On the formation of inner-sphere solvation complexes in dilute acetonitrile solutions of the Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts: a Molecular Dynamics study

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ABSTRACT

The solvation properties of dilute acetonitrile solutions of the Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts have been investigated by using Molecular Dynamics simulations. The Hg^{2+} ion in acetonitrile was found to coordinate both counterions and acetonitrile molecules in its first solvation sphere by forming inner-sphere complexes. However, different geometries of the Hg^{2+} solvation polyhedra are formed depending on the counterion: in the Hg(NO$_3$)$_2$ salt solution, Hg^{2+} forms a 8-fold cluster of acetonitrile and nitrate ligands with a square antiprism symmetry, while in the system containing the Hg(TfO)$_2$ salts, the Hg^{2+} solvation shell is composed of eight ligands arranged in a C$_2$ symmetry.

Introduction

Divalent mercury cation Hg^{2+} is considered one of the most impacting pollutants in respect to environmental contamination and toxicity to living organisms [1]. Such high toxicity is due to its strong affinity for S-containing ligands in proteins and enzymes. Moreover, Hg^{2+} is not biodegradable and accumulates in the living bodies and this causes dysfunction of cells and results in a wide variety of diseases related to the central nervous system [2–5]. Many toxic effects are attributed to the Hg^{2+} divalent ion, including oxidative-assisted damages, neuro-toxicological disorders, and carcinogenicity, and its detection and removal from water resourcers are currently tasks of key importance for environmental and biological concerns [2–5].

In this framework, understanding the solvation properties of the Hg^{2+} ion in organic solvents can be fundamental also to improve the efficiency of removal procedures.[6,7] Another important issue is to shed light on the effect of counterions on the Hg^{2+} coordination chemistry, since they can significantly alter the Hg^{2+} solvation complexes by entering the metal ion coordination sphere. For such reasons, in this paper we have decided to investigate dilute (0.1 M) acetonitrile solutions of the Hg^{2+} ion with two different counterions, namely nitrate (NO$_3^-$) and triflate (trifluoromethanesulfonate, TfO$^-$). Nitrate and triflate have been chosen as counterions since the former anion has a stronger coordination ability as compared to the latter, which is a weakly complexing species. The two counterions can thus show a different behaviour in complexing the Hg^{2+} ion. Moreover, both anions

are relevant from a catalytic point of view since Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ are good catalysts for several organic reactions carried out in acetonitrile solutions [8,9].

In general, acetonitrile is one of the preferred solvents for catalytic reactions because it usually forms weak and labile complexes with metal ions [10]. In many applications, the selection of the counterion is particularly critical in acetonitrile, as even well-known weakly coordinating counterions such as triflates can compete with acetonitrile ligands for metal ions coordination sites, as previously found for lanthanides, as an example [11]. Moreover, the combination of Hg^{2+} and acetonitrile is important in relation to the design and synthesis of selective fluorescent chemosensors based on organic derivatives for the Hg^{2+} ions detection [12]. Since such chemosensors are usually adopted by dissolving them in acetonitrile, reaching a delailed characterization of the Hg^{2+} solvation properties in this solvent can be relevant also to improve the chemosensor detection performance.

Here we have studied the solvation properties of Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ in acetonitrile by means of Molecular Dynamics (MD) simulations, which have been previously used to study the coordination properties of many ions in aqueous and non-aqueous media [13–18]. This work is part of a wider study on the Hg^{2+} coordination chemistry. Indeed, we have recently investigated the solvation properties of dilute aqueous and methanol solutions of the Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts and we have highlighted a different behavior of the Hg^{2+} ion in these solvents [19]: in aqueous solutions of the Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts, the Hg^{2+} first coordination shell is composed only of water molecules, while

