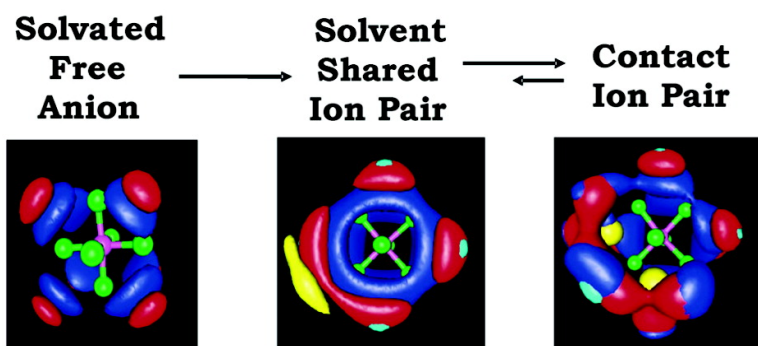Communication

Contact Ion Pair between Na and PtCl Favored in Methanol

Kevin J. Naidoo, Anton S. Lopis, Arjan N. Westra, David J. Robinson, and Klaus R. Koch

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Contact Ion Pair between Na$^+$ and PtCl$_6^{2-}$ Favored in Methanol

Kevin J. Naidoo,*,† Anton S. Lopis,† Arjan N. Westra,‡ David J. Robinson,† and Klaus R. Koch*,‡

Department of Chemistry, University of Cape Town, Rondebosch, 7701, South Africa, and Department of Chemistry, University of Stellenbosch, P Bag X1, Matieland, 7602, South Africa

Received March 26, 2003; E-mail: knaidoo@science.uct.ac.za; krk@sun.ac.za

In dilute water solution, the nature and extent of hydration of simple cations and anions depends on their size, charge, and polarizability; generally cations are strongly hydrated while some bulky anions are relatively weakly hydrated. Moreover, in dilute aqueous solution, the extent of cation−anion pair formation is generally low, but increases with increasing solute concentration.[1] However, in solvents with a lower dielectric constant than water, ion pairing (or ion−ion associations) becomes more pronounced, as is well demonstrated by the numerous liquid−liquid anion exchange and ion-pair extraction processes that are known.[2] Solvent separated (SSIP), solvent shared (SSHIP), and contact ion pairs (CIP) have been observed for H$_3$O$^+$ and Cl$^-$.[3] The most studied ion pair in simple ionic systems, using theoretical methods, has been Na$^+$Cl$^-$ in water[4] with the predictions being supported by recent Fourier transform microwave rotational spectrocopic experiments of dilute Na$^+$Cl$^-$ aqueous solutions.[5] We show here the formation, and discuss the geometry, of Na$^+$ and PtCl$_6^{2-}$ solvent shared and contact ion pairs favored in methanol, using potential of mean force computational methods as well as multinuclear NMR spectroscopy experiments.

