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Raman and Infrared Study of Nitrate Complexes of Bismuth(III)[1]

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Raman spectra (160–1700 cm^{-1}) were recorded for aqueous solutions containing various ratios of nitrate to bismuth and also for a $Bi(NO_3)_3 \cdot 5H_2O$–KNO_3 melt. Infrared spectra (400–1800 cm^{-1}) were obtained for several of the solutions and the hydrate melt. The spectra are consistent with the presence of nitrate of C_{2v} symmetry, and from the polarization of the highest frequency Raman line (at *ca.* 1500 cm^{-1}), bidentate coordination is inferred. There is no evidence of nitrate bridging. The appearance of a polarized Raman band at *ca.* 235 cm^{-1}, which is assigned to the symmetric bismuth–nitrate stretching motion, is evidence for covalency in the metal–ligand bond. Raman intensity measurements indicate the existence of stepwise complexes containing one through four nitrates per bismuth. In each of these species, water is also bound to bismuth, as is shown by a polarized band at *ca.* 370 cm^{-1}, attributed to the symmetric bismuth–water stretching vibration.

Introduction

There is considerable evidence for the association of Bi(III) and nitrate ions in both aqueous solution and solids. Conductance measurements[3] on nitric acid solutions of $Bi(NO_3)_3 \cdot 5H_2O$ point toward partially ionized $Bi(NO_3)_3$ species, and from a study of the solubility[4] of $BiONO_3$ in HNO_3 at 25° the formation constant for $Bi(NO_3)^{2+}$ is calculated as $K_1 = 18$. Anion-exchange results suggest that at least one negatively charged nitrate complex of Bi(III) exists to some extent in solution.[5] A recent X-ray structure determination[6] of $Bi(NO_3)_3 \cdot 5H_2O$ reveals that each Bi(III) ion is surrounded by three bidentate nitrate groups which are unsymmetrically coordinated, as well as by three oxygen atoms from water molecules. Both infrared and Raman[7] spectra of solid $Bi(NO_3)_3 \cdot 5H_2O$ are consistent with this structure, insofar as more bands are observed than would be expected for uncoordinated nitrate with D_{3h} symmetry. Early photographic Raman spectra[8] of acidic bismuth nitrate solutions clearly indicate extensive complexing.

Quantitative analysis of Raman and infrared spectra in solution should indicate (1) whether or not a stepwise series of nitrate complexes of Bi(III) is formed, as has been found with chloride ion as ligand,[9] (2) whether bound nitrate is mono- or bidentate, and (3) whether the bismuth(III) nitrate species are strictly ion pairs or whether there is a bond with some covalent character.

Experimental Section

Solutions.—All chemicals were reagent grade, used without further purification. A stock solution in which the formal ratio $[NO_3^-]/[Bi(III)]$ equaled 1.5/1 was prepared by adding a 0.49 *M* solution of bismuth oxide in *ca.* 9 *M* $HClO_4$ to a 0.98 *M* solution of bismuth nitrate pentahydrate in *ca.* 4.5 *M* $HClO_4$. Higher formal ratios were obtained by diluting this stock solution with nitric acid. Spectrophotometric analysis for bismuth(III)[10] was done using a Beckman DU spectrophotometer. For this purpose, the bismuth nitrate stock solution was diluted with 6 *N* HCl so that $[Bi(III)] \backsim 5 \times 10^{-5}$ *M*. Nitrate was analyzed both by gravimetry as nitron nitrate and by acid titration of anhydrous sodium carbonate, using methyl orange–indigo carmine as indicator.[11] The concentration of perchlorate ion, the internal Raman intensity standard, was known by preparing all solutions by quantitative dilution.

Hydrate Melt.—An extremely viscous liquid phase was formed when the two solids, $Bi(NO_3)_3 \cdot 5H_2O$ and KNO_3, were ground together (arbitrary ratio) in a mortar slightly above room temperature. The melt was first filtered through a coarse glass frit to remove the larger suspended particles and then centrifuged at 7000 rpm for *ca.* 90 min. Although the resulting liquid was still slightly cloudy, an excellent Raman spectrum was nevertheless obtained.