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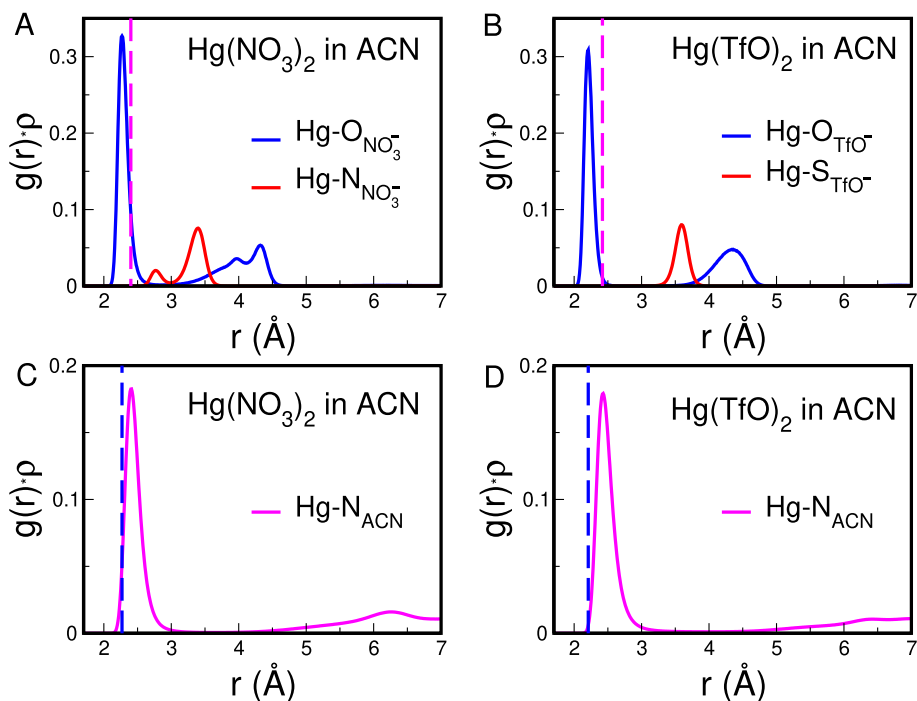
Fig. 1. A) $Hg-O_{NO_3^-}$ (blue line) and $Hg-N_{NO_3^-}$ (red line) radial distribution functions $g(r)$'s multiplied by the numerical density of the observed atoms ρ ($g(r)\rho$), where O and N are the oxygen and nitrogen atoms of the nitrate anions, respectively, calculated from the MD simulation of the $Hg(NO_3)_2$ acetonitrile solution. B) $Hg-O_{TfO^-}$ (blue line) and $Hg-S_{TfO^-}$ (red line) $g(r)\rho$, where O and S are the oxygen and sulphur atom of the triflate anions, respectively, calculated from the MD simulation of the $Hg(TfO)_2$ acetonitrile solution. C) $Hg-N_{ACN}$ $g(r)\rho$, where N is the nitrogen atom of the acetonitrile molecules, calculated from the MD simulation of the $Hg(NO_3)_2$ acetonitrile solution. D) $Hg-N_{ACN}$ $g(r)\rho$, where N is the nitrogen atom of the acetonitrile molecules, calculated from the MD simulation of the $Hg(TfO)_2$ acetonitrile solution. The dashed lines in each panel represent the positions of the $g(r)$ first peak maximum related the other competing ligand (either counterion or solvent).

in methanol solutions of the same salts the Hg^{2+} cation coordinates both counterions and methanol molecules in its first solvation sphere [19]. One important issue that we have addressed here is whether the Hg^{2+} nitrate and triflate salts are able to form inner-sphere complexes also in acetonitrile, as previously found for the methanol solutions. Moreover, a careful analysis of the MD simulations allowed us to obtain detailed structural information on the interactions formed among the Hg^{2+} cations, the solvent molecules and the counterions and to shed light on the formation of different complexes in which solvent molecules are replaced by the anionic ligands.

