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Hydration of Hg^{2+} in Aqueous Solution Studied by Neutron Diffraction with Isotopic Substitution

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The structural parameters of Hg^{2+} hydration were studied in 0.225 mol/L solutions of Hg^{2+} in DNO_3/D_2O by means of neutron diffraction with isotopic substitution of ^{199}Hg for ^{nat}Hg. It was found that Hg^{2+} is hydrated by a first solvation shell of six water molecules. The observed Hg−O and Hg−H distances are equal to 2.48 ± 0.05 and 3.08 ± 0.05 Å, respectively. The angle ϕ between the plane of the water molecule and the cation−water oxygen axis is ∼ 35°. The solvation of Hg^{2+} therefore mimics very closely that of Ca^{2+} (the Ca−O and Ca−H distances are 2.40 and 3.03 Å, respectively) and helps to account for the extreme toxicity of mercury(II). We note also that the Hg−O distance obtained in the neutron diffraction experiment is larger by ∼0.1 Å than that obtained by X-ray diffraction. This difference is consistent with a shift of the oxygen electron density toward the mercury cation due to the covalency of the Hg−O interaction.

Mercury is the most toxic inorganic compound for a large variety of living organisms,[1] and its emissions have steadily increased since the XIXe century due to mining activity, chloralkali industry, coal power plants, and municipal waste combustion. It forms salts in two ionic states, Hg^{1+} and Hg^{2+}, but those formed by the latter are much more common and stable in the environment than Hg^{1+} salts. The properties of aqueous solutions of Hg^{2+} are very important for the environmental sciences, because they control mercury bioavailability and toxicity.[1] Hydration is one of the most crucial factors controlling the sorption of cations at the surface of oxides, hydroxides,[2,3] and clay minerals,[4] and it plays a significant role in the retardation of heavy metal migration. Therefore, information about the structural parameters of Hg^{2+} hydration is a key parameter for modeling of mercury transport in aqueous environments and interactions of Hg^{2+} with biological molecules and proteins.[5] It is particularly important to resolve the ability of Hg^{2+} to mimic ions such as Ca^{2+} in aqueous environments, since this similarity will lead to Hg uptake and toxicity.[6]

The structural parameters of Hg^{2+} hydration have previously been studied by X-ray diffraction (XRD),[7−9] nuclear magnetic resonance (NMR),[10] and ab initio molecular dynamics (MD) simulations.[11] The coordination number for water molecules around Hg^{2+} as obtained by the different methods is equal to 6, with the exception of a smaller value of 4.9 revealed by NMR. This last result is likely due to the fast exchange between the hydration shell of the ion and bulk water. However, there is significant uncertainty about the Hg−O distance, with the experimental results varying in the range 2.33−2.42 Å. It is worth noticing that this distance is very close to the observed distance Ca−O in aqueous solutions.[12] Furthermore, the available experimental data do not contain data on the crucial Hg−H coordination, which is important for determining the orientation of water molecules around Hg, and also for detailed comparison with other divalent cations. More pragmatically, knowledge of cation−water distances and coordination numbers can be very useful for the analysis of extended X-ray absorption fine structure (EXAFS) data obtained on mercury ions sorbed on mineral samples.[3−5,13] Likewise, experimental Hg−O and Hg−H radial distribution functions obtained for aqueous solutions can be used to refine the pair potential parametrization for MD simulations.[11] The aim of the work we now present is to fill these important gaps in the available experimental information, and to explore in detail the water coordination around the Hg^{2+} ion with the use of neutron diffraction with isotopic substitution.