Spectra.—A Cary Model 81 Raman spectrophotometer with 4358-Å mercury excitation was used to record the Raman spectra, the 933-cm^{-1} band of ClO_4^- serving as the internal intensity standard. All solutions were filtered through a fine glass frit and their spectra were then recorded at 46°, the ambient lamp compartment temperature. Depolarization ratios (ρ) were measured by surrounding the sample tube with cylindrical polaroid sheets which had been calibrated with CCl_4, $CHCl_3$, and C_6H_6.[12] Sheets of Kodak Wratten 2A gelatin filter were inserted in the polaroid wraparounds to isolate the 4358-Å mercury line. The Raman spectrum of crystalline $Bi(NO_3)_3 \cdot 5H_2O$ was recorded without difficulty using the customary conical sample holder.

Infrared spectra (400–1800 cm^{-1}) of the hydrate melt and several solutions were recorded on a Perkin-Elmer 521 grating infrared spectrophotometer as smears between silver chloride plates. Indene was used to calibrate the wavelength scale.[13]

Spectral Resolution.—Raman bands were analyzed using a Du Pont 310 curve resolver. In general, broad spectral envelopes were satisfactorily resolved into Gaussian components, whereas narrow, intense bands were best fitted with curves approximating a Lorentz–Gaussian product function.

Results

The viscous $Bi(NO_3)_3 \cdot 5H_2O$–KNO_3 mixture gives the Raman and infrared spectra shown in Figures 1 and

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(1) Sponsored by a research grant from the Office of Saline Water, U. S. Department of the Interior.

(2) National Science Foundation Predoctoral Fellow, 1966–1968.

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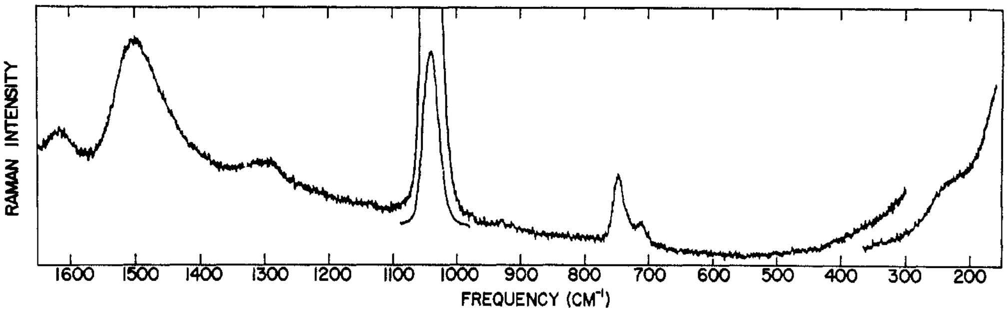

Figure 1.—Raman spectrum of bismuth nitrate pentahydrate–potassium nitrate melt. Cary Model 81, RD 4, lamp current 15 A, slit width 10 cm^{-1}, scan speed 15 cm^{-1}/min, gain 3 × 20 (1 × 20 for 1036-cm^{-1} band), single slit 160–360 cm^{-1}, double slit 300–1700 cm^{-1}.

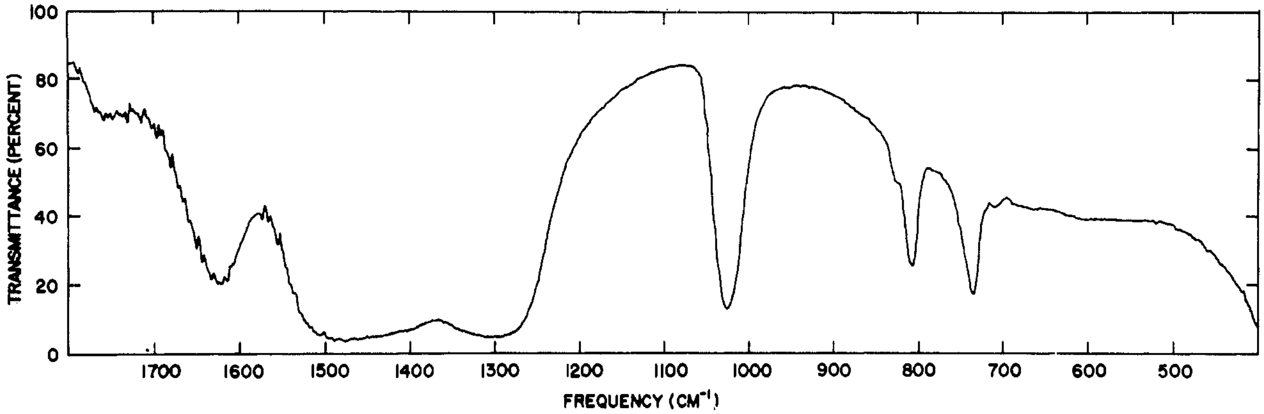

Figure 2.—Infrared spectrum of bismuth nitrate pentahydrate–potassium nitrate melt. Perkin-Elmer 521, twice routine slit program, gain 5, scan time 20 cm^{-1}/min; between silver chloride plates.

