

Effect of geometric restraints on lability of amino-cobalt(III) complexes

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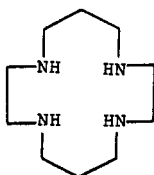
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Abstract - The kinetics of the uncatalysed and base-catalysed aquation of the complexes $trans-[Co(tn)_2BCl]^{n+}$ ($tn = 1,3$ -diaminopropane; $B = OH^-, Cl^-, NCS^-, N_3^-, NH_3, CN^-$), are reported and the rate constants compared to those of the corresponding 1,2-diaminoethane complexes. For those species whose aquation takes place with stereochemical change, the increase in ring size from five to six-membered causes a reactivity increase of 3 orders of magnitude. For others, the reactivity increase is only about 10-20 fold. It is suggested that those complexes that can aquate through a trigonal bipyramidal intermediate experience the greatest release of strain in the transition state. The effect does not appear to be carried over into the base-catalysed hydrolysis.

In 1960 it became clear to us that the 'duality of behaviour' encountered in the dependence of the rate constants for the aquation of cis - and $trans$ - $[Co(en)_2BX]^{n+}$ ($en = 1,2$ -diaminoethane; X is the leaving group) upon the electron displacement properties of B was not, as Ingold had suggested (ref. 1) a duality of mechanism, but rather a duality of the shape of the incipient five-coordinate intermediate of a dissociatively activated process.

It appeared that, in addition to what proved to be the generally observed ground-state bond weakening that related to the σ -donor ability of B and was most effective when B was $trans$ to the leaving group ($trans$ influence), there was a labilisation that arose from strong π -donors which were more effective when B was cis to the leaving group. The π donor labilization appeared to involve the stabilisation of a trigonal-bipyramidal intermediate, and hence stereochemical change, while the other, going through a square based pyramid, took place with complete retention of configuration.

It occurred to us that one of the tests that could be applied would be to see the effect on the reactivity of replacing the diaminoethane chelates with multidentate amine ligands that exhibited very strong steric preference, either preventing or promoting a trigonal bipyramidal geometry. Our first approach used 1,4,8,11-tetraazacyclotetradecane (cyclam = I), designed initially to prevent the formation of a trigonal bipyramid (refs. 2,3) and our first impressions, later confirmed by the much more extensive studies of Poon (refs. 4-7), were that, apart from the $trans-[Co(cyclam)(OH)Cl]^+$ cation, which was much more labile than the en_2 analogue, the replacement of two diaminoethane ligands by one cyclam reduced the reactivity of all the complexes by approximately two orders of magnitude (Table 1). Although it has still not been possible to prepare a similar series of cis complexes, the enormous reactivity difference between the available cis and $trans$ -dichloro species did not in



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any way parallel the behaviour of the corresponding en_2 complexes. (Table 2). We were certain that this effect was due to the differences of the configurations of the ligands in the two geometric isomers but it was not until much later that the $trans$ and cis isomers of the same ligand configuration could be compared. The nitrogen configurations in the $RRRR$ isomers,

TABLE 1. Rate constants ($10^4 k_{aq}/s^{-1}$) for the aquation of $trans-[Co(A_4)B Cl]^{n+}$ at 25°C.

B	A = en ₂	A = cyclam	k_{cyclam}/k_{en}
A OH ⁻	16	120	7.5
Cl ⁻	.42	.011	.026
NCS ⁻	.00042	.000011	.026
B N ₃ ⁻	2.5	.026	.010
C NO ₂ ⁻	9.8	.43	.044
CN ⁻	.82	.0048	.0059
NH ₃	.0034	.00073	.215

A trigonal bipyramid main pathway
 B possibly parallel pathways
 C square pyramidal pathway.

TABLE 2. Comparison of the rate constants ($10^4 k_{aq}/s^{-1}$) for the aquation of $cis-$ and $trans-$ $[CoA_4Cl_2]^+$ at 25°C.

