small isotope effects (k_H/k_D(296 K) ~ 1–2,[23] and hydrogen atom abstractions from methane which proceed through a linear "three"-centered TS (C⋯H⋯X) have large isotope effects (k_H/k_D(298 K) ~ 9).[16b,24] A linear four-centered TS for the methane reaction (Rh⋯C⋯H⋯Rh) can potentially produce kinetic isotope effects comparable to a linear three-centered TS (C⋯H⋯X) because there are the same number and type of isotope sensitive (H (D)) vibrations in both transition states. This situation for C–H bond reactions contrasts with that for H_2 where the presence of two hydrogens produces twice as many isotope sensitive modes in a linear four-centered TS as there are in a linear three-centered TS.

In summary, the reaction of (TMP)Rh$^•$ with hydrogen proceeds through a four-centered TS that provides a low activation enthalpy pathway for the concerted formation of two (TMP)Rh–H. The kinetic isotope effect is relatively small, but this result cannot at this time be used in differentiating between linear and bent transition states because of the inability to determine both the vibrational structure of the TS and the contribution of tunneling to k_{H_2}/k_{D_2}. Linear four-centered transition states can be expected to produce substantially smaller kinetic isotope effects than the better known three-centered TS because of the reduction of both the EXC and ZPE terms that results from doubling of the isotope-sensitive vibrations in the TS. Bonding and steric considerations suggest that a linear four-centered TS is preferable, but confirming experimental evidence is lacking. Reactions of (TMP)Rh$^•$ and other radicals with substrates like H_2 and CH_4, where atom abstractions are thermodynamically unfavorable, can be accomplished by an alternate low activation enthalpy pathway involving the concerted reaction of two radicals through a four-centered TS.

Experimental Section

Materials. (Tetramesitylporphyrinato)rhodium(II) was prepared by published procedures.[13] H_2 and D_2 were purchased from Matheson Gas Products. Deuterated NMR solvents were degassed by freeze–pump–thaw cycles and then refluxed over sodium/benzophenone until the indicator turned purple.

General Methods. All manipulations were performed in an inert-atmosphere box under nitrogen/argon or by vacuum-line techniques. NMR data were recorded on an IBM-Bruker WP200SY spectrometer at ambient temperature unless otherwise noted.

Kinetic Studies. All reactions of hydrogen and deuterium were performed in 507 PP Wilmad sealed NMR tubes immersed in a constant-temperature bath (±0.10 °C). The progress of each reaction was evaluated by monitoring the changes in relative concentrations of (TMP)Rh$^•$ and (TMP)Rh–H as observed by ^{1}H NMR spectroscopy. Absolute concentrations of rhodium porphyrin species were measured with respect to a known concentration of H_2 as an internal standard. The molar concentration of H_2 in benzene as a function of temperature and hydrogen pressure is given by the following expression: $[H_2] = [2.3421 \times 10^{-3} + 2.2592 \times 10^{-5}(T_2\ (°C)][T_2(K) \times P_1\ (Torr)/T_1\ (K)][1/760\ Torr]$, where T_1 and P_1 are the temperature and pressure at which the concentration is calculated. The solubility of D_2 in benzene is assumed to be the same as H_2.

Kinetic experiments were monitored at a series of hydrogen pressures (P_{H_2} = 150–650 Torr) and used to determine that the reaction is first order in H_2. Plots of $[(TMP)Rh^•]^{-1}$ versus time yielded straight lines until completion of the reaction, which clearly indicates that reaction 1 is second order in $[(TMP)Rh]^•$ and thus third order overall (rate = $k[(TMP)Rh^•]^2[H_2]$). Rate constants (k_{H_2}(296 K) = 2.5 ± 0.4 $L^2\ mol^{-2}\ s^{-1}$; k_{D_2}(296 K) = 1.6 ± 0.2 $L^2\ mol^{-2}\ s^{-1}$; k_{H_2}(353 K) = 11.2 ± 1.3 $L^2\ mol^{-2}\ s^{-1}$; k_{D_2}(353 K) = 8.4 ± 1.6 $L^2\ mol^{-2}\ s^{-1}$) are averages from four independent kinetic measurements for each reaction. The error ranges correspond to one standard deviation from the mean. Rate constants measured for independent samples are observed to agree within approximately ±15%, but the absolute error in any single measurement could be as large as 30%.

