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Further Observations on the Case for Pentaco-ordinate Intermediate Formation in Octahedral Cobalt(III) Aquation

W. G. JACKSON*
Department of Inorganic Chemistry, University of Melbourne, Parkville, 3052, Melbourne, Victoria, Australia

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The steric course for Hg^{2+} and NO^+ promoted aquation of some bis(ethylenediamine)cobalt(III) cations has been accurately determined at 23° C. Some are re-examinations of other work for which precision has been improved or different results obtained. Previous discussion related to the factors affecting aquation stereochemistry is amplified in the light of new results and some new correlations are noted.

Introduction

It has long been recognized that stereochemistry is an important aspect of studies in aquation kinetics of octahedral complexes. Much of the pioneering work concerned "spontaneous" aquation of Co(III) amine complexes, and it became common to rationalize the steric course in terms of five co-ordinate "intermediates". More recently, Taube[1,2], Buckingham and Sargeson[3,4], and others have studied so-called "induced" or promoted aquation and have shown, on the basis of precise stereochemical results, that these reactions proceed *via* genuine but extremely short lived pentaco-ordinate intermediates and that their spontaneous aquation counterparts proceed in general by a different mechanism. Pentaco-ordination in Co(III) substitution has only recently been reviewed in its own right[5,6].

We wish to report here our results for the stereochemistry of the Hg^{2+} promoted aquation of *cis*-$Co(en)_2Br_2^+$, *cis*- and *trans*-$Co(en)_2(OH_2)Br^{2+}$, *cis*- and *trans*-$Co(en)_2(OH_2)Cl^{2+}$, and the NO^+ promoted aquation of the azido complexes *cis*- and trans-$Co(en)_2(N_3)_2^+$, *cis*- and *trans*-$Co(en)_2(OH_2)N_3^{2+}$, *trans*-$Co(en)_2ClN_3^+$ and *trans*-$Co(en)_2BrN_3^+$. Several of these are re-examinations of previous work[1,2,3] for some of which we obtain different results. Where appropriate, comparisons are made between promoted and spontaneous aquation, and we amplify certain aspects of previous discussions on the relationship between steric course of aquation and the nature of both the leaving and undisplaced groups.

Experimental Section

Complexes

The following compounds were all known previously and were prepared by the best literature procedures available without essential modification. The salts prepared are indicated: *cis*-$Co(en)_2Br_2^+$ ($Br \cdot H_2O$, NO_3, ClO_4), *trans*-$Co(en)_2Br_2^+$(Br,ClO_4), *cis*-$Co(en)_2(N_3)_2^+$(NO_3, ClO_4), *trans*-$Co(en)_2(N_3)_2^+$(ClO_4), *trans*-$Co(en)_2ClN_3^+$(ClO_4), *trans*-$Co(en)_2BrN_3^+$(ClO_4), *cis*-$Co(en)_2(OH_2)Cl^{2+}$ ($Br_2 \cdot H_2O$, $SO_4 \cdot 2H_2O$), *trans*-$Co(en)_2(OH_2)Cl^{2+}$(SO_4), *trans*-$Co(en)_2(OH)Cl^+$($Cl \cdot H_2O$), *cis*-$Co(en)_2(OH_2)Br^{2+}$($Br_2 \cdot H_2O$, $(NO_3)_2 \cdot H_2O$), *trans*-$Co(en)_2(OH_2)Br^{2+}$(SO_4), *trans*-$Co(en)_2(OH)Br^+$ ($Br \cdot H_2O$), *cis*-$Co(en)_2(OH_2)N_3^{2+}$($SO_4 \cdot H_2O$), *trans*-$Co(en)_2(OH_2)N_3^{2+}$($SO_4 \cdot 2H_2O$), *cis*-$Co(en)_2(OH_2)_2^{3+}$ ($(NO_3)_3$), *cis*-$Co(en)_2(OH_2)(OH)^{2+}$($Br_2 \cdot H_2O$), *trans*-$Co(en)_2(OH_2)_2^{3+}$ ($(NO_3)_3$), *trans*-$Co(en)_2(OH_2)(OH)^{2+}$(Br_2, $(ClO_4)_2$), and *cis*-$Co(en)_2(CO_3)^+$(Cl,ClO_4). All compounds analysed well. Support for the stoichiometry came from the agreement between the spectra of the different salts (see ahead). *Cis*-$[Co(en)_2(OH_2)N_3]SO_4 \cdot H_2O$, prepared as only one salt, has been formulated as both anhydrous[7] and as a monohydrate[3,7]. Our sample analysed as indicated. Calcd. for $[Co(en)_2(OH_2)N_3]SO_4 \cdot H_2O$: C, 13.6; H, 5.7; N, 27.8; S, 9.1. Calcd. for $[Co(en)_2(OH_2)N_3]SO_4$: C, 14.3; H, 5.4; N, 29.2; S, 9.6. Found: C, 13.4; H, 5.8; N, 28.0; S, 9.2%.

