Structural and Mechanistic Studies of Co-ordination Compounds. Part V.[1] The Preparation, Aquation, and Base Hydrolysis of Octahedral Cobalt(III)-Amine Complexes Containing Isothiocyanate as an Orienting Ligand

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The preparation and characterization of *trans*-$[Co(NH_3)_4(NCS)Cl]^+$ cation is described. The kinetics of the aquation and base hydrolysis of this complex cation and those of *trans*-$[Co(cyclam)(NCS)Cl]^+$ have been studied over a range of temperature. These results are discussed in terms of the influence of nephelauxetic effects of these amine ligands on the central cobalt(III) ion.

THE substitution of *trans*-$[Co(cyclam)Cl_2]^+$, where cyclam represents 1,4,8,11-tetra-azacyclotetradecane, by thiocyanate in aqueous acidic solution was described by Poon and Tobe.[2] In the presence of an excess of competing chloride ion, the kinetics were interpreted in terms of reactions (1) and (2) with the second step (k_2)

$$\textit{trans}\text{-}[Co(cyclam)Cl_2]^+ + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}[Co(cyclam)(NCS)Cl]^+ + Cl^- \quad (1)$$

$$\textit{trans}\text{-}[Co(cyclam)(NCS)Cl]^+ + NCS^- \xrightarrow{k_2} \textit{trans}\text{-}[Co(cyclam)(NCS)_2]^+ + Cl^- \quad (2)$$

sufficiently slow for the first almost to reach a pseudo-equilibrium. This implied that *trans*-$[Co(cyclam)(NCS)Cl]^+$ lost its thiocyanate more readily than its chloride. This interpretation was surprising in view of the known[3] behaviour of the analogous *cis*- and *trans*-$[Co(en)_2(NCS)Cl]^+$ where en represents ethylenediamine. In order to examine the role played by the co-ordinated thiocyanate in the cyclam complex it is desirable to study the aquation of an authentic sample of *trans*-$[Co(cyclam)(NCS)Cl]^+$. The studies of these reactions and those of the corresponding *trans*-$[Co(NH_3)_4(NCS)Cl]^+$ would also be desirable in substantiating the suggested influence of a nephelauxetic effect on the thermodynamic and kinetic behaviour of octahedral cobalt(III)-amine complexes.[4,5]

EXPERIMENTAL

Preparation of the Complexes.—*trans*-Chloroisothiocyanato-(1,4,8,11-tetra-azacyclotetradecane)cobalt(III) perchlorate was prepared by the method of Bosnich, Poon, and Tobe[6] and was recrystallized four times by adding an excess of concentrated sodium perchlorate solution to a clear saturated solution of the complex. The *crystals* were filtered off, washed with a small amount of cold water, then with alcohol and ether, and were air-dried [Found: C, 29·1; H, 5·55; N, 15·4; S, 7·3; co-ordinated Cl, 7·9. $Co(C_{10}H_{24}N_4)(NCS)Cl(ClO_4)$ requires C, 29·2; H, 5·3; N, 15·5; S, 7·1; co-ordinated Cl, 7·84%].

trans-*Chloroisothiocyanatotetra-amminecobalt*(III) *perchlorate.*—*trans*-$[Co(NH_3)_4Cl_2]NCS$ (10 g), prepared by the rapid addition of a cold saturated solution of *trans*-$[Co(NH_3)_4Cl_2]Cl$[7] to an ice-cold saturated solution of potassium thiocyanate, was suspended in dimethyl sulphoxide (100 ml) at room temperature for 24 h. The solid was slowly dissolved and the solution gradually changed from green to dark purple. After the undissolved dichloro-complex was filtered off, the volume of the solution was reduced under vacuum at room temperature until bluish crystals of *trans*-$[Co(NH_3)_4(NCS)Cl]Cl$ appeared. The crystals were filtered off, and washed with an excess of 95% ethanol until the washing was colourless. They were then washed with ether and were air-dried (yield: 10%). The perchlorate was prepared by adding dropwise a saturated solution of sodium perchlorate to a saturated solution of the chloride. The solution was cooled in an ice-bath and dark purple crystals began to separate. These were filtered off and washed with alcohol and ether. The *compound* was recrystallized at least ten times by repeatedly adding sodium perchlorate solution to the complex solution (yield: 60% per recrystallization) [Found: C, 3·85; H, 3·75; N, 22·1; Cl, 22·3. $Co(NH_3)_4(NCS)(Cl)(ClO_4)$ requires C, 3·75; H, 3·75; N, 21·9; Cl, 22·2%].