A ₄	en ₂	RRSS-cyclam	RRRR-cyclam
<i>trans</i> -Cl	0.32 ⁹	.011 ²	17.5 ¹⁴
<i>cis</i> -Cl	2.4 ⁹	-	160 ³
k_{cis}/k_{trans}	7.5	(1.45x10 ⁴)	9.1

TABLE 3. Rate constants ($10^4 k_{aq}/s^{-1}$) at 25°C, enthalpies ($\Delta H^\ddagger/kJ.mol^{-1}$), and entropies ($\Delta S^\ddagger/J.K^{-1}.mol^{-1}$) of activation for the aquation of $trans-[Co(AA)_2B Cl]^{n+}$

	AA = en			AA = tn			k_{tn}/k_{en}
	$10^4 k_{aq}$	ΔH^\ddagger	ΔS^\ddagger	$10^4 k_{aq}$	ΔH^\ddagger	ΔS^\ddagger	
OH ⁻	16	107	+61	8	7600		470
Cl ⁻	.42	109	+36	9	680	92	+36
NCS ⁻	.00045	125	+30	10	0.62	114	+59
N ₃ ⁻	2.5	87	-25	11	360	83	-1
NO ₂ ⁻	9.8	87	-8	1	180	86	+9
CN ⁻	.82	94	-8	12	5.8	88	-10
NH ₃	.0034	97	-46	13	.064	102	-4
SO ₃ ²⁻	5560 (a)				67500		12
	821 (b)				8100		10
	400 (c)				10000		25

(a) Displacement of N₃⁻; (b) displacement of NO₂⁻;(c) displacement of NCS⁻: Data from ref. 20.TABLE 4: Rate constants ($k_{OH}/dm^3 mol^{-1} s^{-1}$) at 10.0°C for the base catalysed hydrolysis of $trans-[Co(AA)_2 B Cl]^{n+}$

	AA = en	AA = tn	k_{tn}/k_{en}
Cl ⁻	167 ²³	2670 ²³	16
NCS ⁻	1.47 ¹⁰	28.8	20
NO ₂ ⁻	0.43 ¹	5.7	13

which allow the folding in the *cis* isomer, also allow the *trans* isomer to go to the trigonal bipyramidal intermediate and to undergo aquation with stereochemical change. It is now clear that the *trans* $-[Co(RRRR-cyclam)B Cl]^{n+}$ series would have been more illuminating but, apart from the case where B = Cl, the other members have not yet been prepared.

The behaviour of the two *trans* $-[Co(cyclam)Cl_2]^+$ isomers brought to mind the qualitative observations of Werner (ref 15) that *trans* $-[Co(tn)_2Cl_2]^+$ (tn = 1,3-diaminoethane) is much more labile than *trans* $-[Co(en)_2Cl_2]^+$. It was shown much later to be a rate enhancement of some 3 orders of magnitude (ref. 16). House (ref. 17) showed that the replacement of only one of the diaminoethanes was insufficient to produce this effect, and that the Cr(III) analogues did not respond in this way and had labilities that were much less sensitive to the nature of the amine ligands. He suggested that the labilization was due to the release of the strain in the six-membered rings when the trigonal bipyramid was formed. He also showed that the lability of Co(III) complexes of the type *trans* $-[Co(A_4)Cl_2]^+$ is very sensitive to the nature of A₄ (ref. 18).

It therefore seemed reasonable to predict that, if this is correct, the duality of geometry should show up as a duality of response to the change from the five- to the six-membered rings. House has already shown that, while primary amines (am) in *cis* $-[Co(tn)_2(am)Cl]^{2+}$ can increase the reactivity by two orders of magnitude compared to that of the diaminoethane complex, the NH₃ complex is only 15 times more reactive (ref. 19). In the reactions of *trans* $-[Co(tn)_2(SO_3)X]$ (X = N₃⁻, NO₂⁻, NCS⁻), in which SO₃²⁻ is a specific *trans* labilizing ligand, the change from AA = en to tn leads only to a 15 fold increase in rate constant (ref. 20). Complexes of the type *trans* $-[Co(tn)_2B Cl]^{n+}$ with B = NO₂⁻, NCS⁻ have already been described (ref. 21) and we have prepared these and other members of the series by methods analogous to those used for the preparation of the corresponding diaminoethane series. The complex with B = NH₃ was prepared by the action of concentrated hydrochloric acid saturated with lithium chloride on *trans* $-[Co(tn)_2(NH_3)(SO_3)ClO_4]$ and the *trans* arrangement has been confirmed by a single-crystal X-ray diffraction study of the chloride hydrate. The *trans* configuration of the other substrates has been confirmed by ¹H n.m.r. spectra in d₆-dimethyl sulphoxide. The *trans* chloro-azido perchlorate, prepared by Jackson's method (ref. 22), could not readily be freed from *trans* dichloro and *trans* diazido impurities but the rate constant was determined quite precisely at 600 nm, an isosbestic point for the aquation of the dichloro complex. All attempts so far to make a solid sample of a *trans* $-[Co(tn)_2(OH)Cl]^+$ salt

