tronegativities (x_{opt}) as defined by Jørgensen.[9] The resultant values are listed and compared with the corresponding values for halo complexes in Table IV.

TABLE IV
OPTICAL ELECTRONEGATIVITIES

	Oxo compds	Halides[a]		Oxo compds	Halides[a]
F		3.9	V(V)	2.7	
O	3.5	3.5 (H_2O)[b]	Mo(VI)	2.5	
Cl	3.0[c]	3.0[c]	W(VI)	2.3	2.2[d]
Br	2.8	2.7	Nb(V)	2.0	2.0[d]

[a] Reference 9. [b] This value was estimated from the lowest charge-transfer band of $Ru(H_2O)_6^{3+}$. [c] x(Cl) was chosen as the reference. See the text. [d] The lowest charge-transfer bands given in Table III were used. Smaller literature values are based on the Laporte-allowed transitions occurring at higher energies.

The derived x_{opt}'s follow the trend generally accepted. We also note that on going from $3d^0$ to $4d^0$ and from $4d^0$ to $5d^0$ in the same oxidation states the x_{opt}'s decrease by 0.7 and 0.2, respectively. A similar shift between 4d and 5d was noted for the halo complexes.[8] On going from Nb(V) to Mo(VI), the x_{opt} increases by 0.5. The x_{opt} of Nb(V) is larger than that of Zr(IV) by 0.2.[10]

Now the question is, "Which molecular orbitals are involved in this charge transfer?" Kon and Sharpless[4,5] assigned this to $b_1^b \rightarrow b_2^*$, but, as a recent molecular orbital calculation for $VOCl_4^{2-}$ shows, about 20 kK below the b_2^* orbital there is a group of close-lying nonbonding and bonding orbitals which are of mainly ligand character. The e_π^b and b_1^b orbitals lie more than 30 kK below this group of orbitals.[6] Thus it is more likely that the LCT band comes from the former group of orbitals for chlorides and bromides.

Another point is that the transition energy for the second lowest charge transfer is always about 6 kK higher than that of the LCT band for metal oxychlorides with no d electron (see Table I). Since this energy is much smaller than the lowest d–d transition energy for the corresponding d^1 system, the second LCT band must be attributed to another orbital on chlorine, probably the b_2^b orbital which is about 6 kK below the nonbonding orbitals b_1^n and a_2^n.[6] Thus the assignment of the CT bands for $MoOCl_5^{2-}$ based on a single bonding orbital[3] is doubtful.

In many iso- and heteropoly anions the metal ion is surrounded octahedrally by six oxygen atoms, one of which is an oxo-type oxygen.[12] The original motivation for the present study was to identify the oxygen responsible for the LCT bands of these compounds. Although the LCT bands have usually been assigned to $e_\pi^b \rightarrow b_2^n$ for oxo compounds on the basis of the molecular orbital treatment, x_{opt} of H_2O is so similar to that of oxygen in eq 2 that the bands may equally well be attributed to the "equatorial" oxygens. When the spectra of $PW_{12}O_{40}^{3-}$ and $P_2W_{18}O_{62}^{6-}$ are compared, the appearance of another band in the spectrum of the latter suggests that the equatorial oxygens are involved in the low-energy charge transfers. However, no such splitting is observed for $P_2Mo_{18}O_{62}^{6-}$, and the origins of the LCT bands of poly anions are still not clear.

The spectra of the reduced "heteropoly blue" complexes show intervalence charge-transfer transitions, *e.g.*, Mo(V) → Mo(VI). We may use the metal x_{opt}'s derived above to predict the position of the LCT bands in such compounds; see eq 3 and Table V.

$$E = 9 + \overset{\text{donor}}{\begin{Bmatrix} \mathrm{V} & 80 \\ \mathrm{Mo} & 75 \\ \mathrm{W} & 68 \end{Bmatrix}} - \overset{\text{acceptor}}{\begin{Bmatrix} \mathrm{V} & 80 \\ \mathrm{Mo} & 75 \\ \mathrm{W} & 68 \end{Bmatrix}} \qquad (3)$$

