In situ generation and characterization of gold(I) complexes from $K[AuCl_4]$ in aqueous solutions

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Abstract

A highly reactive gold(I) species, assigned as $[AuCl_2]^-$, is electrogenerated and its subsequent chemical reactions with L-cysteine, D-penicillamine and imidazole are monitored by electrochemical methods. By this *in situ* method, electrochemical data for (L-cysteinato)gold(I) and (D-penicillaminato)gold(I) were determined and compared to relevant gold(I) species. Electrochemical and spectroelectrochemical data for the reduction of $[AuCl_4]^-$ in water is also presented.

Introduction

We recently reported [1] the electrochemical and spectroelectrochemical properties of the gold(III) complex, $K[AuCl_4]$, and the gold(I) complexes, $Au[P(R)_3]Cl$ and $Au[P(R)_3]_2^+$, where $R = C_6H_5$, C_2H_5, OC_6H_5 and OC_2H_5, in non-aqueous solvents. In addition to providing data on the electron transfer properties of these species, we were able to monitor and enhance the generation of $Au[P(R)_3]Cl$ and $Au[P(R)_3]_2^+$ from $[AuCl_4]^-$ and PR_3. In this manuscript we will extend the non-aqueous studies to examine the electron transfer properties and ligand addition reactions of $K[AuCl_4]$ in an aqueous solvent system. The change of solvent will allow examination of gold(I) compounds that have relevance to the treatment of rheumatoid arthritis [2–4] which were not examined in the non-aqueous study due to solubility and/or stability factors.

Previous electrochemical data on $[AuCl_4]^-$ in aqueous media has focussed on the formation of $[AuCl_4]^-$ from a gold electrode [5] and how this reaction affects the behavior of gold electrodes in various solvent conditions [6, 7]. Although cyclic voltammetric data for $K[AuCl_4]$ in HCl with a carbon paste electrode [8, 9] has been reported, voltammetric investigations of aqueous gold solutions have not been extensive. Our voltammetric data at a platinum electrode is consistent with the mechanism proposed for the reduction of $HAuCl_4$ in CH_3CN [10]. Of significance to our studies, the observation of a gold(I) species, $[AuCl_2]^-$, was reported. In aqueous systems, we also observe the formation of a gold(I) species and we can electrochemically monitor the reaction of this species with specific ligands.

By this method, the generation of (L-cysteinato)gold(I) and (D-penicillaminato)gold(I), were monitored by electrochemical techniques and consequently we were able to measure electrochemical data on these complexes. Cysteinatogold(I) is directly used in the treatment of rheumatoid arthritis, while penicillamine is administered in conjunction with the gold drugs to reduce the toxicity of gold [11]. The effect of the penicillamine is to redistribute gold in the body, presumably by formation of a gold penicillamine complex. Our study presents the first electrochemical data on either (L-cysteinato)gold(I) or (D-penicillaminato)-gold(I), which will be compared with $Au[P(R)_3]Cl$ and $Au[P(R)_3]_2^+$.

Steric and electronic effects across P–Au–N linkages are of interest due to reports of antitumor activity of auranofin (2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranosato-5-triethyl phosphine gold(I)) against P388 Leukemia [12, 13] and possible binding to DNA [14]. Hence, the results from electrochemical studies of the addition of imidazole to the electrogenerated gold(I) species will also be presented and discussed.

Equipment and techniques

Electrochemical experiments were performed on either a BAS-100A or an EG&G Princeton Applied Research 273 potentiostat/galvanostat coupled to an EG&G Princeton Applied Research model RE0091-XY recorder. A platinum-button working electrode,

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approximate area 0.008 cm^2, a platinum wire counter electrode and a SCE reference electrode, separated from solution with a bridge, comprise the three-electrode system for the voltammetric studies. In the bulk electrolysis studies, the three-electrode system consisted of a large platinum mini-grid working electrode, approximate area 0.025 cm^2, and a SCE reference electrode separated from solution by a bridge in one compartment of a two compartment cell. A platinum wire counter electrode is placed in the second compartment, and the two sides of the cell are separated by a frit. The supporting electrolyte was 0.6 M $NaClO_4$ unless otherwise stated.