The ratio of rate constants (k_{H_2}/k_{D_2}) was determined from kinetic runs utilizing H_2 and D_2 samples prepared at the same gas pressure and initial molar concentration of (TMP)Rh$^•$ so as to minimize the accumulation of errors in k_{H_2}/k_{D_2} (k_{H_2}/k_{D_2}(296 K) = 1.6 ± 0.2; k_{H_2}/k_{D_2}(353 K) = 1.3 ± 0.2). Activation parameters for reaction 1 were derived from four k_1 measurements at both 296 and 353 K. The error ranges correspond to one standard deviation ($\Delta H_1^‡(H_2)$ = 4.9 ± 1.0 kcal mol^{-1}; $\Delta S_1^‡(H_2)$ = −40 ± 5 cal $K^{-1}\ mol^{-1}$; $A(H_2) = 2.9 \times 10^4$; $\Delta E_1^‡(H_2)$ = 5.5 ± 1.0 kcal mol^{-1}; $\Delta H_1^‡(D_2)$ = 5.5 ± 1.0 kcal mol^{-1}, $\Delta S_1^‡(D_2)$ = −39 ± 5 cal $K^{-1}\ mol^{-1}$, $A(D_2) = 5.0 \times 10^4$, $\Delta E_1^‡(D_2)$ = 6.1 ± 1.0 kcal mol^{-1}). Thermodynamic parameters from equilibrium studies could not be derived from the observations because reaction 1 effectively proceeded to completion for the range of conditions examined.

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Infrared Spectroscopic Study on the Hydration of Mercury(II), Cadmium(II), and Zinc(II) in Aqueous Solution and in the Hexahydrated Perchlorate Salts

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Introduction

In a recent theoretical study (SCF calculation) on the hexahydrated d^{10} ions zinc(II), cadmium(II), and mercury(II),[1] it was inferred that a comparatively broad distribution of the Hg–O bond lengths, as observed in a solution X-ray diffraction study,[2] could be explained in terms of a weak second-order Jahn–Teller (SOJT) effect.[3,4] This means that vibronic couplings between the nuclear and electronic motions occur in the hexaaquamercury(II) complex, primarily mixing the electronic A_g ground state of the mercury(II) ion with the lowest excited E_g state with an open d orbital, involving a vibrational mode of E_g symmetry. The calculations showed the d to s excitation energy to be lower for the hexaaqua complex of mercury(II) than for the zinc(II) and cadmium(II) complexes, implying a higher degree of vibronic coupling.[1]

In the present study, the hydration of the mercury(II) ion was investigated both in aqueous solution, using an infrared spectroscopic double-difference method,[5-7] and in the solid hexahydrate. In line with the theoretical calculation,[1] a comparative study of the hydrated Zn^{2+}, Cd^{2+}, and Hg^{2+} ions is presented.

Experimental Section

Materials. The solid hexahydrates of cadmium(II) and mercury(II) perchlorates were prepared as previously described.[8] The hydrated zinc perchlorate was obtained from GFS Chemicals. For the acidified solutions, perchloric acid was added to 0.05 mol dm^{-3}. The cation concentrations were determined by acid–base titrations of the eluate from a Dowex 50W resin and by standard EDTA titrations.[9] Partial deuteration (8.0 mol % HDO) was obtained by adding D_2O (99.98%) to the solution by weight. Three parallel preparations were made which differed by less than 0.5% in OD peak absorbance. Partial deuteration of the $Cd(ClO_4)_2 \cdot 6L_2O$ and $Hg(ClO_4)_2 \cdot 6L_2O$ compounds was obtained by recrystallization from an aqueous solution with an H/D ratio of 0.975.

Measurements. The infrared spectra were recorded at 8-cm^{-1} resolution with a Digilab FTS-45 spectrometer on line with a Digilab 2360-SPC computer. The solutions were contained between CaF_2 windows and a Teflon spacer (path length 49.8 ± 0.3 μm determined interferometrically) in a cell thermostated to 20.0 °C by circulating water in its metal frame.