2, with frequencies and spectral features as listed in Table I. These particular spectra are presented because they are also characteristic of aqueous bismuth nitrate solutions but are free of the interferences due to HNO_3 (at *ca.* 1300 cm^{-1}) and ClO_4^- (at *ca.* 1120 cm^{-1}), which are observed in spectra of the more dilute solutions used for Raman intensity measurements. The latter solutions were prepared in order to apply the Job method of continuous variations[14] to this system. They contained a fixed sum of stoichiometric concentrations [Bi(III)] + $[NO_3^-]$ equal to 2.45 *M*, with *R* (the formal ratio $[NO_3^-]/[Bi(III)]$) ranging from 1.5 to 7.0 ($[H^+]$ = 7.3–4.0 *M*). Variations with changing *R* in the observed Raman spectra, both in intensity and band position, are best described by dividing the spectrum into six frequency regions.

TABLE I

VIBRATIONAL FREQUENCIES[a] AND SPECTRAL FEATURES[b] OF THE $Bi(NO_3)_3 \cdot 5H_2O$–KNO_3 MIXTURE

Infrared[c]	Raman	Description[d]
1760 m		1029 + 738 cm^{-1} combination
1628 s	1616 m	H_2O bend + B_1 overtone
1475–1290 vs, b	1500 s, p	A_1, bound NO_3^- str
	1450 w, b, dp(?)	Bound NO_3^-
	1422 m, dp	Solvated free NO_3^-
	1355 w, dp	Solvated free NO_3^-
	1294 m, dp	B_2, bound NO_3^- str
	1048 s, p	A_1', free NO_3^- str
1029 vs	1036 vs, p	A_1, bound NO_3^- str
828 w		A_2'', free NO_3^-, out-of-plane def
810 s	810 vw, dp	B_1, bound NO_3^-, out-of-plane def
738 s	747[e] m, p	A_1, bound NO_3^- bend
712 w	714 w, dp	B_2, bound NO_3^- bend
	239 w, p	Sym Bi–NO_3^- str

[a] In cm^{-1}. [b] s, strong; m, medium; w, weak; b, broad; v, very; p, polarized; dp, depolarized. [c] The ~1400-cm^{-1} region was not resolved in the infrared region. [d] def, deformation; sym, symmetric. [e] Slightly asymmetric, probably owing to the underlying 719-cm^{-1} band of free nitrate.

1400-Cm^{-1} Region.—The highest frequency nitrate band is strong, broad (width at half-height $\omega_{1/2}$ = 80 cm^{-1}), and polarized (ρ = 0.6) and gradually moves from 1510 cm^{-1} (*R* = 1.5) to 1491 cm^{-1} (*R* = 7.0). At the same time, at *ca.* 1440 cm^{-1} a weak, broad, and probably depolarized band is always seen. As *R* increases, two depolarized bands gain intensity at *ca.* 1420 and 1360 cm^{-1}. These are due to uncoordinated nitrate, perturbed in some way by solvent water, and are observed in aqueous alkali metal nitrate solutions as well.[15] A polarized line at 1308 cm^{-1} grows in as *R* is raised in solutions with [Bi(III)] + $[NO_3^-]$ = 2.45 *M*, $[H^+]$ = 7.3–4.0 *M*. Although this band, which appears even in the absence of Bi(III), might be due to an hydronium–nitrate ion pair, it is somewhat difficult to rule out undissociated HNO_3 molecules, because additional bands characteristic of HNO_3 (*e.g.*, at 677 and 926 cm^{-1})[16] probably are obscured by overlapping

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spectral features. The lowest frequency band in this region is very weak and smoothly disappears under the 1308-cm^{-1} line from a position at *ca.* 1275 cm^{-1} in the $R = 1.5$ solution. Because of its location, its ρ value is doubtful, although in the hydrate melt (at 1294 cm^{-1}) it is definitely depolarized.

