

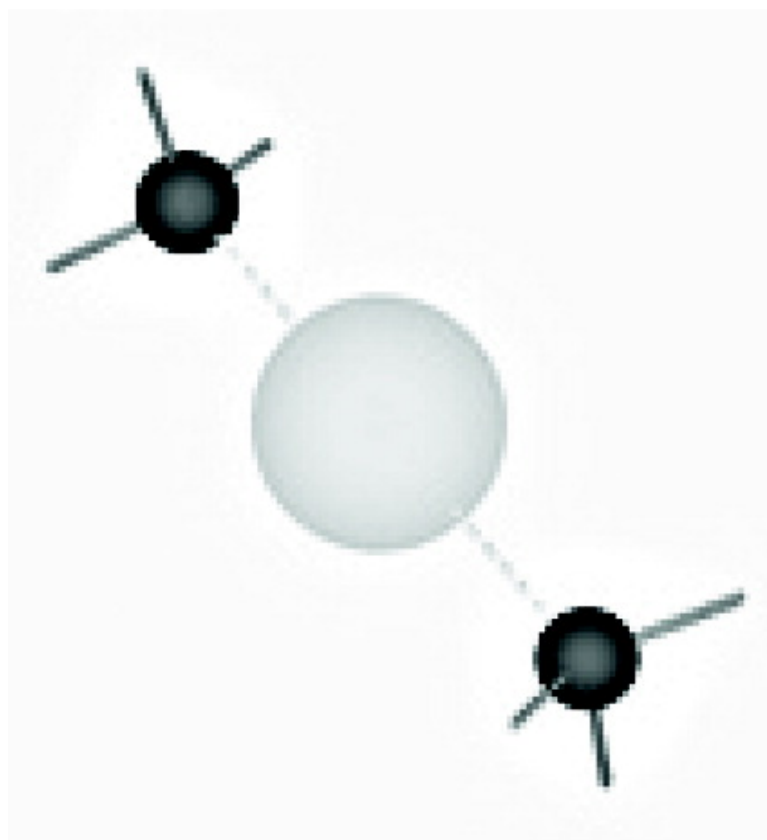
Communication

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## Gold(I) in Liquid Ammonia: Ab Initio QM/MM Molecular Dynamics Simulation

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In aqueous solution, the Au(I) ion forms a flexibly four-coordinated hydration structure in the first solvation shell.<sup>7</sup> In contrast, a Au(I)-diamine complex is supposed to be formed when dissolving gold in ammoniacal solution with the aid of an appropriate oxidant.<sup>1</sup> Some theoretical studies of Au(I)-ammonia interactions have been carried out in the last years<sup>2,3</sup> without giving a satisfactory description of this system, and therefore, further investigations of structural and dynamical properties of Au(I) in liquid ammonia are of considerable interest.

Nowadays, computer simulations with high-end computer technology can be used for analyzing structural and dynamical properties of solvated ions.<sup>4-6</sup> In particular, the quantum mechanical/molecular mechanical (QM/MM) method has proven to be a suitable tool for elucidating details of metal ion solvates in dilute solution with water<sup>7,8</sup> and/or ammonia<sup>9-12,19</sup> as solvent. Following a recent QM/MM simulation for Au(I) in water<sup>7</sup> and also due to the importance of leaching gold metal using ammoniacal solutions,<sup>1</sup> this work treats liquid ammonia as solvent. The highly CPU-time-demanding QM/MM method is required for including quantum mechanical effects into the part of major chemical interest. Therefore, ion plus first solvation shell were defined as the QM region, which was treated at the Hartree-Fock level using LANL2DZ with relativistic corrected ECP<sup>14</sup> (gold) and DZP Dunning<sup>15</sup> (ammonia) basis sets. The remaining region was treated by classical molecular mechanics (MM region) based on pair potential functions including three-body corrections. A parallel implementation of *Turbomole 5.1*<sup>16</sup> was used for the quantum mechanical calculations.