The intensity, $I(Q)$, of scattered neutrons is measured as a function of the scattering vector $Q = 4\pi/\lambda \sin\theta$, where 2θ is a scattering angle and λ is the neutron wavelength, and can be expressed as $I(Q) = I^{self}(Q) + F(Q)$.[14] The first term results from self-scattering. Due to the inelastic scattering effects, it gives a sloping background, which can be taken into account by the following empirical formula:[15]

$$I^{self}(Q) = \sum_{\alpha} c_{\alpha}\overline{b_{\alpha}^{2}} + A_1Q^2 + A_2Q^4 \qquad (1)$$

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TABLE 1: Parameters of the First Hydration Shell of Hg Obtained by Different Methods [Mean Hg^{2+}−O Distance (r_{Hg-O} in Å) and Mean Number of Oxygen Atoms around Hg^{2+} (n_O)]

salt	H_2O/salt molar ratio	r_{Hg-O}	n_O	method	ref
$Hg(ClO_4)_2$	19.7	2.42	6	XRD	7
$Hg(ClO_4)_2$	15.8	2.41	6	XRD	8
$Hg(BF_4)_2$	27	2.33	6	XRD	9
$Hg(NO_3)_2$	55		4.9	NMR	10
Hg^{2+}	499	2.42	6.2	QM/MM-MD	11

where c_α is the atomic fraction and $\overline{b_\alpha^2}$ is the mean scattering length of species α (α = Hg, O, D, or N in our case). A_1 and A_2 are adjustable parameters. The structural information is contained in the second, distinct scattering term:

$$F(Q) = \sum_\alpha \sum_\beta c_\alpha c_\beta b_\alpha b_\beta [S_{\alpha\beta}(Q) - 1] \tag{2}$$

where b_α is the mean coherent scattering length of element α and $S_{\alpha\beta}(Q)$ is the partial structure factor. Fourier transformation yields $g_{\alpha\beta}(r)$, the partial distribution function of the particles β around α:

$$g_{\alpha\beta} = 1 + \frac{1}{2\pi^2 \rho_n} \int_0^\infty [S_{\alpha\beta}(Q) - 1] Q^2 \frac{\sin Qr}{Qr} \, dQ \tag{3}$$

where ρ_n is the atomic number density of the sample.

When we measure diffraction patterns for two samples that are identical except for the isotopic composition of one of the elements, for example, Hg (^{nat}Hg) and its isotope Hg′ (^{199}Hg), the difference in the two $F(Q)$'s is

$$\Delta_{Hg}(Q) = c_{Hg}^2 (b_{Hg'}^2 - b_{Hg}^2)[S_{HgHg}(Q) - 1] + \sum_{\alpha \neq Hg} 2 c_{Hg} c_\alpha (b_{Hg'} - b_{Hg}) b_\alpha [S_{Hg\alpha}(Q) - 1] \tag{4}$$

In other words, all partial structure factors not involving the substituted element (Hg in our case) are eliminated in this first order difference function. By Fourier transforming, one gets $\Delta G_{Hg}(r)$, the weighted sum of partial $g_{Hg\beta}(r)$'s

$$\begin{aligned}\Delta G(r) &= \frac{1}{2\pi^2 \rho_n r} \int_0^{Q_{max}} \Delta_{Hg}(Q) Q \sin(Qr) \, dQ \\ &= A[g_{HgO}(r) - 1] + B[g_{HgD}(r) - 1] + \\ &\quad C[g_{HgN}(r) - 1] + D[g_{HgHg}(r) - 1]\end{aligned} \tag{5}$$

with

$$\begin{aligned} A &= 2 c_{Hg} c_O b_O (b_{Hg'} - b_{Hg}) \\ B &= 2 c_{Hg} c_D b_D (b_{Hg'} - b_{Hg}) \\ C &= 2 c_{Hg} c_N b_N (b_{Hg'} - b_{Hg}) \\ D &= c_{Hg}^2 (b_{Hg'}^2 - b_{Hg}^2) \end{aligned} \tag{6}$$

The upper limit of the integral (eq 5) is the maximum experimental value of the scattering vector, that is, 16.6 $Å^{-1}$.

For the preparation of our samples, we used a 1 M solution of DNO_3 in D_2O, natural mercury ^{nat}Hg, and isotope ^{199}Hg in the form of oxide HgO. Two samples with ^{nat}Hg and ^{199}Hg (0.225 mol/L solutions) were prepared using a 1 M solution of a noncomplexing acid DNO_3[16] in D_2O (Table 2). The neutron diffraction measurements were performed on the D4C diffractometer on the reactor neutron source of the Institut Laue Langevin, France.[17] The incident wavelength was 0.6986 Å, measured using a Ni powder reference. The samples were contained in an 8.05 mm inner diameter, 8.9 mm outer diameter cylindrical null coherent scattering Ti/Zr container. Diffraction patterns were measured at ambient temperature (298 K) for each of the samples, the empty sample container, the instrument background, and the 8 mm diameter vanadium rod.

