kinetic and thermodynamic studies have been reported,[7,9] likely due to the low chemoselectivity of such reactions.

The oxidation reactions of catechols which selectively produce *o*-quinones conform to either of the following two equations:

$$\text{catechol} + \tfrac{1}{2}O_2 \rightarrow o\text{-quinone} + H_2O \qquad (10)$$

$$\text{catechol} + O_2 \rightarrow o\text{-quinone} + H_2O_2 \qquad (11)$$

To the best of our knowledge, only two kinetic and mechanistic studies have been reported in the literature. Tsuruya and coworkers[7a] have studied the kinetics of cobalt(II)–chelate catalyzed oxidation of $DTBCH_2$ to DTBQ in $CHCl_3$ showing that the rate of the reaction, conforming to eq 10, is first order with respect to the concentrations of the metal catalyst and substrate and also first order in the partial pressure of dioxygen. In a previous paper, Martell and Tyson[7b] reported a kinetic study on Mn(II)-catalyzed oxidation of $DTBCH_2$ conforming to eq 11. Despite the complexity of the system, they were able to demonstrate that the oxidation reaction follows simple first-order kinetics for dioxygen uptake. Our results on the oxidation of $DTBCH_2$ in $CHCl_3$ are, therefore, unprecedented, as the rate of the reaction has been shown to be independent on free dioxygen over a large range of partial pressures (15–725 psi).

Concluding Remarks

The present study has revealed that the catecholate complex $[(\text{triphos})\text{Ir}(\text{DTBC})]^+$ is an effective homogeneous catalyst for the selective oxidation of $DTBCH_2$ to DTBQ by molecular oxygen and has served to shed some light on the mechanism of the reaction in which the formation of the O_2 adduct $[(\text{triphos})\overline{\text{Ir}(\text{O}}\overline{\text{O})}(\text{DTBSQ})]^+$ and its bimolecular reaction with free catechol are obligatory steps. In particular, we believe that this is the first well-documented example of a catalytic oxidation conforming to eq 11 in which the rate is first order in catalyst and substrate concentrations and zero order in free dioxygen over a large range of partial pressures.

The identification of the catalyst and the interception of the catalyst–O_2 adduct are of particular relevance. Their isolation and characterization have certainly been made possible by the use of the tripodal ligand triphos. In effect, tripodal tri- and tetradentate ligands are being largely used to study reaction mechanisms due to their ability to provide the resulting complexes with a remarkable kinetic inertness.[9,10,32]

Finally, it is worth stressing that the oxygenation of $DTBCH_2$ to DTBA (*intra*diol C–C cleavage) competes with *o*-quinone formation at high pressure of O_2. This unprecedented result will probably stimulate further studies with the prospect of using high pressures for oxygenation reactions of severe pollutants such as substituted aromatics.

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Infrared Study on the Hydration of Mn^{2+}, Fe^{2+}, Co^{2+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} Ions in Dilute Aqueous Solution

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OD stretching vibration spectra of Mn^{2+}, Fe^{2+}, Co^{2+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} perchlorates in dilute (0.2–0.4 M) aqueous solution were obtained using infrared spectroscopy. Intensities, bandwidths, and peak positions of the hydrated cation bands are reported. The currently studied first-row transition-metal ions all have a similar effect on the coordinated water (HDO) molecules and give rise to OD stretching vibration bands at 2427 (2) cm^{-1}. Qualitatively similar spectra were obtained for the trivalent lanthanide perchlorate solutions, with a single OD band from cation-perturbed HDO molecules. This implies that the lanthanide ions only perturb the nearest-neighboring water molecules, which thus constitute the primary hydration shell, and to a similar extent as do the divalent cations. The obtained hydration numbers for the lanthanide ions are 7.8 (6) (La), 8.0 (6) (Nd), 8.7 (6) (Dy), and 8.8 (6) (Yb).