Molecular Dynamics details

Two MD simulations of 0.1 M acetonitrile solutions containing either $Hg(NO_3)_2$ or $Hg(TfO)_2$ have been performed by means of the Gromacs package [20]. The acetonitrile solvent was described by the six-site model developed by Grabuleda et al.[21], which provides a good description of bulk liquid acetonitrile, while the force field parameters for the triflate and nitrate anions were taken from Lopes and Padua [22,23]. As regards the Hg^{2+} cation, we have used a Lennard-Jones potential previously developed by us in Ref.19. Mixed Lennard-Jones parameters for all of the different atom types were obtained from the Lorentz-Berthelot combination rules, with the exception of the interaction between the Hg^{2+} cation and the O atoms of the NO_3^- anions for which the Lennard-Jones parameters used to describe the interaction between Hg^{2+} and the water oxygen atom have been used [19]. Note that such combinations of the force field parameters for the Hg^{2+} ions and the nitrate and triflate anions have been previously used to describe the solvation properties of dilute aqueous and methanol solutions of the $Hg(NO_3)_2$ or $Hg(TfO)_2$ salts.[19] In particular, the use of such parameters allowed us to reproduce the delicate balance between Hg^{2+}-counterions and Hg^{2+}-solvent interactions in both water and methanol, in

agreement with the X-ray absorption spectroscopy results.[19] As long as the validity of the force field has been demonstrated in aqueous and methanol solution, we reasonably assume here that such validity can be transfered also to the systems investigated in this work. The systems were composed of 5 Hg^{2+} cations, 10 anions and 957 acetonitrile molecules in a cubic box, created by randomly assigning initial positions to all ions and molecules placed in a very large cubic simulation box that was then compressed in the NPT ensemble. The box edge lengths to be used in the production phase were then determined by equilibrating the systems in the NPT ensemble at 1 atm and 300 K for 5 ns. The simulations have then been carried out in the NVT ensemble at 300 K for a total time of 20 ns, after a 3 ns equilibration run, using a 1 fs time step. The Nosé-Hoover thermostat [24,25], with a relaxation constant of 0.5 ps, was used to control the system temperature. Long-range interactions have been evaluated by the particle-mesh Ewald method [26], while the cut-off of the nonbonded interactions was set to 12 Å. Periodic boundary conditions have been applied in order to simulate the bulk material.

Results

The first question that we addressed is whether the Hg^{2+} nitrate and triflate salts form inner-sphere complexes in acetonitrile. To give an answer to this question, we have calculated from the MD simulations of acetonitrile solutions containing either the $Hg(NO_3)_2$ or the $Hg(TfO)_2$ salt the $g(r)$'s between the Hg^{2+} cations and the oxygen atoms of either the nitrate ($Hg-O_{NO_3^-}$) or the triflate ($Hg-O_{TfO^-}$) anions. The $g(r)$'s are depicted in Fig. 1 multiplied by the numerical density of the observed atoms (ρ). These functions are very useful to properly compare $g(r)$'s involving species with different densities (such as the solvent molecules and the counterions) since the simple comparison of the $g(r)$'s could be misleading, as previously pointed out in several works [27,28]. However, for the sake of simplicity, in the following discussion we refer to the

Table 1
Structural parameters calculated from the MD simulations of acetonitrile solutions of the Hg(NO$_3$)$_2$ and the Hg(TfO)$_2$ salts.

	Hg(NO$_3$)$_2$ in ACN		
interaction	R (Å)	N	cutoff (Å)
Hg $-$N$_{ACN}$	2.40	3.8	3.56
Hg $-$O$_{NO_3^-}$	2.27	3.9	2.84
Hg $-$N$_{NO_3^-}$			
first peak	2.76	0.4	3.00
second peak	3.39	3.1	4.10

	Hg(TfO)$_2$ in ACN		
interaction	R (Å)	N	cutoff (Å)
Hg $-$N$_{ACN}$	2.42	4.3	3.96
Hg $-$O$_{TfO^-}$	2.21	3.1	2.90
Hg $-$S$_{TfO^-}$	3.59	3.1	5.00

Position of the $g(r)$ first peak maximum (R) and coordination number (N) related to the listed interactions. The cutoff values used to calculate the coordination numbers by integration of the corresponding $g(r)$ first peak are also reported.

depicted functions as the $g(r)$'s. The structural parameters of all the $g(r)$'s are listed in Table 1. The Hg $-$O$_{NO_3^-}$ and Hg $-$O$_{TfO^-}$ $g(r)$'s calculated from the simulations show well defined first shell peaks with maxima at 2.27 Å and 2.21 Å, respectively, showing that both nitrate and triflate anions in acetonitrile enter the Hg^{2+} first solvation shell, by forming inner-sphere complexes. The Hg $-$O$_{NO_3^-}$ and Hg $-$O$_{TfO^-}$ first shell coordination numbers, obtained by integrating the $g(r)$ first peaks up to the first minima, are 3.9 and 3.1, respectively. Note that the Hg $-$O$_{NO_3^-}$ and Hg $-$O$_{TfO^-}$ first peak maxima are very similar to the values previously obtained for the Hg $-$O$_{NO_3^-}$ and Hg $-$O$_{TfO^-}$ distances in methanol solution [19], indicating that the positioning of the counterions in the Hg^{2+} surrounding is independent on the nature of the solvent.

