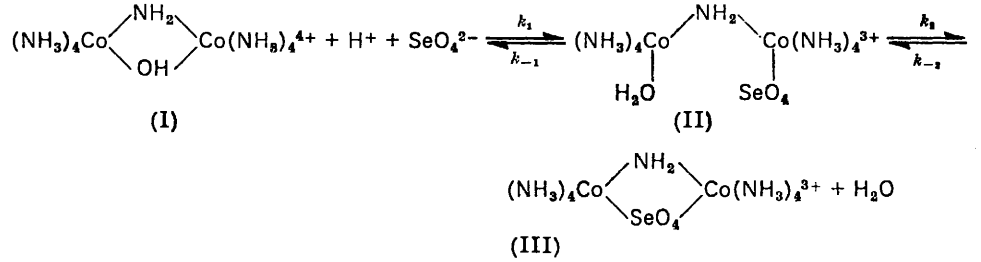
Reactions of μ-Hydroxo-dicobalt(III) Complexes. Part IX.[1] Equilibrium and Kinetic Studies of the Reaction of the μ-Amido-μ-hydroxo-bis[tetra-amminecobalt(III)] Complex with Selenate Ions in Aqueous Perchloric Acid Solutions, and Characterisation of the μ-Amido-μ-selenato-bis[tetra-amminecobalt(III)] Complex

By (Miss) **Siew-Wan Foong** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

Perchlorate and bromide salts of the μ-amido-μ-selenato-bis[tetra-amminecobalt(III)] complex have been prepared and characterised. Equilibrium and kinetic studies on the interconversion [equation (i)] of the μ-amido-μ-hydroxo- (I) and μ-amido-μ-selenato-complexes (III) at $I = 2{\cdot}0\text{M}$ ($NaClO_4$) are described. From spectrophotometric studies at 25 °C, the overall equilibrium constant $K_{12} = 265 \pm 5$ l^2 mol^{-2}. For the forward reaction,



(I) (II) (III) (i)

the conversion of (I) into (II) is rate determining and first-order rate constants, k_f, show the dependence $k_f/\text{s}^{-1} = k_{1a}[H^+][SeO_4^{2-}]$. At 25 °C, $k_{1a} = 1{\cdot}35 \times 10^{-2}$ l^2 mol^{-2} s^{-1}, $\Delta H_{1a}^{\ddagger} = 18{\cdot}2 \pm 0{\cdot}3$ kcal mol^{-1} and $\Delta S_{1a}^{\ddagger} = -6{\cdot}3 \pm 0{\cdot}9$ cal K^{-1} mol^{-1}. The reverse reaction shows a dependence on $[H^+]$ of the form $k_r/\text{s}^{-1} = a + b[H^+]$ over the temperature range 45—60 °C, where $k_r = k_{-2}k_{-1}/k_2$. At 25 °C extrapolated values of a and b are $3{\cdot}85 \times 10^{-5}$ s^{-1} and $8{\cdot}6 \times 10^{-6}$ l mol^{-1} s^{-1} respectively. Activation parameters are $\Delta H_a^{\ddagger} = 16{\cdot}4 \pm 0{\cdot}4$ kcal mol^{-1}, $\Delta S_a^{\ddagger} = -30{\cdot}2 \pm 1{\cdot}4$ cal K^{-1} mol^{-1}; and $\Delta H_b^{\ddagger} = 16{\cdot}4 \pm 1{\cdot}6$ kcal mol^{-1} and $\Delta S_b^{\ddagger} = -36{\cdot}3 \pm 4{\cdot}6$ cal K^{-1} mol^{-1}.

WHEREAS the μ-amido-μ-sulphato-bis[tetra-amminecobalt(III)] complex $(NH_3)_4Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(NH_3)_4^{3+}$ (ref. 2) is well characterised,[3] the analogous complex with the selenato-group has not been extensively studied.[4] We present here details of the preparation of the μ-amido-μ-selenato-complex from the μ-amido-μ-hydroxo-bis[tetra-amminecobalt(III)] complex, (I), the preparation of which is described elsewhere.[5] The i.r. and u.v.-visible spectra and elemental analyses support the structure (III). Kinetic studies on the interconversion of (I) and (III), equation (1), exhibit similar features to those reported earlier for the reaction with sulphate ions.[6]

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[1] Part VIII, R. K. Wharton and A. G. Sykes, *J.C.S. Dalton*, 1973, 439.

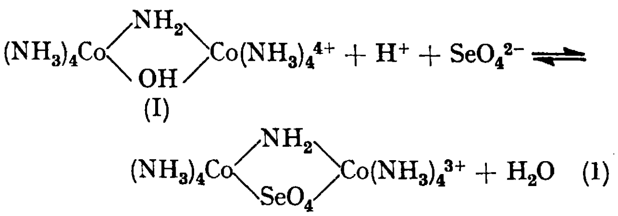
[2] A. Werner, *Annalen*, 1910, **375**, 51; the preparation of the ethylenediamine complex $(en)_2Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(en)_2^{3+}$ is also given. Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1969, **42**, 146 give details of the preparation of the propylenediamine complex $(pn)_2Co{\cdot}\mu(NH_2,SO_4){\cdot}Co(pn)_2^{3+}$.

[3] For a recent review of dicobalt(III) complexes see A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, vol. XIII, ed. J. O. Edwards, 1970, pp. 1—106.

[4] J. Meyer, G. Dirska, and F. Clemens, *Z. anorg. Chem.*, 1924, **139**, 333. Studies on the Cr^{2+} and V^{2+} reductions of the μ-amido-μ-selenato-bis[tetra-amminecobalt(III)] complex have already been reported [R. S. Taylor, M. Green, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 277 and M. Green, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 509].

[5] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc.* (*A*), 1970, 2979; R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, vol. XII, ed. R. W. Parry, 1970, p. 210.

