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^{1}H NMR Studies of the Bi^{3+}–HO^- System: Stoichiometric Composition of the Hexanuclear Complex and Rate of Proton Exchange of Coordinated H_2O and HO^- in Mixed Acetone/Water Solution

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The hydroxide proton content of the hexanuclear bismuth hydroxide complex has been determined in a mixed water/acetone solvent by using ^{1}H NMR spectroscopy and peak integration. From these data, we established the stoichiometry of the complex as $Bi_6O_4(HO)_4{}^{6+}$, in agreement with the previous X-ray diffraction studies by Sundvall.[3,5] The composition $Bi_6(HO)_{12}{}^{6+}$, proposed by others, is thus in error. The rate of proton exchange between the coordinated HO^- groups and the bulk solvent is considerably lower than the rate of exchange of coordinated water. The HO^- proton exchange is characterized by the following parameters: $k_{298} = 9 \times 10^4$ s^{-1}, $\Delta H^* = 32$ kJ·mol^{-1}, and $\Delta S^* = -42$ J·mol^{-1}. The water exchange could not be measured even at the lowest temperature investigated, 170 K. A lower limit of the rate of exchange between protons in Bi^{3+}(aq) and the bulk was estimated to be 5×10^6 s^{-1} at 298 K.

Introduction

The first step in an analysis of complex formation in solution is often a thermodynamic study of the composition and the equilibrium constants of the species formed. This may be followed by studies of the structure and bonding of the complexes, e.g. by using diffraction and/or spectroscopic methods, studies of the reactivity of the complexes, etc. The structural and mechanistic interpretations are facilitated by precise information on the stoichiometry of the complexes. However, this information is limited to the components whose concentrations can be varied during the experiment; cf. ref 1, pp 23–24. As an example, we can take the hydrolysis of metal ions

$$pM^{n+} + qH_2O \rightleftarrows M_p(HO)_q{}^{np-q} + qH^+ \qquad (1)$$

where the stoichiometric coefficients p and q and the equilibrium constant for (1) can be determined by standard methods.[1] In dilute and moderately concentrated solutions, the water concentration is very nearly constant during an experiment. Hence, $2HO^- \equiv O^{2-} + H_2O$, and all of the stoichiometries $M_p(OH)_q$, $M_pO(OH)_{q-2}$, ..., $M_pO_n(OH)_{q-2n}$, ... are equivalent from the standard experimental point of view. There is an obvious need to obtain additional information on the composition of these species; large-angle X-ray scattering,[2,3] IR and Raman data,[4,5] and also ^{17}O NMR[6] have been used for this purpose.

Proton NMR data at low temperature have been used extensively to obtain information on the hydration of metal ions.[6] Akitt and Duncan[7] determined the number of coordinated water molecules in various beryllium hydroxide complexes to obtain information on the complete composition of the complexes.

The ^{1}H NMR peak area method can only be used if the overall rate of proton exchange between bulk and "bonded" protons is slow. This condition can often be achieved by decreasing the temperature. In order to avoid freezing, one may have to add another solvent; methanol and acetone are often used for this purpose. We used low temperature and a mixed water/acetone solvent in this study.

Akitt and Duncan observed the presence of a narrow peak, which they assigned to the protons in the bridging HO^- group in $Be_3(HO)_3{}^{3+}$. Protons in coordinated HO^- are exchanged more slowly than those of coordinated H_2O with the bulk water.[7] Hence, it is surprising that no ^{1}H NMR studies of coordinated HO^- seem to have been made on labile metal hydroxide complexes (some investigations of this type have been made on isopolyanions[8]). We have selected the Bi^{3+}–HO^- system as a test case for this type of studies. There are several reasons for this:

(1) The hydrolysis of Bi^{3+} has been extensively studied by several different methods,[3,5,9] and there is one complex, "$Bi_6(HO)_{12}{}^{6+}$", that predominates over a large concentration range. This facilitates both the experiments and the data interpretation.

