

Geometric Hydration Shells for Anionic Platinum Group Metal Chloro Complexes

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Solvation shells surrounding complex inorganic anions have not been extensively studied and are often mentioned with an amorphous picture in mind. We use a computational model previously validated against experimental results and ab initio quantum calculations (Lienke, A.; Klatt, G.; Robinson, D.; Koch, K. R.; Naidoo, K. J. *Inorg. Chem.* **2001**, *40*, 2352–2357) to investigate the nature of the hydration shells about simple platinum group metal chloro complexes ($[\text{PtCl}_6]^{2-}$, $[\text{RhCl}_6]^{3-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$). Our simulations show that the hydration shells surrounding these complexes are symmetric and take on familiar geometric forms. We find that only the $[\text{RhCl}_6]^{3-}$ complex has a clearly defined second hydration shell while the $[\text{PtCl}_6]^{2-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$ second hydration shells are more diffuse.

Introduction

The behavior of metal ions in solution is strongly influenced by the nature of the solvent and consequently the nature of the ion–solvent interaction. For example, in aqueous systems, the solvation and indeed desolvation of complex platinum group metal (PGM) anions is an important factor in their dissolution and precipitation. More subtly, their relative degree of solvation is important in the selective separation of these elements by more modern analytical techniques, for example, high-pressure liquid chromatography, capillary electrophoresis, ion exchange, and solvent extraction.² However, the degree of solvation and the nature of the solvation shell(s) of particularly these complex PGM chloroanions as well as transition metal complexes, in general, remains scarcely studied and poorly understood.

Just as the solvent affects the physical and chemical properties of the solute, so the solute affects the solvent. The changes a solvent undergoes upon addition of a solute have been under investigation for nearly 100 years.³ Current theories of solute effects on surrounding water structure are

based on classical hydration models.^{4,5} Using these models, solutes can be classified phenomenologically as “structure-making” (promoting the structure of water) or “structure-breaking” (disrupting the water structure). Hydration shells have been investigated both experimentally and computationally for various alkaline and alkaline earth (e.g., Ca^{2+} , Na^+),^{6,7} halide (e.g., Cl^- , Br^-),^{8,9} and transition metal (e.g., $\text{Fe}^{2+/3+}$, Ni^{2+} , Cr^{3+})^{6,10,11} ions in water. These and other hydration shells about monatomic ions have been reviewed elsewhere from both experimental and theoretical perspectives.^{12–14} However, the number of investigations involving transition metal complexes, such as those of the chloroanions of the PGMs, remains limited. In this regard it is interesting to note the recent study of the interaction of water with square planar platinum(II) complexes.¹⁵ This study models the

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electrostatic attractions and repulsions using static quantum mechanics calculations. The approach of water molecules along the z axis of the complex is used to estimate the degree and nature of hydrogen-bonding interactions. However, the general concern with static model studies, albeit at a high level of theory, is that only a limited number of solvent molecules and configurations about a metal complex can be studied in this way. The occurrence of axially coordinated solvent molecules in square planar complexes is the topic of an ongoing debate with evidence supporting^{16,17} and refuting^{18,19} the case for axially bound waters being continually presented.

We apply models of the PGM chloroanions that are based on classical physics and make use of parameters derived from both quantum mechanical and experimental data,¹ with the aim to investigate the condensed phase solute–solvent interaction with varying solvents, such that a picture of their “solvation sphere structure” will emerge. Thus far, we have considered the complex chloroanions of platinum(IV), rhodium(III), platinum(II), and palladium(II) ($[\text{PtCl}_6]^{2-}$, $[\text{RhCl}_6]^{3-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$) and their interactions with water molecules. Molecular mechanics PGM force fields for each of these ions have been described elsewhere¹ except for the $[\text{PtCl}_4]^{2-}$ complex, which we briefly describe below.

The structural arrangement of water around a solute is often described by a radially averaged probability density distribution, i.e., a radial distribution function (RDF). This function provides a convenient means with which to corroborate condensed-phase molecular dynamics (MD) or Monte Carlo (MC) computer simulation results with diffraction experiments.¹ However, a drawback of the RDFs is the loss of detail found in highly structured solvents from radial averaging. In this paper we have developed our study to produce geometric descriptions of the hydration shells of $[\text{PtCl}_6]^{2-}$, $[\text{RhCl}_6]^{3-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$ from 1 ns MD simulations without radial averaging. This results in spatial probability distribution functions (SDFs) that provide three-dimensional probability density distributions of the water surrounding the metal complexes.

