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SUBSTITUTION REACTIONS OF A COBALT(III) CYCLIC TETRAAMINE COMPLEX

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The ligand 1,4,8,11-tetraazacyclotetradecane ("cyclam") is the simplest member of the 2-3-2-3 carbon linked cyclic tetraamines and is the skeleton of the ligand already described by Curtis[1]. He described a hexa-C-methyl derivative which was prepared rather elegantly by forming a Schiff's base between acetone and ethylenediamine coordinated on a nickel(II) template, during which process the acetone dimerises to form the 3-carbon links. Reduction of the coordinated Schiff's base gave the tetraamine. Cyclam, which was originally described by Van Alphen[2] and later unambiguously synthesised by Stetter and Mayer[3], was prepared by a slight modification of Van Alphen's method whereby ethylenediamine and 1,3-dibromopropane were reacted to give the 2-3-2 open chain tetraamine which was then cyclised by further reaction with 1,3-dibromopropane.

So far we have characterised the cobalt(III) complexes[4], some nickel(II) complexes[5] and we are currently characterising some Cr^{III} complexes[6]. The cobalt(III) complexes that have so far been characterised are listed in Table I. They bear a very close resemblance to the corresponding [Co en_2 XY] complexes and there is a remarkable similarity of spectrum. In all cases where the *cis* and *trans* isomers of the bisethylenediamine have sufficiently different spectra, the spectrum of the cyclam complex resembles that of the *trans* isomer. The complexes were prepared by two main methods, (*a*), the air oxidation of a solution containing the ligand, a suitable cobaltous salt and a salt of the anionic ligand; subsequent treatment with acid was necessary in the case of the dichloro and dibromo complexes, and, (*b*), by the displacement of the chloride from *trans*-[Co cyclam Cl_2]$^+$. This second method is essential for the preparation of the mixed complexes and the

TABLE I

CYCLAM COMPLEXES OF COBALT(III) THAT HAVE BEEN CHARACTERISED[4]

trans-[Co cyclam Cl_2]$^+$	*trans*-[Co cyclam $(NO_2)_2$]$^+$
cis-[Co cyclam Cl_2]$^+$	*trans*-[Co cyclam $(NH_3)_2$]$^{3+}$
trans-[Co cyclam Br_2]$^+$	*trans*-[Co cyclam NCSCl]$^+$
trans-[Co cyclam $(N_3)_2$]$^+$	*trans*-[Co cyclam N_3Cl]$^+$
trans-[Co cyclam $(NCS)_2$]$^+$	

diammine complex. The dinitro complex was also prepared by the action of the ligand on a solution of sodium cobaltinitrite. All of the substitution reactions proceed with complete retention of configuration and there is only one example of a *cis* isomer. This was found in very small quantities in the *trans*-dichloro complex formed by aerial oxidation of a cobaltous chloride solution. It is possible that other *cis* isomers might be obtained from this one.

The nickel(II) complexes that have been described[5] are of the type, [Ni cyclam X_2] where X = Cl, Br, I or ClO_4. The chloro and bromo complexes are mauve and paramagnetic in the solid state, $\mu_{eff} = 3.1$ *B.M.* at 20°, whereas the iodide and perchlorate are brown and diamagnetic. All complexes dissolve in water and methanol to give brown diamagnetic solutions and the conductivity in water is that of a 2:1 electrolyte. The structure of [Ni cyclam Cl_2] has been determined by X-ray diffraction[7]. The four nitrogens are in a square plane with the chlorines approximately in the octahedral positions, with the Ni–Cl bond length some 0.2 Å longer than is usual. The chlorines are displaced towards the amine hydrogens which are arranged two above and two below the plane, the pairs being on either end of the 3-C links. The infrared spectra of [Ni cyclamI_2] and *trans*-[Co cyclam Cl_2]Cl are virtually identical, both in the number and position of peaks and their relative intensities. This is certainly consistent with a *trans* configuration in the cobalt(III) complex and, since the nickel salts are readily interconvertible, it is not unlikely that the configuration of the ligand is the same as in the nickel chloride complex.

