Structural and Mechanistic Studies of Co-ordination Compounds. Part VI.[1] Preparation, Aquation, and Base Hydrolysis of Some Octahedral *trans*-Chlorocyanocobalt(III) Amine Complexes

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The preparation of the complex *trans*-$[Co(NH_3)_4(CN)Cl]^+$ is described. The kinetics of aquation and base hydrolysis of this complex and the base hydrolysis of the complex *trans*-$[Co(cyclam)(CN)Cl]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) have been studied over a range of temperature, and the following parameters have been obtained: *trans*-$[Co(NH_3)_4(CN)Cl]^+$, k_{OH_2} (at 25 °C) = $9{\cdot}8 \times 10^{-4}$ s^{-1}, $\Delta H_{OH_2}^{\ddagger} = 20{\cdot}7$ kcal mol^{-1}, $\Delta S_{OH_2}^{\ddagger} = -3$ cal K^{-1} mol^{-1}, and k_{OH} (at 0 °C) = $3{\cdot}5 \times 10^{-2}$ l mol^{-1} s^{-1}, $\Delta H_{OH}^{\ddagger} = 23{\cdot}8$ kcal mol^{-1}, $\Delta S_{OH}^{\ddagger} = 22$ cal K^{-1} mol^{-1}; *trans*-$[Co(cyclam)(CN)Cl]^+$, k_{OH} (at 0 °C) = $8{\cdot}1 \times 10^{-1}$ l mol^{-1} s^{-1}, $\Delta H_{OH}^{\ddagger} = 22{\cdot}6$ kcal mol^{-1}, $\Delta S_{OH}^{\ddagger} = 24$ cal K^{-1} mol^{-1}. Thermodynamically, it was found that the extent of aquation of complexes of the type *trans*-$[Co(amine)_4(CN)Cl]^+$ increases in the order cyclam < $(en)_2$ < $(NH_3)_4$ (en = ethylenediamine). Kinetically, the aquation rate constants of these complexes increase, but the base-hydrolysis rate constants decrease in the above order. The results support the proposed nephelauxetic effects which these amine ligands exert on the central cobalt(III) ion. Spectroscopic evidence is produced to support the above conclusion.

THE influence of the nephelauxetic effects of some closely related saturated amine ligands on the thermodynamic and kinetic stability of octahedral cobalt(III) amine complexes has been discussed previously.[2-4] It was predicted that, for a given pair of unidentate ligands L and X (L denotes an orienting ligand and X a leaving group) of complexes of the type *trans*-$[Co(amine)_4LX]^{n+}$ [amine = NH_3, $\frac{1}{2}$en (en = ethylenediamine), or $\frac{1}{4}$cyclam (cyclam = 1,4,8,11-tetra-azacyclotetradecane)], the aquation rate constants would decrease along the above series in the order $(NH_3)_4 < (en)_2 <$ cyclam. On the other hand, the base-hydrolysis rate constants would be expected to vary in the opposite direction. In an earlier paper[5] we reported that the aquation rate constant of the complex *trans*-$[Co(cyclam)(CN)Cl]^+$ was indeed slower than that of the bis(ethylenediamine) analogue by a factor of $1{\cdot}7 \times 10^2$ at 25 °C. However, the corresponding rate constant of the tetra-ammine analogue was not available for comparison. This paper describes the preparation, aquation, and base hydrolysis of the complex *trans*-$[Co(NH_3)_4(CN)Cl]^+$ and the base hydrolysis of the complex *trans*-$[Co(cyclam)(CN)Cl]^+$.

EXPERIMENTAL

Preparations.— trans-*Chlorocyano*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *nitrate*, $[Co(cyclam)(CN)Cl]NO_3$. This complex was prepared by the published method,[5] except that the *trans*-$[Co(cyclam)(SO_3)Cl]$ intermediate was prepared by a modified method which increased the yield to 90%. Here, the chlorosulphito-complex was prepared by stirring an equivalent amount of finely powdered sodium sulphite into a saturated solution of the complex *trans*-$[Co(cyclam)Cl_2]Cl$[6] in methanol until all the solid had dissolved and the solution became red in colour. Addition of an excess of light petroleum to the filtered solution precipitated the desired product.