TABLE V
CALCULATED AND EXPERIMENTAL LOWEST INTERVALENCE CHARGE-TRANSFER BANDS IN HETEROPOLY BLUES

Donor	Acceptor	Calcd	Obsd	Compd	Ref
V	V	9	9	$MnV^{IV}V_{12}O_{38}^{8-}$	*a*
V	Mo	14	14	$PV^{IV}Mo_{11}O_{40}^{5-}$	*b*
V	W	21	20	$PV^{IV}W_{11}O_{40}^{5-}$	*b*
Mo	Mo	9	9	$H_2P_2Mo_2^{V}Mo_{16}O_{62}^{6-}$	*c*
Mo	W	16	16	$PMo^{V}W_{11}O_{40}^{4-}$	*d*
W	W	9	8.0	$PW^{V}W_{11}O_{40}^{4-}$	*e*
			8.6	$SiW^{V}W_{11}O_{40}^{5-}$	*e*
			8.5	$FeW^{V}W_{11}O_{40}^{6-}$	*e*
			11	$P_2W^{V}W_{17}O_{62}^{7-}$	*e*

[a] C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92,** 85 (1970). [b] M. T. Pope, D. P. Smith, J. J. Altenau, and J. Bender, *Proc. Int. Conf. Coord. Chem., 13th,* **1,** 127 (1970). [c] E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **9,** 667 (1970). [d] J. J. Altenau, M.S. Thesis, Georgetown University, Washington, D. C., 1970. [e] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, **9,** 662 (1970).

The constant, 9 kK, is attributed to a many-phonon jump with a large electron–phonon coupling constant following Hush.[13]

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[12] M. T. Pope, *Inorg. Chem.*, in press.

[13] N. S. Hush, *Progr. Inorg. Chem.*, **8,** 391 (1967).

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The Hydrolysis of *trans*-Dichloro- and *trans*-Chlorohydroxobis(propylenediamine)chromium(III) Cations in Basic Solution

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An appreciable amount of kinetic and mechanistic data is available for the base hydrolysis of *cis*- and *trans*-dihalo- or -halopseudohalobis(diamine)cobalt(III) cations.[1] On the other hand, very little attention has been focused on the chromium(III) analogs. Some time ago Basolo, *et al.*,[2] reported a brief investigation of the base hydrolysis of *cis*- and *trans*-dichlorobis(ethylenediamine)chromium(III) cations. More recently we have reported a more complete study of the *trans*-dibromo analog.[3] Tobe, *et al.*,[4] have studied *cis*- and *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)chromium(III) cations. The present study was undertaken

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 3.

[2] R. G. Pearson, R. A. Munson, and F. Basolo, *J. Amer. Chem. Soc.*, **80,** 504 (1958).

[3] M. S. Nozari and J. A. McLean, Jr., in "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 217.

[4] E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, **9,** 1781 (1970).

to gain information concerning the effect of *C*-alkyl substitution on base hydrolysis rates and stereochemistry and to make more meaningful comparisons between Cr(III) and Co(III) analogs.

Experimental Section

Preparation of Complexes.—*trans*-Chloroaquobis(propylenediamine)chromium(III) cation was prepared from aged solutions of the dichloro salt[5] and isolated by cation exchange as previously reported.[6] In order to obtain a pure concentrated solution, five separate columns were used and the resin bands containing the desired species were all combined in one column (kept below 0°) and eluted with 50 ml of 3.5 *N* HNO_3 (the eluate was collected in a flask and kept in an ice–salt bath). Chloroaquo solutions were adjusted to a pH of *ca.* 2 by titrating at 0° with Dowex 2-X8 resin (OH^- form) and used immediately for kinetic measurements.

trans-Diaquobis(propylenediamine)chromium(III) bromide was prepared by using *trans*-$[Cr(pn)_2Br_2]Br \cdot HgBr_2$ as the starting material.[7] Woldbye's method[8] was used to convert this double salt to the corresponding hydroxoaquo complex. The pink precipitate which formed immediately was washed with 50% ethanol to remove excess KBr and dried *in vacuo* over $CaCl_2$ overnight. *Anal.* Calcd for $[Cr(pn)_2(OH_2)(OH)]Br_2$: Cr, 13.16. Found: Cr, 13.15. The visible absorption spectrum of the corresponding bis-aquo complex was quickly recorded after dissolving this compound in cold 0.1 *N* HNO_3. The spectrum[9] has maxima at 448 (31.2) and 365 (41.3) and a minimum at 408 (21.2).

