Coordination Chemistry Reviews
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

STEREOCHEMICAL CHANGES DURING OCTAHEDRAL SUBSTITUTION REACTIONS

RONALD D. ARCHER

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002 (U.S.A.)

(Received March 14, 1969)

CONTENTS

ABBREVIATIONS

en = ethylenediamine
bipy = 2,2′-bipyridine
ophen = 1,10-phenanthroline
trien = triethylenediamine (1,4,7,10-tetraazadecane)
2,3,2-tet = 1,4,8,11-tetraazaundecane
cyclam = 1,4,8,11-tetraazacyclotetradecane
DMA = dimethylacetamide
DMF = dimethylformamide
DMSO = dimethylsulfoxide
TMS = tetramethylenesulfoxide (sulfolane)
pn = propylenediamine (1,2-diaminopropane)
diars = *o*-phenylenebisdimethylarsine
NSSN = 1,10-diaza-4,7-dithiodecane (or its 5-methyl derivative)

A. INTRODUCTION

The interest in octahedral substitution reaction stereochemistry and the reaction mechanisms of such reactions is enjoying a continued upward surge. And while a general consensus has been reached regarding the reaction modes for most cobalt(III) substitution reactions; *i.e.*, dissociation and dissociative interchange[1–5], the ability to predict which substitution reactions will undergo stereochemical rearrangements during the substitution process is lacking[6,7]. A few general statements can be made:

(i) Stereochemical changes occur more often during cobalt(III) substitution reactions than during the corresponding reactions of other inert trivalent transition metal ions for which data is available; *i.e.*, chromium(III), ruthenium(III), rhodium(III), and iridium(III)[6,8,9].

(ii) Stereochemical change (stereomobility)[10] and ligand field strength appear to have an inverse relationship within a series of metal ions with the same electronic configuration; such as iron(II), cobalt(III), rhodium(III), iridium(III), and platinum(IV), which are all $t_{2g}{}^6$ in inert, low spin, octahedral complexes[6,10,11]. Only the first two show stereochemical changes during substitution reactions.

(iii) Within a series of similar cobalt(III) species in which only one non-substituting ligand is varied, aquation stereomobility appears related to the π-donor abilities of the varied ligand[12,13]. However, the simple S_N1 explanation of the stereochemical changes observed during the spontaneous aquation reactions for the *trans*-$[Co(en)_2LCl]^{n+}$ ions relative to the retention observed for the corresponding *cis* ions lacks validity since induced aquations, which are more likely to have true five-coordinate (S_N1) intermediates, often produce different stereoisomers than the spontaneous aquations[14–17]. Extension of the π-bonding concept to base hydrolysis stereochemical observations also shows promise[18].

With the availability of better instrumentation and the guidelines of past research successes and failures as guides, new significant results in this area are rapidly appearing. Therefore, even though Basolo and Pearson[8] published a long chapter on stereochemical changes in octahedral complexes in their revised text, Basolo[6] published a more significant and updated review with the same copyright year (1967). Since the Basolo review was written an appreciable number of significant experimental and theoretical articles have appeared which makes the current review both timely and important. To illustrate, examples of recent experimental results from Australia include induced[17,19,20] and spontaneous[20] aquation stereochemistry, base hydrolysis stereochemistry[19,21], differing stereochemical results for ion-pair and ion-triplet anation reactions[22], a compilation of isomerization, solvolysis, ion association, and solvation effects for *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ in six solvents[23], etc.

A slightly earlier review by Tobe[7] also has been valuable to the reviewer. The well-written and now classical octahedral reaction stereochemical review by

Basolo^{24} and modified versions thereof$^{25-27}$ are noteworthy because of their usefulness for more than a decade.

B. INTERMEDIATES AND REACTION PRODUCT STEREOCHEMISTRY

(i) *Dissociative reactions*

Although up to thirty stereoisomers can exist for an octahedral complex $[\mathrm{MBCDEFG}]^n$ produced by the general reaction

$$[\mathrm{MABCDEF}]^m + \mathrm{G} \rightarrow [\mathrm{MBCDEFG}]^n + \mathrm{A} \qquad (1)$$

where M is a metal ion and A, B, C, D, E, F, and G are electron pair donor atoms; *i.e.*, ligands or donor atoms of chelating ligands, only five such isomers are expected by normal dissociative (D)^{28} or unimolecular $(\mathrm{S_N1})^{24}$ reaction paths from a specific $[\mathrm{MABCDEF}]^m$ isomer as shown in Figure 1. This general scheme also can be used to predict substitution products for more symmetrical complexes and for chelated species^{10}. The general diagram is used by letting the ligand donor atoms of an actual octahedral complex replace A through F with the leaving group in position A, and any chelated ligands in sterically possible positions. If any of the products are sterically impossible they are deleted. Furthermore, two or more of the five products are often identical in more symmetrical cases. Figure 2 illustrates the use of the general scheme to predict possible substitution products for an

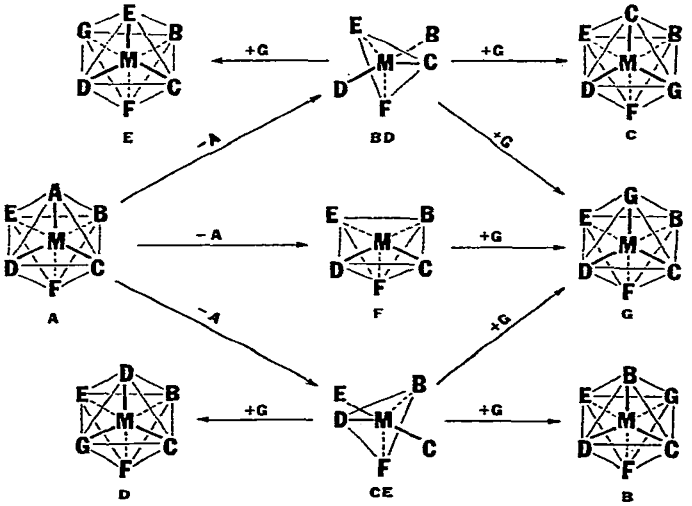


Fig. 1. General substitution stereomobility illustrating dissociative intermediates. Octahedral species named according to ligand *trans* to F. The intermediates named according to the ligand(s) on the principal C_n axis.

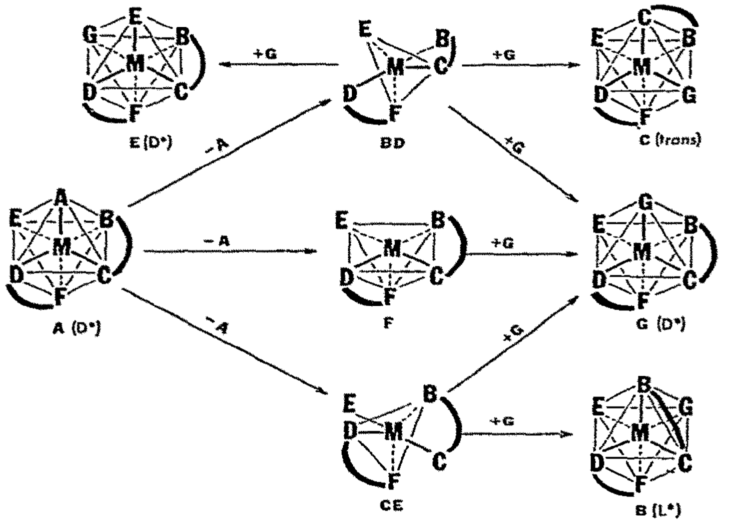


Fig. 2. Use of the general substitution stereomobility diagram for a *cis* complex with two bidentate and two unidentate ligands.

octahedral complex with two bidentate ligands and two *cis* unidentate ligands, one of which is replaced. Note that isomer D is deleted since a normal chelate ring of five or six atoms cannot span *trans* positions. Note that the two D* products may be different for species with unsymmetrical bidentate ligands, but are identical for complexes with two symmetrical ligands. The D* and L*cis isomer designations are the right- and lefthandedness of the complexes relative to the C_2 axis[29] of

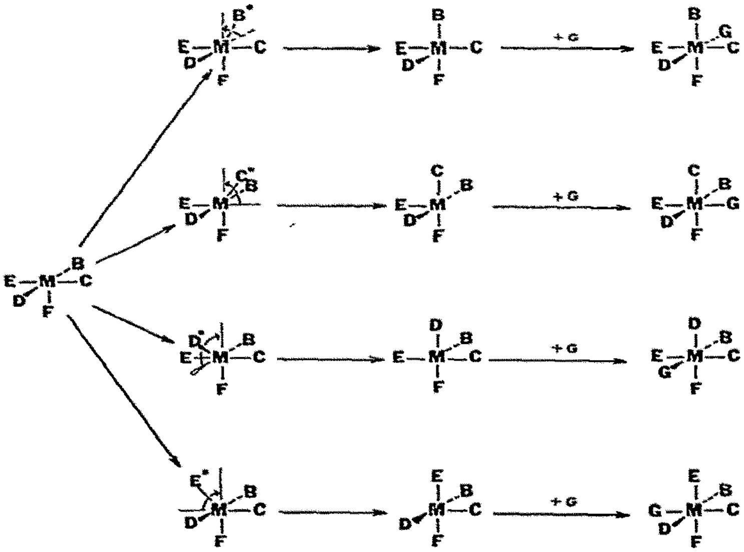


Fig. 3. Rearrangement of tetragonal pyramid F of Fig. 1. Multiple rearrangements would give other isomers in addition to those shown in these figures.

cis complexes which have two identical unidentate ligands and two identical, symmetrical bidentate ligands.

Rearrangement of the tetragonal pyramid shown in Figure 1 to other tetragonal pyramids would also give the products labeled B, C, D, and E in Figure 1 as is shown in Figure 3, where B*, C*, D*, and E* are anticipated transition states. Multiple rearrangements of this type would allow other isomers, such that a scrambling to the most thermodynamically stable tetragonal pyramid should occur if the time of rearrangement is considerably less than the time required for the addition of a sixth ligand. Currently available data do not support multiple rearrangements of this type as frequent (or even infrequent) occurrences[7]. Entropy considerations[3] appear to eliminate them for normal aquation rearrangements.

(ii) *Interchange reactions*

The same five product possibilities are predicted for an interchange process, in which one of the solvent or other nucleophilic species in the second coordination sphere exchanges with one of the ligands in the normal coordination sphere. Although seven groups are bonded to the metal in the interchange mechanism, two of the seven are normally only weakly bonded in the dissociative interchange process (I_d)[28] believed to predominate in reactions of octahedral complexes of the first transition series. If the entering group appreciably affects the substitution process, the reaction may lie on the associative side (I_a-interchange associative) See, for example, reference 30. If the interchange occurs *cis* to the leaving group (Figure 4) the product should have a retained configuration (G of Figure 1),

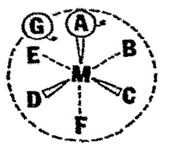


Fig. 4. Interchange reaction with *cis* attack; retained product results.

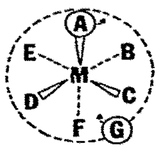


Fig. 5. Interchange reaction with *trans* attack; rearrangement to isomers B, C, D, and E of Fig. 1 should occur.

