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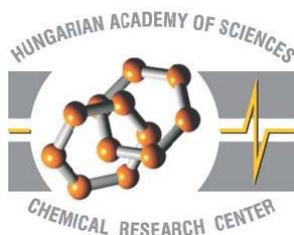
**BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS  
FACULTY OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY  
GYÖRGY OLÁH DOCTORAL SCHOOL**

**Structure of some transition-metal complexes and supramolecules in solution,  
studied by X-ray diffraction and molecular dynamics simulation**

Ph. D. Thesis

**Szabolcs Bálint**

Supervisor: Tünde Megyes, Dr.  
Consulent: Tamás Radnai, Prof.



Chemical Research Center of the Hungarian Academy of Sciences  
Institute of Structural Chemistry, Liquid Structure Laboratory

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## 1. Introduction

Since the discovery of X-ray radiation, several methods were developed to study the molecular structure of substances. The diffraction method, which has been extended to liquids, is a well-known method developed earlier. For now, a combination of X-ray diffraction with computer simulation, resulted in a powerful tool with one can get deeper insight to the liquid structure, and this was a breakthrough in the liquid structure research.

The solution X-ray diffraction had a great history in our institute in studying the structure of inorganic salts in aqueous and non-aqueous solutions, and it was extended to analyse more complex systems. Thus, e.g., the NMR results were complemented by X-ray diffraction data, which gave more information on the static structures that exist in solution.<sup>1</sup> This had led to the recognition that even supramolecules (here the term “supramolecule” denotes a molecule beyond a molecule – a molecule built up from molecules) can be studied in solution. Their structural study became a rapidly growing field thanks to the special properties of supramolecules. For example, non-linear optical properties, size and/or shape selectivity are of major interest. Another important feature of these complexes is self-assembling.

Due to the large size (many atoms) of these complexes only a limited range of computer simulation methods can be used, for example classical molecular dynamics simulation. My task was first to learn how to model liquid structure and structure of solutions, starting from simple liquids to the highly complex supramolecular solutions. The results calculated from molecular dynamics simulation is compared to the results obtained from X-ray diffraction measurement.

The studies have been started with the structure of the potential solvents: nitromethane, methylene chloride, methanol and acetic acid. Most important are nitromethane and dichloromethane, due to their application during the synthesis of metal containing supramolecules. Nitromethane has been studied widely by using molecular dynamics simulation,<sup>2</sup> because the fact that it serves as a model compound for high-energy explosives, but according to our knowledge no X-ray diffraction experiment is performed yet on the liquid. Methylene chloride is an ideal media in important chemical reactions. The studies carried out on this liquid were focusing on the testing of the newly developed classical pair potentials, comparing their results with spectroscopic data and no structural analysis has been performed.<sup>3</sup> Furthermore, only one X-ray diffraction measurement has been published up to now, but the results coming out are questionable.<sup>4</sup>

In order to compare the simulated and experimental data of the gold(I) containing supramolecule, we had to develop gold(I) interaction potential, while no classical pair potential is published. Due to the limited solubility of the gold(I) salts in organic solvents, we selected the most soluble solvent-salt pairs for potential fitting, they are: gold(I) in liquid nitromethane and potassium dicyanoaurate(I) in nitromethane and methanol. It should be noted, that we focused on the classical pair potential fitting and then testing it by comparison of molecular dynamics simulation with diffraction data.

The first supramolecule studied is the tetrakis( $\mu_2$ -acetato-O,O)tetraplatinum(II) ( $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$  or octaacetatotetraplatinum(II)) in glacial acetic acid solution. This complex was

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<sup>1</sup> E. Holló-Sitkei, G. Tárkányi, L. Párkányi, T. Megyes, G. Besenyeyi, *Eur. J. Inorg. Chem.* 1573 (2008)

