H^+]^{-1} \qquad (5)$$

over the range $[H^+] = 0{\cdot}1$—$1{\cdot}0$M. The absence of a detectable contribution from the conjugate pathway, k_b, for $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ is best explained in terms of an S_N2 mechanism, since increasing S_N2 character would increase the rate of the k_a path which, in turn, might mask any contributions from k_b.

It is expected that rate constants for an associative mechanism would be more dependent on the incoming ligand than for a dissociative mechanism. It is convenient here for us to consider k_{NCS}/k_{Cl} values as diagnostic of either dissociative or associative character. The danger in considering only limited information in this way is that one of the ions may be exhibiting non-typical behaviour. At present however we see no compelling evidence for supposing that NCS^- or Cl^- might be behaving in such a way. The ratios k_{NCS}/k_{Cl} for k_a in Table 5 exceed an order of magnitude in all cases, and it is unlikely that different ion-pair formation constants between the 3+ and 1− reactants are able to account for these divergent values.[27] Rather do they suggest varying degrees of associative character. While it is possible that k_a has associative character for $[Cr(H_2O)_6]^{3+}$, $[Fe(H_2O)_6]^{3+}$, and $[Co(H_2O)_6]^{3+}$, the k_b path is most probably S_N1. The basis for this is the close similarity in rate constants k_b for NCS^- and Cl^- complexing, Table 6, which is consistent with an S_N1 process, where the mechanism may be S_N1 (limiting). The conjugate-base pathway k_b may not be favourable for $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ since electron donation from a hydroxo-ligand in the conjugate-base cannot have a significant effect on the bonding of other aquo-ligands when empty *d*-orbitals are available.

TABLE 6

A comparison of $[H^+]^{-1}$-dependent k_b values (25 °C) for chloride and thiocyanate anation of hexa-aquo-metal ions

Metal ion	k_{Cl} / s^{-1}	k_{NCS} / s^{-1}	k_{NCS}/k_{Cl}	Ref.
Ti^{3+}	Not detected	Not detected		19
V^{3+}	Not detected	Not detected		15, 16
Cr^{3+}	$4{\cdot}2 \times 10^{-9}$	$7{\cdot}2 \times 10^{-9}$	1·75	18
Mo^{3+}	Not detected	Not detected		This work
Fe^{3+}	28	16·5	0·6	20
Co^{3+}	40	79·6	2·0	22—24

Associative character for anation reactions of $[Cr(H_2O)_6]^{3+}$ is supported by other evidence including a graph of log k_a against log K (formation constant),[28] and volumes of activation.[29] For $[Fe(H_2O)_6]^{3+}$ rate constants k_a for Cl^-, Br^-, $HC_2O_4^-$, and NCS^- give a spread of values,[20] which is of similar magnitude to that observed for $[V(H_2O)_6]^{3+}$, and therefore consistent with an associative mechanism. Enthalpies of activation are not sufficiently small or entropies of activation sufficiently negative however in the case of $[Cr(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ to indicate a high degree of S_N2 character. We also note that rate constants for water exchange of $[Fe(H_2O)_6]^{3+}$,[20b] and particularly for $[Ti(H_2O)_6]^{3+}$ [14] and $[V(H_2O)_6]^{3+}$,[17] are in excess of those for anation. These are more difficult to explain in terms of an S_N2 mechanism since H_2O is generally considered to be a poor nucleophile compared to NCS^-. Data at present available for water exchange reactions should however be regarded with some caution, since $[H^+]$-variations do not appear to have been investigated. Thus for the $[Ti(H_2O)_6]^{3+}$ study [14] $[H^+] = ca.\ 8 \times 10^{-3}$M was not varied ($[H^+] = 0{\cdot}4$—$1{\cdot}0$M for anation study); moreover, for $[Fe(H_2O)_6]^{3+}$ [20b] and $[V(H_2O)_6]^{3+}$ [17] conditions of $[H^+]$ have not been reported, and with $[Cr(H_2O)_6]^{3+}$ [18b] the $[H^+]$-effect is uncertain. Here are systems clearly demanding more extensive study.