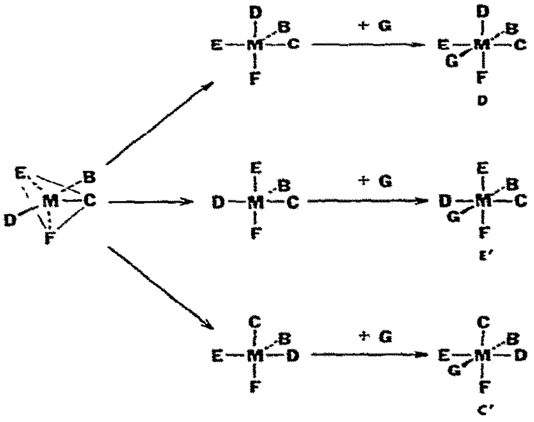


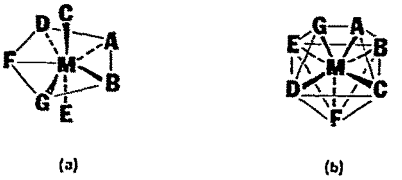
Fig. 6. Trigonal bipyramidal rearrangements would give isomers other than those indicated in Fig. 1. Only the rearrangements which place B in the plane are shown; similar rearrangements for D in the plane could also occur. Trigonal bipyramid CE would give new isomers, too.

whereas a *trans* type interchange (Figure 5) should produce the other four isomers (B, C, D, and E of Figure 1). The relative amounts of these latter four isomers should depend upon the size, shape, polarity, and bonding character of ligands B through F. The *cis* interchange to *trans* interchange ratios should depend on the same factors noted above for all six ligands and on the electronic configuration of the metal ion. Hence, isomer predictions are difficult for such reactions.

The return of one of the trigonal bipyramids of Figure 1 to a tetragonal pyramid prior to the restoration of coordination number six might be possible through an interchange process. Such a rearrangement gives unique isomer possibilities (Figure 6), but appears unnecessary at present[7].

(iii) *Bimolecular reactions*

True bimolecular nucleophilic substitution reactions (S_N2 or A)[28] should also produce the same five isomers. Again several factors (the same ones noted above) determine the relative isomer ratios. Again, attack near the leaving group (*cis* attack) produces a retention of configuration. With reference to A of Fig. 1, attack by G above the BCDE plane will produce isomer G if A is displaced. A 2:4:1 octahedral wedge (Figure 7) is the logical intermediate for such bimolecular retention reactions[31], which differ from the corresponding interchange retention reactions only in the relative amounts of bond making and bond breaking in the transition state of lowest energy. Attack from a position well removed from the leaving group (*trans* attack) will logically give the other four isomers. For example, again with reference to species A of Figure 1, a group G attacking $[\text{MABCDEF}]^m$ in the CDF face is expected to produce isomer C or D when A is displaced. Similar attack of facial regions DEF, EBF, and BCF should produce D or E, E or B, and B or C, respectively. Again steric or electronic effects will give varied isomer ratios.



(a) (b)

Fig. 7. Bimolecular or associative intermediates for octahedral substitution reactions; (a) pentagonal bipyramid of pseudo D_{5h} symmetry; (b) octahedral wedge of pseudo C_{2v} symmetry.

Attempts to rationalize the activation energy and mechanistic observations for octahedral substitution reactions in terms of crystal field theory[32], ligand field theory[33], and molecular orbital theory[34,35] are less than satisfactory in terms of predicting reactions which will give stereochemical changes. None of the calculations give results which allow the trigonal bipyramid to compete with the tetragonal pyramid for d^6 ions. One reason is the lack of non-bonding interactions in the calculations. In fact, both the crystal field[10,32] and ligand field[33] calculations suggest the pentagonal bipyramid as the logical intermediate for d^6 stereochemical changes, even though it is a bimolecular intermediate—in direct opposition to mechanistic conclusions that most of the reactions are more dissociative than associative[1–5].

C. AQUATION STEREOCHEMICAL CHANGES

(i) *Spontaneous cobalt(III) aquation reactions*

In water, aquation is synonymous with the term acid hydrolysis. For octahedral complexes both terms imply the general reaction

$$[\mathrm{MABCDEF}]^n + \mathrm{H_2O} \rightarrow [\mathrm{MBCDEF(H_2O)}]^{n-a} + \mathrm{A}^a \tag{2}$$

using the symbolism developed in Section B(i). The term spontaneous aquation means that no catalyst has been added, in contrast to induced aquation reactions, which are chemically or photochemically catalyzed.

Aquation stereochemistry has been studied for a large number of cobalt(III) complexes. Sometimes the aquation reaction is followed by an isomerization reaction, and in a few cases the latter is so rapid that the aquation stereochemistry is difficult, if not impossible, to follow. Systematic results for the spontaneous aqua-

TABLE 1

SPONTANEOUS AQUATION STEREOCHEMISTRY AND ACTIVATION PARAMETERS FOR SOME *trans*-COBALT-(III) COMPLEXES[a]

$[\mathrm{CoABCDEF}]^n + \mathrm{H_2O} \rightarrow [\mathrm{CoBCDEF(H_2O)}]^{n-a} + \mathrm{A}^a$

A	*BCDE*	*F*	*k(sec⁻¹, 25°)*	*ΔH‡, kcal mole⁻¹*	*ΔS‡, e.u.*	*% stereo-change*	*Ref.*
$\mathrm{Cl^-}$	SS-trien	$\mathrm{Cl^-}$	3.5×10^{-3}	25.5	+16	100	35, 37
$\mathrm{Cl^-}$	RR, SS-2,3,2-tet	$\mathrm{Cl^-}$	[b]	25.1	+ 9	95	7
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{OH^-}$	1.6×10^{-3}	25.9	+20	75	38
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{NCS^-}$	5×10^{-8}	30.2	+ 9	60 ± 10	39, 40
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{Br^-}$	4.5×10^{-5}	24.9	+ 3	50	41
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{Cl^-}$	3.5×10^{-5}	26.2	+14	35	38, 42
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{N_3^-}$	2.2×10^{-4}	22.5	0	20	43
$\mathrm{Cl^-}$	RS-2,3,2-tet	$\mathrm{Cl^-}$	[b]	23.7	− 1	0	7
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{CN^-}$	8.2×10^{-5}	22.5	− 2	0	44
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{NO_2^-}$	9.8×10^{-4}	20.9	− 2	0	45
$\mathrm{Cl^-}$	cyclam	$\mathrm{Cl^-}$	1.1×10^{-6}	24.6	− 3	0	46
$\mathrm{Cl^-}$	cyclam	$\mathrm{OH^-}$	1.2×10^{-2}	18.1	− 7	0	46
$\mathrm{Cl^-}$	$\mathrm{(en)_2}$	$\mathrm{NH_3}$	3.4×10^{-7}	23.2	−11	0	47
$\mathrm{Br^-}$	$\mathrm{(NH_3)_4}$	$\mathrm{NH_3}$	6.3×10^{-6}	23.3	− 4	0[c]	48, 49

[a] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values based on recent values of Tobe[3].

[b] Unpublished; see ref. 3.

[c] Stereochemistry based on *trans*-$[\mathrm{Co(NH_3)_4(ND_3)Br}]^{2+}$ aquation[20]. *trans*-$[\mathrm{Co(NH_3)_4Cl_2}]^+$ shows about 55 ± 10% stereochemical change, $k = 2 \cdot 10^{-3}$, $\Delta H^* = 23.6$, $\Delta S^* = 9$ [ref. 148].

tion of several cobalt(III) complexes for which both stereochemical and activation parameter data is available are given in Table 1. The enthalpies of activation ($\Delta H^{\ddagger}$) entropies of activation ($\Delta S^{\ddagger}$) are based largely on a recent compilation by Tobe[3]. The corresponding *cis* isomers for which data is available show complete retention of configuration during the spontaneous aquation reactions. A comparison of the

TABLE 2

ACTIVATION PARAMETERS FOR THE SPONTANEOUS AQUATION OF SOME COBALT(III) COMPLEXES[a]

$[CoL_4L'Cl]^n + H_2O \rightarrow [CoL_4L'H_2O]^{n+1} + Cl^-$

Complex		$\Delta H^{\ddagger}$ *(cis)*	$\Delta S^{\ddagger}$ *(cis)*	$\Delta H^{\ddagger}$ *(trans)*	$\Delta S^{\ddagger}$ *(trans)*
L_4	L'				
trans ion rearranges but *cis* ion does not					
en$_2$	OH^-	23	+10	26	+20
en$_2$	Cl^-	21½	− 5	26	+14
en$_2$	Br^-	23½	+ 5	25	+ 3
en$_2$	NCS^-	20	−14	30	+ 9
en$_2$	N_3^-	21	− 4	22½	0
trien[b]	Cl^-	α21	− 6	25½	+16
		β20	− 3		
RR, SS-2,3,2-tet	Cl^-	[c]	[c]	25	+ 9
both *cis* and *trans* ions aquate with retention of configuration					
en$_2$	NH_3	24½	− 6	23	−11
en$_2$	NO_2^-	22	− 3	21	− 2
cyclam	Cl^-	18½	− 6	24½	− 3

[a] $\Delta H^{\ddagger}$ (kcal/mole) and $\Delta S^{\ddagger}$ (e.u.) values based on compilation by Tobe[3].

[b] trien complexes: SS-trien for *β-cis* and *trans* species; see ref. 37 for a detailed discussion of coordinated trien configurations.

[c] Unavailable, see ref. 3.

activation parameters for a number of *cis* and *trans* ions are shown in Table 2. Results to date suggest several tentative conclusions:

(i) No apparent relationship exists between reaction rate and stereochemical change. Hence, no $\Delta G^{\ddagger}$ relationships are found since

$$k = \frac{RT}{Nh} \exp\left(-\Delta G^{\ddagger}/RT\right) \tag{3}$$

from transition state theory, where k is the specific rate constant, R is the gas law constant, T is the absolute temperature, N is Avogadro's number, h is Planck's constant, and $\Delta G^{\ddagger}$ is the free energy of activation. As written any changes in the transmission coefficient is included in the activation free energy. Furthermore, the equation is valid for an assumed equilibrium between the ground and activated states. Even though no regularities can be observed from the free energy of activation, a breakdown into enthalpy and entropy of activation terms indicates regularities (ii) and (iv).

(ii) The *trans* ions which exhibit stereochemical changes during aquation have higher entropies of activation than do the isomers which aquate with retention of configuration[3]. Tobe[3] has interpreted this observation to mean that "...the grosser aspects of the steric course of aquation are determined in the rate-determining transition state", and has concluded that the entropy of activation can be used, at least in complexes with four amine groups *cis* to the leaving group, to decide which reactions undergo at least some stereochemical change. He suggests that the higher entropies imply an incident if not actual trigonal bipyramid, whereas the lower entropies are associated with an incipent tetragonal pyramid, or at least a retained reaction product; *i.e.*, an interchange or solvent dissociated reaction doesn't change the arguments. Alternatively, the higher entropy of activation could result from a change in spin state. Both spin-free and triplet states allow the trigonal bipyramid to compete better energetically with the tetragonal bipyramid[11,33], and higher entropies are associated with higher spin states.

