

# Neutron Scattering Techniques for Studying Metal Complexes in Aqueous Solution

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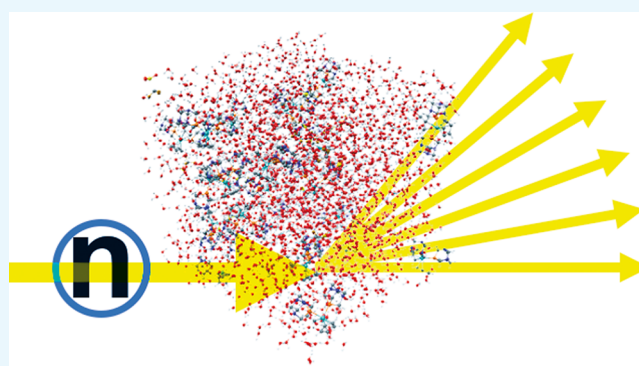
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**ABSTRACT:** Neutron scattering combined with *ab initio* calculations provides a powerful tool for studying metal complexes in different solvents and, particularly, in water. The majority of traditional characterization techniques in catalysis provide only limited information on homogeneous catalytic processes. Neutron scattering, on the other hand, thanks to its sensitivity to hydrogen atoms, and therefore water molecules, can be used to build detailed models of reaction paths and to observe, at a molecular level, the influence of solvent molecules on a catalytic process. In this Mini-Review we describe several examples on how neutron scattering combined with *ab initio* calculations can be used to examine the nature of the interaction of water molecules with catalytically active metal complexes in solution.



## INTRODUCTION

Organometallic chemistry, and particularly catalysis in water, have attracted increasing interest in recent years because of their potential roles in the development of new eco-benign synthetic processes.<sup>1</sup> Water offers many advantages over more common organic solvents in terms of abundance, renewability, low cost, modest environmental impact, stability, and safety, among others. Despite these advantages, water is still only scarcely used in industrial chemical processes in comparison to organic solvents. The main reasons for this are (a) the high dielectric constant of water, which makes it difficult or impossible to solubilize many metal complexes, and (b) its non-innocence, as it often leads to the decomposition of the catalyst. Additionally, and crucially, investigating water's behavior and participation in a chemical process can be difficult to achieve using routine spectroscopic techniques such as IR and NMR. This fact often complicates the proper interpretation of reaction mechanisms, which is fundamental for their optimization.

One of the most powerful techniques for studying the structure of water and aqueous systems is neutron scattering with hydrogen/deuterium isotopic substitution.<sup>2</sup> For convenience, in the following we will refer to this technique as *liquid diffraction*, in analogy to powder diffraction, even though they are technically and theoretically different. Using this method, the spherically averaged (or radial) pair distribution function (RDF), which is a linear combination of all the atom–atom correlations from every pair of atoms that constitute the solution at fixed moment in time, can be derived either directly, in the simplest cases, or indirectly with the help of classical molecular dynamics or Monte Carlo simulations. In the past three decades,

the combination of improved neutron diffraction sources and instruments and powerful molecular modeling software has made it possible to disentangle contributions from different atomic species, opening the possibility of understanding the chemical environment around atoms and molecules in solution. These approaches are providing unprecedented insight into the nature of the interaction between water molecules and solutes.<sup>3</sup> The work presented in this Mini-Review has made use of liquid diffraction measurements along with molecular modeling based on the Empirical Potential Structure Refinement (EPSR) method developed by Soper and co-workers.<sup>4</sup>

The application of liquid diffraction for determining the interaction of water with coordination compounds is a recent development, to which this group of authors has made important contributions. Its successful implementation still requires the combination of several experimental and modeling techniques. In particular, we have pioneered the use of quantum-mechanical *ab initio* simulations, along with the well-established EPSR method, to substantially enhance the level of insight into the structure, dynamics, and electronic properties of hydrated systems of catalytic interest. In our approach, we use a subset of the molecular structures determined from EPSR simulations and

