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Study of the interaction of water with the aqua-soluble dimeric complex [RuCp(PTA)2-µ-CN-1κC:2κ2N-RuCp(PTA)2](CF3SO3) (PTA = 1,3,5-triaza-7-phosphaadamantane) by Neutrons and X-ray diffraction in solution.

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Study of the interaction of water with the aqua-soluble dimeric complex [RuCp(PTA)$_2$-μ-CN-1κC:2κ^2N-RuCp(PTA)$_2$](CF$_3$SO$_3$) (PTA = 1,3,5-triaza-7- phosphaadamantane) by Neutrons and X-ray diffraction in solution.

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The study of an aqueous solution of [RuCp(PTA)$_2$-μ-CN-1κC:2κ^2N-RuCp(PTA)$_2$](CF$_3$SO$_3$) by neutron and X-ray diffraction revealed surprising details as to how the water molecules interact with the complex and affect its properties. The present paper demonstrates the applicability of sophisticated scattering techniques in combination with theoretical calculations to the study of coordination compounds in aqueous solution.

Coordination/organometallic complexes[1] are potential candidates for a variety of applications such as magnetism,[2] nonlinear optics,[3] electrocatalysis,[4] photocatalysis,[5] photovoltaics,[6] template formation of ordered networks,[7] advanced electrode materials,[8] and conjugated coordination polymers.[9] Traditional analysis techniques (IR-RAMAN, UV-vis, NMR, powder X-ray diffraction, etc.) are generally very effective at obtaining characterisation such as the chemical structure of the molecule. Moreover and more importantly, they provide the needed information from which chemical and physical properties can be inferred. Nevertheless, generally these techniques are not useful for the determination of how water molecules interact with the metal complexes. In particular information on how the water molecules interact with water-soluble organometallic complexes is frequently lacking.

Neutron scattering is a sophisticated technique that can provide detailed information on the position of hydrogen atoms, and consequently water molecules, both in the solid state and aqueous solution. The primary drawbacks that limit its application are its relatively high cost, the need to transport samples to large scale facilities or to prepare them on site, and the low flux and consequent need for relatively large samples at concentrations higher than the ones usually adopted in this field. In addition to this, many metal complexes dissolve poorly or decompose in water and therefore these systems have rarely be considered suitable for neutron experiments.

Here we report how the continuous advances in the data analysis techniques that combine neutron experiments with theoretical calculations have now reached the point where carefully designed experiments on these systems of interest can be performed. Far from being limited to the specific compound examined in the single experiment, the information thus extracted can shed light on the solvation of a number of chemically related compounds, and, indirectly, on how they interact with other molecules in water solution.

The first air-stable water soluble poly-metallic polymer that includes mixed P,N ligands as metal coordinating spacers was reported by us[10] and it formed from two metal-containing moieties, {CpRu}$^+$ and {AgCl$_2$}$^-$, bridged by the cage-like water soluble monodentate phosphine PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) in an *unprecedented P,N coordinating mode*. Later on, we also demonstrated the water soluble, air stable hetero-poly-metallic polymer {[{(PTA)$_2$CpRu−μ-CN−RuCp(PTA)$_2$}-μ-Au(CN)$_4$]}$_n$.[11] Both complexes display new interesting properties never previously found for organometallic complexes, such as the fact that they form gels in water. From these initial findings other examples of metal-polymers containing PTA have been reported.[12]

To extend the synthesis of these kinds of complexes, the dimeric ruthenium complex [RuCp(PTA)$_2$-μ-CN-1κC:2κ^2N-RuCp(PTA)$_2$](CF$_3$SO$_3$) (**1**) was synthesized. In this water-soluble complex the metals are electronically connected and

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their optical properties are clearly dependent on the solvent. The complex was synthesized by reaction of the previously reported $[RuCp(CN-\kappa C)(PTA)_2]$ complex[3] with the starting complex $[RuCpCl(PTA)_2]$ in water (Scheme 1). Complex **1** is stable in air both in the solid state and solution, it displays a high water solubility ($S_{25°C}$ = 320 mg mL^{-1}) and it does not decompose for weeks, even at 60 ºC and when in contact with metals like Ti and Al. The high water solubility of **1(CF$_3$SO$_3$)**, the dependence of its optical properties on the solvent and its high stability in air and in contact with metals, make this compound ideal for experimental analysis based on neutron diffraction.
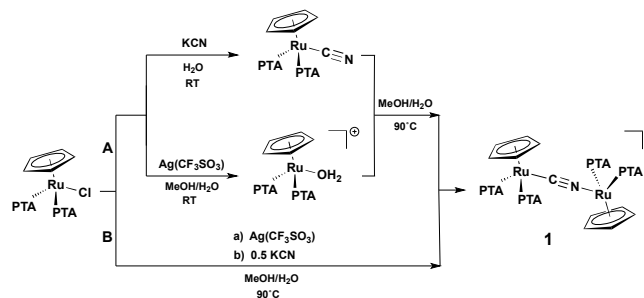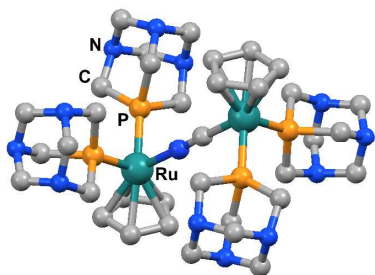
Scheme 1. Synthesis of **1**