The Job method of analysis ([Bi(III)] + [NO_3^-] = 2.45 *M*) was applied to the highest frequency band and peak heights (normalized to a known ClO_4^- concentration) were taken at 5-cm^{-1} intervals between 1485 and 1510 cm^{-1} and also at 1530 cm^{-1}. Plots of the normalized heights *vs.* *R* exhibit local maxima at $R < 1.5$ and $R = 2.5$, 3.5, and 5.0.

1040-Cm^{-1} Region.—This part of the spectrum is complicated by the presence of the ν_3 vibration of ClO_4^- at *ca.* 1120 cm^{-1}, as well as by a weak shoulder at 1046 cm^{-1} which appears in concentrated $HClO_4$ solutions and is enhanced by added Bi(III).[9] The broad polarized envelope ($\rho = 0.3$) due to nitrate overlaps these bands, its apparent maximum shifting from 1032 cm^{-1} ($R = 1.5$) to 1048 cm^{-1} ($R = 7.0$). To resolve the envelope into its component bands, the frequency scale was doubled and the slit width almost halved compared to Figure 1, and the following was done. First, the spectral contours of several additional solutions with $R \geqslant 7$, but containing no ClO_4^-, were matched with two bands at 1048 and 1035 cm^{-1} having $\omega_{1/2} = 13$ and 24 cm^{-1}, respectively. The position, width at half-height, and shape of these bands were kept fixed for all remaining solutions and only their heights were allowed to vary. Second, the maximum in spectra of the envelope from additional solutions in which $R < 1.5$ moved no lower than 1032 cm^{-1}. It was assumed, therefore, that the band needed to fit the low-frequency contour in the $R = 1.5$ solution was indeed the lowest frequency band in this region. It is located at 1026 cm^{-1} and was given the same band parameters (except height) as those of the 1035-cm^{-1} band. Third, spectra of solutions with $1.5 < R < 7.0$ could not all be fit satisfactorily without introducing an intermediate band at 1031 cm^{-1} with parameters identical with those at 1035 and 1026 cm^{-1}. A Job analysis ([Bi(III)] + [NO_3^-] = 2.45 *M*) of the normalized heights of the four nitrate bands gives the following results: (1) the 1026-cm^{-1} band intensity has a maximum at some $R < 1.5$ and decreases as *R* is raised; (2) the 1031-cm^{-1} intensity maximizes at $R = 2.0$ with a pronounced shoulder at $R = 3.0$; (3) the 1035-cm^{-1} band height has a sharp maximum at $R = 5.0$; and (4) the 1048 cm^{-1} peak intensity steadily increases as *R* is raised.

The resolution procedure is illustrated in Figure 3, in which solid lines indicate those bands due to NO_3^- species. As the figures show, it is possible to fit the various contours with a single set of nitrate bands of fixed shape and frequency. Because the data from the resolved curves correlate well with those from the NO_3^- spectra in both the 1400- and 740-cm^{-1} regions (see below), it appears that the 1040-cm^{-1} region is best explained by assuming the overlap of bands of fixed shape and position, rather than considering one band of varying shape and position.

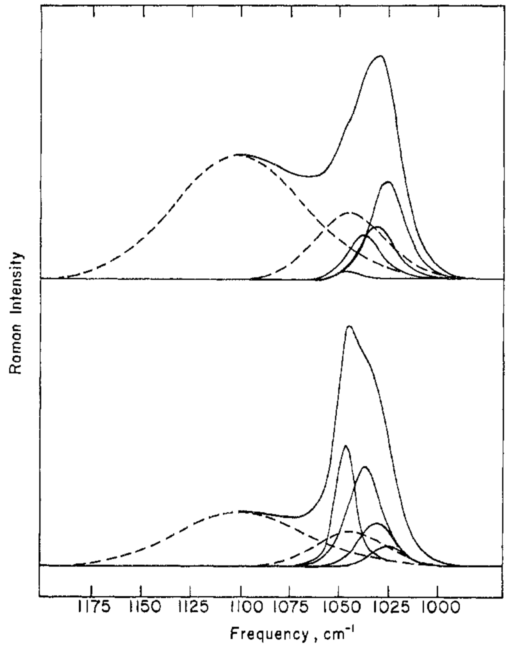

Figure 3.—Resolved Raman spectral envelope in 1040-cm^{-1} region. Top: $R = 1.5$, [Bi(III)] = 0.98 *M*, [NO_3^-] = 1.47 *M*, [ClO_4^-] = 7.3 *M*, [H^+] = 7.3 *M*. Bottom: $R = 3.5$, [Bi(III)] = 0.55 *M*, [NO_3^-] = 1.90 *M*, [ClO_4^-] = 4.1 *M*, [H^+] = 5.0 *M*. The over-all envelope very closely matches the observed spectrum; solid lines indicate those curves due to NO_3^- species.