(2) There is conflicting evidence on the composition and geometry of the complex; two models have been suggested, $Bi_6(HO)_{12}{}^{6+}$ and $Bi_6O_4(HO)_4{}^{6+}$. Both models have an octahedral arrangement of six Bi atoms. In the first model, the 12 HO^- groups span all the octahedral edges; in the latter, the HO^- and O^{2-} ions are located above the triangular faces of the octahedron, forming a $Mo_6Cl_8{}^{4+}$ type of arrangement. Sundvall[3,5] has made a thorough discussion of the pros and cons of the two models and presented convincing evidence for the $Bi_6O_4(HO)_4{}^{6+}$ model. Nevertheless, the first model is presented in modern textbooks.[10,11]

Experimental Section

Preparations and Analysis. A solution with the mole ratio Bi^{3+}:ClO_4^- = 1:1 (Z = 2, where Z = total concentration of HO^-/total concentration of Bi^{3+}) was prepared by dissolving purified Bi_2O_3 in 6 M $HClO_4$. The stock solution (2.09 mol·kg^{-1}) was analyzed for Bi^{3+} by using EDTA and for ClO_4^- by using ion exchange. Throughout this paper the concentrations are given in moles per kilogram of solution. More concentrated solutions (2.33 and 2.53 mol·kg^{-1}) were prepared by evaporation of a known quantity of water from a known quantity of the stock solution. The evaporation was made under vacuum at room temperature. The solutions contain more than 97% of the total bismuth as hexamers, as estimated by the stability constants of Olin.[9] The rest is Bi^{3+}(aq) and $Bi(HO)^{2+}$.

$Bi(ClO_4)_3$ solutions ($Z \sim 0$) were prepared by dissolving Bi_2O_3 in an excess of $HClO_4$. The excess was constant (0.45 mol·kg^{-1}) in all solutions used.

NMR Measurements. The NMR measurements were carried out on a Bruker WP200 instrument. The samples were prepared by mixing weighed quantities of the aqueous Bi solutions and acetone (99.95% acetone-d_6, Ciba Geigy). All measurements were made at low temperature by using a Bruker B-VT-1000 variable-temperature-control unit. The temperature was measured by using the methanol thermometer

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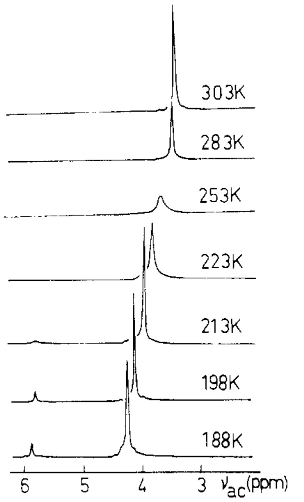

Figure 1. Typical ^{1}H NMR spectra of the Bi^{3+}–HO^- system at different temperatures. $[Bi^{3+}]_{total} = 2.53$ mol·kg^{-1}; $Z = 2$; $n_{acetone}{:}n_{water} = 13$.

method.[12] The instrumental parameters were chosen to obtain optimal values of the various band integrals.[13,14]

Calculations. The proton content of the complex was calculated from

$$A_C/(A_C + A_B) = n_{Bi}(x/n_H) \qquad (2)$$

where A_B and A_C are the integrals of the peaks from bulk water and complex, respectively, n_{Bi}, n_H, and $n_{H,C}$ are the total quantities of Bi and H and quantity of coordinated protons in moles, respectively, and $x = n_{H,C}/n_{Bi}$ is the average proton number for bismuth in the complex (2 for $Bi_6(HO)_{12}{}^{6+}$ and 0.67 for $Bi_6O_4(HO)_4{}^{6+}$).

The pseudo-first-order rate constant for the proton exchange bulk water ↔ complex was calculated by using the approximate formula for the fast-exchange region in a two-site exchange case[15]

$$k_A = 4\Pi p_A p_B{}^2(\delta\nu)^2[w' - (p_A T_{2A} + p_B T_{2B})/\Pi T_{2A} T_{2B}]^{-1} \qquad (3)$$

p_A and p_B are the fractional populations of sites A and B, $\delta\nu$ is the chemical shift difference in hertz between the sites, w' is the bandwidth of the exchange-broadened signal in hertz, and T_{2A} and T_{2B} are the transverse relaxation times. $\delta\nu$ has been linearly extrapolated from the slow- to the fast-exchange region. The temperature dependence of T_2 and the broadening due to field inhomogeneities have been taken into account by using the method suggested by Sandström,[16] with *tert*-butyl alcohol as the reference standard. The main reason for using only the fast-exchange region for determining rate constants and activation parameters was the large uncertainty in T_2 for the complex and to some extent also for the bulk water in the slow-exchange region.