Computational Methods

The program CHARMM²⁰ was used for all MD simulations. Bulk solutions of $[\text{PtCl}_6]^{2-}$, $[\text{RhCl}_6]^{3-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$ were simulated using periodic boundary conditions in cubic boxes of sides of 24.57 Å, respectively. The TIP3P water model²¹ was used as implemented in CHARMM,²² and the number of water molecules

was varied for each metal complex solution to maintain a density of 1.051 g/mL. Sodium counterions were added into the solutions to maintain an overall charge of 0. We used the Ewald summation method to calculate electrostatic interactions. The data was then collected over 1 ns of dynamics, during which time box size and particle number were kept constant. The data was collected in a microcanonical ensemble. The temperature fluctuated around 300 K, and the total energy was well conserved. In the case of the $[\text{PtCl}_6]^{2-}$ complex we used charges of -0.545 and $+0.180$ on the chlorine ligands and metal ion, respectively. These charges were derived by using the Merz–Kollman–Singh scheme²³ and applied to the platinum group metal complexes as previously described by us in detail.¹ The rest of the parameters were the same as reported for the $[\text{PtCl}_6]^{2-}$ complex,¹ except the reference bond length ($r_0 = 2.272$ Å), which was changed to be consistent with that of the square planar complex, and a quadratic distortion constant ($k_w = 59.0$ kcal Å² mol⁻¹), which was added to maintain this geometry. Here we must emphasize that r_0 and the force constant k_i as used in the harmonic expression for the metal–chloro bond are not synonymous with the equilibrium bond length and the bond specific force constant as referred to in many molecular mechanical calculations based on purely harmonic functions. The reason is that in this model we include 1,3 nonbonded interactions; consequently r_0 and k_i no longer have this relation to experiment. The equilibrium bond lengths computed in our systems are determined by the sum of the harmonic bond potentials and the interligand interaction potentials. Moreover, the simulated equilibrium bond lengths match the experimentally observed values very closely.¹

We calculated three-dimensional water probability density matrixes for each solution of metal complex by removing the rotational and translational diffusion of the solute throughout the trajectories. This was done by reorienting the solute in each stored coordinate set to the best least-squares fit with the metal complex ion in a reference coordinate set. The coordinate transformation was applied to all the atoms in the system. The complete 1 ns data set was used to analyze the water structure in the metal complex solution. Furthermore, the statistical independence of each frame was maintained by separating the frames by at least 0.5 ps from each other. We follow closely a computational method, which we previously reported in detail, for the calculation of spatial distribution functions of solvents about a solvated molecule.²⁴ Only the water oxygen atoms were used to calculate the probability densities from a grid with a mesh size of 0.5 Å placed on the solution simulation box. We used a Gaussian distribution function centered on each water oxygen atom to accurately represent the distribution of the atom across the mesh. The densities in each box were summed for all the selected frames from the dynamics run and then normalized and averaged over the 1 ns simulation data set. The graphical plots of the SDFs shown in Figures 2 and 4 were produced using gOpenMol.²⁵

Results and Discussion

The radial distribution functions for the metal complex–water configurations have been calculated in the same way as described in our previously published study¹ and are shown in Figure 1. The metal–water oxygen (O(w)) radial

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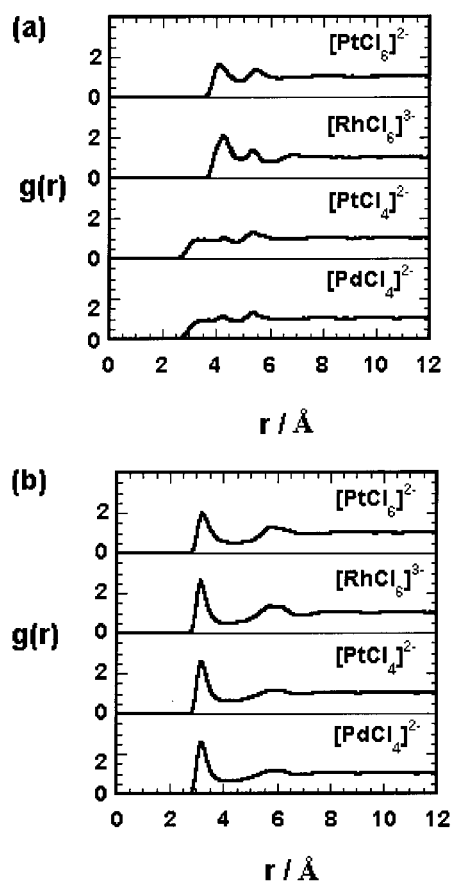