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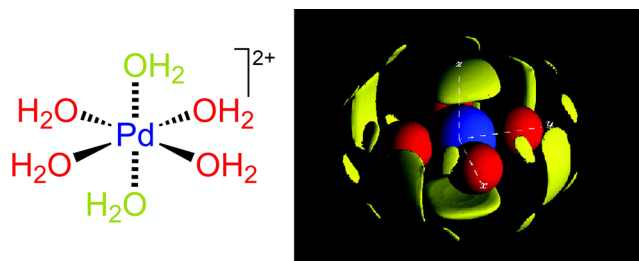
experimental neutron data to calculate UV–vis spectra in an “accelerated way”. This step is used to validate the *ab initio* calculations, through a direct comparison to experimental UV–vis measurements. We then run full *ab initio* molecular dynamics (AIMD) simulations, which do not require empirical parameters, to compare the structure of the solvation shell around a metal complex to the one derived from neutron data and EPSR. Finally, we use advanced *ab initio* calculations based on time-dependent density functional theory (TD-DFT) to determine the optical properties of the complexes in solution. Additionally, for all of the EPSR simulations involved, equilibrium ground-state energy structures and atomic charges (to be used as “seeding potential”) are also calculated.

Initially, we showed that by combining a traditional workhorse spectroscopic technique, nuclear magnetic resonance (NMR), with “exotic” neutron scattering on the experimental side, and classic along with quantum calculations on the computational side, an unprecedented insight into the interaction of solvated coordination compounds with water, and therefore into reaction mechanisms, can be achieved. In this Mini-Review we aim to bring together the many lessons learned during this process, with the hope that they will inspire more “coordination complex chemists” with the will to take up this challenging, but extremely rewarding, approach.

## ■ CISPLATIN

Cisplatin,  $[\text{PtCl}_2(\text{NH}_3)_2]$ , is a well-known anticancer compound extensively used in medicine. Along with a number of related complexes, cisplatin has been studied extensively, largely with the aim to elucidate its mechanism of action in cancer. Once administered, cisplatin dissolves in physiological fluids, which are mainly composed of water. It is therefore very important to understand how water interacts with this complex, in order to obtain detailed information on its anticancer action mechanism.

Studies explicitly targeting the interaction of water with Pt(II), a  $d^8$  cation, have shown the existence of a very complex scenario.<sup>5,6</sup> An important study has targeted a concentrated solution of  $[\text{Pd}(\text{OH}_2)_4]^{2+}$  in acidic conditions ( $\text{HClO}_4$ ), to prevent the hydrolysis of this aqua complex.  $\text{Pt}^{2+}$  and  $\text{Pd}^{2+}$  display similar behavior in water, although palladium ions are more stable and soluble in water than platinum ones. Importantly, they are sufficiently soluble to allow probing with X-ray absorption techniques<sup>7</sup> and neutron scattering.<sup>8</sup> Analysis of this data has revealed the existence of a meso-shell around  $\text{Pd}^{2+}$  ions in water, with two water molecules located on the same side of the molecular plane, interacting with the metal ion. This study also puts forward evidence for an axial coordination of perchlorate anions. An analogous coordination is observed in the case of the meso-shell water molecules, and the coordination region is stabilized by the cooperative effects of the square-planar cation and the water molecules around it (Figure 1). Interestingly from a chemical point of view, these results suggest that the coordination of a ligand in the axial region of a  $d^8$  metal can be affected by the presence of counterions and charged species. Therefore, it is important to pay special attention to the specific effects of counterions in the reaction medium. The results obtained in this study demonstrate the applicability and power of neutron scattering techniques in providing information about the solvation structure of a metal complex in water.

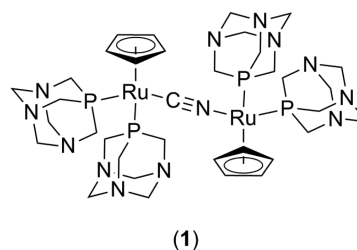


**Figure 1.** Left: Schematic representation of the aqua-Pd(II) ion. Right: Spatial density function of equatorial water molecules (red spheres), axial water molecules (inner yellow surfaces), and second hydration sphere (outer yellow surfaces) around the  $\text{Pd}^{2+}$  cation (blue sphere). Reproduced with permission from ref 8. Copyright 2012 American Chemical Society.

