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Aquation of Coordinated Chlorides in *cis*-α & *cis*-β Dichloro(triethylenetetramine) Co(III) Chlorides

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Aquation of *cis*-α- and *cis*-β-dichloro(triethylenetetramine) Co(III) chlorides has been studied at room temperature (25-26°) and *p*H around 4·0. Substitution of the two chlorides takes place in two steps. For both the isomers, the first step is faster by about fifteen times as compared to the second step. *cis*-β-Complex aquates about four times faster than the *cis*-α-complex.

THE mechanism of ligand substitution in cobalt (III) complexes could be by interchange '*d*' (*Id*), dissociative (*D*) and interchange '*a*' (*Ia*)[1]. Ligand exchange mechanism is influenced not only by the central atom, but equally by the ligands (incoming, outgoing and nonlabile ligands) as well as the solvent.

Tobe[2] has described an approximate but simple way of assigning a mechanism by comparing the substitution rate constant with the aquation rate constant (instead of water exchange rate constant) under similar conditions. For such a comparison the rates of aquation for *cis*-α and *cis*-β dichlorotriethylenetetramine Co(III) chlorides are required. This paper describes determination of rate constants of aquations and also discusses the overall mechanism of two steps of aquation and comparison of rates and mechanism of aquation of the two isomers.

Materials and Methods

Preparation and characterization — Dichloro(triethylenetetramine) Co(III) chloride complexes (*cis*-α and *cis*-β) were prepared by the methods given by Sargeson and Searle[3]. Their purity and identity were checked by comparing the visible and infrared spectra with those given in literature[4,5].

Procedure — Accurately weighed amounts of *cis*-α *cis*-β were dissolved in distilled water to make solutions of $5\times10^{-3} M$ and $4{\cdot}86\times10^{-3} M$ respectively. The solutions of *cis*-α and *cis*-β showed a *p*H of 4·0 and 3·8 respectively. The spectra in the visible region (Bausch and Lomb and Beckman DU spectrophotometers) were taken immediately and after different intervals of time after dissolution.

Results and Discussion

For both the isomers it was observed that the optical densities increased in the range of 440 to 510 nm, while these decreased in the region 510 to 600 nm during the process of aquation. Representative spectra for *cis*-α-[Co(trien)Cl_2]Cl are shown in Fig. (1).

Aquation of cis-α isomer — The variations in optical density at 310 and 600 nm were followed as a function of time for the determination of rate constants. Optical density after completion of the aquation reaction is taken as OD_∞ and that at at time '*t*' as 'OD_t'. The plot of log $(OD_\infty - OD_t)$ vs time could be resolved into linear portions giving two rate constants for the two steps of aquation. A typical plot of log $(OD_\infty - OD)$ vs *t* is given in Fig. 2. Points after 6 hr were well beyond the scale, hence not shown. The situation applied to Fig. 3 also.

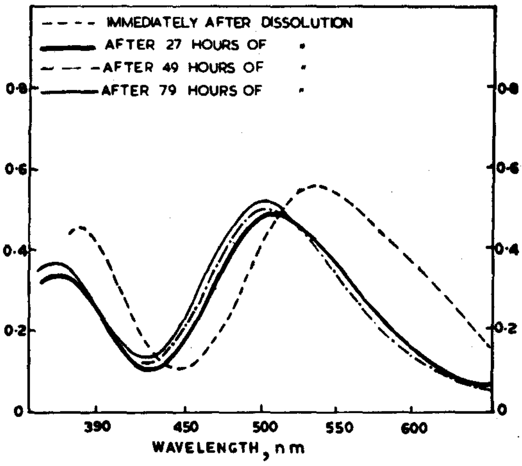

Fig. 1 — Spectra of *cis*-α-[Co(trien)Cl_2]Cl ($5\times10^{-3}M$) solution in water immediately after dissolution and after few days of dissolution

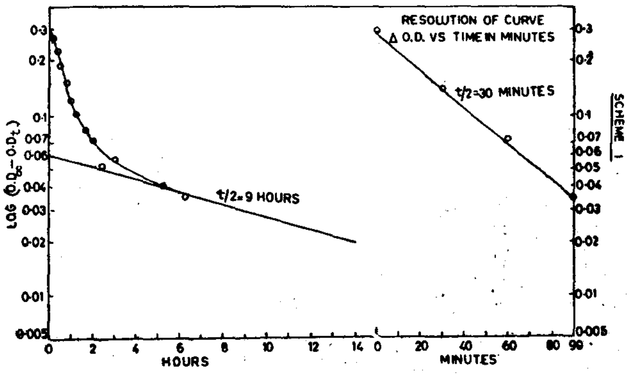

Fig. 2 — Aquation of 0·005*M* *cis*-α-[Co(trien)Cl_2]Cl solution [wavelength 600 nm]

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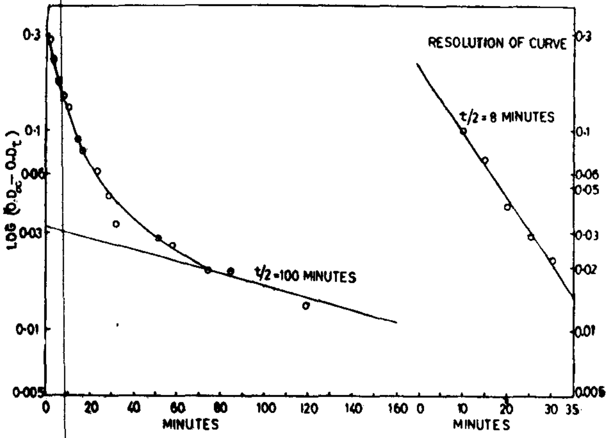