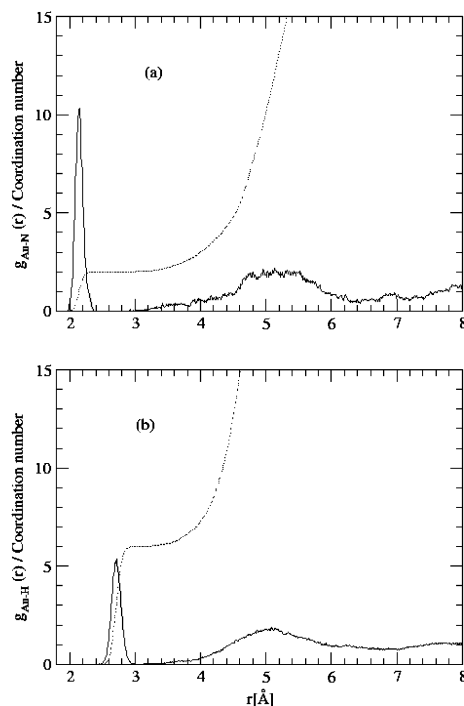
The QM/MM simulation was performed using a cubic box with 1 Au(I) ion and 215 ammonia molecules corresponding to the density of 0.690 g/cm<sup>3</sup> at the simulation temperature of 235 K. Details of the simulation protocol are given in ref 7 and the Supporting Information. From the simulation data, structural (RDF, CND, ADF) as well as dynamical properties (ion-ligand stretching frequency, mean residence times)<sup>13,17,18</sup> were evaluated.

The Au<sup>+</sup>-NH<sub>3</sub> energy reaches the optimal value of -45.0 kcal/mol at a Au-N distance of 2.19 Å. The calculated BSSE is small, amounting to only 0.8 kcal/mol. The Au(NH<sub>3</sub>)<sub>n</sub><sup>+</sup> binding energies obtained from MP2 and CCSD(T) calculations (see Table 1) are considerably lower than the HF energies. The Au-N distances, in particular that of the most stable structure (Au-diamine complex), are not changed to an extent that would produce larger structural changes in the simulation. The lowest binding energy was obtained for *n* = 2 at each level of theory, predicting a very stable linear conformation. The Au-N distance of this stable complex obtained from the highest correlated molecular orbital approach, CCSD(T), has a value identical to the HF result, whereas the MP2 calculation yields an underestimated value. The calculation for Au(NH<sub>3</sub>)<sub>3</sub><sup>+</sup>

**Table 1.** Binding Energies and Au-N Distances<sup>a</sup> Obtained from the Optimized Structure, Au(NH<sub>3</sub>)<sub>n</sub><sup>+</sup>, Relative to the Single Component

	<i>n</i> = 1		<i>n</i> = 2		<i>n</i> = 3	
	$\Delta E_{\text{bind}}$	$r_0$	$\Delta E_{\text{bind}}$	$r_0$	$\Delta E_{\text{bind}}$	$r_0$
HF	-45.0	2.19	-47.8	2.13	-36.2	4.36, 2.13 <sup>b</sup>
MP2	-56.9	2.14	-60.3	2.10	-46.2	4.12, 2.10 <sup>b</sup>
CCSD(T)	-54.9	2.15	-60.4	2.13	-45.9	4.22, 2.11 <sup>b</sup>

<sup>a</sup>  $r_0$  is the distances in Å, and  $\Delta E_{\text{bind}}$  is the energy in kcal/mol. <sup>b</sup> An average of two short bonds.



**Figure 1.** (a) Au-N and (b) Au-H radial distribution functions (solid line) and their corresponding running integration numbers (dotted line).

system shows only the two ligands close to the ion, again pointing out the stable complex for Au(NH<sub>3</sub>)<sub>2</sub><sup>+</sup>.

The Au-N and Au-H radial distribution functions (RDFs) and their running integration numbers are displayed in Figure 1, and the main structural parameters are listed in Table 2. A narrow and well-separated peak located at 2.15 Å is observed for the first solvation shell, indicating a rigid structure of the first shell. A single coordination number of 2.0 was found for this shell corresponding to a diamine complex, quite in contrast to the flexible, mainly four-coordinated hydrate complex.<sup>7</sup> The higher coordination number in the case of H<sub>2</sub>O seems to reflect the higher affinity of Au<sup>+</sup> to H<sub>2</sub>O compared to NH<sub>3</sub><sup>3</sup>, and the preference for the lower coordination number in the case of ammonia is certainly also related to the bulkier ligands, making the two-fold coordinated complex a more

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**Table 2.** Characteristic Value of the Radial Distribution Function  $g_{\alpha\beta}(r)$  for Au<sup>+</sup> in Liquid Ammonia Obtained from QM/MM Simulation<sup>a</sup>

atom pair		$r_{m1}$	$r_{m1}$	$N_{\alpha\beta}(m_1)$	$r_{m2}$	$r_{m2}$	$N_{\alpha\beta}(m_2)$
$\alpha$	$\beta$						
Au	N	2.15	2.4	2.0	5.01	6.4	~27
Au	H	2.71	3.69	6.0	5.07	7.0	~90

<sup>a</sup>  $r_{m1}$  and  $r_{m2}$  are the distances in Å of the  $i$ th maxima and minima of  $g_{\alpha\beta}(r)$ .  $N_{\alpha\beta}(m_i)$  is the average coordination number integrated up to  $r_{mi}$  of the  $i$ th shell.