## ■ WATER-SOLUBLE RUTHENIUM COMPLEXES

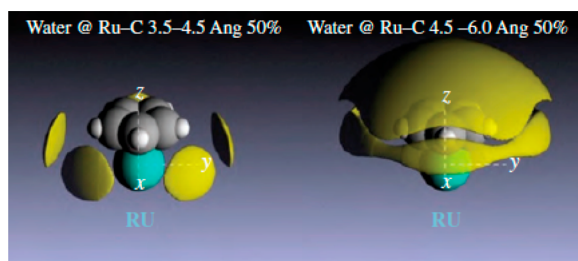
The first example of the determination of the water solvation structure around a metal complex in water solution was published in 2014.<sup>9</sup> The organometallic complex  $[\text{RuCp}(\text{PTA})_2-\mu\text{-CN-1}\kappa\text{C:2}\kappa^2\text{N-RuCp}(\text{PTA})_2](\text{CF}_3\text{SO}_3)$  (**1**) (PTA = 1,3,5-triaza-7-phosphaadamantane) (Scheme 1) is very

**Scheme 1.** Structure of **1**



soluble in water ( $S_{25^\circ\text{C}} = 320 \text{ mg mL}^{-1}$ ) and stable in aqueous solution. This metal complex is therefore an ideal candidate for the application of neutron diffraction methods. Both neutron and X-ray experimental data were used as starting points to perform EPSR Monte Carlo simulations. Neutron and X-ray diffraction are complementary techniques, as neutrons provide detailed information on the hydrogen-rich solvent structure, while X-rays can be used to investigate the nature of the solute–solvent interactions. The radial pair distribution function (RDF) obtained from the EPSR simulations shows that water molecules interact with the Ru complex. Unsurprisingly, a strong correlation is observed for water molecules interacting through hydrogen bonds with the amine groups of the ligands. However, other interactions were also observed. In particular, water molecules were found to interact with the hydrophobic cyclopentadiene (Cp) ligand. The RDF peak for these interactions is not well-defined, but non-negligible peaks are observed at distances of 2.5 Å ( $\text{C-H}_{\text{water}}$ ) and 3.5 Å ( $\text{C-O}_{\text{water}}$ ), which strongly support the existence of direct interactions between water molecules and the CH groups of the Cp ligand (Figure 2).

These results were validated by comparison of experimental UV–vis spectra in water and DMSO with the spectra computed with TD-DFT using structural models derived from EPSR simulations. It is important to note that the combination of molecular Monte Carlo EPSR simulations with smaller scale *ab initio* calculations (with explicit solvent molecules) presented in this work is a novel approach. A bathochromic shift is observed

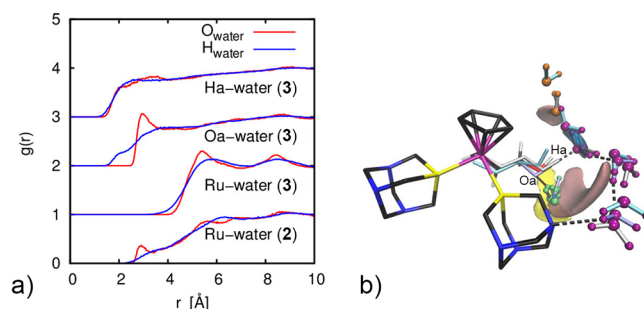


**Figure 2.** Space-filled areas represent those with 50% probability to find a water molecules around the Cp ligand (schematically represented) in **1** at different distances from the Ru center (left: 3.5–4.5 Å; right: 4.5–6.0 Å). Reproduced from ref 9 with permission from the Royal Society of Chemistry.

in the UV–vis spectrum of the water solution, at variance with anhydrous DMSO solutions. This shift can be interpreted as a solvation-driven change in the strength of the ligand field induced on the Ru atom by the presence of the coordinating Cp groups. The *ab initio* calculations show that the charge transfer involving the Cp ligand is strongly influenced by the interaction with water molecules. It is also important to emphasize that the results showed that water molecules are not innocent ligands, as they are capable of interacting with a lipophilic ligand, such as the Cp, and this interaction can be strong enough to change the electronic distribution in the entire complex, thus modifying its absorption properties.

