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COMMUNICATION

The first quantitative detection of silver ion at micromolar levels in water using a redox-switchable ligand

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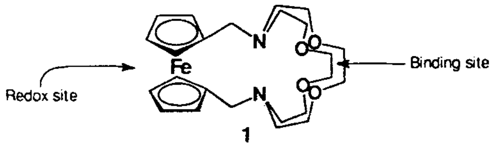
1,1′ - (1,4,10,13 - Tetraoxa - 7,16 - diazacyclooctadecane - 7,16-diyldimethyl)ferrocene, 1, is the first redox-switchable ligand that is useful in aqueous solution. This ligand can then be used to quantitatively detect Ag^+ ion at micromolar concentration levels in such media. The efficacy of this unique ligand results, at least partially, from a novel direct interaction between the ferrocenyl iron atom and the bound silver cation. Differential pulse or square wave voltammetric methods were used to demonstrate the quantitative and reproducible detection of Ag^+ ion in the important concentration range 5–60 μM.

In the quarter of a century since the discovery of crown ethers, literally thousands of cation binders have been developed, each of which exhibits an intrinsic selectivity profile and binding dynamics.[1] During the past decade various approaches to *binding switching* have made it possible to alter these intrinsic properties on demand.[2] In particular, *redox-switchable* ligands have held forth the promise of bringing together binding switching and microscale cation sensing.[3] We report here *proof-of-concept* results for this long-standing goal.

Redox-switchable ligands require a cation binding site, such as a crown ether, in proximity to a redox-active residue such as nitrobenzene,[4] anthraquinone,[5] ferrocene,[6] and others.[7] When the redox-active residue is electron deficient, cation binding is enhanced by reduction of the neutral material whereas, in ligands bearing an electron-rich ferrocene subunit, oxidation of neutral ferrocene introduces a repulsive positive charge into the cation binder.[6] In compound **1** this positive charge is centrosymmetric with respect to the diaza-18-crown-6 portion of this macrocyclic ligand (shown below).



1

The voltammetric behaviour of **1** in acetonitrile has been described in detail elsewhere.[8] In the absence of metal cations, **1** shows a reversible redox couple centered at 0.126 V *vs* SSCE in acetonitrile. This corresponds to the reversible oxidation of the ferrocene subunit. Oxidation of **1** to generate the positively charged ferricinium form is expected to impair the ligand's cation binding ability due to the repulsive electrostatic interaction between the ferricinium group and the macrocycle-bound cation. This electrostatic interaction also makes the oxidation of metal cation complexes of **1** more difficult than that of free **1**, resulting in a substantial positive shift of $E^{o\prime}$ upon cation binding. We have shown that if the binding constant (between **1** and the metal cation) is greater than $10^5\ M^{-1}$, the voltammetric behavior of **1** in the presence of substoichiometric concentrations of metal cation exhibits two resolved sets of waves that correspond to the $\mathbf{1}^+/\mathbf{1}$ and $\mathbf{1}^+\cdot M^+/\mathbf{1}\cdot M^+$ redox couples.[8] It is clear then that, under these conditions, the concentration of M^+ can be evaluated from the peak current of the $\mathbf{1}^+\cdot M^+/\mathbf{1}\cdot M^+$ redox couple. In acetonitrile solution we have observed cation-dependent voltammetric behavior of **1** with several alkali and alkaline-earth metal cations as well as with silver ion.[8,9] However, for reasons of practicality, it would be desirable to extend these interactions to aqueous media. In this communication, we demonstrate that compound **1** maintains a strong affinity for silver ions in aqueous media and, thus, it is the first redox-switchable ligand which is effective in water. This is, at least partially, due to a novel interaction between the ferrocenyl ion atom and the bound Ag^+ ion.[8]

The voltammetric behavior of **1** in aqueous solution is strongly pH dependent. The ligand's two amine nitrogens can undergo protonation and, due to their proximity to the ferrocene subunit, substantially affect its oxidation potential. The corresponding proton exchange equilibria are:

$$\mathbf{1} + H^+ \rightleftharpoons \mathbf{1}\cdot H^+ \qquad (1)$$

$$\mathbf{1}\cdot H^+ + H^+ \rightleftharpoons \mathbf{1}\cdot H_2^{2+} \qquad (2)$$

As the extent of protonation of **1** increases,[10] electron density is withdrawn from the ferrocene nucleus and oxidation becomes thermodynamically more difficult. Thus, the observed oxidation potential of **1** is 0.18 V *vs* SSCE at pH 10, 0.33 V at pH 7, and 0.55 V in acidic medium. As protonation hinders cation complexation, we conducted our experiments at a pH high enough to avoid extensive protonation of the ligand but not so high that would cause precipitation of metal hydroxides. We found that the pH range 8.5–10 fulfills both requirements.