Kinetics.—The aquation of *trans*-$[Co(cyclam)(NCS)Cl]ClO_4$ was followed by sampling the reaction solution, made up at room temperature, into different Pyrex tubes which were sealed and placed 'simultaneously' in a thermostat. After thermal equilibrium had been attained (about 20 min), tubes were withdrawn at intervals and quickly cooled in an ice-bath. The solutions were then warmed to room temperature and the absorbances at 556 nm were measured with a Unicam SP 700 spectrophotometer. For the faster aquation of *trans*-$[Co(NH_3)_4(NCS)Cl]ClO_4$ the reaction was started by dissolving a known weight of the complex in a given volume of the appropriate solvent which had previously been brought to the reaction temperature. The solution was immediately transferred to a silica cell in the temperature-controlled cell holder of a Unicam SP 800 recording spectrophotometer and the reaction was followed *in situ* by repeatedly scanning the full spectrum over the 700—400 nm range at regular intervals. The base hydrolysis of *trans*-$[Co(cyclam)(NCS)Cl]ClO_4$ and *trans*-$[Co(NH_3)_4(NCS)Cl]ClO_4$ was studied spectrophotometrically *in situ* by following the changing absorbance with time at a constant wavelength (590 and 570 nm respectively) with a Unicam SP 700 spectrophotometer.

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[1] Part IV, C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216.

[2] C. K. Poon and M. L. Tobe, *Co-ordination Chem. Rev.*, 1966, **1**, 81.

[3] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691.

[4] C. K. Poon, *J. Amer. Chem. Soc.*, 1970, **92**, 4467.

[5] C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.

[6] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.

[7] S. M. Jörgensen, *Z. anorg. Chem.*, 1897, **14**, 404; 'Handbook of Preparative Inorganic Chemistry,' vol. 2, 2nd edn., ed. G. Brauer, Academic Press, New York, 1965, p. 1537.

Physical Measurements.—The visible and u.v. absorption spectra of freshly prepared solutions were measured on either a Unicam SP 700 or SP 800 spectrophotometer as convenient. I.r. spectra of Nujol mulls between KBr windows were measured with a Perkin-Elmer 337 spectrophotometer. ^1H N.m.r. spectra of freshly prepared $[^2H_6]$-dimethyl sulphoxide solutions were measured with a 60 MHz Perkin-Elmer R-20 spectrometer. The pH of buffer solutions was measured with a Radiometer pH meter type RHM 26.

RESULTS

The behaviour of *trans*-[Co(cyclam)(NCS)Cl]ClO$_4$ in 0·01M-perchloric acid was very similar to that of other complexes of the same type, *trans*-[Co(cyclam)(L)Cl]$^+$ where L = Cl$^-$,[6] NO$_2^-$,[8] and CN$^-$.[8] The visible absorption spectrum slowly changed with time with the absorption peak moving very slightly towards a shorter wavelength with increasing absorbance, while an isosbestic point was maintained at 604 nm throughout the reaction. The initial spectrum was identical with that of the starting chloroisothiocyanato-complex. Addition of an excess of chloride forced the reaction to re-trace its own path. It can, therefore, be concluded that *trans*-[Co(cyclam)(NCS)Cl]$^+$ aquates reversibly with complete retention of configuration to an equilibrium mixture according to equation (3).

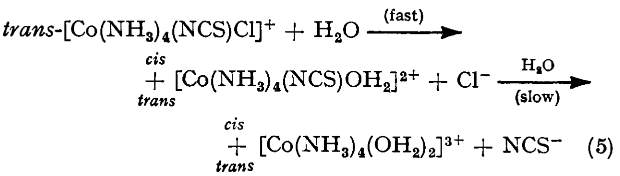
$$trans\text{-}[\mathrm{Co(cyclam)(NCS)Cl}]^+ + \mathrm{H_2O} \rightleftharpoons trans\text{-}[\mathrm{Co(cyclam)(NCS)OH_2}]^{2+} + \mathrm{Cl}^- \quad (3)$$