Fig. 3 — Aquation of 0·01*M* *cis*-β-[Co(trien)Cl_2] solution [wavelength 600 nm]

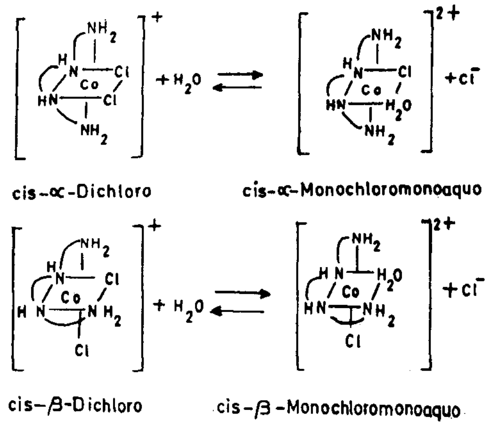

Fig. 4 — Effect due to relative position of ligands with different electron donating and electron accepting capacities

Aquation of cis-β isomer — With this isomer, the variations in optical density with time were followed at wavelengths 310, 480 and 600 nm at different concentrations. A typical plot of log ($OD_\infty - OD_t$) vs time is given in Fig. 4.

First order rate constants (k_1 and k_2, sec^{-1}) for *cis*-α and *cis*-β isomers for the concentrations studied are given in Table 1.

The important observation which is common to both *cis*-α and *cis*-β is that the first step is 13 to 18 times faster than the second step. The fact that the first step is faster by more or less the same factor with both the isomers would indicate that the circumstances responsible for the differences in reactivities fo dichloro cations and monoaquomonochloro cations of the two isomers should be the same. The two common criteria-which are not affeoted by stereochemical differences of *cis*-α and *cis*-β isomers could be as discussed below.

(a) *Effect of charge* — The effect of charge on the reaction centre could be one of the factors. For the replacement of the first chloride, the metal-chloride bond has to be weakened while the central metal atom has a formal charge of $+1[Co(trien)Cl_2]^+$, but for the replacement of the second chloride, the complex cation will have a dipositive charge. The leaving group will have to overcome the 2^+ charge while getting detached. Therefore the removal of the second chloride can be expected to be slower than the first. This can also be the explanation for the fact that substitution takes place in two steps rather than in a single step. So long as the unipositive cation is there, dipositive cation may not be undergoing aquation. Because of this difference in rates, the identification of both the steps by same experiment could be possible.

(b) *Effect of non-labile groups* — This effect is due to the relative positions of ligands with different electron donating and electron accepting capacities. As shown in Fig. 4, imino and the ammine groupings are common in all the four cations. What changes is the influence due to H_2O instead of Cl. The increasing order of electron donor capacity of these groups is given as $NH_2^{\delta-} > Cl^- > H_2O$ (ref. 6).

For the replacement of the first chloride two NH and Cl^- are there to donate electrons to the centre, i.e. cobalt(III), which could result in an increase in the electron density at the centre and hence assist in dissociation. Whereas in the second step, in the case of both the isomers, the two $NH_2^{\delta-}$ remain common as at the time of removal of the first chloride, but one chloride is replaced by H_2O, which is a harder base than chloride. Therefore electron density at the centre gets reduced and dissociation is affected.

Explanation based on these two criteria leads to the support of a dissociative mode of activation in the present case.

Another observation is that in the present concentration range and short *p*H range (3·8 to 4) rate constants increased with increasing concentration of complexes. Sargeson and Searle[4] have studied the equation for both *cis*-α and *cis*-β isomers in the broad *p*H range 0 to 4 and have found it to be independent of ionic strength and concentration of the complex. In this case increase in rate constant could be attributed to higher *p*H. No attempt was made to keep the ionic strength constant, the reason being that rates of aquation were required for comparison with substitution rates. For substitution experiments, a constant ionic strength could not be maintained for solubility reasons.

TABLE 1 — RATE CONSTANTS FOR AQUATION OF *cis*-α AND *cis*-β-Co(TRIEN)Cl_2/Cl

Wave-length nm	[Complex] mole/litre	$t_{1/2}$ (1st step) min	$t_{1/2}$ (2nd step) hr	$10^4 \times k$ (1st step) sec^{-1}	$10^5 \times k$ (2nd step) sec^{-1}
	cis-α-Co(TRIEN)Cl_2/Cl				
310	$1·25 \times 10^{-3}$	59	12·6	1·96	1·53
600	$2·5 \times 10^{-3}$	45	10·4	2·57	1·89
600	$5·0 \times 10^{-3}$	30	9·0	3·85	2·14
	cis-β-Co(TRIEN)Cl_2/Cl				
310	$2·43 \times 10^{-3}$	14	3·5	8·25	4·619
480	$4·86 \times 10^{-3}$	8	2·16	14·46	5·346
600	$1·0 \times 10^{-2}$	8	1·66	14·46	6·956

Comparison of aquation rates of cis-α and cis-β isomers — A comparison of rate constant values (k) given in Table 1 shows that both the steps for aquation of *cis*-β isomer were faster than those of *cis*-α isomer. The first step is faster by 3 to 4 times and the second step 3·5 to 5 times in the range of concentrations studied. An explanation for this lies in the stereochemistry of the two isomers. For *cis*-β there are three nitrogen atoms in the central plane and only two in the case of *cis*-α. Therefore electron density at the centre of *cis*-β is more favourable for dissociation than for *cis*-α. Another reason for higher activity of *cis*-β is the fact, as already discussed by Sargeson and Searle[4], that *cis*-β is less solvated.

Further work involving the use of DMSO and mixtures of DMSO-DMF in place of water is in progress and will be published elsewhere.

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