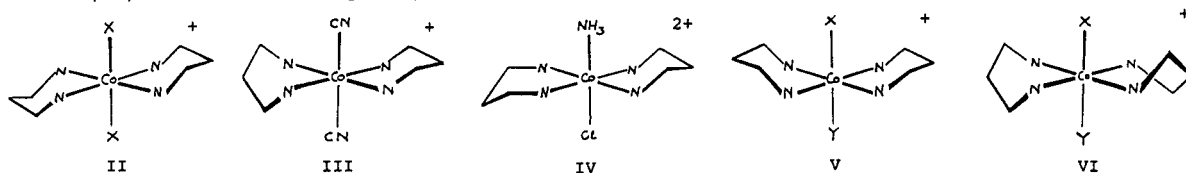
have failed, but since this is the dominant product of the first stage of the base hydrolysis of the dichloro complex, a rough estimate of its aquation rate constant was made by extrapolating the rate constant for the second stage (which is not greatly dependent upon $[\text{OH}^-]$) to zero base concentration. The rate constants at 25°C and activation parameters are collected in Table 3.

We have not yet been able to determine the steric course of these reactions. The final product of the displacement of the first Cl^- from *trans*- $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$ is mainly the *cis* aquo-chloro species but a definite spectrophotometric induction period at 530 nm is very similar to that observed in the aquation of the corresponding diaminoethane complex and consistent with the initial formation of a product that is much richer in the *trans* chloro-aquo species. Preliminary studies indicate that the *trans-cis* isomerisation of the chloro-aquo species is considerably faster than the reactions that form them. If the relationship between the stereochemistry and the entropy of activation observed in the diaminoethane case also holds, there should be stereochemical change in this system and also when $\text{A} = \text{NCS}^-$.

It would appear that the complexes that aquate with stereochemical change in the diaminoethane series are accelerated by approximately three orders of magnitude when en is replaced by tn. The rest are only accelerated by a factor of 10 or so. The *trans*- $[\text{Co}(\text{en})_2(\text{N}_3)\text{Cl}]^+$ cation is anomalous in the sense that the reaction has been shown to proceed with stereochemical change (ca 10%) (ref. 22) and yet ΔS^\ddagger is $-25 \text{ J K}^{-1} \text{ mol}^{-1}$. It is possible that, in this case ΔG^\ddagger values for the trigonal bipyramidal and square pyramidal intermediates are sufficiently similar for both pathways to contribute over the range of temperature studied. A curved Eyring plot would be predicted and the steric course ought to be very temperature sensitive. However, it would also follow that the change from en to tn ought to favour the trigonal bipyramidal pathway and remove the anomaly. There is no doubt that the change of diamine increases the lability of the chloro-azido complex by a factor that lies between the 10-fold of the retentive pathways and the 10^3 fold of the steric change pathways, but the entropy of activation is still too small. This anomaly remains but in general the results are consistent with the idea that the major accelerating effect of the tn_2 system is confined to those complexes that aquate with stereochemical change.

Since the base catalysed solvolyses of the Co(III) complexes of the type $[\text{Co}(\text{AA})_2\text{B Cl}]^{n+}$ are thought to take place dissociatively through a trigonal bipyramidal intermediate it seemed likely that the base catalysed hydrolysis would be much accelerated on going from the $\text{AA} = \text{en}$ to $\text{AA} = \text{tn}$ systems. This does not appear to be the case in the complexes examined so far (Table 4).