Introduction

In dilute aqueous salt solutions, the vast majority of the water molecules are hydrogen bonding to other water molecules, thus constituting the bulk. Infrared spectroscopic studies of such solutions are hindered by the intense absorption of bulk water, which conceals the information to be gained from ion-perturbed water molecules. Furthermore, the spectrum of H_2O is rather complex, with a great deal of overlap of the two fundamental OH stretching vibrations, ν_1 and ν_3, and the first overtone of the bending vibration, ν_2.[1] By addition of a small amount of D_2O, which rapidly reacts with H_2O to form HDO, and the observation of the OD stretching vibrations of the HDO molecules, the situation is greatly improved and simpler spectra can be obtained of the decoupled OD oscillator. This technique of isotopic dilution has been known for a long time.[1–3] Although the problem of the complicated H_2O spectrum can be reduced by isotopic dilution, there is still a substantial amount of HDO molecules in the bulk that contributes to the infrared spectra. By the combination of isotopic dilution and a spectral double-difference technique where the absorption from HDO molecules in the bulk is subtracted, OD vibration spectra of ion-perturbed HDO molecules can be obtained.[4]

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The double-difference method allows the effect of single ions on the neighboring water molecules in aqueous solution to be monitored through the shift in the OD stretching vibration of HDO molecules. In dilute solutions, the polarized water molecule coordinated to a cation will form hydrogen bonds to water molecules in the second sphere with strengths varying with the polarizing power of the cation. Small cations with a large charge/radius ratio cause a strengthening of the hydrogen bond and shift the OD stretching vibration to lower frequency,[4,5] whereas large monovalent or divalent cations have a minor effect and give rise to OD stretching vibration frequencies closer to the value obtained for water molecules in the bulk.[6]

As for the hydration of anions, it is known that the water molecules neighboring anions in aqueous solution are in rapid exchange.[7-9] Nevertheless, the number of intramolecular stretchings of the HDO molecule, $\sim 10^{14}$ s^{-1}, is still orders of magnitudes faster, and vibrational spectroscopic double-difference studies have reported well-characterized OD hydration bands for a number of anions, e.g., $CF_3SO_3^-$,[10] BF_4^-,[4] ClO_4^-,[4,11] NO_3^-,[11] SO_4^{2-},[11] and the halide ions.[11]

In the present investigation, the hydration of Mn^{2+}, Fe^{2+}, Co^{2+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} ions was studied with the use of infrared spectroscopy. We used isotopically diluted HDO molecules and a double-difference technique and obtained OD stretching vibration bands of ion-perturbed water molecules.[4] This investigation is one in a series of infrared studies on the hydration of ions in aqueous solution performed at this laboratory.[4-6,10-13]

Experimental Section

Materials. Analytic grade $Mn(ClO_4)_2{\cdot}6H_2O$ (KEBO), $Co(ClO_4)_2{\cdot}6H_2O$ (Fluka), and $Fe(ClO_4)_2{\cdot}6H_2O$ (GFS Chemicals) were used in the preparation of stock solutions. The lanthanide ion perchlorates were prepared by treating the corresponding lanthanide oxide with perchloric acid. Concentrations were determined by passing the solutions through a cation-exchanger and titrating the eluate using a standard base. Deuterated solutions were prepared by adding a weighed amount of D_2O (99.98%) to a weighed amount of solution. Three independent preparations were made of each solution, differing less than 0.5% in the OD peak absorbance of the corresponding recorded spectra. The pH values of all solutions were ≤ 5. In consideration of the stability constants for the formation of hydrolysis products,[14] this means that the concentration of hydrolysis products in the solutions is negligible.

Measurements. Spectra were recorded on a Perkin-Elmer 580B spectrometer on line with a Perkin-Elmer 3500 data station (La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} spectra) with a chosen resolution of 10 cm^{-1}. Spectra were also recorded with 8-cm^{-1} resolution on a Digilab FTS-45 FTIR spectrometer on line with a Digilab 2360-SPC computer (Mn^{2+}, Fe^{2+}, and Co^{2+} spectra). The solutions were contained between CaF_2 windows with a Teflon spacer setting the cell path length to 0.050 mm, as determined interferometrically. The temperature was kept at 20.0 °C by circulating thermostated water through the metallic fitting holding the CaF_2 plates in place.

Double-Difference Method

The double-difference method involves the calculation of spectral differences, which results in the removal of the unwanted spectral contributions from H_2O and from HDO molecules in the bulk, and gives infrared spectra of ion-perturbed HDO. A detailed description of the procedure can be found in ref 4; only a short summary is given here.