Spectroelectrochemical data were recorded on a Perkin-Elmer 3B UV–Vis spectrometer using a BAS CV-27 potentiostat coupled to an IBM 7424 MT X-Y recorder and an IBM PS/2 model 50 computer. The three electrodes used were a large platinum mini-grid working electrode, a platinum wire counter, and a platinum wire pseudo-reference electrode. The supporting electrolyte was 0.6 M $NaClO_4$ unless otherwise stated. The pH of the solutions were measured on a SA 720 Orion pH meter with an Orion combination pH electrode. The electrochemical cells are home built and are designed for inert-atmosphere studies [15–17].

It is well known that $[AuCl_4]^-$ undergoes hydrolysis in aqueous solutions [18–20] and establishes itself in equilibrium with other chlorogold(III) species. Therefore, allowing hydrolysis to occur would complicate the electrochemical investigations by increasing the number of gold species present. Hence, the pH was adjusted to near 1.7 to limit the extent of the hydrolysis for all reported studies.

Chemicals

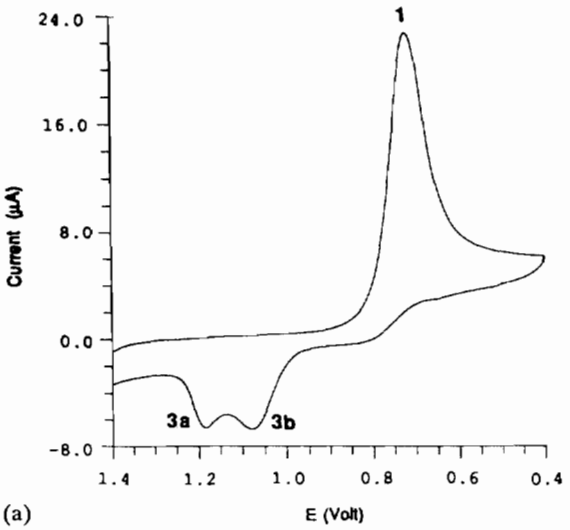
$K[AuCl_4]$ was purchased from AESAR, L-cysteine (97%), imidazole (99%), and D-penicillamine (99+%) were purchased from Aldrich and all were used without further purification. The HCl (0.1000 N) and HNO_3 (concentrated, 99.999+%) were purchased from Fisher Scientific Company and Aldrich, respectively, and used to adjust the pH of the doubly distilled water/$NaClO_4$ solution. The $NaClO_4$ (99+%) was purchased from Aldrich and used without further purification. The doubly distilled water was from a Milli-Q purification system.

Results and discussion

$K[AuCl_4]$ and generation of $[AuCl_2]^-$

Cyclic voltammetric results for $K[AuCl_4]$ added to a solution acidified to pH 1.67 with HNO_3 are shown in Fig. 1(a). Under these conditions, there is a reduction wave (wave 1, Fig. 1(a)), a reduction wave due to proton (wave 2, not shown in Fig. 1(a)) and two overlapping oxidation waves (waves 3a and b, Fig. 1(a)) which are present only after scanning through wave 1. The value of E_{pc} for wave 1 (Fig. 1(a)) is 0.75 V versus SCE. Wave 3a and b have E_{pa} values of 1.17 and 1.09 V versus SCE. See Table 1 for wave analysis data under these conditions.