In a second study,<sup>10</sup> we addressed the interaction of water with a catalytic intermediate in the isomerization of linear allylic alcohols mediated by the complex  $[\text{RuCp}(\text{H}_2\text{O}-\kappa\text{O})(\text{PTA})_2]-(\text{CF}_3\text{SO}_3)_2$ , **2** ( $\text{CF}_3\text{SO}_3$ ). This reaction is strongly dependent on the allylic alcohol size and on the amount of water.<sup>11,12</sup> Reaction of **2** ( $\text{CF}_3\text{SO}_3$ ) with 1-propen-3-ol in water gives very slow isomerization of the alcohol into propanal (12% in 2 days at 80 °C). During the first step of the catalytic cycle, an intermediate forms which is stable enough to be studied using NMR. The intermediate was characterized as the water-soluble  $\eta^2$ -allyl-complex  $[\text{RuCp}(\text{exo-}\eta^2\text{-CH}_2=\text{CH-CH}_2\text{-OH})(\text{PTA})_2]^+$  (**3**), whose stability relative to competing conformations is also supported by *ab initio* calculations.

Neutron diffraction was performed on both **2** and **3**. The resulting neutron data sets were used to drive EPSR simulations, which provided the RDF (Figure 3, left) and its three-dimensional reconstruction (spatial density function, or SDF, Figure 3, right). The presence of one water molecule coordinated to the Ru in **2** is demonstrated by the presence of a clear peak at approximately 2.6 Å in the RDF (bottom), which is consistent with the Ru–OH<sub>2</sub> distance in the crystal structure of **2** ( $\text{CF}_3\text{SO}_3$ ) (Ru1–O1 = 2.1784(16) Å).<sup>12</sup> Furthermore, in the RDF of **3**, two water molecules are observed in the vicinity of the hydroxyl group of the allylic alcohol: one molecule acts as a hydrogen bond donor and the other as a hydrogen bond acceptor. Most surprisingly, AIMD simulations show that one of the water molecules interacting with the hydroxyl group is part of a stable water bridge that connects the OH group of the alcohol to the nitrogen atom of the PTA ligand, driving the complex to assume an *exo* conformation that differs from the lowest *exo* conformation calculated in gas phase. The water chain found around this particular *exo* isomer of **3** is stable up to 20 ps, according to AIMD simulations. In this way, in aqueous solution, the substrate in **3** can adopt a conformation that may facilitate the catalytic reaction. For the *endo* isomers of **3**, which were found to be at least 6.5 kcal/mol higher in energy in gas-



**Figure 3.** Comparison of AIMD and EPSR results for **3**. (a) Radial pair distribution function (RDF) for water ( $\text{O}_{\text{water}}$  in red,  $\text{H}_{\text{water}}$  in blue) around the ruthenium atom in catalyst **2** and complex **3**. For the latter, the RDFs for water around the allylic hydroxyl group (Oa, Ha) are also shown. (b) Overlay of AIMD snapshots from with EPSR results. Space-filled areas show those of water probability >50% at 1–2 Å (blue), >25% at 2.7–3.5 Å (pink), and >15% at 3.5–4.5 Å (yellow) distance from Ha. Reproduced with permission from ref 10. Copyright 2018 American Chemical Society.

