# Kinetics of the Acid Hydrolysis of Nitrito-complexes. Part III.[1] Nitritochromium(III) Complexes

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Kinetic studies of the acid-catalysed hydrolysis of the nitrito-ligand from the complexes *trans*-$[Cr(NH_3)_4(ONO)Cl]^+$, *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$, *cis*-$[Cr(NH_3)_4(ONO)OH_2]^{2+}$, *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(ONO)]^{4+}$, and *cis*-$[Cr(en)_2(ONO)(NCS)]^+$ (en = ethylenediamine) have been carried out by the stopped-flow method. Below pH 1, a common rate law applies: $-d[Complex]/dt = (k_1'[H^+] + k_2'[H^+]^2)[Complex]$. At 283·1 K and $I$ = 1·0 mol l$^{-1}$ ($NaClO_4$): $10^2\ k_1'$ = 2·59 ± 0·07, 12·7 ± 1·6, 5·9 ± 0·2, 3·6 ± 0·2, 13·8 ± 0·4 l mol$^{-1}$ s$^{-1}$; and $10^2\ k_2'$ = 6·27 ± 0·13, 86·1 ± 3·1, 12·9 ± 0·3, 2·9 ± 0·1, and 40·9 ± 0·5 l$^2$ mol$^{-1}$ s$^{-1}$ for these complexes respectively. For the complexes *trans*-$[Cr(NH_3)_4(ONO)Cl]^+$ and *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$, activation parameters at 298·1 K are $\Delta H^‡(k_1')$ = 20·3 ± 0·3 and 15·3 ± 0·1 kcal mol$^{-1}$, $\Delta S^‡(k_1')$ = +6 ± 1 and −8·4 ± 0·2 cal K$^{-1}$ mol$^{-1}$, $\Delta H^‡(k_2')$ = 14·7 ± 0·2 and 11·9 ± 0·1 kcal mol$^{-1}$, and $\Delta S^‡(k_2')$ = −12 ± 1 and −16·7 ± 0·2 cal K$^{-1}$ mol$^{-1}$ respectively. Neighbouring-group interaction between the ligands $ONO^-$ and $NCS^-$ is postulated to account for the low value of $\Delta H^‡(k_1')$ in the complex *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$. All the reactions proceed with retention of configuration, and the results are consistent with a mechanism involving nitrogen–oxygen bond cleavage.

PREVIOUSLY we have shown that the acid-catalysed hydrolysis of complexes of the type $[CrL_5ONO]^{2+}$ ($L = NH_3$ or $H_2O$) proceeds with the rate law (1).

$$-d[CrL_5ONO^{2+}]/dt = (k_0 + k_1'[H^+] + k_2'[H^+]^2)[CrL_5ONO^{2+}] \quad (1)$$

The following mechanism is postulated to account for this behaviour, where $k_1' = k_1K_1$ and $k_2' = k_2K_1K_2$ ($K_1$ and $K_2$ are the successive protonation constants).

TABLE 1

Spectral maxima and minima (nm) of some nitritochromium(III) complexes [extinction coefficients (l mol$^{-1}$ cm$^{-1}$) in parentheses]

| Complex | $\lambda_{max.}$ | | $\lambda_{min.}$ | |
|---|---|---|---|---|
| *trans*-$[Cr(NH_3)_4(ONO)Cl]^+$ | 366 (76·5) | 535 (31·6) | 350 (73·4) | 435 (14·2) |
| *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$ * | 367 (90·1) | 493 (82·2) | | 421 (19·6) |
| *cis*-$[Cr(en)_2(ONO)NCS]^+$ * | 363 (113) | 483 (121) | 349 (106) | 412 (30) |
| *cis*-$[Cr(NH_3)_4(ONO)OH_2]^{2+}$ | 364 (94) | 491 (54) | 317 (69) | 422 (21) |
| *trans*-$[Cr(NH_3)_4(ONO)OH_2]^{2+}$ † | 363 (75) | 492 (32) | 313 (62) | 421 (16) |
| *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4ONO]^{4+}$ | 368 (114) | 502 (106) | 304 (67) | 428 (28·2) |
| $[Cr(NH_3)_5ONO]^{2+}$ | 355 (79·4) | 477 (47·2) | | |
| $[Cr(H_2O)_5ONO]^{2+}$ | 365 (44·8) | 563 (18·1) | 339 (34·7) | 479 (4·7) |
| *cis*-$[Cr(NH_3)_4(ONO)_2]^+$ *† | 362 (121) | 492 (65) | 311 (91) | 421 (15) |
| *trans*-$[Cr(NH_3)_4(ONO)_2]^+$ † | 325 (146) | 488 (38·7) | 309 (140) | 422 (11·8) |