Figure 1. Pair distribution functions $g(r)$ for (a) metal...O(w) configurations and (b) chlorine...O(w) configurations.

distribution functions (RDFs) for the platinum and rhodium octahedral complexes (Figure 1a) have a similar form, clearly showing two hydration shells. The RDFs of the two square planar complexes (Pt(II) and Pd(II)) show similar solvent structure, appearing to have only one hydration shell. This first shell appears to extend from around 3.5 Å through to 5.5 Å. This structure is not diffuse though and is the result of radial averaging as can be seen by two small peaks at around 4 Å through to 5 Å. The chlorine–O(w) RDFs for both octahedral complexes and both square planar complexes (Figure 1b) resemble each other more closely than the corresponding metal–O(w) RDFs in Figure 1a. In the case of all the structures there are two well-defined peaks (in the chlorine–O(w) RDFs) at a distance approximately 3 Å through 6 Å from the chlorine atoms. This indicates that the surrounding water molecules are closely correlated to the chlorine atoms. However, in the case of the square planar complexes the second peak corresponding to a possible second hydration shell is weaker compared to that of the octahedral platinum and rhodium complexes.

The spatial probability densities for $[\text{PtCl}_6]^{2-}$ and $[\text{RhCl}_6]^{3-}$ were first analyzed at a level 100% greater than that found in bulk water, while for $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$ we analyzed the water positional probabilities at 75% greater than bulk density. In Figure 2 we show these metal...oxygen and metal...hydrogen isoprobability surfaces. In all three complexes there are on average 8 nearest neighbor water molecules, which can be considered to be the first hydration shell.

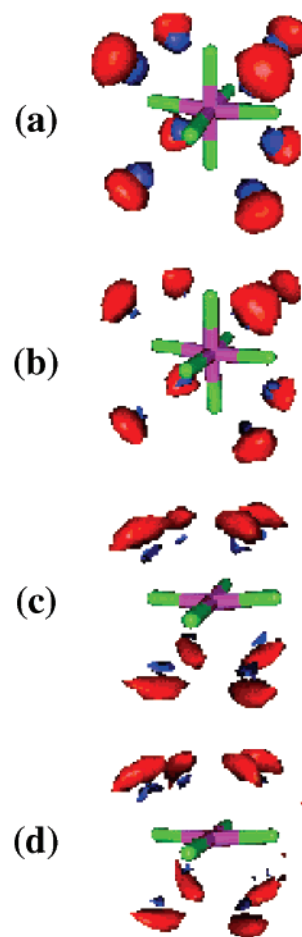


Figure 2. PGM complex chloroanions with water isoprobability density surfaces (oxygen in red and hydrogen in blue), at 100% greater than bulk for (a) $[\text{PtCl}_6]^{2-}$ and (b) $[\text{RhCl}_6]^{3-}$ and at 75% greater than bulk for (c) $[\text{PtCl}_4]^{2-}$ and (d) $[\text{PdCl}_4]^{2-}$.

Table 1. Average Interatomic Distances (Å), as Calculated from the Maxima of the Metal–Oxygen SDFs^a

complex		first solvation shell	second solvation shell
$[\text{PtCl}_6]^{2-}$	Pt...O	4.07	4.91
	Cl...O	3.33	3.65
	O...O	4.70 ^a	4.91 ^a 2.85 ^b
$[\text{RhCl}_6]^{3-}$	Rh...O	4.03	4.49
	Cl...O	3.29	3.32
	O...O	4.65 ^a	4.48 ^a 2.64 ^b
$[\text{PtCl}_4]^{2-}$	Pt...O	3.58	
	Cl...O	3.31	
	O...O	3.11 ^a 5.66 ^c	
$[\text{PdCl}_4]^{2-}$	Pd...O	3.62	
	Cl...O	3.29	
	O...O	3.32 ^a 5.52 ^c	

^a Distance between adjacent intrashell water oxygens. ^b Distance between adjacent intershell water oxygens. ^c Distance between adjacent intrashell water oxygens across the σ_h symmetry plane.

Interatomic distances between the metal complexes and the water oxygens O(w) and various interwater oxygen distances (O(w)...O(w)) are given in Table 1.