The known[6] visible spectrum of *trans*-[Co(cyclam)(Cl)OH$_2$]$^{2+}$ predicts that the release of the isothiocyanate group in the forward reaction would have shifted the absorption peak to a longer wavelength with decreasing intensity. The reaction was followed spectrophotometrically at 556 nm and the first-order rate constants k were obtained from the slopes of standard plots for an opposed first- and second-order reaction according to expression (4)[9a] where a

$$2{\cdot}303 \log \frac{aX_e + X(a - X_e)}{a(X_e - X)} = k\,\frac{2a - X_e}{X_e}\,t \quad (4)$$

represents the initial concentration of the chloro-complex and X and X_e represent the concentration of the aquo-complex at time t and at equilibrium respectively. X And X_e were determined from the changing absorbance and the molar absorptivities of *trans*-[Co(cyclam)(NCS)Cl]$^+$ and *trans*-[Co(cyclam)(NCS)OH$_2$]$^{2+}$ at 556 nm (118·0 and 153·4 l mol^{-1} cm^{-1} respectively). Although any attempt to isolate *trans*-[Co(cyclam)(NCS)OH$_2$]$^{2+}$ in pure crystalline form has been unsuccessful, this complex cation has been adequately characterized in solution and its visible spectrum has been accurately determined by an indirect approach.[8]

When *trans*-[Co(NH$_3$)$_4$(NCS)Cl]ClO$_4$ was dissolved in 0·50M-nitric acid, the absorption peak of the visible spectrum slowly moved from 571 to 515 nm with isosbestic points maintained at 544 and 438 nm for the first two half-lives of the reaction. The intensity of the entire spectrum then began to decrease at a much slower rate with a new peak finally developed at 500 nm, the intensity of which was only about 1/6 of that of the initial spectrum. This observation is consistent with the reaction scheme (5).



$$trans\text{-}[\mathrm{Co(NH_3)_4(NCS)Cl}]^+ + \mathrm{H_2O} \xrightarrow{\text{(fast)}} \underset{trans}{\overset{cis}{+}} [\mathrm{Co(NH_3)_4(NCS)OH_2}]^{2+} + \mathrm{Cl}^- \xrightarrow[\text{(slow)}]{\mathrm{H_2O}} \underset{trans}{\overset{cis}{+}} [\mathrm{Co(NH_3)_4(OH_2)_2}]^{3+} + \mathrm{NCS}^- \quad (5)$$

It is not possible to determine the steric course of the first aquation step because we have not been able to prepare the pure *cis*- and *trans*-[Co(NH$_3$)$_4$(NCS)OH$_2$]$^{2+}$ cations or to measure their visible absorption spectra indirectly. Since the electronic spectra of tetra-amminecobalt(III) complexes are expected to be very similar to those of the corresponding bisethylenediamine and cyclam analogues, a knowledge of the visible spectra of *cis*- and *trans*-[Co(en)$_2$(NCS)OH$_2$]$^{2+}$ [3] (with absorption peaks at 490 and 538 nm respectively) enabled us to conclude that the aquation of *trans*-[Co(NH$_3$)$_4$(NCS)Cl]$^+$ is probably accompanied by stereochemical change. The studies of the aquation were complicated by the participation of the second step at the later stage of the reaction. The reaction was followed spectrophotometrically by repeatedly scanning the entire visible spectrum at regular intervals until the spectrum began to deviate from the isosbestic points. The first-order aquation rate constant was obtained by Guggenheim's treatment[9b] of the changing absorbance at 600 nm. Good linear plots were obtained. At this wavelength the change of absorbance for the first step is conveniently large while the subsequent change corresponding to the second step is much smaller than that at other wavelengths between the two isosbestic points where the absorption peaks of the reaction products occur. The rate constants so determined, which correspond to the rate of disappearance of *trans*-[Co(NH$_3$)$_4$(NCS)Cl]$^+$, agreed well with those determined by following the amount of ionic chloride released by Volhard's method with use of the calculated infinity for the complete release of the co-ordinated chloride. These data are in Table 1.

TABLE 1

First-order rate constants for the aquation of *trans*-[Co(am)$_4$(NCS)Cl]ClO$_4$

(am)$_4$	t/°C	10^5k [a]/s^{-1}
(NH$_3$)$_4$ [b]	40·4	3·15 ± 0·08
(NH$_3$)$_4$ [b]	40·4	3·04 [c]
(NH$_3$)$_4$ [b]	50·9	13·0 ± 1·0
(NH$_3$)$_4$ [b]	61·15	44·8 ± 1·6
(NH$_3$)$_4$ [b]	71·7	149·0 ± 5·0
(cyclam) [d]	82·5	3·40 ± 0·06
(cyclam) [d]	86·0	4·78 ± 0·10
(cyclam) [d]	90·0	7·03 ± 0·10
(cyclam) [d]	94·5	10·9 ± 0·80

[a] An average of 2 determinations. [b] In 0·5M-nitric acid. [c] By titrimetric method. [d] In 0·01M-nitric acid.