* The complex is rather unstable and the extinction coefficients are, therefore, only approximate. † Recorded for comparison; the complex was not investigated kinetically.

$$\begin{array}{llr}
[CrL_5ONO]^{2+} + H_2O \xrightarrow{k_0} & [CrL_5OH_2]^{3+} + NO_2^- & (2) \\
\quad K_1 \Big\updownarrow (H^+)\ \text{rapid} & & \\
[CrL_5(HONO)]^{3+} + H_2O \xrightarrow{k_1} & [CrL_5OH_2]^{3+} + HNO_2 & (3) \\
\quad K_2 \Big\updownarrow (H^+)\ \text{rapid} & & \\
[CrL_5(H_2ONO)]^{4+} + H_2O \xrightarrow{k_2} & [CrL_5OH_2]^{3+} + H_2NO_2^+ & (4)
\end{array}$$

Path (2) is unimportant below pH 1 where (3) and (4) predominate, whilst path (4) is more important when $L = H_2O$ than when $L = NH_3$.[1] A kinetic study of complexes of the type *cis*- and *trans*-$[Cr(en)_2(ONO)X]^{n+}$ (en = ethylenediamine; X = $ONO^-$, $OH_2$, $OH^-$, $F^-$, $Cl^-$, $Br^-$, dimethylformamide, or dimethyl sulphoxide) at 11·5 > pH > 0·8 gave evidence for paths (2) and (3), but (4) was not reported.[2] Studies of the complex $[Co(NH_3)_5ONO]^{2+}$ also indicate a rate law of type (1),[3-4] although activity effects were originally suggested to account for the non-linear dependence on acidity in this case.[3]

In the present study we have tried to substantiate the above mechanism, and investigate the factors affecting $k_1'$ and $k_2'$ by studying a variety of nitritochromium(III) complexes of different charge and geometry. The results are also of interest in relation to the catalytic effect of nitrous acid on the aquation of *cis*-anionoaquochromium(III) complexes.[5] Four new nitritochromium(III) complexes are reported, three of which were investigated kinetically.

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[1] Parts I and II, T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1969, 219, 1997.

[2] W. W. Fee, J. N. MacB. Harrowfield, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 290.

[3] B. E. Crossland and P. J. Staples, *J. Chem. Soc.* (*A*), 1971, 2853.

[4] E. Klimek, B. Grossman, and A. Haim, *Inorg. Chem.*, 1972, **11**, 2382.

[5] T. C. Matts and P. Moore, *J. Chem. Soc.* (*A*), 1971, 1632.

## RESULTS

*Stoicheiometry*.—The complexes were synthesised by *O*-nitrosation of the aquochromium(III) precursors.[6] The

$$\mathrm{Cr^*OH_2}^{n+} + \mathrm{HNO_2} \rightleftharpoons \mathrm{Cr^*ONO}^{(n-1)+} + \mathrm{H_3O^+} \quad (5)$$

isolated products were established as nitrito-isomers by means of i.r. spectra {except *cis*-$[\mathrm{Cr(en)_2(ONO)NCS}]^+$, see ref. 7}, u.v.–visible spectra in dipolar aprotic solvents,[7] and their behaviour in an excess of aqueous perchloric acid.[1] The latter treatment caused a rapid reversal of reaction (5) to give a product with a u.v.–visible spectrum identical to that of the original aquochromium(III) complex plus 1 mole of nitrous acid. The latter was rapidly oxidised to nitrate ion with hydrogen peroxide[8] to reveal a second $\mathrm{Cr^{III}}$ peak in the spectrum at *ca.* 350—370 nm. Final spectra indicated that these reactions proceed with complete retention of configuration, as is expected since nitrogen–oxygen bond cleavage is known to be involved from tracer studies.[2] Maxima and minima in the spectra of the nitrito-complexes are recorded in Table 1.

TABLE 2

Pseudo-first-order rate constants ($k$) for the acid hydrolysis of nitritochromium(III) complexes [$I$ = 1·0 mol l$^{-1}$ ($\mathrm{NaClO_4}$)]

*trans*-$[\mathrm{Cr(NH_3)_4(ONO)Cl}]^+$

273·7 K

| | | | | | |
|---|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·102 | 0·188 | 0·370 | 0·600 | 0·800 |
| $10^3k$/s$^{-1}$ | 1·06 | 2·37 | 6·45 | 13·6 | 23·2 |

283·1 K

| | | | | | |
|---|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·0511 | 0·102 | 0·201 | 0·301 | 0·400 |
| $10^3k$/s$^{-1}$ | 1·56 | 3·46 | 7·49 | 12·7 | 20·3 |
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·500 | 0·600 | 0·800 | 0·975 | |
| $10^3k$/s$^{-1}$ | 30·0 | 38·3 | 60·6 | 84·7 | |