In the case of the triflate solution, the Hg $-$O$_{TfO^-}$ average coordination number coincide with the average number of anions entering the Hg^{2+} first shell complex. Indeed the triflate anion acts only as a monodentate ligand, as evident from the single peak found in the Hg $-$S$_{TfO^-}$ $g(r)$ shown in Fig. 1B. Conversely, the nitrate anion can coordinate Hg^{2+} both in a monodentate and bidentate fashion. The Hg $-$N$_{NO_3^-}$ $g(r)$ shows indeed the presence of two peaks: when the nitrate ion acts as bidentate ligand with two oxygen atoms pointing towards the Hg^{2+} ion, the Hg $-$N$_{NO_3^-}$ most probable distance is 2.76 Å, whereas when the nitrate ion acts as monodentate ligand with only one oxygen atom directed towards the cation, the Hg $-$N$_{NO_3^-}$ distance moves to 3.39 Å. However, inspection of Table 1 indicates that the monodentate coordination is the dominant coordination mode: about 0.4 and 3.1 nitrate anions adopt the bidentate and monodentate coordination, respectively, for a total of 3.5 nitrate ions surrounding Hg^{2+}. It is interesting to point out that the presence of more than two counterions in the Hg^{2+} first solvation shell is made possible by the fact that some anions act as a bridge between two different Hg^{2+} cations.

Besides interacting with the counterions, Hg^{2+} forms short-range interactions with the acetonitrile molecules, as shown by the $g(r)$'s calculated between the Hg^{2+} cations and the acetonitrile nitrogen atom (Hg $-$N$_{ACN}$) shown in Fig. 1C and Fig. 1D for the Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salt solutions, respectively. In the presence of nitrate counterions, Hg^{2+} is coordinated by an average number of 3.8 acetonitrile molecules, while in the triflate case the average number of acetonitrile molecules in the Hg^{2+} solvation complex is 4.3. The maxima of the Hg $-$N$_{ACN}$ $g(r)$ first shell peaks are very similar to each other suggesting similar interactions between the cation and the solvent molecules in the presence of both counterions. Since the Hg^{2+} first solvation shell is composed of both acetonitrile molecules and either nitrate or triflate counterions, it is interesting to calculate a total average coordination number
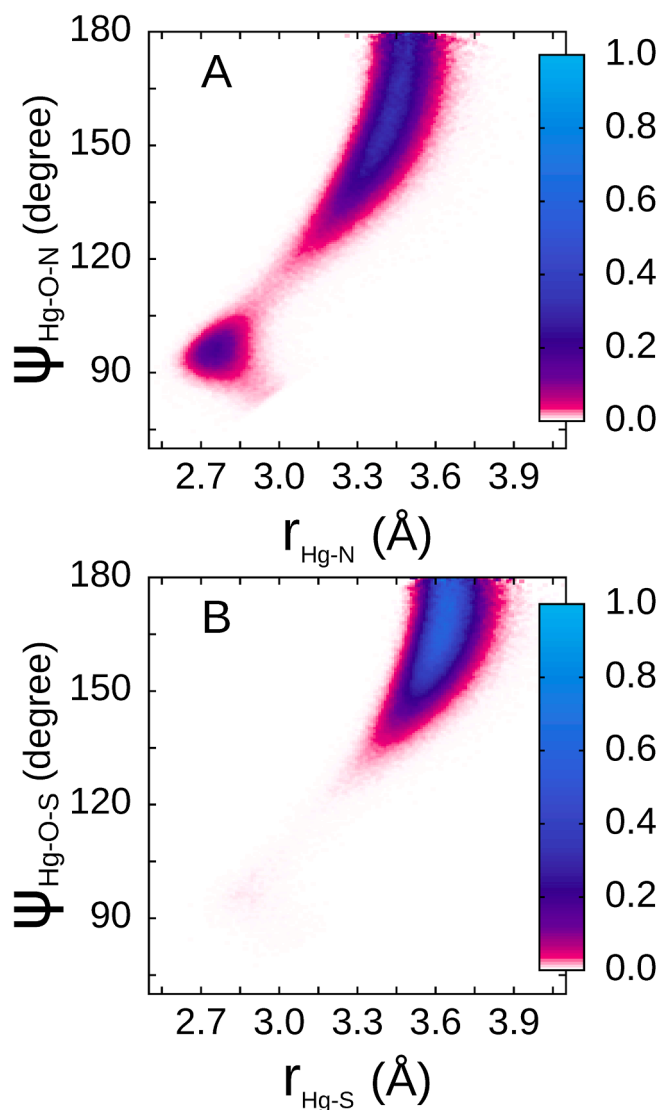