Fig. 1. Complex unit single crystal X-ray structure of **1**, including the atomic labelling scheme. For clarity hydrogen atoms are not included.

The single crystal structure of **1(CF$_3$SO$_3$)6H$_2$O** (Fig. 1) and its main properties are discussed in the Supporting Information (SI). Neutron diffraction enhanced by hydrogen/deuterium isotopic substitution (NDIS) and white-beam (Ag source) X-ray diffraction has been used to study a 0.1M solution of **1(CF$_3$SO$_3$)6H$_2$O** in water. The experimental spectra are used to constrain a computer simulation produced using empirical potential structure refinement (EPSR, see the Experimental Section). EPSR allows maximum exploitation of the neutron and X-rays scattering data and a direct comparison with the results of traditional simulation methods, such as molecular dynamics. In particular, neutron data provide a strong constraint on the solvent structure while the X-ray data complement the information on the solute-solvent interaction. Diffraction patterns and the corresponding EPSR models can be found in the SI.
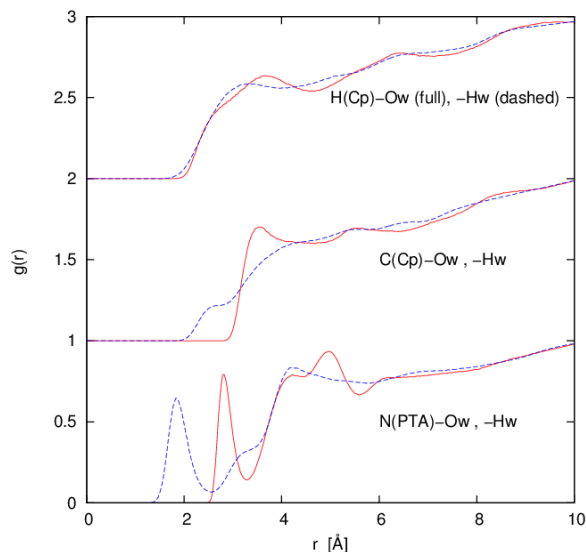

Fig. 2 Pair correlation functions extracted through EPSR simulation for water around **1**. These function express the probability of finding atom **b** at a given distance from atom **a**. Probability to find water oxygen (Ow, full line) or water hydrogen (Hw, dashed line) around three atoms belonging to **1**, namely H and C on the Cp ligand and N on the PTA ligand. Lines have been shifted vertically for clarity.

Figure 2 shows a selection of the radial atom-atom correlation functions g(r) extracted through EPSR simulation for water around **1**. As expected, the shorter and better-defined correlation is around the N_{PTA} acceptors for the water protons. These g(r)s present a very well defined peak, supporting the presence of a strong bond between N_{PTA} atoms and water molecules. The water molecule points its hydrogens (Hw) towards the N_{PTA} atoms, in a rather linear N-Hw-Ow configuration (d_{N-Hw} = 1.85 Å – dashed line; d_{N-Ow} = 2.8 Å – continuous line). Vertically shifted are the g(r)s corresponding to the interaction of water molecules with the cyclopentadiene (Cp) group; these are not characterized by a well-defined peak. Nevertheless, a non-negligible intensity at a distance as short as 2.5 Å (C-Hw) and 3.5 Å (C-Ow) is a strong indication of water molecules and the Cp ligand interacting, which is somewhat surprising as the Cp is thought to be hydrophobic.