(iii) Aquation reactions of cobalt(III) give retained configurations unless the group *trans* to the leaving group has unpaired electrons and the four groups *cis* to the leaving group do not[13]. This observation has been used in the past to imply that *trans* hydroxo or chloro ligands must rearrange toward a trigonal bipyramid in order to labilize the leaving group; *e.g.*, ref. 50. The results with cyclam[46] should dispel the idea that the *trans* ligands with extra unshared pairs must rearrange. In fact, the enthalpy of activation for one of the cyclam complex reactions is considerably lower than the corresponding ethylenediamine complex reaction, even though the cyclam species reacts without rearrangement. The induced aquation results discussed below in Section C(ii) are most readily interpreted if the spontaneous aquations of at least some of the stereomobile species are not simple dissociation processes. The fact remains though that many cobalt(III) complexes with four amine donors with negligible π interactions *cis* to the leaving group and a π donor ligand *trans* to the leaving group do undergo at least partial stereochemical changes during spontaneous aquation; whereas cobalt(III) complexes with one or more π donor ligands *cis* to the leaving group aquate without any stereochemical change.

(iv) The complexes for which changes in configuration occur during spontaneous aquation of the *trans* but not the *cis* ions exhibit spontaneous aquation activation parameters

$$\Delta H^{\ddagger}(cis) < \Delta H^{\ddagger}(trans) \tag{4}$$

and

$$\Delta S^{\ddagger}(cis) \leq \Delta S^{\ddagger}(trans) \tag{5}$$

That is, a comparison of both the *cis* and *trans* complexes in Table 2 indicates that invariably the stereomobile *trans* ions are inherently less inclined to react in terms of enthalpy than are the retentive *cis* species. On the other hand, species which react with retention of configuration for both isomers have *trans* ions with lower enthalpies of activation than the corresponding *cis* species. It appears probable that if these latter *trans* complexes needed more energy for spontaneous aquation, stereomobility might have been observed for these as well. In fact, isomerization and retentive aquation energetics can be fairly similar. For example, the reaction path which allows the isomerization of *trans*-$[Co(en)_2NH_3H_2O]^{3+}$ is only about five kcal/mole less favored than the water exchange, which goes by retention of configuration[51].

Attempts to calculate which complexes should rearrange and which should not have not been too successful to date. Noting that the ground states for a d^6 trigonal bipyramid and a d^6 pentagonal bipyramid (the two intermediates which can give rearrangement) are triplet states, Spees, Perumareddi, and Adamson[33] conclude by ligand field calculations that the pentagonal bipyramid is the one which should compete with the tetragonal pyramid for cobalt(III) complexes, anyway. This conclusion is at odds with the general interpretations made for cobalt(III) complexes by most investigators in the field[1-5]. The molecular orbital approach of Yatsimirskii[34,35] when modified to give energies for species in which all groups are not equal does indicate that the trigonal bipyramid rather than the pentagonal bipyramid has the lower energy, but for real species with parameters based on spectral data the trigonal bipyramid does not compete with the tetragonal pyramid by such calculations[52]. However, the fact that good results are not obtained by such calculations should not be surprising considering the number of approximations made in the calculations. Normally no modification of σ bond strength is made in going from one geometry to another even though electronic interactions should change appreciably in going to a trigonal or pentagonal bipyramid due to repulsion between antibonding electrons in the d_{xy} and or $d_{x^2-y^2}$ orbitals and the σ electron pairs in the xy plane. Furthermore, most calculations have not included ligand–ligand repulsions, considerations of the solvent interactions of the outer sphere, or the interactions of the incoming group, which must affect the energy of the system in an interchange process to some extent.

The entropies of activation also tend to affirm the idea that these reactions should be treated as interchange reactions rather than as simple dissociative processes. A comparison of the $\Delta S^{\ddagger}$ values in Tables 1 and 2 with those for water exchange about aluminum(III) and gallium(III)[53] are enlightening. Aluminum(III), which is smaller than cobalt(III), exhibits water exchange with an entropy of activation of +28 e.u., consistent with a dissociative (D or S_N1) process in which disorder occurs as the transition state is approached; whereas, gallium(III), which is larger than cobalt(III), has an entropy of activation of −22 e.u., as expected for an associative (A or S_N2) reaction which undergoes the ordering of an added group in the transition state or activated intermediate. The entropies of activation for the cobalt(III) species are intermediate, consistent with the interchange (I_d or I_a) process. The arguments favoring the I_d mechanism over the I_a one for cobalt(III) complexes have been detailed elsewhere[1-5].

A recent aquation study by Lincoln and Stranks[54] with the *cis* $[Co(en)_2(OH)(PO_4)]^-$ and $[Co(NH_3)_4(OH)(PO_4)]^-$ anions is inconclusive since isomerization reactions are too fast for the investigators to separate from the aquation. Lincoln and Stranks[54] do bring out an interesting point regarding the calculations of entropies of activation. If one realizes that the rate of an interchange reaction is dependent on water availability, a specific rate constant that excludes the water concentration from the observed rate constant gives an entropy of activation which differs from a water inclusion value by 8 e.u.

(ii) *Induced cobalt(III) aquation reactions*

Chemically induced aquation reactions have yielded some surprises. In fact, the induced aquations of cobalt(III) species as tabulated in Table 3 are indicative

TABLE 3

SPONTANEOUS *vs.* CHEMICALLY INDUCED AQUATION COBALT(III) STEREOCHEMISTRY[a]

$[Co(en)_2LX]^{n+} + H_2O \rightarrow [Co(en)_2L(H_2O)]^{n-x} + X^x$

Reactant	*Product*	*%Stereochemical change*			
LX	*LH_2O*	*Spontaneous*	*HONO*	*H^+*[c]	*Hg^{2+}*[d]
D*-*cis* $(N_3)_2$	N_3H_2O		16 *trans* (84 D*)[e]		
cis $(N_3)_2$	N_3H_2O			<5	
D*-*cis* N_3Cl	N_3H_2O	0 (100 D*)[e]			16 *trans* (84 D*)[e]
D*-*cis* ClN_3	ClH_2O		21 *trans* (79 D*)[e]		
D*-*cis* Cl_2	ClH_2O	0 (100 D*)			24 *trans* (77 D*)[e]
cis ClBr	ClH_2O	<5			
D*-*cis* H_2ON_3	$(H_2O)_2$		0 (100 D*)		
D*-*cis* H_2OCl	$(H_2O)_2$				0 (100 D*)
cis H_2OCl	$(H_2O)_2$	0–10			
cis H_2OBr	$(H_2O)_2$				0–5
D*-*cis* NH_3Cl	NH_3H_2O	0[f]			0[g]
D*-*cis* NH_3Br	NH_3H_2O				0[g]
D*-*cis* NH_3N_3	NH_3H_2O				
trans $(N_3)_2$	N_3H_2O		0	0	Little
trans N_3Cl	N_3H_2O	20			0
trans ClN_3	ClH_2O		27		
trans Cl_2	ClH_2O	35			28
trans ClBr	ClH_2O	20; 35			
trans BrCl	BrH_2O	50[f]			
trans H_2OCl	$(H_2O)_2$	0–50			40
trans $(H_2O)_2$	$(H_2O)_2$	38 *calcd*			
trans H_2ON_3	$(H_2O)_2$		40		
trans NH_3Cl	NH_3H_2O	0[h]			0[g]
trans NH_3N_3	NH_3H_2O		0[g]		

[a] Data based largely on tabulation by Loeliger and Taube[16].

[b] Reaction rate considered accelerated by the reaction sequence $HONO \rightleftarrows NO^+ + OH^-$ (fast, reversible); $NO^+ + L_5M{-}N_3^- \rightarrow L_5M + N_2\uparrow + N_2O\uparrow$

[c] $L_5M{-}N_3^- + H^+ \rightarrow L_5M + HN_3$

[d] $L_5M{-}Cl^- + Hg^{++} \rightarrow L_5M + HgCl^+$, etc.

[e] Ref. 17.

[f] Ref. 20.

[g] Ref. 3.

of the difficulty in predicting reaction stereochemistry of transition metal ion substitution reactions.

Whereas *cis*-$[Co(en)_2Cl_2]^+$ reacts slowly with water to give 100% *cis*-$[Co(en)_2Cl(H_2O)]^{2+}$, Sargeson[14] noted that the addition of Hg^{2+} induces a rapid aquation reaction which gives a mixture of *cis*- and *trans*-$[Co(en)_2Cl(H_2O)]^{2+}$. A more recent study[17] indicates

$$\text{D}^*\text{-}cis\text{-}[Co(en)_2Cl_2]^+ \xrightarrow[\text{Hg}^{2+}\text{ induced}]{\text{H}_2\text{O}} \left.\begin{array}{r} 76\text{–}78\%\ \text{D}^*\text{-}cis\text{-} \\ 24\%\ \ trans\text{-} \end{array}\right\} [Co(en)_2Cl(H_2O)]^{2+}$$

$$\xrightarrow[\text{spontaneous}]{\text{H}_2\text{O}} 100\%\ \text{D-}cis\text{-}[Co(en)_2Cl(H_2O)]^{2+} \qquad (6)$$

None of the mirror image (L*) isomer was observed in either the spontaneous or the chemically induced aquation reactions of the optically active dichloro ion. The mechanistic implications are discussed below.

Studies with the D*-*cis* and *trans* isomers of $[Co(en)_2N_3X]^+$ type species are equally important. Whereas the D* species where X = Cl spontaneously aquates with complete retention of configuration, the Hg^{2+} induced aquation yields about 16% *trans* aquation product. Conversely, although the *trans* ion where X = Cl aquates with about 20% stereochemical change, the Hg^{2+} induced aquation reaction gives very little, if any, *cis* product. Furthermore, the intermediates in these induced reactions appear to be five coordinate ones inasmuch as the HONO catalyzed aquations for similar species but where X = N_3 give identical stereochemical product compositions as do the Hg^{2+} aquations where X = Cl. (See Table 3 for details and references.) If the leaving group had an effect on the reaction stereochemistry, changing from chloride to azide should show some variation in stereomobility. Azide is known to be more strongly bonded to cobalt(III) than is chloride. Evidence for this is found in the spontaneous aquation reactions of chloroazido complexes; *i.e.*, these reactions only yield aquaazido species.

Assuming the nitrous acid and mercuric ion induced aquations involve five coordinate intermediates, the product stereochemistries indicate that two intermediates are involved in *cis* induced aquations. The appropriate intermediates are the BD and F intermediates of Fig. 2. The lack of any inverted or racemic product eliminates the CE intermediate. The antibonding effect calculated for the intermediates generated by the loss of one chloride from *cis*-$[Co(en)_2Cl_2]^+$ (Table 4) are consistent with the experimental results inasmuch as the trigonal bipyramid with the chloro ligand in the trigonal plane has 16,000 cm^{-1} (about 46 kcal.) less antibonding repulsions than the trigonal bipyramid with the chloro ligand in the axial position. As noted earlier, however, these calculations make the tetragonal pyramid much more stable than either trigonal bipyramid, but steric and solvation effects are completely neglected in such calculations.