293·1 K

| | | | | |
|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·010 | 0·0209 | 0·0512 | 0·102 |
| $10^3k$/s$^{-1}$ | 0·939 | 2·05 | 5·20 | 10·7 |
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·200 | 0·300 | 0·400 | 0·500 |
| $10^3k$/s$^{-1}$ | 24·0 | 40·3 | 61·9 | 84·8 |
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·600 | 0·800 | 0·975 | |
| $10^3k$/s$^{-1}$ | 113 | 175 | 246 | |

303·1 K

| | | | | | |
|---|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·050 | 0·100 | 0·200 | 0·300 | 0·400 |
| $10^3k$/s$^{-1}$ | 16·6 | 33·3 | 78·3 | 128 | 185 |
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·500 | 0·600 | 0·800 | 1·00 | |
| $10^3k$/s$^{-1}$ | 241 | 327 | 480 | 708 | |

*cis*-$[\mathrm{Cr(NH_3)_4(ONO)NCS}]^+$

| | | | | |
|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·0965 | 0·386 | 0·675 | 0·965 |
| Temp./K | 273·8 | 273·8 | 273·8 | 273·8 |
| $10^3k$/s$^{-1}$ | 8·40 | 98·0 | 213 | 429 |
| Temp./K | 283·1 | 283·1 | 283·1 | 283·1 |
| $10^3k$/s$^{-1}$ | 20·1 | 173 | 487 | 888 |
| Temp./K | 293·3 | 293·3 | 293·3 | 293·3 |
| $10^3k$/s$^{-1}$ | 49·7 | 412 | 1083 | 1742 |

*cis*-$[\mathrm{Cr(NH_3)_4(H_2O)(ONO)}]^{2+}$ at 283·1 K

| | | | | | |
|---|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·20 | 0·40 | 0·60 | 0·80 | 1·00 |
| $10^3k$/s$^{-1}$ | 17·4 | 44·1 | 80·7 | 129 | 190 |

*cis*-$[\mathrm{(NH_3)_5Cr(OH)Cr(NH_3)_4(ONO)}]^{4+}$ at 283·1 K

| | | | |
|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·10 | 0·50 | 1·00 |
| $10^3k$/s$^{-1}$ | 3·90 | 25·0 | 64·8 |

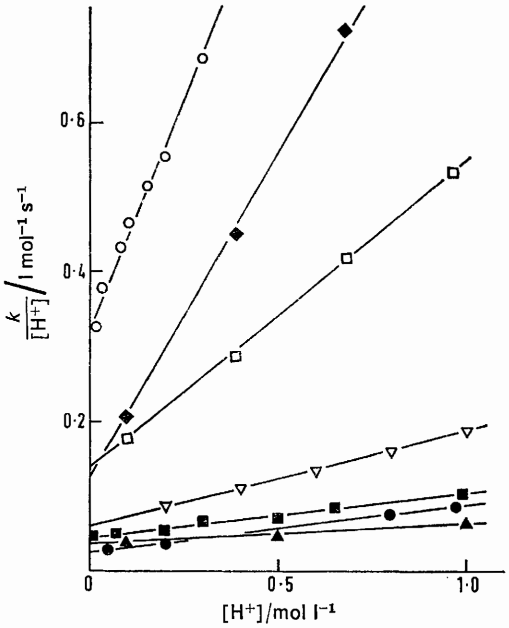
*cis*-$[\mathrm{Cr(en)_2(ONO)NCS}]^+$ at 283·1 K

| | | | | |
|---|---|---|---|---|
| $[\mathrm{H^+}]$/mol l$^{-1}$ | 0·0965 | 0·386 | 0·675 | 0·965 |
| $10^3k$/s$^{-1}$ | 17·3 | 122 | 307 | 537 |

*Kinetic Studies*.—The reactions were studied between 240 and 250 nm by the stopped-flow method under pseudo-first-order conditions with $[\mathrm{H^+}]$ (0·01—1·0 mol l$^{-1}$) in large excess over the complex (*ca.* $5 \times 10^{-5}$ mol l$^{-1}$). A constant ionic strength of 1·0 mol l$^{-1}$ was maintained with $\mathrm{NaClO_4}$. Good first-order rate plots were observed for more than three half-lives in each case. Infinity absorbance readings were occasionally estimated by the method of non-linear least squares.[9] Average values (from 3 to 4 estimations) of the pseudo-first-order rate constants ($k$) are collected in Table 2. It can be seen from equation (1) that when $k_0$ is negligible (6) is applicable. Therefore, a plot of $k/[\mathrm{H^+}]$ against $[\mathrm{H^+}]$ should give a straight line with gradient $k_2'$

$$k = k_1'[\mathrm{H^+}] + k_2'[\mathrm{H^+}]^2 \quad (6)$$

and intercept $k_1'$. Such a plot is shown in the Figure for all the results obtained at 283·1 K. Values of $k_1'$ and $k_2'$ were estimated by a weighted linear least-squares analysis and are collected in Table 3, together with the activation parameters and the results obtained previously.[1-4]