<sup>2</sup> H. E. Alper, F. Abu-Awwad, P. Politzer, *J. Phys. Chem. B* **103**, 9738 (1999); D. C. Sorescu, B. M. Rice, D. L. Thompson, *J. Phys. Chem. B* **101**, 798 (1997); D. C. Sorescu, B. M. Rice, D. L. Thompson, *J. Phys. Chem. A* **105**, 9336 (2001); J. M. Seminario, M. C. Concha, P. Politzer, *J. Chem. Phys.* **102**, 8281 (1995)

<sup>3</sup> M. Ferrario, M. W. Evans, *Chem. Phys.* **72**, 141 (1982); H. J. Böhm, R. Aldrichs, *Mol. Phys.* **54**, 1261 (1985); G. R. Kneller, A. Geiger, *Mol. Phys.* **68**, 487 (1989); H. Torii, *J. Mol. Liq.* **119**, 31 (2005)

<sup>4</sup> B. R. Orton, R. L. T. Street, *Mol. Phys.* **34**, 583 (1977)

synthesized by method of Basato et al.<sup>5</sup> In the octaacetatotetraplatinum(II) the platinum(II) ions are arranged in square planar geometry, and the acetate ions are coordinated from the axial and equatorial positions. Due to its reactivity it is a promising molecule for synthesizing water-soluble complexes by replacing the acetate groups.

Based on the previous results, the bis( $\mu_2$ -xantphos-P,P)digold(I)dinitrate (gold(I)xantphos) supramolecule<sup>6</sup> in nitromethane is studied. Beyond the comparison of pure solvent and bulk solvent structure in the solution, the solvation sphere and the ion pair formation is also studied. Further on, a possible reason for the luminescence property of the molecule is given.

These results and applied joint methods were the first detailed studies in the literature, showing their effectiveness in the case of more complicated systems.

## 2. Applied methods

Philips X'Pert MPD X-ray diffractometer using  $\theta - 2\theta$  arrangement and Bragg-Brentano geometry with a pyrographite monochromator in the scattered beam is applied for measurement. The samples were measured in capillary at room temperature using Mo  $K_\alpha$  radiation. The scattering angle ranges  $1.28^\circ < 2\theta < 130.2^\circ$ , corresponding to a range of  $0.2 \text{ \AA}^{-1} < k < 16.06 \text{ \AA}^{-1}$ . Over 100 000 points are collected at 150 discrete points. The measured data were treated on the usual way, already published several times.<sup>7</sup>

Molecular dynamics simulations were performed using DL\_POLY 2.15 program. The collected trajectories were analysed using in-house software. The resulted data were always compared to the corresponding X-ray data, in order to check the goodness of the simulation. This always showed that the size of the simulated system and the simulation parameters were carefully and correctly chosen.

Ab initio calculations have been carried out by using Gaussian 03 Rev. B05 program package. The nature of the geometries are characterised by the frequency calculation, and were always compared to either previous findings or the experimentally available data.

## 3. New scientific results

### 3.1. Liquid nitromethane

Quantum chemical calculations showed that there are two different conformers, eclipsed and staggered, of nitromethane molecule, with nearly the same total energy. The rotation barrier between these two minima is less than 0.01 kcal/mol, therefore the rotation of  $\text{NO}_2$  group around the C–N bond is almost free. The optimised geometry for the dimer nitromethane was obtained to be molecules shifted antiparallel and it has been found that in the nitromethane dimer the  $\text{CH}\cdots\text{O}$  interaction cannot be considered as H-bonded interaction.

According to the molecular dynamics simulation study no predominant occurrence of nitromethane dimers in the liquid nitromethane could be detected; however, the position and orientation of the nearest neighbour molecules resemble to some extent the configuration of the theoretically calculated energy-minimised dimer. Neighbouring C–N bond vectors slightly prefer

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<sup>5</sup> M. Basato, A. Biffis, G. Martinati, C. Tubaro, A. Venzo, P. Ganis, F. Benetollo, *Inorg. Chim. Acta* **355**, 399 (2003)

<sup>6</sup> A. Deák, T. Megyes, G. Tárkányi, P. Király, G. Pálinkás, P. J. Stang, *J. Am. Chem. Soc.* **128**, 12668 (2006)

<sup>7</sup> T. Radnai, Az alkáli kloridok vizes oldatainak szerkezetvizsgálata röntgendiffrakcióval, *Magyar Fizikai Folyóirat*, **28**, 339, (1980);

an antiparallel configuration in the liquid. In the liquid state CH...O type weak hydrogen bonds could not be detected.<sup>[1.]</sup>

The total radial distribution functions of MD simulation and X-ray diffraction agree very well. The small discrepancy between the experimental and theoretical radial distribution functions may be due to both the potential model applied in the simulation and to the experimental uncertainties, but the theoretical and experimental findings are in general accordance.

