

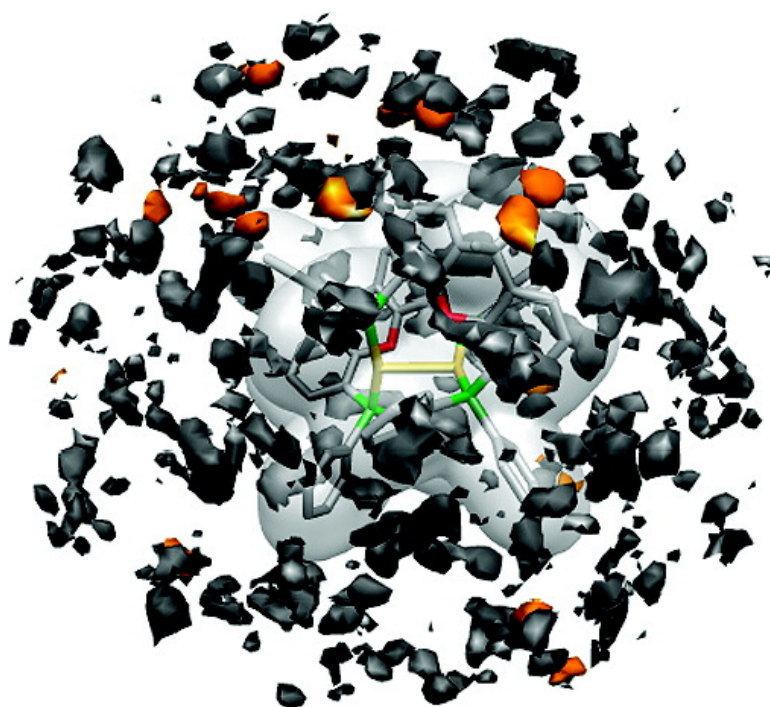
Communication

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Complete Structural Characterization of Metallacyclic Complexes in Solution-Phase Using Simultaneously X-ray Diffraction and Molecular Dynamics Simulation

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A major challenge in all of supramolecular chemistry and self-assembly, including the metal directed approach, is the proper structural characterization. This task is made all the more difficult because of the complexity and nanoscale dimensions of supramolecular ensembles and architectures. Mass spectrometry and multinuclear NMR spectroscopy are most commonly employed to provide proof of composition and to deduce structural information, respectively. In cases where a suitable single crystal can be obtained, classical single crystal X-ray diffraction provides the most reliable structural data, but in the solid state only. It is recognized that very weakly coordinated network compounds form in the solid state only upon crystallization and do not exist as discrete species in solution.¹ With the development of modern electronics and high-speed computers, interest in liquid and solution structures of molecules have steadily grown.² Only a few attempts have been made on the description of the structure of different complex solutions.³ These studies were focused on the determination of the structure of the solvated supramolecules and no description of the solvation sphere and modification in the structure of the solvent was given.

In the present work, we report the complete structural characterization of a nitromethane solution of a recently synthesized and reported^{3b} 16-membered gold(I) ring showing short 1,9-transannular Au...Au aurophilic interactions: $[\text{Au}_2(\mu\text{-xantphos})_2](\text{NO}_3)_2$ (**1**). In the previous study^{3b} solution X-ray measurement was performed to determine the structure and the aurophilicity of **1** after dissolution. The aim of the present study was at first to obtain structural information about the solvation of complex **1**, then to describe the often-neglected complex-solvent interaction in an intricate system like the present one. Finally the resulting change in the bulk structure of the solvent due to the presence of a big solute was also the subject of this study. To perform the complete structural characterization of the solution of **1** in nitromethane, X-ray diffraction combined with molecular dynamics simulation was applied on a 179 mM solution. To follow up the structural variation in the bulk, a molecular dynamics simulation of a very dilute (4 mM) solution was also performed.