Isomeric Purity

Clearly this is important for the accurate measurement of aquation stereochemistry and therefore we prepared different salts of most of the complexes, each of which was recrystallized until a constant visible absorption spectrum (ε, $< \pm 0.5\%$) was obtained. The

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* Present address: The University Chemical Laboratory, Lensfield Road, University of Cambridge, Cambridge, CB2 1EW, U.K.

agreement between the spectra of different salts of the same cation was taken as evidence for isomeric purity. The spectra of aquo complexes were obtained from both solid hydroxo and aquo salts, and since the $Co(en)_2(OH_2)_2{}^{3+}$ and $Co(en)_2(OH)_2{}^{+}$ spectra do not change rapidly with time[8], these were also measured in $1M$ NaOH as well as $1M$ $HClO_4$ using both solid hydroxo–aquo and diaquo salts, as an additional internal check on isomeric purity. For the *cis* spectra we also used *cis*-$[Co(en)_2(CO_3)]ClO_4$ which initially was reacted with $HClO_4$. Each spectrum was independent of the starting compound.

The spectra measured here were in close agreement with the best available published data, possibly with the exception of *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ for which we find differences in ε up to 10% at some wavelengths, principally around 500 nm (*e.g.*, $\varepsilon^{492} = 17.6\ M^{-1}\ cm^{-1}$, *cf.* 19.2[9]). This difference, however, corresponds to only a 2% *cis* impurity in the spectrum published for the *trans* isomer[9].

Promoted Aquation and Stereochemistry

The techniques used in performing the Hg^{2+} and NO^{+} assisted aquations have been described before[1,2,3]. Generally 0.1–0.5M Hg^{2+}, $1M$ $HClO_4$, and 5.0–10.0 × $10^{-3}M$ [Complex] solutions were used; between 10% excess and double the required stoichiometric amount of $NaNO_2$ was used in the nitrosations ($1M$ $HClO_4$). AR reagents were used throughout. Solutions of HgO in excess $HClO_4$ were filtered through fine porosity sintered glass immediately prior to use to remove barely perceptible opalescence; this precaution significantly improved the results.

The steric course for most aquations was determined as follows: Sufficient reagent was added to the complex to effect rapid dissolution and then complete conversion to $Co(en)_2(OH_2)_2{}^{3+}$; the conditions were such that the spontaneous processes made a negligible contribution to reaction. The spectrum of the product mixture was then immediately scanned (340–700 nm) and this was usually constant within 1 min. after mixing. Several final spectra could be measured before any appreciable interference from the very slow *cis-/trans*-$Co(en)_2(OH_2)_2{}^{3+}$ isomerization was experienced[8]. The product isomeric proportions were then determined by simple spectral analysis at several wavelengths. The best results were obtained at 492 nm where the diaquo isomers differ most in their spectra ($\varepsilon_{cis}{}^{492} = 80.9$, $\varepsilon_{trans}{}^{492} = 17.6M^{-1}$ cm^{-1}). The steric course for the promoted aquations of *trans*-$Co(en)_2ClN_3{}^{+}$ and *trans*-$Co(en)_2BrN_3{}^{+}$ were determined similarly by rapidly generating $Co(en)_2(OH_2)X^{2+}$ (X = Cl, Br or N_3) and analysing the product spectrum in terms of the appropriate species (X = N_3, $\varepsilon_{cis}{}^{500} = 294.0$, $\varepsilon_{trans}{}^{500} = 102.5$; X = Br, $\varepsilon_{cis}{}^{530} = 90.7$, $\varepsilon_{trans}{}^{530} = 11.5$; X = Cl, $\varepsilon_{cis}{}^{510} = 91.2$, $\varepsilon_{trans}{}^{510} = 11.0M^{-1}$ cm^{-1}). Only small corrections to the product spectra were required to allow for slow product interconversion[3,10,11]. The presence of the promoting reagent does not significantly affect these isomerization rates[3].