favorable conformation. This is also reflected by the sharp decay of stabilization energy per ligand from  $n = 2$  to  $n = 3$ . The obtained Au<sup>+</sup>–N distance is relatively short compared to other monovalent ions, e.g. Na<sup>+</sup> in liquid ammonia,<sup>10</sup> forming a Na(NH<sub>3</sub>)<sub>5</sub><sup>+</sup> complex with a Na–N distance of 2.55 Å. Li<sup>+</sup> in liquid ammonia<sup>9</sup> forms a Li(NH<sub>3</sub>)<sub>4</sub><sup>+</sup> complex with a Li<sup>+</sup>–N distance of 2.15 Å. The short Au<sup>+</sup>–N distance is not very surprising, as the ion coordinates only to two ligands, whereby ligand–ligand repulsion (which is complex with more ligands giving rise to increased ion–ligand distances) remains very small. This gold(I)–diamine complex has already been predicted from the electrochemical equilibrium of the gold ore leaching process using ammoniacal solution in the presence of iodine as oxidant.<sup>1</sup>

The well-defined second peak of the Au–N RDF corresponding to the second solvation shell is centered at 5.01 Å. The value of the Au–N RDF between first and second hydration shell reaches zero, thus indicating no significant ligand exchange processes. The second peak of the Au–H RDF is centered at almost the same distance as that of the Au–N RDF, thus showing a highly disordered second shell with no recognizable dipole orientation.

The unusually large second shell coordination number of ~27 NH<sub>3</sub> molecules confirms the rather loose order and appears to be a specific characteristic of Au(I) as a similar value (~33) was found for Au(I) in water.<sup>7</sup> The fact that there are only two ammonia molecules in the first shell opens the possibility of binding a larger number of ammonia molecules in the second shell, as the ion charge is not well shielded considering the size of the ion and the small number and size of the ligands, both in the case of H<sub>2</sub>O and NH<sub>3</sub>. This appears to be the reason for the large second coordination number. The N–Au–N angle distribution function shows a single peak located at 175° which corresponds to a linear configuration of the first-shell diamine complex.

The power spectra of the Au–N stretching vibration in the first solvation shell obtained by approximative normal coordinate analysis shows a well-defined single peak, thus supporting the rigid structure of the first solvation shell. The peak maximum of 350 cm<sup>-1</sup> corresponds to a force constant of 100 Nm<sup>-1</sup>.

Experimental structures, especially EXAFS data, being the best comparable ones due to the low concentration used, are not available yet for Au<sup>+</sup> in liquid ammonia, but the good agreement of structural properties obtained from QM/MM simulations of other ions where experimental data are available proves the reliability of the QM/MM method (see Table 3).

As no first-shell exchange processes were observed, the mean residence time of ammonia molecules in the second shell was calculated from the QM/MM simulation, using the “direct” method<sup>18</sup>

**Table 3.** Structural Properties of First Solvation Shell of Several Ions<sup>a</sup>

ion	system	$r_{ion-N}$	$n$	method	ref
Au <sup>+</sup>	liquid ammonia	2.15	2	QM/MM	this work
Cu <sup>2+</sup>	liquid ammonia	2.05/2.17	6	QM/MM	19
Cu <sup>2+</sup>	liquid ammonia	2.00/2.17	6	EXAFS	20
Co <sup>2+</sup>	liquid ammonia	2.22	6	QM/MM	21
Co <sup>2+</sup>	Co(NH <sub>3</sub> ) <sub>6</sub> (PF <sub>4</sub> ) <sub>2</sub>	2.19	6	XRD	22

<sup>a</sup>  $r_{ion-N}$  is the ion–N distances in Å,  $n$  is the average coordination number.

with a  $t^*$  value of 0.5 ps. A mean residence time of 7.1 ps in the second solvation shell was observed. This value is slightly higher compared to the corresponding result for water (4.6 ps).<sup>7</sup> In contrast, the mean residence time of Ag(I)’s second hydration shell is significantly shorter (2.6 ps)<sup>18</sup> despite the smaller coordination number of 17.1.<sup>8</sup>

Ab initio QM/MM molecular dynamics simulation was used to characterize structural and dynamical properties of the solvated Au(I) in liquid ammonia leading to a linear rigid structure of the first-shell diamine complex. The large second-ordination shell amounting to 27 NH<sub>3</sub> molecules seem to be a specific characteristic of the solvated Au(I) ion, as a similar behavior was obtained for Au(I) in water.

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**Supporting Information Available:** Potential functions, simulation protocol, video clip, ref 21. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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