Figure 1(b) is a representative cyclic voltammogram of $K[AuCl_4]$ when added to a solution acidified to pH 1.71 with HCl. Wave 1 (solid line, Fig. 1(b)) has an E_{pc} of 0.63 V versus SCE and wave 3, now one broad wave (solid line, Fig. 1(b)) has an E_{pa} of 1.08 V versus SCE. Wave 1 is 120 mV more negative in the presence



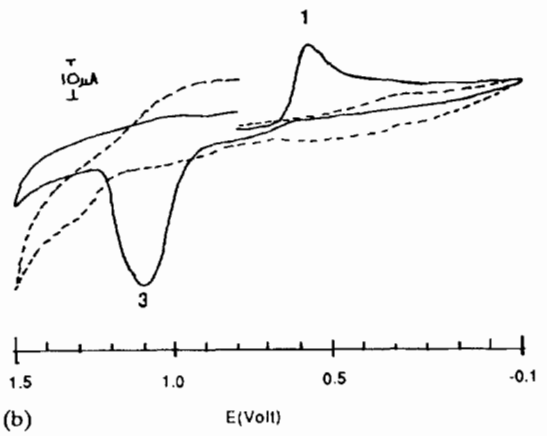


Fig. 1. (a) Cyclic voltammogram of 0.0023 M $K[AuCl_4]$ in 0.6 M $NaClO_4/H_2O$ acidified to pH 1.67 with HNO_3 at a scan rate of 100 mV/s. Potential range 1.4–0.4 V. (b) Cyclic voltammogram of 0.0033 M $K[AuCl_4]$ in 0.6 M $NaClO_4/H_2O$ acidified to pH 1.71 with HCl at a scan rate of 100 mV/s. Potential range 1.5 to −0.1 V. The dotted line is the result obtained in the absence of $K[AuCl_4]$.

TABLE 1. Electrochemical wave analysis of $K[AuCl_4]$ in aqueous solutions

Solution conditions	Figure	Wave	E_p[a]	$E_p - E_{p/2}$[b]	$ip/v^{1/2}$	Scan rate dependence[c]
pH 1.67 HNO_3 $NaClO_4/H_2O$	1(a)	1	0.75	66	constant	negative
		2/2'	−0.39[d]			
		3a	1.17	53	constant	positive
		3b	1.09	46	constant	positive
pH 1.71 HCl $NaClO_4/H_2O$	1(b)	1	0.63	55	constant	negative
		2/2'	−0.43[d]			
		3	1.08	88	constant	positive

[a]Volts vs. SCE, scan rate of 100 mV/s. [b]Millivolts, scan rate of 100 mV/s. [c]Shift of E_p as a function of increased scan rate. [d]$E_{1/2}$ values for wave 2 (reduction) and 2' (reoxidation) due to the presence of proton. The proton reduction and reoxidation waves are not shown in the Figures.

of Cl^- relative to the solution acidified with HNO_3. Wave 3 is coupled to wave 1 since it is not present until scanning through the reduction wave. The dotted line in Fig. 1(b) is the background scan obtained in HCl at pH 1.71. Also present under these conditions, but not shown in Fig. 1(b), is the proton reduction process (wave 2) located at $E_{1/2} = -0.43$ V versus SCE. Wave analysis data under these conditions can also be found in Table 1.

Although waves 1 and 3 are coupled, the separation between them is too large for a reversible electron transfer. For example, ΔEp is 330 mV in Fig. 1(a) and 450 mV in Fig. 1(b). These data imply that a chemical reaction is coupled to the reduction of $[AuCl_4]^-$ (wave 1) and that wave 3 is due to the oxidation of the product of the chemical reaction. A reversible reoxidation wave is not observed for wave 1 up to scan rates of 1000 mV/s. Bulk electrolysis at 0.55 V versus SCE results in a value of n of 2.55 ± 0.21 with the formation of a gold film on the electrode, indicating reduction to Au metal. Hence, this suggests that process 3 (Fig. 1(a) and (b)) is due primarily to the oxidation of the Au film, which is generated by the reduction of $[AuCl_4]^-$. Wave 1 is the principal wave observed after scanning through wave 3 in multiple cyclic voltammetric experiments and hence regeneration of Au(III) occurs by wave 3.