The hydration shell geometries of the two octahedral complexes, $[\text{PtCl}_6]^{2-}$ and $[\text{RhCl}_6]^{3-}$, are similar in their profiles, with the most highly occupied sites centered above

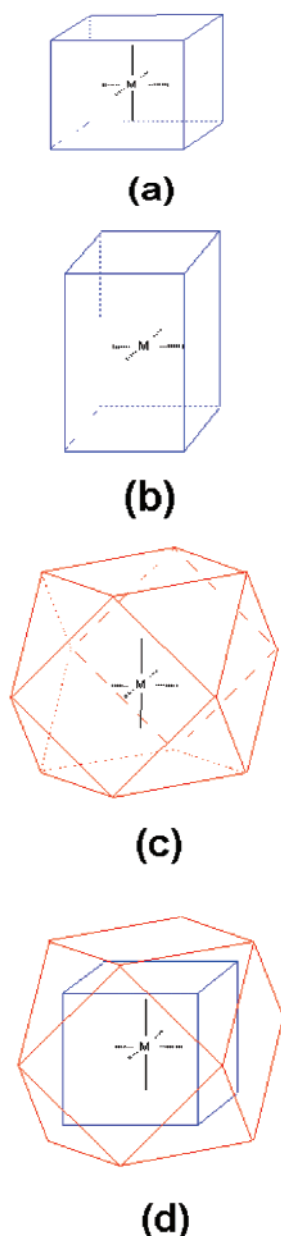


Figure 3. Schematic representation of the hydration shell architectures as constructed from the maxima of the metal–oxygen SDFs: (a) cubic arrangement of first shell around $[\text{MCl}_6]^{n-}$, (b) tetragonal prism arrangement of first shell around $[\text{MCl}_4]^{2-}$, (c) cuboctahedral arrangement of second shell around $[\text{MCl}_6]^{n-}$, and (d) combined first and second shell around $[\text{MCl}_6]^{n-}$.

the 8 faces, equidistant from the three cofacial chlorine ligands. Figure 2a,b clearly shows these water molecules aligned with hydrogen density closest to the chloroanion and average $\text{Cl}\cdots\text{O}(\text{w})$ distances (Table 1) of 3.33 and 3.29 Å for the platinum and rhodium complexes, respectively, well within the accepted donor–acceptor distance of 3.5 Å for a hydrogen bond.²⁶ Furthermore, these values are in accord with RDF peaks calculated from simulations of solvated chloride^{14,27} and $\text{Cl}\cdots\text{O}(\text{w})$ distances obtained from neutron diffraction experiments.²⁸ These water molecules occupy the

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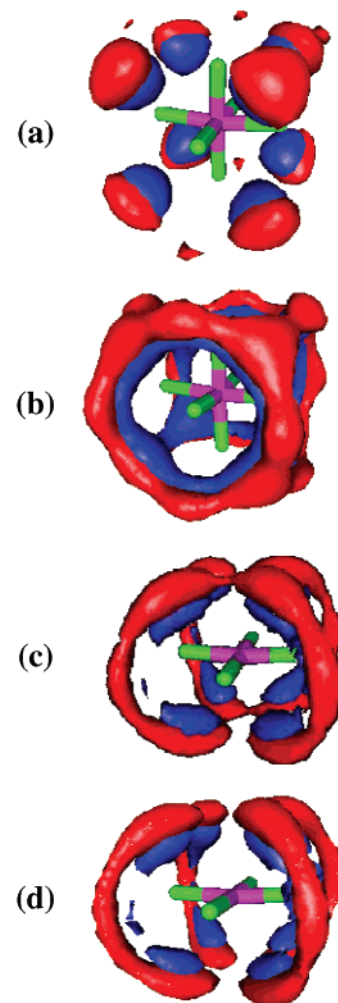


Figure 4. PGM complex chloroanions with water isoprobability density surfaces (oxygen in red and hydrogen in blue), at 50% greater than bulk for (a) $[\text{PtCl}_6]^{2-}$, (b) $[\text{RhCl}_6]^{3-}$, (c) $[\text{PtCl}_4]^{2-}$, and (d) $[\text{PdCl}_4]^{2-}$.

corners of virtual cubes around the platinum and rhodium complex anions with sides of length 4.70 and 4.65 Å and volumes of 104 and 100 Å³, respectively (schematically shown in Figure 3a).