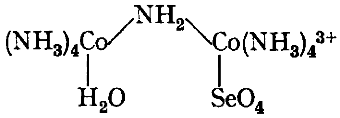
[6] M. B. Stevenson, A. G. Sykes, and R. S. Taylor, *J. Chem. Soc.* (*A*), 1970, 3214.



$$(NH_3)_4Co\overset{NH_2}{\underset{OH}{\lt\gt}}Co(NH_3)_4^{4+} + H^+ + SeO_4^{2-} \rightleftharpoons (NH_3)_4Co\overset{NH_2}{\underset{SeO_4}{\lt\gt}}Co(NH_3)_4^{3+} + H_2O \quad (1)$$

(I) (III)

As in the latter study, it is necessary in invoke formation of the aquo-complex, (II), as a transient intermediate.



$$(NH_3)_4Co\overset{NH_2}{\lt\gt}Co(NH_3)_4^{3+}$$

(II)

RESULTS

Characterisation of the μ-Amido-μ-selenato-complex.—Samples of the bromide and perchlorate salts of the complex were prepared as described in the Experimental section. Elemental analyses on the perchlorate salt indicated a molecular formula of $[(NH_3)_4Co\cdot\mu(NH_2,SeO_4)\cdot Co(NH_3)_4](ClO_4)_3$ with no water molecules of crystallisation. A solution of complex (3×10^{-3}M) in 0·1M-$LiClO_4$ (25 °C) gave an initial pH reading of 5·5 decreasing to 4·0 after *ca.* 10 min. The initial pH is consistent with a μ-amido-μ-selenato-structure (no co-ordinated water); subsequent changes in pH are in accordance with the conversion of (III) into (I) which results in the release of H^+. U.v.-visible spectra of complexes (I) and (III) are shown in Figure 1. The spectrum of (III) is similar to that of the μ-amido-μ-sulphato-bis-[tetra-amminecobalt(III)] complex which is also shown in the Figure. Spectra of the μ-amido-μ-phosphato-bis[tetra-amminecobalt(III)] complexes (protonated and unprotonated forms) are also similar,[7] and peak positions and absorption coefficients are characteristic of bridging tetrahedral oxo-anions.[8]

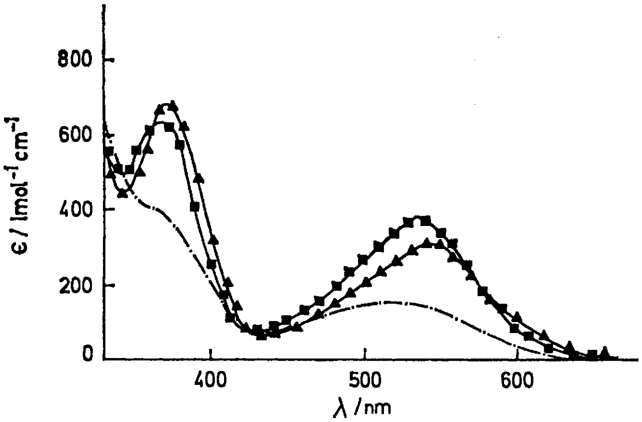
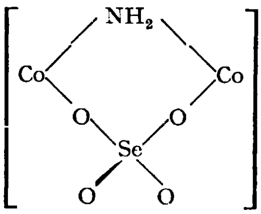


FIGURE 1 U.v. and visible spectra of the μ-amido-μ-hydroxo- (— · — · —), μ-amido-μ-selenato- (▲), and μ-amido-μ-sulphato-complexes (■) in 0·1M-$HClO_4$

The i.r. spectrum of the μ-amido-μ-selenato-complex indicated a lowering of symmetry to C_{2v} and metal–oxygen bonding as in (IV). Frequencies observed are listed in Table 1 and Figure 2 illustrates the splitting of the ν_3 fundamental on bridging. The frequency ν_4 was also split (Table 1) and ν_1 and ν_2, which are not i.r.-active for uncomplexed selenate ion, were observed for the bridging selenato-group. There was some uncertainty in the position of the ν_4 bands and our assignment should be regarded as tentative. The complex $(NH_3)_3Co\cdot\mu(SeO_4,SeO_4,OH)\cdot Co(NH_3)_3^+$ has recently been prepared and its i.r. spectrum reported.[9] An interesting feature is the more extensive splitting of the ν_3 band in the case of the triple bridged complex.



(IV)

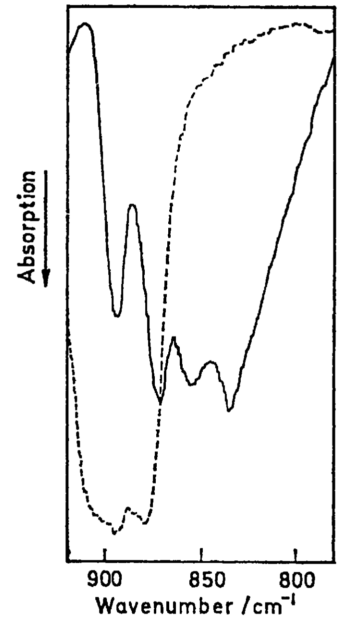


FIGURE 2 I.r. spectra of the complexes $[(NH_3)_4Co\cdot\mu(NH_2,SeO_4)\cdot Co(NH_3)_4](ClO_4)_3$ (——) and Na_2SeO_4 (- - - -) in KBr discs

The Selenate–Hydrogenselenate Ion Equilibrium.—Information as to the extent of protonation of selenate ions, (2), in aqueous solution is limited. Data obtained at I = 0·0007—0·019M and corrected to $I = 0$ using the Davies equation give a value $K_B = 46$ l mol⁻¹ at 25 °C.[10] Corrections using the Debye–Hückel limiting expression for activity coefficients give values in the range K_B = 50—60 l mol⁻¹, depending on the choice of the ion-size parameter.[11]

$$SeO_4^{2-} + H^+ \overset{K_B}{\rightleftharpoons} HSeO_4^- \qquad (2)$$

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[7] J. D. Edwards, S. W. Foong, and A. G. Sykes, *J.C.S. Dalton*, 1973, in the press.

[8] A. G. Sykes and R. S. Taylor, *J. Chem. Soc. (A)*, 1970, 1424.

[9] K. Wieghardt and J. Eckart, *Z. anorg. Chem.*, 1971, **383**, 240.

[10] V. S. K. Nair, *J. Inorg. Nuclear Chem.*, 1964, **26**, 191.

[11] A. K. Covington and J. V. Dobson, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1435.

Other work gives $K_B = 83$ l mol^{-1} at 25 °C and $I = 0$ (corrected using the Debye–Hückel equation).[12] Earlier investigations over a range of temperatures indicated that K_B is essentially the same as that for the formation of the hydrogensulphate ion.[13] No other information is at present available as to values of K_B at the higher ionic strengths used in this work.