We have used the same technique to determine the steric course for the $Co(en)_2X_2{}^{+}$ complexes having two readily replaced ligands, *e.g.*, *cis*-$Co(en)_2Br_2{}^{+}$. In these instances the promoted aquation stereochemistry was determined from the observed isomeric $Co(en)_2(OH_2)_2{}^{3+}$ proportions in the completely aquated product knowing the contributions made by each of the intermediate $Co(en)_2(OH_2)X^{2+}$ isomers under identical conditions. This technique is accurate when *cis*- and *trans*-$Co(en)_2(OH_2)X^{2+}$ have quite different promoted aquation stereochemistries which indeed is generally the case. Moreover, this method obviates difficulties associated with the alternative of directly observing the first aquation step. The control of stepwise aquation necessarily involves nearer stoichiometric amounts of reagents and therefore this increases the time for complete reaction. Thus, under these conditions, and where the background spontaneous aquation has been kept negligible, the product spectrum must be corrected for secondary reaction. In addition to $Co(en)_2(OH_2)X^{2+}$ isomerization which, incidentally, is faster than $Co(en)_2(OH_2)_2{}^{3+}$ isomerization, the second stage of promoted aquation is often significant.

All electronic spectra were measured at 23° C using matched 1 cm silica cells and a Hitachi EPS–3T self recording instrument. Wavelength and photometric accuracy was ensured with holmium and didymium filters (λ) and standard chromate solutions ($\varepsilon^{372.5} = 4830M^{-1}$ cm^{-1} [12]). The spectra showed no detectable dependence on $[Hg^{2+}]$. HNO_2 absorption was destroyed with urea;[13] HNO_2 does not absorb much above 400 nm[13].

The water exchange rates (k_{cc}, k_{tt}) of Taube[8] together with some more recent isomerization rate data (k_{tc}, k_{ct})[8,14] were used to calculate[2] the steric course of "aquation" of the $Co(en)_2(OH_2)_2{}^{3+}$ and $Co(en)_2(OH_2)(OH)^{2+}$ isomers*. The two *cis/trans* equilibrium constants K(= k_{ct}/k_{tc})[14,15,16] were used to obtain the k_{ct} and k_{tc} constants from the measured rates of approach to equilibrium ($k_{ct} + k_{tc}$). We remeasured the $Co(en)_2(OH_2)_2{}^{3+}$ equilibrium since it strongly favours the *cis* isomer and the value for the equilibrium constant is therefore liable to error. Widely different results have been reported depending upon the supporting medium (nitrate[9,15] or perchlorate[15,16]). We found $\varepsilon^{492} = 77.8 \pm 0.4M^{-1}\,cm^{-1}$ for an equilibrated

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* k_{cc} and k_{ct} are the rate constants for *cis* to *cis* water substitution and *cis* to *trans* isomerization respectively. The % *cis* product in *cis* substitution is given by $100k_{cc}/(k_{cc}+k_{ct})$; similarly for the *trans* substrates. Taube has shown (ref. 8) that each act of isomerization leads to the exchange of one water. Therefore the calculated steric course refers to the stereochemistry of water substitution.

solution of either *cis*- or *trans*-$Co(en)_2(OH_2)_2^{3+}$ in 0.1–1.0*M* $HClO_4$ at 23° C, which corresponds to 95.0 ± 0.5%*cis*, K = 19.0 ± 2.0. This agrees with some published data for perchlorate (K = 18.3, temperature independent)[15,16] but not for nitrate media (K = 58)[9,15]. Undoubtedly the source of discrepancy is due to nitrate co-ordination; we have noted that the observed isosbestic points for *cis/trans* isomerization are in precise agreement with those expected only in perchlorate media. Facile nitrate co-ordination has been noted in other diaquotetramine cobalt(III) systems,[17] and indeed, a sparingly soluble red nitrato complex can be readily isolated from *cis*-$Co(en)_2(OH_2)_2^{3+}$ or $Co(en)_2(CO_3)^+$ and HNO_3. Nitrate, like perchlorate, is usually considered an "inert" anion.