Our data in HNO_3 and HCl solutions are consistent with earlier studies [6, 7] of the oxidation of gold electrodes in the presence of chloride ion, in which an oxidation wave located at potentials near $E_{pa} = 1.0$ V versus SCE is reported. These studies demonstrated that the electron transfer process involves the adsorption of chloride onto the gold surface to produce a soluble Au(I) chloride species. The exact gold species generated is very sensitive to solvent conditions, particularly the chloride ion concentration. This sensitivity of the oxidation process (wave 3) to solvent conditions is evidenced, in our studies, by the difference in wave 3 in HNO_3 and HCl solutions.

An incidental aspect of the electrochemical response of $[AuCl_4]^-$ is that for both acid solutions multiple scans in the cyclic voltammogram show the development of a second reduction wave at $E_{pc} = 0.81$ V versus SCE. This process is small in current and is found only after scanning through wave 3. Hence, this wave may be due to the reduction of an electrogenerated aqueous Au(I) species, as found under non-aqueous conditions [1]. However, characterization of this process was not performed.

Spectroelectrochemical data in aqueous solution demonstrates the total loss of Au from solution upon reduction. Figure 2 is representative spectroelectrochemical data for reduction of $K[AuCl_4]$ at −0.2 V versus SCE. $K[AuCl_4]$ is characterized by absorbance bands at 225 and 305 nm, under our conditions. At this concentration (approximately 4×10^{-3} M) the absorbance band at 225 nm is off-scale as shown in Fig. 2(a). Upon reduction this band decreases to baseline and no new absorption processes are observed. Similar results are obtained for the band at 305 nm, as shown in Fig. 2(b). Hence, reduction results in a decrease to baseline of the bands at 225 and 305 nm without the formation of any additional bands.

After the reduction of $K[AuCl_4]$, if the potential is set negative of wave 3, no spectral changes are observed. If the potential is set positive of wave 3, regeneration of the original spectrum is observed. Hence, $[AuCl_4]^-$ is the product of the oxidation process at wave 3. This is in agreement with the multiple scans in the cyclic voltammetric data and further demonstrates that wave 3 is due to the reoxidation of the gold film on the electrode generated upon reduction.

These data for the aqueous solvent system are qualitatively similar to the results reported for the reduction of $K[AuCl_4]$ in CH_2Cl_2, THF and CH_3CN [1]. In CH_3CN,