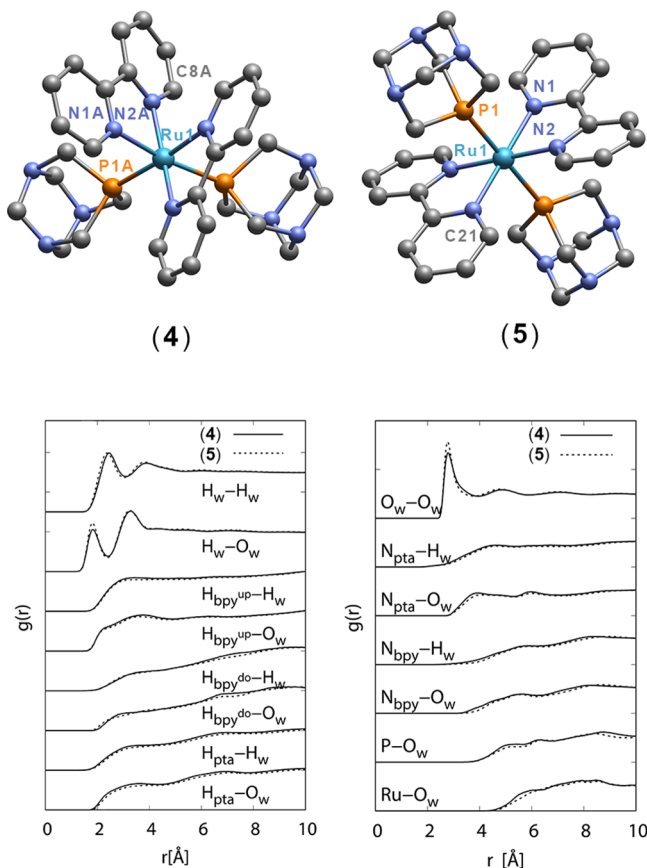
phase calculations than the lowest-lying *exo* one, a similar behavior was not observed in AIMD simulations. This was the first combined experimental and computational evidence supporting the existence of stable closed chains of water molecules and their influence on reactivity.<sup>13</sup> The AIMD simulations also indicate that water molecules occupy relatively stable positions around the solute over time scales sufficient for detection with neutron techniques, and they play a dominant role during the course of the reaction.

As previously mentioned, the catalytic isomerization of 1-propen-3-ol by **2** in water has a very low conversion (12% at 80 °C, 2 days), in contrast with faster reactions in the case of longer linear allylic alcohols; for example, the 1-penten-3-ol occurs at 55 °C in minutes.<sup>12</sup> The reaction is, however, faster than in dry MeOH and 1-propen-3-ol as solvent. AIMD simulations carried out in methanol solutions indicate the absence of a hydrogen bond network linking the substrate to the PTA ligand, which results in a less favorable orientation of the alkyl hydrogen atom with respect to the catalytic ruthenium center. These results suggest that the isomerization reaction catalyzed by **2** is strongly influenced by the water environment and by the solvation process, rather than the simple coordination of water molecules to the metal center, with the water chain determining the conformation of the substrate in **3**. In this example, neutron scattering experimental results and *ab initio* calculations and simulations indicate that water, as a reaction medium, promotes the formation of a more reactive isomer of **3**.

## ■ OPTICALLY ACTIVE WATER-SOLUBLE RUTHENIUM COMPLEXES

*cis*- and *trans*- $[\text{Ru}(\text{bpy})_2(\text{PTA})_2]^{2+}$  complexes containing bpy (bpy: bipyridyl) ligands are known for their optical properties, which are technologically important for their use in photosensitizers, antitumoral prodrugs, and catalysts.<sup>14,15</sup> The photochemical properties of these species depend dramatically on the nature of the ancillary ligands coordinated to the metal. In addition, interactions of the complex ligands with molecules in the environment, for example solvent molecules, can induce strong modifications of their properties, which makes these complexes ideal for use as sensors for a plethora of molecular species in solution.<sup>16</sup>

Two examples of this family of complexes are *cis*-[Ru(bpy)<sub>2</sub>(PTA)<sub>2</sub>]Cl<sub>2</sub> (**4**) and *trans*-[Ru(bpy)<sub>2</sub>(PTA)<sub>2</sub>]OTf (**5**) (Figure 4), whose photophysical and photochemical properties are