The structural arrangement of water around a solute is often described by a radially averaged probability density distribution, that is, a pair distribution function $g(r)$. However, a drawback of the $g(r)$'s is the loss of detail found in the structure of the solvent shells due to radial averaging. We have recently produced geometric descriptions of the hydration shells of PtCl$_6^{2-}$, RhCl$_6^{3-}$, PtCl$_4^{2-}$, and PdCl$_4^{2-}$ from nanosecond molecular dynamics (MD) simulations without radial averaging.[6] This results in spatial (three-dimensional) probability distribution functions (SDFs) of the solvent density distributions surrounding the metal complexes. The structures of the solvation shells formed from polar molecules surrounding the metal complexes observed in these SDFs have been independently verified using X-ray diffraction and computational methods.[7] We performed 2 ns isothermal isobaric simulations ($P = 1$ bar, $T = 298$ K) of a PtCl$_6^{2-}$ complex in methanol containing two Na$^+$ ions using the CHARMM program.[8] The methanol parameters (listed in Tables 1−3 of the Supporting Information) have been developed by us on the basis of the Jorgensen solvent model and have been tested to match diffusion and structural experimental data.[9] We find that on calculation of the SDFs in methanol solution, both the SSHIP (Figure 1a) and the CIP (Figure 1b) configurations are favored for the {Na$^+$ PtCl$_6^{2-}$}$^-$ ion pair. This is in contrast to the (Na$^+$)$_2$PtCl$_6^{2-}$ water solution simulations, for which no ion pair is found, using the same MD protocol. In Figure 1a, the Na$^+$ ion is located in a dispersed probability density about two octahedral PtCl$_6^{2-}$ ion faces. When the CIP forms (Figure 1b), the Na$^+$ ion can be aligned in either of two geometrically symmetrical positions, both perpendicular to the faces of the PtCl$_6^{2-}$ octahedron. The hydroxyls of the methanol molecules orientate
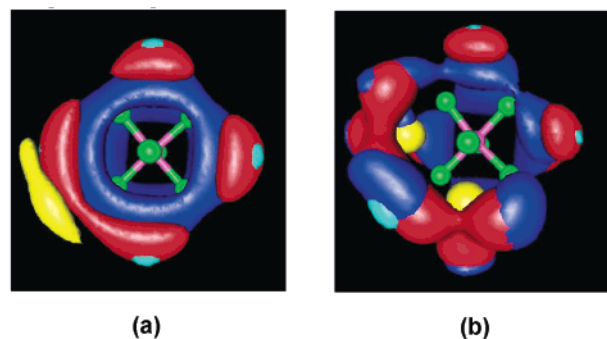
† University of Cape Town.
‡ University of Stellenbosch.

Figure 1. The spatial distribution functions (SDFs) for the {Na$^+$ PtCl$_6^{2-}$}$^-$ ion pair. The Pt metal (violet) complexed with chorine (green) ligand forms (a) a SSHIP with the Na$^+$ ion (yellow) located in a dispersed probability density volume and (b) a more favored CIP, with the Na$^+$ ion (yellow) displayed in direct contact with the PtCl$_6^{2-}$ anion positions. The methanol [oxygens (red), hydrogens (blue), and methyl groups (light blue)] solvation shell is distorted by the CIP.
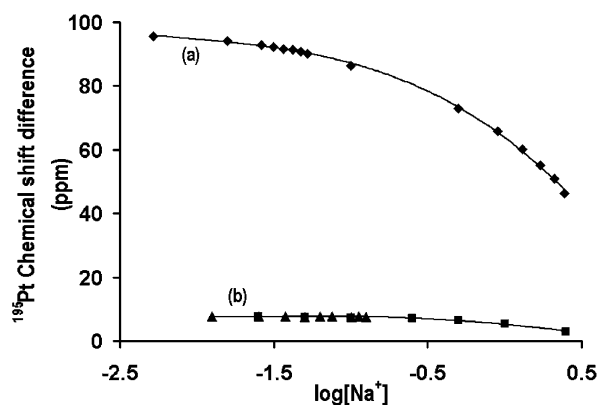

Figure 2. Na$^+$ concentration dependence of $\delta(^{195}$Pt) in (a) methanol solution (as NaClO$_4$) and (b) water (▲ as NaCl and ■ as NaClO$_4$ at 303 K). All chemical shift differences were measured relative to a reference solution in a 2 mm coaxial capillary, thus compensating for any magnetic susceptibility effects; see Supporting Information for experimental details.

themselves around the remaining faces of the PtCl$_6^{2-}$ octahedron with the hydrogen atoms pointing toward the faces of the octahedron, while the oxygen atoms and methyl groups point away. This is similar to the orientation of water molecules in a previous aqueous solution simulation.[10]

