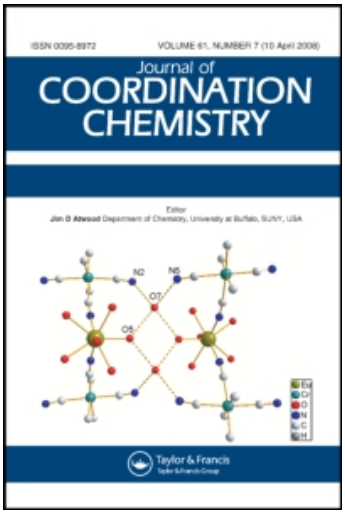

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Rapid Reduction of $[Cu^{II}(Sarcophagine)]^{2+}$ Ion and Elimination of Cu^{1} From the Cage: A Pulse Radiolysis Study

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NOTE

RAPID REDUCTION OF $[Cu^{II}(SARCOPHAGINE)]^{2+}$ ION AND ELIMINATION OF Cu^{I} FROM THE CAGE: A PULSE RADIOLYSIS STUDY

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INTRODUCTION

The electrochemical reduction of $[Cu^{II}(sar)]^{2+}$ ion[1] (Figure 1) in aqueous solution is essentially irreversible (Figure 2) and leads to extrusion of Cu from the cage, leaving the organic framework intact.[1] This extrusion process also appeared to be very rapid on the cyclic voltammetry time scales available (up to 200 V/s). We were prompted, therefore, to look at the reduction process by pulse radiolysis over a shorter time scale (ns → 10 ms) using the hydrated electron in order to probe for the events which lead to extrusion of the metal ion in such a facile way.

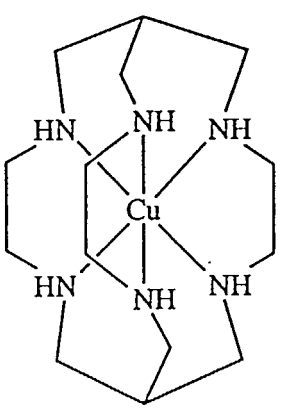


FIGURE 1 Six-coordinate $[Cu(sar)]^{2+}$ ion.[1]

* Author for correspondence.
** In recognition of Arthur Martell's distinguished service to our discipline.

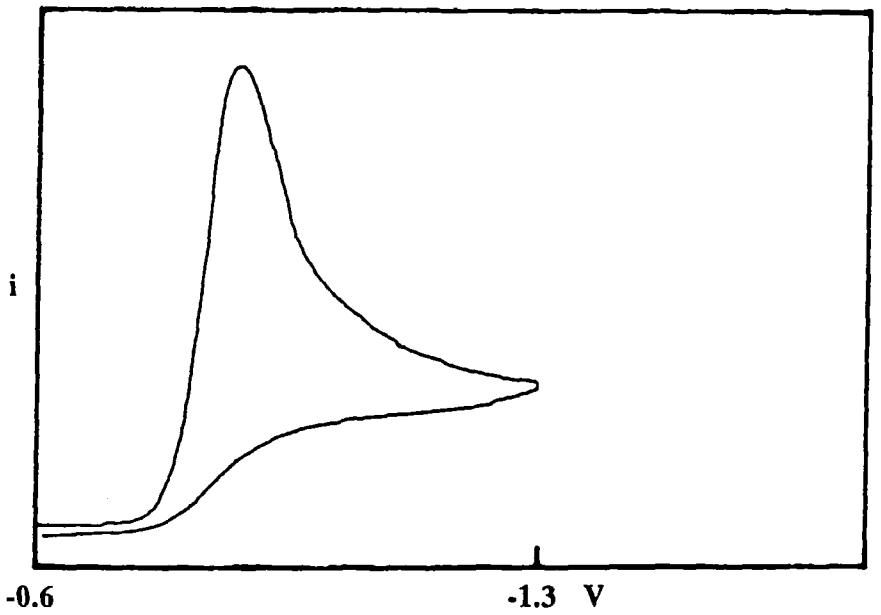


FIGURE 2 Cyclic voltammogram of $[Cu(sar)]^{2+}$ (22°C in 0.1 M $Na[CF_3SO_3]$ at pH 6.0 *versus* saturated calomel, 500 mV s^{-1}.