Differential pulse voltammetry (DPV) was used throughout the experiments reported here to allow work with concentrations of ligand and metal cation much lower than can be detected with linear sweep or cyclic voltammetry.[11] Figure 1A shows the DPV response of a glassy carbon electrode in an aqueous solution containing a concentration of 70 μM **1**. As expected, the only peak observed in the anodic scan corresponds to the reversible oxidation of the ferrocenyl subunit of **1**. Figure 1B shows the response of the same electrode after addition of 30 μM of Ag^+ ion to the solution. The new peak at more positive potentials (labelled II in the figure) corresponds to the reversible oxidation of the $\mathbf{1}\cdot Ag^+$ complex. Although the complete resolution of peaks I and II was not possible, the shape of the differential voltammogram permits the accurate determination of the peak currents for the oxidation of the $\mathbf{1}\cdot Ag^+$ complex (peak II) and the free ligand **1** (peak I). As noted, the high equilibrium constant for complex formation between **1** and Ag^+ ion means that the concentration of $\mathbf{1}\cdot Ag^+$ complex in solution is approximately equal to the added concentration of Ag^+ ion. Thus, we can take this peak current ($i_{pa,II}$) as an analytical signal to monitor the concentration of Ag^+ ion in the solution. This is clearly demonstrated by the data plotted in Figure 2 which shows the linear correlation between $i_{pa,II}$ and the concentration of Ag^+ ion added to the solution in the range from 10 to 60 μM. Figure 2 also shows the variation of the peak current corresponding to the oxidation of the free ligand ($i_{pa,I}$) which decreases linearly as the concentration of added Ag^+ ion increases. Essentially identical results were obtained with square wave voltammetry which allows the use of faster scan rates.

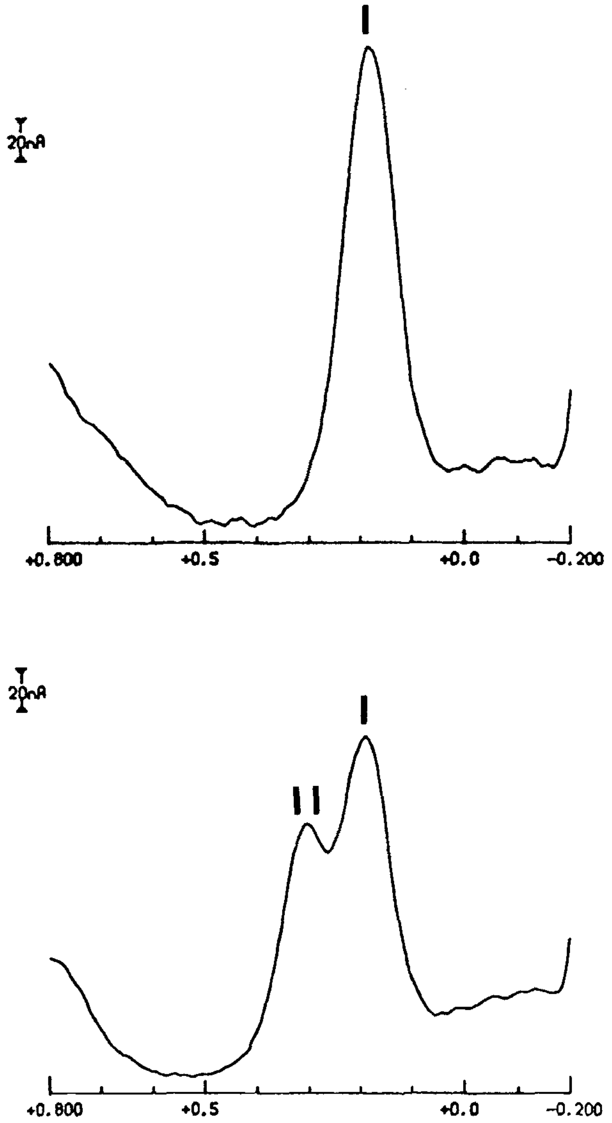


Figure 1 DPV response of a glassy carbon electrode (0.08 cm^2) immersed in an aqueous 0.1 M KNO_3 solution (pH adjusted to 9.7 by addition of NH_3) also containing (A) 70 μM **1**, and (B) 70 μM **1** + 30 μM $AgNO_3$. Voltammetric parameters were as follows: scan rate, 2 mV/s; pulse amplitude, 10 mV; and pulse width, 50 msec.