Other Chemicals.—A 2 *N* stock solution of $LiClO_4$, a 0.040 *M* solution of propylenediamine, and Dowex 2-X8 resin, 20–50 mesh in the OH^- form, were prepared according to published procedures.[10] Sodium hydroxide solutions were made from standard Acculate solutions and kept in sealed plastic containers. These solutions were standardized with standard HCl before use. All other chemicals were reagent grade.

Analytical Methods.—Visible absorption spectra were obtained with a Cary Model 14 spectrophotometer using matched quartz cells. Chromium analyses on solid samples as well as chromatographic fractions were performed by methods described previously.[6] All pH measurements were made with a Sargent Model DR pH meter.

Kinetic Measurements.—Temperature was maintained constant within ±0.04° by a thermostatically controlled bath. Light was routinely excluded by using actinic glassware. The reaction of *trans*-$Cr(pn)_2Cl_2^+$ in basic solution was carried out with the initial complex concentration, c_0, either equal to or half the initial base concentration, b_0. After mixing the appropriate amounts of thermostated NaOH solution and complex, aliquots were withdrawn with a fast-flowing thermostated pipet, quenched in 0.01 *N* HNO_3, and Cl^- release was followed by potentiometric titration.[6] When b_0 was equal to c_0, the second-order rate constant could be obtained from the slope of a plot of $1/(c_0 - x)$ *vs.* t, where x is the amount of Cl^- released at time t.

The rate of the above reaction was also followed by measuring the unreacted *trans*-$Cr(pn)_2Cl_2^+$ present at time t. The various components in the reaction mixture were separated by the elution procedure previously used in acid hydrolysis studies[6] except that the diaquo species were eluted with 250 ml of 6 *N* HNO_3.

The chromatographic procedure was also used to study the hydrolysis of *trans*-$Cr(pn)_2Cl_2^+$ in buffered alkaline solution. The reaction was begun in the same manner as the Cl^- release studies above except that NaOH was replaced by a buffer solution[11] at the desired pH (10.35–11.02). Aliquots were quenched in 0.25 *N* HNO_3 and passed through the cation-exchange column, and the unreacted complex was eluted with 1.4 *N* HNO_3 and analyzed for Cr. The pseudo-first-order rate constant was obtained by plotting $\ln [c_0/(c_0 - x)]$ *vs.* t. These values were in turn plotted against the hydroxide ion concentration,[12] giving a slope equal to the second-order rate constant for the base hydrolysis of *trans*-$Cr(pn)_2Cl_2^+$ and an intercept equal to the aquation rate constant. The latter rate constant was also measured independently at 25.0° in 0.10 *N* HNO_3 in the absence of light by following the disappearance of complex chromatographically as previously described.[6]

The hydrolysis of *trans*-$Cr(pn)_2(OH)Cl^+$ was studied exclusively at the desired pH in buffered alkaline solution. This cation was generated in solution by adding 25 ml of the propylenediamine buffer and 75 ml of 2.0 *M* $LiClO_4$ to 75 ml of the chloroaquo solution. This solution was transferrred to a dry 10-cm spectrophotometer cell, thermostated at 25.0°, and immediately the spectrum was repeatedly scanned from 350 to 650 nm at a rate of 50 Å/sec, until an equilibrium spectrum was obtained. The pseudo-first-order rate constants were obtained from plots of $-\ln (A_t - A_\infty)$ *vs.* t, where A_t and A_∞ are the observed absorbancies at time t and equilibrium, respectively. Rate data were calculated at 440 and 430 nm. At the completion of a kinetic run the pH of the solution was adjusted quickly to *ca.* 2 with $HClO_4$, instantly converting the dihydroxo product to the corresponding diaquo species. The isomeric ratio of the products was determined spectrophotometrically by the usual methods using our experimental molar absorbancy indices for the *trans*-diaquo isomer and reported values[13] for the *cis*-diaquo isomer.

Results and Discussion

Hydrolysis of *trans*-$Cr(pn)_2Cl_2^+$.—When the chromatographic procedure was used to follow the disappearance of the *trans*-dichloro species in basic solution at 25.0°, in kinetic runs where $b_0 = c_0$, we obtained a second-order rate constant of $5.4 \times 10^{-2}\ M^{-1}\ sec^{-1}$. On the other hand, plots obtained from Cl^- release data gave a value of $12.0 \times 10^{-2}\ M^{-1}\ sec^{-1}$. These results show that the stoichiometric ratio of 1:1 for the reactants assumed in plotting $1/(c_0 - x)$ *vs.* t, when $c_0 = b_0$, is not valid here.