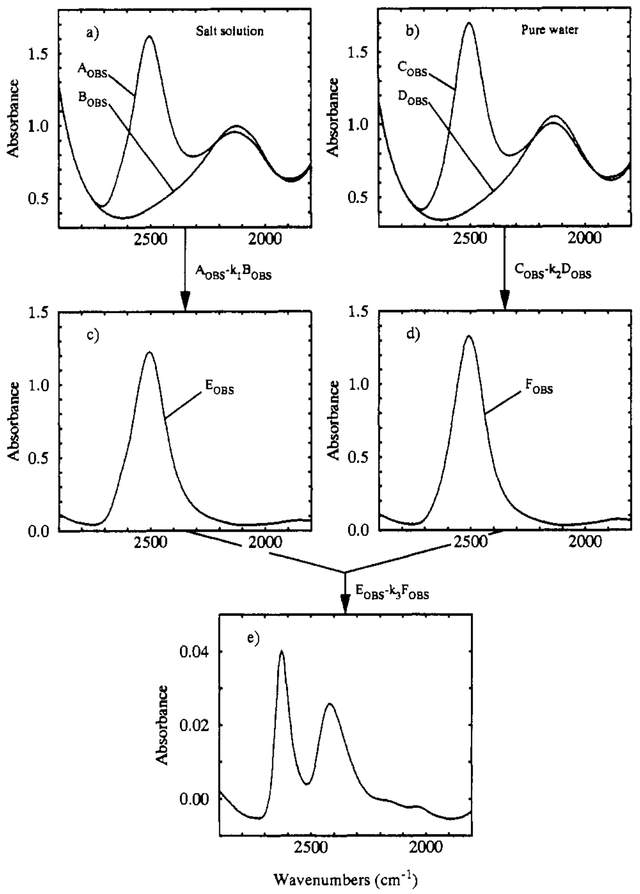

Figure 1. Double-difference method as illustrated by the registered infrared spectra. The four spectra in (a) and (b) are from solutions (A) 0.239 M $Co(ClO_4)_2$ in 8.00 mol % HDO in H_2O, (B) 0.239 M $Co(ClO_4)_2$ in H_2O, (C) 8.00 mol % HDO in H_2O, and (D) pure H_2O. The difference spectra in (c)–(e) have been calculated as indicated in the figure (see text for further details).[4] Note the change in the absorbance scale in (e).

Infrared spectra of four solutions of different compositions are recorded, here exemplified for the cobalt solution: (A) 0.239 M $Co(ClO_4)_2$ in 8.00 mol % HDO in H_2O; (B) 0.239 M $Co(ClO_4)_2$ in H_2O; (C) 8.00 mol % HDO in H_2O; (D) pure H_2O. The corresponding four spectra are denoted A_{OBS}, B_{OBS}, C_{OBS}, and D_{OBS}, respectively, in Figure 1a,b. The difference $(A_{OBS} - k_1B_{OBS}) - k_3(C_{OBS} - k_2D_{OBS})$ is calculated, resulting in the spectra seen in Figure 1c–e. The constants k_1 and k_2 are calculated stoichiometrically.[4] In the first step, the spectral contribution from H_2O is subtracted from the salt solution (Figure 1c) and the reference bulk (Figure 1d). In step 2, the contribution from HDO in the bulk is eliminated by subtracting the bulk HDO spectrum (Figure 1d), multiplied with a constant k_3, from the ion solution spectrum (Figure 1c). The remaining spectrum in Figure 1e consists of OD bands from ion-perturbed HDO molecules. The two bands are assigned to the hydrated anion (ν_{OD} = 2630 cm^{-1}) and cation (ν_{OD} = 2421 cm^{-1}). The constant k_3 is related to the number of ion-perturbed water molecules (HDO) per formula unit of the salt, α, by the relation

$$k_3 = (1/C_{H_2O}(D))(C_{H_2O}(B) - C(s)\alpha) \qquad (1)$$

where $C_{H_2O}(X)$ is the concentration of water in solution X and C(s) is the salt concentration in moles per liter. The entity α is related to the individual ion hydration numbers by

$$\alpha = am + bn/2 \qquad (2)$$

where m and n are the coordination numbers for the cation and

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Table I. Band Parameters for OD Stretching Difference Spectra of $Mn(ClO_4)_2$, $Fe(ClO_4)_2$, $Co(ClO_4)_2$, $La(ClO_4)_3$, $Nd(ClO_4)_3$, $Dy(ClO_4)_3$, and $Yb(ClO_4)_3$ (T = 20.0 °C, d = 0.0495 mm, C(HDO) = 8.00 mol %)