Comparisons of substitution behaviour of metal III ions in the second and third transition series with those of metal ions in the first series have been made previously but are not well established. A direct comparison of $[Ru(H_2O)_6]^{3+}$ [21] and $[Rh(H_2O)_6]^{3+}$ [30] with their first-row congeners is not meaningful, since $[Fe(H_2O)_6]^{3+}$ is high spin and $[Co(H_2O)_6]^{3+}$ may be partially high spin. Thus $[Mo(H_2O)_6]^{3+}$ provides the first example in which direct comparison between hexa-aquo-ions of first- and second-row transition-metal ions of identical electronic configurations is possible. Comparisons of the substitution behaviour of $[Co(NH_3)_5(H_2O)]^{3+}$, $[Rh(NH_3)_5(H_2O)]^{3+}$, and $[Ir(NH_3)_5(H_2O)]^{3+}$ are possible.[31] It is now well established that anation reactions of $[Co(NH_3)_5(H_2O)]^{3+}$ proceed by an S_N1 mechanism,[32] which might be quite unique in the context of III-state ions. In spite of considerable increase in crystal-field-stabilization-energy (c.f.s.e.) the enthalpy of activation for water exchange and Cl^- complexing with $[Rh(NH_3)_5(H_2O)]^{3+}$ is less than those of $[Co(NH_3)_5(H_2O)]^{3+}$.[31] This seems to indicate increasing S_N2 character in going from Co to Rh. This view is further supported by the ratio of rate constants for Cl^- complexing to that of water exchange,[33] and by the volume of activation for water exchange.[25] What is clear from a consideration of enthalpies of activation, Table 4, is that the anation of $[Mo(H_2O)_6]^{3+}$ must proceed with appreciably more associative character than those of $[Cr(H_2O)_6]^{3+}$. Whether greater S_N1 character will become apparent in the third series as the c.f.s.e. increases still further, as the data for $[Ir(NH_3)_5(H_2O)]^{3+}$ may suggest,[31] is of considerable interest. Although it is not a subject for direct comparison, it is possibly worth mentioning also in this context that the aquation of $[ReCl_6]^{2-}$ [34] is

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[34] J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1973, 902.

very slow compared to that for the aquation of $[MoCl_6]^{3-}$,[35] where rhenium(IV) like molybdenum(III) has a d^3 electronic configuration.

Data for the aquation of $[Mo(H_2O)_5Cl]^{2+}$ may be compared with that for $[Cr(H_2O)_5Cl]^{2+}$, k (25 °C) = $2{\cdot}77 \times 10^{-7}$ s^{-1}, $\Delta H^\ddagger = 24{\cdot}3$ kcal mol^{-1}, $\Delta S^\ddagger = -7{\cdot}1$ cal K^{-1} mol^{-1},[36] and this gives further support to an associative mechanism. Differences in rate constants are much smaller than for anation reactions however. The formation constants for $[Mo(H_2O)_5Cl]^{2+}$ and $[Mo(H_2O)_5NCS]^{2+}$ are *ca.* 10^3 and *ca.* 10^4 times bigger than those for $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_5NCS]^{2+}$. This is mainly due to the large difference of anation rates. While aquation rates of rhodium(III) complexes are not generally faster than those of cobalt(III), the faster rate of aquation of $[Mo(H_2O)_5Cl]^{2+}$ compared to $[Cr(H_2O)_5Cl]^{2+}$ gives further support to the suggested associative mechanism.

To summarize the situation for $[Mo(H_2O)_6]^{3+}$ we have no hesitation in invoking a mechanism for substitution with considerable S_N2 character, certainly in excess of that for $[Cr(H_2O)_6]^{3+}$. The evidence is certainly as compelling as for $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$. A study of the water-exchange reaction, including $[H^+]$ and temperature variations, would be most appropriate.