The base hydrolysis of *trans*-[Co(cyclam)(NCS)Cl]ClO$_4$ was most conveniently studied in the pH 7·0—8·0 range (γ-collidine–nitric acid buffer system). A study of the changing visible spectrum showed that isosbestic points were maintained at 536 and 448 nm throughout the entire reaction. The initial spectrum was identical to that of the starting compound while the spectrum of the acidified final solution was virtually the same as that of *trans*-[Co(cyclam)(NCS)OH$_2$]$^{2+}$. It can be concluded that the base hydrolysis of *trans*-[Co(cyclam)(NCS)Cl]$^+$ is complete and stereoretentive. The reaction was followed *in situ* at

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[8] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

[9] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961, (*a*) p. 186, (*b*) p. 49.

590 nm and the pH of the solution was measured at the same reaction temperature. The hydroxide-ion concentration was obtained from the appropriate value of the ionic product of water at the same temperature.[10] The pseudo-first-order rate constants and hence the second-order rate constants were obtained from standard plots described previously.[1] The base hydrolysis of the same complex ion was also followed in another buffer system (borax–boric acid) in order to check the effect of different buffers on the rate constants. The base hydrolysis of *trans*-$[Co(NH_3)_4(NCS)Cl]ClO_4$ was similarly studied at 570 nm in the pH 10·5—12·0 range (2,6-dimethylpiperidine–nitric acid). Isosbestic points were maintained at 543 and 418 nm. These data are in Table 2.

TABLE 2

Second-order rate constants for the base hydrolysis of *trans*-$[Co(am)_4(NCS)Cl]ClO_4$ in buffer solutions

$(am)_4$	t/°C	k[a]/l mol^{-1} s^{-1}
$(NH_3)_4$[b]	11·1	0·426 ± 0·025
$(NH_3)_4$[b]	17·6	1·43 ± 0·06
$(NH_3)_4$[b]	26·2	6·32 ± 0·27
(cyclam)[c]	22·0	(0·618 ± 0·005) × 10^3
(cyclam)[c]	29·5	(1·50 ± 0·03) × 10^3
(cyclam)[c]	38·1	(4·18 ± 0·13 × 10^3
(cyclam)[d]	22·0	(0·507 ± 0·02) × 10^3
(cyclam)[d]	31·0	(1·52 ± 0·03) × 10^3

[a] From 6 different runs over a span of 0·8 pH unit. [b] In 2,6-dimethylpiperidine–nitric acid buffer solutions and at μ = 0·21M. [c] In γ-collidine–nitric acid buffer solutions and at μ = 0·25M. [d] In borax–boric acid buffer solutions and at μ = 0·25M.

DISCUSSION

The assignment of a *trans*-configuration to the new tetra-ammine complex was made on the basis that only one NH_3 resonance peak was observed in the n.m.r. spectrum of the $[^2H_6]$dimethyl sulphoxide solution of the complex at 1·01 p.p.m. downfield of the dimethyl sulphoxide peak. That the thiocyanate ligand is *N*-bonded was shown by the absence of any peak assignable to the *S*-bonded ν(C–S) in the 680—750 cm^{-1} region in the i.r. spectrum of the complex.[11] On the other hand, bands characteristic of *N*-bonded ν(C–S) and ν(C–N) are present at 850 and 2160 cm^{-1} respectively.

It is clear in the present study that the *N*-bonded *trans*-$[Co(cyclam)(NCS)Cl]^+$, like the corresponding bisethylenediamine and tetra-ammine analogues, loses its chloride much more readily than the thiocyanate. This observation implied either that Poon and Tobe's interpretation [2] of the kinetics of the substitution of *trans*-$[Co(cyclam)Cl_2]^+$ by thiocyanate was incorrect or that the first substituted product was not the *N*-bonded *trans*-$[Co(cyclam)(NCS)Cl]^+$. Closer re-examination of the substitution suggested that the reaction was more complicated than that formulated previously and that the *S*-bonded *trans*-$[Co(cyclam)(SCN)Cl]^+$ could well be the first reaction product.[12] This problem is at present under investigation.