trans-*Tetra-amminechlorocyanocobalt*(III) *chloride*. Concentrated hydrochloric acid (40 cm^3) was added dropwise with stirring to a filtered concentrated solution of the complex *trans*-$[Co(NH_3)_4(CN)OH]Cl$[7] (1·0 g, 4·8 mmol) in glacial acetic acid (200 cm^3). Fine crystals of the complex *trans*-$[Co(NH_3)_4(CN)Cl]Cl$ began to form. After allowing the fine crystals to settle at the bottom of the solution, the supernatant liquid was decanted off. The yellow crystalline *product* was filtered off, washed with methanol, acetone, and light petroleum, and air-dried (yield 0·4 g) {Found: C, 5·15; H, 5·4; Cl, 31·9; N, 29·6. $[Co(NH_3)_4(CN)Cl]Cl$ requires C, 5·35; H, 5·35; Cl, 31·7; N, 31·2%}. Attempts to recrystallize the complex from aqueous solution only resulted in the formation of the aquocyano-complex. On the other hand, the complex was not sufficiently soluble in most organic solvents to permit recrystallization. Attempts to prepare a different salt of the complex have also been unsuccessful.

Kinetics.—The aquation of the complex *trans*-$[Co(NH_3)_4(CN)Cl]Cl$ in 0·1M-nitric acid was followed spectrophotometrically *in situ* at 480 nm using a Unicam SP 700 recording spectrophotometer, which was equipped with an absorbance scale-expansion accessory and an external recorder of the type Unicam AR 25. The reaction was initiated by addition of the finely ground complex to the solvent in a silica optical cell, which had been previously brought to reaction temperature in the thermostatted cell holder of the spectrophotometer, and the resulting solution stirred rapidly to dissolve the complex. The entire process between addition of the complex to the solvent and commencement of measurements took *ca.* 6 s. A blank experiment showed that the dissolving and stirring process only very slightly altered the solution temperature at the beginning of the reaction, which rapidly (*ca.* 4 s) reverted to the run temperature. The latter was maintained to within ±0·1 °C by circulating water from a thermostat bath through the cell holder. The base hydrolysis of both complex cations was similarly studied in thermostatted buffer solutions. The pH of the solutions at the reaction temperature was measured, as described elsewhere,[8] using a set of Radiometer microelectrodes of the types K4112 (calomel) and G222C (glass).

Visible and u.v. electronic absorption spectra were measured on either a Unicam SP 700 or 8000 spectrophotometer. The pH of buffer solutions was measured with a Radiometer pH meter type PHM26.

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[4] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

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

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[7] I. B. Baranovskii and A. V. Babaeva, *Russ. J. Inorg. Chem.*, 1964, **9**, 1168.

[8] W. K. Lee and C. K. Poon, *Inorg. Chem.*, in the press.

RESULTS

When the complex *trans*-$[Co(NH_3)_4(CN)Cl]Cl$ was dissolved in 0·1M-nitric acid, its visible absorption spectrum slowly changed with time. Both ligand-field bands were slightly blue-shifted with a slight decrease in intensity and with isosbestic points maintained at 331, 388, and 448 nm for the entire reaction. The initial spectrum was identical with that of the *trans*-chlorocyano-complex and the final spectrum was indistinguishable from that of an authentic sample of the complex *trans*-$[Co(NH_3)_4(CN)OH_2]^{2+}$. Titration of the amount of ionic chloride at the end of the reaction indicated that the release of the co-ordinated chloride was complete. It can, therefore, be concluded that the aquation of the *trans*-$[Co(NH_3)_4(CN)Cl]^+$ complex is complete and stereoretentive.

The aquation reaction was followed spectrophotometrically at 480 nm, where the difference in absorbance between the initial and final visible spectra was greatest. First-order rate constants, which were independent of the small amount of ionic chloride present (0·01M), were obtained from gradients of plots of log $(A_t - A_\infty)$ against time, where A_t and A_∞ are respectively the absorbances at time t and after 10 half-lives. These plots were linear to three half-lives. Data determined at three different temperatures are collected in Table 1.

TABLE 1

First-order aquation rate constants of the complexes *trans*-$[Co(amine)_4(CN)Cl]^+$

(Amine)$_4$	Temp./°C	k_1/s^{-1}
$(NH_3)_4$	23·9	$(8{\cdot}59 \pm 0{\cdot}10) \times 10^{-4}$ [a]
$(NH_3)_4$	40·8	$(6{\cdot}13 \pm 0{\cdot}10) \times 10^{-3}$ [a]
$(NH_3)_4$	52·7	$(2{\cdot}08 \pm 0{\cdot}04) \times 10^{-2}$ [a]
$(NH_3)_4$	25·0	$9{\cdot}8 \times 10^{-4}$ [b]
$(en)_2$	25·0	$8{\cdot}2 \times 10^{-5}$ [c]
(cyclam)	25·0	$4{\cdot}8 \times 10^{-7}$ [d]