Method. In the infrared spectroscopic method, the OD stretching vibration spectrum of the isotopically isolated, ion-perturbed HDO

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Table I. Fitted Band Parameters of the Difference Spectra of $Zn(ClO_4)_2$, $Cd(ClO_4)_2$, and $Hg(ClO_4)_2$ Solutions, with and without Added Acid ($HClO_4$)

soln	c_{salt}, mol dm^{-3}	c_{acid}, mol dm^{-3}	ion	C[a]	ν_{OD}, cm^{-1}	fwhh,[b] cm^{-1}	α[c]	R_u–R_l,[d] pm
$Zn(ClO_4)_2$	0.242		ClO_4^-	0.045	2633	74		2.2
			Zn^{2+}	0.030	2427	155	10.7	1.4
$Cd(ClO_4)_2$	0.243		ClO_4^-	0.045	2633	77		2.4
			Cd^{2+}	0.032	2425	156	11.1	1.4
$Zn(ClO_4)_2$	0.236	0.0515	ClO_4^-	0.047	2632	80		2.4
			Zn^{2+}	0.033	2425	144	11.7	1.3
$Cd(ClO_4)_2$	0.240	0.0505	ClO_4^-	0.049	2632	82		2.5
			Cd^{2+}	0.036	2423	148	12.4	1.3
$Hg(ClO_4)_2$	0.242	0.0505	ClO_4^-	0.050	2632	84		2.6
			Hg^{2+}	0.035	2416	193	12.1	1.7

[a] Band height in absorbance units. [b] Full width at half-height, fwhh.[6] [c] The number of ion-perturbed OD oscillators per salt unit. [d] Hydrogen bond distance range calculated from $\nu_{OD} \pm {}^1/_2$fwhh.[14]

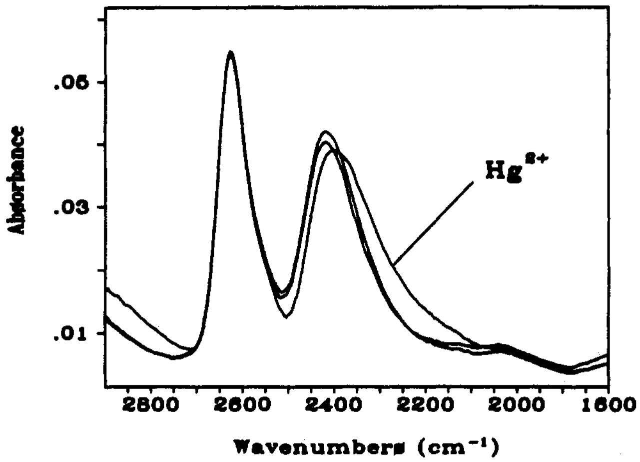

Figure 1. OD difference spectra of the acidified $Zn(ClO_4)_2$, $Cd(ClO_4)_2$, and $Hg(ClO_4)_2$ solutions superimposed after scaling to equal concentration (0.240 M).

molecules is extracted by removing the contributions from HDO in the bulk and from H_2O in a double-difference procedure, described in detail in ref 5. The hydrolysis of the mercury ion in aqueous solution is well-known, and acid was added in order to suppress the formation of hydroxide complexes.[10] A slight modification of the previously described method was thus necessary, since acidic reference solutions[5] were used to match the acidified metal ion solutions.

Results and Discussion

Aqueous Solutions. The final difference OD spectra are shown in Figure 1. Two bands dominate in each spectrum, a high-wavenumber OD band at 2632–3 cm^{-1} from the water molecules hydrogen-bonded to the perchlorate ion and a low-wavenumber OD band from water molecules neighboring the metal ion. The OD band parameters are given in Table I. From these, it is obvious that the hydrogen bonding in the corresponding zinc(II) and cadmium(II) solutions is very similar. However, when the results from corresponding solutions with and without added acid are compared, some differences become apparent (Table I). For the acidified solutions, the bandwidth of the perchlorate band is larger, whereas the metal ion bandwidth is smaller despite the increase in the number of affected OD oscillators per formula unit of salt, α, of about 1.2.