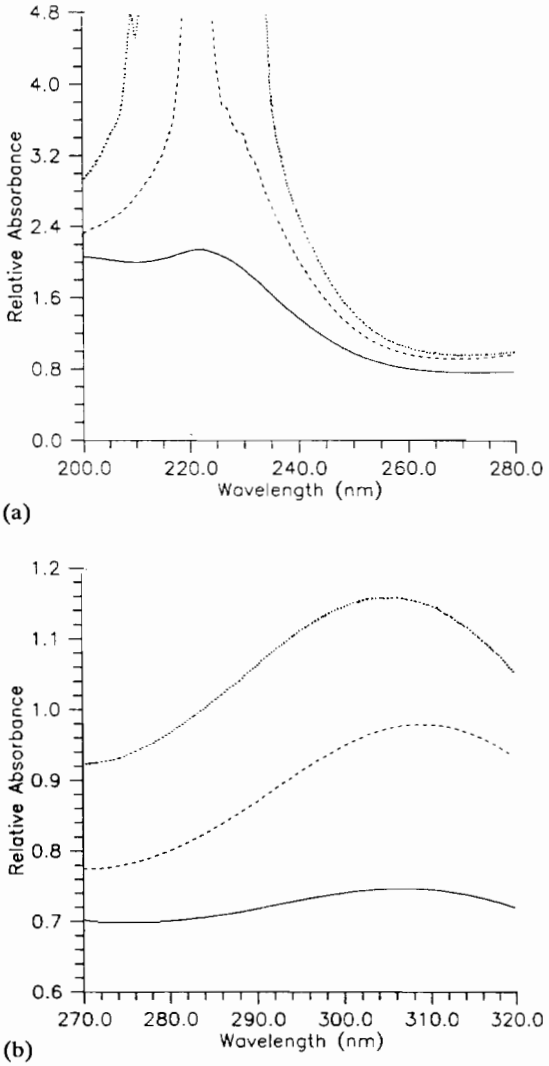


Fig. 2. Spectroelectrochemical data for a 0.0040 M K[$AuCl_4$] in 0.6 M $NaClO_4/H_2O$ acidified to pH 1.67. (a) Spectral range 200–280 nm, $E = -0.2$ V; (b) spectral range 270–320 nm, $E = -0.2$ V. Key: original complex (· · · · ·); $T = 20$ s (– – –); $T = 2$ min (——). Potentials are vs. a Pt wire pseudo-reference.

however, wave 1 consists of two overlapping reduction waves, due to the stabilization of Au^I by this solvent. Our titration studies with cysteine and penicillamine will demonstrate that in an aqueous system wave 1 also consists of two overlapping reduction waves (vide infra). This suggests that wave 1 consists of two reduction steps that sequentially form Au(I) and Au(0).

In agreement with the data in the non-aqueous solvents, the ratio of the peak current to the square root of the scan rate ($i_p/v^{1/2}$) of wave 1 in the present study is constant which indicates a diffusion controlled process. In addition, wave 1 shifts negative with increasing scan rate which is indicative of coupled chemical reaction(s). The $E_p - E_{p/2}$ values of 50–60 mV for wave 1 are probably a deceptive coincidence and *not* evidence of a one electron transfer process in the diffusion controlled step.

The reduction mechanism previously reported for $[AuCl_4]^-$ in acetonitrile has two reversible electron transfer steps with coupled chemical reactions [21]. Based on the similarity of our data, we propose that the mechanism is the same in both aqueous and non-aqueous solvents, provided hydrolysis is limited in the aqueous system. This mechanism is represented in Scheme 1 (eqns. (1)–(3)). Of note is the formation of the gold(I) species,

$$[AuCl_4]^- \rightleftharpoons [AuCl_2]^+ + 2Cl^- \quad (1)$$

$$[AuCl_2]^+ + 2e^- \rightleftharpoons [AuCl_2]^- \quad (2)$$

$$[AuCl_2]^- + e^- \rightleftharpoons Au + 2Cl^- \quad (3)$$

Scheme 1.

assigned as $[AuCl_2]^-$ (eqn. (2)). We clearly see the formation of a gold(I) complex in our ligand addition studies which would, based on Scheme 1, be $[AuCl_2]^-$. However, exact determination of the gold(I) complex in our studies has not been performed. Since the focus of this study is to electrochemically generate and characterize specific gold(I) complexes via ligand addition to this intermediate species, the identity of this species is not critical. However, to be concise, we will refer to this species as $[AuCl_2]^-$ throughout the text.

Addition of cysteine

The reaction of cysteine with the electrogenerated $[AuCl_2]^-$ was examined by monitoring the change in the electrochemical response as a function of the molar ratio of cysteine to gold. An example of the effect of the presence of cysteine is shown in Fig. 3(a)–(c) which are representative cyclic voltammograms at 0, 0.5 and 1:1 molar ratios of L-cysteine to K[$AuCl_4$]. Upon addition of cysteine, the reduction wave (wave 1, Fig. 3(a)) splits into two waves (waves 1a and 1b, Fig. 3(b)). At a 1:1 cys:Au ratio, wave 1b is almost reduced to background levels with wave 1a remaining relatively unchanged, as shown in Fig. 3(c). Wave 1a has an E_{pc} of 0.77 V versus SCE and a value of $E_p - E_{p/2}$ of 40 mV (Fig. 3(c)). This value of $E_p - E_{p/2}$ indicates that wave 1a is a two electron process. Similarly, the oxidation waves (waves 3a and 3b, Fig. 3(a)) also undergo observable changes as the amount of cysteine is increased. Waves 3a and 3b merge and shift to form one broad oxidation wave centered at $E_{pa} = 1.19$ V versus SCE, as shown in Fig. 3(c).