800-Cm^{-1} Region.—Only in spectra of concentrated bismuth nitrate solutions does any Raman intensity appear in this region, and even then it is very weak. The spectrum of the $Bi(NO_3)_3 \cdot 5H_2O$–KNO_3 melt (run at higher gain than in Figure 1) shows a band at 810 cm^{-1} (vw, dp), while in a more dilute solution ([Bi(III)] = 1.3 *M*, $R \sim 7$) it is seen at 805 cm^{-1} (vw, dp).

740-Cm^{-1} Region.—At least two bands are clearly resolvable: the first (m, p; $\rho = 0.4$) moves from 747 cm^{-1} ($R = 1.5$) to 743 cm^{-1} ($R = 7.0$), while the second (w, dp) shifts from 711 cm^{-1} ($R = 1.5$) to 718 cm^{-1} ($R = 7.0$). The higher frequency band was analyzed using the Job method ([Bi(III)] + [NO_3^-] = 2.45 *M*). Normalized heights at 750, 745, and 740 cm^{-1} were plotted *vs.* *R* and exhibit local maxima at $R < 1.5$ and $R = 2.5$, 4.0, and 5.5.

370-Cm^{-1} Region.—Although not present in the Raman spectrum of the hydrate melt (Figure 1), a polarized band of medium intensity is seen for the more dilute bismuth nitrate solutions and gradually shifts from 363 cm^{-1} ($R = 1.5$) to 381 cm^{-1} ($R = 7.0$). Furthermore, the height at peak maximum (normalized to a known ClO_4^- concentration) per mole of Bi(III) does not tend toward zero over the ratio range $R = 1.5$–7.0 ([Bi(III)] + [NO_3^-] = 2.45 *M*); in fact, it is found to be essentially constant. We previously assigned a line at *ca.* 390 cm^{-1} to the symmetric bismuth(III)–water stretching motion in $HClO_4$ solution.[9]

235-Cm^{-1} Region.—The weak, polarized Raman line seen for the melt at 239 cm^{-1} (Figure 1) appears at 232 cm^{-1} for a concentrated aqueous solution ([Bi-

(III)] = 1.3 *M*, $R \sim 7$). Owing to its position on the shoulder of the Rayleigh line, it was not studied quantitatively.

Discussion

The vibration spectra in Figures 1 and 2 and the data reported above clearly indicate a symmetry for nitrate lower than D_{3h} in the aqueous bismuth nitrate system. For D_{3h} symmetry, only four frequencies due to nitrate are expected: $\nu_1 = 1048\ \text{cm}^{-1}$ (A_1', Raman active); $\nu_2 = 828\ \text{cm}^{-1}$ (A_2'', infrared active); $\nu_3 = 1390\ \text{cm}^{-1}$ (E', Raman and infrared active); and $\nu_4 = 719\ \text{cm}^{-1}$ (E', Raman and infrared active). However, even spectra of dilute aqueous alkali metal nitrates reveal splitting of the ν_3 (E') degeneracy, presumably owing only to solvent interaction,[15] and thus exhibit lines at *ca.* 1420 and 1360 cm^{-1}. If the total of five lines from solvated nitrate is subtracted from the bismuth nitrate spectra, there is left a pattern of frequency, spectral activity, and polarization (Table I) which is consistent with nitrate of local symmetry reduced to C_{2v} owing to metal ion coordination.[17] Such a symmetry generates six frequencies: $3\ A_1$ (p) + B_1 (dp) + $2\ B_2$ (dp). Each is both Raman and infrared allowed. Only the bands at *ca.* 1620, 1450, and 239 cm^{-1} seem extraneous at this point; these will be discussed below.