### **3.2. Liquid methylene chloride**

On the basis of quantum chemical calculations it can be seen that the structure determining forces, electrostatic (dipole-dipole and quadrupole-quadrupole) and van der Waals interactions, play similar role in formation of the dimer structure.

The essential features of the partial radial distribution function in three different molecular dynamics simulations agree with each other, meaning that the obtained results are rather insensitive on the charge distribution of methylene chloride molecule. Analysing these distribution functions it can be observed that the number of neighbours belonging to the first coordination shell can only be determined with high inaccuracy meaning that the first coordination shell is not very well defined in this liquid. The characteristic values of these functions indicate that in liquid methylene chloride no hydrogen bond like interaction appears.

Neighbouring molecules slightly prefer an antiparallel, tail-to-tail orientation to parallel one. For C...C distances longer than 4.0 Å, the antiparallel tail-to-tail orientation is lost very quickly and slight preference of parallel head-to-tail and L-shaped orientations can be detected. On the other hand some orientational correlations between rather distant molecules can also be observed.

The total radial distribution functions of MD simulation and X-ray diffraction agree very well and the theoretical and experimental findings are in general accordance.<sup>[2]</sup>

### **3.3. Pair potential of gold(I)–nitromethane**

The MP2 and HF level of theory using the LANL2DZ basis set for gold and D95V for each other elements at the level of BSSE corrected interaction energies showed no significant difference. With the increasing the number of the solvent molecules coordinating to the metal ion the interaction energy shows nearly linear increment after the coordination of the first two molecules. Thus the corrected interaction energies are calculated, and potential parameters are fitted between the nitromethane solvent and two nitromethane coordinated to the gold(I) ion. The total radial distribution functions obtained from MD simulation using this newly developed potential and X-ray diffraction measurements of the AuCl in nitromethane show a good agreement, meaning that the fitting of potential parameters resulted an acceptable parameter set.<sup>[3]</sup>

### **3.4. Pair potential of [Au(CN)<sub>2</sub>]<sup>-</sup>–nitromethane**

The method was identical already mentioned at the previous point. Using the above introduced analysis, it has been found that with increasing of the number of the solvent molecules coordinating to the central ion, the interaction energy shows a nearly linear dependence. Thus the analytical potentials are fitted to the BSSE corrected interaction energy of one anion and one solvent molecule. The total radial distribution functions obtained from MD simulation and X-ray diffraction measurement of the K[Au(CN)<sub>2</sub>] in nitromethane are in good agreement.

The cation-anion pair potential fitted to the same potential function as the anion-solvent and the resulted agreement between the experiment and theory is acceptable.<sup>[4.]</sup>

### **3.5. Pair potential of [Au(CN)<sub>2</sub>]<sup>-</sup>–methanol**

Here we applied a pseudopotential<sup>8</sup> for gold(I) downloaded from EMSL basis set library and aug-cc-pVDZ for all the other elements. The BSSE interaction energies fitted to an analytical formula and the molecular dynamics simulation results showed good agreement with those obtained from the X-ray diffraction measurement.