The lack of racemization during the advent of some stereochemical change in these induced aquations eliminates seven coordinate and other intermediates of

TABLE 4

ANTIBONDING EFFECTS FOR SEVERAL COBALT(III) COMPLEXES AND INTERMEDIATES

Complex	*d-orbital antibonding energies (kK)*[a]	*Total spin-paired* d^6 *antibonding effect (kK)*[b]
cis-$[Co(en)_2Cl_2]^+$	8, 8, 16, 69, 69	64
$\{Co(en)_2Cl\}^{2+}$tetragonal pyramid Cl in plane	0, 8, 8, 46, 69	32
$\{Co(en)_2Cl\}^{2+}$trigonal bipyramid Cl at xy coordinate	4, 4, 26, 34, 63	68[c]
$\{Co(en)_2Cl\}^{2+}$trigonal bipyramid Cl in axial position	8, 8, 26, 26, 63	84[d]
cis-$[Co(en)_2Cl(H_2O)]^{2+}$	2, 8, 10, 67, 69	40
trans-$[Co(en)_2Cl(H_2O)]^{2+}$	0, 10, 10, 67, 69	40

[a] Calculations based on angular parameter model[55,56] used for ML_6 species by Yatsimirskii[34,35] as modified[52] to allow for complexes with nonequivalent ligands. kK = 1000 cm^{-1} = 2.86 kcal/mole. Parameters based on spectral data tabulated by Wentworth and Piper[57], but using nomenclature of Yatsimirskii[34,35]. $\Delta\sigma(en) = 23\ kK$; $\Delta\pi(en) = 0\ kK$; $\Delta\sigma(Cl) = 23\ kK$; $\Delta\pi(Cl) = 8\ kK$; $\Delta\sigma(H_2O) = 21\ kK$; $\Delta\pi(H_2O) = 2\ kK$.

[b] Calculations assume electrons are paired in lowest energy orbitals.

[c] If intermediate is ground state triplet, intermediate total antibonding effect = 76 *kK* (pairing energy).

[d] If intermediate is ground state triplet, intermediate total antibonding effect = 84 *kK* (pairing energy).

appreciable bond formation. The seven coordinate intermediates which give *trans* products from *cis* reactants also give some inverted *cis* products, contrary to the induced aquation results.

One curious result—whereas the nitrous acid induced aquation of *cis*-$[Co(en)_2(N_3)_2]^+$ exhibits considerable (~16%) stereochemical change, the H^+ induced aquation appears to give only a little (<5%). The latter result is similar to the spontaneous reaction of the *cis*-azidochloro complex and suggests the possibility of an interchange or concerted reaction. The corresponding *trans*-diazido ion exhibits very little stereomobility using either HONO or H^+ induction.

Substitution reactions of cobalt(III) can also be induced by photochemical *d-d* excitation. (Excitation of the charge transfer bands yields mainly redox reactions.) The aquation quantum yields for the *d-d* transitions are quite small, especially when compared with the *d-d* excitations of chromium(III)[58]. Unfortunately, the stereochemical information available on cobalt(III) photochemical substitution reactions is only fragmentary[58,59].

Similar to the spontaneous and chemically induced substitution reactions, the *trans*-$[Co(en)_2Cl_2]^+$ ion undergoes photochemical aquation with some isomerization[60]. Unfortunately, the percent of stereochemical change is unknown because the study[60] only followed the production of *cis*-$[Co(en)_2Cl(H_2O)]^{2+}$. The corresponding D*-*cis* dichloro ion aquates with at least 50% retention[61], and while a loss in optical activity was observed, the cause could have been photoracemization, photoisomerization, or photoaquation. More information on this topic, still in its infancy, can be found in two recent review articles[58,59]. Note that the cobalt(III) complexes without any π-donor ligands other than the displaced ligand do not undergo any stereochemical changes during either spontaneous or induced aquation reactions. Hence the conclusion may be drawn that cobalt(III) complexes with four amine type ligands *may* undergo stereochemical change during aquation if, and only if, the fifth unreplaced ligand is a π-donor.

Since cobalt(III) complexes with stronger field nitrogen donors such as bipyridine do not show rearrangement during substitution, attempts to correlate ligand field strength and stereochemical change have been made by the present writer[10,11]. Basolo[6] has concurred.

One question has not been answered to date: Which is more important, that one group is a π-donor, or the overall ligand field strength? Aquation studies with complexes containing weaker field ligands should give the answer. Unfortunately, cobalt(III) complexes with several oxygen donor ligands and a halide or two are not available in appropriate stereochemical forms. Use of the *cis* and "*trans*" isomers of $K[Co(NH_3)_2(CO_3)_2]$ (ref. 62) for stereochemical studies[63,64] has led to the discovery that the "*trans*" isomer is mainly $[Co(NH_3)_4(CO_3]$ [*cis*-$Co(NH_3)_2(CO_3)_2$] plus some aquation products, but no evidence for stereomobility has been obtained[65]. Similarly, studies with β-diketone complexes have led to an extreme example of the octahedral *trans* effect (*i.e.*, *trans*-$[Co(acac)_2(NO_2)_2]^-$ aquates orders of magnitude faster than the corresponding *cis* isomer[66,67] but no direct aquation stereomobility has been observed).

Of related interest are the acid cleavage reactions of dimeric complexes bridged with hydroxo ligands. No changes in configuration have been observed during the acid cleavage of $[(en)_2Co(OH)_2Co(en)_2]^{4+}$ with either perchloric or nitric acid—the only product is the *cis* isomer[68] of $[Co(en)_2(H_2O)_2]^{3+}$. Other cleavage reactions of $[(NH_3)_4Co(OH)_2Co(NH_3)_4]^{4+}$ and $[(C_2O_4)_2Co(OH)_2Co(C_2O_4)_2]^{4-}$ probably give retention reactions as well[68]. The latter system is difficult to study since the $[Co(C_2O_4)_2(H_2O)_2]^{2-}$ ion decomposes rapidly to cobalt(II) species. Addition of nitrate to the dimeric oxalate ion while adding sufficient acid to maintain a slight acidity gives a $[Co(C_2O_4)_2(NO_2)_2]^{3-}$ species (along with some cobalt(II) decomposition products)[69]. The dinitro ion has infrared spectral properties consistent with a *cis* configuration[69]. However, no information is available as to the stereospecificity of the latter reaction.

(iii) *Chromium(III) aquation reactions*

As opposed to the cobalt(III) species just discussed, relatively few chromium(III) ions appear to exhibit any stereochemical change during aquation. Retention of configuration appears to be the general rule for most chromium aquation reactions. In fact, the few chromium(III) amine complexes which show such changes appear to do so in competition with nitrogen bond breaking rather than just showing simple halide displacements[70]. For example, while approximately 14% *cis* aquation products appear during the *trans*-$[Cr(en)_2Cl_2]^+$ aquation[71], the results are complicated by *ca.* 10% release of ethylenediamine. One case of stereochemical change[72]

$$\alpha\text{-}cis\text{-}[Cr(trien)Cl_2]^+ \xrightarrow{H_2O} \beta\text{-}cis\text{-}[Cr(trien)Cl(H_2O)]^{2+} \qquad (7)$$

may be due to nitrogen rearrangement. In fact, the authors assumed a retention aquation reaction followed by rapid isomerization by analogy with the retention observed for the corresponding cobalt(III) aquation. The possibility of a concerted reaction path is possible and should not be eliminated. Isolation of the corresponding *α-cis* aquachloro complex may be necessary in order to solve the ambiguity.

Several other chromium(III) complexes have been studied where no rearranged aquation products have been found but where an upper limit of rearrangement has been given. Pertinent data are collected in Table 5.

TABLE 5

CHROMIUM(III) AQUATION STEREOCHEMICAL CHANGE LIMITS[a]

Reactant	*Ligand(s) displaced*	*% Stereochemical change*	*Reference*
α-cis-$[Cr(trien)Cl_2]^+$	Cl^-	≤100[b]	70
trans-$[Cr(en)_2Cl_2]^+$	Cl^- (~90%) en (~10%)	≤ 14[c]	69
trans-$[Cr(en)_2Br_2]^+$	Br^-	≤ 4[c]	71
trans-$[Cr(NH_3)_4Cl_2]^+$	Cl^-	< 8[d]	72
trans-$[Cr(NH_3)_4ClBr]^+$	Br^- (≥87%)	< 5[d]	72
cis-$[Cr(en)_2Cl_2]^+$	Cl^-	< 1[d]	69
cis-$[Cr(en)_2Br_2]^+$	Br^-	< 5[d]	71
cis-$[Cr(en)_2(H_2O)Br]^{2+}$	Br^-	< 10[d]	71
cis-$[Cr(en)_2(NCS)Cl]^+$	Cl^- (≥96%)	≤ 4	73
cis-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$	Cl^-	≤ 5	72

[a] See reference 68 for references to more retention reactions.

[b] The *β-cis* product may arise from product isomerization or aquation (see text).

[c] The *cis* product may arise from reactant isomerization or aquation.

[d] Experiments preclude the detection of stereochemical changes up to this limit.

Rationalization of the greater retention which is normally observed for chromium(III) aquation reactions is often done in terms of π-donor considerations[76]. This line of reasoning suggests that when fewer electrons exist in the t_{2g} metal orbitals, π-donation from a ligand is less apt to perturb the system sufficiently for a change in configuration. The conclusion is also in agreement with the small differences in rate found for base and acid hydrolysis for chromium(III), especially when compared[77] with cobalt(III). Unfortunately, calculations using just the *d*-like orbitals invariably indicate that the energy difference between the tetragonal pyramid, which gives only retention of configuration, and the trigonal bipyramid, which allows changes in configuration, is less for chromium(III) than for cobalt(III)

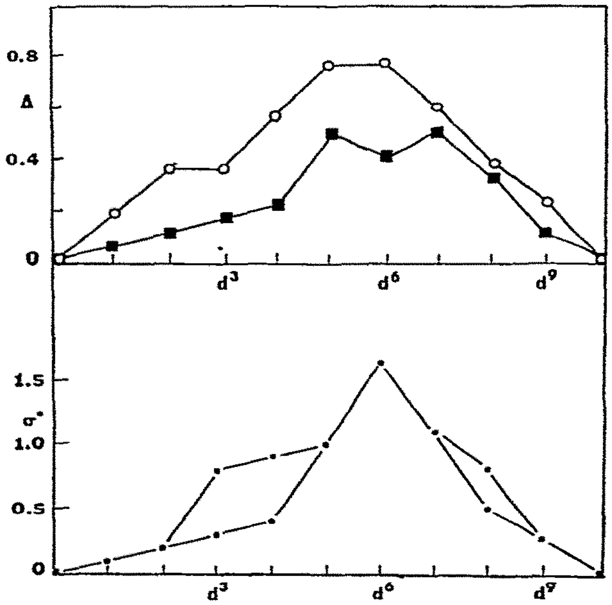


Fig. 8. Extra energy required for trigonal bipyramidal intermediate relative to tetragonal pyramid based on ○—○—○ crystal field or ■—■—■ ligand field where no spin change, and spin change to ground state of intermediate are used, respectively, based on ref. 8 and ref. 33. Lower diagram is angular overlap model calculations for 20% π donation; ■ is for no change in spin from ground state and ● is for ground state of the intermediate, based on Yatsimirskii, ref. 34, 35.

as shown in Figure 8. The steric, solvation, and σ-bonding effects, which are difficult to consider quantiatively in these systems apparently shift the relative energies to a considerable extent.

(iv) *Aquation of other inert metal ions*

Stereochemical data for the aquation reactions of other inert metal ion octahedral complexes are very limited. Platinum(IV), rhodium(III), and ruthenium(III) complexes appear to undergo substitution reactions with almost complete retention of configuration in all cases for which stereochemical data is available[6,76]. The information on inert, spin-paired iron(II) is less certain. Iron(II) forms some inert complexes with two diimine bidentate ligands (*e.g.*, ophen and bipy) and two monodentate ligands, provided the latter are high in the spectrochemical series; ligands such as nitro, cyano, or fulminato[78]. Complexes with weaker field monodentate ligands have quintet or triplet ground states[78,79]. Therefore, water substitution gives labile species not amenable to classical stereochemical studies. However, the tris(diimine) complexes of iron(II) racemize faster than substitution by water takes place[80], hence stereomobility should be observed in the bis(diimine) iron(II) species.

