The degeneracy of $\nu_3(E')$ of NO_3^- (*ca.* 1384 cm^{-1}) is lifted by water alone[2,3] and the separation of the two maxima is increased by long-range coulombic perturbation from cations. However, in three cases—LiNO$_3$,[2] Zn(NO$_3$)$_2$,[4] and now Mg(NO$_3$)$_2$—it has been shown that a doublet in the region of $\nu_4(E')$ (*ca.* 720 cm^{-1}) appears when cation–anion contact results from packing requirements. For LiNO$_3$ a band at $\sim$740 cm^{-1} increases in intensity relative to the more intense 720-cm^{-1} line as the water:salt ratio decreases below 6:1.[2] For Zn(NO$_3$)$_2$ a band at $\sim$750 cm^{-1} similarly appears when water:salt < 6:1 and is as intense as the 720-cm^{-1} band when the ratio is 2.5:1.[4] For Mg(NO$_3$)$_2$ a band at $\sim$750 cm^{-1} appears alongside the 718-cm^{-1} band when water:salt < 6:1. Thus a band in the 740–750-cm^{-1} region of the Raman spectrum appears to be diagnostic of cation–nitrate ion contact. Two bands in this region indicate two types of nitrate in the solutions, a solvated type and a bound type (*cf.*, for example, studies of nitrate solutions of Ca^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, In^{3+}, Ce^{4+}, and Bi^{3+} given in ref 4). Although the 1300–1500-cm^{-1} region of the Raman spectrum consists of a contour with two broad maxima, comparison of spectra and curve resolution by computer techniques reveals at least four bands for these concentrated solutions. Two bands at about 1344 and 1412 cm^{-1} are being replaced by two maxima at about 1340 and 1460 cm^{-1} for Mg(NO$_3$)$_2$ with a minimum at 1400 cm^{-1}. These features, somewhat different in frequency and less obvious, are present for concentrated LiNO$_3$ solutions also.

Our Raman spectra of 1.3 M aqueous Al(NO$_3$)$_3$ solutions exhibit only a single line at 718 cm^{-1}. This, together with the relatively small separation of the bands at 1341 and 1414 cm^{-1}, is consistent with the presence of nitrate ion perturbed by aquated Al^{3+}. Our infrared spectra contain two maxima at 1347 and 1410 cm^{-1}. No way has yet been found to extract information about solvent-shared ion pairs from vibration spectra. The study of Al(NO$_3$)$_3$ solutions of low water content would be of value to confirm the criterion, but these systems appear to be unstable.

(2) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).
(3) A. R. Davis, J. W. Macklin, and R. A. Plane, *J. Chem. Phys.*, **50**, 1478 (1969).
(4) D. E. Irish, A. R. Davis, and R. A. Plane, *ibid.*, **50**, 2262 (1969).

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Some Comments on the Mechanism of Substitution Reactions of Cobalt(III) Complexes of the Pentaammine Class

Sir:

Following the attempt by Haim and Taube[1] to elucidate the mechanism of substitution reactions of