		ν_{max}, cm^{-1}	fwhh,[a] cm^{-1}	C[b]	A,[c] cm^{-1}	A/C_n,[d] L cm^{-1} mol^{-1}	α[e]
$Mn(ClO_4)_2$ (0.242 M)	Mn^{2+}	2426	143	0.0285	5.0	20.5	10.3 (5)
	ClO_4^-	2633	72	0.0454	4.0	8.3	
$Fe(ClO_4)_2$, (0.238 M)	Fe^{2+}	2428	152	0.0299	5.5	23.2	11.1 (5)
	ClO_4^-	2633	76	0.0452	4.2	8.8	
$Co(ClO_4)_2$ (0.239 M)	Co^{2+}	2428	152	0.0299	5.5	23.2	10.3 (5)
	ClO_4^-	2633	73	0.0450	4.0	8.4	
$La(ClO_4)_3$[f] (0.236 M)	La^{3+}	2421	133	0.0347	5.6	23.9	13.5 (5)
	ClO_4^-	2630	74	0.0666	6.0	8.5	
$Nd(ClO_4)_3$[f] (0.342 M)	Nd^{3+}	2421	141	0.0498	8.6	25.1	13.7 (5)
	ClO_4^-	2630	74	0.0978	8.8	8.6	
$Dy(ClO_4)_3$[f] (0.366 M)	Dy^{3+}	2414	158	0.0726	14.8	40.4	14.4 (5)
	ClO_4^-	2631	73	0.0980	9.3	8.4	
$Yb(ClO_4)_3$[f] (0.375 M)	Yb^{3+}	2414	159	0.0737	15.1	40.3	14.5 (5)
	ClO_4^-	2630	73	0.1008	9.5	8.5	
est stdard devs		0.1%	3%	2%	5%	5%	

[a] Full width at half-height. [b] Peak height in absorbance units. [c] Band area.[1] [d] C_n is the concentration of respective cation or anion. [e] The number of ion-perturbed OD oscillators per salt unit (see text) with the estimated standard deviation (within parentheses) referring to the last significant digit. [f] The rare-earth perchlorate intensity data have been scaled from 6.00 mol % HDO and path length = 0.0444 mm.

anion, respectively, for a salt M_aN_b. The value of k_3, and thereby α (eq 1), is obtained from a band-shape analysis. In a least-squares fit procedure the bulk HDO spectrum is removed until the best description of the OD bands is reached in terms of the peak positions, bandwidths, and band heights. In the current study, we have used the perchlorate anion as the counterion. The hydration number of the perchlorate ion has previously been determined using the double-difference method; a value of 4.6 (8) was reported.[4] This value was the average obtained for a range of concentrations, and it contains an estimated correction of 0.3 water molecules, due to an expected OH/OD fractionation effect. However, the effect of OH/OD fractionation on the hydration numbers for divalent metal ions has recently been studied,[15] and it was concluded that the effect is small and barely significant. If this correction is disregarded, a perchlorate ion hydration number 4.1 (8) is obtained at concentrations comparable to the current study. In a recent double-difference study on the hydration of anions,[11] the perchlorate ion hydration number was redetermined to 3.8 (3). [The number given in parentheses, here and in the following, is the standard deviation referring to the last significant digit, as estimated from measurements made on at least three independently prepared samples.] This value is used in the current study. The knowledge of the anion hydration number means that the value of k_3 (eq 1) can be directly related to the number of cation-affected water molecules (eq 2). The extent of outer-sphere complexation in aqueous ionic solutions has previously been investigated in a concentration study of $Ni(ClO_4)_2$ and $Mg(ClO_4)_2$.[16] A linear increase in the number of solvent-shared ion pairs, or outer-sphere complexes, was observed with the increase of ion concentration; <5% complexation occurs for salt concentrations of 0.5 mol/kg. As outer-sphere complexes are formed, the effect on the spectra is a decrease of the cation band intensity and a broadening of the anion band. The results from this study clearly exclude the possible use of an ionic medium (i.e. a solution of high ionic strength) in the present ion hydration studies, since a substantial amount of outer-sphere complexes would form. The current concentrations have been chosen to minimize outer-sphere complexation and yet give reliable data in terms of signal to noise ratio.

