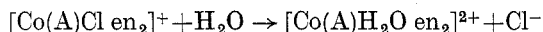


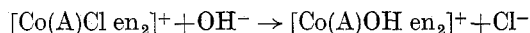
THE LABILIZING INFLUENCES OF THE HYDROXO LIGAND IN THE SUBSTITUTIONS OF COBALT(III) COMPLEXES*

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In the unimolecular substitution of $[\text{Co}(\text{A})\text{Cl en}_2]^+$ complexes by water (solvolytic aquation), where en represents ethylenediamine and A denotes either OH or Cl,



it has been universally accepted¹ that the dissociation of the leaving chloro ligand is brought about largely by the electropositive electromeric effect ($+E$) of the labilizing hydroxo or chloro ligands. An estimate of the $+E$ effects of these ligands may be obtained by comparing the first-order rate constants for the solvolytic aquation of the appropriate complexes, allowance being made for the statistical factor of two in the dichloro cation. These rate constants¹ indicate a greater (by 100-fold) $+E$ effect for the hydroxo ligand than for the labilizing chloro ligand. On the other hand, the mechanism for the substitution of these complexes by hydroxide ion (base hydrolysis) is not yet definite:



In spite of their earlier statement² that the "stereochemistry of the reaction product is often not in itself diagnostic of the mechanism involved", Pearson and Basolo³ recently claimed that the available *stereochemical* data support a dissociation process for the base hydrolysis of octahedral cobalt(III) complexes. We now wish to show that the available *rate* data can be quite inconsistent with their $S_N1\text{CB}$ mechanism, particularly when the labilizing influences of the hydroxo ligand is being considered.

According to the $S_N1\text{CB}$ mechanism, the observed second-order rate of reaction depends on the product of two constants, namely, (a) the equilibrium constant for the ionization of a proton from an amine ligand in the complex; and (b) the first-order rate constant for the unimolecular aquation of the resulting conjugate base, the dissociation of the leaving chloro ligand being brought about by the $+E$ effects of both the amido group and the non-replaced unidentate ligands A. For the reactions with the $[\text{Co}(\text{A})\text{Cl en}_2]^+$ series of cations, the amido group (and hence its $+E$ effect) is the same throughout the series, and so the reactivities of the various complexes should depend mainly on the acid-strengthening effect, as well as the $+E$ effect, of A. It is not possible to quote figures for the ionization constants of the amine-amide system, but an estimate of the acid-strengthening effect of the hydroxo ligand

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¹ Baldwin, M. E., Chan, S. C., and Tobe, M. L., *J. chem. Soc.*, 1961, 4637.

² Basolo, F., and Pearson, R. G., "Mechanisms of Inorganic Reactions." p. 220. (John Wiley: New York 1958.)

³ Pearson, R. G., and Basolo, F., *Inorg. Chem.*, 1965, 4, 1522.

relative to that of the non-replaced chloro ligand may be obtained by comparing the available values⁴ for the corresponding aquo complexes, where the proton is lost from oxygen (K_a is 1.3×10^{-8} and 6.3×10^{-8} respectively when A is *trans*-OH and *trans*-Cl at 25°). Although the acid-strengthening effect of Cl is some five times greater than that of OH, it is more than offset by its smaller (100-fold) +*E* effect, so that the S_N1CB mechanism would require that the $[\text{Co}(\text{OH})\text{Cl en}_2]^+$ complex undergoes base hydrolysis at a higher rate than the $[\text{Co}(\text{Cl})\text{Cl en}_2]^+$ cation. Reference to available data (k_2 is 0.56 and 1500 respectively for A = *trans*-OH and A = *trans*-Cl at 25°)⁵ shows that this requirement is clearly not supported by experiment, since the observed labilizing influences of the hydroxo ligand are only 1/2700 those of the non-replaced chloro ligand. Although Pearson *et al.*⁶ reported obtaining a rate constant of 200 l. mole⁻¹ sec⁻¹ at 25° for the *trans*-chlorohydroxobis(ethylenediamine)-cobalt(III) cation by an indirect method subject to considerable error, their value appears to be incorrect (see, e.g., ref. 12 in Olson and Garner⁷).

In an attempt to explain the extremely large reduction in rate for the base hydrolysis of the dichlorobis(ethylenediamine) complexes when the non-replaced chloro ligand is changed to the nitro group, Pearson *et al.*⁸ introduced another rate-determining factor, namely, the repulsive π -type interaction between the filled *p* orbitals of nitrogen in the amido group and the filled d_{xy} -type orbitals on the cobalt atom. This repulsion, which is a quantum-mechanical rather than a purely electrostatic interaction, provides a driving force for the departure of the chloride ion. The chloronitro complexes, in which the electronegative conjugation ($-T$) of the nitro ligand reduces the electron occupancy of the d_{xy} -type cobalt orbital, will not supply as much driving force for this process, and consequently the reaction is much slower. Clearly this explanation cannot be satisfactorily applied to the observed slow reaction for the chlorohydroxo complexes, since the hydroxo ligand, with no vacant *p* orbitals, is incapable of metal-to-ligand π -bonding. In fact, in this aspect, the labilizing influences of the hydroxo ligand should be quite similar to those of the non-replaced chloro ligand, which is not supported by experiment. For reasons⁹ which we shall not repeat here, we believe that the driving force for the breaking of the bond joining the cobalt to the outgoing chloro ligand in the $[\text{Co}(\text{Cl})\text{Cl en}_2]^+$ complex is derived, not from quantum-mechanical interactions involving the amido group, but rather from those involving the non-replaced chlorine. In this way, the relatively small reactivity of the chlorohydroxo complexes can be easily accounted for.