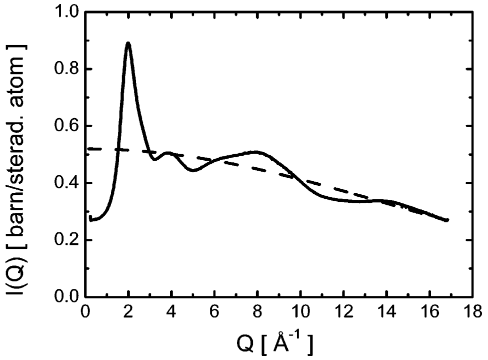

Figure 1. $I(Q)$ for the solution of ^{nat}Hg in D_2O (solid line) and self-scattering, $I^{self}(Q)$, fitted by a polynomial (eq 2) (dashed line).

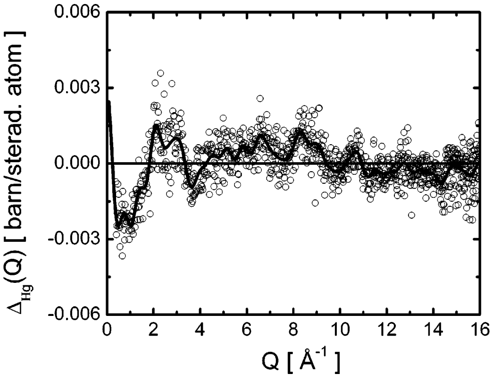

Figure 2. Difference function $\Delta_{Hg}(Q) = F_{Hg'}(Q) - F_{Hg}(Q)$ (circles) and Fourier transformation of space function $\Delta G(r)$.

TABLE 2: Coherent Scattering Lengths, Concentrations, and Coefficients (eq 6)

element	b (fm)	c		
O	5.803	0.341	A (b)	4.8×10^{-4}
D	6.671	0.652	B (b)	2.2×10^{-4}
N	9.36	0.0058	C (b)	5.9×10^{-6}
^{nat}Hg	12.69	0.00132	D (b)	2.2×10^{-6}
^{199}Hg	16.9			

An example of $I(Q)$, corrected for background, empty container, attenuation, and multiple scattering, normalized to the scattering from vanadium is shown in Figure 1. In order to estimate the self-scattering, $I^{self}(Q)$, we fitted $I(Q)$ at higher Q values by the polynomial function (eq 1). $F(Q)$ functions were obtained after subtraction of $I^{self}(Q)$ from $I(Q)$. The difference function $\Delta_{Hg}(Q) = F_{Hg'}(Q) - F_{Hg}(Q)$ and its Fourier transform $\Delta G(r)$ (eq 5) are shown in Figures 2 and 3, respectively. The back Fourier transform of the real-space function $\Delta G(r)$ is also shown in Figure 2. The Fourier transformations were done by numerical integration without using any other treatment. Due to the small difference in scattering lengths of ^{nat}Hg and ^{199}Hg and the low concentration of Hg in solution, the difference $\Delta_{Hg}(Q)$ is rather noisy and the resulting function $\Delta G(r)$ also contains significant errors. Nevertheless, the accuracy of our data was high enough to obtain the information on the first hydration shell of Hg^{2+} cation.

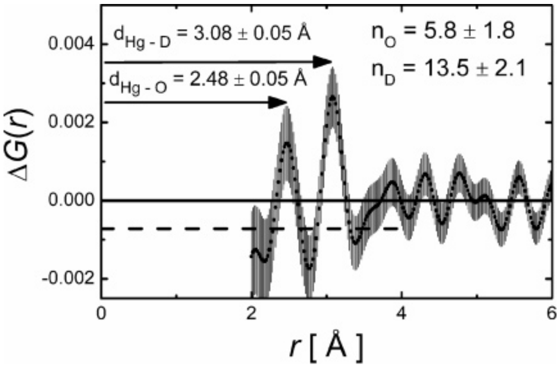

Figure 3. Real-space difference function $\Delta G(r)$. The horizontal dashed line shows the level $\Delta G(0) = -(A + B + C + D)$.