Results and Discussion

Mn^{2+}, Fe^{2+}, and Co^{2+}. The OD spectra of the first-row transition-metal ion solutions are presented in Figure 2, and the corresponding refined band parameters are given in Table I. The current OD band parameters for Mn^{2+}, Fe^{2+}, and Co^{2+} add to the data previously obtained at this laboratory for first-row divalent transition-metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}).[4,12,13] According to the present infrared results, the Mn^{2+}, Fe^{2+}, and Co^{2+} ions coordinate 6.5 (5), 7.3 (5), and 6.5 (5) water molecules, respectively. It is noted that the Fe^{2+} hydration number is significantly higher than the commonly expected coordination number of 6 for divalent transition-metal ions.[17] The OD bandwidths of the iron(II) and cobalt(II) ions are somewhat broader than for the corresponding manganese(II) band (Table I), which in turn is approximately the same as found for the nickel(II) ion.[4]

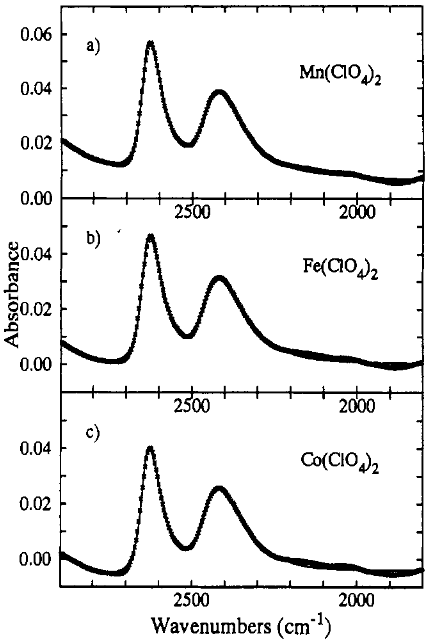

Figure 2. Difference OD stretching spectra (crosses) of (a) 0.242 M $Mn(ClO_4)_2$, (b) 0.238 M $Fe(ClO_4)_2$, and (c) 0.239 M $Co(ClO_4)_2$ in aqueous solution. The solid lines are the functions fitted to the spectra. The band parameters are given in Table I. T = 20.0 °C, path length = 0.0495 mm, and C(HDO) = 8.00 mol %.

Several of the transition-metal ions have previously been studied using infrared spectroscopy.[18,19] It was established that the first-row transition-metal ions Mn^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} have a similar effect on the hydrating water molecules. Using a deconvolution technique, the positions of OD bands of cation-perturbed HDO molecules were obtained, ranging from 2418 to 2442 cm^{-1} for dilute solutions (<1.0 m).

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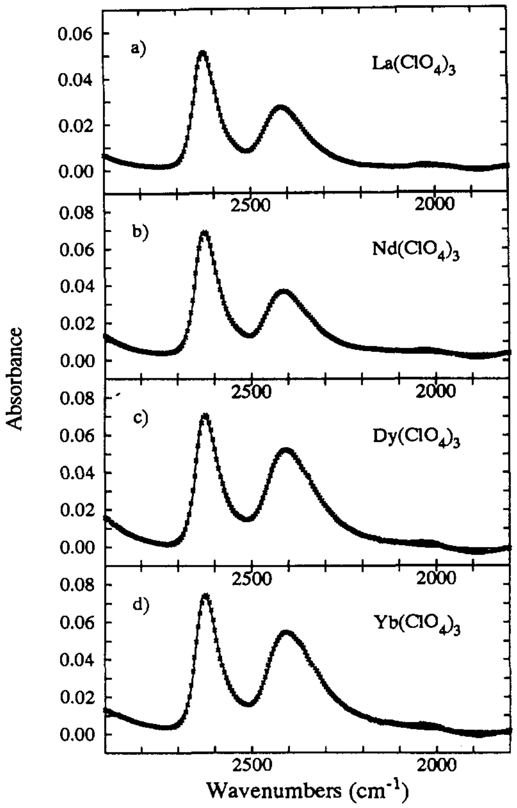