Plots of $k/[\mathrm{H^+}]$ against $[\mathrm{H^+}]$ at 283·1 K and $I$ = 1·0 mol l$^{-1}$ ($\mathrm{NaClO_4}$) for the complexes: (○), $[\mathrm{Cr(H_2O)_5ONO}]^{2+}$; (◆), *cis*-$[\mathrm{Cr(NH_3)_4(ONO)NCS}]^+$; (□), *cis*-$[\mathrm{Cr(en)_2(ONO)NCS}]^+$; (▽), *cis*-$[\mathrm{Cr(en)_2(OH_2)ONO}]^{2+}$; (■), $[\mathrm{Cr(NH_3)_5ONO}]^{2+}$; (●), *trans*-$[\mathrm{Cr(NH_3)_4(ONO)Cl}]^+$; and (▲), *cis*-$[\mathrm{(NH_3)_5Cr(OH)Cr(NH_3)_4ONO}]^{4+}$. Some of the points (○) (ref. 1) and (◆) (Table 2) are off the scale

## DISCUSSION

It is evident from the Figure that equation (6) can be applied to all the complexes investigated and the

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[6] F. Basolo and G. S. Hamaker, *Inorg. Chem.*, 1962, **1**, 1.

[7] W. W. Fee, C. S. Garner, and J. N. MacB. Harrowfield, *Inorg. Chem.*, 1967, **6**, 87.

[8] D. J. Benton and P. Moore, *J. Chem. Soc.* (*A*), 1970, 3179.

[9] P. Moore, *J.C.S. Faraday I*, 1972, **68**, 1890.

mechanism postulated previously[1] [equations (2)—(4)] is assumed to apply in the present cases. Examination of the relative values of $k_1'$ and $k_2'$ in Table 3 also shows why previous workers[2] failed to detect the term involving $[H^+]^2$ in the rate law (1), since their studies of nitritochromium(III) complexes were carried out above pH 0·8. At pH 2, the second term in equation (6) is always negligible compared with the first, although between pH 1 and 2 evidence for the term involving $[H^+]^2$ is apparent, especially for the *cis*-complexes of charge 1+. The rather poor activation parameters reported[2] for the complex *cis*-$[Cr(en)_2(ONO)_2]^+$ could possibly arise from neglect of the second term in equation (6), although this complex {like *cis*-$[Cr(NH_3)_4(ONO)_2]^+$ (ref. 5)} is very unstable and rather difficult to investigate.[2]

In cases where $k_1'$ and $k_2'$ are of comparable magnitude, the mechanistic significance of the term involving $[H^+]^2$ [equation (6)] is debatable since activity effects may be important at the high acidities required to measure $k_2'$ accurately. For example, this is the situation reported for $[M(NH_3)_5ONO]^{2+}$ [M = $Cr^{III}$ (ref. 1) or $Co^{III}$ (ref. 3)] complexes. However, in those cases where $k_2'$ is larger (as shown by the lines of considerable gradient in the Figure), there is no question of activity effects accounting for the non-linear dependence of of $k$ on $[H^+]$, and it seems reasonable, therefore, to apply the proposed mechanism [(2)—(4)] to all the nitrito-complexes investigated so far. A similar conclusion was reached recently[4] following studies of the complex $[Co(NH_3)_5ONO]^{2+}$, where activity effects were reduced to a minimum by using lithium perchlorate instead of sodium perchlorate[3] to adjust the ionic strength.

A comparison of the activation parameters in Table 3 shows that, apart from the results for the complex *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$, the values are all very similar irrespective of the charge or geometry the complex studied. This is good evidence that all these acid-catalysed reactions proceed with a common mechanism involving nitrogen–oxygen bond cleavage,[1] a belief which is confirmed by the tracer studies of previous workers.[2] It is noteworthy that the acid-independent reactions proceed with chromium–oxygen bond cleavage.[2]