[a] This work; each entry represents an average of three different determinations in 0·1M-nitric acid. [b] Obtained by extrapolation; $\Delta H^\ddagger = 20{\cdot}7$ kcal mol^{-1} and $\Delta S^\ddagger = -3$ cal K^{-1} mol^{-1}. [c] In neutral aqueous solution; S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514. [d] In 0·01M-nitric acid; K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

The base hydrolysis of the complex *trans*-$[Co(NH_3)_4(CN)Cl]Cl$ was most conveniently studied in 2,6-dimethylpiperidine–nitric acid buffer solutions (pH 10·3—11·7). The visible spectrum slowly increased in absorbance without establishing any isosbestic point. The initial spectrum was identical with that of the starting complex. When the final solution was acidified with an excess of nitric acid and the visible spectrum was immediately measured, it was found that the spectrum was very similar to that of the complex *trans*-$[Co(NH_3)_4(CN)OH_2]^{2+}$. It can be concluded that the base hydrolysis of the *trans*-$[Co(NH_3)_4(CN)Cl]^+$ complex is complete and virtually stereoretentive.

The base-hydrolysis reaction was followed at 350 nm and observed pseudo-first-order rate constants, k_{obs}, were obtained from standard semilogarithmic plots. The hydroxide-ion concentration in each of the runs was obtained by measuring the pH of the reaction solution at the reaction temperature in the manner described elsewhere.[8] Second-order rate constants were obtained from gradients of linear plots of k_{obs} against hydroxide-ion concentration. The base hydrolysis of the complex *trans*-$[Co(cyclam)(CN)Cl]^+$ was similarly studied at 465 nm in the same buffer system. Here, the changing visible spectrum showed isosbestic points at 335, 357, and 564 nm. The spectrum of the acidified final solution was identical with that of the complex *trans*-$[Co(cyclam)(CN)OH_2]^{2+}$.[5] Data are collected in Table 2.

TABLE 2

Second-order rate constants for the base hydrolysis of the complexes *trans*-$[Co(amine)_4(CN)Cl]^+$

(Amine)$_4$	Temp./°C	k_2/l mol^{-1} s^{-1}
$(NH_3)_4$	12·7	$0{\cdot}26 \pm 0{\cdot}01$ [a]
$(NH_3)_4$	22·5	$1{\cdot}04 \pm 0{\cdot}04$ [a]
$(NH_3)_4$	28·4	$2{\cdot}40 \pm 0{\cdot}10$ [a]
(cyclam)	13·6	$5{\cdot}87 \pm 0{\cdot}20$ [a]
(cyclam)	21·9	$18{\cdot}7 \pm 0{\cdot}60$ [a]
(cyclam)	27·2	$37{\cdot}0 \pm 0{\cdot}80$ [a]
$(NH_3)_4$	0	0·035 [b]
$(en)_2$	0	0·13 [c]
(cyclam)	0	0·81 [d]

[a] This work; from six different runs in 2,6-dimethylpiperidine–nitric acid buffer solutions at $I = 0{\cdot}1$M ($NaNO_3$) and over a span of 1·0 pH unit. [b] Obtained by extrapolation; $\Delta H^\ddagger = 23{\cdot}8$ kcal mol^{-1} and $\Delta S^\ddagger = 22$ cal K^{-1} mol^{-1}. [c] At $I = 0{\cdot}012$M; S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514. [d] Obtained by extrapolation; $\Delta H^\ddagger = 22{\cdot}6$ kcal mol^{-1} and $\Delta S^\ddagger = 24$ cal K^{-1} mol^{-1}.

DISCUSSION

The assignment of a *trans*-configuration to the new $[Co(NH_3)_4(CN)Cl]^+$ complex was made, tentatively, on the basis that the complex was prepared under mild conditions by anating the complex *trans*-$[Co(NH_3)_4(CN)OH_2]^{2+}$ with an excess of chloride ions in glacial acetic acid solution. Acid hydrolysis of the present complex gave, in a single-step process, the *trans*-aquocyano-complex, and base hydrolysis also gave a *trans*-product. With reference to stereoretentive-substitution reactions of the corresponding complex *trans*-$[Co(en)_2(CN)Cl]^+$ (ref. 9) and other tetra-ammine complexes containing the π-accepting NO_2^- group[10] as an orienting ligand, it was inferred that the new tetra-amminechlorocyano-complex had a *trans*-configuration. Attempts to characterize this complex by a different method were not successful. The powerful ^1H n.m.r. method, which has been successfully used to characterize other tetra-ammine complexes,[1,10] was not applicable here because of the poor solubility of the complex in most common organic solvents, such as $[^2H_6]$dimethyl sulphoxide, and the rapid hydrolysis of the complex in deuterium oxide. I.r. spectra of the *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ complexes have been discussed by Faust and Quagliano and a difference between the spectra was noted.[11] However, for the less symmetrical monosubstituted tetra-ammine complexes, the absence of any *cis*-isomer prevents determination of the stereochemistry of these complexes on the basis of the *trans*-isomers alone.