We have attempted to determine K_B at $I = 2{\cdot}0$M ($NaClO_4$), first using the colorimetric procedure described by Reynolds and Fukushima for sulphate ion.[14] Cresol Red indicator was used and measurements were made at 560 nm. Results obtained showed a wide scatter. Attempts were also made to measure K_B by pH titration and a value K_B *ca.* 8 l mol^{-1} was obtained, *i.e.* $HSeO_4^-$ is a slightly stronger acid than the ion HSO_4^- in agreement with ref. 11. From these observations we conclude that K_B is of the same order of magnitude as that for the formation of HSO_4^-. In the first instance we have assumed K_B to have the same value as that for HSO_4^-, *i.e.* 11·9 l mol^{-1} at 25 °C and $I = 2{\cdot}0$M ($NaClO_4$), but because of the uncertainty a range of values from 4 to 40 l mol^{-1} has also been considered.

Preliminary Experiments.—The conversion (I) ⟶ (III), at 25 °C with initial concentrations [(I)] *ca.* 10^{-3}M, $[H^+] = 2{\cdot}0$M, and $[SeO_4^{2}]_T = 1{\cdot}00$M, had a half-life of *ca.* 9 min and gave isosbestic points at 406 and 460 nm. For the reverse reaction, with initial concentrations of [(III)] *ca.* 5×10^{-4}M, $[H^+] = 2{\cdot}0$M, and temperature 50 °C, the half-life was *ca.* 33 min and isosbestic points were observed at 415 and 460 nm. Cross-over points for complexes (I) and (III) in the absence of free selenate ions are at 418 and 460 nm, but will not necessarily be in the same positions in the presence of these ions which are known to have an effect on the spectrum of (I) (see Experimental section). We conclude that there is no spectroscopic evidence for any build-up of complex (II) during either the forward or reverse reactions. Free selenate ion absorbs below 350 nm.

Details of the overall equilibrium and the kinetics of conversion of complexes (I) ⟶ (III) and (III) ⟶ (I) are considered below. The inclusion of the ion SeO_4^{2-} on the left-hand side of equation (1) does not necessarily exclude that of $HSeO_4^-$ as a possible reactant.

Determination of the Overall Equilibrium Constant.—The overall equilibrium constant K_{12} for the formation of complex (III) is as defined in (3). Since there is no significant build-up of complex (II), concentrations of (I) and (III) can readily be obtained from spectrophotometric measurements. Absorption coefficients, ε_{obs}, were determined at 542 nm for solutions of complex (I) which had been allowed to equilibrate in the presence of varying amounts of $[H^+]$ and $[SeO_4^{2-}]_T$ (Table 2). The variation of ε_{obs} with $[SeO_4^{2-}]_T$ at $[H^+] = 2{\cdot}0$M is shown in Figure 3. Taking into account (2), equation (3) can be modified to (4),

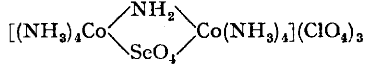
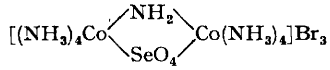
$$K_{12} = \frac{[(NH_3)_4Co{\cdot}\mu(NH_2,SeO_4){\cdot}Co(NH_3)_4{}^{3+}]}{[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4{}^{4+}][H^+][SeO_4^{2-}]} \quad (3)$$

$$\frac{\varepsilon_S - \varepsilon_{obs}}{\varepsilon_{obs} - \varepsilon_{OH}} = \frac{1}{K_{12}} \cdot \frac{(1 + K_B[H^+])}{[H^+][SeO_4^{2-}]_T} \quad (4)$$

where ε_{OH} (137—188 l mol^{-1} cm^{-1} depending on $[H^+]$ and $[SeO_4^{2-}]_T$, see Table 2) and ε_S (306 l mol^{-1} cm^{-1} from Figure 3) are for complexes (I) and (III) respectively; a value $K_B = 11{\cdot}9$ l mol^{-1} at 25 °C (that for sulphate ion) was assumed. The constant K_{12} was obtained graphically by plotting the left-hand side of (4) against $(1 + K_B[H^+])[H^+]^{-1}[SeO_4^{2-}]_T^{-1}$ (Figure 4). The decomposition of complex (I) is not effective for the range of conditions investigated. At 25 °C and $I = 2{\cdot}0$M ($NaClO_4$), $K_{12} = 265 \pm 5$ l^2 mol^{-2}. The error was computed by a least-squares program with each data point given equal weight-

TABLE 1

Evidence for a bridging selenate ligand from i.r. spectra (cm^{-1})

Complex	Symmetry	ν_1	ν_2	ν_3	ν_4
Free selenate ion [a]		833	335	875	432
Na_2SeO_4	T_d			880—890	430
 $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}SeO_4)Co(NH_3)_4](ClO_4)_3$	C_{2v}	844	384	893 872 854	518 480 [b] 408
 $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}SeO_4)Co(NH_3)_4]Br_3$	C_{2v}	836 [c]	381	893 [c] 873 [c] 856 [c]	519 488 [b] 410

[a] Raman and i.r.-active bands from K. Nakamoto, ' Infra-red Spectra of Inorganic Coordination Compounds, 2nd edn., 1970, p. 111. [b] The Co–N stretching band (470 cm^{-1}) is in this region; it is generally weak and does not appear to be resolved in this spectrum. A further weak band at 534 cm^{-1} was not assigned. [c] Not as well resolved as that for the perchlorate salt.

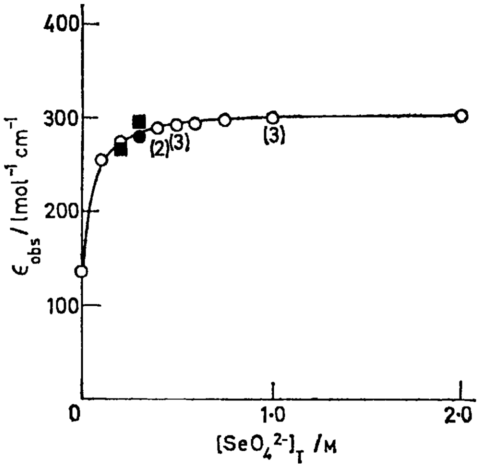


FIGURE 3 Variation of ε_{obs} with $[SeO_4^{2-}]_T$ at $[H^+] = 2{\cdot}0$M and 25 °C, (○). Points at 35 (●) and 40 °C (■) are also included

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[12] A. V. Pamfilov and A. L. Agafonova, *Zhur. fiz. Khim.*, 1950, **24**, 1147.