(1) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

cobalt(III) complexes of the pentaammine class

$$Co(NH_3)_5OH_2^{3+} + X^{n-} \rightleftharpoons Co(NH_3)_5X^{(3-n)+} + H_2O \qquad Q \quad (1)$$
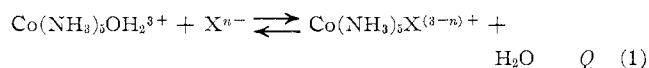
there has been a great deal of interest in the subject.[2] An important observation was made by Langford[3] when he noted that a plot of log k_a (k_a is the rate constant for aquation, the reverse reaction in eq 1) *vs.* $-$log Q (Q is the equilibrium quotient for eq 1) for the uninegative ions F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and H$_2$PO$_4^-$ yielded a straight line with a slope of 1.0. With the recent addition of data points for N$_3^-$ and SCN$^-$,[4] Langford's linear correlation, presented in Figure 1, covers *ca.* 5 orders of magnitude. Since a
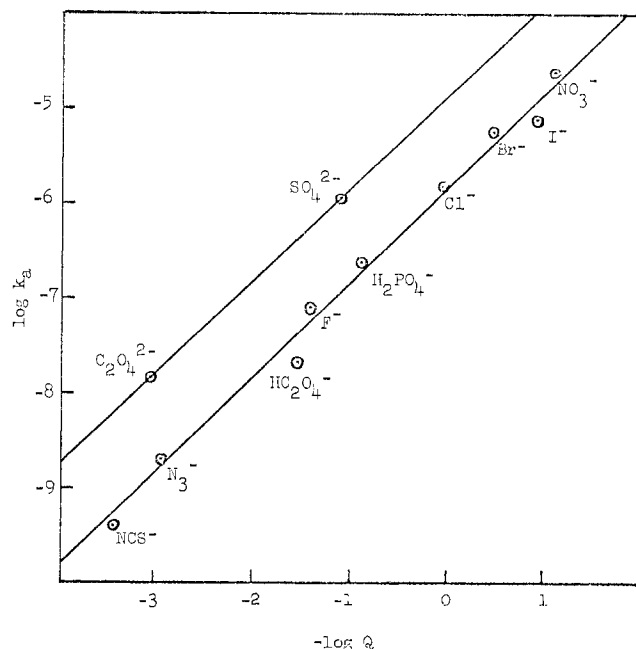

Figure 1.—Plot of log k_a *vs.* log Q for acidopentaamminecobalt-(III) complexes: upper line, log k_a = $-4.84 - 0.98$ log Q; lower line, least-squares equation log k_a = $-5.78 - 1.03$ log Q.

linear free energy correlation with slope 1.0 between $\Delta G^{\ddagger}$ and ΔG° indicates that the transition state is very similar to the products,[5] Langford concluded that the leaving group X^{n-} is, at most, weakly bound to the cobalt(III) center in the transition state.[3,6]

The linear correlation between log k_a and log Q is somewhat surprising when it is recognized that the overall reaction represented by eq 1 actually proceeds in two stages[2] and, therefore, that k_a and Q actually refer to different processes.[7] The first stage corre-

(2) For a comprehensive review, see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.
(3) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).
(4) T. W. Swaddle and G. Guastalla, *ibid.*, **8**, 1604 (1969).
(5) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963.
(6) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.
(7) For the reactions of Be^{2+} with F$^-$, HF, and SO$_4^{2-}$, a linear free energy relation has been reported between the rate and equilibrium parameters pertaining to the outer sphere–inner sphere interconversion reaction: W. G. Baldwin and D. R. Stranks, *Australian J. Chem.*, **21**, 2161 (1968).
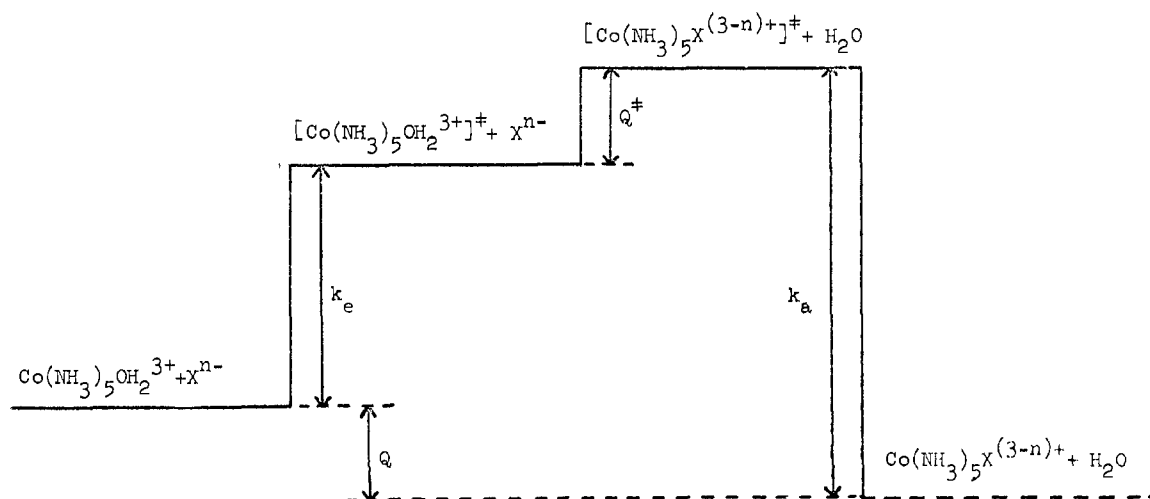
Figure 2.—Schematic free energy diagram showing the relation between water exchange (eq 5), aquation (eq 6), and equilibration (eq 1) reactions, and the relative stabilities of the corresponding transition states.