Observation of two reduction waves in the presence of cysteine is due to the rapid reaction of the electrogenerated gold(I) species, $[AuCl_2]^-$, with cysteine to form cysteinatogold(I) at the electrode surface. Wave 1a which is due to the formation of $[AuCl_2]^-$ is un-

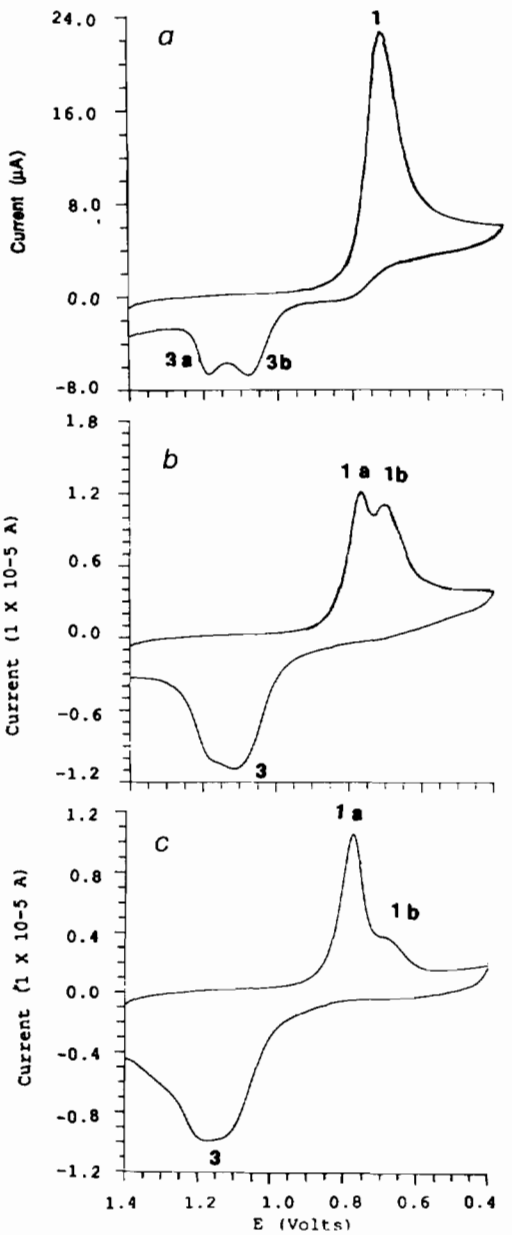


Fig. 3. Cyclic voltammograms of 0.0023 M $K[AuCl_4]$ in 0.6 M $NaClO_4/H_2O$ acidified to pH 1.67 with HNO_3. (a) No cysteine, (b) 0.5:1 cys:Au, (c) 1:1 cys:Au. Potential range 1.40–0.4 V.

affected by the addition of cysteine. However, wave 1b which is assigned to the reduction of $[AuCl_2]^-$ to Au metal is affected by the addition of cysteine. The shift in potential for this process that occurs as cysteine is added is due to the presence of the added chemical reaction between cysteine and $[AuCl_2]^-$. Cyclic voltammetric investigations of cysteine and cystine have been performed under the conditions of the above experiment and the results indicate that the electrochemical response is not due to either the oxidation of free cysteine or reduction of free cystine. Similar electrochemical data for cysteine and cystine have been presented and discussed in the literature [22–24]. Hence, the changes observed upon addition of cysteine (Figs. 3(b) and (c)) are due to the reaction of the electrogenerated gold(I) with cysteine to form cysteinatogold(I). Only at an excess of cysteine is an electrochemical response due to the presence of free cysteine observed during the titration experiment. This data and interpretation is basically the same as what was observed upon addition of $P(R)_3$ to $K[AuCl_4]$ in CH_3CN, THF and CH_2Cl_2 [1].