The intermolecular radial distribution functions obtained from the experiment and simulation are shown in Figure 1. The agreement is good. The intermolecular radial distribution functions describing the complex-solvent interactions together with those obtained for solvent-solvent interactions and the interaction of the gold ion with the solvent are also shown. It can be observed that the complex-solvent interaction appears as a slightly increasing background and contributes in a very small amount to the total intermolecular radial distribution function. The gold-solvent contribution is very low, representing about 10% of the total intermolecular radial distribution function at long distances. Owing to their complexity the interactions between the solute and solvent molecules can only be approximated. Therefore the solvation properties of a metallacycle

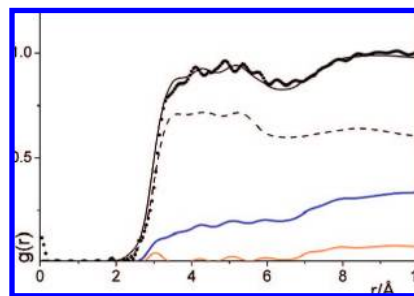


Figure 1. Intermolecular radial distribution functions for solution of complex **1** obtained from X-ray diffraction and molecular dynamics simulation: (black dots) XD experiment, (black line) MD simulation, (dashed line) solvent-solvent contribution, (blue line) complex-solvent contribution, (orange line) Au-solvent contribution.

cannot be described applying the diffraction method alone. However evaluating the diffraction measurement data using the complex-solvent and solvent-solvent radial distribution functions, determined from molecular dynamics simulation, the structure of metallacyclic complexes could be determined in a straightforward way.

Figure 2a shows the partial radial distribution functions describing the solvation sphere of the complex. It can be observed that at a distance of 5.87 Å from the oxygen atom (O_{cplx}) the solvation sphere is starting to build up; at 9 Å the solvation sphere is formed. Similarly, at a distance of 6.35 Å from the P_{cplx} , the solvation sphere in the surroundings of phosphorus atoms is formed, and at 9 Å the complete solvation sphere is evolved. Spatial distribution of the nitromethane neighbor molecules in the solvation shell around complex **1** is presented in Figure 2b. The solvation sphere of the complex is slightly distorted following the shape of the molecule. It has been found that a relatively diffuse solvation shell is formed around the complex. The nitrate ions are distributed in the solvation shell and are not directly bonded to the gold ions. They are located on the more positive side of the complex **1**, due to its dipole moment, oriented perpendicular to the Au-Au bond. Figure 2c represents the spatial distribution of nitromethane molecules around the anion when $\text{N}_{\text{anion}} \cdots \text{N}_{\text{solvent}}$ distances are shorter than 10 Å. There are two layers of molecules in the solvation shell of the anion: the closer layer is in the direction of the bisector of ONO angle and the other one in the direction of the oxygen atoms.

The orientations of the neighboring molecules can be characterized by the angle dependent pair distribution function. Figure 3a shows the orientation of nitromethane molecules relative to the complex. The peak at 6.4 Å and 45° appears because of the nitromethane molecules directly bound to the gold ions by their nitrate groups. The nitromethane molecules in the solvation sphere are distributed randomly; no special orientation can be detected.