Polarization of the highest frequency line due to bound nitrate (*ca.* 1500 cm^{-1}), together with depolarization of the *ca.* 1290-cm^{-1} band, is evidence for bidentate (or bridging) coordination.[18] This follows from considering the highest frequency mode for bidentate (or bridging) nitrate to be mainly the terminal N–O stretching motion (hence symmetric and polarized), whereas the lower frequency band represents predominantly the bound NO_2 asymmetric stretching motion (hence depolarized). This criterion has also been applied to the highest frequency Raman band from aqueous solutions of cerium(IV) nitrate[19] (1538 cm^{-1}) and scandium(III) nitrate[20] (1534 cm^{-1}). In both cases, bidentate nitrate coordination was inferred. For the present system, nitrate bridging can probably be ruled out for several reasons: (a) previous workers[3,4] invoked the existence of only simple monomeric species to explain their conductance and solubility data; (b) the structure of $Bi(NO_3)_3 \cdot 5H_2O$ involves bidentate nitrates with no bridging;[6] (c) the Raman spectrum of this solid,[7] with bands at 1302 and 1486 cm^{-1}, corresponds closely to the solution spectra.

The polarized Raman line in the 235-cm^{-1} region for both the hydrate melt and the concentrated aqueous bismuth nitrate solutions is readily ascribed to the symmetric $Bi–O_2NO$ stretching motion. There is a corresponding line at 236 cm^{-1} in the Raman spectrum of crystalline $Bi(NO_3)_3 \cdot 5H_2O$. Bands in this region have been similarly assigned for other metal ions, *e.g.*, Ce(IV)[19] (238 cm^{-1}) and Sc(III)[20] (280–290 cm^{-1}). The presence of such a band here suggests that the interaction between bidentate nitrate and Bi(III) is not totally ionic in nature; rather, there is some covalent character.

Thus far, the spectral data have revealed both the method of nitrate coordination to Bi(III) (bidentate) and also the nature of the bonding involved (partially covalent). There remains the identification of the species which must be present in solution to account for the observed frequency shifts with changing *R* value. To this end, the Job analysis should be useful, for although, in a system containing several successive equilibria, the unambiguous stoichiometries can seldom be learned from the Job method, the minimum number of species will nevertheless be indicated. For such a complex system, the normalized spectral intensity due to the highest species is expected to show a maximum at a formal ratio slightly greater than that of the appropriate stoichiometry.[21] The fact that the normalized 1035-cm^{-1} band intensity maximizes at $R = 5.0$ and all of the other analyzed peak intensities in the 1400- and 740-cm^{-1} regions exhibit local maxima at $R = 5.0–5.5$ suggests, then, that there are four nitrates per Bi(III) in the highest species. The three lower *R* values at which the normalized intensities show additional maxima ($R < 1.5$, $R = 2.0–2.5$, and 3.0–4.0) probably refer to species containing one, two, and three nitrates per Bi(III).

The direction of frequency shift with increasing *R* value can easily be understood in terms of such a stepwise series of complexes. In both the 1400- and 740-cm^{-1} spectral regions, the splitting of the E' mode of D_{3h} nitrate diminishes as *R* increases, while simultaneously the *ca.* 1040-cm^{-1} band moves closer to the 1048-cm^{-1} position in D_{3h} nitrate. In other words, the nitrates in the higher consecutive complexes appear to be less distorted from D_{3h} symmetry than the nitrates in the lower species. This must be related to the lower polarizing ability of the central metal as an increased number of nitrate ligands reduces its effective charge. With stepwise metal halide complexes, the same effect is frequently manifested in the lowering of stretching frequency as higher complexes are formed.[9]

The weak band appearing near 1450 cm^{-1} in all solution spectra which were resolved can be associated with one or more of the complex species, since the same line is found in both the infrared and Raman spectra of solid $Bi(NO_3)_3 \cdot 5H_2O$ (ref 7 and verified by us). Its origin probably lies in coupling between bound nitrates.

Still unassigned in Figures 1 and 2 is the band at *ca.* 1620 cm^{-1}. Basing his conclusions on earlier claims[22] that $Bi(OH)^{2+}$ and $Bi(OH)_2^+$ predominate in acidic bismuth nitrate solutions, Ollano[8] attributed this line in his photographic Raman spectra to $Bi(OH)^{2+}$, while that at *ca.* 1500 cm^{-1} was assigned to $Bi(OH)_2^+$. It is now known, however, that the major Bi(III) hydrolysis product (at least in ClO_4^- media) is the hexamer, $Bi_6(OH)_{12}^{6+}$, whose Raman spectrum[23] reveals

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no bands in this area. Furthermore, other work in our laboratory shows that spectra of even monomeric hydroxy species (of As(III)) do not have bands in this region. The $\sim$1620-cm^{-1} peak may be ascribed in part to the ν_2 bending mode of water for the following reason. As [Bi(III)] increases ([Bi(III)] + $[NO_3^-]$ = 2.45 *M*), this band shifts from 1640 cm^{-1} ($R = 7.0$) to 1618 cm^{-1} ($R = 1.5$) and considerably narrows in width. Cations are expected to influence mainly the bending mode of water, and the spectral behavior which we observe has been predicted and found elsewhere for other ions.[24] In addition, there is probably some contribution to the 1620-cm^{-1} band from the Raman- and infrared-allowed overtone of the B_1 mode of bound NO_3^-, as well as from the Raman-allowed overtone of the A_2'' mode of free NO_3^-.