The water probability densities of the square planar anions, $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$, are shown in Figure 2c and Figure 2d. In this case however, the water molecules do not display cubic symmetry but form a less symmetric tetragonal prism. The 8 water oxygen atoms are each equidistant from two adjacent chlorine atoms, either above or below the σ_h plane of symmetry. These water molecules align with the hydrogens toward the ion with average $\text{Cl}\cdots\text{O}(\text{w})$ distances of 3.31 and 3.29 Å, respectively, suggestive of the presence of hydrogen bonding. Interestingly, there is no evidence of an axial water molecule approaching through the δ^- oxygen atom to the δ^+ metal atom of either complex. While this observation may be a limitation of our model, there is experimental NMR¹⁸ and X-ray¹⁹ data indicating the absence of axial waters above square planar complexes. In our model the first hydration shell could then be considered to consist of these 8 water molecules located at the vertexes of a

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tetragonal prism. The solvation prism for $[\text{PtCl}_4]^{2-}$ has sides 3.11 and 5.66 Å and a relatively small volume of 55 Å³, while for $[\text{PdCl}_4]^{2-}$ the sides are of lengths 3.32 and 5.52 Å and the contained volume is 61 Å³. The 4 long sides of these structures straddle the plane of the complex chloroanion as schematically indicated in Figure 3b.

When the water probability density analyses are repeated for the octahedral complexes at 50% above bulk (Figure 4a,b), a second hydration shell comprising 12 occupied sites emerges. The waters are positioned above saddle positions symmetrically between each pair of chlorine atoms. Examination of the geometric arrangement indicates that the 12 water molecules occupy the vertexes of a regular 14-sided cuboctahedron (with 8 triangular faces and 6 square faces). The dimensions of these structures are 4.91 and 4.48 Å with contained volumes of 250 and 190 Å³ for the platinum and rhodium complexes, respectively. The framework of this rather complex solvation structure around these octahedral complex ions is depicted in Figure 3c,d. These results imply that $[\text{RhCl}_6]^{3-}$ has a relatively more strongly bound second hydration shell while the $[\text{PtCl}_6]^{2-}$ second hydration shell is more diffuse. We are not aware of experimental evidence for a second hydration shell around PGM complex anions; however, recently such hydration shells have been observed for cationic (Cr^{3+} , Rh^{3+} , and Zn^{2+}) transition metal aqueous solutions^{11,29} and chromochloroquo complexes of the type $[\text{CrCl}_n(\text{H}_2\text{O})_{6-n}]^{(3-n)+}$ ($n = 1-3$),³⁰ by extended X-ray methods.

Analysis of the interatomic distances associated with the water molecules in these positions (Table 1) indicates that they may be bound to the first shell water molecule or to one of the chlorine ligands. The $\text{O}(\text{w})\cdots\text{O}(\text{w})$ distances are 2.85 and 2.64 Å between the first and second shell water oxygens in the platinum and rhodium solutions, respectively. The $\text{Cl}\cdots\text{O}(\text{w})$ distances for the second shell waters are 3.65 Å for the $[\text{PtCl}_6]^{2-}$ solution and 3.32 Å for $[\text{RhCl}_6]^{3-}$ solution. The fact that the second shell waters for the rhodium complex are drawn in closer to the metal complex is further supported by the decrease in the intershell $\text{O}(\text{w})\cdots\text{O}(\text{w})$ distance (2.64 Å) from that of 2.8 Å found in simulations of bulk TIP3P water (experimental value³¹ = 2.8 Å).

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The second hydration shell of the square planar complexes (Figure 4c,d) is less clearly defined but resembles that seen for the octahedral complexes above. The next occupied positions are 4 sites above the saddle positions associated with two adjacent chlorine atoms, with the hydrogen atoms aligned toward the ion appropriately for hydrogen bonding.

Conclusion

We have used a force field based molecular dynamics model, that was previously validated against diffraction experiments and quantum mechanical calculations, to investigate the hydration spheres about platinum group metal chloro complexes. These calculations show that at a probability density of 75% above the spatial probability density of bulk water the solvent molecules surrounding the $[\text{PtCl}_6]^{2-}$, $[\text{RhCl}_6]^{3-}$, $[\text{PtCl}_4]^{2-}$, and $[\text{PdCl}_4]^{2-}$ complexes are geometrically ordered. This implies that most of the time the charged metal complexes are ordering the water molecules that solvate them, which is particularly interesting for relatively large anionic complexes that are often regarded as poorly solvated.

While this result makes intuitive sense, these hydration spheres have not previously been visualized to this level of detail. The reason for this is that experimental diffraction data and computer simulation data in the form of radial distribution functions radially average the relative distances between the metal complex and the water. This method removes a significant portion of the 3-D structural information of the surrounding solvent. Instead of radially “smearing out” information about the water...complex distances, we have calculated the probability densities anisotropically. This approach has (we believe for the first time) allowed us to observe in detail a large degree of symmetry in the first hydration shell. While second hydration shells for metal complexes have been recently seen experimentally, it appears that only the more highly charged $[\text{RhCl}_6]^{3-}$ complex has a strongly bound second hydration shell.

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