A similar intermediate can be drawn with a hydride ion as the bridging ligand, again rearranging to $(CH_3)_3$-NBH_3 + $LiHB^*F_3$. This mechanism also involves a transfer of trimethylamine from the labeled to the un-labeled boron. While the single hydrogen bridges are known in other cases,[6] the fluorine bridge should be favored here for steric reasons. It should be easier to develop a coordination member of five for boron with four hydrides and a fluoride than with three fluorides, a hydride, and a trimethylamine. However, the nature of the bridging ligand is unimportant to the argument below.

To test these hypotheses, a series of exchange and tracer studies was conducted. No exchange was apparent between $(CH_3)_3NB^{10}H_3$ and $LiB^{11}H_4$. When $B^{10}_2H_6$ and $LiB^{11}H_4$ had equilibrated and had been converted to $(CH_3)_3NBH_3$, their n.m.r. spectra were identical (see Experimental section). Similarly, $B^{11}_2H_6$ and $(CH_3)_3NB^{10}H_3$ were found to give a random distribution of isotopes. Moreover, the reaction

$$(CH_3)_3NB^{10}F_3 + {}^1/_2B^{11}_2H_6 + (C_2H_5)_2O =$$
$$(CH_3)_3NB^{11}H_3 + B^{10}F_3 \cdot (C_2H_5)_2O$$
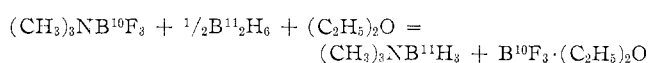
goes to completion with only a small (10–50%) excess of B_2H_6.[7]

In the reaction between $(CH_3)_3NB^{10}F_3$ and $LiB^{11}H_4$, both boron isotopes were randomly distributed between the amine borane and the diborane products. This gives no indication as to the course of the reaction, since this exchange could occur through the diborane produced. Lithium hydride in large excess was added to another reaction between normal $LiBH_4$ and $(CH_3)_3$-NBF_3 enriched in B^{10} where the ratio of salt to adduct was 1.2:1. Diborane generated was consumed by the reaction

$$LiH + {}^1/_2B_2H_6 = LiBH_4$$
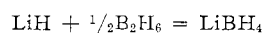
Thus the quantity of free B_2H_6 in the system was kept low and its exchange with other species reduced. In this system the $B^{10}:B^{11}$ ratio in the borane adduct was 1.1, while in the $LiBH_4$ it was 1.6. That the B^{10} would accumulate in the salt implies that the conversion of $(CH_3)_3NBF_3$ to the borane involves a cleavage of the nitrogen–boron bond, with displacement of BF_3 by BH_3 (or BH_4^-) as the more favored of the two reaction paths. There is some mixing of the isotopes. This might arise either from some exchange of F^- for H^- without cleavage of the B–N bond or from exchange between the diborane and the borane adduct before reaction with LiH.

(6) D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963).
(7) Best available values for the heats of association of the BH_3 and BF_3 complexes with $N(CH_3)_3$ are about equal [F. G. A. Stone, *Chem. Rev.*, **58**, 101 (1958)]. The driving force in this case appears to be the formation of $BF_3 \cdot (C_2H_5)_2O$, which is considerably less dissociated than the corresponding borane.

Solvation of Metal Ions in Aqueous Solutions: the Metal–Oxygen Bond

By R. E. Hester and R. A. Plane

In the course of a series of studies of complex compound formation in aqueous solutions of strong electrolytes by the Raman spectroscopic method, we have obtained considerable evidence of the formation in solution of aquo–metal ion complexes involving a significant degree of electron sharing in the metal–oxygen bond. The appearance of a vibrational Raman line is dependent upon there being a change in bond polarizability with bond length ($I \propto (\partial \bar{\alpha}/\partial r)^2$), which in turn depends on a finite electron density in the bond. Thus purely ionic or ion–dipole bonding does not give rise to a Raman line characterizing the bond.[1] Table I lists Raman lines observed from nitrate, sulfate, and perchlorate salts of various metals after the lines due to the oxyanions and to the solvent water have been subtracted.[2–4] In each case the new lines were best observed from very concentrated, near-saturated solutions of the salts listed in Table I. Spectra were obtained using a Cary Model 81 Raman spectrophotometer, with calibrated polarizing screens wrapped around the sample tubes for depolarization measurements.

Table I

Low Frequency, Polarized Raman Bands from Aqueous Salt Solutions

Salt	Raman line, cm.$^{-1}$
$Cu(NO_3)_2$	440
$Zn(NO_3)_2$	390
$Hg(NO_3)_2$	380
$Mg(NO_3)_2$	370
$In(NO_3)_3$	410 and 460 overlapping bands
$CuSO_4$	440
$MgSO_4$	360
$ZnSO_4$	400
$Ga_2(SO_4)_3$	475, shoulder on 435 cm.$^{-1}$ $\nu_2(E)$ line of SO_4^{2-}
$In_2(SO_4)_3$	350–550
Tl_2SO_4	470
$Cu(ClO_4)_2$	440
$Hg(ClO_4)_2$	380
$In(ClO_4)_3$	*ca.* 420, shoulder on 465 cm.$^{-1}$ $\nu_2(E)$ line of ClO_4^-
$Mg(ClO_4)_2$	360

The new lines were in all cases highly polarized and therefore readily distinguishable from the restricted rotational[4] water band at 450 cm.$^{-1}$. However, the

