TABLE III

EQUILIBRIUM CONSTANTS FOR RHODAMINE B; TEMP. = 25°

Constant	Chloride	Bromide	Perchlorate
$[RHCl]_s$	1.7×10^{-4}		
D'	2.8×10^{3}		
K_1	1.0×10^{-3}		
K_2'	4.3×10^{-4}		
K_2	6×10^{-4}		6×10^{-4}
K_3	3.4×10^{-3}		1.3×10^{-3}
K_4	1.9×10^{-3}		
K_5'	2.1×10^{-1}	1.8×10^{-1}	1.5×10^{-1}
K_6 K_7	Probably small		
K_8	8.0×10^{-4}	8.5×10^{-5}	4.0×10^{-6}

Little significance is attached to these values; those determined spectrophotometrically are considered much more reliable.

Summary of Values of Equilibrium Constants.—Table III lists the values of the constants determined in this work. The values refer to solutions which are 1 M in the particular anion, with the exception of the values for K_2 and K_3 which are the thermodynamic values.

Acknowledgment.—We are grateful to the Dow Chemical Company for a fellowship held by R. W. R. in 1952–1953.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. X. π-Bonding in Dissociation Reactions of Octahedral Complexes[1,2]

BY RALPH G. PEARSON AND F. BASOLO

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In order to account for the high rates of hydrolysis of chloroamido and chlorohydroxo complexes of cobalt(III) and other rate data, it is proposed that π-bonding stabilizes the transition state. This π-bonding consists of the sharing of an additional pair of electrons on the donor atom with the cobalt. The stereochemical requirements and consequences of such bonding are discussed. An explanation is given for the failure of the "*trans-effect*" rule in the case of octahedral complexes.

In previous papers[1] we have reported results strongly supporting an SN1CB[3] mechanism for the base hydrolysis of complex ions of cobalt(III). The steps in a typical example would be

$$Co(NH_3)_5Cl^{+2} + OH^- \overset{\text{fast}}{\rightleftarrows} Co(NH_3)_4NH_2Cl^+ + H_2O \quad (1)$$

$$Co(NH_3)_4NH_2Cl^+ \xrightarrow{k_{CB}} Co(NH_3)_4NH_2^{+2} + Cl^- \quad (2)$$

$$Co(NH_3)_4NH_2^{+2} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_4NH_2H_2O^{+2} \quad (3)$$

$$Co(NH_3)_4NH_2H_2O^{+2} \xrightarrow{\text{fast}} Co(NH_3)_5OH^{+2} \quad (4)$$

The kinetics follow a second-order course if the complex ion is a weak enough acid so that 1 is very incomplete. The rate equation would then be

$$\text{rate} = k_{CB}\, K_a/K_w\, [OH^-][\text{Complex}] \quad (5)$$

and the observed second-order constant is the product of a first-order constant, k_{CB}, for reaction 2 and the equilibrium constant K_a/K_w for reaction 1.

The values of K_a cannot be measured, in general, because of the rapid reaction of the complex ions with alkali. However, an estimate can be made of the magnitude of the acid ionization constants involved by considering some related compounds. The aquo complexes of cobalt(III) are acidic enough so that their K_a values can be measured and the values found are of the order of 10^{-5} for tripositive cations and 10^{-7} for dipositive cations.[4]

From a consideration of such data and by comparing the acidities of $Pt(NH_3)_6^{+4}$ and $Pt(NH_3)_5H_2O^{+4}$, which differ by a factor of 10^5, Anderson, Briscoe and Spoor[5] estimated that K_a for $Co(NH_3)_6^{+3}$ would be approximately 10^{-11}. However, one might argue that the comparison should involve the acidities of NH_4^+ and H_3O^+ (factor of 10^{11}) which would lead to a K_a for $Co(NH_3)_6^{+3}$ of 10^{-17}. An intermediate value of 10^{-13} seems reasonable based on the greater resemblance of Co^{+3} to Pt^{+4} than to H^+.

We have tried to measure the K_a for several complex ions such as $Coen_3^{+3}$ directly using a conventional titration procedure and a pH meter. A good "constant" was in fact obtained for such ions as shown in Table I. However, spectroscopic examination in the visible and near ultraviolet regions of alkaline solutions of $Coen_3^{+3}$ showed no shifts to longer wave lengths as is expected for the loss of a proton.[6] Instead, a shift to longer wave lengths occurred in the far ultraviolet indicating ion pair formation.[7] Such ion pair formation should in fact occur between hydroxide ion and $Coen_3^{+3}$ and the constants recorded in Table I are of the expected order of magnitude[7] if the data are reinterpreted in this way.