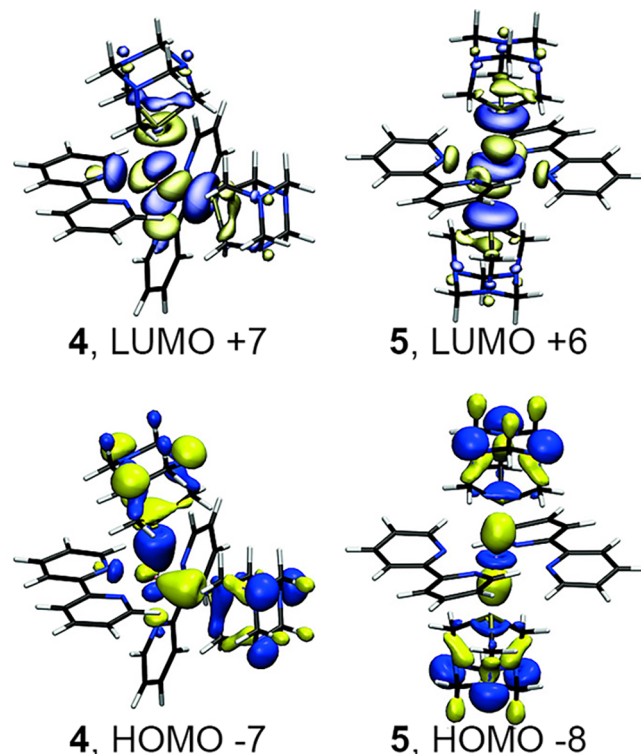


**Figure 4.** Representation of the crystal structures of **4** and **5**. A selection of RDFs are given for water oxygen,  $O_w$ , and water hydrogen,  $H_w$ , around relevant sites on compounds **4** (*cis*, full line) and **5** (*trans*, broken line). The 1,3,5-triaza-7-phosphaadamantane ligand atoms are labeled “pta”, while the bipyridine is labeled “bpy”.  $C^{up}$ ,  $C^{do}$ ,  $H^{up}$ , and  $H^{do}$  are sites on the bipyridine ligands (labeled according to their charges). Water–water correlations are also presented.<sup>17,20</sup> Reproduced with permission from ref 17. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

solvent- and pH-dependent. Furthermore, these complexes exhibit good solubility in water, which makes it possible to study them using neutron scattering.<sup>17</sup> Typically, the fluorescence properties of metal complexes degrade in water, as protic solvents quench molecular luminescence through nonradiative decay promoted by hydrogen bonds and electron transfers.<sup>18,19</sup> The quenching chain usually involves the interaction of water with specific ligands; for this reason, neutron diffraction combined with *ab initio* calculations has the potential to provide important information on the optical properties.

The solute–water RDFs for **4** and **5** (Figure 4) are found to be very similar, and they indicate the presence of a large number of water molecules in the vicinity of the solute. This is consistent with the good solubility of these compounds in water. Water molecules concentrate near the bipyridine ligand, in preference to the PTA ligand. The electronic distributions, according to the TD-DFT calculations, are consistent enough in both complexes to produce few significant hydration differences but different enough to induce clearly different optical effects.

The molecular orbitals of the *cis* and *trans* complexes, which are coordination isomers, are energetically similar, but the electron density distribution on the Ru ion differs in the two cases. The PTA ligands are strong  $\sigma$  donors and strongly interact with the ruthenium d orbitals. DFT calculations show that, due to the different PTA coordination, this interaction is predominantly with the Ru  $d_{x^2-y^2}$  orbital in the *cis* complex **4** (left in Figure 5) but with the  $d_{z^2}$  orbital of ruthenium in the *trans*

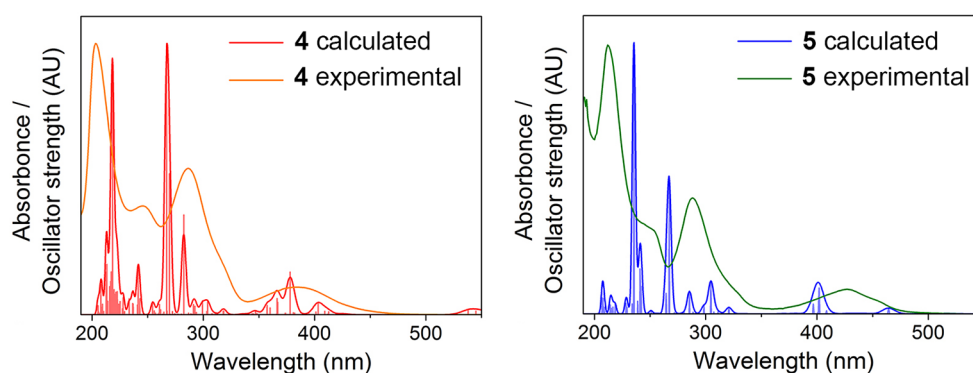


**Figure 5.** Selected orbitals of **4** and **5** from density functional theory calculations at the B3LYP/def2-TZVPP level of theory. Reproduced with permission from ref 17. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