The $[Cu^{II}sar]^{2+}$ ion is kinetically and thermodynamically stable under the pH conditions of the experiments,[2] except towards reduction of Cu(II) to Cu(I) (E_{red} − 0.8 V *versus* the saturated calomel electrode at 22°C in 0.1 M $NaCF_3SO_3$ at pH 6.0). The reduction process for $LCu^{2+} + e^-_{aq} \rightarrow LCu^+$ can be followed spectrophotometrically but thereafter the $d^{10}Cu^I$ species have little or no spectral features which are readily accessible. However, the changes after the initial reduction can be are readily accessible. However, the changes after the initial reduction can be followed conductimetrically in principle[3,4] and this avenue was therefore explored.

The initial conductivity increase following the electron pulse arises from the production of H^+, e^-_{aq} and OH^- primarily and the rate determining decreases in conductivity come primarily from the consumption of H^+. Reduction of Cu(II)→ Cu(I) by e^-_{aq} also leads to a conductivity decrease but this is small compared with the changes due to H^+ consumption.

EXPERIMENTAL

Solutions of the complex were prepared in He saturated aqueous solutions with 0.01 M ethanol added as OH scavenger. The pH was adjusted to values of between 3.5 and 5.7 by addition of either perchloric acid or NaOH. The solutions were irradiated with single pulses (0.25 microseconds, *ca* 15 Gy) from the ANL 15 MeV electron linear accelerator, and the transient conductivity change during and after the pulse was measured. The details of the pulse radiolysis technique, conductivity and spectrophotometric detection systems have been described in previous publications.[3,4] The dosimetry was defined in terms of the electron charge entering the conductivity

cell. The dose calibration factor was determined by measurement of the conductivity signal produced in a standard system ($CHCl_3$ in acidified water).

The complex $[Cu(sar)](CF_3SO_3)_2$ was synthesised by mixing equimolar amounts of the sarcophagine ligand (3,6,10,13,16,19-hexaazabicyclo[6,6,6]eicosane)[5] and $Cu(CF_3SO_3)_2$ in aqueous solution and crystallization effected by CF_3SO_3Na. Anal.: Calc. for (Found) $CuC_{16}H_{32}N_6F_6O_6S_2$: C, 29.74 (29.6); H, 4.99 (5.2); N, 13.01 (13.2); S, 9.93 (9.6)%.

RESULTS AND DISCUSSION

The reduction of $[Cu(II)(sar)]^{2+}$ (5×10^{-4} M) to $[Cu(I)(sar)]^{+}$ by the hydrated electron was followed spectrophotometrically at 600 nm on a sub-microsecond time scale to yield a second order rate constant k_{e^-} of $7 \times 10^{10}\,M^{-1}\,s^{-1}$ at 25°C. Subsequent events associated with the $[Cu^{I}(sar)]^{+}$ decay were not observable by this technique but conductivity changes associated with proton consumption by the product (5) were readily observed. Over the time scale 10^{-7}–10^{-2} s they are detailed in Figures 3 and 4. These secondary events fall into two time domains and they are both pH dependent. The first observable conductivity change in the pH range 3–5 is essentially first order in H^+ concentration and consumes one proton with a second order rate constant of $2 \times 10^{10}\,M^{-1}\,s^{-1}$. This relatively rapid decay path is followed by a slower process which also appears to be first order in H^+ concentration with a second order rate constant of $2 \times 10^{7}\,M^{-1}\,s^{-1}$ and it also consumes a proton.