The behaviour of the dichloro complex has already been explained in terms of rate limiting deprotonation (ref. 24) since it is known that the ratio of the rate constants for the reprotonation (k_{-1}) and dissociation (k_2) of the amido conjugate base is about 5 at 10°C. It does not require a great increase in k_2 for the general expression $k_{\text{OH}} = 8 k_1 k_2 / (k_{-1} + k_2)$ (where k_1 is the rate constant for the exchange of the 8 equivalent amine protons) to simplify to $k_{\text{OH}} = 8 k_1$. The temperature dependence of k_{OH} for the 1,3-diaminopropane complex is consistent with this proposal. However, there is no reason to believe that the much less labile chloro-isothiocyanato and chloro-nitro complexes can be explained in this way and the fact that the activation parameters for the base hydrolysis of *trans*- $[\text{Co}(\text{tn})_2(\text{NCS})\text{Cl}]^+$ ($\Delta\text{H}^\ddagger = 96 \text{ kJ mol}^{-1}$; $\Delta\text{S}^\ddagger = +121 \text{ J K}^{-1} \text{ mol}^{-1}$) are sufficiently similar to those of the corresponding en_2 complex ($\Delta\text{H}^\ddagger = 96 \text{ kJ mol}^{-1}$; $\Delta\text{S}^\ddagger = +113 \text{ J K}^{-1} \text{ mol}^{-1}$) rules out any change in the rate determining step. Clearly the reasoning applied to the solvolytic aquation does not extend to the base catalysed aquation where the orientation of the amido nitrogen becomes important. It has been shown, in this context, that the rate constants for the base hydrolysis of complexes of the type $[\text{Co}(\text{A}_5)\text{X}]^{2+}$ are very sensitive to the ability of the A_5 set of nitrogen donors to allow the deprotonated amido nitrogen, *cis* to the leaving group, to orient its coordination plane perpendicular to the trigonal plane of the trigonal-bipyramidal cobalt (ref. 24).



Some comment is called for on the possibility that the lability of the complexes is somehow related to the conformations that are adopted by the six-membered rings. Several single crystal X-ray diffraction studies of the structures of complexes of the type *trans*- $[\text{Co}(\text{tn})_2\text{X}_2]^+$ have been published and, although the centrosymmetric chair-chair conformation (II) is common [$\text{X} = \text{Cl}^-$ (ref. 25); NO_3^- (ref. 26); NO_2^- (ref. 27); CN^- (ref. 28)], the extent of

"flattening" of the chair changes from compound to compound and changes in the degree of hydration can lead to much more fundamental changes. For example, while the cation in *trans* -[Co(tn)₂(CN)₂]Cl₂·3H₂O has structure II, the monohydrate, *trans* -[Co(tn)₂(CN)₂]Cl₂·H₂O has the skew-chair conformation, (III), (ref. 28). The symmetry is reduced in the *trans* -[Co(tn)₂ B X]ⁿ⁺ complexes but less structural data are available. We have just shown that the cation in *trans* -[Co(tn)₂(NH₃)Cl]Cl₂·H₂O has two non-equivalent rings, one of which has the chair conformation while the other has the cobalt, the two nitrogens and the two carbons adjacent to them all essentially coplanar (IV). This is very much a flattened (hydrogen atoms eclipsed) modification of the unsymmetrical chair-chair conformation (V). The double skew conformation (VI) should also be considered for both the symmetrical and the unsymmetrical complexes (as well as its conformer with the two skew rings of opposite chirality). It is reasonable to conclude that, as in the case of the various conformers of [Co(en)₃]³⁺, packing and interionic hydrogen bonding dominate and the energy differences between the various conformers cannot be large.

It is therefore unwise to assume that the solid state conformations are carried over into solution, or indeed that the conformation in one solvent, e.g., dimethyl sulphoxide is the same as in water. The ¹H n.m.r. spectra of such solutions are very informative and will be discussed elsewhere. However, if the energy differences between the conformers is not large and the interconversion is fast, it is unlikely that reactivity differences can be ascribed to the conformations adopted by the six-membered rings in solution. Nevertheless, we are currently examining the various *trans* -[Co(AA)₂B X]ⁿ⁺ complexes where AA is 2,4-diaminobutane, where the steric restraints favouring the equatorial disposition of the methyl groups freezes the skew-skew conformation for the *RR* ligand and the chair-chair conformations for the *RS* ligand (refs. 29, 30).

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