

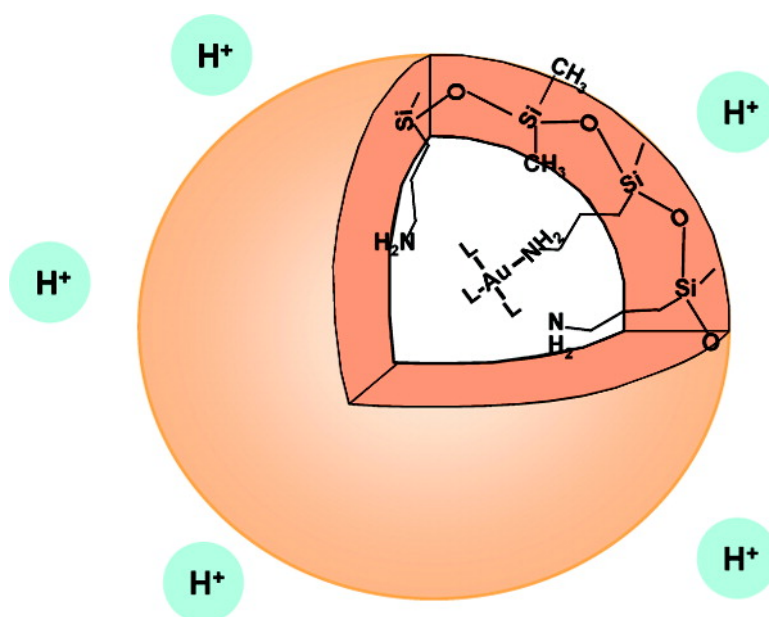
Communication

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Striking Confinement Effect: AuCl_4^- Binding to Amines in a Nanocage Cavity

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It is well-known that the protonation constant of an amine and dissociation constant of a carboxylic acid are strongly influenced by the ability of their environment to stabilize charges. Thus, they are affected by the dielectric constant of the medium and presence of other charged or polarizable groups nearby. For example, the protonation constant of the second lysine in acetoacetate decarboxylase is shifted from a pK_a of 10 to ~ 6 due to electrostatic repulsion between two charged ammonium ions and the low dielectric constant of the hydrophobic environment of a protein,¹ where solvation stabilization and charge screening are much weaker than those in an aqueous medium. This phenomenon of pK_a shift is also observed in nonbiological systems. For example, a pK_a shift of 1–2 pH units is observed for the amines in the interior of a G4-PAMAM dendrimer,² ~ 1 unit in a vesicle,³ 1–2 units in a micelle,^{4,5} and as much as 4–5 units at the air–water interface.³ Likewise, a difference of ~ 2 pH units between the protonation constants of propylamine and octylamine in an aqueous solution has been attributed to the agglomeration of octylamine consequent to its hydrophobic octyl group, thus affecting solvation stabilization of the ammonium ion.⁶ These shifts are all attributed to a combination of effects of electrostatic repulsion and a hydrophobic medium.

The magnitude of pK_a shift should be concentration dependent, since factors such as electrostatic repulsion involves interaction between molecules. One consequence of this can be illustrated with a simplistic example of amines in a small water droplet. Neglecting the effect of ionic strength, protonation of one amine increases the pH of a 2 nm diameter water droplet to ~ 13.5 and a 10 nm droplet to ~ 11.5 (Supporting Information, Figure S1). Since the protonation constant of primary amines is ~ 10 , these values suggest that no more than one amine group could be protonated in a nm-size water droplet.

Recently, we have synthesized siloxane and carbosilane nanocages with 2–5 nm diameter cavities.^{7,8} One of these nanocages was designed to possess 7–9 amines as aminopropyl groups tethered to the interior surface of a porous siloxane shell that forms a 2 nm cavity.⁷ Because of the considerations mentioned above, we expect that, in a near neutral pH solution of these nanocages, no more than one of the amine groups in each cavity would be protonated. The remaining amine groups, being neutral, should then be available for interactions that utilize the electron lone pair on the N atom.