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<sup>8</sup> K. A. Peterson, C. Puzzarini *Theor. Chem. Acc.* 114, 283 (2005)

### 3.6. Solution structure of octaacetatotetraplatinum(II) in glacial acetic acid

Our results obtained from the diffraction study of the acetic acid are in accordance with previous findings,<sup>9</sup> from X-ray and neutron diffraction experiments. It has been found that the acetic acid molecules mainly form chain structure by hydrogen bonds, where the hydroxyl and carbonyl groups of a molecule play role as proton donor and acceptor to other molecules, respectively. From solution X-ray diffraction study the platinum–platinum distances obtained from the least-squares fit of the difference structure function  $kh(k)$  are  $2.56 \pm 0.01$  Å for the bonding Pt–Pt and  $3.53 \pm 0.05$  Å for the nonbonding Pt···Pt distances, respectively. This means that the  $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$  complex retains its shape in the solution.<sup>[5.]</sup>

Total radial distribution functions of MD simulation and X-ray diffraction agree well. The discrepancy between these functions obtained from simulation and X-ray diffraction may be due to both the potential model applied in the simulation and to the experimental uncertainties but the theoretical and experimental findings are in general accordance.

From the analysis of the partial radial distribution functions of the acetic acid and solution obtained from simulations a significant change can be detected on the solvation sphere of the methyl group (Fig. 1.). The hydrogen-bonded structure of the acetic acid is not destroyed in the solution compared to the pure liquid.

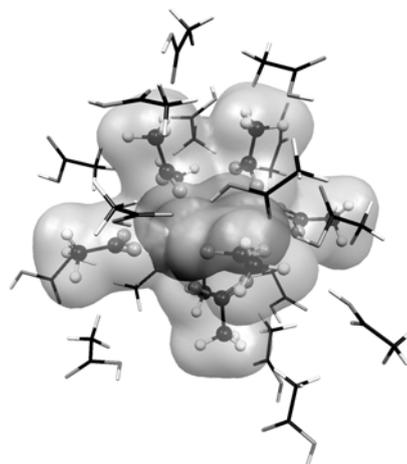


Figure 1. A snapshot obtained from simulation showing the arrangement of the acetic acid molecules around the  $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$  complex

### 3.7. Solution structure of the gold(I)xantphos in nitromethane

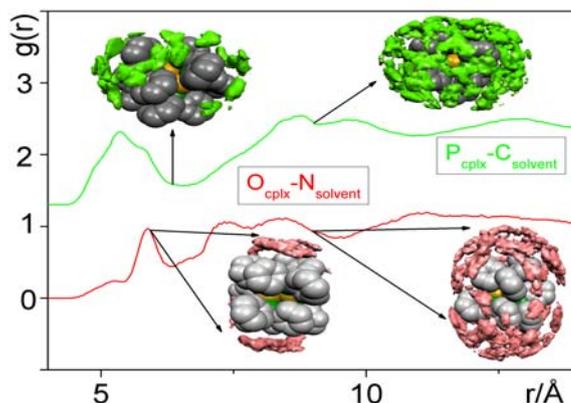
By the joint application of the two methods (MD simulation and X-ray diffraction) we were able to describe not only the structure of the complex, but the solvation properties of the  $[\text{Au}_2(\mu\text{-xantphos})_2](\text{NO}_3)_2$  (gold(I)xantphos) complex in nitromethane by analysing the solvation sphere, and the effect of the solvation on the bulk structure as well.<sup>[6]</sup>

It is revealed from X-ray diffraction measurement that the gold(I)xantphos complex retains its structure in solution. Thus for the molecular dynamics simulation the geometry obtained from single crystal X-ray diffraction structure refinement was used.

The agreement between the X-ray diffraction experiment in solution and MD simulation is good. 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 (Fig. 2.). The nitrate ions are located on the more positive side of the complex, due to its dipole moment, oriented perpendicular to the Au–Au bond. From analysing the partial radial distribution functions and the orientation of the neighbouring nitromethane molecules, it is observed that there is a nitromethane molecule coordinated by its nitrate group directly to the gold anion by  $-10$  kcal/mol interaction energy. This can be an evidence of the luminescence property of the gold(I)xantphos supramolecule in solution.

Analysing the structure of nitromethane in the solvent sphere shows no significant orientation not taking into account the solvent molecules coordinated to the gold ions. The bulk structure of nitromethane solvent in the solution shows antiparallel arrangement, which is lost very quickly as distance increases. Besides the antiparallel orientation the T-shape arrangement has been found as well.

