

terms of coordination of the perchlorate to the metal.

The occurrence of two bands in the  $\sim 1100\text{-cm}^{-1}$  region ( $1190$  and  $1022\text{ cm}^{-1}$ ) and in the  $\sim 620\text{-cm}^{-1}$  region ( $618$  and  $612\text{ cm}^{-1}$ ) of the class 1 perchlorate complexes is thus consistent with the presence of monodentate perchlorate groups. The moderately intense band at  $912\text{ cm}^{-1}$  also indicates the presence of coordinated perchlorate. The class 1 perchlorate complexes may therefore be assigned structure A, consistent with their stoichiometry and infrared spectra.

The assignment of infrared bands for the class 2 perchlorate complexes is somewhat more difficult. If these compounds contain both monodentate and bridging perchlorates as in structure B, there will be two types of perchlorate local symmetry,  $C_{3v}$  and  $C_{2v}$ . The observation of three bands in the  $\sim 1100\text{-cm}^{-1}$  region (Table II) may be interpreted in terms of the presence of bridging bidentate perchlorate groups. The two bands originating from the monodentate perchlorates are probably overlapped by the bridging bidentate perchlorate bands. The totally symmetric stretch of the perchlorate ion, of  $T_d$  symmetry, at about  $935\text{ cm}^{-1}$  is nondegenerate and normally infrared inactive. Therefore, even if the symmetry of the perchlorate groups was lowered to  $C_{2v}$ , only a single band should appear in the infrared spectrum in the  $935\text{-cm}^{-1}$  region. The occurrence of two bands at  $896$  and  $906\text{ cm}^{-1}$  indicates the presence of two different types of coordinated perchlorates in the class 2 complexes. The assignment of structure B to the class 2 perchlorates is thus consistent with their stoichiometry and infrared spectra. It should be noted, however, that a structure containing a monodentate and a bidentate perchlorate coordinated to a single mercury cannot be ruled out.

**Nitrate Compounds.**—The ionic nitrate group has four fundamental vibrations, three of which are infrared active at about  $1400$ ,  $830$ , and  $700\text{ cm}^{-1}$ . Coordination lowers the local symmetry of the nitrate with splitting of the  $1400\text{-}$  and  $700\text{-cm}^{-1}$  bands into two components each. In addition, the normally infrared-inactive symmetric stretch ( $\sim 1050\text{ cm}^{-1}$ ) becomes active. Differentiation of mono- and bidentate nitrate bonding is usually possible only through Raman depolarization studies.<sup>15</sup>

The observation of four bands in the  $1400\text{-cm}^{-1}$  re-

(15) R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, **5**, 1308 (1966).

gion, two bands in the  $700\text{-cm}^{-1}$  region, and a moderately intense band at  $1017\text{ cm}^{-1}$  in the infrared spectra of the class 1 nitrate compounds implies the presence of coordinated nitrate. Lattice effects can be ruled out on the bases of the large splittings in the  $1400\text{-cm}^{-1}$  region and the presence of the band at  $1017\text{ cm}^{-1}$ . The presence of four bands in the  $1400\text{-cm}^{-1}$  region, instead of the two expected, may be attributed to vibration coupling between the two nitrate groups attached to mercury. The four bands may be divided into two groups. The bands at  $1438$  and  $1430\text{ cm}^{-1}$  may be assigned to the out-of-phase and in-phase  $\text{-NO}_2$  asymmetric stretch vibrations, respectively. Those at  $1275$  and  $1260\text{ cm}^{-1}$  may be assigned, respectively, to out-of-phase and in-phase symmetric stretch vibrations. A similar effect was observed in a recent vibrational spectroscopic study of mercury(II) nitrate solutions.<sup>16</sup> The class 1 nitrate complexes are therefore assigned structure A consistent with their infrared spectra and stoichiometry. The same conclusion has been reached for the similar compound bis(pyridine)mercury(II) nitrate.<sup>17</sup>

The presence of two bands at  $807$  and  $800\text{ cm}^{-1}$ , in the region where only a single nondegenerate band resulting from a nitrate out-of-phase deformation is expected, implies the presence of two kinds of nitrate in the molecule. In the compound  $\text{Ni}(\text{dien})(\text{NO}_3)_2$  a band at  $816\text{ cm}^{-1}$  has been assigned to monodentate nitrate, while a band at  $807\text{ cm}^{-1}$  has been assigned to bidentate nitrate.<sup>18</sup> The two bands in the class 2 nitrates are similarly assigned.

The presence of two types of nitrate is consistent with structure B if two of the nitrates act as bidentate bridges between mercury atoms and two others are bonded in a monodentate manner. This structure should result in the observation of six bands in the  $1400\text{-cm}^{-1}$  region, two due to monodentate nitrate and four due to bridging nitrate groups. The experimental results (Table II) are in agreement with this expectation. Unfortunately, the insolubility of the class 2 nitrates prevented a Raman depolarization study and a molecular weight determination. Therefore, an unbridged monomeric structure containing a monodentate and a bidentate nitrate cannot be ruled out.

(16) A. R. Davis and D. E. Irish, *ibid.*, **7**, 1699 (1968).

(17) J. I. Bullock and D. G. Tuck, *J. Chem. Soc.*, 1897 (1965).

(18) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

## Correspondence

### Concerning Cation-Nitrate Ion Contact in Aqueous Solutions

Sir:

Recently Matwiyoff, *et al.*,<sup>1</sup> have obtained a hydration number of 6 for  $\text{Al}^{3+}$  in  $\text{Al}(\text{NO}_3)_3$  solutions by proton magnetic resonance spectroscopy. They therefore

(1) N. A. Matwiyoff, P. E. Darley, and W. G. Movius, *Inorg. Chem.*, **7**, 2173 (1968).

concluded that nitrate ion does not occupy the primary hydration sphere of  $\text{Al}^{3+}$ . They then suggested that this result is in disagreement with previous conclusions from Raman and infrared data. We wish to point out that our present understanding of the vibrational spectrum of aqueous nitrate solutions leads to a similar conclusion—*viz.*, that nitrate ion does not contact  $\text{Al}^{3+}$  in aqueous solution.