[13] M. S. Sherrill and E. H. Lyons, jun., *J. Amer. Chem. Soc.*, 1932, **54**, 979.

[14] W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, 1963, **2**, 176.

TABLE 2

Data used in the determination of the equilibrium constant, K_{12}, for the formation of the μ-amido-μ-selenato-complex (ε_S 306 l mol^{-1} cm^{-1}) from the μ-amido-μ-hydroxo-complex {ε_{OH} 137—188 l mol^{-1} cm^{-1} depending on [H$^+$] and [SeO_4^{2-}]} at 25 °C, I = 2·0M (NaClO$_4$), and λ = 542 nm. The number of determinations is indicated in parentheses

[H$^+$] M	[SeO_4^{2-}]$_T$ M	10^4[Complex] M	ε_{OH} [c] l mol^{-1} cm^{-1}	ε_{obs} l mol^{-1} cm^{-1}
2·0	2·0	3·94	188	302
2·0	1·0	3·91	164	300 (3)
2·0	0·75	3·94	158	298
2·0	0·6	3·94	154	295
2·0	0·5	3·94	152	293 (3)
1·5	0·5	3·96	151	289 (3)
1·0	0·5	3·82	150	294
2·0	0·4	3·84	149	290 (2)
1·5	0·4	3·85	148	295 (2)
1·0	0·4	3·91	147	290 (3)
0·5	0·4	3·96	146	288 (2)
1·5	0·3	4·00	146	286 (2)
1·0	0·3	3·88	145	287 (2)
0·5	0·3	*a*	144	280 (3)
2·0	0·2	3·87	145	274
1·5	0·2	3·79	144	275
0·5	0·2	*b*	142	269 (2)
2·0	0·1	4·15	142	252
1·0	0·1	7·82	140	250

[a] [Complex] = 3·86 × 10^{-4}—32·3 × 10^{-4}M. [b] [Complex] = 3·87 × 10^{-4}—31·7 × 10^{-4}M. [c] The effects of [H$^+$] (0—2·0M) and [SeO_2^{2-}]$_T$ (0—0·5M) were determined separately as indicated in the Experimental section. It is assumed that the two effects are additive; a linear dependence on [SeO_4^{2-}]$_T$ was assumed over the range 0—2·0M.

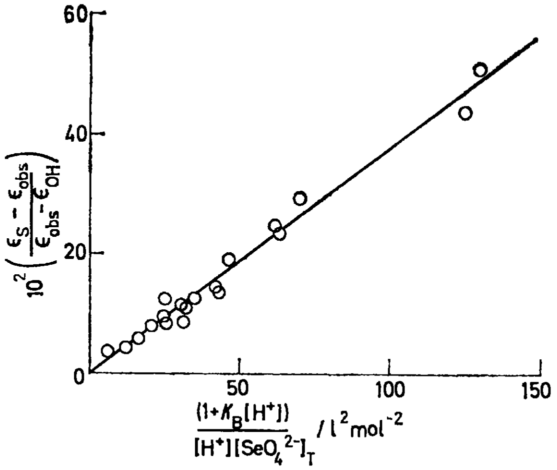

FIGURE 4 Determination of K_{12} for the formation of the μ-amido-μ-selenato-complex [equation (5)]

ing, and the program as a whole was weighted so that the line passed through the origin.

The reaction of H$^+$ and selenate ions with complex (I) did not proceed to effective completion until such conditions as [H$^+$] = 2·0M and [SeO_4^{2-}]$_T$ = 1·0M were employed (Figure 3). Since pseudo-first-order rate constants k_f for the conversion (I) ⟶ (III) were, with one exception, obtained with [SeO_4^{2-}]$_T$ ⩽ 0·5M, an allowance for the reverse reaction (k_r) is necessary. We consider first therefore the determination of the rate constant k_r.

Kinetics of the Reverse Reaction.—Temperatures in the range 45—60 °C were selected so that rates were sufficiently rapid. First-order plots of log ($OD_t - OD_\infty$) against time for the disappearance of complex (III) at 542 nm were linear to at least 80% completion (OD_∞ calculated from known ε values). The overall reaction was sufficiently rapid as to virtually exclude contributions from the decomposition of (I).* First-order rate constants, k_r, from such plots are listed in Table 3. On varying [H$^+$] from 0·5 to 2·0M, k_r gave the dependence (5) which is illustrated

$$k_r = a + b[H^+] \qquad (5)$$

in Figure 5. Values of *a* and *b* (Table 4) were obtained by a least-squares treatment where each data point was given equal weighting. Activation parameters $\Delta H_a^\ddagger$, $\Delta H_b^\ddagger$, $\Delta S_a^\ddagger$, and $\Delta S_b^\ddagger$ were obtained in a similar manner and are summarised in Table 7. Values of k_r at temperatures 25—40 °C were obtained by extrapolating activation plots for *a* and *b* respectively.

TABLE 3

Pseudo-first-order rate constants, k_r, for the conversion of the μ-amido-μ-selenato-complex (III) to the μ-amido-μ-hydroxo-complex (I), I = 2·0M (NaClO$_4$) except where stated otherwise

Temp. °C	[H$^+$] M	10^4[Complex] M	10^4k_r s^{-1}
45·0	0·5	4·12	1·62
	1·0	3·61	1·71
	1·5	3·61	1·88
	2·0	3·61	2·09
50·0	0·5	3·64	2·55
	1·0	4·09	2·94
	1·0	4·19 [a]	3·05
	1·0	3·70	2·83
	1·5	2·32 [a]	3·19
	1·5	3·58	3·04
	2·0	3·56	3·40
	2·0	4·06	3·52
	2·0	4·22 [a]	3·60
55·0	0·5	2·85	3·78
	0·5	2·70	3·61
	1·0	2·93	4·07
	1·5	2·77	4·30
	1·5	2·46	4·26
	2·0	2·85	5·00
60·3	0·5	3·87	5·50
	1·0	3·64	6·10
	1·5	3·58	6·63
	2·0	3·61	7·20

[a] I = 2·0M (LiClO$_4$).