The concentration of ligand **1** used in the experiment sets the maximum concentration of Ag^+ ion that can be determined by this method. The presence of uncomplexed Ag^+ is problematic because the initial potential of these experiments is enough to drive the cathodic deposition of free Ag^+ on the surface of the working electrode. This results in a sharp anodic stripping peak at 0.11 V corresponding to the process $Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$. In the presence of excess ligand **1**, however, no Ag stripping peak is observed because essentially all the Ag^+ ions are bound to the ligand, thus preventing deposition of metallic silver on the electrode surface. Under these conditions, *it is clear that* $i_{pa,II}$ *provides an accessible and convenient analytical signal to monitor* Ag^+ *solution concentrations.* The linearity of peak current vs $[Ag^+]$ makes possible the use of either calibration curve or standard addition approches. Furthermore, the use of

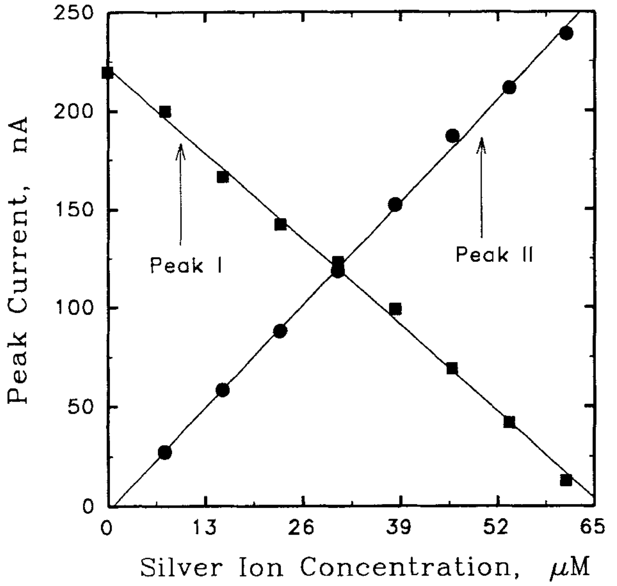


Figure 2 Anodic peak current of peak II (●) and peak I (■) as a function of added silver ion concentration. Currents were recorded using DPV under the conditions of Figure 1.

voltammetric methods results in faster analysis times than those feasible with potentiometric techniques since the equilibration of the system usually takes longer in the latter case. It is interesting to note that the method proposed here—like any other method based on a complexation reaction—will detect either free Ag^+ ions or Ag^+ bound to ligands weaker than **1**. Indeed, Ag^+ ions which are more strongly complexed by other ligands will be effectively masked in the analysis.

We are currently assessing the selectivity of this method for Ag^+ determinations in aqueous solution. Our results indicate that the presence of large excesses of hard cations, such as alkali and alkaline-earth metal cations, does not interfere at all with the determination of Ag^+. This is presumably due to the strong solvation of these cations in aqueous media which decreases substantially the stability of their complexes with **1**. As expected, transition metal cations seem to compete more effectively with Ag^+ ions for the macrocyclic cavity of **1**. For instance, DPV of **1** in the presence of less than 1 equiv of Cu^{2+} or Pb^{2+} exhibits only one peak. The two-peak behavior observed with Ag^+, characteristic of strong binding of the metal ion, is not observed for Cu^{2+} and Pb^{2+}. However, more than 1 equivalent of these metal cations causes shifting and broadening of the single peak observed for the oxidation of the ligand. The determination of Ag^+ in the presence of substantial excess of either Cu^{2+} or Pb^{2+} is made difficult by the shifting and broadening of the voltammetric peaks that the interfering transition metal ions cause. Therefore, synthetic modifications of the structure of **1** that increase its selectivity for Ag^+ *vs* other transition metal ions would be highly desirable for demanding analytical situations.

The principle of using a redox-active ligand, such as cryptand **1**, for the detection and quantitative determination of metal cations can be utilized in a variety of analytical approaches. For instance, compound **1** can be incorporated into a carbon paste electrode which becomes sensitive to the presence of Ag^+ ions in the contacting solution. The square wave voltammograms of Figure 3 demonstrate the difference between the anodic responses of such an electrode in solutions containing no Ag^+ ion (Fig 3A) and increasing concentrations of Ag^+ ion (Figs 3B–G). Indeed, the electrode response in the presence of Ag^+