Fig. 2. A) Combined distribution functions (CDFs) between the Hg-N distances and the Hg-O-N angles, where N and O are the nitrogen and oxygen atoms of a nitrate anion belonging to the Hg^{2+} first coordination shell, respectively, calculated from the MD simulation of the Hg(NO$_3$)$_2$ acetonitrile solution. B) CDFs between the Hg-S distances and the Hg-O-S angles, where S and O are the sulphur and oxygen atoms of a triflate anion belonging to the Hg^{2+} first coordination shell, respectively, calculated from the MD simulation of the Hg(TfO)$_2$ acetonitrile solution.

(Hg $-$O$_{NO_3^-/TfO^-}$ + Hg $-$N$_{ACN}$) which is 7.7 and 7.4 for the nitrate and triflate salt solutions, respectively. Interestingly, such values are similar to the total average Hg^{2+} first shell coordination numbers previously obtained for the aqueous and methanol solutions of Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts [19]. Our findings thus show that both nitrate and triflate anions in acetonitrile enter the Hg^{2+} first solvation shell, by forming an inner-sphere complex, in agreement with their behaviour in methanol solutions and at variance with their behaviour in water, where Hg(NO$_3$)$_2$ and Hg(TfO)$_2$ salts are fully dissociated [19]. Altogether our results indicate that the affinity of nitrate and triflate towards the Hg^{2+} ion only depends on the nature of the solvent: in water, due to the strong solvation ability of the solvent, they do not enter the cation first shell complex, while in methanol and acetonitrile they are able to coordinate Hg^{2+} also in dilute solution where the solvent molecules are present in great excess.

It is interesting to evaluate the geometric orientation of the counterions around Hg^{2+}, by calculating the combined distribution functions
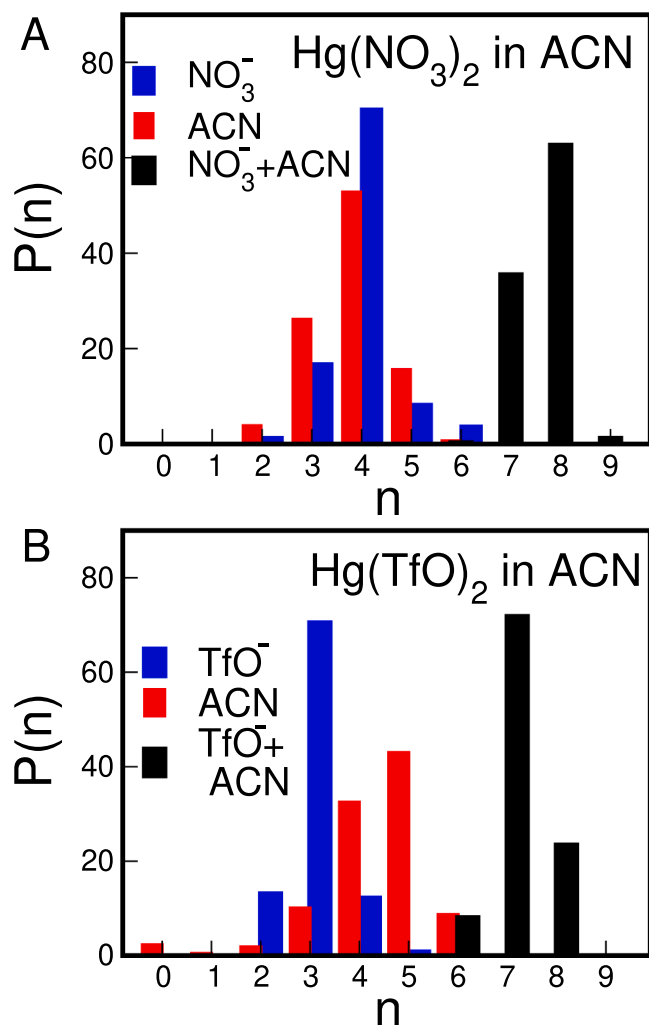
Fig. 3. Coordination number distributions (P(n)) of the acetonitrile molecules (red bars), of the counterions (blue bars) and of the sum of acetonitrile molecules and counterions (black bars) in the Hg^{2+} first solvation shell calculated from the MD simulations of the $Hg(NO_3)_2$ (A) and $Hg(TfO)_2$ (B) acetonitrile solutions.