Results and Discussion

Table I summarizes the results of the present research; included are some selected results from previous work on both spontaneous and promoted aquation of $Co(en)_2AX^{n+}$ complexes. The data refer mainly to ambient temperature (23° C). We find no detectable dependence of the aquation stereochemistry on the concentration of $HClO_4$ or the promoting reagent (Hg^{2+} or NO^+).

We recently reported[10] the unusual and particularly clear example of a *cis*-tetraamine cobalt(III) complex which spontaneously aquates with appreciable stereochemical change, namely *cis*-$Co(en)_2Br_2^+$. One other example exists, *cis*-$Co(en)_2N_3Cl^+$ [7]. Previously *cis* complexes have been found to undergo stereochemical change only in promoted aquation or base hydrolysis; in these cases the steric course is invariably independent of leaving group suggesting the intervention of reduced co-ordination number intermediates[1–4,6]. Therefore we studied the Hg^{2+} promoted aquation of *cis*-$Co(en)_2Br_2^+$ to see if the aquation stereochemistry exactly matched that of the spontaneous process. We find this is clearly not so (Table I). The only conclusion that can be drawn at present is that the spontaneous and promoted aquations do not proceed by a common stoichiometric[18] mechanism. This represents the only example of a *cis* complex aquating with steric change and not giving an identical product distribution to the promoted aquation.

It is important to note that at ~ 60° C we find the steric course of Hg^{2+} promoted and spontaneous aquation of *cis*-$Co(en)_2Br_2^+$ to be identical; the steric course of spontaneous aquation is appreciably temperature dependent[10] (*e.g.* 15° C, 77 ± 1% *cis;* 40° C, 65 ± 1%*cis*). Caution is therefore elicited in concluding that a common intermediate is involved when a common steric course is found at a specific temperature for only two reactions; some other common property need be established (*e.g.* nucleophile competition ratio[4]). Temperature dependence of the aquation stereochemistry is potentially useful but in the very few studies made it is not generally observed and has been established in only one instance[10].

To obtain the *cis*-$Co(en)_2Br_2^+$ result required an examination of the Hg^{2+} promoted aquations of *cis*- and *trans*-$Co(en)_2(OH_2)Br^{2+}$ under identical conditions (see Experimental). The *cis* isomer has been studied previously; the reported aquation steric course was 99 ± 2%*cis*[2]. We found 95.0 ± 0.5%*cis*, and therefore re-examined the promoted aquations of *cis*-$Co(en)_2(OH_2)Cl^{2+}$ (Hg^{2+}, 100 ± 2% *cis*)[2] and *cis*-$Co(en)_2(OH_2)N_3^{2+}$ (NO^+, 100 ± 4% *cis*)[1,3] to see if this difference in steric course was real. We now find the latter reactions also give 95.0 ± 0.5% *cis*-$Co(en)_2(OH_2)_2^{3+}$. It is interesting to note that the promoted aquation product has been reported to be 94.5 ± 2.5% active[2], which indicates full retention of optical configuration for the *cis* component, a universal feature of both spontaneous and promoted aquation[6]. The 5% *trans* product must of course be inactive.

Previously no conclusion could be drawn from these results since in stereoretentive aquation the product ratio is not defined. However, the revised results now reveal a common product distribution (*cis/trans* = 19.0 ± 2.0), *i.e.* the steric course is leaving group independent. The inference is that a common pentacoordinate intermediate is involved. Accurate stereochemical data for the spontaneous aquations cannot be obtained, although note *cis*-$Co(en)_2(OH_2)_2^{3+}$ in water exchange gives this same steric course (Table I).