It has been discussed in great detail elsewhere[2-4] that the thermodynamic and kinetic behaviour of cobalt(III) amine complexes is closely related to the extent of electronic delocalization of the weakly antibonding or nonbonding d electrons away from the central metal ion. The extent of delocalization is affected by the nature of

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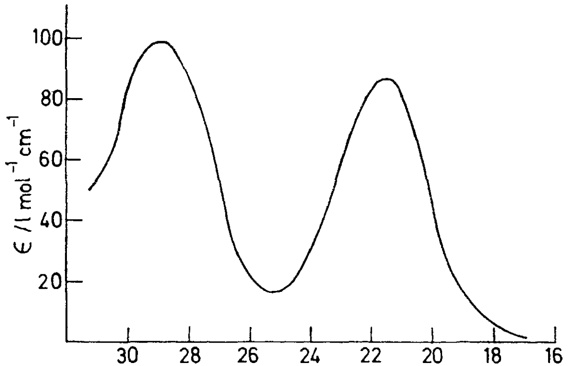
[9] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514.

[10] C. K. Poon and H. W. Tong, *J. Chem. Soc.* (*A*), 1971, 2151.

[11] J. P. Faust and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1954, **76**, 5346.

the ligands and it was found spectroscopically[2] to decrease in the following order of saturated amine ligands: cyclam > en > NH_3. Since the average ligand-field strength of chloride and cyanide ligands, according to Wentworth and Piper,[12] is very similar to that of $\frac{1}{4}$(amine)$_4$, it is expected, as observed, that the splitting of the octahedral $^1T_{1g}$ and $^1T_{2g}$ states in complexes of the type *trans*-[Co(amine)$_4$(CN)Cl]$^+$ is very small. The visible absorption spectrum of the complex *trans*-[Co(cyclam)(CN)Cl]Cl is shown in the Figure. The separation of the two visible bands arises from a larger electronic repulsion between the *d* electrons in the $^1T_2$* electronic configuration.[13] For the series of *trans*-[Co(amine)$_4$(CN)Cl]$^+$ complexes, it would be expected, at least qualitatively, that the probability of electronic excitation to the $^1T_2$* state relative to that of the $^1T_1$† state would be parallel with the ability of the amine ligands to expel *d* electrons from the central cobalt(III) ion. Since the two absorption bands (Figure) are sufficiently well separated to make estimation of the band intensities fairly reliable, it was found that the intensity ratio (high-frequency band) : (low-frequency band) indeed decreased in the order cyclam > (en)$_2$ > $(NH_3)_4$ (1·54, 1·18, 1·09). In the above comparison of the intensity ratio, other effects which strongly affect the absolute intensity of a transition, such as static dissymmetric field,[14] approximately cancel, thus making their difference unimportant in the above discussion. Intensity ratios of the complexes *trans*-[Co(amine)$_4(NH_3)_2]^{3+}$ also decrease in the same order (1·42, 1·11, 0·91).



Visible absorption spectrum of the complex *trans*-[Co(cylam)-(CN)Cl]$^+$ in aqueous solution

The trend in thermodynamic stability of these chlorocyano-complexes with respect to aquation also varied in the direction predicted by the thermodynamic nephelauxetic effect of the amine ligands on the cobalt(III) ion. For the cyclam and bis(ethylenediamine) complexes, as the nitrate salts, equilibrium was reached with 90 and 95% aquation respectively. For the tetra-ammine complex, even as the chloride salt, aquation was virtually complete. In fact, there was no sign of chloride anation when the reaction was carried out in *ca.* 3M-hydrochloric acid.

Kinetically, the variation of aquation and base-hydrolysis rate constants of these complexes with the nature of the amine ligands (Tables 1 and 2) fully supports the earlier proposition[2] concerning the influence of kinetic nephelauxetic effect on the lability of octahedral cobalt(III) amine complexes. Other effects, such as steric and solvation, predict that both aquation and base hydrolysis should vary in the same direction with the nature of the amine ligands.[4] Once again, for the present strain- and sterically-free systems, Tobe's correlation,[15] of square-pyramidal intermediate and retention of configuration with lower entropies of activation, is supported.

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* This band should be a composite of $^1B_2$ and ^1E.

† This band should be a composite of $^1A_2$ and ^1E.

[12] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.

[13] H. Yamatera, *Bull. Chem. Soc. Japan*, 1958, **31**, 95.

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