The broad oxidation wave (wave 3, Fig. 3(c)) is assigned to the oxidation of cysteinatogold(I). Wave analysis of wave 3 (Fig. 3(c)) is not practical under these conditions, however, authentic gold(I) complexes, $Au[P(R)_3]Cl$ and $Au[P(R)_3]_2^+$, where $R = C_6H_5$, C_2H_5, OC_6H_5 and OC_2H_5, in non-aqueous solvents give similar broad oxidation waves [1]. Analysis of the electrochemical response for these complexes indicated that the broad waves were due to chemical reaction(s) coupled to the electron transfer process. Also, we do not see a wave for the reduction of the electrogenerated cysteinatogold(I) to gold metal out to a potential of −1.0 V versus SCE. This is similar to results found for gold(I) complexes of the form $Au(PR_3)Cl$ and $Au[PR_3)_2]^+$ [1].

The addition of excess L-cysteine to $[AuX_4]^-$, where X is a halide ion, results in the formation of (L-cysteinato)gold(I) [25]. The cysteine acts as a reducing agent and the HX prevents the precipitation of the oxidation product, cystine (eqn. (4)). This reaction also occurs under our conditions. Hence, coincident with the change in waves 1 and 3, addition of cysteine results in the formation of cysteinatogold(I). This is evidenced by

$$3CysH + AuBr_4^- \xrightarrow[HBr]{0.1\ M} Cys\text{–}Cys + AuCys + 4Br^- + 3H^+ \quad (4)$$

the precipitation of Au(cysteine), a general decrease in the current for all waves and an increase in the ratio of the current of wave 3 (oxidation of cysteinatogold(I)) to the current of wave 1 (reduction of $[AuCl_4]^-$.

Addition of penicillamine

Ligand addition reactions of penicillamine to electrogenerated $[AuCl_2]^-$ in HNO_3 were also followed by cyclic voltammetric methods. Similar to the addition of cysteine, waves 1a and 1b separate and at a 0.16 molar ratio of penicillamine to $K[AuCl_4]$ have an E_{pc} value of 0.80 and 0.65 V versus SCE, respectively. Wave 1a again has the characteristic $E_p - E_{p/2}$ of a two electron transfer. As the titration progresses wave 1b shifts in potential and decreases in current and at a 0.55 molar

ratio only wave 1a is observed at an E_{pc} of 0.82 V. The cyclic voltammogram at a 1:1 molar ratio of penicillamine to $K[AuCl_4]$ has only the two electron reduction wave (wave 1a) at $E_{pc} = 0.82$ V, similar to the cysteine addition (Fig. 3(c)). Hence, under these conditions, only the reduction of Au(III) to Au(I) is observed in the presence of penicillamine. Addition of excess penicillamine results in total loss of any electroactive species in solution. Cyclic voltammetric investigations of penicillamine were performed under the conditions of this experiment and the data indicate the results obtained are not due to free penicillamine. The interpretation of these results is similar to the cysteine case, however, the chemical reaction between electrogenerated $[AuCl_2]^-$ and penicillamine must occur at a faster rate since a lower concentration of penicillamine is required to observe only wave 1a in the cyclic voltammogram.

Wave 3 also undergoes significant changes as the titration experiment progresses. Ultimately a broad wave at $E_{pa} = 1.14$ V versus SCE is observed which is assigned to the oxidation of Au(I)penicillamine. In addition, a second oxidation wave at $E_{pa} = 1.35$ V is also observed. No reduction wave for Au(I) penicillamine species was found.

Addition of imidazole

The addition of imidazole to electrogenerated $[AuCl_2]^-$ in HNO_3 was also monitored by cyclic voltammetry in the same manner as cysteine and penicillamine. The titration up to a 5:1 molar ratio of imidazole to $K[AuCl_4]$ resulted in no change in the electrochemical response in the cyclic voltammetric experiments. Hence, there is no indication of reaction between the electrogenerated gold(I) species and imidazole.