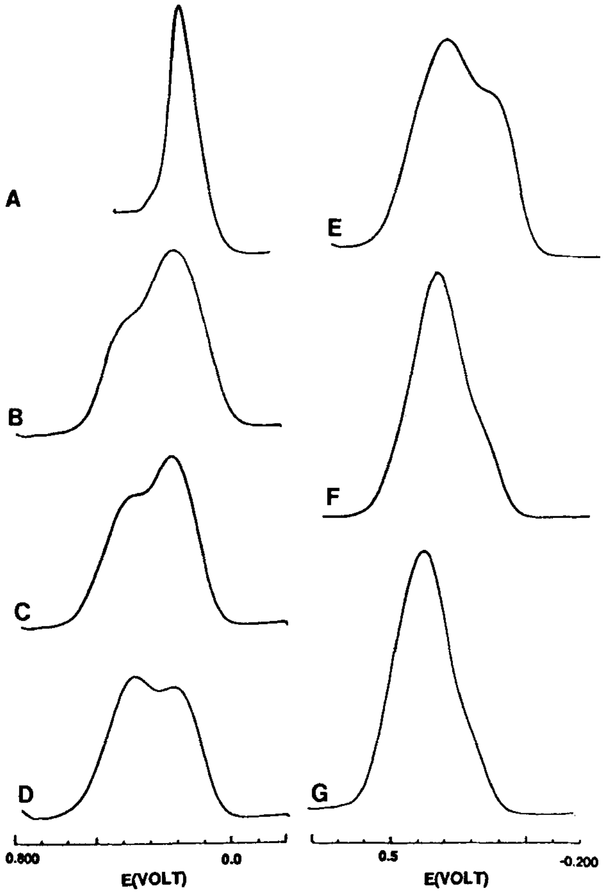


Figure 3 SWV response of a modified carbon paste electrode (containing **1**, see Experimental Procedures for details of carbon paste preparation) immersed in an aqueous 0.1 M KNO_3 solution (pH adjusted to 9.7 by addition of NH_3). The electrode had been previously exposed to solutions containing (A) no $AgNO_3$, (B) 1.4 mM $AgNO_3$, (C) 2.8 mM $AgNO_3$, (D) 4.2 mM $AgNO_3$, (E) 5.5 mM $AgNO_3$, (F) 6.9 mM $AgNO_3$, (G) 8.3 mM $AgNo_3$. Voltammetric parameters were as follows: square wave amplitude, 20 mV; frequency, 15 Hz; scan rate, 75 mV/s.

follows the same pattern described before. The peak corresponding to the oxidation of the complex increases as the concentration of Ag^+ increases in the analyzed solution. In fact, we verified that the peak current for the oxidation of the complex is linearly related to $[Ag^+]$ in the range 1–10 mM for the electrode of Figure 3. In an entirely different approach, we are also trying to incorporate the essential structural features of ligand **1** into a more elaborate compound designed to self-assemble on a gold electrode surface. Our objective here is the preparation of electroactive, cation-sensitive monolayers.[12]

In summary, we have demonstrated for the first time the principle of using a redox-switchable ligand for the analytical determination of a cation (Ag^+) under a practical set of conditions in the ubiquitous aqueous solvent system.

Experimental procedure

Compound **1** was prepared as reported elsewhere.[8,9] The voltammograms were recorded with a BAS-100 electrochemical analyzer using a single-compartment cell fitted with a glassy carbon working electrode (Bioanalytical Systems, West Lafayette, Indiana), a platinum flag counterelectrode, and a home-built sodium chloride saturated calomel reference electrode. Differential pulse voltammograms were obtained at a scan rate of $2\,\mathrm{mV\,s^{-1}}$, using a pulse amplitude of 10 mV and a pulse width of 50 ms. The supporting electrolyte was 0.1 M KNO_3. To avoid the protonation of the ligand's nitrogens the pH was adjusted to 9.7 by addition of aqueous NH_3. Silver ion complexation by NH_3 is not relevant under these conditions because the corresponding stepwise equilibrium constants for the formation of $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$ (2.3×10^3 and 6.0×10^3, respectively)[13] are relatively low. We have checked this point by performing additional experiments in which the solution pH was adjusted to the same value of 9.7 by addition of NaOH. The voltammetric results were essentially identical under these conditions (no NH_3 in the system), showing that NH_3 does not play a significant role in the data plotted in Fig 2.

Modified carbon paste electrodes[14] were prepared by thoroughly mixing 0.3 g of graphite powder (Ultra Carbon, Bay City, Michigan), 3.4 mg of cryptand **1**, and 1.0 mL of Nujol oil (Aldrich) in a mortar and pestle. This paste was packed into a homemade electrode assembly consisting of two concentric lengths of glass tubing and a bronze rod arranged in a piston-like configuration for easy surface renewal. Weighing paper was used to polish the exposed carbon paste electrode surface. Silver preconcentration was performed by immersing the electrode for exactly 1 min in a solution containing a given concentration of $AgNO_3$. After rinsing thoroughly with distilled water, the electrode was submitted to square wave voltammetric analysis in pure supporting electrolyte solution (0.1 M KNO_3, pH = 9.7 adjusted with NH_3).

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