sponds to the diffusion-controlled formation of an ion-pair or outer-sphere complex

$$Co(NH_3)_5OH_2{}^{3+} + X^{n-} \rightleftharpoons Co(NH_3)_5OH_2{}^{3+},X^{n-} \qquad Q_0 \quad (2)$$

and is followed by the slow outer sphere–inner sphere interconversion reaction

$$Co(NH_3)_5OH_2{}^{3+},X^{n-} \underset{k_a}{\overset{k_x}{\rightleftharpoons}} Co(NH_3)_5X^{(3-n)+} + H_2O \quad (3)$$
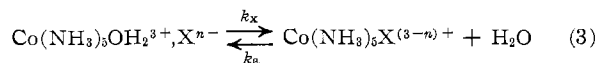
Since $Q = Q_0 k_x/k_a$, the slope of 1.0 in the linear log k_a *vs.* $-\log Q$ plots implies that the first term on the right-hand side of eq 4 is independent of the nature

$$\log k_a = \log k_x Q_0 - \log Q \qquad (4)$$

of the ligand X^{n-}.[8] The term $\log k_x Q_0$ will obviously be constant if the individual values of k_x and Q_0 remain constant as the ligand X^{n-} is varied. Since the value of Q_0 is determined principally by the charge of the ligand, Langford's linear correlation for the uninegative ligands implies that the values of k_x are independent of the nature of the ligand[9] and, therefore, that there is little assistance by the incoming ligand in the outer sphere–inner sphere interchange reaction. Using microscopic reversibility considerations, Langford's conclusion that the leaving ligand in the aquation reaction is at most weakly bound to the cobalt center in the transition state follows immediately.

Now, if the charge of the ligand X^{n-} is increased, provided that k_x remains constant[9] and that the outer-sphere formation constants Q_0 are determined mainly by the charges of the ligands, we would expect that a plot of $\log k_a$ *vs.* $\log Q$ would give a family of straight lines with slope 1.0 but increasing intercept with increasing negative charge on the ligand. Unfortunately, this prediction cannot be tested rigorously because the necessary data are available only for sulfate[10,11] and oxalate[12] ions. However, it is noteworthy, as

shown in Figure 1, that the points for sulfate and oxalate deviate considerably from the linear relation for the uninegative ions.[13] Moreover, the straight line (defined by two points!) for the dinegative ions has a slope of 0.98, in remarkable agreement with the expected value of 1.0. From the difference in the intercepts between the two lines in Figure 1, it is possible to calculate the ratio of the outer-sphere formation quotient for a dinegative ion to the corresponding value for a mononegative ion, provided that k_x is independent of charge. The calculation gives a ratio of 8.7, a value of the correct order of magnitude.[14] We conclude, therefore, that the present interpretation of Langford's correlation and the extension to include ions of higher negative charge strengthens Langford's suggestion that the ligand X^{n-} forms, at most, a weak bond to the cobalt(III) center in the transition state for the interchange reaction given by eq 3.

An alternate and, as will be seen, equivalent treatment of the aquation and equilibrium data can be developed on the basis of formal calculations of equilibrium quotients between transition states.[15] Consider the water-exchange, aquation, and equilibration reactions

$$[Co(NH_3)_5OH_2{}^{3+}]^{\ddagger} \rightleftharpoons Co(NH_3)_5OH_2{}^{3+} \qquad 1/k_e \quad (5)$$

$$Co(NH_3)_5X^{(3-n)+} \rightleftharpoons [Co(NH_3)_5X^{(3-n)+}]^{\ddagger} \qquad k_a \quad (6)$$

$$Co(NH_3)_5OH_2{}^{3+} + X^{n-} \rightleftharpoons Co(NH_3)_5X^{(3-n)+} + H_2O \qquad Q \quad (1)$$

By adding these reactions, we obtain

$$[Co(NH_3)_5OH_2{}^{3+}]^{\ddagger} + X^{n-} \rightleftharpoons$$
$$[Co(NH_3)_5X^{(3-n)+}]^{\ddagger} + H_2O \qquad Q^{\ddagger} \quad (7)$$

The equilibrium quotient $Q^{\ddagger} = k_a Q/k_e$ that governs reaction 7 pertains to the substitution of a water molecule in the transition state for water exchange by the ligand X^{n-} to produce the transition state for the interchange reaction (eq 3). In this inter-

(8) This point has already been noted: see ref 2, p 202.