Finally from the biological point of view, it is necessary to collect more information to elucidate the behaviour of molybdenum in enzymes, and further work aimed at investigating substitution and redox behaviour of the different oxidation states of molybdenum is highly relevant.[37]

EXPERIMENTAL

Preparation of Potassium Hexachloromolybdate(III).—This compound was prepared according to the method in the literature.[38] The absorption spectrum of $[MoCl_6]^{3-}$ in 12M-HCl was measured and gave $\lambda_{max.}$ 422 nm (ε 45·4 l mol^{-1} cm^{-1}) and $\lambda_{max.}$ 526 nm (ε 32·6 l mol^{-1} cm^{-1}). The molybdenum concentration was determined by oxidation to molybdenum(VI) with cerium(IV). Details of absorption spectra previously reported are not consistent with each other.[6,35,39] This is most likely due to difficulties in preparing pure $[MoCl_6]^{3-}$ salts and failure to maintain a sufficiently high concentration of HCl (>9M) when determining the spectrum.

Preparation of Ammonium Aquopentachloromolybdate(III).—This complex has been prepared and characterised previously.[40] The procedure used in this study was to electrolyse molybdic acid hydrate, $H_2MoO_4{\cdot}H_2O$ (AnalaR, B.D.H.) (20 g) in concentrated HCl (150 ml) mixed with water (50 ml) for several hours at 3—4 V. The molybdenum(VI) is reduced at the mercury-pool cathode to give a red solution of the molybdenum(III) product. A platinum (or carbon) electrode in 6M-HCl is used in the anode compartment, which is separated from the cathodic solution by a No. 4 sinter. After transference of the cathodic solution to a flask, NH_4Cl (8 g) was added. The solution was then evaporated to leave *ca.* 30 ml of clear red solution. Brick-red crystals were obtained after a few hours at 0 °C, and were filtered off, washed with ethanol, and dried *in vacuo*.

p-*Toluenesulphonic Acid* (*HPTS*).—B.D.H. Laboratory Reagent Grade of this acid was recrystallised once from hot water. Aqueous solutions of the recrystallised sample had no absorption at >300 nm.

Lithium p-*Toluenesulphonic Acid*.—The acid HPTS (50 g) was dissolved in water (200 ml). To this solution Li_2CO_3 (10 g) (Hopkin and Williams, Laboratory Grade Reagent) was added slowly with stirring. Unchanged Li_2CO_3 was filtered off, and the filtrate was reduced in volume to *ca.* 70 ml on a water-bath (80 °C) until crystals were deposited. The solution was cooled to 0 °C for 1 h during which time white crystals were deposited; these were filtered; further evaporation gave more crystals. The product was recrystallised once from hot water as in the case of HPTS, and dried *in vacuo* for one day. An aqueous solution had no absorption >300 nm. A solution *ca.* 2M was prepared and standardised using an ion-exchange resin [Amberlite IR(H) 120]. This procedure gave H^+ for Li^+, and could be determined by titration.

Sodium p-*Toluenesulphonic Acid*. Laboratory grade reagent (B.D.H.) was recrystallised once from water.

Preparation of Hexa-aquomolybdenum(III) *Solutions*.—The following procedure was carried out under rigorous oxygen-free conditions. Either $K_3[MoCl_6]$ or $[NH_4]_2$-$[MoCl_5(H_2O)]$ (0·5 g) was dissolved in oxygen-free 0·2—0·5M-HPTS (500 ml) and kept at *ca.* 20 °C for 2 days. The solution diluted to 0·2M (in HPTS) was then exchanged onto a column of Dowex 50W-X12 cation-exchange resin. No special precautions to remove possible oxidising impurities from the resin were used; the column was however first washed with oxygen-free water (*ca.* 250 ml). A greenish yellow band was obtained on the column with a smaller brown band at the top of the column. The column was washed with 0·2M-HPTS (100 ml), followed by 0·5M-HPTS (100 ml) which eluted small amounts of a yellow component. With 1·0M-HPTS (200—300 ml) a light yellow solution of $[Mo(H_2O)_6]^{3+}$ was obtained. The resin was covered with aluminium foil to avoid photochemical reactions. All solutions were transferred using Teflon tubing and nitrogen-gas pressure. Solutions of $[Mo(H_2O)_6]^{3+}$ were stored at *ca.* 0 °C.