To extend the discussion of quantum mechanical interactions from the case of $\text{Co}-\ddot{\text{Cl}}:$ to those of $\text{Co}-\ddot{\text{O}}\text{H}$ and $\text{Co}-\ddot{\text{N}}\text{H}_2$, it is necessary to consider, not only the number of non- σ -bonded lone-pairs of electrons in the respective donating atoms, but also their stereochemistries. First, the magnitude of these quantum-mechanical repulsions is smaller when there are fewer lone-pairs of electrons, and this would

⁴ Tobe, M. L., *Sci. Prog., Lond.*, 1960, **48**, 492.

⁵ Chan, S. C., and Tobe, M. L., *J. chem. Soc.*, 1962, 4531.

⁶ Pearson, R. G., Meeker, R. E., and Basolo, F., *J. Am. chem. Soc.*, 1956, **78**, 709.

⁷ Olson, D. C., and Garner, C. S., *Inorg. Chem.*, 1963, **2**, 558.

⁸ Pearson, R. G., Munson, R. A., and Basolo, F., *J. Am. chem. Soc.*, 1958, **80**, 504.

⁹ Chan, S. C., *Nature*, 1966, **212**, 815.

lead to the following order of decreasing labilizing power for these ligands: $\text{Cl} > \text{OH} > \text{NH}_2$. Secondly, it also depends on the directional properties of the orbitals at which the lone-pairs of electrons are supposed to reside, being greatest if perpendicular to the Co-A σ -bond.⁹ There is little error in assuming that the stereochemistries of these donating atoms in complexes are similar to those in the corresponding simpler compounds where the atoms are joined to hydrogen, i.e. $\text{H}-\ddot{\text{Cl}}:$, $\text{H}-\ddot{\text{O}}\text{H}$, and $\text{H}-\ddot{\text{N}}\text{H}_2$. For the water (or ammonia) molecule, it is well known that the oxygen (or nitrogen) atom has a tetrahedral disposition of orbitals, with the lone-pairs of electrons residing in two (or one) of the sp^3 hybrid orbitals making an approximately tetrahedral angle with the σ -bonds. This is because the overlap integral involving the $2s$ orbital on these elements and another σ -orbital at equilibrium distance is appreciably greater than that involving the $2p$ orbital and so there is much to be gained in overlap by bringing the s orbital into a hybrid scheme. On the other hand, the corresponding overlap of σ -orbitals is greater with the $3p$ than with the $3s$, and so for HCl no hybridization will be necessary, and two of the three lone-pairs of electrons in chlorine will reside in the pure p orbitals, mutually perpendicular to the σ -bond. The result is that, in cobalt(III) complexes, the magnitude of the quantum mechanical repulsions will be considerably greater when $\text{A} = \text{Cl}$ than when $\text{A} = \text{OH}$, corresponding to the marked reduction in reactivity⁵ observed on changing A from *trans*-Cl to *trans*-OH in the reactions of the $[\text{Co}(\text{A})\text{Cl en}_2]^+$ cations. This repulsion is clearly least for the amido ligand, thus indicating strongly that the importance, if any, of the amido conjugate base in the base hydrolysis of halogenoamminecobalt(III) complexes is extremely small.

On the basis that the proposed modification is followed, we further suggest that the transmission of these quantum mechanical interactions does not require or permit a dissociative process. This is evidenced by the fact that such interactions are not operative in the solvolytic aquation of $[\text{Co}(\text{Cl})\text{Cl en}_2]^+$ and $[\text{Co}(\text{OH})\text{Cl en}_2]^+$ cations, for which the assignment of a unimolecular mechanism has been universally accepted, and in which the rate-determining factor is the $+E$ effect ($\text{OH} > \text{Cl}$). Presumably some degree of nucleophilic interaction is required for the transmission of the quantum mechanical repulsions ($\text{Cl} > \text{OH}$) in the base hydrolysis of these cations, so that the reaction may be visualized as a displacement process in which bond-breaking is more important than bond-making in the transition state.

In conclusion, it can be said that the labilizing influences of the hydroxo ligand in the substitutions of cobalt(III) complexes depend on the nature of the nucleophile, being an electropositive conjugation in solvolytic aquation, and a quantum mechanical repulsion in base hydrolysis.