Fig. 4. Combined distribution functions (CDFs) between the Hg-X distances and X-Hg-X angles where X is either the nitrogen atom of the acetonitrile molecules or the oxygen atom of the counterions (nitrate/triflate) belonging to the Hg^{2+} first coordination complex. A) CDFs calculated for the 8-fold configurations only extracted from the MD simulations of the acetonitrile solution of the $Hg(NO_3)_2$ salt. (B) CDFs calculated for the 7-fold configurations only extracted from the MD simulations of the acetonitrile solution of the Hg $(TfO)_2$ salt.

(CDFs) between the Hg-N or Hg-S distances and the Hg-O-N or Hg-O-S angles, where N and S are the nitrate nitrogen atom and the triflate sulphur atom, respectively (see Fig. 2A and 2B). In these calculations, only the oxygen atoms belonging to the Hg^{2+} first coordination shell are considered and only triplets of atoms Hg-O-N/S in which O and N/S belong to the same ligand. Analysis of the CDFs related to the nitrate counterions shows that the bidentate coordination gives rise to a peak centered at a Hg-O-N angle of 98° with an Hg-N distance of 2.76 Å. This peak is quite narrow suggesting the formation of a stable and ordered coordination. Conversely, when the nitrate ions adopt a monodentate coordination, a more disordered structure with a higher orientational freedom is found, as it can be inferred from the broad peak found at angles comprised between 150° and 180°. As concerns the triflate counterion, the presence of a single probability spot in the CDFs is in line with the existence of a single monodentate coordination mode. The CDF peak is centered at a Hg-S distance of 3.62 Å and Hg-O-S angles comprised between 150° and 180°. Such features show that both triflate and monodentate nitrate coordinate the Hg^{2+} ion by aligning the O-N/S vector along the Hg-O direction forming a nearly linear configuration.