D. BASE HYDROLYSIS STEREOCHEMICAL CHANGES

(i) *Cobalt(III) reactions*

Convincing evidence has accumulated for the conjugate base nature of cobalt(III) amine base hydrolysis reactions[1,7,77]. For an acidopentamminecobalt(III) ion the dissociative conjugate base (S_N1CB) reaction sequence is

$$[Co(NH_3)_5X]^{2+} + OH^- \rightleftarrows \underset{\text{Conjugate base}}{[Co(NH_3)_4(NH_2)X]^+} + H_2O \tag{8}$$

followed by the slower, rate determining step

$$[Co(NH_3)_4(NH_2)X]^+ \rightarrow [Co(NH_3)_4(NH_2)]^{2+} + X^- \tag{9}$$

and the rapid pickup of water and subsequent proton transfer

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightarrow \rightarrow [Co(NH_3)_5(OH)]^{2+} \tag{10}$$

If a negligible amount of the conjugate species is present the rate law is that expected for a second order reaction, first order in complex and first order in hydroxide[81].

An interchange pathway, catalyzed by conjugate base formation, where S is any second (or outer) sphere species of charge s:

$$[Co(NH_3)_5X]^{2+} \cdot S^s + OH^- \rightleftarrows [Co(NH_3)_4(NH_2)X]^+ \cdot Ss + H_2O \tag{11}$$

$$[Co(NH_3)_4(NH_2)X]^+ \cdot S^s \rightarrow [Co(NH_3)_4(NH_2)S]^{s+1} + X^- \tag{12}$$

$$[Co(NH_3)_4(NH_2)S]^{s+1} + H_2O \rightarrow [Co(NH_3)_5S]^{s-2} + OH^- \tag{13}$$

can also be a useful way of considering some of the results[82]. Evidence for the interchange process is found in the concentration dependence of the Bailar inversion reactions [see section D(ii)], the isotope fractionation studies[83] with $[Co(NH_3)_5F]^{2+}$, and the base hydrolysis stereochemistry of *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl](ClO_4)_2$ in the presence of added azide ion[84]. The base hydrolysis studies of Buckingham, Olsen and Sargeson[21,84] with *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ ions, where X- = Cl^-, Br^-, and NO_3^-, are interesting in this mechanistic consideration. Normally the base hydrolysis product is 50 ± 5% *cis*-$[Co(NH_3)_4(^{15}NH_3)(OH)]^{2+}$ and 50 ± 5% is *trans*-$[Co(NH_3)_4(^{15}NH_3)(OH)]^{2+}$. The authors[21] interpreted the results in terms of the S_N1CB intermediate shown in Figure 9a, where the two trigonal edges next to the somewhat negative NH_2 ligand statistically add water only half as fast as the *trans* edge. Alternate explanations are either some retention of the *trans* structure by a tetragonal pyramid plus a more statistical distribution in the trigonal pyramid, or an interchange process

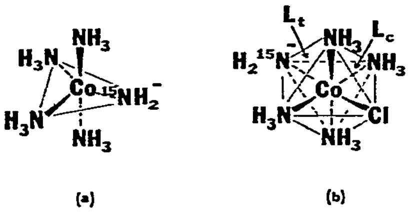


Fig. 9. Conjugate base species postulated for *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ base hydrolyses; (a) S_N1CB and (b) interchange conjugate base, where L_c or L_t is a ligand entering *cis* or *trans* to leaving groups Cl^-.

catalyzed by the conjugate base. The latter statistically gives 50% of each product since half of the faces are *trans* and half are *cis* to the $^{15}NH_3$ ligand (Figure 9b). Furthermore, in competition experiments between water (or hydroxide) and azide, 70% of the azido product is *cis*-$[Co(NH_3)_4(^{15}NH_3)N_3]^{2+}$, but only about 40% of the aqua product obtained after acidification shows rearrangement[84]. (The conclusion of the investigators[84] that the azide acts statistically through a trigonal bipyramid is in opposition to electrostatic considerations, since water is more apt to approach a negative group than is the azide ion, whereas the product ratios are in the reverse order). On the other hand, base hydrolysis competition experiments with $[Co(en)_2(NH_3)X]^{2+}$ type species (X as above) with azide and thiocyanate indicate that the product stereochemical distributions are the same for the aqua and the anated product[19].

The base hydrolysis stereomobility of the cobalt(III) bis(ethylenediamine) complexes has been discussed recently in terms of electromeric effects[18], electron transfer[85], and spin changes[10]. The overall stereochemical changes which are observed are noted in Table 6. The base hydrolysis stereochemistries can be rationalized in terms of the two conjugate base trigonal bipyramidal intermediates available after proton removal[95] [(BD) and (CE) in Figure 2], and the leaving groups appear to have very little effect on the product stereochemistry[19,93]. Even so, the S_N1CB explanation does not satisfactorily account for all base hydrolysis observations unless an interchange, ion-pair, or related concept is coupled with the conjugate base mechanism as noted above.

The observed stereochemistries for the base hydrolysis reactions noted in Table 6 are in agreement with the idea and calculations noted in the aquation section, namely that π-donors tend to occupy trigonal plane positions in the bipyramidal intermediates[18]. Whereas this concept gives only D* and *trans* products from D* reactants in the induced aquation reactions (*i.e.*, ethylenediamine is not a π-donor), D*, L*, and *trans* products all logical products if the conjugate base of ethylenediamine is formed, since the conjugate base is a strong π-donor. (Recent evidence for the π-donor character of RNH^- is found in the conjugate base studies of tris(aminoacido)cobalt(III) species; the conjugate base species are paramagnetic[96] as expected for strong π-donation). With reference to Figure 2, the (CE)

TABLE 6

THE AQUEOUS BASE HYDROLYSIS STEREOCHEMISTRY OF COBALT(III) ETHYLENEDIAMINE COMPLEXES

$[Co(en)_2LX]^{n+} + OH^- \rightarrow [Co(en)_2L(OH)]^{n+} + X^-$

Reactant		*Stereochemical changes(%)*[a]			*Reference*	*cis Reactant conjugate base intermediates based on Fig. 2*[b]
L	*X*	*trans→cis*	*trans-cis*	$D^* \rightarrow L^*$		
$OH^{(-)}$	Cl^-	94[c]	3	< 8[d]	86–88	(BD) > (CE)[d]
$OH^{(-)}$	Br^-	90	4		86	e
$NCS^{(-)}$	Cl^-	76	20	24	43, 89	(BD) > (CE)
$NCS^{(-)}$	Br^-	81			89	
$NCS^{(-)}$	N_3^-	70	30		90, 91	(BD) > (CE)
NH_3	Cl^-	64, 76[f]	22, 16[f]	15, 24[f]	19, 92	(BD) > (CE)
NH_3	Br^-		23, 15[f]	17, 26[f]	19, 92	
NH_3	NO_3^-	63[f]	23, 14[f]	15[f]	19, 92	(BD) > (CE)
$N_3^{(-)}$	Cl^-	27[g]	41[g]		15, 43	(BD) > (CE)
$NO_2^{(-)}$	Cl^-	6[h]	33	21	45, 84	(CE) > (BD)
$NO_2^{(-)}$	NCS^-	12	50		94	
$Cl^{(-)}$	Cl^-	5	63	16[i]	84	(BD) > (CE)
$Cl^{(-)}$	Br^-	5	70		84	(BD) > (CE)
$Cl^{(-)}$	DMA		74[j]		122	
$Cl^{(-)}$	DMF		42[j]		122	
$Cl^{(-)}$	DMSO		82[j]		122	
$Br^{(-)}$	Cl^-	0	60		84	(BD) > (CE)

[a] The percent figures are probably good to about 5% since small spectral differences between one study and another often give results which differ considerably; see footnotes f and g.

[b] The intermediates are based on the assumption that dissociative conjugate base reactions with trigonal bipyramidal intermediates occur; *cf.* ref. 95.

[c] Ref. 38 suggested a lower value; ref. 87 suggested a *trans-trans* equilibrium refuted by ref. 88; value quoted from ref. 86 may include some isomerized product.

[d] Ref. 86 had a higher value (36%) refuted by ref. 87; the smaller $D^* \rightarrow L^*$ value is more consistent with (BD) > (CE). See Table 8 for more details.

[e] Indeterminant since small errors give large differences; see ref. 18. Similar configurational changes have been observed where $X^- = OAc^-$ and F^-, ref. 98 and 99.

[f] Second number refers to values from ref. 92. Relative purity in the studies difficult to ascertain.

[g] Original study, ref. 43, listed 13% and 49% but ref. 15 absorption values considered preferable (ref. 7).

[h] Ref. 7 lists 13% but references cited list 6%.

[i] Probably high; see ref. 87; may be concentration dependent.

[j] Based on composition of $[Co(en)_2H_2OCl]^{2+}$ after acidification. See Table 7 for total experimental results.

TABLE 7

ACIDIFIED BASE HYDROLYSIS PRODUCTS FOR SOME *cis*-$[Co(en)_2Cl(SOL)]^{2+}$ COMPLEXES WITH MIXED PRODUCTS[122]

Reactant SOL	*%*$[Co(en)_2Cl(H_2O)]^{2+}$		*%*$[Co(en)_2(H_2O)_2]^{3+}$	
	cis	*trans*	*cis*	*trans*
DMA	16	46	14	24
DMF	18	13	13	56
DMSO	10	47	21	22

intermediate should occur more often if E is not a good π-donor, and as indicated in Table 6, only with nitrite, a π-acceptor, does the (CE) intermediate appear favored over the (BD) intermediate. The only other ligand in the table which is not a π-donor is ammonia, but ammonia should be a fairly strong acid relative to ethylenediamine[18], so that the (BD) intermediate can predominate. The F end of ethylenediamine DF should be a stronger acid than the D end (since NH_3 *trans* to a halide is deuterated more rapidly than if *cis* to the halide)[20], and it appears to be[97], so the BF edge (CE) should not be as suited for nucleophilic addition as the BD edge. But the recent stereochemical results[19] show that the stereochemistry requires a little extra attack on the negative side which is not too likely. The earlier values[92] require more than a two to one attack along the wrong side if the simple interpretation is maintained. Even more seriously difficulties arise with the thiocyanate complex if a simple S_N1CB trigonal bipyramidal explanation is adhered to since one of the two open edges predominates infinitely over the other one[10,95]. Once again an interchange or similar modification can ease the dilemma, but such a modification does not make for predictability in other reactions.

Recently reported stereochemical changes during base hydrolysis include the $[Co(N,N'\text{-bis}\,\{L\text{-2-amino-3-phenylpropyl}\}\;D,D\text{-1,2-diaminocyclohexane})Cl_2]^+$ ion of *β-cis* configuration to a *trans* configuration[100]. The same change was obtained upon heating, so the base hydrolysis reaction occurs in such a way as to relieve steric strain[100].