The complexes *trans*-$Co(en)_2(OH_2)X^{2+}$ (X = Cl, N_3) were shown previously[1,2,3] to give 60% *trans* product in promoted aquation, the same stereochemistry as water exchange in *trans*-$Co(en)_2(OH_2)_2^{3+}$. We now find the Hg^{2+} reaction with *trans*-$Co(en)_2(OH_2)Br^{2+}$ fits this pattern. The case for intermediate formation here is particularly strong since when *cis* and *trans* products are formed in comparable amounts the product ratio is well defined[3,6]. The improved precision of these results (62.0 ± 0.5% *trans*) in this work emphasizes this conclusion. Again, no accurate steric course information can be obtained for the spontaneous aquations (X = Cl, Br, N_3).

A common product is also found for the promoted aquation of the *trans*-$Co(en)_2BrX^+$ complexes (91.5 ± 1.0% *trans*), whereas in spontaneous aquation the stereochemistry is both quite different and leaving group dependent. Again a reduced co-ordination number intermediate is indicated for the promoted aquations. It should be noted that here there is decidedly less steric change than in spontaneous reaction; more usually the reverse is true, particularly for *cis* complexes' (Table I). The quite different steric course of water entry into the $Co(en)_2X^{2+}$ intermediate for X = Cl and Br is also noteworthy; this is found for the (different) intermediate in both *cis* and *trans* aquation.

TABLE I. Stereochemistry of Aquation $Co(en)_2AX \xrightarrow{H_2O} Co(en)_2A(OH_2) + X$[a]

Complex[b]	Aquation Method	Product	% Retention[c]	Ref.
cis-Br Br^{+}	spont	$Br(OH_2)^{2+}$	73 ± 1	d
cis-Br Cl^{+}	spont	$Br(OH_2)^{2+}$	100	e
cis-Br Br^{+}	Hg^{2+}	$Br(OH_2)^{2+}$	58 ± 1	this work
cis-$(OH_2)Cl^{2+}$	Hg^{2+}	$(OH_2)_2^{3+}$	95.0 ± 0.5	this work
			100 ± 2	f
cis-$(OH_2)Br^{2+}$	Hg^{2+}	$(OH_2)_2^{3+}$	95.0 ± 0.5	this work
			99 ± 2	f
cis-$(OH_2)N_3^{2+}$	NO^{+}	$(OH_2)_2^{3+}$	95.0 ± 0.5	this work
			100 ± 4	g, h
cis-$(OH_2)(OH_2)^{3+}$	spont	$(OH_2)_2^{3+}$	95.5 (calc.)	i
trans-Br Br^{+}	spont	$Br(OH_2)^{2+}$	70 ± 2	e, j
trans-Br Cl^{+}	spont	$Br(OH_2)^{2+}$	50 ± 5	e
trans-Br Br^{+}	Hg^{2+}	$Br(OH_2)^{2+}$	92 ± 1	this work
trans-Br N_3^{+}	NO^{+}	$Br(OH_2)^{2+}$	91.0 ± 0.5	this work
trans-$(OH_2)Cl^{2+}$	Hg^{2+}	$(OH_2)_2^{3+}$	62.0 ± 0.5	this work
			60 ± 5	f
trans-$(OH_2)N_3^{2+}$	NO^{+}	$(OH_2)_2^{3+}$	62.5 ± 0.5	this work
			60 ± 5	g, h
trans-$(OH_2)Br^{2+}$	Hg^{2+}	$(OH_2)_2^{3+}$	62.0 ± 0.5	this work
trans-$(OH_2)(OH_2)^{3+}$	spont	$(OH_2)_2^{3+}$	63 (calc.)	i
trans-Cl Cl^{+}	spont	$Cl(OH_2)^{2+}$	65	k
trans-Cl Br^{+}	spont	$Cl(OH_2)^{2+}$	80 ± 5	e
trans-Cl Cl^{+}	Tl^{3+}	$Cl(OH_2)^{2+}$	71 ± 3	l
trans-Cl Cl^{+}	Hg^{2+}	$Cl(OH_2)^{2+}$	72	h
trans-Cl N_3^{+}	NO^{+}	$Cl(OH_2)^{2+}$	73.0 ± 0.5	this work
			73 ± 3	f, g
cis-N_3Cl^{+}	spont	$N_3(OH_2)^{2+}$	85	m
cis-N_3Cl^{+}	Hg^{2+}	$N_3(OH_2)^{2+}$	85 ± 2, 84 ± 2	m, h
cis-$N_3N_3^{+}$	NO^{+}	$N_3(OH_2)^{2+}$	83 ± 1	this work
			84 ± 2	h
trans-N_3 N_3^{+}	Hg^{2+}	$N_2(OH_2)^{2+}$	97 ± 3	f
trans-N_3 N_3^{+}	NO^{+}	$N_3(OH_2)^{2+}$	100	g
			99 ± 1	this work
trans-N_3 Cl^{+}	Hg^{2+}	$N_3(OH_2)^{2+}$	100 ± 3	m
			99.5 ± 0.5	this work
trans-N_3 Br^{+}	Hg^{2+}	$N_3(OH_2)^{2+}$	100	m
			99.5 ± 0.5	this work
cis-Cl Cl^{+}	spont	$Cl(OH_2)^{2+}$	100, 100 ± 2	k, h
cis-Cl Br^{+}	spont	$Cl(OH_2)^{2+}$	100	e
cis-Cl N_3^{+}	NO^{+}	$Cl(OH_2)^{2+}$	79 ± 2	h
cis-Cl Cl^{+}	Hg^{2+}	$Cl(OH_2)^{2+}$	77 ± 3	h
cis-Cl $(dmso)^{2+}$	spont	$Cl(OH_2)^{2+}$	85 ± 5	n
cis-Cl $(dma)^{2+}$	spont	$Cl(OH_2)^{2+}$	83 ± 3	n
trans-$(OH)(OH_2)^{2+}$	spont	$OH(OH_2)^{2+}$	29 (calc.)	i
trans-(OH) Br^{+}	spont	$OH(OH_2)^{2+}$	27 ± 2	e
trans-(OH) Cl^{+}	spont	$OH(OH_2)^{2+}$	25	k