TABLE 4

Summary of rate constants *a* and *b* for the reverse reaction (III) ⟶ (I) at various temperatures, I = 2·0M (NaClO$_4$)

Temp. °C	10^4a s^{-1}	10^4b l mol^{-1} s^{-1}
45·0	1·43 ± 0·05	0·32 ± 0·04
50·0	2·27 ± 0·09	0·58 ± 0·06
55·0	3·27 ± 0·15	0·77 ± 0·12
60·3	4·95 ± 0·02	1·13 ± 0·02

Kinetics of the Forward Reaction.—To avoid precipitation of the selenate salt of (I) it was preferable to keep [H$^+$] > [SeO_4^{2-}]$_T$. The reaction was studied over the concentration

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* This involves loss of ammonia ligands from the complex (R. S. Taylor and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1426) and is much more effective in the corresponding reaction of the μ-amido-μ-sulphato-complex (ref. 6) which is an order of magnitude slower. As a result the linearity of plots in the latter study was reduced to 30—40% completion.

ranges $[H^+] = 0{\cdot}5$—$2{\cdot}0$M and $[SeO_4^{2-}]_T = 0{\cdot}1$—$0{\cdot}5$M (one run was carried out at 1·0M), with $I = 2{\cdot}03 \pm 0{\cdot}02$M ($NaClO_4$). Ionic strengths were calculated, allowing for the protonation of the SeO_4^{2-} ion with the K_B values in Table 6. Kinetic runs were followed spectrophotometrically at 542 nm and pseudo-first-order rate constants k_0 determined from plots of log ($OD_\infty - OD_t$) against time, where the final absorbance (OD_∞) was that recorded after 6—8 half-lives. Initially, some difficulty was experienced in reproducing runs to within ±20% with singly distilled water and triply distilled water was therefore used, when much better agreement was obtained. Plots at wavelengths 520—560 nm were linear to >80% completion, except at 45 and 55 °C (*ca.* 60% completion) when some contribution from the decomposition of complex (I) is expected. At 500 nm the optical density change was smaller and the linearity was reduced to *ca.* 50% completion. For three runs at 45 °C and $[SeO_4^{2-}]_T = 0{\cdot}1$M, OD_∞ was calculated and not observed. In all cases an allowance was made for the reverse reaction, thus the rate constant k_f for the forward reaction is given by ($k_0 - k_r$), where k_r (from Figure 5) values are at identical conditions of temperature and $[H^+]$ (Table 5).

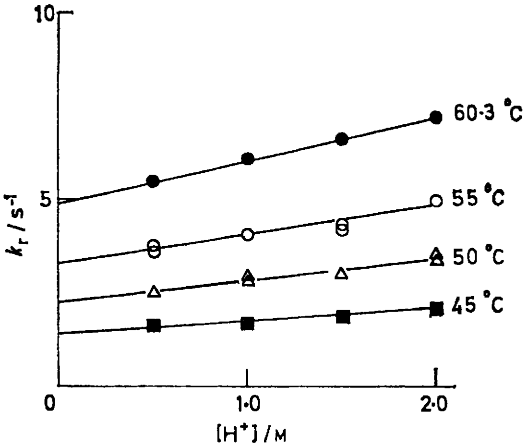


FIGURE 5 Dependence of k_r on $[H^+]$ for the reverse reaction (III) $\longrightarrow$ (I), $I = 2{\cdot}0$M ($NaClO_4$)

By analogy with the study on the μ-amido-μ-sulphato-complex,[6] a dependence as in (6) would be expected. On

$$k_f = k_{1a}[H^+][SeO_4^{2-}] + k_{1b}[H^+][HSeO_4^-] \qquad (6)$$

introducing K_B and $[SeO_4^{2-}]_T$, (6) gives (7). The left-hand

$$\frac{k_f(1 + K_B[H^+])}{[H^+][SeO_4^{2-}]_T} = k_{1a} + k_{1b}K_B[H^+] \qquad (7)$$

side of this equation is referred to as F, see for example Table 5. For runs at constant $[SeO_4^{2-}]_T$, no dependence of F on $[H^+]$ was apparent (Figure 6) and we are uncertain as to possible contributions from k_{1b} (if any). From a consideration of the reverse reaction and the $[H^+]$ dependence of k_r [equation (5)], contributions from k_{1b} are to be expected. The most accurate estimate we can make at 25 °C is that from the quantities K_{12}, K_B, and b [equation (8)],

$$k_{1b} = bK_{12}/K_B \qquad (8)$$

where K_{12} and b are as already determined and K_B is as indicated above. These give k_{1b} *ca.* 2×10^{-4} l^2 mol^{-2} s^{-1} at 25 °C in good agreement with the value observed for the reaction of the hydrogensulphate ion. The gradient of the broken line in Figure 6 is that required for such a value of k_{1b}. However this value should be regarded as an upper limit since still steeper gradients would be necessary at the higher temperature. Making no allowances for k_{1b}, activation parameters for k_{1a} are $\Delta H_{1a}^‡ = 18{\cdot}2 \pm 0{\cdot}3$ kcal mol^{-1} and $\Delta S_{1a}^‡ = -6{\cdot}3 \pm 0{\cdot}9$ cal K^{-1} mol^{-1}. The inclusion of k_{1b} is unlikely to decrease k_{1a} by more than 5—10% and the effect on the activation parameters for k_{1a} is probably not significant. Table 7 summarises the data obtained.