Figure 3. OD stretching spectra of aqueous solutions of (a) 0.236 M La(ClO$_4$)$_3$, (b) 0.342 M Nd(ClO$_4$)$_3$, (c) 0.366 M Dy(ClO$_4$)$_3$, and (d) 0.375 M Yb(ClO$_4$)$_3$. The crosses are the observed points, and the solid line is the function fitted to the spectra. See Table I for band parameters. T = 20.0 °C, path length = 0.0444 mm, and C(HDO) = 6.00 mol %.

In a previous Raman study on the hydration of first-row transition-metal ions, it was inferred that the shift of the symmetric intermolecular M–OH$_2$ vibration approximately follows the variation in hydration enthalpy.[20] The hydration enthalpies for the first-row transition-metal ions are known to vary with the atomic number, and thus with the number of d-electrons, following the Irving–Williams trend.[17] The hydration enthalpy increases from Mn^{2+}, reaches a maximum for Ni^{2+} and Cu^{2+}, where it is greater than expected from a simple electrostatic model, and decreases again for Zn^{2+}. This trend is roughly explained by crystal field effects. The main contribution to the hydration enthalpy of cations comes from the coordination of water molecules in a more or less well-defined first sphere. The strength of this interaction is expected to reflect not only on intermolecular ion–water stretching vibrations but also on the polarization of the coordinating water molecules and thus the strength of the hydrogen bonds formed to water molecules outside the first hydration sphere. The position of the present cation hydration bands ranges from 2426 to 2428 cm^{-1}. The corresponding positions of the previously studied Ni^{2+} and Zn^{2+} are 2423 and 2427 cm^{-1}, respectively.[13,16] The [Cu(H$_2$O)$_6$]$^{2+}$ complex is influenced by the Jahn–Teller effect, and two peaks from cation-perturbed water molecules can be discerned, corresponding to the two types of water molecules expected from the tetragonal distortion of the [Cu(H$_2$O)$_6$]$^{2+}$ complex.[12] This excludes the copper ion from further comparison, and the interested reader is referred to ref 12 for further reading on this issue. In view of the estimated standard deviations of the peak positions (0.1%), the OD stretching frequency of these cation-perturbed HDO molecules is the same. It is thus concluded that the OD stretching frequency of HDO molecules perturbed by transition-metal ions does not reflect the difference in hydration enthalpies.

Lanthanide Ions. The final difference spectra of the lanthanide ion perchlorate solutions are shown in Figure 3, and the band parameters are reported in Table I. The perchlorate peak is positioned at 2630 cm^{-1}, and a single cation peak is observed at ~2420 cm^{-1}.

The hydration numbers obtained for La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} are 7.8 (6), 8.0 (6), 8.7 (6), and 8.8 (6), respectively (Table I). For a considerable amount of time there has been a controversial discussion going on in the literature about the hydration number of the lanthanide ions. On the basis of the X-ray diffraction studies of highly concentrated solutions, it has been suggested that the hydration number is 9 (average 9.1 (2)) in the beginning of the series, which decreases to 8 (average 8.1 (2)) for the heavier ions.[21] The phenomenon of a hydration number change along the series is supported by the results of Kanno et al.,[22,23] who used Raman spectroscopy on aqueous chloride solutions in the glassy state (liquid-nitrogen temperature) and observed that the ν_1(Ln^{3+}–OH$_2$) vibration frequency (ν_1 is the totally symmetric stretching vibration of the [Ln(H$_2$O)$_n$]$^{3+}$ complex) changes abruptly for the intermediate lanthanide ions (Eu^{3+}, Gd^{3+}). This was interpreted as a hydration number change from 9 to 8 in going from the light to the heavy rare-earth ions. On the other hand, Johansson et al.[24,25] found a hydration number of 8.0 (3) consistent with their X-ray diffraction results in the concentration range 0.8–4.6 m for both light and heavy lanthanide ions (La^{3+}, Sm^{3+}, Tb^{3+}, Er^{3+}). Neutron diffraction studies have given hydration numbers of 8.5 (2)[26] and 8.9 (2)[27] for Nd^{3+}, 8.5 (2) for Sm^{3+},[27] 7.8 (2) for Yb^{3+},[28] and 8.0 (2)[28] and 7.4 (5)[29] for Dy^{3+}.