We then examined the system to determine if the second step was an extremely rapid follow-up to the first. The observed rate would simply be that of a single second-order process but with the provision that 2 mol of OH^- is reacting with each mole of the dichloro complex. We found that we were not dealing with this limiting case by using 2:1 stoichiometry and applying the steady-state approximation to the intermediates.

The ratio of products obtained in unbuffered basic solution also indicated that the second chloride is released faster than the first. Aliquots of the stoichiometric ratio of 2:1 were quenched in acid at various reaction times[14] and the different chromium species were separated by ion-exchange chromatography. The concentrations of some species were too small to follow their column separation visually; however, chromium analysis of the various eluents showed little variation of the product ratios during a reaction time of 4 hr. The approximate amounts of products were 5% each of *cis*- and *trans*-chloroaquo, 35% *cis*-diaquo, and 55% *trans*-diaquo.

The kinetic data obtained from reactions carried out in buffer solution over a range of pH values proved to be more meaningful than the studies carried out in unbuffered basic solution. Buffered solutions of different pH were studied chromatographically to obtain a

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(5) J. A. McLean, Jr., and R. R. Barona, *Inorg. Nucl. Chem. Lett.*, **5**, 385 (1969).

(6) R. R. Barona and J. A. McLean, Jr., *Inorg. Chem.*, **10**, 286 (1971).

(7) J. A. McLean, Jr., and R. I. Goorman, *Inorg. Nucl. Chem. Lett.*, **7**, 9 (1971).

(8) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

(9) The first numbers are wavelengths in nanometers and the numbers in parentheses are molar absorbancy indices in $M^{-1}\ cm^{-1}$.

(10) D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 558 (1963).

(11) This buffer solution consists of 25.0 ml of 0.040 *M* propylenediamine (pH adjusted with $HClO_4$), 5.00 ml of 2.0 *M* $LiClO_4$, and 70 ml of distilled water.

(12) The hydroxide ion concentration was calculated from the relation $[OH^-] = 1.34$ antilog (pH − 14) given in ref 10.

(13) M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

(14) Spectral scans of solutions *in situ* could not be analyzed because the spectra of the hydroxo forms of the species assumed to be present in the reaction solutions are not known.

series of rate constants which were plotted *vs.* OH^- concentration. These plots were linear over the $[OH^-]$ range of $(2.0–14) \times 10^{-4}$ *M*. The slope of such a plot gives a second-order rate constant, due to base hydrolysis, of 1.48×10^{-2} M^{-1} sec^{-1} and the intercept gives a first-order rate constant, due to aquation, of 2.84×10^{-5} sec^{-1} at 25.0°. The directly measured k_{aq} for the *trans*-dichloro complex at 25.0° is $(3.35 \pm 0.27) \times 10^{-5}$ sec^{-1}. These values are within acceptable agreement when one considers the larger experimental errors associated with the intercept method. When the directly measured k_{aq} was used to correct the rate data for the disappearance of the *trans*-dichloro species in unbuffered basic solution, a value of 1.6×10^{-2} M^{-1} sec^{-1} was obtained. Considering the larger experimental error associated with this value, it is in acceptable agreement with the value 1.48×10^{-2} M^{-1} sec^{-1} obtained from reactions in buffered solutions. The experimental results obtained here indicate that *trans*-$Cr(pn)_2Cl_2^+$ undergoes base hydrolysis at 25.0° at a rate comparable with its aquation rate. The second-order rate constant in Table I for *trans*-$Cr(en)_2Cl_2^+$ $(3.7 \times 10^{-2}$ M^{-1} $sec^{-1})$ at 25.0° would require a pH of *ca.* 11 before base hydrolysis could release chloride ion as fast as aquation can at 25.0° (in contrast to the Co(III) analog for which the corresponding pH is *ca.* 6). The value of 1.48×10^{-2} M^{-1} sec^{-1} obtained in the present study for the base hydrolysis of the propylenediamine analog also requires a pH above 11 before the rate of the reaction of this complex with OH^- can equal that of aquation at 25.0°. Our results show that aquation cannot be ignored in reactions of certain Cr(III) complexes with hydroxide ion. Furthermore, studies based solely on chloride release or hydroxide consumption are insufficient to characterize complex reaction schemes of this type.