It thus appears that the ionization constant as

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(1) For previous papers in this series see F. Basolo, J. G. Bergmann, R. E. Meeker and R. G. Pearson, THIS JOURNAL, **78**, 2676 (1956).

(2) This investigation supported by the U. S. Atomic Energy Commission under Contract AT(11-1)89. Project No. 2.

(3) SN1CB refers to substitution, nucleophilic, unimolecular, conjugate base, in the convenient terminology of Hughes and Ingold, see D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

(4) (a) R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956); (b) F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *ibid.*, **76**, 3079 (1954).

(5) J. S. Anderson, H. V. A. Briscoe and N. F. Spoor, *J. Chem. Soc.*, 361 (1943).

(6) A. A. Grunberg and G. P. Faerman, *Z. anorg. Chem.*, **193**, 193 (1930); C. K. Jorgensen, private communication.

(7) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

an acid of $Coen_3^{+3}$ cannot be directly measured in water but must be less than 10^{-13}. The complex ions containing replaceable ligands such as $Co(NH_3)_5Cl^{+2}$ and $Coen_2Cl_2^+$ must be weaker acids still. The exact value need not be known for present purposes, so a maximum value of 10^{-14} will be assumed for this discussion. The rather large variations expected from one ion to another due to substituent groups and electrical charges will be ignored.

TABLE I

APPARENT pK_a VALUES OF SOME COMPLEX IONS OF COBALT(III) AT 25° IN WATER

Complex	pK_a (apparent)	K_{form}[a]
$[Coen_3^{+3}]$	12.50	31[b]
$[Copn_3^{+3}]$	12.73	19
[Cod,l-bn_3^{+3}]	12.97	11

[a] If interpreted on the basis of ion pair formation. [b] For comparison the formation constant for this complex ion with bromide ion is 21 (ref. 6). J. A. Caton and J. E. Prue have measured a constant of 71 for ion pair formation between $[Co(NH_3)_6^{+3}]$ and hydroxide ion (private communication).

Contribution of π-Bonding to Rapid Base Hydrolysis Reactions.—Table II shows the results of calculating rate constant for (2) using some of the experimental rate constants for base hydrolysis reported earlier,[4a] the estimated K_a of 10^{-14}, and a K_w of 10^{-14}, since the data refer to water at 25°. Also included for comparison are the acid hydrolysis rate constants for the parent complexes, assumed to be the same as for the dissociation

$$Co(NH_3)_5Cl^{+2} \xrightarrow{k_{H_2O}} Co(NH_3)_5^{+3} + Cl^- \qquad (6)$$

$$Co(NH_3)_5^{+3} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5H_2O^{+3} \qquad (7)$$

TABLE II

RATE CONSTANTS FOR DISSOCIATION OF COMPLEX IONS, k_{H_2O}, AND THEIR CONJUGATE BASES, k_{CB}, IN WATER AT 25°

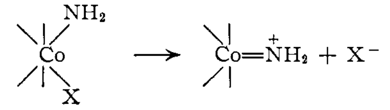
Compound	k_{H_2O}, sec.$^{-1}$	k_{CB}, sec.$^{-1}$	k_{CB}/k_{H_2O}
$Co(NH_3)_5Cl^{+2}$	6.7×10^{-6}[a]	8.5×10^{-1}	1.3×10^5
cis-$Co(en)_2NH_3Cl^{+2}$	1.4×10^{-6}[a]	5.4×10^1	3.9×10^7
cis-$Co(trien)NH_3Cl^{+2}$	6.7×10^{-7}[a]	1.6×10^2	2.4×10^8
cis-$Co(en)_2Cl_2^+$	2.5×10^{-4}	1×10^3	4×10^6
trans-$Co(NH_3)_4Cl_2^+$	1.8×10^{-3}	1.8×10^3	1.0×10^6
trans-$Co(en)_2Cl_2^+$	3.2×10^{-5}	3.0×10^3	9×10^7

[a] At 35°. Divide by three to approximate values at 25°.

Similar ratios are found for a number of complexes of cobalt(III) which contain an acidic hydrogen.[4a] It should be remembered that these ratios will be even greater if K_a is taken as less than 10^{-14}.

This large difference in rates of release of halide ion is unexpected. It is true that the conjugate base has one less positive charge than its parent complex. This would certainly facilitate the dissociation of a negatively charged ion. However, a comparison of the doubly-charged complexes of Table II with the singly-charged complexes indicates that this electrical factor is of the order of 10^3 at most. This latter figure is also in agreement with calculations based on electrostatic theory and with other experimental data on the effect of electrical charges on reactant molecules.[8]

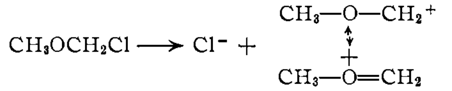
Thus, there remains an unexplained factor of 10^3 to 10^5 and perhaps even larger favoring the conjugate bases. Since all of these contain an amido group with an unshared pair of electrons, it is proposed that the increased rate of dissociation is due to π-bonding[9] in the reaction intermediate. Such π-bonding where the unshared electrons of the amido group move toward the cobalt helps to displace the halide ion and to stabilize the five-coördinated intermediate after the loss of the halide ion.



