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MECHANISM OF SUBSTITUTION REACTIONS OF COMPLEX IONS. XV. ACID AND BASE HYDROLYSIS OF *CIS*- AND *TRANS*-DICHLORO-BIS-(ETHYLENEDIAMINE)-CHROMIUM(III) ION.[1]

Sir:

The rates of acid hydrolysis of chloro complexes of chromium(III) are always greater than those of the corresponding complexes of cobalt(III).[2] This is as expected on the basis of crystal field theory[3] since cobalt(III), with six electrons in the stable d_{xy}, d_{xz}, and d_{yz} orbitals, will resist changes in the octahedral arrangement of ligands more strongly than chromium(III) with only three electrons in these orbitals. We recently have measured the rates of both acid and basic hydrolysis for *cis* and *trans*-$Cr(en)_2Cl_2^+$. The results together with those[4] for *cis* and *trans* $Co(en)_2Cl_2^+$ are

RATE CONSTANTS AT 25° IN WATER

	k_{acid}, sec.$^{-1}$	k_{base}, M.$^{-1}$ sec.$^{-1}$
cis-$Cr(en)_2Cl_2^+$	3.5×10^{-4}	2.7×10^{-2}
trans-$Cr(en)_2Cl_2^+$	3.9×10^{-5}	3.7×10^{-2}
cis-$Co(en)_2Cl_2^+$	2.5×10^{-4}	1.0×10^{3}
trans-$Co(en)_2Cl_2^+$	3.2×10^{-5}	3.0×10^{3}

The remarkable result is that the rates of base hydrolysis are about $1/10^5$ *slower* for chromium(III) than for cobalt(III). This demonstrates, at the very least, that a common mechanism is not operating throughout. The slower reaction with hydroxide ion for chromium compared to cobalt is not compatible with an S_N2 mechanism on either the basis of crystal field or valence bond theory.

The result is explicable on the basis of an S_N1CB mechanism as previously postulated.[4] The acidities of corresponding chromium and cobalt complexes, where measurable, are found to be about equal.[5] Hence the conjugate bases are formed with about equal ease from either $Cr(en)_2Cl_2^+$ or $Co(en)_2Cl_2^+$. The great reactivity of the conjugate base has been ascribed to repulsive π-type interaction between the filled p orbitals of nitrogen in the amido group and the filled d_{xy} type orbitals on the metal atom.[6] This repulsion provides a driving force for loss of chloride ion accompanied by a rearrangement to a trigonal bipyramid intermediate which allows an attractive π-type interaction with the now empty $d_{x^2-y^2}$ orbital.

It is obvious that chromium with only half as many electrons in the d_{xy} type orbitals will not supply as much driving force for this process. Hence the over-all much lower rate of release of chloride ion in the presence of alkali can be understood. A similar explanation will hold for *cis*-$Co(en)_2NO_2Cl^+$, which also reacts very slowly with hydroxide ion.[7] In this case π-bonding from the metal atom to the nitro group reduces the electron occupancy of the d_{xy} type orbital.

The rates of chloride ion release were measured both in acid and in alkali by amperometric titration of chloride ion. The concentration of complex ion was 2.00×10^{-3} *M*. Ionic strength was maintained at 0.10 by $NaNO_3$. Rates in alkali were measured in a series of solutions containing up to 0.10 *M* hydroxide ion. The pseudo first order rate constant was found from the experimental half-life for one chloride ion. A plot of rate constant *vs.* hydroxide ion concentration was linear. From the slope, the second order rate constant given in the table was calculated. The rate constants for acid hydrolysis were found directly in 0.1 *M* nitric acid and also in acetate–acetic acid buffers of *p*H 4.2 to 4.6 containing 0.1 *M* acetate ion. The same rates were obtained in the two media showing that there was no direct reaction with acetate ion. The rate constant for acid hydrolysis could also be found from the intercept of the above mentioned plot. The intercept was equal to about twice the directly measured value, since in alkaline solution the intermediate $Cr(en)_2OHCl^+$ would rapidly lose the second chloride ion.[8]

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A NEW CYCLOPROPYL CORRELATION IN THE NEAR-INFRARED REGION

Sir:

During a recent investigation of certain cyclopropyl derivatives in the near-infrared region of 1.1–2.7 microns, we have noted that in every case of nine derivatives examined, an absorption band has occurred at 1.63–1.65 microns and another at 2.22–2.27 microns.

The spectra were determined using a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. All compounds were run as 10% solutions in carbon tetrachloride in a 3.0 mm. fixed thickness sodium chloride cell. Wave length was calibrated using chloroform and benzene.