<sup>9</sup> D. J. Frurip, L. A. Curtiss, M. Blander, *J. Am. Chem. Soc.* **102**, 2610 (1980); H. Bertagnolli, H. G. Hertz, *Phys. Status Solidi, A Appl. Res.* **49**, 463 (1978); H. Bertagnolli, *Chem. Phys. Lett.* **93**, 287 (1982)



**Figure 2.**  $P_{\text{cplx}-\text{C}_{\text{solvent}}}$  and  $O_{\text{cplx}-\text{N}_{\text{solvent}}}$  partial radial distribution functions (obtained from MD) showing how the solvation sphere of gold(I)xantphos complex is built up.  $P_{\text{cplx}-\text{C}_{\text{solvent}}}$  was up-shifted with 1.3

#### 4. Thesis points

- I have shown that in liquid nitromethane the C–H···O type interaction cannot be considered as hydrogen bond. The nearest neighbours slightly preferring the shifted antiparallel arrangement liquid state.
- I presented that the structure of liquid methylene chloride is rather insensitive to the charge distribution on the molecule.
- The first coordination shell of dichloromethane is not very well defined. The neighbouring molecules slightly prefer the arrangements obtained from quantum chemical calculations.
- I developed the first pair potentials available in the literature for gold(I) in nitromethane and methanol.
- Through the example of  $[\text{Pt}(\text{CH}_3\text{COO})_2]_4$  in acetic acid I have shown, that the complex retains its structure in solution. The hydrogen bonded structure of the solvent is not destroyed in the solution.
- I pointed out that the bis( $\mu_2$ -xantphos-P,P)digold(I)dinitrate (gold(I)xantphos) in nitromethane retains its structure in the solution. Furthermore, the solvent molecules are randomly arranged on the surface of the supramolecule.
- I proved that the solvent molecules are directly coordinating to the gold(I) in the gold(I)xantphos solution, while the nitrate ions are arranged in the direction of the dipole moment of the complex, on its surface.
- I clarified that the bulk solvent structure can be found in the space between the solvated gold(I)xantphos supramolecules.

### Publication list related to the thesis:

- [1.] Megyes, T.; **Bálint, S.**; Grósz, T.; Radnai, T.; Almásy, L.; Bakó, I.: *Structure of Liquid Nitromethane: Comparison of Simulation and Diffraction Studies*, J. Chem. Phys. **126**, 164507, 2007;  
Impact factor: 3.044, Cited: 2
- [2.] **Bálint, S.**; Bakó, I.; Grósz, T.; Megyes, T.: *Structure of Liquid Methylene Chloride: Molecular Dynamics Simulation Compared to Diffraction Experiments*, J. Mol. Liq. **136**, 257, 2007,  
Impact factor: 1.1; Cited: 1
- [3.] Injan, N.; Megyes, T.; Radnai, T.; Bakó, I.; **Bálint, S.**; Limtrakul, J.; Spangberg, D.; Probst, M.: *Potential Energy Surface and Molecular Dynamics Simulation of Gold(I) in Liquid Nitromethane*, J. Mol. Liq., **147**, 64, 2009,  
Impact factor: 1.188
- [4.] Injan, N.; Megyes, T.; Radnai, T.; Bakó, I.; **Bálint, S.**; Limtrakul, J.; Probst, M.: *Au(CN)<sub>2</sub><sup>-</sup> in nitromethane: energetics, X-ray diffraction and molecular dynamics simulation*, J. Mol. Liq. 2009 Submitted,  
Impact Factor: 1.188
- [5.] Megyes, T.; **Bálint, S.**; Grósz, T.; Kótai, L.; Bakó, I.: *Solution structure determination of tetranuclear platinum (II) cluster complex in acetic acid: X-ray diffraction and molecular dynamics simulation study*, J. Mol. Liq. **143**, 23, 8, 2008,  
Impact factor: 1.188
- [6.] Megyes, T.; Bakó, I.; **Bálint, S.**; Grósz, T.; Pálinkás, G.: *Complete Structural Characterization of Metallacyclic Complexes in Solution-Phase Using Simultaneously X-ray Diffraction and Molecular Dynamics Simulation*, J. Am. Chem. Soc. **130**, 9206, 2008,  
Impact factor: 8.091