The cyclam complexes were prepared in order to see the effect of conferring some rigidity on the ligand system upon the rates and steric courses of aquation of complexes of the type, [Co am_4 ACl]$^{n+}$ where A = OH, Cl, Br, NCS, N_3, H_2O, NH_3, NO_2, CN, etc.; especially of interest were those ligands that lead to a trigonal bipyramidal 5-coordinate intermediate, *e.g.*, OH, Cl, Br, N_3, and NCS. We had hoped to see that such complexes were considerably stabilised. This work however has barely started because of other effects that were not anticipated and proved to be of considerable interest. This paper is concerned with some of the other effects.

The first unexpected effect was the unusual thermodynamic stability of the dichloro complex. The aquation equilibrium,

$$[\mathrm{Co\ am_4\ Cl_2}]^+ + \mathrm{H_2O} \rightleftharpoons \underset{+\mathrm{Cl}^-}{[\mathrm{Co\ am_4\ Cl\ H_2O}]^{2+}} \rightleftharpoons \underset{+\mathrm{Cl}^-}{[\mathrm{Co\ am_4\ (H_2O)_2}]^{3+}}$$

which is well over to the right in the case of the bisethylenediamine complex, does not, in the case of cyclam, reach the complete displacement of the first chlorine. In nitric acid solution, pH = 2, the complex, provided as the nitrate, has only lost about 70% of the first chloride at equilibrium. The equilibrium constant for the first step is 6.0×10^{-3} moles/litre at 80°. At higher pH the position of equilibrium is moved to the right and, in the absence of added acid, the equilibrium solution contains only the chloro-aquo complex. The reversibility of the aquation reaction made a direct study of rate inaccurate and it was decided instead to study the rate of ligand exchange and substitution in aqueous solution. This type of reaction had not previously been observed in octahedral substitution in aqueous solution, although it was typical of the behaviour in non-aqueous solvents, and it seems to be a good opportunity to examine the role of solvent. We were reasonably convinced at first that the rate determining step was aquation and this was followed by a rapid anation. The reactions with four reagents were examined, Cl^-, NCS^-, N_3^- and NO_2^-. The behaviour of the non-basic reagents could be studied in acid solution and this presents the clearest picture.

Chloride exchange was studied in $0.01N\ HNO_3$ (HCl was also used) at 60.5°. The McKay plot showed that the two chlorines were equivalent and the rate constant for the chloride substitution was shown to be independent of chloride concentration over the range $2\times10^{-2}M < [Cl^-] < 1.3\times10^{-1}\ M$ and equal to $7.5\times10^{-3}\ \text{min}^{-1}$.

Substitution by the other ions was then studied. The basic ions, N_3^- and NO_2^-, in the absence of added acid reacted very much more rapidly than did chloride in acid solution and this aspect of the reaction was set aside until the acid behaviour was fully characterised. For this purpose thiocyanate proved to be most suitable. Within the pH range 2–3 the rate of reaction was independent of pH and the replacement of the first chlorine was very much faster ($t_{\frac{1}{2}} = 2.5$ h) than the replacement of the second ($t_{\frac{1}{2}} = 60$ h). On measuring the visible absorption spectrum over the range 400–800 mμ from time to time during the course of the reaction the first set of spectra observed had a common isosbiestic point at 630 mμ and these corresponded to the change *trans*-[Co cyclam $Cl_2]^+ \rightarrow$ *trans*-[Co cyclam NCS Cl$]^+$. At later stages of the reaction, and much more slowly, the absorption at the iosbiestic point started to fall and two new isosbiestic points appeared at 555 and 448 mμ corresponding to the change,

$$trans\text{-}[\text{Co cyclam NCS Cl}]^+ + NCS^- \rightarrow trans\text{-}[\text{Co cyclam }(NCS)_2]^+ + Cl^-$$

The reaction was followed spectrophotometrically at 555 mμ where the second step did not interfere. In the presence of excess thiocyanate the reaction was cleanly of first order and the rate constant was independent of the concentration of thiocyanate: *e.g.*, at 60.5°,

$$[SCN^-] = 5\times10^{-3},\quad k_1 = 4.5\times10^{-3}\ \text{min}^{-1};$$
$$[SCN^-] = 1.0\times10^{-2},\quad k_1 = 4.4\times10^{-3}\ \text{min}^{-1}.$$

Therefore, although the rates of entry of chloride and thiocyanate are independent of the concentration of the anionic reagent they are dependent upon its nature. A closer examination of this phenomenon was considered to be of interest in order to see whether this was some type of environmental effect and an attempt was made to study the entry of one reagent in an environment of the other. This was most conveniently done by studying entry of thiocyanate in the presence of a large excess of chloride. In any spectrophotometric study the entry of chloride in the complex would not cause any interference.