The *cis*-$[Co(glycine)_2(NO_2)_2]^-$ preparation from *fac*-$[Co(glycine)_3]$ appears to involve a stereochemical change[101], but the reaction conditions of the preparation (hot solution and long reaction time) preclude any conclusions as to mechanism, although basic conditions suggest labilization to give the most thermodynamically stable product. This change is consistent with the observation that the conjugate base species of the tris species is paramagnetic[94], and an earlier suggestion[10] that cobalt(III) stereomobility is related to the availability of a non-

TABLE 8

PRODUCTS FORMED IN THE BASE HYDROLYSIS OF D*-*cis*-$[Co(en)_2Cl_2]^+$

Approximate molarity		*%*					*Approximate reaction time, sec.*
D-ClCl*[a]	*OH⁻*	*Total trans*	*D*-ClOH*	*L*-ClOH*	*D*-OHOH*	*L*-OHOH*	
0.1[b]	0.03	77[c]	22	1	0	0	50
0.03[b]	0.03	84[c]	12	1	1	3	45
0.1[b]	0.1	81[c]	10	2	2	5	20
0.1	0.2	72[c]	4	1	10	13	35
0.1	0.3	66[c]	3	2	12	16	25
0.3	0.3	63[c]	1	1	16	20	50

[a] Column headings indicate the two monodentate ligands coordinated in the bis (ethylenediamine) cobalt(III) species.

[b] Not all of the dichloro ion is consumed at the lower hydroxide concentrations.

[c] Breakdown of *trans* products is questionable, but total appears consistent.

singlet state of moderate energy. The magnetic moments observed for the amino acid conjugate base species and the bond strength parameters of the triplet iron(II) species isolated by Konig and Madeja[79] suggest that the triplet excited states as well as completely spin-free quintet states need to be considered in detailed mechanistic considerations. Furthermore, a triplet ground state exists for both the d^6 trigonal bipyramid and pentagonal bipyramid, logical intermediates for stereochemical rearrangements[33].

(ii) *Bailar inversion reactions*

One of the most interesting stereochemical results in coordination chemistry dates back to 1934 when Bailar and Auten[102] noted that $\text{D}^*\text{-}[\text{Co(en)}_2\text{Cl}_2]^+$ reacts with an aqueous paste of Ag_2CO_3 to give a $[\text{Co(en)}_2(\text{CO}_3)]^+$ product which has more inverted than retained product. The relative configurations were deduced by reverse chemical reactions with aqueous hydrochloric acid and a comparison with other reactions thought to give retention of configuration[102,103]. Optical rotatory dispersion and circular dichroism studies[104] verified the conclusion. A number of other studies have been conducted in order to learn more about this reaction[86,87,105,107]. Together the studies indicate a concerted reaction since

$$\text{D}^*\text{-}[\text{Co(en)}_2\text{Cl}_2]^+ + \text{OH}^- \rightarrow \underset{\textit{trans} > \text{D}^* > \text{L}^*}{[\text{Co(en)}_2\text{Cl(OH)}]^+} + \text{Cl}^- \tag{14}$$

$$\text{D}^*\text{-}[\text{Co(en)}_2\text{Cl(OH)}]^+ + \text{OH}^- \rightarrow \underset{\text{D}^* \gg \textit{trans} \text{ and } \text{L}^*}{[\text{Co(en)}_2(\text{OH})_2]^+} + \text{Cl}^- \tag{15}$$

But,

$$\text{D}^*\text{-}[\text{Co(en)}_2\text{Cl}_2]^+ + \text{OH}^- \rightarrow \underset{\textit{trans} \text{ and } \text{L}^* > \text{D}^*}{[\text{Co(en)}_2(\text{OH})_2]^+} + 2\text{Cl}^- \tag{16}$$

The concentration dependence can be accommodated by

(i) a *trans* attack inversion such as is shown in Figure 10;

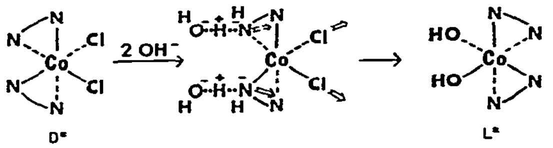


Fig. 10. Possible mechanism for the Bailar inversion of $[\text{Co(en)}_2\text{Cl}_2]^+$.

(ii) an intermediate with one monodentate ethylenediamine, provided both chlorides are replaced prior to rechelation (since if only one chloride is removed prior to recombination the chlorohydroxo species should also be inverted);

(iii) a *cis* ion-pair mechanism in which the first chloride released from the complex sufficiently blocks *cis* attack during the second chloride replacement (which would require the second step to be faster than diffusion of the chloride); and

(iv) a trigonal twist mechanism.

The latter two are considered unlikely on the basis of diffusion rates and the relative amounts of inversion noted at various concentrations, respectively. The apparent silver and hydroxide ion stereochemical dependence do rule out a simple S_N1CB reaction, even though an unsymmetrical trigonal bipyramid could accommodate any individual set of data for the reaction[95]. However, the role of silver in the inversion is a little uncertain at the presence since silver ion is unnecessary at higher hydroxide ion concentrations and the studies conducted at lower concentrations normally only give partial hydrolysis in the absence of the silver ion.

Related inversions have been observed for the base hydrolyses of the optically active isomers of $[Co(en)_2BrCl]^+$ (ref. 108), $[Co(en)_2Br_2]^+$ (ref. 108), and $[Co([-]pn)_2Cl_2]^+$ (ref. 105). Base hydrolysis reactions with other bidentate ligands and with other monodentate ligands do not show such inversions, nor do the corresponding bis (ethylenediamine) complexes of other metals.

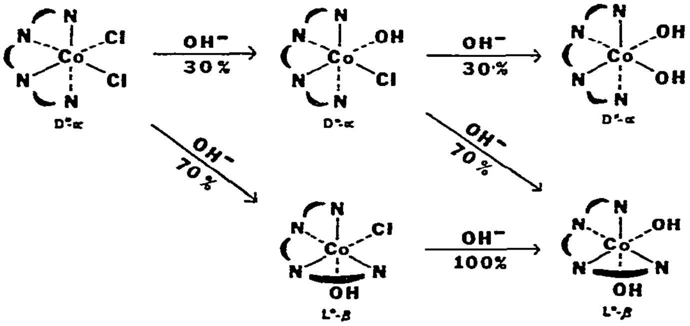


Fig. 11. $[Co(trien)Cl_2]^+$ base hydrolysis inversion stereochemistry.

Several D* → L* type inversions have been observed with tetradentate ligands, where the movement of one end of the D*-*α-cis* isomer converts the species to a L*-*β-cis* isomer as in Figure 11. Ions which undergo such a D*-α to L*-β inversion during base hydrolysis include $[Co(trien)Cl_2]^+$; the original article[109] indicated retention, but reanalysis[110] after the base hydrolysis of the *β-cis* had been reported[111] suggests inversion. $[Co(trien)Cl(OH)]^+$ also gives inversion[109], but the $[Co(NSSN)X_2]^+$ ions do not[112]. Steric factors coupled with the base hydrolysis probably are responsible for the trien inversions. Similar tetradentate inversions probably occur in the *α-cis*-$[Cr(trien)Cl_2]^+$ aquation discussed previously and appears to occur in the reaction of amino acids with D*-*α-cis*-$[Co(L,L\text{-}\alpha,\alpha'\text{-}dimethyltrien)ClH_2O)]^{2+}$ (ref. 113). Again ring mobility is probably responsible.

A multistep reaction involving the rearrangement of two terminal ends of a linear sexadentate ligand[114] is an inversion of the type under discussion[115] as is one of the following two reactions—the reaction of ethylenediamine with $[Co(PDTA)]^-$ or the corresponding reaction[116] with $[Co(EDTA)]^-$. Although the original investigators considered the reaction with the PDTA complex as inversion and the one with the EDTA complex as 2/3 retention[116], other assignments of relative configurations suggest that the two reactions are retention and 2/3 inversion, respectively[115,117]. The difference depends on the PDTA methyl group, which is situated such that it can be considered as responsible for weakening the two chelate rings on the end next to the methyl group. Addition of ethylenediamine to one of the weak positions followed by the addition of another one to the other carboxyl coordination positions, and the complete removal of the PDTA is then followed by a third ethylenediamine ligand addition giving a retained configuration, using the MacDermott and Sargeson[115] and Douglas, Haines, and Brushmiller[117] assignment of configuration. On the other hand, in the EDTA complex the in-plane (ONNO) ring strain places one end of the first ethylenediamine molecule in the plane, but if the other three carboxyl groups have an equal probability of being removed, only the one on the same nitrogen as the one first removed gives retained configuration, so 2/3 of the product is inverted. For more details on this and other Bailar inversions, see refs. 8, 110, 118, 119.

(iii) *Other metal ion reactions*

As in the case of aquation reactions, stereochemical change is not observed for the base hydrolysis reactions of rhodium(III) or ruthenium(III)[8,120–122]. Furthermore, no evidence has been presented to indicate any appreciable stereochemical changes for base hydrolysis reactions of chromium(III). In light of the lower sensitivity of the chromium(III) complexes to hydroxide, this reviewer would be surprized if much is uncovered except in the cases of ring strain or other ring opening reactions. Such are observed in isomerization and racemization reactions[8] of chromium(III).

E. ANATION AND ANION EXCHANGE STEREOCHEMICAL CHANGES

Anation reaction stereochemistry has been relatively neglected. An anation reaction can be represented by the general equation

$$[M(SOL)BCDEF]^{n+} + X^- \rightarrow [MXBCDEF]^{n-1} + SOL \qquad (17)$$

where SOL is a solvent molecule. That is, anation is the reverse of solvolysis. Even though less is known about anation stereochemistry than would be desirable, some interesting stereomobility has been observed for the cobaltamine systems, and retention has normally been noted for anation reactions of the other inert ions.

(i) *Aqueous anation reactions*

Aqueous anation reactions normally appear to yield products with the same stereochemistry as the corresponding aqua complexes. For example, $[Co(en)_2NO_2(H_2O)]^{2+}$ anation products have retained configurations[123], and in dilute aqueous solution the reactions of *trans*-$[Co(en)_2Cl_2]^+$ with nitrite gives about 70% *trans*- and 30% *cis*-$[Co(en)_2(NO_2)_2]^+$,[124] similar to the stereochemistry of the normal aquation reaction of the *trans*-dichloro ion[38]. On the other hand, Norris and Tobe[124] have been able to vary the reaction conditions such that the dinitro product is essentially all *cis* or all *trans*. In the presence of cobalt(II) and ethylenediamine a catalyzed redox reaction produces the *trans* ion. The cobalt(II) intermediate is thought to contain one ethylenediamine and three nitrite ligands and to abstract Cl from the reactant producing the *cis*-nitrochloro species, which gives the *cis*-dinitro species by a normal aquation and anation path. The *trans*-dinitro results by a catalyzed path are still under investigation[124]. Such redox possibilities must be kept in mind in other apparent substitution reactions[85].

(ii) *Non-aqueous anation reactions*

The anation of *cis*-$[Co(en)_2NO_2(DMSO)]^{2+}$ in dimethylsulfoxide appears to give complete (>95%) retention with chloride, nitrite, and thiocyanate ions, even when ion pairs are involved[125], similar to the aquation of nitrohalo complexes. A number of earlier studies with *cis* and *trans*-$[Co(en)_2NO_2X]^{n+}$ complexes also found only retention[7].