If π-bonding is a factor in rates of dissociation, then the effect should occur with all ligands which have unshared pairs of electrons. The magnitude of the effect would depend on the tendency of the ligand to release electrons and, in particular, would increase in the series $Cl^- < OH^- < NH_2^-$. Data in Tables II and III show that this expected trend is observed for analogous cobalt(III) complexes. In spite of the statistical factor of two, the chlorohydroxo complexes react considerably faster than the corresponding dichloro complexes, the factor being between 10^1 and 10^2. Thus, just as anticipated, the acceleration in rate due to a hydroxo group is less than that due to an amido group but greater than that due to a chloro group.

It is not necessary to postulate π-bonding to explain these relative reactivities. Another explanation would be based on the inductive effects of the groups involved. It is known that electron releasing groups (base strengthening) accelerate the rate of acid hydrolysis of cobalt(III) complexes.[1] This would increase in the observed order $Cl^- < OH^- < NH_2^-$ which is that of increasing base strength. However, the increase in rate due to such inductive effects is very small[1] and may be insufficient to account for the observed rates shown in Tables II and III.

The situation is similar to that encountered in organic chemistry in explaining the high reactivity of α-haloethers. The accepted explanation for this reactivity is that a resonance structure involving π-bonding from the oxygen atom's unshared electron pairs stabilizes the carbonium ion.



$$CH_3OCH_2Cl \longrightarrow Cl^- + \begin{matrix} CH_3{-}O{-}CH_2^+ \\ \updownarrow \\ CH_3{-}\overset{+}{O}{=}CH_2 \end{matrix} \qquad (8)$$

In the above case it is known that the proper geometry can be reached readily so that π-bonding can occur. It will now be necessary to examine the octahedral complexes of cobalt(III) to see if the postulated π-bonding is geometrically possible. Kimball[10] has given an excellent analysis of the possibilities for π-bonding between a ligand and a central atom for all the common coördination numbers.

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[8] F. H. Westheimer and M. Shookhoff, THIS JOURNAL, **62**, 269 (1940).

[9] The π-bonding referred to here involves the partial transfer of *p* orbital electrons on the ligand atom toward the central metal. This is not to be confused with the more familiar type of π-bonding in complexes involving the partial transfer of *d* orbital electrons on the central metal toward the ligand atom; L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 250.

[10] (a) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940); (b) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1944, p. 227, *et seq.*

His discussion is based on the symmetry properties of atomic and equivalent hybridized atomic orbitals.

Stereochemical Requirements of π-Bonding.—In the coördination complexes of cobalt(III) the six ligands are bonded to cobalt through $d^2 sp^3$ hybrid orbitals which are directed toward the corners of a regular octahedron. The cobalt atomic orbitals involved, in the notation of Eyring, Walter and Kimball,[10b] are d_{z^2}, $d_{x^2-y^2}$, s, p_x, p_y and p_z where x, y and z, are the cartesian coördinate axes of the system. In addition there are the d_{xy}, d_{xz} and d_{yz} orbitals of cobalt all of which are filled with electrons. In the normal octahedral condition the only π-bonding that can occur is one involving the donation of electrons from these filled cobalt orbitals to an empty p or d orbital in the ligand. This is the kind of π-bonding originally proposed by Pauling,[9] but it does not concern us here.

Upon dissociation of a ligand, a five-coördinated reaction intermediate is formed. The nature of this intermediate has been discussed by several authors.[11] We need consider only two possible forms for this intermediate—the tetragonal or square pyramid and the trigonal bipyramid. The orbital hybridization for each of these intermediates will be examined to see if π-bonding of the type in which cobalt is the electron acceptor is feasible.

The intermediate formed directly upon dissociation of a ligand would be the tetragonal pyramid, wherein four ligands are located in a plane and the fifth ligand is situated normal to that plane. No change in the orbital hybridization need be involved in the formation of this intermediate. One vacant $d^2 sp^3$ hybrid orbital would simply project outward normal to the tetragonal plane.