TABLE 5

Rate constants k_0 (observed) and k_f (after correction of k_0 for k_r) for the conversion of the μ-amido-μ-hydroxo-complex (I) to the μ-amido-μ-selenato-complex (III) at $I = 2{\cdot}03 \pm 0{\cdot}20$M ($NaClO_4$) and [Complex] $= 3{\cdot}60 \times 10^{-4}$—$31{\cdot}70 \times 10^{-4}$M

Temp. / °C	[H$^+$] / M	[SeO$_4^{2-}$]$_T$ / M	10^4k_0 / s^{-1}	10^4k_f / s^{-1}	10^4F / l^2 mol^{-2} s^{-1}
25	2·00	0·5	6·60	6·04	150
	1·50	0·5	6·40	5·89	148 [a]
	1·00	0·5	6·23	5·76	149
	0·50	0·5	5·12	4·69	130
	0·50	0·5	5·58	5·15	143
	2·00	0·4	5·28	4·72	146
	2·02	0·4	4·83	4·27	133
	1·00	0·4	5·06	4·59	148
	2·01	0·3	3·98	3·42	141
	1·00	0·3	3·61	3·14	135
	0·50	0·3	3·38	2·95	137
	2·00	0·2	2·87	2·31	143
	2·01	0·2	2·73	2·17	134
	2·01	0·2	2·70	2·14	132
	1·51	0·2	2·93	2·42	152
	1·51	0·2	2·57	2·06	130
	1·51	0·2	2·57	2·06	130
	1·02	0·2	2·45	1·98	128
	1·02	0·2	2·58	2·11	136
	2·00	0·1	1·62	1·06	132
	1·51	0·1	1·60	1·09	137
35	0·5	0·1	3·32	2·53	400
	2·0	0·1	3·91	2·83	402
	1·5	0·3	9·17	8·19	394
	2·0	0·3	9·53	8·45	400
40	0·5	0·2	8·97	7·80	652
	2·0	0·2	10·4	8·82	653
	0·5	0·3	12·9	11·8	654
	2·0	0·3	14·4	12·8	648
45	0·5	0·1	7·40	5·74	1021
	1·0	0·1	8·05	6·20	1035
	2·0	0·1	8·53	6·40	1036
	0·5	0·3	19·1	17·4	1036
	1·5	0·3	20·8	18·8	1025
	2·0	0·3	21·2	19·1	1030
55	2·01	0·3	44·2	39·2	2480
	2·01	0·3	45·8	40·9	2390
	1·5	1·0	141	137	2510 [a]

[a] Ionic strength adjusted with $LiClO_4$.

The effect which other values of K_B might have on our interpretation has been checked at 25 °C. Thus with $K_B = 4{\cdot}0$ l mol^{-1}, $k_{1a} = 0{\cdot}52 \times 10^{-2}$ l mol^{-2} s^{-2} and with $K_B = 40$ l mol^{-1}, $k_{1a} = 4{\cdot}3 \times 10^{-2}$ l mol^{-2} s^{-2}. Again contributions from k_{1b} remain uncertain. Clearly rate constants reported in this section are dependent on K_B and are subject to modification as more precise values become available. However the allowance that has been made here is we feel a generous one.

Examination of the data at 25 °C suggests that there is need for a third term $c[\mathrm{SeO_4}^{2-}]_\mathrm{T}$ on the right-hand side of equation (7). Thus for runs at constant [H⁺] (Table 5), an increase in F was observed on increasing $[\mathrm{SeO_4}^{2-}]_\mathrm{T}$ from 0·1 to 0·5M. Similar terms have been observed for corresponding studies on the μ-amido-μ-sulphato-[6] and μ-amido-μ-phosphato-complexes[7] and here the term implies a $[\mathrm{SeO_4}^{2-}]_\mathrm{T}{}^2$ dependence. On making an allowance for the c term at 25 °C, the value of k_{1a} is still within the range given in Table 6. The trend observed from less extensive data at higher temperatures was not as marked and it is difficult therefore to make a correction for this term.

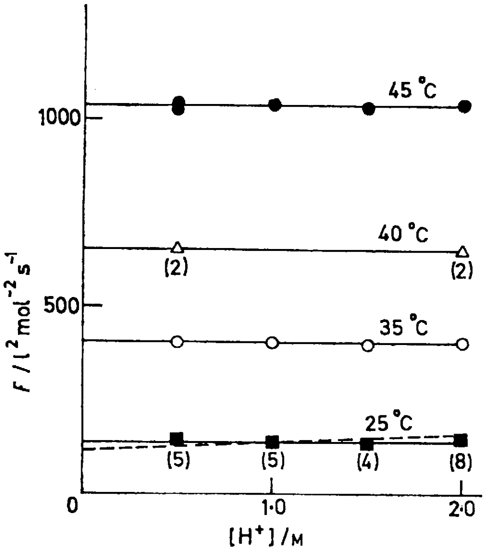


FIGURE 6 Dependence of the term F, *i.e.* the left-hand side of equation (7), on [H⁺], $I = 2{\cdot}03 \pm 0{\cdot}02$M (NaClO₄). The gradient of the broken line at 25 °C corresponds to $k_{1b}K_\mathrm{B}$ where k_{1b} has been calculated from K_{12}, b, and K_B [equation (8)]

TABLE 6

Summary of K_B values at different temperatures and corresponding values of k_{1a} for the conversion of the μ-amido-μ-hydroxo-complex (I) to the μ-amido-μ-selenato-complex (III), $I = 2{\cdot}03$M (NaClO₄)

Temp. / °C	K_B / l mol⁻¹	10^4k_{1a} / l² mol⁻² s⁻¹	10^4k_{1b} / l² mol⁻² s⁻¹
25·0	(4·0) [a]	(52) [c]	
	11·9 [b]	135 ± 4	*ca.* 2 [d]
	(40·0) [a]	(430) [c]	
35·0	13·7 [b]	397 ± 2	
40·0	14·7 [b]	651 ± 2	
45·0	15·7 [b]	1031 ± 3	
55·0	17·7 [b]	2435 ± 48	

[a] Assuming limiting values of K_B at 25 °C. [b] The value of K_B is assumed to be the same as that for the formation of the hydrogensulphate ion (A. J. Zielen, *J. Amer. Chem. Soc.*, 1959, **81**, 5022); the temperature dependence is that used in ref. 6. The tempreature dependence for the hydrogenselenate ion is assumed to be the same as that for the hydrogensulphate ion; ref. 9. [c] Value not included in computations to determine the activation parameters. [d] Deduced from K_{12}, b, and K_B [equation (8)].

TABLE 7

Summary of kinetic data for the forward and reverse reactions, $I = 2{\cdot}0$M (NaClO₄)

Path	Rate constant at 25 °C	$\Delta H^\ddagger$ / kcal mol⁻¹	$\Delta S^\ddagger$ / cal K⁻¹ mol⁻¹
k_{1a}	1·35 × 10⁻² l² mol⁻² s⁻¹	18·2 ± 0·3	−6·3 ± 0·9
k_{1b}	*ca.* 2 × 10⁻⁴ l² mol⁻² s⁻¹ [a]		
a	3·85 × 10⁻⁵ s⁻¹ [b]	16·1 ± 1·1	−25·7 ± 3·3
b	8·6 × 10⁻⁶ l mol⁻¹ s⁻¹ [b]	14·4 ± 3·2	−33·5 ± 9·7

[a] Deduced from K_{12}, b, and K_B [equation (9)]. [b] Obtained by extrapolation of data at temperatures in the range 45—60 °C.