An interesting finding of the present study is that water is coordinated to Bi(III) in all of the aqueous nitrate complexes. This conclusion follows from the continued presence in all solutions of the symmetric bismuth(III)–water stretching mode at $\sim$370 cm^{-1} and is not wholly unexpected, since in solid $Bi(NO_3)_3 \cdot 5H_2O$ each Bi(III) is capable of coordinating three bidentate nitrates and three water molecules.[6] Moreover, the facts that the normalized molar intensity of this band remains almost constant in all solutions (even though the number of coordinated H_2O molecules is expected to decrease as NO_3^- is coordinated) and that its frequency increases with *R* suggest that the water in the higher complexes is even more strongly bound than in the lower species. However, in the hydrate melt, which might be considered the most concentrated solution of all, the fact that the Bi–H_2O line is not observed indicates that the water has been removed, with a stronger coordination of nitrate. Accompanying this stronger nitrate coordination, the Bi–NO_3^- frequency increases from 232 cm^{-1} in the concentrated aqueous solution to 239 cm^{-1} in the melt.

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Adducts of Group IV Tetrahalides and β-Diketones

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β-Diketones form adducts, without enolization, when combined with various metal halides in inert solvents at low temperatures. Analytical, nuclear magnetic resonance, and infrared data are consistent with the following new complexes being simple 1:1, nonionic adducts having carbonyl groups coordinated to *cis* positions: $SnCl_4 \cdot C_7H_{12}O_2$ (prepared from 3,3-dimethylacetylacetone), $TiCl_4 \cdot C_7H_{12}O_2$, $TiBr_4 \cdot C_7H_{12}O_2$, $TiI_4 \cdot C_7H_{12}O_2$, $ZrCl_4 \cdot C_7H_{12}O_2$, and $SnCl_4 \cdot C_6H_{10}O_2$ (prepared from 3-methylacetylacetone). The product from the low-temperature reaction of acetylacetone and tin tetrachloride is shown to be the adduct $SnCl_4 \cdot C_5H_8O_2$.

Introduction

The purpose of the present work was to prepare and investigate adducts in which β-diketones, without enolization, form chelated structures with metal halides.

3,3-Dimethylacetylacetone, (3,3-AcAc), does not contain readily enolizable hydrogens and therefore was selected as a ligand for the observation of reactivity and of infrared and nmr spectra of β-diketone adducts[1] in this investigation. The previously reported diketone adducts of acetylacetone (AcAcH) and its derivatives were characterized only by elemental analyses and decomposition temperatures except where noted: $BF_3 \cdot C_6H_5COAc$,[2] $Al_2Br_6 \cdot 2AcAcH$,[3] "$[(HAcAc)_2Sn]SnCl_6$" (conductivity),[4] "$[(HAcAc)_2SnCl_2]Cl_2$" (conductivity),[4] $SbCl_5 \cdot AcAcH$,[5] $HgCl_2 \cdot AcAcH$[6] (infrared[7]), $TiCl_4 \cdot AcAcH$,[5] and $ZrCl_4 \cdot AcAcH$.[8] Recently,[9] the "very weak complexes" $SiF_4 \cdot HAcAc$ and $GeF_4 \cdot HAcAc$ and the complex $SnF_4 \cdot HAcAc$ were listed in an nmr investigation but apparently were not isolated and analyzed.

Far more common than adducts of β-diketones are the β-ketoenolate complexes. Of interest in the present investigation are conditions in which reaction 1 is favored over reaction 2. As indicated by the following paragraphs, the reaction of tin tetrachloride and acetylacetone is reported[4,5,10–12] to give at least one ill-defined product in addition to *cis*-dichlorobis(acetylacetonato)-tin(IV).

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(1) The term "adduct" herein refers to Lewis acid–base compounds not having enolate ligands.

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