TABLE I. (Cont.)

Complex[b]	Aquation Method	Product	% Retention[c]	Ref.
trans-$(CH_3CO_2)(CH_3CO_2H)^{2+}$	spont	$(CH_3CO_2)(OH_2)^{2+}$	25 ± 5	o
trans-$(CH_3CO_2)\ Cl^+$	spont	$(CH_3CO_2)(OH_2)^{2+}$	20 ± 10	p
trans-$(CH_3CO_2)\ Cl^+$	Hg^{2+}	$(CH_3CO_2)(OH_2)^{2+}$	25 ± 2	p

[a] Usually 23° C (see text). [b] Last named group is the leaving group. [c] Results of this work are averages of three determinations. [d] 23° C; C.G. Barraclough, R.W. Boschen, W.W. Fee, W.G. Jackson, and P.T. McTigue, *Inorg. Chem., 10,* 1994 (1971). [e] S.C. Chan and M.L. Tobe, *J. Chem. Soc.,* 5700 (1963). [f] D.A. Loeliger and H. Taube, *Inorg. Chem., 5,* 1376 (1966). [g] D.A. Loeliger and H. Taube, *Inorg. Chem., 4,* 1032 (1965). [h] D.A. Buckingham, I.I. Olsen, and A.M. Sargeson, *Inorg. Chem., 6,* 1807 (1967). [i] Water exchangc (see tcxt); W. Krusc and H. Taube, *J. Am. Chem. Soc., 83,* 1280 (1961). [j] Checked in this work by isosbestic point method (ref. d). [k] M.E. Baldwin, S.C. Chan, and M.L. Tobe, *J. Chem. Soc.,* 4637 (1961). [l] S.W. Foong, B. Kipling, and A.G. Sykes, *J. Chem. Soc. (A),* 118 (1971). [m] V. Ricevuto and M.L. Tobe, *Inorg. Chem., 9,* 1785 (1970). [n] I.R. Lantzke and D.W. Watts, *Aust. J. Chem., 19,* 1821 (1966). [o] In this acid catalysed aquation, Co–O fission occurs; T.P. Dasgupta and M.L. Tobe, *Inorg. Chem., 11,* 1011 (1972). [p] T.P. Dasgupta, W. Fitzgerald, and M.L. Tobe, *Inorg. Chem., 11,* 2046 (1972).