The second type of five-coördinated intermediate is the trigonal bipyramid wherein three ligands lie in a central plane with one ligand above and one ligand below that plane. The trigonal plane would involve $(s + d_{z^2})(p_x)(p_y)$ hybrid orbitals which are directed toward the apices of an equilateral triangle, and the orbitals normal to the plane would be $(s + d_{z^2})(p_z)$ hybrids, leaving the $d_{x^2-y^2}$ orbital vacant. This vacant $d_{x^2-y^2}$ orbital consists of four lobes in the trigonal plane directed toward the corners of a square.

The π-bonding would involve a free electron pair from the amido nitrogen in the conjugate base, from the oxygen in a hydroxo complex or from the chlorine in a chloro complex. This electron pair would occupy a p orbital in the ligand. The criterion for π-bonding then is a suitable matching of the vacant cobalt orbital with the p orbital of the ligand which contains the free electron pair. The orbitals must be oriented so that lobes of the same sign can overlap.[12]

Figures 1a and 1b show the orientations of the ligand p orbital with respect to the vacant cobalt orbital for the tetragonal pyramid, with a vacant octahedral hybrid orbital, and for the trigonal bipyramid. For the tetragonal pyramid the positive lobes can overlap, but the negative lobes cannot. Therefore, it is concluded that some "π"-bonding will occur in the tetragonal pyramid but that a weak bond only will be formed. It is noted that this overlap can occur only for a p orbital of a ligand which is located in a position *cis*- to the vacant cobalt orbital. For a ligand in a *trans*-position, the p orbital must always be directed normal to the vacant cobalt orbital, and, therefore, could not properly overlap it.

Other possibilities for a square pyramid according to Kimball would be $d^2 sp^2$ hybridization with a vacant p_z orbital normal to the tetragonal plane and $d^2 p^3$ hybridization with a vacant s orbital. These structures are energetically unfavorable, though the vacant p_z orbital could lead to good π-bonding with a *cis*-ligand. Another possibility is the dsp^3 hybrid discussed by Daudel and Bucher[13] in which the vacant orbital is a $d_z{}^2$ normal to the tetragonal plane. This structure is energetically plausible but cannot undergo π-bonding with either a *cis*- or *trans*-ligand. Presumably if π-bonding can occur to an appreciable extent, the net hybridization will result in less $d_z{}^2$ and more p_z character in the vacant orbital. The resultant in such a case will be very similar to the octahedral orbit and have π-bonding abilities as already discussed.

In the trigonal bipyramid both the positive and negative lobes are well matched for good overlap. It is concluded that the trigonal bipyramid can undergo reasonably strong π-bonding. This strong π-bonding in the trigonal bipyramid would be expected to greatly stabilize the reaction intermediate after the dissociation of the chloride ion but would be expected to be a factor in the displacement of the chloro group only insofar as rearrangement to the trigonal bipyramid form occurs during the stretching of the Co–Cl bond.

Giacometti[14] has discussed the hybridization of orbitals for a trigonal bipyramid structure in a somewhat different way. In this case the possibilities for π-bonding are essentially the same as for our simpler presentation.

Failure of the *trans*-Effect in Octahedral Cobalt(III) Complexes.—Chernyaev[15] observed that in substitution reactions of platinum(II) complexes the position of the substitution depends upon the nature of the ligands in the complex, not that of the entering group. He pointed out that a group *trans* to a negative ligand is replaced more readily than if it were *trans* to a neutral ligand. This phenomenon known as the *trans-effect* has been observed, qualitatively, for numerous reactions of platinum(II) complexes.[16] The same effect, if it occurs at all, is not nearly as well defined for octahedral complexes. However, some evidence can be cited for cobalt(III) complexes where it would appear that the *trans*-effect does play a significant

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[11] (a) F. Basolo, B. D. Stone and R. G. Pearson, This Journal, **75**, 819 (1953); (b) D. D. Brown and R. S. Nyholm, *J. Chem. Soc.*, 2696 (1953); (c) H. M. E. Cardwell, *Chemistry and Industry*, 422 (1955).

[12] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332, 354 (1954), give an account of d-p π-bonding.

[13] R. Dandel and A. Bucher, *J. chim. phys.*, **42**, 6 (1945).

[14] G. Giacometti, *J. Chem. Phys.*, **23**, 2068 (1955).

[15] I. I. Chernyaev, *Ann. Inst. Platine U. S. S. R.*, **4**, 243 (1926); **5**, 118 (1927).