The rate data obtained for the complexes *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$ and *cis*-$[Cr(en)_2(ONO)NCS]^+$, whilst showing the same acid dependence as the other nitrito-complexes, are quantitatively different and show an interesting effect when compared with results reported for the closely related complex, *cis*-$[Cr(en)_2(ONO)F]^+$. For example, values for $k_1'$ are more than fifty times greater for the isothiocyanato-complexes than the fluoro-complex of the same charge and geometry, and this is seen to arise from the much smaller value of $\Delta H^\ddagger(k_1')$. The possibility that this effect arises from differences in the site of protonation (ONO in the isothiocyanato-complexes and F in the fluoro-complex) is considered unlikely since nitrite ion is more basic than fluoride ion, and the rate data reported for *cis*-$[Cr(en)_2(ONO)F]^+$ are in line with the other nitritochromium(III) complexes where such an ambiguity does not exist. A more plausible explanation comes from the

TABLE 3

Values of $k_1'$ and $k_2'$ at 283·1 K associated with the rate law (1), and activation parameters at 298·1 K

| Complex | $10^2k_1'$ / l mol$^{-1}$ s$^{-1}$ | $10^2k_2'$ / l$^2$ mol$^{-2}$ s$^{-1}$ | $\Delta H^\ddagger(k_1')$ / kcal mol$^{-1}$ | $\Delta S^\ddagger(k_1')$ / cal K$^{-1}$ mol$^{-1}$ | $\Delta H^\ddagger(k_2')$ / kcal mol$^{-1}$ | $\Delta S^\ddagger(k_2')$ / cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4ONO]^{4+}$ [a] | 3·6 ± 0·2 | 2·9 ± 0·1 | | | | |
| $[Cr(NH_3)_5ONO]^{2+}$ [b] | 4·6 ± 0·3 | 5·9 ± 0·5 | 19·7 ± 0·8 | +5 ± 3 | | |
| $[Co(NH_3)_5ONO]^{2+}$ [c] | 0·021 [c] | 0·028 [c] | 19·6 [c] | −6 [c] | 17·1 [c] | −14 [c] |
| $[Cr(H_2O)_5ONO]^{2+}$ [b] | 32·2 ± 0·7 | 123 ± 1 | 19·8 ± 0·7 | +9 ± 2 | 13·9 ± 0·3 | −9 ± 1 |
| *cis*-$[Cr(NH_3)_4(OH_2)(ONO)]^{2+}$ [a] | 5·9 ± 0·2 | 12·9 ± 0·3 | | | | |
| *cis*-$[Cr(en)_2(OH_2)(ONO)]^{2+}$ [d] | 2·0 | *e* | 20·1 ± 0·3 | +4·9 ± 0·9 | | |
| *trans*-$[Cr(en)_2(OH_2)(ONO]^{2+}$ [d] | 1·5 | *e* | 19·8 ± 0·8 | +3 ± 3 | | |
| *trans*-$[Cr(en)_2(dmf)(ONO)]^{2+}$ [d] | 1·2 | *e* | 20·1 ± 0·5 | +4 ± 2 | | |
| *cis*-$[Cr(NH_3)_4(ONO)NCS]^+$ [a, f] | 12·7 ± 1·6 | 86·1 ± 3·1 | 15·3 ± 0·1 | −8·4 ± 0·2 | 11·9 ± 0·1 | −16·7 ± 0·2 |
| *cis*-$[Cr(en)_2(ONO)NCS]^+$ [a] | 13·7 ± 0·6 | 45·3 ± 1·7 | | | | |
| *cis*-$[Cr(en)_2(ONO)F]^+$ [d] | 0·23 | *e* | 20·9 ± 0·4 | +3 ± 2 | | |
| *cis*-$[Cr(en)_2(ONO)_2]^+$ [d] | 6·6 | *e* | 22 ± 2 | +18 ± 7 | | |
| *trans*-$[Cr(NH_3)_4(ONO)Cl]^+$ [a, g] | 2·59 ± 0·07 | 6·27 ± 0·13 | 20·3 ± 0·3 | +6 ± 1 | 14·7 ± 0·2 | −12 ± 1 |
| *trans*-$[Cr(en)_2(ONO)Cl]^+$ [d] | 0·41 | *e* | 21·0 ± 0·5 | +5 ± 2 | | |
| *trans*-$[Cr(en)_2(ONO)Br]^+$ [d] | 0·56 | *e* | 20·3 ± 0·8 | +3 ± 3 | | |
| *trans*-$[Cr(en)_2(ONO)_2]^+$ [d] | 0·70 | *e* | 24·3 ± 0·7 | +18 ± 3 | | |

en = ethylenediamine; dmf = dimethylformamide.