DISCUSSION

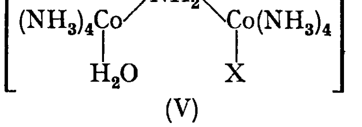
The characterisation of the μ-amido-μ-selenato-complex, (III), is we feel clearcut and decisive. The equilibrium constant K_{12} for the formation of (III) (265 l² mol⁻²) is an order of magnitude smaller than that for the corresponding μ-amido-μ-sulphato-complex (2·24 × 10³ l² mol⁻²) at 25 °C. The agreement between K_{12} and $k_\mathrm{f}/(k_\mathrm{r}[\mathrm{H}^+][\mathrm{SeO_4}^{2-}]_\mathrm{T})$ (351 l² mol⁻² at 25 °C) is regarded as satisfactory, bearing in mind that the reverse reaction was studied in the absence of free selenate ions.

The intermediate (II) has not been isolated or identified spectrophotometrically. There is no evidence for any appreciable build-up of (II) in the study of both the forward and reverse reactions. In the corresponding study of the μ-amido-μ-sulphato-complex, the reduced linearity of first-order plots for the forward reaction (at certain wavelengths) provided some evidence for the sulphato-analogue of (II).

Assuming stationary-state kinetics for (II), where first-order rate constants for (I) $\rightleftharpoons$ (II) are k_1 and k_{-1} and for (II) $\rightleftharpoons$ (III) are k_2 and k_{-2}, equations (9) and (10) can be derived. Two limiting cases of these equations may be considered. The first with $k_2 > k_{-1}$ seems more probable than the second with $k_{-1} > k_2$ for the following reasons. As more data becomes available for reactions of dicobalt(III) complexes it appears that species (V) react rapidly with elimination of H₂O and formation of complexes with X^{n-} as a bridging ligand. Wilkins and Miller[15] have determined a rate constant of 2 s⁻¹ at 25 °C for the elimination of water in (11) (trien = triethylenetetramine), which is fast for a reaction at a

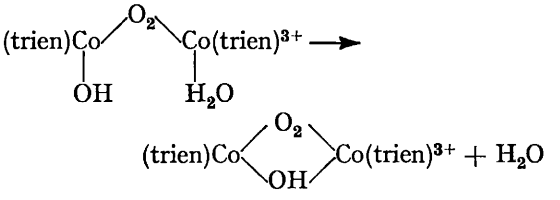
$$k_\mathrm{f} = k_1k_2/(k_2 + k_{-1}) \qquad (9)$$

$$k_\mathrm{r} = k_{-1}k_{-2}/(k_2 + k_{-1}) \qquad (10)$$



$$\left[(\mathrm{NH_3})_4\mathrm{Co}(\mathrm{H_2O})(\mu\text{-}\mathrm{NH_2})\mathrm{Co}(\mathrm{X})(\mathrm{NH_3})_4\right]^{5-n}$$

(V)



$$(\mathrm{trien})\mathrm{Co}(\mathrm{OH})(\mu\text{-}\mathrm{O_2})\mathrm{Co}(\mathrm{H_2O})(\mathrm{trien})^{3+} \longrightarrow (\mathrm{trien})\mathrm{Co}(\mu\text{-}\mathrm{O_2})(\mu\text{-}\mathrm{OH})\mathrm{Co}(\mathrm{trien})^{3+} + \mathrm{H_2O} \qquad (11)$$

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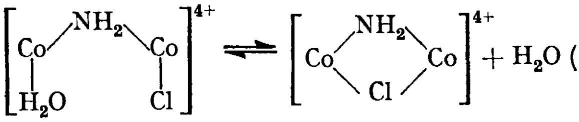
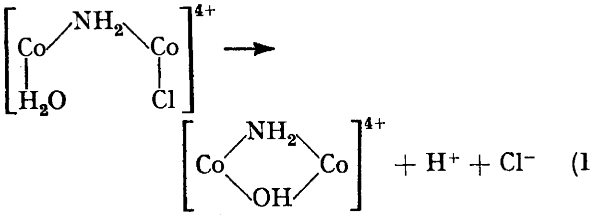
[15] F. Miller and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1970, **92**, 2687.

cobalt(III) centre and consistent with our observations here for the μ-amido-series of complexes. Instances in which appreciable amounts of (V) are present in aqueous solution are with $X^{n-} = Cl^-$ and Br^-, when the halide bridge is itself unstable and readily cleaved. Thus with,



(12)

for example, $X^{n-} = Cl^-$ a relatively rapid equilibrium (12) ensues, which terminates only when the subsequent slower reaction, (13), of the aquochloro-complex occurs.



(13)

The lability of the H_2O possibly arises from crowding of the ligands in complexes of type (V). The H_2O ligand is more reluctant to bridge than X^{n-} (= SO_4^{2-}, SeO_4^{2-}, HPO_4^{2-}, Cl^-, and Br^-) because of the nucleophilic properties of the respective groups and the availability of electron lone-pairs. However even with the bisaquo-complex ($X^{n-} = H_2O$) bridge closure is relatively rapid. On this basis we tentatively conclude that $k_2 > k_{-1}$, when $k_r = k_1$ and $k_r = k_{-1}k_{-2}/k_2$. It follows that $k_2 > k_1$, since there is no build up of complex (II). A further condition is that $k_2 > k_{-2}$ to allow formation of (III) to proceed to completion (Figure 3). An allowance for possible variations of K_B from 4·0 to 40 l mol^{-1} gives values of k_{1a} from $0{\cdot}52 \times 10^{-2}$ to $4{\cdot}3 \times 10^{-2}$ l^2 mol^{-2} s^{-1}, and k_{1a} may be assumed to lie within this range.