TABLE I

HYDROLYSIS OF *trans*-$M^{III}(AA)_2AX^+$ COMPLEXES AT 25°

No.	Ion	$10^5 k_{aq}$, sec^{-1}	k_{OH}, M^{-1} sec^{-1}
1	$Co(en)_2Cl_2^+$	3.2[a]	3000[a]
2	$Co(en)_2OHCl^+$	140[b]	200,[a] 0.56[c]
3	$Co(pn)_2Cl_2^+$	6.2[a]	2300[a]
4	$Co(pn)_2OHCl^+$	130[b]	210[a]
5	$Cr(en)_2Cl_2^+$	2.25 ± 0.03[d]	0.037[e]
6	$Cr(en)_2OHCl^+$	460 ± 30[f]	<0.3[f]
7	$Cr(pn)_2Cl_2^+$	3.35 ± 0.27[g]	0.015[g]
8	$Cr(pn)_2OHCl^+$	401 ± 22[g]	<0.2[g]

[a] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, **78,** 709 (1956). [b] R. G. Pearson, R. E. Meeker, and F. Basolo, *ibid.*, **78,** 2673 (1956). [c] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963). [d] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18,** 219 (1961). [e] Reference 2. [f] Reference 10. [g] This work.

Hydrolysis of *trans*-$Cr(pn)_2(OH)Cl^+$.—The spectrophotometric kinetic data obtained for the reaction of this species in buffered solution at 25.0° showed that this complex undergoes reaction at a faster rate than the dichloro complex. The graphs obtained from plots of $-\ln (A_t - A_\infty)$ *vs.* *t*, as shown in Figure 1, indicate no detectable pH dependence of the rate. Thus, these data suggest that this complex undergoes reaction mainly by aquation in the pH range 9.65–11.3. The calculated k_{aq} for this complex is $(4.01 \pm 0.22) \times 10^{-3}$ sec^{-1}. Spectral analysis of the acidified solutions at the end of the reaction indicated that the product is a mixture composed of *ca.* 90% *trans*- and 10% *cis*-$Cr(pn)_2(OH)_2^+$.

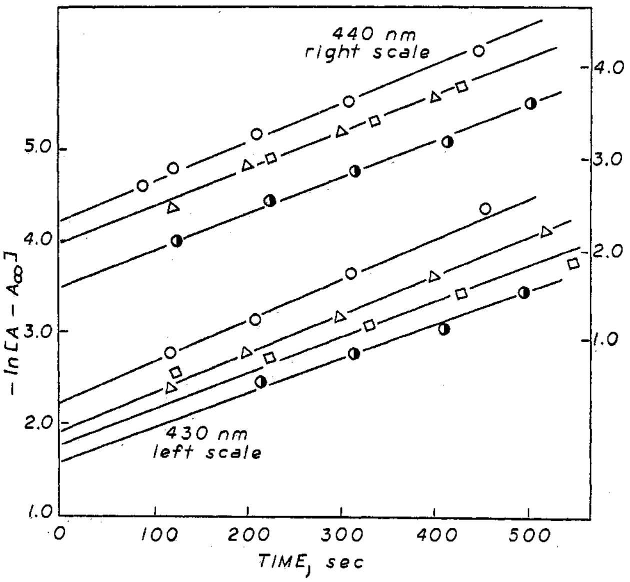

Figure 1.—Pseudo-first-order rate plots for the hydrolysis of *trans*-$Cr(pn)_2(OH)Cl^+$ in 0.1 *M* propylenediamine and 0.1 *M* $LiClO_4$ at 25 ± 0.04°: ◑, pH 9.65; □, pH 10.08; △, pH 11.0; ○, pH 11.3.

When aquation rates in Table I are considered, it is seen that the loss of the first chloride is faster for propylenediamine than for ethylenediamine complexes when the metal is held constant. On the other hand, C-alkylation has little or no effect on the aquation rates of the *trans*-chlorohydroxo species.

Certain limitations should be recognized when one uses k_{OH} data in the last column of Table I for comparative purposes. First, the first value for entry no. 2 and the value for entry no. 4 were calculated by an indirect method subject to considerable error. The second value (0.56 M^{-1} sec^{-1}) for entry no. 2 was measured directly and is believed to be the correct value. Second, the value for entry no. 5 was calculated from Cl^- release measurements and no mention was made whether this value was corrected for the release of the second chloride. Finally, it is seen that only upper limits have been placed on the k_{OH} values for chromium(III)–chlorohydroxo species.