We have examined the binding of AuCl_4^- complexes to these interior amines. AuCl_4^- can bind to an amine either by ligand exchange with a neutral amine that results in changing the Au–Cl coordination number (eq 1) or by forming an ion pair with a protonated amine without any change in the Au–Cl coordination number (eq 2). Since these different modes of binding are sensitive

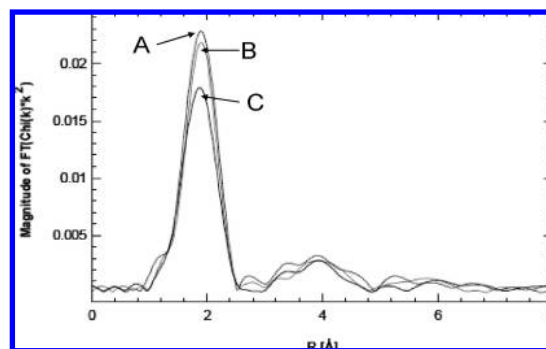


Figure 1. Magnitude of the Fourier transformed EXAFS (without phase correction) for 430 μM Au(III) in anhydrous methanol, $\text{Cl}/\text{Au} = 4$: (A) no added amine, $\log[\text{H}^+] = -3.7$; (B) in the presence of AS, $\text{NH}_2/\text{Au} = 1$, $\log[\text{H}^+] = -4.7$; (C) in the presence of nanocage, $\text{NH}_2/\text{Au} = 1$, $\log[\text{H}^+] = -4.0$. The main peak in curve C is slightly skewed to the left compared with the others because of contribution from a small, shorter bond length component (Au–N).

to the state of the amine, they can be used to probe whether its protonation is affected by the nanocage environment.



The binding of the AuCl_4^- complex was monitored spectroscopically using a combination of EXAFS and UV–vis spectroscopy, assuming that the Au–N coordination can be accurately approximated with the Pt–N coordination. This assumption is reasonable because of the similar electronic configuration of Pt and Au atoms. The Au–Cl bond is longer than the Au–O or Au–N bond, and a Cl atom scatters X-ray more strongly than O or N atoms. Thus, these bonds can be distinguished in EXAFS (Figure 1 and S4). The ligand-to-metal charge transfer band at 227 nm in the UV region is also sensitive to a Cl versus O atom (Figure S2). From the known hydrolysis constants for AuCl_4^- (Table S1) and data from control experiments using different solutions of known pH, Au(III) and Cl^- concentrations, a quantitative correlation between the Au–Cl coordination number (CN), and the extinction coefficient at 227 nm in UV spectroscopy can be established (Figure S3). This correlation was shown to be applicable for both aqueous and methanol solutions. The latter was used to dissolve the nanocages. From this correlation, changes in the Au–Cl CN could be quantified. When the formation of a Au–O bond by hydrolysis was either absent or could be accounted for by control experiments, the Au–N coordination could be determined. In addition to a methanol solution of HAuCl_4 , another set of control experiments used solutions of 3-aminopropylmethylbis(trimethylsilyloxy)silane (AS), which mimics the aminopropyl group in the nanocage.

Changes in the Au–Cl CN in methanol solutions of HAuCl_4 at different H^+ concentrations were followed as a function of time using

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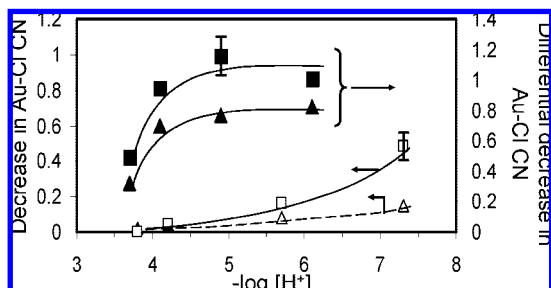


Figure 2. Decrease in Au–Cl CN in methanol solutions of HAuCl₄ and AS adjusted to different H⁺ concentrations after 10 (Δ) or 90 min (□), and differential changes in CN between solutions containing nanocages compared to those containing AS after 90 (▲) or 3000 (■) min. Representative uncertainties are shown. [Au(III)] = 72 μM, Cl/Au = 4.