The activation parameters were obtained by a least-squares fit to the Eyring equation

$$\ln (k/T) = -\Delta H^\ddagger/RT + \Delta S^\ddagger/R + \ln (k_B/h) \qquad (4)$$

The chemical shift of coordinated water, ν_C, in Bi^{3+}(aq) was calculated from the dependence of the chemical shift of the water signals on the total concentration of Bi^{3+}. Assuming six-coordination, we have

$$\bar{\nu} = \nu_B + 12(\nu_C - \nu_B)n_{Bi}/n_H \qquad (5)$$

where $\bar{\nu}$ and ν_B are chemical shifts of the time-averaged water and the bulk water signals, respectively.

Results and Discussion

A typical set of NMR spectra at different temperatures is shown in Figure 1. At room temperature, there is only one band. This broadens with decreasing temperature and is separated into two bands around 220 K. (No broadening of the water band can be observed at lower temperature in the acetone/water solvent in the absence of the Bi complex.) The average number of protons per Bi, x, was determined as a function of the total concentration of Bi and of the acetone:water mole ratio; the data are depicted in Figure 2. The constant value of $x = 0.64 \pm 0.02$ indicates that there is only one Bi species in the solution and that the composition of the complex does not vary with the acetone:water mole ratio. The value 0.64 is in excellent agreement with the stoichiometry $Bi_6O_4(HO)_4{}^{6+}$. x decreases with decreasing Z; hence, the minor peak is due to coordinated HO^- protons only. There are only weak interactions in the solid state between the Bi atoms in $Bi_6O_4(HO)_4{}^{6+}$ and external oxygen atoms.[3,5] This might indicate that there is a corresponding weak interaction between the complex and water also in solution, in agreement with the observation that no separate peak for coordinated water is present in the ^{1}H NMR spectra. However, this observation may also be due to fast exchange between coordinated and bulk water.

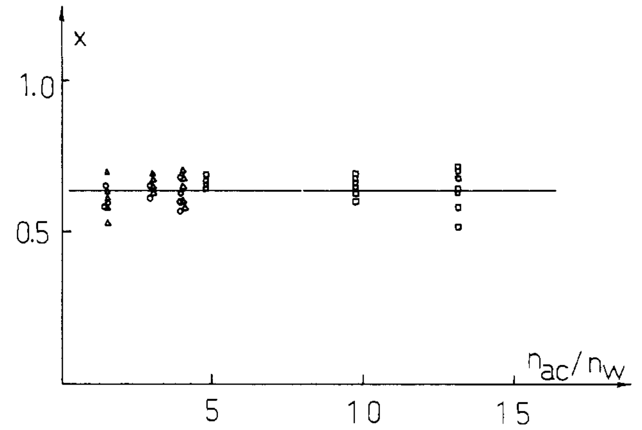

Figure 2. Measured proton:bismuth mole ratios in the bismuth hydroxo complex as a function of the acetone:water mole ratio at different [Bi]: 2.09 (○), 2.33 (△), 2.53 (□) mol·kg^{-1} $BiOClO_4$. (The spectra were recorded at several temperatures, 170 K < T < 230 K.)

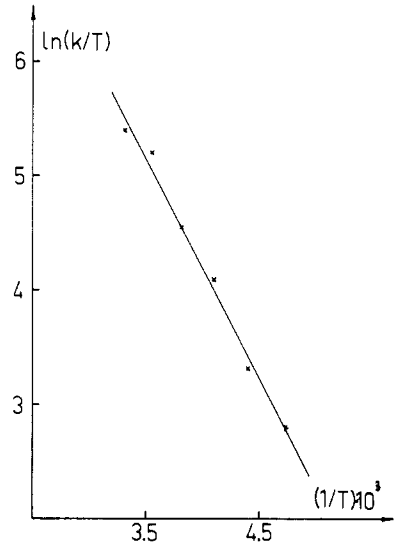

Figure 3. Eyring plot of the pseudo-first-order rate constants evaluated from the ^{1}H NMR spectra shown in Figure 1.

The difference in chemical shifts between the bulk water and coordinated hydroxide is large. This fact made it possible both to obtain precise values of the average number of protons per Bi and to evaluate the rate of exchange of protons in the system.