We here exploit the sensitivity of the ^{195}Pt NMR chemical shift ($\delta(^{195}$Pt))[11] to probe the solvation and ion-pair formation of the PtCl$_6^{2-}$ anion in methanol and water. Figure 2 shows the dependence of the $\delta(^{195}$Pt) of PtCl$_6^{2-}$ (solutions made from anhydrous H$_2$PtCl$_6$) on the Na$^+$ concentration in (a) methanol and (b) water, at 303 K. In methanol, at constant PtCl$_6^{2-}$ concentration (0.059 M), increasing the concentration of NaClO$_4$ results in significant upfield displacement of $\delta(^{195}$Pt), which is not observed in water under comparable conditions. The structure of the ^{195}Pt resonance,
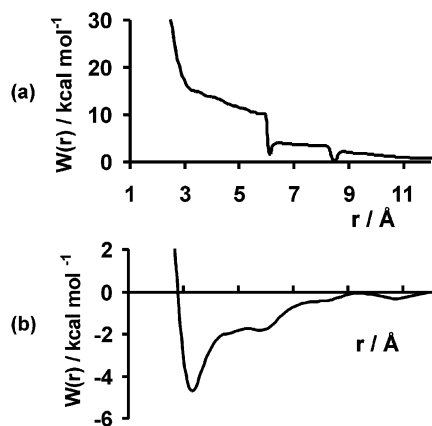
Figure 3. Free energy of association curves (PMFs) of (a) an Na^+ and a $PtCl_6^{2-}$ anion in water and (b) an Na^+ and a $PtCl_6^{2-}$ anion in methanol. The free energy coordinate is the distance between the Na and the Pt atoms.

reflecting the $Pt^{35}Cl/^{37}Cl$ isotopomers of the $PtCl_6^{2-}$ complex,[11] remains invariant throughout all of these experiments, showing that these shift trends do not result from changes in the first coordination sphere of the $PtCl_6^{2-}$ anion, but must result from changes in the solvation shell of the anion. Therefore, the pronounced nonlinearity of shift trends in methanol indicates the formation of ion pairs as $[Na^+]$ increases. Experiments in which the $NaClO_4$ concentration was kept constant ($[Na^+] = 1.004$ M) and the $PtCl_6^{2-}$ concentration varied (in the range $[PtCl_6^{2-}] = 0.00256-0.1014$ M) confirmed that the $\delta^{195}Pt$ variation observed in Figure 2 is not simply a bulk ionic medium effect.

We interpret that these shift trends in methanol at moderate $[Na^+]$ concentrations result from the stepwise formation of an ion pair (with a formation constant $K_1 < 1$). Only at very high $[Na^+]$ is it reasonable to expect the formation of some solvated $\{(Na^+)_2-PtCl_6^{2-}\}$, but solubility limitations of $NaClO_4$ and H_2PtCl_6 in methanol prevent investigations of more concentrated solutions in this way.

The extent of ion pairing for simple salts (e.g., NaI) determined from the ^{23}Na NMR shifts as a function of concentration in nonaqueous solvents (e.g., acetone and sulfolane) is well known, and these shifts have been correlated with the Gutmann donor numbers (DN)[12] (data given in the Supporting Information). However, in our experiments, we monitor the ^{195}Pt shifts of the anion, $PtCl_6^{2-}$, in which the solvating water or methanol molecules interact through hydrogen bonding with the Cl^- ion. Considering the DN and dielectric constant (D) of water and methanol ($DN \approx 17$ and 23.5 vs $D \approx 78.5$ and 32.5), respectively, it appears that the formation of $\{Na^+PtCl_6^{2-}\}^-$ is less a function of the Gutmann donor numbers, and more a consequence of solvent polarity, D.

We use the potential of mean force (PMF), which is the free energy of association, $W(r)$, between a Na^+ cation and a $PtCl_6^{2-}$ anion, to better understand the nature of the ion pairing in solution. The PMF calculations were performed using adaptive umbrella sampling implemented within program CHARMM[13] in combination with the weighted histogram analysis method (WHAM).[14] The PMF curve of the Na^+- - - -$PtCl_6^{2-}$ coordinate in water (Figure 3a) indicates that separation of these two ions is the most favored state. If, however, the ions are forced toward each other, then the SSIP

(minimum at 8.47 Å) followed by a SSHIP (minimum at 6.15 Å) would be the most stable configurations, with a CIP being an unstable configuration. By contrast, in methanol, the Na^+- - - -$PtCl_6^{2-}$ PMF curve (Figure 3b) has a pronounced minimum at 3.28 Å corresponding to a CIP, with a free energy of attraction between a single Na^+ ion and the $PtCl_6^{2-}$ anion of 4.68 kcal/mol. There is a second lesser minimum at 5.84 Å with a free energy of attraction between these ions in methanol of 1.84 kcal/mol, indicative of a SSHIP, but this arrangement is energetically less favorable than the CIP.