The first two peaks of $\Delta G(r)$ are attributed to the Hg−O and Hg−D correlations in the first hydration shell of Hg^{2+} assuming that a water molecule is oriented with its oxygen atom toward the cation. The contribution of Hg−Hg and Hg−N correlations is negligible because the corresponding coefficients C and D are much smaller than A and B (eq 5 and Table 2). Another hint to identify the peaks is the coordination numbers (see below). Integration of $\Delta G(r)$ under these peaks gives the number of oxygen and hydrogen atoms around Hg:

$$n^X_{Hg} = 4\pi\rho_0 c_X \int_{r_1}^{r_2} g_{HgX}(r) r^2\, dr \approx \frac{4\pi\rho_0 c_X}{2c_{Hg}c_X(b_{Hg'} - b_{Hg})b_X} \int_{r_1}^{r_2} (\Delta G(r) - \Delta G(0)) r^2\, dr \quad (7)$$

where X = O or D, $\Delta G(0) = -(A + B + C + D)$ (eq 6), and r_1 and r_2 are coordinates of the minima before and after integrated peak correspondingly.

The number of O atoms, $n_O = 5.8 \pm 1.8$, is obtained with rather large error; the number of D atoms, $n_D = 13.5 \pm 2.1$, is defined with better accuracy. The combination of n_O and n_D gives the number 6 ± 1 of water molecules in the first hydration shell of the Hg^{2+} cation, which is in good agreement with data of other authors[7−11] (Table 1). This agreement can also be considered as an indication of the fact that the formation of ion pairs with NO_3^- anions, which can reduce the number of water molecules in the first hydration shell, is not significant. The first two peaks of $\Delta G(r)$ are well-defined enough to obtain their centroids with about 2% errors (using Gaussian fit) giving the distances $d_{Hg-O} = 2.48 \pm 0.05$ Å and $d_{Hg-D} = 3.08 \pm 0.05$ Å. Analysis of $\Delta G(r)$ for the distances beyond the first hydration sphere is hardly possible due to the poor statistical accuracy of the data. Some spurious oscillations observed in that region arise from the statistical noise of the experimental $\Delta_{Hg}(Q)$ and truncation effects of Fourier transformation. The Hg−O distance observed in the neutron diffraction experiment is larger by ~0.1 Å than that obtained by XRD. This difference might be caused by the shift of the electronic shell of the oxygen toward the mercury cation, so that X-rays scattered by electronic clouds of atoms, and neutrons scattered only by atomic nuclei, find the O atom in slightly different positions relative to the Hg atom. This shift of the electronic density means that the Hg−O interaction is not simply electrostatic. An increase of the covalency of the M−O interaction and also a simultaneous decrease of its electrostatic character in the order $Zn^{2+} < Cd^{2+} < Hg^{2+}$ was indicated in ref 10.

The parameters obtained for the hydration sphere can be compared with those for Ca^{2+} [12,17,18] and Ni^{2+} [19] cations. The angle ϕ between the plane of the water molecule and the cation−water oxygen axis, which can be calculated from the observed cation−oxygen and cation−hydrogen distances, is approximately the same for Hg^{2+} and the above two ions, and is ~35°. The Hg−O and Hg−H distances are very close to those obtained for Ca^{2+} cations (2.40 and 3.03 Å for Ca−O and Ca−H, respectively). This is an important result for the understanding of mercury toxicity. Mimicking of the Ca^{2+} hydration allows the Hg^{2+} ion to penetrate through the Ca^{2+} ionic channels of the cell membranes. Pekel et al. have postulated that the neurotoxic effects of inorganic mercury could be due to the irreversible blockade of voltage-activated calcium channels in neurons.[6] Once in the cell, the larger M−O covalency discussed above for Hg^{2+} compared to Zn^{2+} leads to high toxicity.

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