We have seen that in acetonitrile solutions of the $Hg(NO_3)_2$ and the $Hg(TfO)_2$ salts, the Hg^{2+} first coordination shell is composed of both counterions and acetonitrile molecules. A deeper insight into this behaviour can be obtained by calculating a coordination number
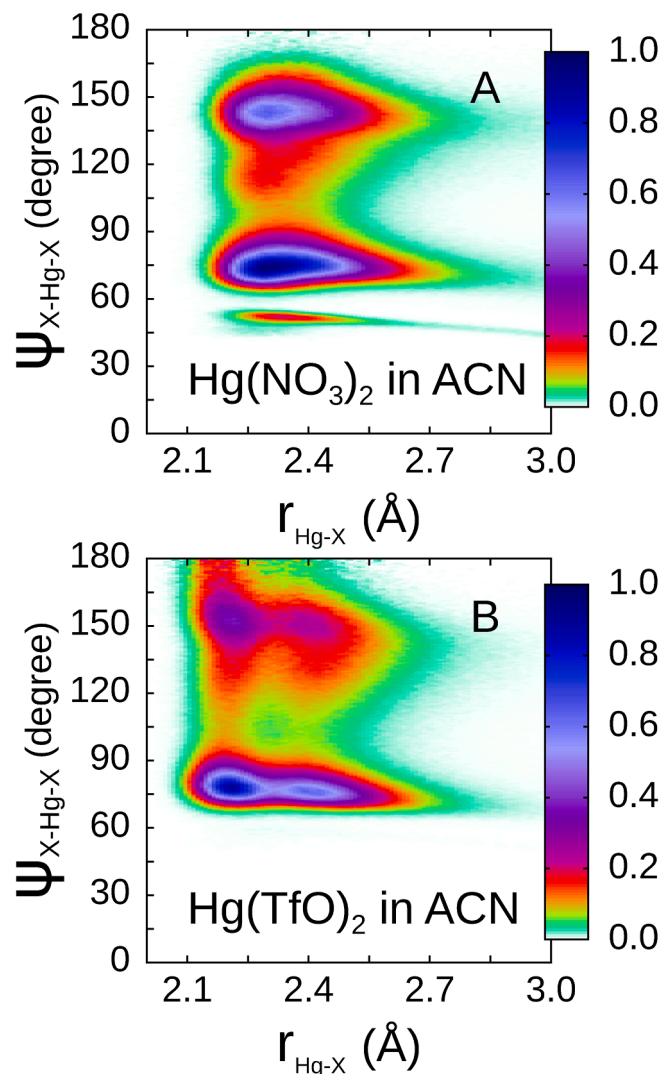
distribution for the acetonitrile molecules, for the oxygen atoms of the nitrate or triflate anions, and for their sum (acetonitrile + counterions). The coordination number distributions of the separated ligands (acetonitrile molecules or counterions) are very broad (Fig. 3A and 3B) indicating that the ligand composition of the Hg^{2+} first solvation shell undergoes strong variations in the course of the simulations. On the contrary, if one considers the Hg^{2+} first-shell complex constituted of either acetonitrile molecules or of counterions, the total coordination number distribution is much less broad. The dominant first shell cluster is different in the solution containing the two different salts: in the nitrate case a dominant percentage of Hg^{2+} first coordination shell contains eight first neighbors, while in the triflate solution the dominant configuration is a 7-fold first shell cluster.

Direct clues into the global geometry of the Hg^{2+} first solvation shell can be gained by calculating the CDFs between the Hg-X distances and the X-Hg-X angles where X is either the nitrogen atom of the acetonitrile molecules or the oxygen atom of the counterions (nitrate/triflate) belonging to the Hg^{2+} first coordination complex. This analysis has been
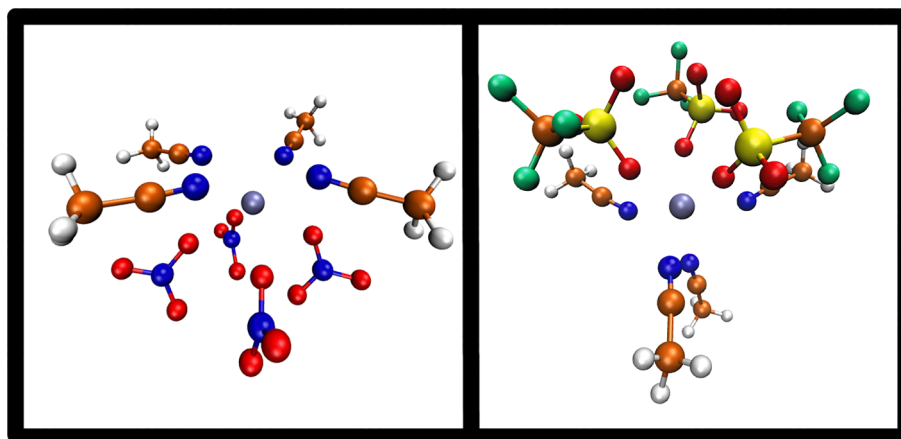
Fig. 5. Solvation complexes formed by the Hg^{2+} ion in the acetonitrile solution containing either the $Hg(NO_3)_2$ (left panel, 8-fold SAP geometry) or the $Hg(TfO)_2$ salt (right panel, 7-fold C_2 symmetry), as obtained from two MD snapshots. Carbon, nitrogen, oxygen, hydrogen, and Hg atoms are represented in orange, blue, red, white, and ice blue, respectively.