[a] This work; $I$ = 1·0 mol l$^{-1}$ ($NaClO_4$). [b] Ref. 1; $I$ = 1·0 mol l$^{-1}$ ($NaClO_4$). [c] Estimated from data in ref. 3 at 278·1 K [$I$ = 1·0 mol l$^{-1}$ ($NaClO_4$)] and in ref. 4 at 298·1 K [$I$ = 1·0 mol l$^{-1}$ ($LiClO_4$)]. Values of $k$ in table 3(a) of ref. 3 were corrected for the spontaneous isomerisation (rate constant estimated as 4 × $10^{-6}$ s$^{-1}$ at 278·1 K from data in ref. 4) and then analysed by a weighted least-squares analysis to give values of $k_1'$ [(1·14 ± 0·12) × $10^{-4}$ l mol$^{-1}$ s$^{-1}$] and $k_2'$ [(1·59 ● 0·26) × $10^{-4}$ l$^2$ mol$^{-2}$ s$^{-1}$] at 278·1 K. [d] Extrapolated to 283·1 K from the results in ref. 2; $I$ = 0·15 mol l$^{-1}$ ($NaClO_4$). [e] Not reported. [f] At 273·8 and 293·3 K: $10^2k_1'$ = 4·80 ± 0·19 and 33·6 ± 1·2 l mol$^{-1}$ s$^{-1}$; and $10^2k_2'$ = 40·4 ± 1·2 and 186 ± 9 l$^2$ mol$^{-2}$ s$^{-1}$ respectively. [g] At 273·7, 293·1, and 303·1 K: $10^2k_1'$ = 0·76 ± 0·03, 9·03 ± 014, and 30·5 ± 0·4 l mol$^{-1}$ s$^{-1}$; and $10^2k_2'$ = 2·59 ± 0·06, 16·2 ± 0·3, and 38·9 ± 0·8 l$^2$ mol$^{-2}$ s$^{-1}$ respectively.

observation that complexes of the type *cis*-$[CrL_4(ONO)X]^+$ are particularly unstable when X = Cl or Br (L = $NH_3$, $H_2O$, or $\frac{1}{2}$en).[2,5] The enhanced lability of $X^-$ has been attributed to an intramolecular interaction between X and the neighbouring nitrito-group,[5] and this may lead to a corresponding weakening of the nitrogen–oxygen bond in some cases (*e.g.* when X = NCS but not when X = F). Which group is lost [$X^-$ or $ONO^-$ (as $NO^+$)] will depend to a large degree on the relative strengths of the Cr–X and CrO–N bonds; when X = NCS, the Cr–N bond is strong and it is the CrO–N bond which is broken, whereas when X = Br or Cl the opposite behaviour is observed.

The difference in behaviour of the complexes *cis*-$[CrL_4(ONO)NCS]^+$ and *cis*-$[CrL_4(ONO)F]^+$ almost certainly arises from the relative stabilities of the ON–X bond (X = F or NCS), together with the size and geometries of the interacting ligands.* The bent geometry of the Cr–NCS group favours interaction between the lone-pair of electrons on the nitrogen atom of the thiocyanate ion and the incipient $NO^+$, and furthermore $NO^+$ is known [4,10] to bond strongly to $NCS^-$. Indeed, free thiocyanate ion is a most effective catalyst for the removal of co-ordinated nitrite ion by assisting nitrogen–oxygen bond cleavage.[4] The order of catalytic effectiveness, $NCS^- > I^- > Br^- > Cl^-$ is reported [4] to be in line with the decreasing ON–X bond strength. The lack of catalysis with the complex *cis*-$[Cr(en)_2(ONO)F]^+$ is, therefore, understandable because of the small size of the fluoride ion, and the weak ON–F bond.

## EXPERIMENTAL

All complexes and standard solutions were prepared from AnalaR materials. The complexes *trans*-$[Cr(NH_3)_4(ONO)Cl]ClO_4$ and *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4ONO]Cl_2(ClO_4)_2,H_2O$ were prepared by published methods.[5,11] The latter complex was converted to the perchlorate salt by dissolving in the minimum possible volume of water, followed by the addition of two equivalents of $AgClO_4$ whereupon the precipitated AgCl was removed at the centrifuge, and the required salt was precipitated by the addition of saturated $NaClO_4$ {Found: Cr, 14·1; $NO_2^-$, 5·9; $H_2O$ (by weight loss on drying at 380 K), 2·3. $[(NH_3)_5Cr(OH)Cr(NH_3)_4(ONO)](ClO_4)_4,H_2O$ requires Cr, 14·1; $NO_2^-$, 6·2; $H_2O$, 2·4%}. The *erythro*-complex was assigned a *cis*-configuration in line with the geometry established for the parent aquo-complex.[12] The spectrum recorded in Table 1 was taken immediately after dissolving a sample in water at *ca.* 283 K.