Table II. Positions and Bandwidths of Infrared Vibrational Bands of the Solid Hydrates $Cd(ClO_4)_2 \cdot 6L_2O$ and $Hg(ClO_4)_2 \cdot 6L_2O$ (L ~97.5% H and ~2.5% D) at Room Temperature

salt	position, cm^{-1}	fwhh,[a] cm^{-1}	assignt	R,[b] pm	R_u–R_l,[c] pm
$Cd(ClO_4)_2 \cdot 6L_2O$	2581	75	ν_{OD}	29.6	1.5
	1617	41	δ_{HOH}		
	1429	23	δ_{HDO}		
$Hg(ClO_4)_2 \cdot 6L_2O$	2567	106	ν_{OD}	29.3	1.9
	1607	81	δ_{HOH}		
	1420	31	δ_{HDO}		

[a] Full width at half-height. [b] Hydrogen-bond distance calculated from the correlation curve in ref 14: $R = [-\ln((2727 - \nu_{OD})/8.97 \times 10^6)]/0.373$. [c] Hydrogen bond distance range calculated from $\nu_{OD} \pm {}^1/_2$fwhh.[14]

These differences are somewhat unexpected, since the contribution of the added acid would be expected to cancel in the double-difference procedure, by the use of reference solutions with the same total concentration of acid as in the metal ion solutions. However, since the probability to find H_3O^+ (or H_2DO^+) ions in the immediate vicinity of the metal ions is low, the local acid concentration in the bulk water of the metal ion solution will be higher than in the also acidified reference solution. A separate double-difference study of the 0.05 mol dm^{-3} perchloric acid solutions, used as references for the metal ion solutions, shows the ClO_4^- band to be broadened and that the hydrated H_2DO^+ ion gives rise to an OD band at about 2390 cm^{-1} with a bandwidth of ca 130 cm^{-1}. We propose that two effects can be ascribed to the local excess of acid in the salt solution. First, the amount of bulk water (H_2O and HDO with unperturbed stretching frequencies) is reduced. As a consequence, a smaller amount of the reference solution OD spectrum has to be subtracted from the salt solution spectrum in the second difference of the double-difference method (see Figure 1, ref 5). A greater α value is thereby obtained for the acidified salt solutions (Table I). Second, the OD bands from the excess acid molecules in the bulk will overlap the OD bands of the salt solution and affect their band shapes (Table I). However, the increase in α obtained at the acidification of the zinc(II) and cadmium(II) solutions is consistent enough to allow a deduction of a corrected α value for the mercury(II) perchlorate solution, $\alpha = 10.9$ (=12.1 − 1.2).

In the comparison of cation OD bands in Figure 1, a broadening and a shift toward lower wavenumbers of the mercury(II) band are apparent. The bandwidth is substantially larger than for other, previously studied, divalent cations (141–152 cm^{-1}).[5,11,12] The lower OD stretching frequency indicates a stronger hydrogen bond and thus a stronger polarization of the water molecules around

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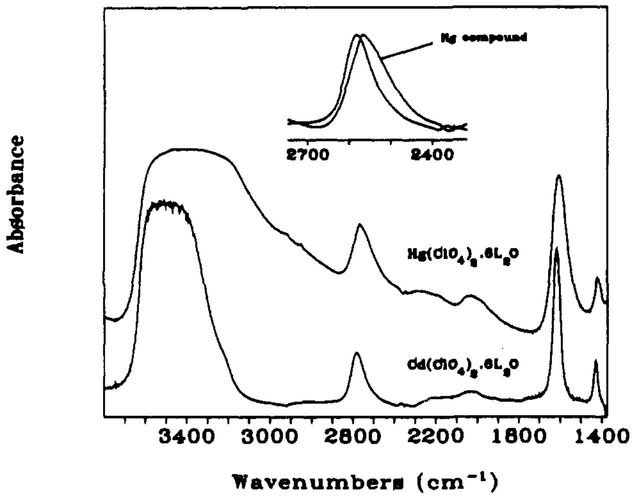

Figure 2. Room-temperature IR spectra of solid $Hg(ClO_4)_2 \cdot 6L_2O$ and $Cd(ClO_4)_2 \cdot 6L_2O$ (95 mol % H_2O and 5 mol % HDO). The inset shows an enlarged view of the OD stretching region, where the OD stretching bands have been scaled to the same height and superimposed, preceded by a baseline correction of the mercury OD band.

the mercury(II) ion. The well-known increase in molar absorptivity with decreasing wavenumber[13] would then be expected to contribute to the increase in the bandwidth. Still, the bandwidth of the mercury(II) ion, 193 cm^{-1}, is >30 cm^{-1} larger than those for the lanthanide cation bands,[12] which are also positioned at 2416 cm^{-1}. We thus conclude that the mercury(II) band is particularly broad.