(1) J. H. B. George, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, **49**, 375 (1953).
(2) G. Herzberg, "Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1945.
(3) R. E. Hester, Thesis, Cornell University, 1962.
(4) P. C. Cross, J. Burnham, and P. A. Leighton, *J. Am. Chem. Soc.*, **59**, 1134 (1937).

often severe overlap of the weak new bands with either this water band or an oxyanion line made quantitative measurements of their intensities, and hence of their degrees of depolarization, impractical in most cases. Depolarization ratios of $\rho = 0.2$ and $\rho = 0.11$ were obtained for the new lines from solutions of cupric and mercuric ions, respectively.[3]

The absence of a low frequency polarized line from the spectrum of liquid water, the lack of dependence of the new lines on the nature of the oxyanion in solution, and the constant frequency obtained from solutions containing the same metal ion lead to the conclusion that the origins of these new lines are in some symmetric forms of vibration within the hydration sheaths of the dissolved metal ions. Evidence in support of this assignment is found in the work of Mathieu[5] and Lafont[6] on solid hydrates containing the ions $Mg(H_2O)_6^{2+}$ and $Zn(H_2O)_6^{2+}$. The polarized nature of the new lines suggests their assignment to metal–water–oxygen symmetric stretching modes, and the smallness of the frequency dependence on the mass of the metal ion then follows from the necessity for the metal to remain stationary in such vibrational modes. Thus all divalent ions except copper listed in Table I give lines in the narrow region 360–400 cm.$^{-1}$, consistent with the formation of hexacoordinated aquo complexes in each case. Jahn–Teller modifications in the case of the copper complex may account for its nonconformity. The line intensities, as well as the frequencies, were higher for the gallium and indium aquo complexes than for the other metals studied. These are clearly related to the stronger bonding of the hydration sheaths brought about by the increased ionic charges. The gallium and indium solutions were also found to be exceptionally viscous—a property fully consistent with a high degree of hydration.[7,8]

(5) J. P. Mathieu, *Compt. rend.*, **231**, 896 (1950).

(6) R. L. Lafont, *ibid.*, **244**, 1481 (1957).

(7) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

(8) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953, Chapter 9.

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A Raman Spectrophotometric Comparison of Interionic Association in Aqueous Solutions of Metal Nitrates, Sulfates, and Perchlorates[1]

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Recent reports from our laboratory have dealt in detail with complex formation in aqueous solutions of calcium nitrate[2] and indium sulfate.[3] These earlier re-

sults arose from the more general study of metal-oxyanion associations in aqueous solutions which we briefly report on here.

The complete Raman spectra of the uncomplexed oxyanions nitrate, sulfate, and perchlorate are well known, that of the nitrate ion being consistent with its D_{3h} symmetry, those of sulfate and perchlorate ions being consistent with T_d symmetries.[4] In concentrated aqueous solutions it is known from a variety of physical measurements that many metal nitrates[5,6] and sulfates[7,8] form associated species, and though the evidence is much less abundant, it appears that in concentrated perchloric acid even the perchlorate ion forms a complex.[9]

We have used a Cary Model 81 Raman spectrophotometer to obtain Raman spectra of a wide range of metal nitrates, sulfates, and perchlorates, taking the usual precautions to ensure precise frequency, intensity, and depolarization values.[2,3] The spectra reported were all obtained from near-saturated solutions at room temperature, in order to force as much ion association as possible. Tables I, II, and III summarize our spectral frequency data and demonstrate that using the criterion that strong association between an oxyanion and a metal ion will distort the symmetry of the oxyanion, it is evident that nitrate complexes are much more common than are sulfate complexes, while there is no evidence here for perchlorate complexes. However, conductivity and solubility measurements show that most metal sulfates are very highly associated even in dilute aqueous solution.[7,8] The Raman frequencies suggest that, with the single exception of indium, these metal sulfate complexes are solvent separated; at least one water molecule being trapped between the metal ion and the sulfate ion. This interpretation is consistent with Eigen's findings from chemical relaxation spectra.[10] The new frequencies arising from nitrate complexes can all be accommodated by a C_{2v} point group assignment, indicative of complexing through oxygen atoms of the NO_3^- ions rather than through the nitrogen atoms, but in no case can a line characterizing the metal–oxygen bonds be assigned. The extreme distortions of nitrate ion symmetry make it probable that the association with metal ions is at least through intimate ion pairing, but some small degree of covalent bond formation cannot be ruled out. The magnitude of the splitting of the $\nu_2(E')$ line of D_{3h} nitrate into ν_4 (B_1) and $\nu_1(A_1)$ lines characteristic of the distorted C_{2v} ion has been used as a measure of the dissymmetry arising in the nitrate group as a result of interaction

(4) G. S. Hertzberg, "Molecular Spectra and Molecular Structure, II," D. Van Nostrand, Princeton, N. J., 1945, Chapter II.

(5) R. A. Robinson, J. M. Wilson, and H. S. Ayling, *J. Am. Chem. Soc.*, **64**, 1469 (1942).

(6) J. P. Mathieu and M. Lounsbury, *Discussions Faraday Soc.*, **9**, 196 (1950).

(7) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London, 1959, Chapter 14.

(8) C. W. Davies, Chapter 3 in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, New York, N. Y., 1959.

(9) F. Klanberg, J. P. Hunt, and H. W. Dodgen, *Inorg Chem.*, **2**, 139 (1963).

(10) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).