*Preparations*—trans-$[Cr(NH_3)_4(OH_2)(ONO)]Cl_2$. The complex *trans*-$[Cr(NH_3)_4(ONO)_2]ClO_4$ (0·2 g, prepared as described [5]) was dissolved in the minimum volume of ice-cold water and one equivalent of hydrochloric acid (1 mol $l^{-1}$) added dropwise with stirring. After 10 min at 273 K, finely ground $MgCl_2$ was added with stirring until a pale pinkish-orange precipitate deposited. The *product* was recrystallised from ice-cold water using saturated $MgCl_2$, and dried *in vacuo* over silica gel. Yield 50 mg. {Found: Cl, 28·4; Cr, 20·1; N, 27·5; $NO_2^-$, 18·0. $[Cr(NH_3)_4(OH_2)(ONO)]Cl_2$ requires Cl, 27·8; Cr, 20·4; N, 27·5; $NO_2^-$, 18·1%}. The spectrum recorded in Table 1 was taken immediately after dissolving at 273 K in a pH 4 phthalate buffer to reduce the possible formation of hydroxo-species. Even in the dark, the complex decomposes in water by loss of ammonia. Acidification of a freshly prepared solution gave a spectrum identical to that of the complex *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$ plus $HNO_2$ (1 mol).

cis-$[Cr(NH_3)_4(OH_2)(ONO)]Cl_2$. The preparation was identical to that given for the *trans*-isomer, except the initial addition of HCl was not necessary. The complex *cis*-$[Cr(NH_3)_4(ONO)_2]ClO_4$ (0·2 g, prepared as described [5]) was simply allowed to aquate in aqueous solution for *ca.* 15 min before addition of $MgCl_2$ (yield 0·1 g). Analysis of three separate *samples* gave a Cr : $NO_2^-$ ratio of 1·0 : 1.

cis-$[Cr(en)_2(ONO)NCS]ClO_4,H_2O$. This complex was prepared *via* the route *trans*-$[Cr(H_2O)_4Cl_2]Cl,xH_2O \longrightarrow [Cr(en)_3]Cl_3 \longrightarrow$ *cis*-$[Cr(en)_2Cl_2]Cl \longrightarrow$ *cis*-$[Cr(en)_2(OH_2)Cl]Br_2,H_2O \longrightarrow$ *cis*-$[Cr(en)_2(NCS)Cl]Br,H_2O \longrightarrow$ *cis*-$[Cr(en)_2(OH_2)NCS]^{2+} \longrightarrow$ *cis*-$[Cr(en)_2(ONO)NCS]ClO_4,H_2O$. The starting material was ' chromic chloride ' (AnalaR) and the intermediate complexes were obtained by published methods.[13-15] Finely powdered *cis*-$[Cr(en)_2(NCS)Cl]Br,H_2O$ (1 g) was suspended in $HClO_4$ (0·01 mol $l^{-1}$, 10 ml) and the mixture stirred in a thermostat in the dark at 298 K for 17 h. In this time the solid dissolved to give a solution of largely the complex *cis*-$[Cr(en)_2(OH_2)NCS]^{2+}$ (the kinetics and stereochemistry have been established [16]). $NaClO_4$ (5 g) was added and, after dissolution, the mixture was poured on to finely ground $NaNO_2$ (1 g), stirred for 2 min at room temperature, and then cooled on ice in the dark. Orange *crystals* separated and after 1 h these were collected, washed with ethanol (20 ml) then ether (50 ml), and air dried. Yield 0·5 g. The i.r. spectrum (Nujol mull) shows a sharp peak at 2095 $cm^{-1}$ (with signs of splitting into 2 peaks) from the co-ordinated thiocyanate group {Found: C, 16·8; H, 4·60; Cr, 13·2; N, 20·9; S, 7·8; $NO_2^-$, 11·5 ± 0·3. $[Cr(en)_2(ONO)NCS]ClO_4,H_2O$ requires C, 15·3; H, 4·6; Cr, 13·2; N, 21·3; S, 8·1; $NO_2^-$, 11·7%}. The visible spectrum (Table 1) was recorded in aqueous solution at 273 K. A spectrum in dimethylformamide showed the expected fine structure [7] in the nitrito-band at *ca.* 350—370 nm ($\lambda_{max.}$ 487, 379, and 367 nm, with shoulders at *ca.* 390 and 360 nm; $\lambda_{min.}$ at 417 and 343 nm).

cis-$[Cr(NH_3)_4(ONO)NCS]ClO_4$. The starting material was the complex *cis*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ (prepared as

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* A referee has pointed out an alternative explanation, which involves an increased value of $K_1$ for the isothiocyanato-complex arising from a favourable interaction between the added proton and the lone-pair of electrons on the nitrogen atom of the thiocyanate group. However, a similar effect might well have been expected for the fluoro-complex since acid-catalysed loss of fluoride ion is well established (T. P. Jones and K. J. Phillips, *J. Chem. Soc.* (*A*), 1968, 674) whereas acid-catalysed removal of co-ordinated thiocyanate ion has not been observed (N. V. Duffy and J. E. Earley, *J. Amer. Chem. Soc.*, 1967, **89**, 272).