[16] J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952); J. Chatt, L. A. Duncanson and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

role. For example, Bailar and Peppard[17] have successfully applied this principle in their synthesis of the geometrical isomers of the ion Coen $(NH_3)_2Cl_2^+$. The key step in this synthesis is the replacement of two NH_3 groups *trans* to two $SO_3^=$ groups, leaving two NH_3 groups *cis* to $SO_3^=$ untouched. Another example is furnished by the data of Bjerrum and Rasmussen[18] on the acid dissociation constants of *cis*- and *trans*-$Coen_2(H_2O)_2^{+3}$. The results obtained are strictly analogous to those reported for the acid strengths of *cis*- and *trans*-$Pt(NH_3)_2(H_2O)_2^{+2}$,[19] the latter having been attributed to the *trans*-effect.[20] Finally, the rate of acid hydrolysis of *trans*-$Coen_2NO_2Cl^+$ is tenfold greater than that of the *cis*-isomer (Table III) in accord with the *trans*-effect.

TABLE III

RATES OF ACID HYDROLYSIS OF SOME GEOMETRICAL ISOMERS OF COBALT(III) COMPLEXES AT 25°

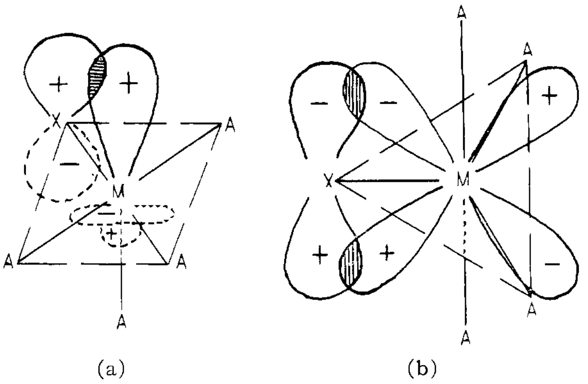
Complex	Isomer	k (sec.$^{-1}$)
$Coen_2NO_2Cl^{+a}$	*cis*	1.1×10^{-4}
	trans	1.1×10^{-3}
$Co(NH_3)_4Cl_2^{+b}$	*cis*	2×10^{-2}
	trans	1.8×10^{-3}
$Coen_2Cl_2^{+b}$	*cis*	2.5×10^{-4}
	trans	3.2×10^{-5}
$Coen_2OHCl^{+c}$	*cis*	1.3×10^{-2}
	trans	1.4×10^{-3}
$Coen_2F_2^{+d}$	*cis*	6×10^{-6}
	trans	1.8×10^{-6}

[a] F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, THIS JOURNAL, **76**, 3079 (1954). [b] R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955). [c] R. G. Pearson, R. E. Meeker, and F. Basolo, THIS JOURNAL, **78**, 2673 (1956). [d] W. R. Matoush, Ph.D. Thesis, Northwestern University, 1957. Measurements were made in 0.001 *M* HNO_3.

Except for the chloronitro complexes, the data in Table III show that for all other isomeric pairs the *trans*-isomer reacts more slowly than does the *cis*-form. This is contrary to what would be predicted merely on the basis of the *trans*-effect.

Failure of the *trans*-effect is believed to be due to the importance of π-bonding in these reactions. In the preceding section it was shown that the maximum overlap of the positive and negative lobes is afforded by a trigonal bipyramid structure (Fig. 1).

It is to be noted that such a structure can be formed from both *cis* and *trans* ligands. However, if π-bonding, accompanied by rearrangement to the trigonal bipyramid, occurs and accelerates the release of chloride ion, it will be more effective if the electron donating ligand is *cis* to the chloro group than if it is *trans*. This conclusion follows by assuming that the transition state for the dissociation of chloride ion will be intermediate between the original octahedral configuration (same orbital arrangement as in the tetragonal pyramid) and the final trigonal arrangement (intermediate between Fig. 1a and Fig. 1b).



(a) (b)

Fig. 1.—Orientation of ligand p orbital with respect to vacant cobalt orbital in five-coördinated intermediates: a, tetragonal pyramid; b, trigonal bipyramid.

The data in Table III show that the *trans*-effect fails only for complexes containing ligands which have available unshared pairs of electrons, *e.g.*, Cl^-, OH^- and F^-. In these cases the π-bonding contribution to the cleavage of the Co–X bond reaches a maximum whenever the electron donating ligands are adjacent (*cis*-) to the group, X, that is being replaced. Therefore, this preferred geometry for π-bonding in *cis* complexes can account for the fact that they react more rapidly than do the analogous *trans* isomers, contrary to predictions based on the *trans*-effect. If this assumption is correct, then complexes containing ligands which cannot produce this type of π-bonding (NO_2^- and SO_3^{-2}) should react in accordance with the *trans*-effect rule. This is, in fact, what is observed. On this basis it is predicted that the *trans-effect should be found in the reactions of octahedral complexes which contain negative ligands that cannot form good π-bonds to the central atom.*[21] If the reaction involved is a proton transfer, however, this does not involve any new possibilities for π-bonding, and the *trans*-effect may be expected.