Since the complexes were at hand, we have re-examined the promoted aquations of several other complexes. Our results (Table I) reaffirm the previous work[1,2,3,7]. No conclusion can be drawn regarding intermediate formation for *trans*-$Co(en)_2N_3X^+$ species ($X = Cl, Br, N_3$) since both the promoted and spontaneous processes proceed with complete retention[1,2,3,7]. The complexes giving steric change (*trans*-$Co(en)_2ClN_3{}^+$* and *cis*-$Co(en)_2(N_3)_2{}^+$ + NO^+) do so in the usual manner – a product distribution is observed which is independent of the leaving group.

Results for the *trans*-$Co(en)_2ClX^+$ species (Table I) are similar to those for *trans*-$Co(en)_2BrX^+$. Here, however, the differences between promoted and spontaneous aquation are not marked, particularly for *trans*-$Co(en)_2Cl_2{}^+$. It has been suggested[19] that, for this complex, the product distributions may even be the same. However, since promoted aquation can lead to either more or less steric change than in spontaneous aquation, as remarked above, it would not be surprising that one example in many could give similar product distributions in the two modes of aquation. *Cis*-$Co(en)_2N_3Cl^+$ (+ Hg^{2+})[7] appears to be the only real case of what could be considered a fortuitous result. The precision with which the steric course of spontaneous aquation is known for two other possibilities, *trans*-$Co(en)_2Cl_2{}^+$ and *trans*-$Co(en)_2(CH_3CO_2)Cl^+$,[20] precludes the definite statement that the stereochemistry is "identical" (say, ± 1%) in spontaneous and promoted aquation. It is interesting to note that the steric course for the TI(III) promoted aquation of *trans*-$Co(en)_2Cl_2{}^+$ (71 ± 3 *trans*) is very similar to that for the other promoted aquations (72.5 ± 0.5% *trans*). TI(III) (and Ag(1)) studies in at least one other system ($Co(NH_3)_5X^{2+}$, $X = Cl, Br, I$)[22] have conclusively shown that a pentaco-ordinate intermediate is not involved in aquation, and further, the entering water may well come from promoting metal ion's co-ordination sphere[21] while the substrate is in the $Co(NH_3)_5X\text{–}M(H_2O)_x{}^{y+}$ ($M = TI, Ag$) binuclear form.

Results obtained by others[3,14,23] for the *cis*-$Co(en)_2ClX^{n+}$ complexes are shown in Table I. Of particular interest is the fact that *cis*-$Co(en)_2(sol)Cl^{2+}$ (sol = dma and dmso)[23] aquate co-ordinated solvent with stereochemical change. It has been argued that since there is a common product distribution (83 ± 3% *cis*) and since, at that time, this was the only established case of *cis* aquation with stereochemical change, a common five co-ordinate intermediate was involved[23]. We have shown, however, that *cis*-$Co(en)_2Br_2{}^+$ aquates with stereochemical change without the intervention of such an intermediate; moreover the leaving groups involved are possibly too similar to each other (and to the solvent water) for the common aquation steric course result to be conclusive in itself. However, this stereochemistry is very close, if not identical, to that found for the promoted aquations of *cis*-$Co(en)_2Cl_2{}^+$ (Hg^{2+}) and *cis*-$Co(en)_2ClN_3{}^+$ (NO^+) where there is a significant leaving group variation; this would seem to indicate that indeed a common pentaco-ordinate intermediate is involved in all these reactions. This conclusion is supported by the fact that the two spontaneous aquations (*cis*-$Co(en)_2ClX^+$, X = Cl and Br) give quite a different steric course (100% *cis*, Table I).

The data for $Co(en)_2(OH)X^{n+}$ complexes ($X = Cl, Br, OH_2$) are interesting because here a common

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* This result appears in the Table in ref. 2 but no details were given in the cited reference.

product distribution is found in spontaneous aquation (Table I). Steric change is marked for the *trans* isomers and the constant product ratio is well defined; however, the *cis* forms aquate with retention[14]. It seems very likely that, at least for the *trans* species, a common intermediate is involved. An argument maintaining fortuitous agreement of the steric course in three cases is difficult to sustain. Moreover, in spontaneous aquation of other complexes (*e.g.* *trans*-$Co(en)_2ClX^+$ and *trans*-$Co(en)_2BrX^+$, Table I) a distinct difference in steric course is found when the leaving group X is changed from Cl to Br. Therefore, in *trans*-$Co(en)_2(OH)X^{n+}$ aquation there should be sufficient difference in the leaving groups for their effects to be manifest if reaction did not involve a common five coordinate intermediate.