Stereochemical changes do occur in anation reactions of the bis(ethylenediamine) complexes of cobalt(III) when the fifth non-reacting ligand is a halo entity; see Table 9. Probably the most interesting results are those of Fitzgerald and Watts[22], who have noted the *cis*-$[Co(en)_2(SOL)X]^{2+}\ldots Y^-$ ion pair (where

TABLE 9

NON-AQUEOUS ANATION STEREOCHEMICAL CHANGES

$[Co(en)_2X(SOL)]^{2+} + Y^- \rightarrow [Co(en)_2XY]^+ + SOL$

X	*SOL*	*Y*	*Solvent*	*Stereochemistry*[a]	*Reference*
Cl	DMF	Cl	DMF	*cis* → *trans*	126
Cl	DMF	SCN	DMF	*cis* → *trans*	126
Br	DMF	Br	DMF	*cis*(IP) → > 50% *trans* *cis*(IT) → < 50% *trans*	22
Cl	DMSO	Cl	DMSO	*cis* → 40–45% *trans*	127
Cl	DMSO	Cl	DMA	*cis*(IP) → > 50% *trans* *cis*(IT) → < 50% *trans*	22
Cl	DMSO	Cl	TMS	*cis*(IP) → > 50% *trans* *cis*(IT) → < 50% *trans*	22

[a] IP = ion-pair with Y^-; IT = ion-triplet with $2Y^-$.

SOL = DMF and $X^- = Y^- = Br^-$ in DMF and where SOL = DMSO and $X^- = Y^- = Cl^-$ in DMA or TMS) gives primarily *trans*-dihalo products whereas the corresponding ion triplets give predominately *cis*-dihalo products. Also, *trans*-products giving way to *cis*-products as the concentration increases has been observed for SOL = DMSO and $X^- = Y^- = Cl^-$ in DMF and for SOL = DMSO and $X^- = Y^- = Br^-$ DMA and TMS, but the mechanisms for these reactions appear to be different. The product stereochemistry is consistent with the predominance of an ion pair positioned opposite the complexes' SOL and X^- ligands (*i.e.*, faces DFC and BCF of the D*-*cis* reactant of Figure 2) and an ion triplet with the second anion adjacent to SOL and/or X^- of the complex. The possibility of ion multiplets effecting the stereochemistry of the reaction products has long been suspected, but is often not observed.

Inasmuch as synthetic chemistry is conducted in concentrated solutions, the concentration aspects of anation stereochemistry are very important. The above results will undoubtedly lead to a flurry of activity in this research area.

(iii) *Anion exchange reactions*

A number of reactions in which one anion is replaced by the same anion (labelled) or another anion show stereochemical changes. The D*-*cis*-$[Co(en)_2Cl_2]^+$ ion reacts with Cl^- in methanol to give 72 to 84% *trans*-dichloro and 14 to 16% L*-dichloro, and the rest (if any) is retained as D*-dichloro, according to a comparison of optical and $^{36}Cl^-$ results[7,128]. The *trans*-dichloro isomer in methanol appears to give almost complete retention[7] based on optical[129] and exchange data[130]. The *cis*-isomer in methanol appears to give almost complete stereochemical rearrangement (*cis* to *trans*) with the azide ion[131], and about one-third *trans* and one-third mirror image[129] with SCN^-. The D*-*cis*-$[Co(en)_2Cl_2]^+ \ldots Cl^-$ ion pair appears to give a slightly different product isomer ratio than thefree ion [7,128]. The ion pair gives about 84% *trans* and 16% racemic product.

In addition to the ethylenediamine complexes of cobalt(III) which show stereochemical changes during anion exchange, the *cis*-$[Co(diars)_2Cl_2]^+$ also isomerizes from the *cis*-dichloro to the *trans*-chlorothiocyanato (~100%), and $^{36}Cl^-$ exchange indicates mainly *trans* product[132]. Furthermore, the racemization and isomerization reactions of complexes with anions predominantly occur by way of exchange reactions as do many of the chelated anionic ligand reactions[6,8]. Inasmuch as no net chemical substitution occurs, the isomerization and racemization reactions will not be discussed further in this review. The reader should refer to references 6 and 8 for more details. (The trigonal twist possibilities, which avoid any substitution, have been detailed[133–135], but appear unnecessary and unlikely in most reactions[135–136].)

F. NON-AQUEOUS SOLVOLYSIS STEREOCHEMICAL CHANGES

Reactions in solvents other than water have been conducted with the hope that less mechanistic ambiguity would result. Whereas a number of interesting anation (Section E) and kinetic parameter results are available, only a limited amount of good stereochemical data on solvolysis reactions in anhydrous solvents is available.

Once again most of the data on stereochemical changes is based on the *cis* and *trans* isomers of $[Co(en)_2Cl_2]^+$ or the bromochloro and dibromo derivatives which give analogous results. Whereas in water both isomers undergo two solvation steps as noted above in Section C, only one solvation step to *cis*-$[Co(en)_2Cl(SOL)]^{2+}$, where SOL = solvent, occurs spontaneously in DMF, DMSO, and perhaps in DMA[23,126,127], regardless of which isomer is the reactant. Any *trans* solvent containing species appear to isomerize to the *cis* species, so that the actual stereochemistry of the direct substitution reaction is uncertain, but stereochemical change appears to predominate the *trans*-dichloro solvolyses in these solvents. In methanol and tetramethylene sulfone only isomerization is observed[82,130,137–139]. Studies in liquid ammonia indicate considerable stereochemical change[11,140–142]. In fact, *trans* and inverted *cis* products are the major products at low temperatures, *i.e.*, a non-aqueous Bailar inversion.

The corresponding trien complex D*-α-*cis*-$[Co(trien)Cl_2]^+$ undergoes D*-α to L*-β inversions in both ammonia[143,144] and ethylenediamine[144]. Only optical rotation data is available, so the amount of *trans* product, if any, in the ammonia reaction is indeterminant. However, by analogy with the base hydrolysis results (Section D) and the one *vs.* two ring movements necessary for the change to L*-β *vs.* trans suggests that the L*-β isomer is the major component of the product.

Some solvent exchange studies by Lantzke and Watts[145] indicate that some stereochemical changes occur for the series

$$Co(en)_2Cl(SOL_1)^{2+} + SOL_2 \rightarrow Co(en)_2Cl(SOL_2)^{2+} + SOL_1 \qquad (18)$$

where SOL_1 = DMA and SOL_2 = DMF or DMSO (*cis* to ~17% *trans*); SOL_1 = DMF and SOL_2 = DMSO (*cis* to ~17% *trans*); and SOL_1 = H_2O and SOL_2 = acidified DMSO (*trans* to ~17% *trans*). These numbers are only approximate and are based on the statistical probability of the two different trigonal bipyramids for the *cis* complexes (Fig. 2). Spectra calculated using that percentage appeared close the experimental results. For a *trans* isomer, though, the percentage should be 33%, since the two trigonal bipyramids are mirror images of each other and each gives 1/3 *trans* product statistically. Other solvent exchange reactions were also investigated, but no meaningful stereochemistry could be obtained.

One final example is a reaction which has been suggested to be an octahedral inversion reaction—the benzene-$[Cr(CO)_6]$ reaction in the benzene tricarbonylchromium synthesis[146,147]. Fischer envisions the reaction as an umbrella type involving three CO groups. Other mechanisms are also possible for this reaction, however[147].

In conclusion, the elucidation of stereochemical changes in octahedral substitution reactions through non-aqueous solvent studies is bound to give added insight into the relationships which exist between reaction stereochemistry and nucleophiles, complexes, and environments. The fragmentary results which are available at the present suggest that the nature of the complex is most important. In other words a delicate balance of metal and ligand properties are necessary in order for any stereochemical changes to occur. The non-aqueous results so far indicate the only major stereochemical role that solvents play in the direct substitution reactions is altering the ion-pairing or solvolysis probabilities, which in turn may alter the stereochemistry to some extent. More studies with other first row transition element complexes are needed, but the lack of completely characterized series of complexes for these elements has caused a heavy reliance on cobalt(III) amines, where the odds for success are considerably greater based on past experience.

REFERENCES

1 C. H. LANGFORD AND T. R. STENGLE, *Ann. Revs. Phys. Chem.*, 19 (1968) 193.
2 F. BASOLO AND R. G. PEARSON, *Mechanisms of Inorganic Reactions* 2nd Ed., John Wiley and Sons, Inc., New York, 1967, pp. 238 ff.
3 M. L. TOBE, *Inorg. Chem.*, 7 (1968) 1260.
4 C. H. LANGFORD AND H. B. GRAY, *Ligand Substitution Processes*, W. Benjamin, New York, 1966, Chapter 3.
5 C. H. LANGFORD AND H. B. GRAY, *Chem. Engr. News*, (April 1, 1968) 68.
6 F. BASOLO, *Advan. Chem. Ser.*, 62 (1967) 402.
7 M. L. TOBE, in J. H. RIDD, Ed., *Studies on Chemical Structure and Reactivity*, Methuen and Co., Ltd., London, 1966, pp. 244 ff.
8 F. BASOLO AND R. G. PEARSON, *Mechanisms of Inorganic Reactions*, (see ref. 2), Chapter 4.
9 M. L. TOBE, in *Studies on Chemical Structure and Reactivity*, (see ref. 7), pp. 228–9.
10 R. D. ARCHER, *Advan. Chem. Ser.*, 62 (1967) 452.
11 R. D. ARCHER, *Proc. VIIIth Internat. Conf. on Coord. Chem., Vienna*, 1964, pp. 111-3.
12 R. G. PEARSON AND F. BASOLO, *J. Amer. Chem. Soc.*, 78 (1956) 4878.
13 C. K. INGOLD, R. S. NYHOLM AND M. L. TOBE, *Nature*, 187 (1960) 477.
14 A. M. SARGESON, *Australian J. Chem.*, 17 (1964) 385.
15 D. LOELIGER AND H. TAUBE, *Inorg. Chem.*, 4 (1965) 1032.
16 D. LOELIGER AND H. TAUBE, *Ibid.*, 5 (1966) 1376.
17 D. A. BUCKINGHAM, I. I. OLSEN AND A. M. SARGESON, *Ibid.*, 6 (1967) 1807.
18 M. GREEN, *J. Chem. Soc. (A)*, (1967) 762.
19 D. A. BUCKINGHAM, I. I. OLSEN AND A. M. SARGESON, *J. Amer. Chem. Soc.*, 90 (1968) 6654.
20 D. A. BUCKINGHAM, I. I. OLSEN AND A. M. SARGESON, *Australian J. Chem.*, 20 (1967) 597.
21 D. A. BUCKINGHAM, I. I. OLSEN AND A. M. SARGESON, *J. Amer. Chem. Soc.*, 89 (1967) 5129.
22 W. R. FITZGERALD AND D. W. WATTS, *Ibid.*, 90 (1968) 1734.
23 W. R. FITZGERALD, A. J. PARKER AND D. W. WATTS, *Ibid.*, 90 (1968) 5744.
24 F. BASOLO, *Chem. Revs.*, 52 (1953) 459.
25 F. BASOLO, in J. C. BAILAR, JR., Ed., *The Chemistry of the Coordination Compounds*, Reinhold Publishing Co., New York, 1956, Chapter 8.