No definite decision can be made from the rates of base hydrolysis listed in Table II as to whether a *cis* or *trans* amido group is more effective since the configurations of the conjugate bases are unknown. A *cis* amido group is always possible in the cases that have been studied.[4a] It is of interest that the greater rate of reaction of *cis*-$Coen_2Cl_2^+$ than *trans* does not hold for base hydrolysis. Also, the greater rate of reaction of $Coen_2ClOH^+$ than $Coen_2Cl_2^+$ does not hold for base hydrolysis.[4a] This can be rationalized by assuming that the acceleration due to chloro or hydroxo π-bonding will not carry over to basic conditions where amido π-bonding dominates.

Stereochemical Consequences of π-Bonding.—It is possible to use the conclusions of the last section to make predictions concerning the stereochemistry of the reaction products of some reactions of cobalt(III) complexes. The guiding principle is that strong π-bonding will cause a rearrangement to a trigonal bipyramid intermediate in reactions proceeding by a dissociation mechanism. Since amido π-bonding is the strongest, and is postulated as always occurring in the base hydrolysis of com-

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[17] J. C. Bailar, Jr., and D. F. Peppard, THIS JOURNAL, **62**, 105 (1940).

[18] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

[19] K. A. Jensen, *Z. anorg. Chem.*, **242**, 87 (1939).

[20] A. A. Grinberg, *Acta Physicochim. U.R.S.S.*, **3**, 573 (1935).

[21] This prediction presupposes a dissociation mechanism.

plexes containing an N–H bond, rearrangement should always accompany the reaction of such complexes with alkali.

The possible modes of reaction of a trigonal bipyramid, penta-coördinated intermediate have been discussed already.[11a] However, this discussion is incomplete and, in part, incorrect. Figure 2 shows a more complete analysis of the products that can be formed by reaction of an entering group with a trigonal bipyramid intermediate derived from [Co(AA)$_2$ax]. It is assumed that the group enters between the groups in the trigonal plane.

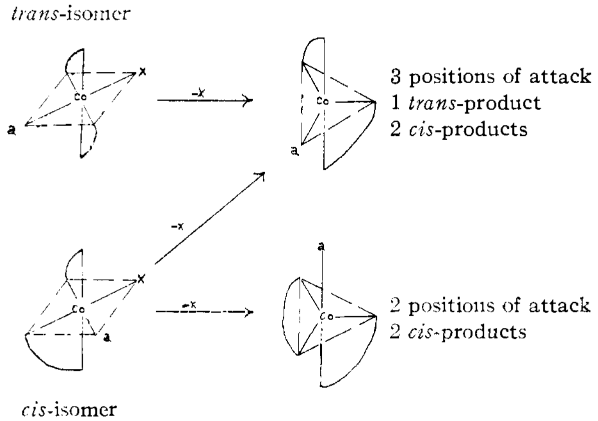

Fig. 2.—Stereochemical changes for a dissociation mechanism involving trigonal bipyramid intermediates.

One of the trigonal forms is the same for both *cis* and *trans* starting material. This can lead to both *cis*- and *trans*-products. However, an active *cis*-reactant will give an active trigonal form, whereas the *trans*-reactant can give only a *d,l*-mixture. A *cis* starting material can also pass through an additional inactive trigonal form which can give only *cis* product. Since the course of the reaction will depend on steric and inductive factors as well as statistical, no exact statement of the stereochemistry of the product can be given.

However, it would appear that considerable rearrangement of both *cis* to *trans* and *trans* to *cis* should occur with *cis* product generally predominating on statistical grounds. Of a pair of *cis-trans* isomers, the *cis* should always give the greater amount of *cis*-product.

If an optically active *cis* starting material is used the product should be active in part with *retention of configuration*. Some inactive *trans* and racemic *cis* will also be formed.[21a] Note that there is no way in which an optically active *cis*-product can be formed with inversion of configuration.[22] If it can be also assumed that reactions not involving π-bonding go primarily through the tetragonal pyramid form (at least in a good coördinating solvent such as water), then the difficulty of obtaining an active product of inverted configuration in reactions of active cobalt(III) complexes can be understood.[23] Presumably such inverted products can be obtained only in circumstances where a dissociation mechanism is not operating.

The facts on the stereochemistry of the immediate products of reaction of cobalt(III) complexes are rather scanty.[14] Reactions in water under acid or neutral conditions seem to give largely retention of configuration. A number of reactions of active *cis*-complexes give active products with retention of configuration, but the degree of optical purity is uncertain.[24] Table IV gives the available data on the products of base hydrolysis of several pairs of *cis–trans* isomers. The predictions made on the basis of π-bonding are seen to be fulfilled in general.