It has been discussed in great detail [4,5] that for a given pair of unidentate ligands L and X of complexes of the type *trans*-$[Co(am)_4(L)X]^{n+}$, the difference in the thermodynamic and kinetic properties for $(am)_4$ = cyclam, $(en)_2$, and $(NH_3)_4$ is governed, among other factors, mainly by the nephelauxetic effect of these amine ligands on the central cobalt(III) ion. Thermodynamically, the relative stability of a lower-charged complex to a higher-charged complex is expected to decrease along the above series of $(am)_4$. Kinetically, the aquation rate constants of analogous complexes would increase but the base hydrolysis rate constants decrease along the same series. In the present investigation the influence of the thermodynamic nephelauxetic effect on the extent of aquation of *trans*-$[Co(am)_4(NCS)Cl]^+$ is prominent. The cyclam complex aquates to *ca.* 35% at equilibrium at 82·5 °C; the aquation of the bisethylenediamine complex is virtually complete but further reaction is not noticeable; for the tetra-ammine complex, not only is the release of the chloride complete, but the release of the co-ordinated thiocyanate also occurs to a great extent giving a mixture of *cis*- and *trans*-$[Co(NH_3)_4(OH_2)_2]^{3+}$.

TABLE 3

First-order rate constants at 25 °C and activation parameters for the aquation of *trans*-$[Co(am)_4(NCS)Cl]^+$

$(am)_4$	k/s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal mol^{-1} K^{-1}
$(NH_3)_4$[a]	3·6 × 10^{-6}	25·7	3
$(en)_2$[b]	4·6 × 10^{-8}	30·2	9
(cyclam)[a]	3·2 × 10^{-8}	24·2	−11

[a] This work. [b] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691; M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.

Some of the rate constants and activation parameters are collected in Tables 3 and 4. The slower aquation rate constant of the tetra-ammine complex than the $(en)_2$ and cyclam analogues is in keeping with the prediction made on the basis of the kinetic nephelauxetic effect. This effect also appears to be operative in the base hydrolysis of these complexes. On the other hand, the aquation rate of the cyclam complex is quite similar to that of the $(en)_2$ complex. This seems to indicate that the kinetic nephelauxetic effect is not a dominating factor here to differentiate between the lability of these two complexes. This similarity in rate, however, is a

TABLE 4

Second-order rate constants at 0 °C and activation parameters for the base hydrolysis of *trans*-$[Co(am)_4(NCS)Cl]^+$

$(am)_4$	k l mol^{-1} s^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$ cal mol^{-1} K^{-1}
$(NH_3)_4$[a]	4·8 × 10^{-2}	29·6	44
$(en)_2$[b]	3·5 × 10^{-1}	23	27
(cyclam)[c]	3·2 × 10	21·1	25
(cyclam)[d]	2·6 × 10	21·1	24

[a] This work, in 2,6-dimethylpiperidine–nitric acid buffer solutions. [b] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377. [c] This work, in γ-collidine–nitric acid buffer solutions. [d] This work, in borax–boric acid buffer solutions.

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[10] 'Handbook of Chemistry and Physics,' 48th edn., ed. R. C. Weast, Chemical Rubber Co., Ohio, 1968, D-92.

[11] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley, New York, 1970, p. 187.

[12] W. K. Lee, unpublished result.

fortuitous compensation of the large difference in the activation energies by the difference in entropies of activation working in the opposite direction. The reason for the exceptionally high activation energy of the aquation of *trans*-[Co(en)$_2$(NCS)Cl]$^+$ as compared with those of other conventional Co^{III}–amine complexes[13] remains a mystery.

The acid hydrolysis of *trans*-[Co(en)$_2$(NO$_2$)Cl]$^+$ is affected by the nature of buffers.[14] The base hydrolysis of *trans*-[Co(cyclam)(NCS)Cl]$^+$ was studied here in two buffer systems. Table 4 shows that although the rate constants do depend slightly on the nature of the buffers the activation energies are equal within experimental error. In other words, the variation of the rate constants with temperature is the same in both buffer systems. This seems to indicate that the rate constants derived from buffer solutions are useful for comparison so long as the comparison is made on the gross difference in order of magnitude rather than on the exact magnitude of these numbers.

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[13] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965, p. 73.

[14] S. C. Chan and C. W. Fung, *J. Inorg. Nuclear Chem.*, 1971, **33**, 569.