### Lectures and posters:

- (1.) **Bálint, S.**; Bakó I.; Grósz T.; Megyes, T.; *Structure of Liquid Methylene Chloride: Molecular Dynamics Simulation Compared to Diffraction Experiments*; poster, EMLG Annual Meeting, Fukuoka, Japan, 2007
- (2.) **Bálint S.**, Megyes T., Grósz T., Radnai T., Bakó I., Pálinkás G.; *Structure of K[Au(CN)<sub>2</sub>] in solution: an X-ray diffraction and theoretical study*; poster, ICSC30, Perth, Ausztralia, 2007
- (3.) **Bálint, S.**, Megyes, T., Bakó, I., Radnai, T.; *Solution structure study of transition metal complexes*; presentation, MTA Doktori Iskolai Beszámoló, presentation, Budapest, Hungary, 2007

- (4.) **Bálint S.**, Megyes T., Grósz T., Radnai T., Bakó I.; *Structure of liquid nitromethane: X-Ray and neutron diffraction studies compared to molecular dynamics simulations*; poster, EMLG06, Spain, Barcelona, 2006

### Other publications:

- (1.) Megyes, T.; **Bálint, S.**; Bakó, I.; Grósz, T.; *Solvation of Calcium Chloride in Formamide: Comparison of Simulation and Diffraction Studies*, J. Phys. Chem. B 2009; submitted, Impact factor: 4.086
- (2.) Megyes, T.; **Bálint, S.**; Bakó, I.; Grósz, T.; Sipos, P.: *The Structure of Gallium in Strongly Alkaline, Highly Concentrated Gallate Solutions: X-ray Diffraction and Molecular Dynamics Simulation*, J. Phys. Chem. B 2009; submitted, Impact factor: 4.086
- (3.) Bakó, I.; Megyes, T.; **Bálint, S.**; Chihaiia, V., Bellissent-Funel, M. C., Krienke, H.; Kopf, A.: *Hydrogen bonded network properties in liquid formamide*, J. Chem. Phys. A accepted for publication 2009; Impact factor: 3.149
- (4.) Megyes, T.; Bakó, I.; Grósz, T.; **Bálint, S.**; H. Krienke: *Solution structure of NaNO<sub>3</sub> in water: diffraction and molecular dynamics simulation study*, J. Phys. Chem. B, **113**, 4054, 2009; Impact factor: 4.189
- (5.) Bakó, I.; Megyes, T.; **Bálint, S.**; Chihaiia, V.: *Water-methanol Mixtures: Topology of Hydrogen Bonded Network*, Phys. Chem. Chem. Phys. **32**, 5004, 2008; Impact factor: 4.064, Cited: 2
- (6.) Megyes, T.; **Bálint, S.**; Bakó, I.; Grósz, T.; Radnai, T.; Sipos, P.: *The Structure of Sodium Hydroxide Solutions – a Combined Solution X-ray Diffraction and Simulation Study*, J. Chem. Phys. **128**, 044501, 2008; Impact factor: 3.149, Cited: 7
- (7.) Megyes, T.; Bakó, I.; **Bálint, S.**; Grósz, T.; Radnai, T.: *Ion pairing in aqueous calcium chloride solutions: molecular dynamic and diffraction study*, J. Mol. Liq. **129**, 63, 2006; Impact factor: 1.106 Cited: 10
- (8.) Megyes, T.; **Bálint, S.**; Bakó, I.; Grósz, T.; Radnai, T.; Pálinkás, G.: *Solvation of calcium ion in methanol: Comparison of Diffraction Study and Molecular Dynamics Simulation*, Chem. Phys., **327**, 415, 2006; Impact factor: 1.934 Cited: 2