It has been suggested that a hydroxo amine Co(III) complex can react by way on an "internal S_N1cb" mechanism;[24] the co-ordinated hydroxo ligand abstracts an amine proton to generate a reactive amido complex. Recent studies in polyamine Co(III) systems (trien[25], cyclam[24], and 3,2,3-tet[26]) have shown that in isomerization, mutarotation, and racemization studies of complexes containing chiral amine donor atoms, deprotonation at a secondary nitrogen atom is in some way intimately connected with deprotonation at oxygen when there is a co-ordinated aquo group. The unusual lability of hydroxo complexes therefore seems to require the presence of an amine group containing an acidic hydrogen. We have recently shown that *Λ-cis*-$Co(diars)_2(OH_2)(OH)^{2+}$, which has no acidic protons on the arsine ligand, is remarkably optically stable and is several orders of magnitude less reactive than its bis(ethylenediamine) analogue[27]. This evidence strongly supports the "internal S_N1cb" mechanism for the unusually rapid *trans*-$Co(en)_2(OH)X^{n+}$ aquations. Therefore these aquations can be considered entirely equivalent to base hydrolysis[28] of *trans*-$Co(en)_2(OH_2)X^{(n+1)+}$ where deprotonation occurs *effectively* at nitrogen. Considered this way, the common stereochemistry in *trans*-$Co(en)_2(OH)X^{n+}$ aquation is not surprising; pentaco-ordination is base hydrolysis of amine Co(III) complexes is well established[28]. We should note in passing that the above rationale is open to experimental verification since each act of *trans*-$Co(en)_2(OH)X^{n+}$ aquation* should lead to the exchange of one nitrogen proton in the product. Proton exchange studies have recently been reported for *trans*-$Co(en)_2(OH)Cl^+$ in connection with base hydrolysis[29] but this particular question seems to remain unanswered.

In conclusion, we should note that some care has been taken in interpreting the stereochemical results since it has been pointed out[18] that leaving group effects can be subtle. This has previously been recognized in applying the criterion of five co-ordinate intermediate formation which requires the aquation product distribution to be strictly leaving group independent[1–4,6]; the close agreement between results for both Hg^{2+} and NO^+ promoted aquations, complemented by competition studies, has provided the strongest evidence for intermediates. The properties of these intermediates are fully discussed elsewhere[6].

It is now generally recognized that dissociation is well advanced at the (first) transition state in Co(III) aquation, yet surprisingly the effect of the leaving group on the steric course of aquation is still usually evident in spontaneous aquation. This would seem to support the case that pentaco-ordination does not generally follow dissociation except in promoted aquation (and in base hydrolysis[28], which we have argued to include the aquation of the hydroxo complexes). Although there is no reason to expect black and white behaviour[18,19], we have attempted to more accurately measure steric course in order to make clearer distinctions in stoichiometric mechanism[18] where possible.

Finally we should note that in the few studies of complexes involving neutral leaving groups and for which reliable steric course data is available, all the reactions would appear to involve genuine five coordinate intermediates (six examples, Table I). It is tempting to relate this to promoted aquation where the leaving groups are also formally neutral but these examples are too few on which to generalize. Note that in at least one case ($Co(NH_3)_5(OH_2)^{3+}$ [18]) it would appear that anation of the neutral aquo group does not proceed *via* the $Co(NH_3)_5{}^{3+}$ intermediate[4,6], although this does preclude the possibility that water exchange involves this species. $Co(NH_3)_5(OH_2)_2{}^{3+}$ can be obtained with a stereospecifically labelled *trans*-$^{15}NH_3$ or ND_3 group but the strict retention in substitution precludes direct experimental testing of this point.

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* By the [OH^-] *independent* path; proton exchange will of course occur in the [OH^-] dependent path.

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