To summarise, present indications are that the reactions of the μ-amido-μ-hydroxo-complex, (I), with both selenate and sulphate ions exhibit similar behaviour with $k_2 > k_{-1}$. Even allowing for a variation in K_B, k_{1a} for the reaction of (I) with selenate is of similar magnitude to that for the reaction with sulphate ions ($2{\cdot}15 \times 10^{-2}$ l^2 mol^2 s^{-1} at 25 °C) [6] and both are appreciably faster than for reactions with anions of 1— charge. Rate constants k_{1b} for the ions $HSeO_4^-$ (estimated value) and HSO_4^- on the other hand are of the same order of magnitude as those observed for Cl^- (9×10^{-4} l^2 mol^{-2} s^{-1}) and Br^- (4×10^{-4} l^2 mol^{-2} s^{-1}) at 25 °C. Both k_{1a} and k_{1b} are composite terms since protonation of the μ-amido-μ-hydroxo-complex is believed to occur prior to bridge cleavage. No evidence was obtained in either of these studies for reactions of SeO_4^{2-} or SO_4^{2-} with the unprotonated μ-amido-μ-hydroxo-complex. Such paths are observed with Cl^- (ref. 16) and Br^- (ref. 17) as the incoming substituents. This different behaviour can be rationalised in terms of electrostatic repulsion between the hydroxo-bridge, formal charge 1—, and the selenate and sulphate ions of charge 2—, assuming that the latter ions must substitute from a position adjacent to the hydroxo-bridge. Paths in which the ions $HSeO_4^-$ and HSO_4^- induce bridge cleavage without prior protonation of the hydroxo-bridge are indistinguishable from the k_{1a} path. A more extensive comparison of data for reactions involving hydroxo-bridge cleavage of complex (I) will be made elsewhere. The rate constant k_r for the reverse reaction is an order of magnitude greater for the μ-amido-μ-selenato-complex than that of the μ-amido-μ-sulphato-complex, which accounts for the difference in K_{12} values.

As in other studies, there is no kinetic evidence for ion-pair formation as a preliminary step to bridge cleavage by k_{1a}. Thus even with 0·5M-selenate ions the k_{1a} path remains strictly first order in [SeO_4^{2-}] and there is no kinetic evidence for formation of ion-pairs reaching or even approaching completion. If ion-pairing does occur prior to bridge cleavage, then the relevant formation constant is much smaller than might be predicted for 2— and 4+ species. However one must make the distinction between ion-pairing near to the negatively charged bridging ligands and that at either extremity of the complex. Selenate ions do have an effect on the absorption coefficients of the μ-amido-μ-hydroxo-complex at 542 nm (see Experimental section) and the ion-pairing which is apparent is presumably at the extremities of the complex.

EXPERIMENTAL

Samples of the chloride salt of the μ-amido-μ-hydroxo-bis-[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4]Cl_4,4H_2O$ were prepared and converted to the perchlorate salt $[(NH_3)_4Co{\cdot}\mu(NH_2,OH){\cdot}Co(NH_3)_4](ClO_4)_4,H_2O$ as described elsewhere.[8] The latter salt was used in all kinetic studies. To prepare samples of the perchlorate salt of the μ-amido-μ-selenato-bis[tetra-amminecobalt(III)] complex, $[(NH_3)_4Co{\cdot}\mu(NH_2,SeO_4){\cdot}Co(NH_3)_4]^{3+}$, the following procedure was used. The chloride salt of the μ-amido-μ-hydroxo-complex (0·4 g) was dissolved in 0·01M-perchloric acid (9—10 ml). The solution was warmed to 30 °C and 12M-perchloric acid (2 ml) followed by 1M-Na_2SeO_4–2M-$HClO_4$ (10 ml) added. The temperature was maintained until a precipitate formed (*ca.* 30—40 min). A further 1 ml of 12M-$HClO_4$ was then added and the solid was filtered off, washed with alcohol and ether, and dried by suction. The crude purple crystals (0·5 g) were recrystallised by first dissolving in 0·01M-$HClO_4$ (20 ml). 12M-$HClO_4$ (3 ml) was then added and the mixture warmed to *ca.* 40 °C. The solution was filtered while hot and the filtrate allowed to cool slowly to room temperature and then to 0 °C. Flaky purple *crystals* formed and were filtered off, washed with alcohol and ether, and dried; yield 48% {Found: H, 3·95, 4·0; Cl, 14·9, 15·3; N, 17·1, 17·7. Calc. for $[(NH_3)_4Co{\cdot}\mu(NH_2,SeO_4){\cdot}Co(NH_3)_4](ClO_4)_3$: H, 3·65; Cl, 15·0; N, 17·7%}. A sample of the bromide salt was prepared for the i.r. studies by adding saturated ammonium bromide solution to a solution of the perchlorate salt.

I.r. studies were carried out on a Perkin-Elmer 457

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[16] S. W. Foong, R. D. Mast, M. B. Stevenson, and A. G. Sykes, *J. Chem. Soc.* (*A*), 1971, 1266.

[17] S. W. Foong and A. G. Sykes, *J.C.S. Dalton*, submitted for publication.

instrument. Samples were prepared as KBr discs. pH Measurements on solutions of the μ-amido-μ-selenato-complexes were made using Radiometer glass (type G202B) and calomel electrodes (type K 401). These were immersed directly in the solution of the complex and the pH measured on a Radiometer pH-meter 4. The latter was calibrated using a buffer of pH 6·5 ± 0·02 (20 °C).

Water which had been triply distilled from alkaline potassium permanganate and acidic potassium dichromate solutions was used to make up all solutions. Spectrophotometer cells were washed with triply distilled water and dried over silica gel in a desiccator. Sodium perchlorate, perchloric acid, and sodium selenate were of AnalaR grade purity. Selenic acid, used in some of the runs, was of laboratory grade purity; check runs using sodium selenate were in good agreement. The μ-amido-μ-selenato-complex has a maximum at 542 nm ($\varepsilon = 306$ l mol^{-1} cm^{-1}). Absorption coefficients for the μ-amido-μ-hydroxo-complex at this wavelength increase from 137 to 140 l mol^{-1} cm^{-1} on increasing [H$^+$] from 0 to 2·0M at $I = 2{\cdot}0$M; a larger increase from 137 to 148 l mol^{-1} cm^{-1} was observed on increasing $[\mathrm{SeO_4^{2-}}]_T$ from 0 to 0·5M, the concentration range employed for the kinetic studies. Appropriate corrections were made for these observations.

We wish to acknowledge the award of a University of Leeds Scholarship (to S. W. F.).

[2/1964 *Received*, *17th August*, 1972]