Preliminary experiments showed that the reactions were slowed down in the presence of excess chloride but that the plot of $\log_{10}(D_\infty - D_t)$ at 555 mμ, using a calculated value for D_∞, against time was no longer linear. Examination of the way in which the full spectra changed showed that, whereas the first step still gave an isosbiestic point, the second stage did not and closer examination showed that the changes were consistent with the scheme:

$$trans\text{-}[\mathrm{Co\ cyclam\ Cl_2}]^+ + \mathrm{NCS}^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-}[\mathrm{Co\ cyclam\ NCS\ Cl}]^+ + \mathrm{Cl}^-$$

$$trans\text{-}[\mathrm{Co\ cyclam\ NCS\ Cl}]^+ + \mathrm{NCS}^- \xrightarrow{\text{slow}} trans\text{-}[\mathrm{Co\ cyclam\ (NCS)_2}]^+ + \mathrm{Cl}^-$$

with the second step sufficiently slow for the first almost to reach a pseudo equilibrium. This implies that the cation, *trans*-[Co cyclam NCS Cl]$^+$ loses its thiocyanate more readily than its chloride.

By using Guggenheim's method and trial and error it was possible to show that a suitable choice of D_∞ led to a linear semilogarithmic plot from which we could obtain the first-order rate constant for approach to equilibrium, k_{obs}, and also, by assuming that the change in medium had no significant effect upon the spectra, the ratio of dichloro to chlorothiocyanato complex at equilibrium and from this the equilibrium constant,

$$K = [\mathrm{Co\ cyclam\ NCS\ Cl^+}]\,[\mathrm{Cl^-}]/[\mathrm{Co\ cyclam\ Cl_2{}^+}]\,[\mathrm{NCS^-}]\,.$$

It was found that, at 60.5°, this value of K was independent of [Cl$^-$] over a tenfold range of concentration but varied with the concentration of thiocyanate. The values are collected in Table 2. A better expression for the equilibrium was found to be:

TABLE II

DEPENDENCE OF K* OF THE THIOCYANATE CONCENTRATION

NCS^-	K
$2.5 \cdot 10^{-3}$ M	67
$5.0 \cdot 10^{-3}$ M	46
$10 \cdot 10^{-3}$ M	36
$20 \cdot 10^{-3}$ M	22

* Equilibrium constant for the *trans*-[Co cyclam Cl$_2$]$^+$+NCS$^-$ ⇌ *trans*-[Co cyclam NCS]$^+$+Cl$^-$ reaction, at 60.5°.

$$K' = \frac{[\mathrm{R\ NCS\ Cl^+}]\,[\mathrm{Cl^-}]\,(1+K''[\mathrm{NCS^-}])}{[\mathrm{R\ Cl_2{}^+}]\,[\mathrm{NCS^-}]}$$

where R = Co cyclam.

This form of expression is consistent with a scheme introducing partial association between cations and anions whereby the chlorothiocyanato complex forms a stronger ion-pair with thiocyanate than does the dichloro complex and neither cations forms a strong ion-pair with chloride.

The kinetics of approach to equilibrium were clearly of first-order and it is possible to show that, if we have a sequence,

$$RCl_2^{+} \xrightarrow{k_1} RCl^{+} + Cl^{-} \tag{1}$$

$$RCl^{2+} + Cl^{-} \xrightarrow{k_{-1}} RCl_2^{+}\,(\text{fast}) \tag{2}$$

$$RCl^{2+} + NCS^{-} \xrightarrow{k_{-2}} R\,Cl\,NCS^{+}\,(\text{fast}) \tag{3}$$

$$RCl\,NCS \xrightarrow{k_2} RCl^{2+} + NCS^{-} \tag{4}$$

the normal mass law retardation expression is modified to

$$\frac{1 + [R\,Cl_2^{+}]_{\text{eqbm.}}/[R\,Cl\,NCS^{+}]_{\text{eqbm.}}}{k_{\text{obs}}} = \frac{1}{k_1} + \frac{k_{-1}[Cl^{-}]}{k_1 k_{-2}[NCS^{-}]}$$