UV–vis (Figure 2). With or without AS, the Au–Cl CN decreased slowly with time and acid concentration (log[H⁺]). The changes in CN after 90 min were ~0, 0.2, and 0.4 for solutions of log[H⁺] of –4.0, –5.5, and –7.5, respectively. That the presence of AS did not affect changes in CN is expected because, at these proton concentrations, the free amine AS would exist predominantly in the protonated form and, hence, reaction (1) cannot proceed. The observed “background” exchange was due to methanolysis by the solvent as well as hydrolysis by the small amount of water introduced with the Au complex, HCl, and NaOH. That the presence of AS did not affect CN also suggests that, in the protonated form, AS does not catalyze solvolysis. The low degree of ligand exchange when the solution is more acidic than log[H⁺] of –4.7 was independently confirmed with EXAFS data. The introduction of nanocages to HAuCl₄ solution (–log[H⁺] 3.6–6.5) resulted in substantial rapid decrease in CN beyond the background ligand exchange described above (Figure 2). Within 10 min, a decrease of ~0.5 was observed, which increased slowly to over 0.8 by 90 min, and approached unity at long times. This additional, rather rapid decrease in Au–Cl is attributed to ligand exchange of chloride by amine in the nanocage. Unlike the free amine in AS in solution, these enclosed amines are not protonated and capable of effecting ligand exchange.

To further establish that, in experiments with nanocages, ligand exchange occurs with amine groups inside the cavity, cyclic voltammetry was conducted. If the Au complexes were in the interior of the nanocages, they would not be accessible to the electrode and no oxidation or reduction peaks of Au could be detected. On the other hand, if the Au complexes were either in solution or anywhere exterior to the nanocages, they would be able to undergo reduction, and characteristic cathodic peaks would be detected at 0.19 and 0.56 V, assignable to reduction of Au(III) in AuCl₄[–] to Au(0) and Au(III) in Au₂O₃ to Au(0), respectively.⁹ These reduction reactions depend little on the nature of the ligand and are not affected by solvolysis.

The cyclic voltammetry results are shown in Figure 3. In the absence of nanocages, the cathodic current decreased slowly with time, losing ~15% in 90 min. In the presence of nanocages (Au/NH₂ ratios <1), the decrease was much faster, and the cathodic current was practically eliminated after 90 min. For Au/NH₂ > 1, however, Faradaic current could be detected whose magnitude increased with increasing amounts of Au (Figure S5). The absence of cathodic current implies that the Au complexes were not accessible to the electrode, consistent with their binding to the interior of the nanocages. That this was observed only when the Au/NH₂ ratio was less than unity was expected; there would not be any amine available to exchange with additional AuCl₄[–]. An additional control experiment was performed using, instead of nanocages, its precursors before cleavage of the carbamate bond to form interior amines and the cavity.⁷ The decrease in cathodic current became similar to that in experiments using AS. This ruled out

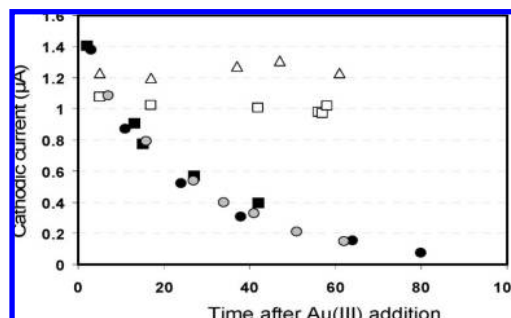


Figure 3. Magnitude of cathodic current in cyclic voltammetry of AuCl₄[–] in: (□) methanol solution at log[H⁺] = –7.4; (Δ) methanol solution of siloxane sphere precursor of nanocages at log[H⁺] = –7.4, a control experiment to test whether Au complexes adsorb on the siloxane shell, by using nanocage precursor before cleavage of carbamate bond to form interior amines; (■) methanol solution of nanocages at log[H⁺] = –7.1; (●, and gray circles) methanol solution of nanocages at log[H⁺] = –7.4.

absorption of the Au complex to the siloxane shell as the cause for current decrease.

In conclusion, quantitative analysis of data from a combination of EXAF and UV–vis spectroscopies and cyclic voltammetry established unequivocally that amines tethered to the interior wall in the cavity of a 2 nm siloxane nanocage have distinct properties from those in bulk solution. They form ligands to Au(III) complexes as expected for neutral amines, even when the exterior solution is acidic. This arises because protonation of more than one amine within the high local concentration inside the nanocages would be deterred by electrostatic repulsion. Consequently, these amines exhibit chemical behavior expected of neutral species. From Figure 2, the shift in the protonation constant of these amines is estimated to be as high as 5–7 pH units, much higher than with many other nanostructures such as dendrimers. This is likely because of the density and restricted mobility of amines within the confined space and hydrophobicity of the shell environment.

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Supporting Information Available: Experimental details including preparation of nanocages, UV–vis, correlation between Au–Cl CN and extinction coefficient, cyclic voltammetry, reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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