The degeneracy of  $\nu_3(E')$  of  $\text{NO}_3^-$  (*ca.* 1384  $\text{cm}^{-1}$ ) is lifted by water alone<sup>2,3</sup> and the separation of the two maxima is increased by long-range coulombic perturbation from cations. However, in three cases— $\text{LiNO}_3$ ,<sup>2</sup>  $\text{Zn}(\text{NO}_3)_2$ ,<sup>4</sup> and now  $\text{Mg}(\text{NO}_3)_2$ —it has been shown that a doublet in the region of  $\nu_4(E')$  (*ca.* 720  $\text{cm}^{-1}$ ) appears when cation-anion contact results from packing requirements. For  $\text{LiNO}_3$  a band at  $\sim 740 \text{ cm}^{-1}$  increases in intensity relative to the more intense 720- $\text{cm}^{-1}$  line as the water:salt ratio decreases below 6:1.<sup>2</sup> For  $\text{Zn}(\text{NO}_3)_2$  a band at  $\sim 750 \text{ cm}^{-1}$  similarly appears when water:salt < 6:1 and is as intense as the 720- $\text{cm}^{-1}$  band when the ratio is 2.5:1.<sup>4</sup> For  $\text{Mg}(\text{NO}_3)_2$  a band at  $\sim 750 \text{ cm}^{-1}$  appears alongside the 718- $\text{cm}^{-1}$  band when water:salt < 6:1. Thus a band in the 740–750- $\text{cm}^{-1}$  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  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Ce}^{4+}$ , and  $\text{Bi}^{3+}$  given in ref 4). Although the 1300–1500- $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  are being replaced by two maxima at about 1340 and 1460  $\text{cm}^{-1}$  for  $\text{Mg}(\text{NO}_3)_2$  with a minimum at 1400  $\text{cm}^{-1}$ . These features, somewhat different in frequency and less obvious, are present for concentrated  $\text{LiNO}_3$  solutions also.

Our Raman spectra of 1.3 *M* aqueous  $\text{Al}(\text{NO}_3)_3$  solutions exhibit only a single line at 718  $\text{cm}^{-1}$ . This, together with the relatively small separation of the bands at 1341 and 1414  $\text{cm}^{-1}$ , is consistent with the presence of nitrate ion perturbed by aquated  $\text{Al}^{3+}$ . Our infrared spectra contain two maxima at 1347 and 1410  $\text{cm}^{-1}$ . No way has yet been found to extract information about solvent-shared ion pairs from vibration spectra. The study of  $\text{Al}(\text{NO}_3)_3$  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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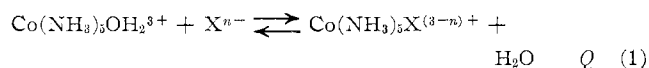
### Some Comments on the Mechanism of Substitution Reactions of Cobalt(III) Complexes of the Pentaammine Class

Sir:

Following the attempt by Haim and Taube<sup>1</sup> 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



there has been a great deal of interest in the subject.<sup>2</sup> An important observation was made by Langford<sup>3</sup> 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  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{H}_2\text{PO}_4^-$  yielded a straight line with a slope of 1.0. With the recent addition of data points for  $\text{N}_3^-$  and  $\text{SCN}^-$ ,<sup>4</sup> Langford's linear correlation, presented in Figure 1, covers *ca.* 5 orders of magnitude. Since a

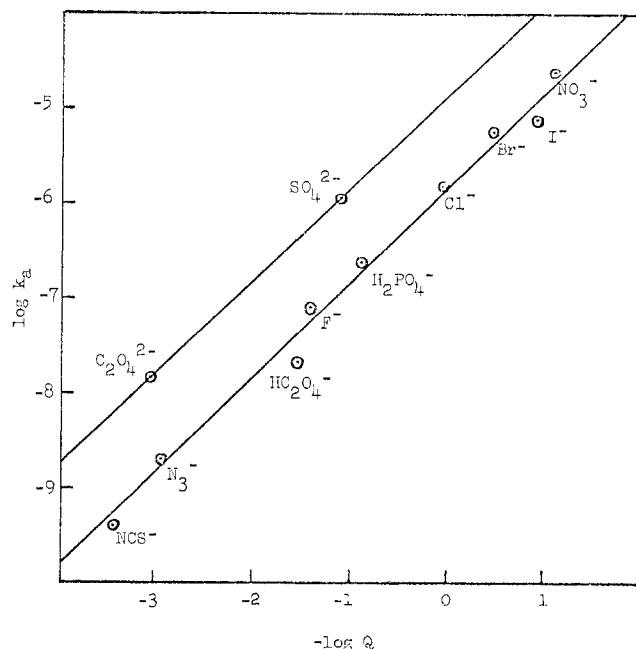


Figure 1.—Plot of  $\log k_a$  vs.  $\log Q$  for acidopentaamminecobalt(III) complexes: upper line,  $\log k_a = -4.84 - 0.98 \log Q$ ; lower line, least-squares equation  $\log k_a = -5.78 - 1.03 \log Q$ .

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

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<sup>2</sup> and, therefore, that  $k_a$  and  $Q$  actually refer to different processes.<sup>7</sup> 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  $\text{Be}^{2+}$  with  $\text{F}^-$ ,  $\text{HF}$ , and  $\text{SO}_4^{2-}$ , 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).