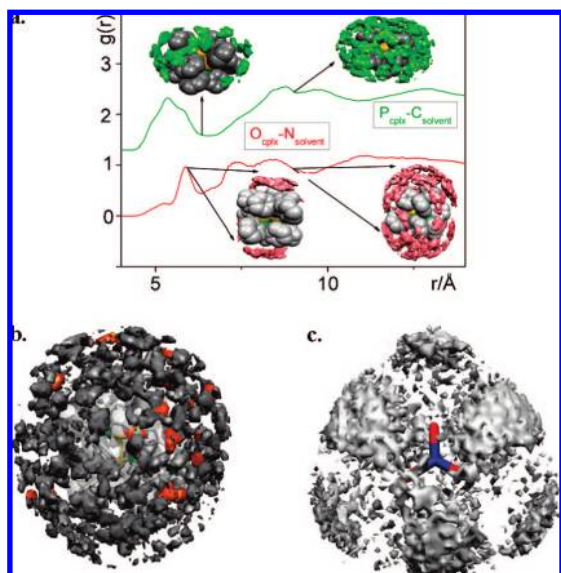


Figure 2. (a) $P_{\text{cplx}}-C_{\text{solvent}}$ and $O_{\text{cplx}}-N_{\text{solvent}}$ partial radial distribution functions (obtained from MD) showing how the solvation sphere of complex **1** is built up. $P_{\text{cplx}}-C_{\text{solvent}}$ was up-shifted with 1.3. (b) Spherical distribution of the nitromethane molecules (dark gray) and nitrate anions (orange) in the solvation sphere of complex **1**. (c) Spherical distribution of the nitromethane molecules in the solvation sphere of the nitrate anion.

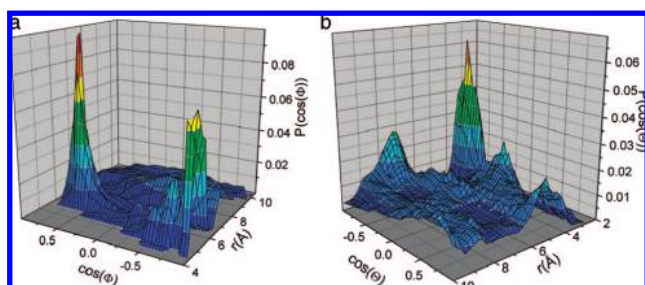


Figure 3. Distance dependent angular distribution function in the case of 179 mM solution: (a) angle (Φ) between the center of complex **1** and C–N bond of the nitromethane molecules (center of the complex defined as the midpoint of the gold–gold bond); (b) angle (Θ) between the dipole moment vector of central and neighboring nitromethane molecules.

Figure 3b shows the distribution of the angle between the dipole moment vector of central and neighboring molecules as a function of N...N distance, showing the orientation of molecules in the bulk. In liquid nitromethane only the first nearest neighbors tend to be oriented in an antiparallel form. For N...N distances longer than 4.0 Å, the angular distribution is almost uniform, indicating that the preference in orientation is lost very quickly.⁴ In solution, besides the antiparallel orientation (3.2 Å), the T-shape orientation of nitromethane molecules appears around 4 Å, and at 7 Å a long-range order of the nitromethane molecules in an antidipole orientation can also be detected.

Figure 4 shows the interaction energy of **1** with nitromethane molecules. The interaction energy is attractive and two regions should be discussed: there is a maximum on the distribution at –10 kcal/mol and 6.4 Å corresponding to the nitromethane molecules coordinated to the gold ions; the other maxima show that the attractive interaction energy in the solvation sphere decreases from –5 to 0 kcal/mol as the distance increases from 7 to 10 Å.

Performing the comparison of the partial radial distribution functions (shown in Supporting Information) obtained for the

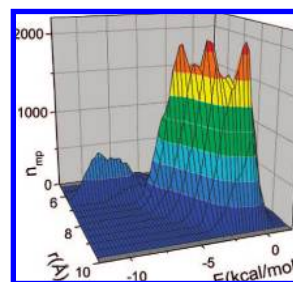


Figure 4. Complex–solvent interaction energy distribution as functions of distance r ; n_{mp} = number of molecular pairs.

solvent in both solutions (4 and 179 mM) and the pure solvent, it has been found that with increase in concentration mainly excluded volume effects appear. The increase of the local density at low r is inversely proportional to the relative volume of solvent in solution. Since this volume decreases with increasing solute concentration, an increase of the height of the solvent–solvent correlations at low r can be detected.⁵

It should be emphasized, that only the combination of diffraction and simulation techniques could result in the complete structural characterization of the solution. By the joint application of the two methods we were able to describe not only the structure of the complex but the solvation properties of **1** in nitromethane by analyzing the solvation sphere, and the effect of the solvation on the bulk structure.

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Supporting Information Available: Experimental and evaluation method for solution X-ray diffraction measurements and the details of molecular dynamics simulation are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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