The present hydration numbers, obtained from dilute solutions (0.2–0.4 M), are ranging from 7.8 (6) to 8.8 (6). Somewhat smaller values are obtained for the lighter lanthanides, contrary to the trend mentioned above. In consideration of the standard deviations, the differences are not significant, and we are forced to conclude that the issue of the lanthanide ion hydration number cannot be solved from the current investigation.

However, the current study certainly provides other interesting structural information. From the comparison of the spectra in Figures 2 and 3, two important observations can be made. First, the immediate reflection is that the trivalent cation solutions give rise to spectra qualitatively very similar to those of the divalent cation solutions. Second, neither the divalent, nor the trivalent, cations give rise to a detectable second hydration sphere. The validity of the latter statement is best demonstrated if we compare the current spectra with a previous infrared study of the smaller Al^{3+}, Cr^{3+}, and Rh^{3+} ions.[5] Significantly different spectral features were observed, with a very broad absorbance due to the hydrated cation, extending far down in frequency. Actually, two cation bands could be discerned, assigned to the first and the second hydration sphere. The single cation hydration bands in Figures 2 and 3 thus tell us that there is no detectable perturbation in terms of vibrations of the second-sphere water molecules for the current lanthanide ions.

The similarity of the transition-metal and the lanthanide spectra at first seems somewhat surprising in consideration of the difference in valence and electronic structure of the ions. It seems as if the influence of the valence is partly compensated for by the difference in ionic radii; the trivalent lanthanides are significantly larger than the transition-metal ions. If we use the charge to radius ratio as a measure of the polarizing power, we find that it is of the same order of magnitude for the two groups of ions: Mn^{2+}, Fe^{2+}, Co^{2+}, 2.5–2.8; La^{3+}, 2.6; Nd^{3+}, 2.9; Dy^{3+}, 3.3; Yb^{3+}, 3.5.

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The Dy^{3+} and Yb^{3+} ratios are slightly larger, and we do indeed observe a small downshift in the peak OD frequency (Table I). Furthermore, the higher coordination number for the lanthanide ions probably also contributes to suppress the effect of the higher valency.

An eye-catching feature of the lanthanide spectra is the different intensities of the cation bands. The two lighter ions, La^{3+} and Nd^{3+}, display intensities similar to those of the divalent transition-metal ions, whereas the heavier Dy^{3+} and Yb^{3+} are much more intense (Table I). We would like to emphasize that the parameters given in Table I indicate that the band-fit procedure works satisfactorily and gives reliable results; the perchlorate band parameters, which should be invariable, are almost the same for the different solutions. Furthermore, a difference in the cation OD band intensity is not necessarily coupled to a difference in hydration number. This is illustrated by a previous ab initio calculation on the $Zn^{2+}{\cdot}H_2O$ and $Mg^{2+}{\cdot}H_2O$ complexes.[30] The calculation showed that the experimentally obtained difference in OD band intensities for these two hexacoordinated ions in aqueous solution[31] could be explained in terms of a 3d-σ orbital overlap for the transition-metal complex.[30] It is also important to stress that the hydration numbers obtained from the double-difference method is derived from band shapes rather than band intensities,[4] and there is no controversy in the fact that large intensity differences are obtained between the lanthanide ions although our results indicate that there is no significant difference in hydration number.