The combination of NMR chemical shift experiments and computed free energies of association of Na^+ and $PtCl_6^{2-}$ confirms that ion-pair formation occurs in methanol and not in water. Furthermore, in methanol, the CIP configuration is strongly favored over the SSHIP configuration. On the basis of these results, the underlying design of separation methodologies for platinum group metal complexes should include the possibility of ion-pair formation in organic solvents and not in water.

Supporting Information Available: Simulation conditions, modified methanol parameters, experimental conditions, and ^{23}Na shift trends (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Marcus, Y. Marcel Dekker: New York, 1997; pp 218−244. (b) Bianchi, A.; Bowman-James, K.; Garcia-Espana, E. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997; pp 217−266.
(2) Moyer, B. A.; Bonnesen, P. V. In *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., Garcia-Espana, E., Eds.; Wiley-VCH: New York, 1997; pp 1−44.
(3) (a) Chialvo, A. A.; Cummings, P. T.; Simonson, J. T. *J. Chem. Phys.* **2000**, *113*, 8093−8100. (b) Chialvo, A. A.; Cummings, P. T.; Simonson, J. T. *J. Mol. Liq.* **2003**, *103−104*, 235−248.
(4) (a) Berkowitz, M.; Karim, O. A.; McCammon, J. A.; Rossky, P. J. *Chem. Phys. Lett.* **1984**, *105*, 577−580. (b) Berkowitz, M.; McCammon, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1755−1761. (c) Dang, L. X.; Rice, J. E. *J. Chem. Phys.* **1990**, *93*, 7528−7529.
(5) Mizoguchi, A.; Ohshima, Y.; Endo, Y. *J. Am. Chem. Soc.* **2003**, *125*, 1716−1717.
(6) Naidoo, K. J.; Klatt, G.; Koch, K. R.; Robinson, D. J. *Inorg. Chem.* **2002**, *41*, 1845−1849.
(7) Brammer, l.; Swearingen, J. K.; Bruton, E. A.; Sherwood, P. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4956−4961.
(8) Brooks, B. R.; Bruccoleri, R. E.; Olafson, B. D.; States, D. J.; Swaminathan, S.; Karplus, M. *J. Comput. Chem.* **1983**, *4*, 187−217.
(9) (a) Jorgensen, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 341−345. (b) Simpson, S. C.; Lopis, A. S.; Naidoo, K. J. 2003, unpublished results.
(10) Lienke, A.; Klatt, G.; Koch, K. R.; Robinson, D. J.; Naidoo, K. J. *Inorg. Chem.* **2001**, *40*, 2352−2357.
(11) (a) Pregosin, P. S. *Chem. Rev.* **1982**, *82*, 247−291. (b) Ismail, F. M.; Kerrison, S. J. S.; Sadler, P. J. *Chem. Commun.* **1980**, 1175.
(12) (a) Burgess, J. Ellis Horwood Ltd: Chichester, 1978; pp 64−68. (b) Popov, A. I. *Pure Appl. Chem.* **1975**, *41*, 275−289. (c) Greenberg, M. S.; Bodner, R. L.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2449−2454. (d) Templeman, G. J.; van Geet, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 5578−5582. (e) Herlem, M.; Popov, A. I. *J. Am. Chem. Soc.* **1972**, *94*, 1431−1434. (f) Erlich, R. H.; Popov, A. I. *J. Am. Chem. Soc.* **1971**, *93*, 5620−5623.
(13) Kuttel, M. M.; Brady, J. W.; Naidoo, K. J. *J. Comput. Chem.* **2002**, *23*, 1236−1243.
(14) (a) Kumar, S.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A.; Rosenberg, J. M. *J. Comput. Chem.* **1992**, *13*, 1011−1021. (b) Kumar, S.; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. *J. Comput. Chem.* **1995**, *16*, 1339−1350.

JA035326X