Therefore, by plotting the left hand expression above, shortened to $\frac{1}{k_{\text{obs}}}$ (corr.), against $[Cl^-]$ for a constant concentration of thiocyanate, a straight line should be obtained with intercept k_1 and slope that is inversely proportional to the concentration of thiocyanate. The results are plotted in Fig. 1 where it will be seen that this simple behaviour is not found. The plot shows a non linear behaviour at low chloride concentration but becomes linear at high chloride concentration. When this linear portion is extrapolated back to $[Cl^-] = 0$ we find that the lines for the

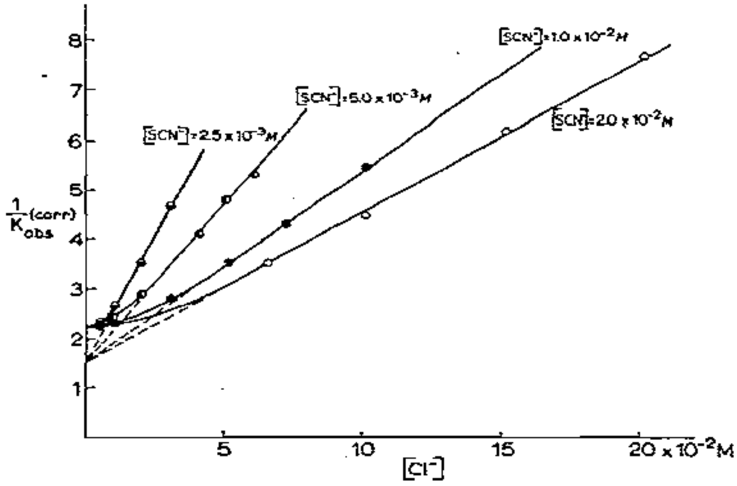

Fig. 1. Plot of $\frac{1}{k_{\text{obs}}}$ (corr) against $[Cl^-]$ for different concentrations of thiocyanate.

different thiocyanate concentrations have the same intercept. This intercept corresponds to a $k_1 = 6.7 \times 10^{-3}$ min^{-1} which agrees very well with the first-order rate constant for chloride exchange $= 7.5 \times 10^{-3}$ min^{-1}. This is readily explained in terms of the environmental effect we were seeking. At the lowest chloride concentration we have a k_1 appropriate for a thiocyanate environment, but, as the chloride concentration increases, k_1 also increases and causes the slope of the plot in Fig. 1 to increase. Above a particular chloride concentration, k_1 has reached a value that is appropriate for a chloride environment and changes no further so that the plot becomes linear and the extrapolation of this line back to the origin gives this value of k_1. In this way we have been able to show that the difference in the first-order rate constants for chloride exchange and thiocyanate substitution was due to some environmental effect.

The dependence of the slopes of the lines in Fig. 1 upon thiocyanate is not as simple as the calculated expression would suggest. These slopes should be inversely proportional to the concentration of thiocyanate but, although a plot of slope *versus* $1/[\mathrm{NCS}^-]$ is linear, it does not pass through the origin. This indicates that the true kinetic expression should be,

$$\frac{1}{k_{\mathrm{obs}}}(\mathrm{corr.}) = \frac{1}{k_{\mathrm{obs}}} + A\,\frac{[\mathrm{Cl}^-]\,(1+B[\mathrm{SCN}^-])}{[\mathrm{SCN}^-]}$$