Preparation of Penta-aquothiocyanatomolybdenum(III) *Solution*.—A solution of $1{\cdot}6 \times 10^{-3}$M-$[Mo(H_2O)_6]^{3+}$ in 0·25M-HPTS (400 ml) was added to NaNCS (0·05 g), and the solution kept for 1 day at 20 °C. The solution, diluted two-fold with water, was then exchanged onto a column of Dowex 50W-X12 (acid form). The column was washed with 0·1M-HPTS (100 ml), and a yellow band eluted with 0·3M-HPTS. Analyses gave a Mo : NCS ratio of 1 : 1.

Sodium Thiocyanate Solutions. General Purpose Reagent (Hopkin and Williams) was recrystallized once from water. Since NCS^- ions are known to give yellow polythiocyanogen in acidic solution,[41] stock solutions of NaNCS in water were prepared and were acidified at the commence-

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[41] C. E. Vanderzee and A. S. Quist, *Inorg. Chem.*, 1966, **5**, 1238.

ment of kinetic runs. A solution 1·0M in HPTS and with $[NCS^-] = 5 \times 10^{-5}$M (conditions appropriate to kinetic runs), gave no absorbance change >300 nm during 1 day.

Standardization of Reactant Solutions.—Solutions of *ca.* 0·05M-$[Mo(H_2O)_6]^{3+}$ (10 ml) were determined by addition of 10 ml of 0·5M-cerium(IV) under oxygen-free conditions. Excess of cerium(IV) was determined by titration with a molybdenum(V) solution (in air). The latter was prepared by dissolving $[NH_4]_2[MoOCl_5]$ [37] in 1M-H_2SO_4, and was standardized by titration with cerium(IV). Solutions of molybdenum(V) were stored in oxygen-free conditions but could be titrated without any such precautions. Ferroin and erioglaucine indicators were used. Molybdenum concentrations were calculated assuming trivalent ions to be present. With $[Mo(H_2O)_5(NCS)]^{2+}$ the consumption of cerium(IV) by NCS^- was taken into account. Under conditions 0·3M-HPTS and 1M-H_2SO_4 six equivalents of cerium(IV) were consumed by each NCS^- ion.

The thiocyanate content of solutions of $[Mo(H_2O)_5(NCS)]^{2+}$ was determined by treating 5 ml of the latter with *ca.* 2M-HNO_3 (0·5 ml) with 0·5 ml of a solution of iron alum as indicated.[42] This solution was then titrated with standard mercury(II) solution. The end-point was determined by extrapolation of absorbance readings at 480 nm against mercury(II) added. This extrapolation procedure is necessary because low $[NCS^-]$ are present. The procedure was checked with known NCS^- solutions.

Kinetic Runs.—Since $[Mo(H_2O)_6]^{3+}$ reacts with ClO_4^- all kinetic runs were in aqueous *p*-toluene-sulphonic acid–*p*-toluenesulphonate media, $I = 1{\cdot}0$M(PTS). Under these conditions no evidence for complexing of PTS to $[Mo(H_2O)_6]^{3+}$ was obtained, and the absorption spectrum obtained was the same in 1M-HPTS as in 1·5M-HBF_4. Runs were carried out under nitrogen using serum caps, nylon syringes, and stainless-steel needles. All kinetics were studied commencing with $[Mo(H_2O)_6]^{3+}$ and Cl^- or NCS^-. It was necessary to use the Guggenheim procedure to evaluate rate constants for some thiocyanate runs because $O.D._\infty$ values were in some cases difficult to determine precisely. This procedure requires a plot of $\log(O.D.' - O.D._t)$ against time where O.D.′ is the absorbance after a time interval $(t + \Delta)$ and Δ corresponds to *ca.* 1·5 half-lives of reaction. Such plots gave good straight lines from which rate constants were evaluated in the customary manner (gradient × 2·303). The Guggenheim plots gave rate constants in satisfactory agreement with those determined by standard methods. Activation parameters were obtained using a standard non-linear least-squares programme.[43]

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