The spatial density[13] of water molecules around the Cp ligand on **1** is shown in Figure 3. The yellow cloud represents the region where the probability of finding a water molecule exceeds 50% (regardless of its orientation). The 3.5 - 4.5 Å distance (left panel) was chosen to match the first peak of the ruthenium-water oxygen g(r) (not shown). The centre of mass of a water molecule (e.g. its oxygen) is likely to sit in correspondence with a triangle formed by a ruthenium atom and two hydrogen atoms on the Cp group. The second plot, on the right hand side, investigates the water molecule density in the distance range 4.5-6.0 Å. Here the most likely position for water molecules approaching the cyclopentadiene group is from the top of the figure e.g. the direction perpendicular to the ring plane.
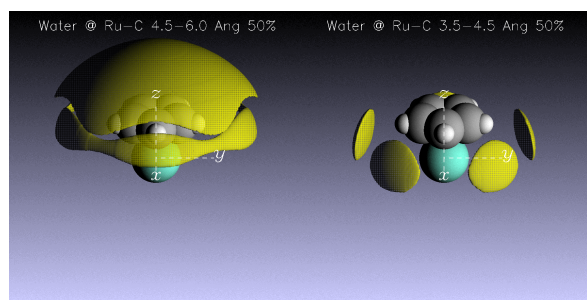
Fig. 3. Spatial Distribution Functions for water molecules around cyclopentadiene ligand on **1**.[14] The yellow cloud represents the region where the probability of finding a water molecule exceeds 50% (regardless of its orientation). The left panel is restricted to distance 3.5-4.5 Å from the central Ru atom, while the right hand panel explores the region between 4.5-6.0 Å. These distances have been chosen to match the first and second peak of the ruthenium-water oxygen g(r).

We have examined the electronic structure and UV/optical response of **1**, both in the gas phase and in the presence of a surrounding shell of water molecules, using Density-Functional Theory (DFT) and Time-Dependent Density-Functional Theory (TD-DFT). The gas-phase structure of the complex was first optimized using crystal phase atomic positions for the starting configuration. For the solvated complex, we considered a series of atomic configurations obtained from the EPSR simulations, containing one complex molecule and up to 50 water molecules to represent the first solvation shell. These structures were not re-optimised to avoid spurious relaxation of the water molecules in the absence of the solvent medium. It is important to mention that combining the output of a full molecular Monte Carlo simulation with a smaller scale ab initio simulation is an original approach, requiring a careful selection of the parameter coupling the two simulation techniques. Further details will appear in future publications. The properties of the solvated complex were obtained by averaging over different configurations, to simulate the effects of the dynamical disorder in the liquid phase. The simulated TD-DFT UV absorption spectra are shown in Figure 4. In the gas phase, the UV response is dominated by two main groups of peaks, at 300-400 nm (localized Ru-4d - 4d transitions) and at 220-300 nm (partial charge-transfer character from Ru-4d to P atoms of PTA). In water solution, the Ru-4d - 4d transitions are shifted to higher wavelengths (bathochromic shift). This result is consistent with experimental UV-vis measurements (Figure 4). An analysis of the atomic charge distribution indicates that this red shift in absorption energies is correlated to electronic charge redistribution on the Cp groups caused by the interaction of the ligand with surrounding water molecules. Mulliken charges on the carbon atoms of the Cp groups are found to fluctuate in solution over ranges of 0.12e around an average value *ca.* 0.1e larger than in the gas phase. The bathochromic shift in the UV spectrum is therefore largely an indirect effect

and can be interpreted as a solvation induced change in the strength of the ligand field induced on the Ru atoms by the presence of the coordinating Cp groups.
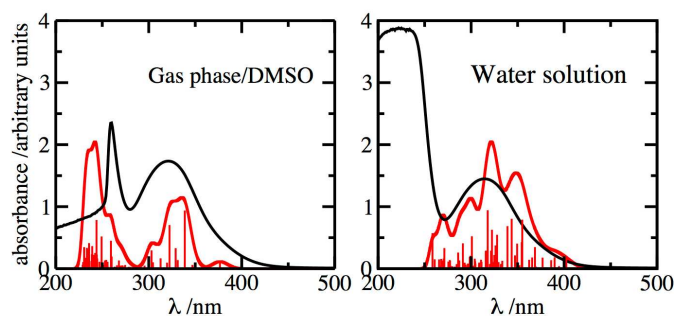
Fig. 4. Experimental (black lines) and TD-DFT (red lines) UV-vis absorption spectra of Complex **1(CF₃SO₃)6H₂O**. The experimental spectra (in DMSO and water solutions) have been recorded at a complex concentration of 5 x 10⁻⁴ M. The thin vertical lines represent the energies of the individual TD-DFT excitations.

These results show how water molecules interact with aqua-soluble Ruthenium cation complex **1** through, as expected, the N_{PTA} but also, unexpectedly, with the Cp ligand. These interactions produce radical changes into the electronic distribution in the molecule and therefore in its properties. Additionally, and very importantly, our work shows that X-ray and neutron diffraction techniques provide powerful methods for understanding the chemical interactions of water molecules with water-soluble complexes at an unprecedented level of detail. It is quite obvious that the effort required by neutron techniques alone mean that they cannot realistically be applied extensively as a routine characterisation method. Work is in progress to address the optimisation of X-ray and neutron diffraction techniques in connection with theoretical tools (EPSR, DFT and TD-DFT) to extend the range of applicability of these techniques. In synthesis, this finding paves the way for further applications in the study of the influence of water molecules in homogeneous catalytic processes mediated by metal complexes.

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