There are two possible proton-exchange mechanisms between coordinated HO^- and the bulk water:

$$Bi_6O_4(\mathit{HO})_4{}^{6+} + HOH \xrightleftharpoons{k_H} Bi_6O_4(HO)_4{}^{6+} + \mathit{H}OH \qquad (6)$$

$$Bi_6O_4(\mathit{HO})_4{}^{6+} + HOH \xrightleftharpoons{k_{HO}} Bi_6O_4(HO)_4{}^{6+} + \mathit{HO}H \qquad (7)$$

By using ^{1}H NMR methods, we can only determine the sum of the rate constants for (6) and (7). From the linear plot of ln (k/T) vs. $1/T$, shown in Figure 3, we obtain $\Delta H^\ddagger = 32$ kJ·mol^{-1}, $\Delta S^\ddagger = -42$ J·mol^{-1}·K^{-1}, and $k_{298} = 9 \times 10^4$ s^{-1}. (The estimated[17]

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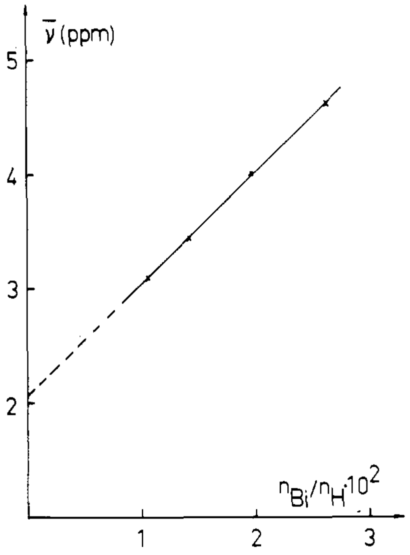

Figure 4. Chemical shift of the time-averaged water band as a function of the n_{Bi}:n_H mole ratio according to eq 5. $n_{acetone}$:n_{water} = 3.0.

rate constants in solutions with different compositions at the coalescence temperature are close to the rate constant[15] log k_{240} = 2.4 from the spectra in Figure 1: log k_{240} = 2.1 at $n_{acetone}$:n_{water} = 1.5 and $[Bi^{3+}]_{total}$ = 2.09 mol·kg^{-1}; log k_{240} = 2.2 at $n_{acetone}$:n_{water} = 5 and $[Bi^{3+}]_{total}$ = 2.53 mol·kg^{-1}. The agreement suggests that the exchange rate does not depend on the acetone:water ratio and/or on the Bi concentration.) These quantities are very similar to the corresponding quantities for the proton dissociation process[18] $Be(H_2O)_4^{2+} + H_2O \rightleftarrows Be(H_2O)_3OH^+ + H_3O^+$.

The rate constant for water exchange in metal aqua complexes is usually smaller than the rate of proton exchange.[19] We expect this to be true also for the *HO*$^-$ and *H*O$^-$ exchanges in metal hydroxide complexes.[7] Hence, k_H for $Bi_6O_4(HO)_4^{6+}$ ought to be of the order of magnitude 10^5 s^{-1} at 25 °C.

This rate constant is smaller than the rate constant for proton exchange in Bi^{3+}(aq). This was estimated by using the calculated chemical shift difference between the coordinated and bulk water molecules. ^1H spectra of acidic Bi^{3+} solutions (Z = 0) contained only one proton signal in the accessible temperature region (293–170 K) and the investigated chemical shift range (−2 to 15 ppm, referred to acetone), indicating fast proton exchange between coordinated and bulk water. The linear plot of $\bar{\nu}$ vs. n_{Bi}/n_H (eq 5) is shown in Figure 4. From this, we obtain ν_C = 10.18 ppm and ν_B = 2.05 ppm, both referred to acetone. From the spectra, one can conclude that the exchange broadening is ≤1 Hz at room temperature and that there is no measurable broadening down to ~170 K.

If we set 1 Hz as the upper limit of the exchange broadening, we can estimate a lower limit of the proton-exchange rate by using eq 3 simplified to $k_A = 4\Pi p_A p_B^2(\delta\nu)^2$.

In a 1.1 mol·kg^{-1} Bi^{3+} solution with a proton excess of 0.45 mol·kg^{-1} and $n_{acetone}$:n_{water} = 3, we have p_A = 0.32 and p_B = 0.64. At room temperature, a value of $\delta\nu = 1.6 \times 10^3$ Hz is obtained from Figure 4; hence, $k_A \geq 5 \times 10^6$ s^{-1}. The only previously published kinetic data for Bi^{3+}(aq) give a lower limit of the rate constant for water exchange[20] larger than 10^4 s^{-1}.

The ^1H NMR method will certainly never be the deus ex machina to solve solution chemical constitution and structure problems. However, the results presented above indicate that it might give important chemical information, particularly in systems where the individual complexes have rather large ranges of existence.

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Registry No. $Bi_6O_4(HO)_4^{6+}$, 85507-34-2; $Bi_6(HO)_{12}^{6+}$, 18866-22-3.

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