TABLE IV

STEREOCHEMISTRY OF PRODUCTS OF BASE HYDROLYSIS FOR SOME *cis–trans* ISOMERS OF COBALT(III) COMPLEXES

Complex ion	Product	
trans-[Coen$_2$ClSCN]$^{+a}$	*cis*-(OH)(SCN)	82%
	trans-(OH)(SCN)	18%
trans-[Coen$_2$BrSCN]$^{+a}$	*cis*-(OH)(SCN)	81%
	trans-(OH)(SCN)	19%
cis-[Coen$_2$NH$_3$Cl]$^{+a}$	*cis*-(NH$_3$)(OH)	84%
	trans-(NH$_3$)(OH)	16%
trans-[Coen$_2$NH$_3$Cl]$^{+a}$	*cis*-(NH$_3$)(OH)	83%
	trans-(NH$_3$)(OH)	17%
cis-[Coen$_2$NO$_2$Cl]$^{+b}$	*cis*-(NO$_2$)(OH)	100%
	trans-(NO$_2$)(OH)	0%
trans-[Coen$_2$NO$_2$Cl]$^{+b}$	*cis*-(NO$_2$)(OH)	50%
	trans-(NO$_2$)(OH)	50%
cis-[Coen$_2$Cl$_2$]$^{+b}$	*cis*-(OH)(Cl)^c	9%
	trans-(OH)(Cl)^c	50%
	cis-(OH)$_2$^{d}	40%
	trans-(OH)$_2$^{d}	60%
trans-[Coen$_2$Cl$_2$]$^{+b}$	*cis*-(OH)(Cl)^c	18%
	trans-(OH)(Cl)^c	55%
	cis-(OH)$_2$^{d}	60%
	trans-(OH)$_2$^{d}	40%

[a] Reference C. K. Ingold, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1691, 1707 (1956). [b] Reference 11a and reference of Table III. [c] From reaction of one mole of NaOH. At the same time 21% of dihydroxo complex is formed from the *cis*-dichloro and 14% of dihydroxo from the *trans*-dichloro complex. The higher yield of *cis*-chlorohydroxo from the *trans*-dichloro than from the *cis*-dichloro complex is not explicable on the basis of π-bonding. Reference is footnote *a* of Table III. [d] From the reaction with excess NaOH.

Evidence for π-Bonding in Complexes of Other Metals.—Wilmarth and co-workers[25] have recently presented magnetic and other evidence that π-bonding similar to the type proposed in this paper occurs in the binuclear basic rhodo chromium(III) ammine complex, (NH$_3$)$_5$Cr–O–Cr(NH$_3$)$_5$$^{+4}$. Similar evidence exists[26] for the complex ion Cl$_5$RuORuCl$_5$$^{-4}$. In the case of the chromium

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(21a) NOTE ADDED IN PROOF.—Ingold, Nyholm and Tobe (see Table IV for reference) have recently confirmed this prediction, though they prefer an S$_N$2 mechanism.

(22) This is a point on which reference 11a is in error in that an inverted product is shown from the asymmetric trigonal bipyramid intermediate.

(23) (a) J. C. Bailar, Jr., and W. Auten, THIS JOURNAL, **56**, 774 (1934); (b) J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940); (c) J. C. Bailar, Jr., J. H. Haslam and E. M. Jones, *ibid.*, **58**, 2226 (1936).

(24) J. P. Mathieu, *Bull. soc. chim.*, [5] **4**, 687 (1937).

(25) W. K. Wilmarth, H. Graff and S. T. Gustin, THIS JOURNAL, **78**, 2683 (1954).

(26) J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 2594 (1953).

complex, a strong labilizing of the other ligands is produced by the π-bonding.

Postmus and King have also shown[27] that in the reaction of the aquo chromium(III) ion with thiocyanate ion, the hydroxo complex $Cr(H_2O)_5OH^{+2}$ is more reactive than $Cr(H_2O)_6^{+3}$. This can be explained in terms of a dissociation mechanism with a five-coördinated intermediate stabilized by π-bonding. A similar situation exists for the acid hydrolysis of $SbCl_6^-$ which is less reactive than $SbCl_5OH^-$.[28] In short, there is no reason to believe that π-bonding is not a common occurrence in all octahedral complexes regardless of the nature of the central atom.

Acknowledgment.—The authors are indebted to Dr. R. E. Meeker for the measurements reported in Table I and Drs. Meeker and H. M. Neumann for stimulating discussions in connection with this paper.