(9) For the cases where values of Q_0 are available, calculations of k_x indeed show that the rate constants k_x are very insensitive to the nature of the ligand X^{n-}. See ref 2 and 6.
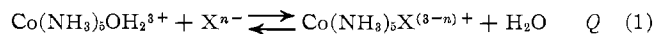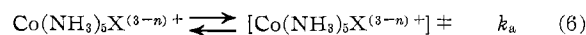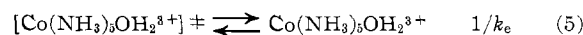
(10) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(11) F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956).

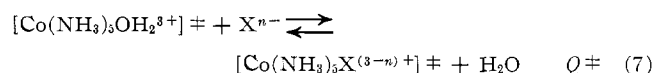(12) C. Andrade and H. Taube, *Inorg. Chem.*, **5**, 1087 (1966).

(13) At the time Langford published his correlation,[3] only the sulfate data were available, and he remarked that the point for $SO_4{}^{2-}$ fell off the line.

(14) The subject of equilibrium quotients for ion-pair formation is controversial. For a recent review, see M. Beck, *Coord. Chem. Rev.*, **3**, 91(1968).

(15) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

TABLE I

FORMAL EQUILIBRIUM QUOTIENTS FOR THE REACTION

$[Co(NH_3)_5OH_2^{3+}]^{\ddagger} + X^{n-} \rightleftharpoons$

X^{n-}	k_a, sec^{-1} [b]	Q, M^{-1} [c]	$[Co(NH_3)_5X^{(3-n)+}]^{\ddagger} + H_2O$ [a] $Q^{\ddagger}$, M^{-1}	Ref [d]
NCS$^-$	4.1×10^{-10} (dilute)	2.7×10^3 (0.5)	0.19	e, f
N$_3^-$	2.1×10^{-9} (dilute)	8.3×10^2 (0.5)	0.30	g, h
HC$_2$O$_4^-$	2.2×10^{-8} (1.0)	35 (1.0)	0.13	i, j
F$^-$	8.6×10^{-8} (dilute)	$\sim$25 (dilute)	0.36	k, l
H$_2$PO$_4^-$	2.6×10^{-7} (1.0)	7.7 (1.0)	0.34	m, m
Cl$^-$	1.7×10^{-6} (dilute)	1.11 (1.0)	0.32	n, o
Br$^-$	6.5×10^{-6} (dilute)	0.35 (1.0)	0.38	p, o
I$^-$	8.3×10^{-6} (1.0)	0.12 (1.0)	0.17	q, q
NO$_3^-$	2.7×10^{-5} (dilute)	0.08 (1.0)	0.37	r, o
C$_2$O$_4^{2-}$	1.5×10^{-8} (1.0)	1.1×10^3 (1.0)	2.8	k, j
SO$_4^{2-}$	1.2×10^{-6} (1.0)	12.4 (1.0)	2.5	s, s