where A and B are constants. This type of expression can be obtained if we assume that the rate law for the second and third steps of the reaction sequence above was not necessarily of second-order. Under what circumstances could this be possible? If the intermediate, written as RCl^{2+} was the five-coordinate species, its reactivity would be such that it could not come to ion-association equilibrium with its environment and the rate-law could not depart from a simple second-order form. On the other hand, if the intermediate was really $\mathrm{RClH_2O}^{2+}$ it would have more than enough time to equilibrate. It has already been pointed out that many octahedral substitution reactions involve a pre-equilibrium between the complex and the reagent that is followed by an exchange of a ligand between the outer sphere and the inner sphere of coordination[8]. If the rate at which the aquo complex reacts with chloride and thiocyanate is controlled by the amount in the form of the ion pair then we can say that, if the chloride ion-pair was not strongly formed its amount would be proportional to the concentration of chloride, whereas if the thiocyanate ion-pair was strong enough its concentration would be related to the function, $[\mathrm{SCN}^-]/(1+B[\mathrm{SCN}^-])$. These expressions would carry through to the final form. One must conclude, therefore, that these substitution reactions proceed by way of a rate determining aquation, the rate of which depends upon the nature of the environment. The anation of the aquo intermediate is fast but, in the case of thiocyanate substitution, the system is approaching a thiocyanate independent rate because of saturation of the ion-pair between thiocyanate and the aquo complex.

The substitution reactions of the dichloro complex under less acid conditions and its base hydrolysis are of considerable interest, although the study is by no means complete. The rate of entry of thiocyanate into the complex in solutions buffered in the pH range 6–8 is linearly dependent upon the concentration of hydroxide and independent of the concentration of thiocyanate. The product of this reaction, however, is *trans*-[Co cyclam NCS OH]$^+$ and it has been shown that this could not be formed by the fast base hydrolysis of a previously formed chlorothiocyanato complex. Careful analysis of the spectra of the solution in the course of the reaction, especially in the early stages, indicate the presence of an intermediate that does not contain thiocyanate and the kinetics are consistent with the reaction sequence:

$$trans\text{-}[\mathrm{Co\ cyclam\ Cl_2}]^+ + \mathrm{OH}^- \xrightarrow{k_2} trans\text{-}[\mathrm{Co\ cyclam\ OH\ Cl}]^+ + \mathrm{Cl}^-$$

$$trans\text{-}[\mathrm{Co\ cyclam\ OH\ Cl}]^+ + \mathrm{SCN}^- \xrightarrow{k_3} trans\text{-}[\mathrm{Co\ cyclam\ OH\ NCS}]^+ + \mathrm{Cl}^-$$

It appears that the second step is essentially a solvolytically controlled process and that thiocyanate does not directly attack the complex. There is no doubt that the chlorohydroxo complex is extremely labile, far more so than the corresponding bisethylenediamine complex.

In the reaction between *trans*-[Co cyclam Cl$_2$]$^+$ and azide at somewhat lower pH ($\mathrm{HN_3/N_3^-}$ buffers) the rate is again proportional to the concentration of hydroxide and the value of k_2 obtained agrees well with that found in the base catalysed thiocyanate substitution. Because the reaction is complicated by the rapid entry of the second azide, it is not possible to say with any certainty whether the first product of the reaction is the *trans*-[Co cyclam N$_3$ Cl]$^+$ or the *trans*-[Co cyclam N$_3$ OH]$^+$ cation but the bulk of the evidence is in favour of the former. When sodium azide is used in the absence of added acid the reaction is much faster (because the pH is higher) and the product is definitely the hydroxoazido complex. The rate of reaction appears to be first-order with respect to azide concentration rather than the half-order dependence one would expect if the rate was proportional to hydroxide concentration. The spectrophotometric rate is not fast enough for the hydroxide substitution to be the rate determining step and it appears that the azide dependent slow step is associated with the replacement of the chloride in the hydroxochloro complex by azide.

The rate of change of optical density of a solution of *trans*-[Co cyclam Cl$_2$]$^+$ in solutions buffered in the pH range 6–7 is first-order with respect to hydroxide concentration and the overall second order rate constant agrees well with the values of k_2 determined above. The product of the reaction is a mixture of *trans*-[Co cyclam OH H$_2$O]$^{2+}$ and *trans*-[Co cyclam (OH)$_2$]$^+$ the ratio being determined by the pH. Attempts to isolate crystalline samples of *trans*-[Co cyclam OH Cl] Cl (or other salts) have all failed because of the ease with which the material disproportionates and substitutes in aqueous solution.

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