Au(III) complexes with nitrogen heterocycles have been investigated [19, 26] and the reaction of $[AuCl_4]^-$ with pyridine and substituted pyridines to generate $(py)Au(Cl)_3$ has been investigated kinetically [27]. The rate of the reaction was found to be directly dependent upon the basicity of the pyridine; as the basicity was increased the kinetics of the reaction also increased. Gold(I) complexes with nitrogen ligands are relatively rare and are only stable when either a strong π-acceptor ligand is coordinated to the Au atom or the N-ligands are able to backbond.

From this viewpoint, the observation of no reaction upon the addition of imidazole is not surprising. Imidazole is less basic than pyridine as evidenced by the $pK_{a'}$ values [28] of 6.8 and 8.6 for imidazole and pyridine, respectively. Hence, direct reaction with $[AuCl_4]^-$ is not observed, in addition, since no stabilizing π-acceptor ligand is available to make a Au(I) complex favorable, *in situ* generation of a Au(I)–N complex was also not found.

Discussion

In our previous work, the reduction of $K[AuCl_4]$ in acetonitrile was found to have two overlapping reduction waves with E_{pc} values of 0.07 and -0.08 V versus SCE. Although a comparison of potential data between different solvent systems presents some uncertainty, it is clear that the reduction of $K[AuCl_4]$ requires much less energy in water than in acetonitrile. This is due to the stabilization of Au(I) compounds by acetonitrile and hence, more energy is necessary for the final reduction to gold metal.

The potential for oxidation of the gold(I) complexes examined in water and in acetonitrile are summarized in Table 2. These data suggest that the gold(I) complexes discussed in the present study are significantly easier to oxidize than $Au[P(R)_3]Cl$ species but significantly more difficult to oxidize than $Au[P(R)_3]_2^+$ species. For example, the oxidation of $Au[P(C_6H_5)_3]Cl$ is 350 mV more positive than Au(cysteine) while the oxidation of $Au[P(C_6H_5)_3]_2^+$ is 410 mV more negative than Au(cysteine). These trends reflect that a simple correlation between the strength and number of π-acid and σ-bonding ligands on a series of transition metal complexes and the potential for electron transfer does not always exist. As expected, complexes such as $Au[P(C_6H_5)_3]Cl$ which contain a π-acid ligand, are much harder to oxidize than Au(cysteine), which has only σ-bonding ligands. However, complexes such as $Au[P(C_6H_5)_3]_2^+$, which contain two π-acid ligands are easier to oxidize than either $Au[P(C_6H_5)_3]Cl$ or Au(cysteine), opposite to what would be predicted. The reason is that the second π-acid ligand of $Au[P(C_6H_5)_3]_2^+$ is not tightly bound. This not only mitigates the ligand electronic effects but presents the

TABLE 2. Oxidation potentials of gold(I) compounds[a]

Compound	Concentration[b] (mM)			E_{pa}[c]	
	Solvent	Au	L		
$Au[P(C_2H_5)_3]Cl$	CH_3CN	3.4		1.51	
$Au[P(C_6H_5)_3]Cl$	CH_3CN	3.4		1.54	
$Au[P(OC_2H_5)_3]Cl$	CH_3CN	4.4	5.8	1.86	
$Au[P(OC_6H_5)_3]Cl$	CH_3CN	4.5	4.6	1.76	
$Au[P(C_6H_5)_3]_2^+$	CH_3CN	4.8	11.2	0.78	
$Au[P(OC_2H_5)_3]_2^+$	CH_3CN	4.4	35.0	1.10	
Au[cysteine]	H_2O/HNO_3	2.3	2.3	1.19	
Au[penicillamine]	H_2O/HNO_3	1.8	2.3	1.14	1.35

[a]Phosphine and phosphite complexes are discussed in detail in ref. 1. [b]Concentration of gold complex and/or ligand in the cyclic voltammetric experiment. [c]Volts vs. SCE.

possibility of ligand replacement prior to electron transfer.

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