26 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 1st Ed., John Wiley and Sons, Inc., New York, 1958, Chapter 5.
27 F. Basolo and R. G. Pearson, *Advanc. Inorg. Chem. Radiochem.*, 3 (1961) 1.
28 C. H. Langford and H. B. Gray, (see ref. 4), Chapter 1.
29 E. Kyuno, L. J. Boucher and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 87 (1965) 4458.
30 H. L. Bott, A. J. Poe and K. Shaw, *Chem. Comm.*, (1968) 793.
31 N. S. Hush, *Australian J. Chem.*, 15 (1962) 378.
32 F. Basolo and R. G. Pearson, (see ref. 2), Chapter 2.
33 S. T. Spees, Jr., J. R. Perumareddi and A. W. Adamson, *J. Amer. Chem. Soc.*, 90 (1968) 6626.
34 K. B. Yatsimirskii, *Teor. Eksp. Khim.* 2 (1966) 451; *Engl. translation*, 342.
35 K. B. Yatsimirskii, T. V. Mal'kova and L. I. Budarin, *Proc. Xth Internat. Conf. on Coord. Chem., Nikko and Tokyo, 1967*, pp. 290–2.
36 A. M. Sargeson and G. H. Searle, *Nature*, 200 (1963) 356.
37 D. A. Buckingham, P. A. Marzilli and A. M. Sargeson, *Inorg. Chem.*, 6 (1967) 1032.
38 M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, (1961) 4637.
39 C. K. Ingold, R. S. Nyholm and M. L. Tobe, *Ibid.*, (1960) 1691.
40 M. E. Baldwin and M. L. Tobe, *Ibid.*, (1960) 4275.
41 S. C. Chan and M. L. Tobe, *Ibid.*, (1963) 5700.
42 S. C. Chan, *Australian J. Chem.*, 20 (1967) 595.
43 P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, (1960) 4803.
44 S. C. Chan and M. L. Tobe, *Ibid.*, (1963) 514.
45 S. Asperger and C. K. Ingold, *Ibid.*, (1956) 2862.
46 C. K. Poon and M. L. Tobe, *J. Chem. Soc. (A)*, (1967) 2069.
47 M. L. Tobe, *J. Chem. Soc.*, (1959) 3776.
48 D. R. Stranks, in J. Lewis and R. G. Wilkins, Eds., *Modern Coordination Chemistry*, Interscience Publishers, New York, 1960, Chapter 2.
49 A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 9 (1955) 1261.
50 F. Basolo and R. G. Pearson, (see ref. 2), pp. 258 ff.
51 D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, (1962), 1388.
52 R. D. Archer, unpublished results.
53 D. Fiat and R. E. Connick, *J. Amer. Chem. Soc.*, 90 (1968) 608.
54 S. F. Lincoln and D. R. Stranks. *Australian J. Chem.*, 21 (1968) 1733.
55 C. K. Jørgensen, R. Pappalardo and H. H. Schmidtke, *J. Chem. Phys.*, 39 (1963) 1422.
56 C. E. Schäfer and C. K. Jorgensen, *Mol. Phys.*, 9 (1965) 401.
57 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4 (1965) 709.
58 A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer and R. D. Lindholm, *Chem. Rev.*, 68 (1968) 541.
59 V. Balzini, L. Moggi, F. Scandola and V. Carassiti, *Inorg. Chim. Acta Rev.*, 1 (1967) 7.
60 L. Moggi, N. Sabbatini and V. Balzani, *Gazz. Chim. Ital.*, 97 (1967) 980.
61 S. T. Spees, Jr., and A. W. Adamson, *Inorg. Chem.*, 1 (1962) 531.
62 M. Mori, M. Shibata, E. Kyuno and T. Adachi, *Bull. Chem. Soc. Japan*, 29 (1956) 883.
63 R. D. Archer and B. D. Catsikis, *J. Amer. Chem. Soc.*, 88 (1966) 4520.
64 R. D. Archer, N. Cooke and B. D. Catsikis, *Abstr. Amer. Chem. Soc. Meeting, Miami, 1967.*
65 O. Hyodo and R. D. Archer, *Abstr. Amer. Chem. Soc. Meeting, Boston, 1968*; to be published.
66 B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, 6 (1967) 800.
67 R. J. York and R. D. Archer, to be published.
68 J. B. Hunt, private communication.
69 M. G. Moffitt, Honors Thesis, Newcomb College, Tulane University, 1967.
70 S. H. Caldwell and D. A. House, *Inorg. Chem.*, 8 (1969) 151.
71 D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, 83 (1961) 4152.
72 C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, 1 (1967) 17.
73 L. P. Quinn and C. S. Garner, *Inorg. Chem.*, 3 (1964) 1348.
74 D. W. Hoppenjans, J. B. Hunt and C. R. Gregoire, *Ibid.*, 7 (1968) 2506.

75 J. M. Veigel and C. S. Garner, *Ibid.*, 4 (1965) 1569.
76 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, (see ref. 2), pp. 273–4.
77 F. Basolo and R. G. Pearson, *Ibid.* Chapter 3.
78 E. König, *Coordin. Chem. Rev.*, 3 (1968) 471.
79 E. König and K. Madeja, *Inorg. Chem.*, 7 (1968) 1848.
80 F. Basolo, J. C. Hayes and H. M. Neumann, *J. Amer. Chem. Soc.*, 76 (1954) 3807.
81 F. J. Garrick, *Nature*, 139 (1937) 507.
82 M. L. Tobe, *Advances in Chem. Ser.*, 49 (1965) 7.
83 M. Green and H. Taube, *Inorg. Chem.*, 2 (1963) 948.
84 D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *J. Amer. Chem. Soc.*, 90 (1968) 6539.
85 R. D. Gillard, *J. Chem. Soc., (A)*, (1967) 917.
86 S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, (1962) 4531.
87 E. A. Dittmar and R. D. Archer, *J. Amer. Chem. Soc.*, 90 (1968) 1468.
88 M. E. Farago, B. Page and M. L. Tobe, *Inorg. Chem.*, 8 (1969) 388.
89 C. K. Ingold, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, (1956) 1691.
90 P. J. Staples, *Ibid.*, (1963) 3227.
91 S. C. Chan and J. Miller, *Rev. Pure Appl. Chem.*, 15 (1965) 11.
92 R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, (1956) 1707.
93 R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, 4 (1965) 433.
94 A. Roger and P. J. Staples, *J. Chem. Soc.*, (1963) 4749.
95 R. G. Pearson and F. Basolo, *Inorg. Chem.*, 4 (1965) 1522.
96 G. W. Watt and J. F. Knifton, *Inorg. Chem.*, 7 (1968) 1159.
97 I. I. Olsen, unpublished work quoted in ref. 19.
98 S. C. Chan and O. W. Lau, *J. Chem. Soc. (A)*, (1966) 1800.
99 V. Carunchio, G. Illuminati and G. Ortaggi, *Inorg. Chem.*, 6 (1967) 2168.
100 R. G. Asperger, private communication.
101 R. G. Denning, M. B. Ćelap and D. J. Radanović, *Inorg. Chim. Acta*, 2 (1968) 58.
102 J. C. Bailar, Jr. and R. W. Auten, *J. Amer. Chem. Soc.*, 56 (1934) 774.
103 J. C. Bailar, Jr., F. G. Jonelis and E. H. Huffman, *Ibid.*, 58 (1936) 2224.
104 J. P. Mathieu, *Bull. Soc. Chim. France*, [5] 3 (1936) 476.
105 J. C. Bailar, Jr. and J. P. McReynolds, *J. Amer. Chem. Soc.*, 61 (1939) 3199.
106 F. P. Dwyer, A. M. Sargeson and I. K. Reid, *Ibid.*, 85 (1963) 1215.
107 L. J. Boucher, E. Kyuno and J. C. Bailar, Jr., *Ibid.*, 86 (1964) 3656.
108 J. C. Bailar, Jr., and J. C. Peppard, *Ibid.*, 62 (1940) 820.
109 E. Kyuno, L. J. Boucher and J. C. Bailar, Jr., *Ibid.*, 87 (1965) 4458.
110 R. D. Archer, in S. Kirschner, Ed., *Coordination Chemistry*, Plenum Press, New York, 1969, pp. 18ff.
111 E. Kyuno and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 88 (1966) 1120.
112 J. H. Worrell and D. H. Busch, *Amer. Chem. Soc. Meeting, Atlantic City, 1965*; private communication, 1969.
113 R. G. Asperger and C. F. Liu, *J. Amer. Chem. Soc.*, 89 (1967) 1533.
114 F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *Ibid.*, 74 (1952) 4188.
115 T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, 16 (1963) 334.
116 D. H. Busch, K. Swaminathan and D. W. Cooke, *Inorg. Chem.*, 1 (1962) 260.
117 B. E. Douglas, R. A. Haines and J. G. Brushmiller, *Ibid.*, 2 (1963) 1194.
118 J. C. Bailar, Jr., *Rev. Pure Appl. Chem.*, 16 (1966) 91.
119 A. M. Sargeson, in F. P. Dwyer and D. P. Mellor, Eds., *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964, Chapter 5.
120 J. A. Broomhead and L. Kane-Maquire, *Inorg. Chem.*, 7 (1968) 2519.
121 A. Panunzi and F. Basolo, *Inorg. Chim. Acta*, 1 (1967) 223.
122 I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, 19 (1966) 1821.
123 M. N. Hughes and M. L. Tobe, *J. Chem. Soc.*, (1965) 1204.
124 A. R. Norris and M. L. Tobe, *Inorg. Chim. Acta*, 1 (1967) 41.
125 W. R. Muir and C. H. Langford, *Inorg. Chem.*, 7 (1968) 1032.
126 I. R. Lantzke and D. W. Watts, *Australian J. Chem.*, 19 (1966) 949.
127 M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, (1964) 2991.

128 B. Bosnich, C. K. Ingold and M. L. Tobe, *Ibid.*, (1965) 4074.
129 D. D. Brown and R. S. Nyholm, *Ibid.*, (1953) 2696.
130 R. G. Pearson, P. M. Henry and F. Basolo, *J. Amer. Chem. Soc.*, 79 (1957) 5382.
131 D. W. Watts, unpublished results quoted in ref. 7.
132 A. Peloso and M. L. Tobe, *J. Chem. Soc.*, (1964) 5063.
133 C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, 6 (1967) 852.
134 J. J. Fortman and R. E. Sievers, *Ibid.*, 6 (1967) 2022.
135 E. A. Muetterties, *J. Amer. Chem. Soc.*, 90 (1968) 5097; 91 (1969) 1636.
136 N. Serpone and R. C. Fay, *Inorg. Chem.*, 6 (1967) 1835.
137 W. R. Fitzgerald and D. W. Watts, *J. Amer. Chem. Soc.*, 89 (1967) 821.
138 D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, (1953) 2696.
139 R. G. Pearson, P. M. Henry and F. Basolo, *J. Amer. Chem. Soc.*, 79 (1957) 5379.
140 J. C. Bailar, Jr., J. H. Haslam and E. M. Jones, *ibid.*, 58 (1936) 2226.
141 R. D. Archer and J. C. Bailar, Jr., *ibid.*, 83 (1961) 812.
142 E. L. Greenwood, B. S. Thesis, University of Illinois, 1936.
143 A. M. Sargeson, private communication, 1964.
144 E. Kyuno and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 88, 1125 (1966).
145 I. R. Lantzke and D. W. Watts, *Ibid.*, 89 (1967) 815.
146 E. O. Fischer, K. Ofele, H. Essler, W. Frohlich, J. P. Mortensen and W. Semmlinger, *Chem. Ber.*, 91 (1958) 2763.
147 D. A. Brown, *Inorg. Chim. Acta. Rev.*, 1 (1967) 35.
148 R. G. Linck, *Inorg. Chem.*, 8 (1969) 1016.