To further analyze this intensity difference, we reevaluated the OD band intensities for fixed lanthanide hydration numbers of 9 for the light and 8 for the heavy ions. This resulted in an intensity decrease for the heavy ions of ~6% and an increase for the light ions of ~10%. The intensity difference between the two groups thus becomes smaller, but is still substantial; it originally amounted to ~40% (Table I). If we believe these hydration numbers to be true, which has been suggested from several authors,[21–23,26–29] it is reasonable to expect an intensity increase for the heavier lanthanide ions. The heavier ions are smaller, and stronger bonds are probably formed to the neighboring water molecules, especially if the primary hydration shell consists of 8 water molecules, in which case they can come closer to the cation than in the case of 9. The reported $R(M{\cdots}O)$ distances are 2.58 Å (La), 2.51 Å (Nd), 2.39 Å (Dy), and 2.33 Å (Yb).[21b,27,28] We thus expect a larger dipole moment derivative in the vibrations of the hydrating water molecules for the heavier lanthanide ions.

It thus seems clear that in terms of intensities a grouping in two categories, the light and the heavy lanthanide ions, is established. Due to the fact that the heavy lanthanide OD bands are shifted somewhat downward in frequency (Table I), an increase intensity is expected, in line with the well-known increase in molar absorptivity with decreasing wavenumber.[32] However, this cannot at all account for the very large increase of intensity. Further studies in relation to this issue are needed to reach a better understanding of the phenomenon. An ab initio calculation on lanthanide–water complexes, similar to the one mentioned above for Zn^{2+} and Mg^{2+},[30] could probably give more information. It would then be necessary to take into account all the electrons of the ions, in order to clarify for example the influence of the inner f-orbitals.

Conclusions

The Mn^{2+}, Fe^{2+}, and Co^{2+} transition-metal ions have a similar effect on the coordinated water molecules, giving rise to OD stretching bands at 2427 (2) cm^{-1}. The obtained hydration numbers are 6.5 (5), 7.3 (5), and 6.5 (5), respectively.

Water molecules neighboring the La^{3+}, Nd^{3+}, Dy^{3+}, and Yb^{3+} ions give rise to OD bands similar to the transition-metal ion bands. Single OD bands are assigned to cation-perturbed water molecules, at frequencies ranging from 2414 to 2421 cm^{-1}. This means that there is no perturbation of water molecules beyond the primary cation hydration sphere. The double-difference method allows no significant differences in terms of hydration numbers to be detected between the light (7.8 (6) (La) and 8.0 (6) (Nd)) and the heavy (8.7 (6) (Dy) and 8.8 (6) (Yb)) lanthanide ions. However, a significantly increased OD hydration band intensity is observed for the heavy lanthanide ions compared to the light, and a grouping in two categories can be made.

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Registry No. Mn^{2+}, 16397-91-4; Fe^{2+}, 15438-31-0; Co^{2+}, 22541-53-3; La^{3+}, 16096-89-2; Nd^{3+}, 14913-52-1; Dy^{3+}, 22541-21-5; Yb^{3+}, 22537-40-2.

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Notes

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Disproportionation of Alkoxyborohydrides: A ^{11}B NMR Study of the Reaction between Sodium Borohydride and Fluorinated Alcohols and Phenols. The Preparation of Tris(fluoroalkoxy)- and Tris(fluorophenoxy)borohydrides

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^{11}B NMR studies have shown that alkoxyborohydrides, when formed in THF solution at 0 °C from sodium borohydride and methanol or fluoroalcohols, disproportionate over time to yield tetraalkoxyborohydride and BH_4^- ions. In contrast to alkoxyborohydrides, triphenoxy and tris(pentafluorophenoxy)borohydrides appear to be stable at 0 °C toward disproportionation. Consequently, modification of $NaBH_4$ with various fluoro alcohols and fluorophenols will yield a class of reducing agents that may be very promising in designing selective and asymmetric reductions.

Modification of alkali metal borohydrides with alkoxy groups has been reported to afford trialkoxyborohydrides which give reductions with high chemo- and stereoselectivity.[1,2] These trialkoxyborohydrides are usually prepared via a Lewis acid/base reaction from the corresponding trialkoxyborane and a metal hydride and stored over excess metal hydride to prevent any disproportionation reaction.[3,4] Direct reactions of alcohols with

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