[a] Values at 25° calculated from the expression $Q^{\ddagger} = k_aQ/k_e$. [b] Rate constant for aquation (reverse of eq 3) and ionic strength in parentheses. [c] Equilibrium quotient for reaction 1 and ionic strength in parentheses. [d] First and second entries refer to aquation and equilibrium, respectively. [e] Calculated from data of D. L. Gay and G. C. Lalor, *J. Chem. Soc., A*, 1179 (1966). [f] Calculated in ref 4 from data in ref e and data of J. W. Moore and R. G. Pearson, *Inorg. Chem.*, 3, 1334 (1964). [g] G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963). [h] Reference 4. [i] Reference 12. [j] Calculated from data in ref 12 and the dissociation constants of oxalic acid given by E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 5, 1866 (1966). [k] S. C. Chan, *J. Chem. Soc.*, 2375 (1964). [l] Estimated in ref 3 from data in ref k. [m] W. Schmidt and H. Taube, *Inorg. Chem.*, 2, 698 (1963). [n] F. J. Garrick, *Trans. Faraday Soc.*, 33, 486 (1937); S. C. Chan, *J. Chem. Soc., A*, 291 (1967). [o] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 6, 1027 (1967). [p] Value reported by A. W. Lamb and J. W. Marden, *J. Am. Chem. Soc.*, 33, 1873 (1911), multiplied by 2.303. [q] R. G. Yalman, *Inorg. Chem.*, 1, 16 (1962). [r] J. N. Brønsted, *Z. Physik. Chem.*, 122, 383 (1926). [s] References 10 and 11.

pretation,[16] the formal equilibrium quotient $Q^{\ddagger}$ represents a measure of the relative affinity of a transition-state cobalt(III) center for water and the ligand X^{n-}, and consequently should provide some insight into the role of the ligand X^{n-} in the transition state for substitution. The relations between the ground states and transition states given by eq 1, 5, and 6 are depicted schematically in Figure 2.

The values of k_a and Q necessary to perform the calculation of $Q^{\ddagger}$ are given in columns 2 and 3 of Table I. The rate constant k_e for water exchange is 5.9×10^{-6} sec^{-1}.[17] The results of our calculations are presented in column 4 of Table I. Three noteworthy features emerge from an examination of the values of $Q^{\ddagger}$. First, for the uninegative ligands the

(16) For an alternate interpretation of the quantity $Q^{\ddagger}/Q_0$, see the discussions in ref 2, p 202, and ref 6, p 87.
(17) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, 80, 2642 (1958).

values of $Q^{\ddagger}$ cover the narrow range 0.13–0.38, with most of the values being encompassed in the interval 0.30–0.38. Second, the values of $Q^{\ddagger}$ for the dinegative ions are significantly larger than those for the uninegative ions. Third, while the values of Q for the uninegative ligands cover a range of *ca.* 4×10^4, the values of $Q^{\ddagger}$ cover only a range of *ca.* 3; for the dinegative ligands, the values of Q differ by a factor of *ca.* 10^2, but the values of $Q^{\ddagger}$ differ by only 10%. Referring to Figure 2, these results mean that, for a given charge on the ligand X^{n-}, the energy levels of $Co(NH_3)_5OH_2^{3+}$, $[Co(NH_3)_5OH_2^{3+}]^{\ddagger}$, and $[Co(NH_3)_5X^{(3-n)+}]^{\ddagger}$ are unchanged as the ligand X^{n-} is varied. In contrast, the energy level of the ground-state $Co(NH_3)_5X^{(3-n)+}$ moves vertically depending on the stability (referred to $Co(NH_3)_5OH_2^{3+} + X^{n-}$) of the complex. This feature is emphasized in Figure 2 by representing the level of $Co(NH_3)_5X^{(3-n)+}$ by means of a dotted line.

The strong discrimination displayed by the ground-state cobalt(III) center toward various ligands contrasted with the insensitivity of the $Q^{\ddagger}$ values to the nature of the ligand suggests, at most, a very weak bond between the ligand X^{n-} and the cobalt(III) center in the transition state. The dependence of $Q^{\ddagger}$ on the charge, but not the identity, of the ligand indicates that the interaction between the cobalt(III) and X^{n-} is primarily electrostatic in nature. Taken all together, these trends indicate that the role of the ligand X^{n-} in the transition state is much like the role in an ion-pair or outer-sphere complex.

Finally, it is noteworthy that Langford's linear correlation and the present treatment of equilibrium quotients involving transition states are mathematically equivalent. As already pointed out, the slope of 1.0 in the log k_a *vs.* $-\log Q$ plots implies that k_xQ_0 is a constant for ligands with the same charge. Similarly, the constancy of $Q^{\ddagger}$ for ligands of the same charge implies that Qk_a is constant. However, since $Q = Q_0k_x/k_a$, it follows immediately that k_xQ_0 is a constant.

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