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described [12]). This was partially converted to the complex *cis*-$[Cr(NH_3)_4(OH_2)NCS]^{2+}$ by reaction with aqueous potassium thiocyanate, separated by cation-exchange chromatography, and precipitated as the perchlorate salt (method to be described later) [$\lambda_{max.}$ 494 ($\varepsilon$ 65·7) and 371 nm ($\varepsilon$ 43·3 l mol$^{-1}$ cm$^{-1}$); $\lambda_{min.}$ 422 nm ($\varepsilon$ 13·1 l mol$^{-1}$ cm$^{-1}$) in $HClO_4$ (0·1 mol l$^{-1}$)]. The complex *cis*-$[Cr(NH_3)_4(OH_2)NCS](ClO_4)_2$ (0·125 g) was treated with perchloric acid (0·3 mol l$^{-1}$, 2 ml) and the resulting slurry poured on to finely ground sodium nitrite (0·41 g). The mixture was stirred at room temperature for 1 min, filtered, and the residue washed with perchloric acid (0·3 mol l$^{-1}$, 2 × 0·2 ml). The combined filtrates and washings were poured on to sodium perchlorate monohydrate (2 g) and cooled in ice in the dark for 30 min. Filtration, washing with ice-cold absolute ethanol (4 × 1 ml) then ether (5 × 1 ml), air drying and finally drying *in vacuo* over $P_4O_{10}$ at room temperature gave the salmon-pink product (0·037 g, 36%) {Found: C, 3·8; H, 3·6; Cr, 16·2; N, 25·8; $NO_2^-$, 14·3; S, 9·8. $[Cr(NH_3)_4(ONO)NCS](ClO_4)$ requires C, 3·7; H, 3·7; Cr, 16·1; N, 26·0; $NO_2^-$, 14·2; S, 9·9%}. Treatment of an aqueous solution of the complex with perchloric acid gave 100% *cis*-$[Cr(NH_3)_4(OH_2)NCS]^{2+}$.

TABLE 4

I.r. spectra (cm$^{-1}$) of some nitritochromium(III) complexes [a]

| Complex | $\nu(NH_3)$ | $\delta_d(NH_3)$ | $\nu_{as}(ONO)$ | $\delta_s(NH_3)$ | $\nu_s(ONO)$ | $\delta(ONO)$ | $\rho_r(NH_3)$ | $\nu(M-N)$ | $\nu(Cr-O)$ |
|---|---|---|---|---|---|---|---|---|---|
| *cis*-$[Cr(NH_3)_4(OH_2)(ONO)]Cl_2$ | 3290s | 1610m | 1475m | 1300s | 1030s | 835m | 765s | 475w | 355m |
| | 3150s | | | | | | | | |
| *trans*-$[Cr(NH_3)_4(OH_2)(ONO)]Cl_2$ | 3295s | 1610m | 1480s | 1300s | 1030s | 845m | 750s | 485m | 365m |
| | 3150s | | | | | | | 465m | |
| | | | | | | | | 445m | |
| *cis*$[Cr(NH_3)_4(ONO)NCS]ClO_4$ [c] | 3325s | 1613m | 1455m | 1303s | | 844m [b] | 744s | 480w | 350w |
| | 3255s | | | 1326(sh) | | | | 445w | |
| *cis*-$[Cr(en)_2(ONO)NCS]ClO_4,H_2O$ | [ν(CN) | 2095s] | | | | 828m [b] | | 546m | |
| | | | | | | | | 491m | 380m |
| | | | | | | | | 439m | 345w |
| | | | | | | | | 417m | |

[a] I.r. spectra of other nitritochromium(III) complexes studied are given in ref. 5. [b] Weaker peaks due to $\nu_s(C-S)$ were observed between 840 and 850 cm$^{-1}$ in the complexes *cis*-$[Cr(NH_3)_4(NCS)_2]^+$ and *cis*-$[Cr(NH_3)_4(OH_2)NCS]^{2+}$. [c] ν(CN) at 2105s cm$^{-1}$. This spectrum recorded with a Perkin-Elmer 621 spectrometer.

*Spectra, Kinetic Studies, and Analyses.*—Procedures described previously were used.[1] I.r. spectra (KBr disc) are recorded in Table 4.

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