performed for the dominant configurations found in the studied systems, namely the for the 8-fold and 7-fold cluster in the nitrate and triflate acetonitrile solutions, respectively. The CDF calculated for the $Hg(NO_3)_2$ salt solution (Fig. 4A) shows three main peaks centered at angle values of about $75°$, $118°$ and $145°$, in line with the existence of a square antiprismatic (SAP) symmetry of the ligands around the Hg^{2+} ion [29]. This geometry is a typical arrangement of 8-fold complexes formed by multicharged metal ions in solution, such as heavy lanthanoid $3 +$ ions in water [30]. At variance with this finding, in the CDF of the system containing the triflate salt two broad peaks centered at angle values of $75°$ and $145°$ can be clearly observed, pointing to the existence of a C_2 symmetry of the ligands around the Hg^{2+} ion. Such solvation structure is the same formed by the water molecules coordinating Hg^{2+} in aqueous solution of the $Hg(NO_3)_2$ and the $Hg(TfO)_2$ salts. Note that the peaks are splitted into two separated peaks due to the fact that the Hg^{2+} ion coordinates the acetonitrile molecules and the triflate anions at longer and shorter distances, respectively. In Fig. 5, two MD snapshots are shown highlighting, as examples, the coordination geometries of the Hg^{2+} solvation complexes in acetonitrile solutions of the $Hg(NO_3)_2$ and Hg $(TfO)_2$ salts.

Conclusions

In this work we have investigated the solvation properties of dilute acetonitrile solutions of the $Hg(NO_3)_2$ and $Hg(TfO)_2$ salts by means of the MD technique. The first important result we have obtained is that in such solutions the Hg^{2+} ion coordinates both counterions and acetonitrile molecules in its first solvation sphere by forming inner-sphere complexes. This is in line with the behaviour of the $Hg(NO_3)_2$ and Hg $(TfO)_2$ salts previously found in methanol solutions, while it is at variance with what happens in water, where such salts are fully dissociated [19]. On the basis of our results, the affinity of nitrate and triflate towards Hg^{2+} only depends on the nature of the solvent: in water, due to the strong solvation ability of the solvent, they do not enter the cation first shell complex, while in methanol and acetonitrile they are able to coordinate Hg^{2+} also in dilute solution where the solvent molecules are present in great excess. Moreover, a larger number of counterions coordinates Hg^{2+} in acetonitrile as compared to the methanol solution in line with the very weak solvation ability of the acetonitrile solvent, which favours the coordination of other ligands to the metal ion. In acetonitrile solutions different geometries of the Hg^{2+} solvation polyhedra are found depending on the counterion: in the $Hg(NO_3)_2$ salt solution, the Hg^{2+} ion prefers to form a 8-fold cluster of acetonitrile and nitrate ligands with a SAP symmetry, while in the system containing the $Hg(TfO)_2$ salts, the Hg^{2+} solvation shell is composed of eight ligands

whose coordinating atoms are arranged in a C_2 symmetry. Another difference found in the solutions containing the two salts is that triflate coordinates Hg^{2+} only in a monodentate fashion, while nitrate can act both as a monodentate and bidentate ligand.

The overall geometries of the Hg^{2+} solvation complexes and the spatial arrangement of the single first-shell ligands derive from the delicate balance between the maximization of electrostatic forces and the minimization of the repulsion among the ligands. The slightly higher coordination number shown by Hg^{2+} in the nitrate solution can be in part related to the presence of a small percentage of bidentate coordination of nitrate towards Hg^{2+}, which allows one additional oxygen atom of a nitrate ligand to be bound, resulting in a 8-fold solvation complex. These findings can help in the rationalization of the Hg^{2+} coordination chemistry, which is of great interest from a fundamental research point of view and it is also a key step in any applications involving such heavy metal ion.

CRediT authorship contribution statement

Valentina Migliorati: Conceptualization, Investigation, Data curation, Writing - original draft. **Paola D'Angelo:** Conceptualization, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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