complex **5** (right in Figure 5). These differences affect the UV–vis spectra of the two compounds. The optical spectra calculated using TD-DFT are in good agreement with the experimental ones, and they show that the lowest absorption band wavelength decreases by ca. 50 nm in the *trans* isomer relative to the *cis* one (Figure 6). The UV–vis spectrum between 350 and 450 nm contains mainly metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge-transfer (LMCT) bands, which in the case of the *cis* isomer are affected by the presence of water molecules in the immediate vicinity.

## CONCLUSION

Neutron scattering measurements and their interpretation based on EPSR simulations and *ab initio* calculations provide a powerful tool for studying organometallic complexes in water solution and for understanding their properties and reactivity in solution. Our work has shown that the combination of different experimental and computational techniques provides a unified and powerful framework in the study of aqueous solutions, which can be difficult to probe using traditional spectroscopic methods. The generality of our approach makes it suitable also in the study of hydrogen-containing non-aqueous solutions of transition metal complexes.



**Figure 6.** Calculated and experimental UV-vis spectral region below 600 nm of 4 and 5. Reproduced with permission from ref 17. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

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### Notes

The authors declare no competing financial interest.

### Biographies



Franco Scalambra received a degree in pharmaceutical chemistry in 2010 (Università di Ferrara, Italy) and obtained his Ph.D. in 2016, working in the group of Prof. Antonio Romerosa, at the University of Almería, in the field of coordination and organometallic chemistry. He is currently working in the Chemistry and Physics Department of the

University of Almería. His main research interests concern the fields of materials, catalysis, bioinorganic, and phosphorus chemistry.



Silvia Imberti graduated in physics in 2001 (U. of Milano Bicocca) and received her Ph.D. in Physics (U. of Roma Tre) in 2005. In 2006, she was a postdoc for CNR (ISC Firenze), seconded to the ISIS Neutron and Muon source on the INES instrument. A year later, she became instrument scientist on SANDALS, for the then CCLRC (now STFC). In 2019, she joined the ACS International team in Oxford as a Publishing Editor for *ACS Omega*. She is still very much interested in chemical physics, green chemistry, molecular liquids, and hydrogen bonding.



Nicole Holzmann obtained her Ph.D. in Theoretical Chemistry from the Philipps-Universität Marburg in 2013, working on DFT bonding analyses of main group complexes. She was a postdoc at CNRS (Centre National de la Recherche Scientifique) in Nancy, France, in the area of MD simulations of membrane protein systems. During her time at STFC Rutherford Appleton Laboratory, she worked in close

cooperation with experimental groups, applying a range of computational methods. She currently works as a Senior Quantum Scientist at Riverlane Ltd., where she explores quantum computing for pharmaceutical applications.



Leonardo Bernasconi received a degree in chemistry (University of Milan) in 1998 and a Ph.D. in Physical and Theoretical Chemistry (University of Oxford) in 2001. He worked as a postdoc at the University of Cambridge and at the Vrije Universiteit Amsterdam, and as a Principal Scientist at STFC Rutherford Appleton Laboratory. He is currently a Research Assistant Professor and Consultant at the Center for Research Computing, University of Pittsburgh. His research interests focus on the development and application of electronic structure methods to extended systems and on *ab initio* molecular dynamics.



Antonio Romerosa graduated in chemistry in 1987 (U. of Granada) and received his Ph.D. (U. Autònoma de Barcelona) in January 1992. The same year he undertook a postdoctoral research position at the ISSECC CNR (now ICCOM CNR) in Florence, Italy, before becoming Lecture Professor (1997) and finally Full Professor (2009) at the University of Almería, Spain. His research interests range over homogeneous catalysis and organometallic chemistry in water, phosphorus chemistry, photoinorganic chemistry, bioinorganic chemistry, and natural stones.

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