As mentioned above, a consequence of the SOJT effect on the hydrated mercury(II) ion would be a wider distribution of the Hg–O distances. The polarization of the coordinated water molecules is affected by the distance to the mercury(II) ion, and consequently, the hydrogen-bond strengths in the second sphere vary. A broader OD stretching band would then be expected, and we propose that the broadening observed for the mercury(II) band is due to the influence of the SOJT effect on the hydrated mercury(II) ion.

Solid Hydrates. The room-temperature infrared spectra of the solid compounds $Hg(ClO_4)_2 \cdot 6L_2O$ and $Cd(ClO_4)_2 \cdot 6L_2O$ (5% HDO, 95% H_2O) are shown in Figure 2, with band positions and bandwidths given in Table II. Also included are hydrogen-bond O···O distances derived from a correlation curve.[14]

The isomorphous crystal structures of the solid hexahydrates of cadmium(II) and mercury(II) perchlorates have previously been determined at room temperature, using X-ray diffraction.[8] The water oxygen atoms form a string of face-sharing octahedra with C_3 symmetry, in which every second octahedron is occupied by a metal ion. Each string of octahedra is surrounded by six parallel columns of perchlorate ions on 3-fold axes. The hexaaquazinc(II) perchlorate has a similar type of structure but is known to have considerable disorder in the distribution of the metal atoms in the octahedra.[15-17] Also, the crystal structure of the hexaaquacadmium(II) perchlorate shows some disorder at room temperature, mainly in the direction of the perchlorate ion columns. However, even though no disorder was found in the corresponding mercury compound,[8] its OD stretching fundamental is even broader, 106 cm^{-1}, and more asymmetric (Table II, Figure 2), which can be explained by an appreciable SOJT effect.

Comparisons of the metal–oxygen distributions in the aqueous solution and in the solid hydrate, as estimated from the OD bandwidths, can provide a relative measure of the SOJT effect. The increase in distance ranges for the mercury compounds in the solids and in the solutions are similar (Tables I and II), and we conclude that the SOJT effect affects the Hg–O bonding to a similar extent in the solid structure and in the aqueous solution.

The OD stretching frequencies in the spectra of the solid cadmium(II) and mercury(II) hexahydrate spectra are ~150 cm^{-1} higher than those for the aqueous solutions (Figure 1 and 2, Tables I and II). This indicates that the water molecules coordinated to the cations form considerably stronger hydrogen bonds in the aqueous solution, where they hydrogen-bond to other water molecules, than in the solid hydrates, where perchlorate ions act as hydrogen-bond acceptors. In a previous study of $Ni(ClO_4)_2$ solutions,[6] a similar influence on the cation-coordinated water molecule by this type of hydrogen-bond acceptor was observed. A band, upshifted ca. 200 cm^{-1} from the cation hydration band at 2423 cm^{-1}, was observed at high concentrations and assigned to water molecules in solvent-shared ion pairs,[6] i.e. water molecules coordinated to the cation and simultaneously hydrogen-bonding to the perchlorate ion. The OD band of the solid $[Ni(L_2O)_6](ClO_4)_2$ (L ~5% D) is found at 2585 cm^{-1},[6] downshifted 35 cm^{-1} with respect to the concentrated aqueous solution due to crystal field effects.

Conclusions

Water molecules in the hydration spheres of the Zn^{2+}, Cd^{2+}, and Hg^{2+} ions, respectively, give rise to single OD bands in the infrared spectra. The band of the mercury(II) ion is significantly broader than those of zinc(II) and cadmium(II) in solution as well as in the solid hexahydrated perchlorate salts. The increase in the covalent character of the Hg–O bonds and in the polarization of the coordinated water molecules is shown by the lower frequency of the OD stretching band. We interpret the broadening of the OD bands for the hydrated mercury(II) ion as an effect of second-order Jahn–Teller couplings of vibrational and electronic motions influencing the bond strength, although the vibronic couplings are not strong enough to give rise to static distortions of the octahedral coordination geometry.

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