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[27] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

[28] H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. XI.[1] Rates of Hydrolysis and Racemization of Difluoro-bis-(ethylenediamine)-cobalt(III)[2,3]

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The rates of acid and base hydrolysis of *trans*-$[Coen_2F_2]^+$ were determined and found to be much slower than the corresponding rates of reaction of *trans*-$[Coen_2Cl_2]^+$. In addition, unlike the dichloro complex, the rate of acid hydrolysis of the difluoro compound is acid catalyzed. A mechanism is proposed to account for this which involves the intermediate formation of a protonated complex. Finally the loss of optical rotation of *d-cis*-$[Coen_2F_2]^+$ was found to proceed in two steps. The first step is a mutarotation due to the formation of *d-cis*-$[Coen_2H_2OF]$ and this then slowly undergoes racemization.

The synthesis and reactions of some fluoroamminecobalt(III) complexes, as well as the resolution of *racemic* isomers, was described earlier.[4] Investigations on these complex ions have now been extended to kinetic studies of hydrolysis reactions and the mutarotation and racemization of optically active isomers. These data are presented here and compared with similar data for the corresponding chloro and bromo complexes.

Experimental

Compounds.—The coördination compounds used were prepared as previously described;[4] all other compounds were commercially available and of reagent grade.

Kinetic Methods for Rates of Acid Hydrolysis.—Three different methods were used to follow the rate of acid hydrolysis. The selection of a method depended, to some extent, on the nature of the complex under investigation.

1. **Spectrophotometric Method.**—This method was applicable to a study of *trans*-$[Coen_2F_2]^+$, since there is a large difference in the optical density of this complex and the product, $[Coen_2H_2OF]^{2+}$, at 500 mμ. The change in optical density at this wave length was followed until the replacement of one fluoride ion was substantially complete and a "leveling off" of the rate was observed. The second fluoride is replaced much more slowly than the first and therefore does not interfere greatly with the determination of the rate of the first step. All measurements were made on a Beckman Model DU Spectrophotometer using cells of 1-cm. path length. Temperature control to within ±0.1° was achieved by pumping water from a constant temperature bath through the compartment surrounding the cells. At low temperatures where the reaction is quite slow, the reaction mixture was kept in the thermostat and aliquots were periodically withdrawn for measurement of optical density. The data obtained gave good first order plots of t *vs.* log $(D_\infty - D)$ and the rate constant k was estimated from the slope of the line (Table II).

2. **Chemical Method.**—The spectrophotometric method was not applicable to the *cis*-difluoro complex because of only negligible spectral changes during hydrolysis. It was therefore necessary to devise a method to follow this reaction by determining the fluoride ion concentration in these colored solutions. This chemical method was also used to check the results obtained by the spectrophotometric method for the *trans* isomer; results by the two methods were in good agreement.

The standard procedure[5] of fluoride analysis by titration with thorium nitrate solution using a sodium alizarin sulfonate indicator was finally adapted to a study of these systems. The primary difficulty was that of visually detecting the end-point in these colored solutions. The possibility that the colored complex could be removed on a cation exchange resin and thus permit the usual determination of fluoride on the resulting colorless solution was first examined. The results obtained were not satisfactory as it appeared that adsorption of the complex on the resin induced the release of coördinated fluoride ion. A technique was finally developed that gave satisfactory results for solutions containing the colored complex ion. In a typical determination, two aliquots were withdrawn from the thermostated reaction mixture. One of these was used in combination with the standard indicator blank, such that on horizontally viewing through both solutions, an approximation to the end-point color was observed. The second aliquot was also placed in front of the standard indicator blank and in the same way viewed horizontally through both solutions. Titration was then carried out with thorium nitrate solution and the end-point detected by reference to the first aliquot plus indicator blank combination. Although this method was tedious, it did give satisfactory results for the first half-life of the reactions studied. Beyond this point the intensity of color increased and deviations in fluoride analyses became correspondingly larger. The data obtained gave good first order plots of t *vs.* log $(T_\infty - T)$, where T is the gross thorium nitrate titer, and the rate constant k was estimated from the slope of the line (Table IV).

3. **Fractional Life Method.**—An approximate but rapid method of determining the acid hydrolysis rate of the *trans* difluoro complex was to observe the time required for the originally green colored solution to become almost colorless or gray in color. This marked the point at which the combined optical absorption due to the green reactant, *trans*-$[Coen_2F_2]^2$, and the red product, $[Coen_2H_2OF]^{2+}$,

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[1] Previous paper in this series, R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

[2] This investigation supported by a National Science Foundation Grant (NSF-G58) and by the U. S. Atomic Energy Commission under Contract AT(11-1)-89—Proj. No. 2.

[3] Presented in part at the International Conference on Coordination Compounds in Amsterdam, April, 1955.

[4] W. R. Matoush and F. Basolo, THIS JOURNAL, **78**, 3972 (1956).

[5] H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.*, **5**, 7 (1933).