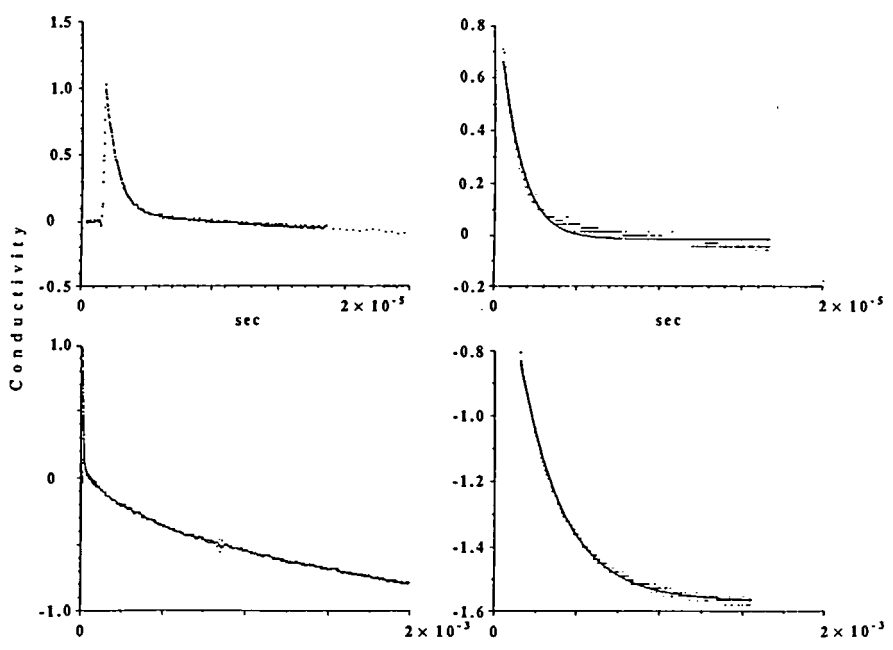


FIGURE 3 Conductivity changes following e^-_{aq} reduction (expressed as H^+ consumption per mole of $[Cu(sar)]^+$ *versus* time (sec) at 25°C and pH 4.40). The figures on the right show the separate rate processes and the fitted data to assess the rate constant.

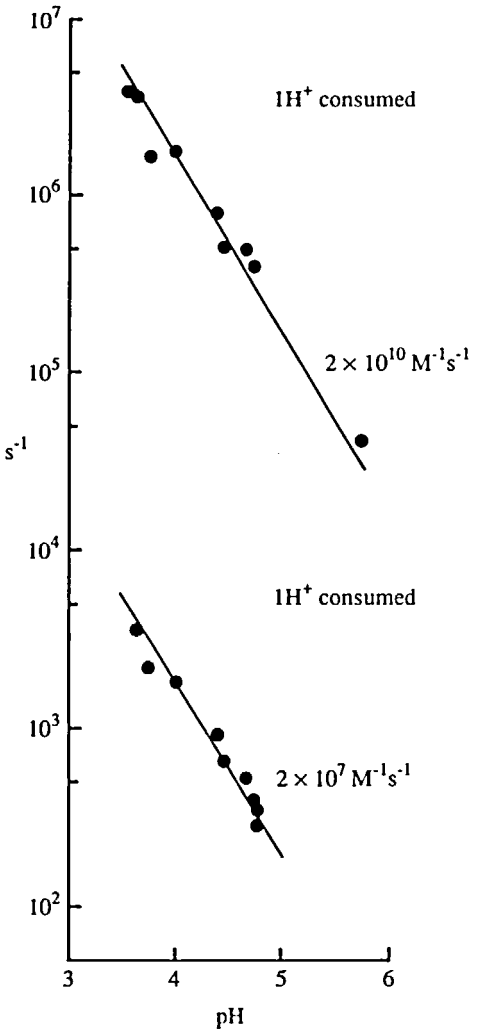


FIGURE 4 Plot of first order rate constants *versus* pH for the consumption of H^+ by $[Cu(sar)]^+$ generated by e^-_{aq}.

The rationalisation of these observations in the light of known chemistry of the encapsulated metal ion follows. Relevant pieces of additional information are, the basicity of the free sarcophagine cage and the effect that the metal ion oxidation state has on the basicity of amine substituents on the periphery of the cage. In the first instance, the free sarcophagine cage has only been protonated observably by four H^+ ions despite the six basic sites available.[5] The four pK_a values at $\mu = 0.1$ and 25°C are 11.09, 9.79, 6.68 and 2.5. In the crystal structures of the different forms, each proton appears to be associated with only a specific N site and does not appear to bridge two adjacent N sites, for example. This, of course, only describes what happens in the lattice and it does not necessarily indicate what happens in solution. Even so, it does imply that two adjacent amine sites are too far apart effectively to share a proton between them in the form of a hydrogen bridge.

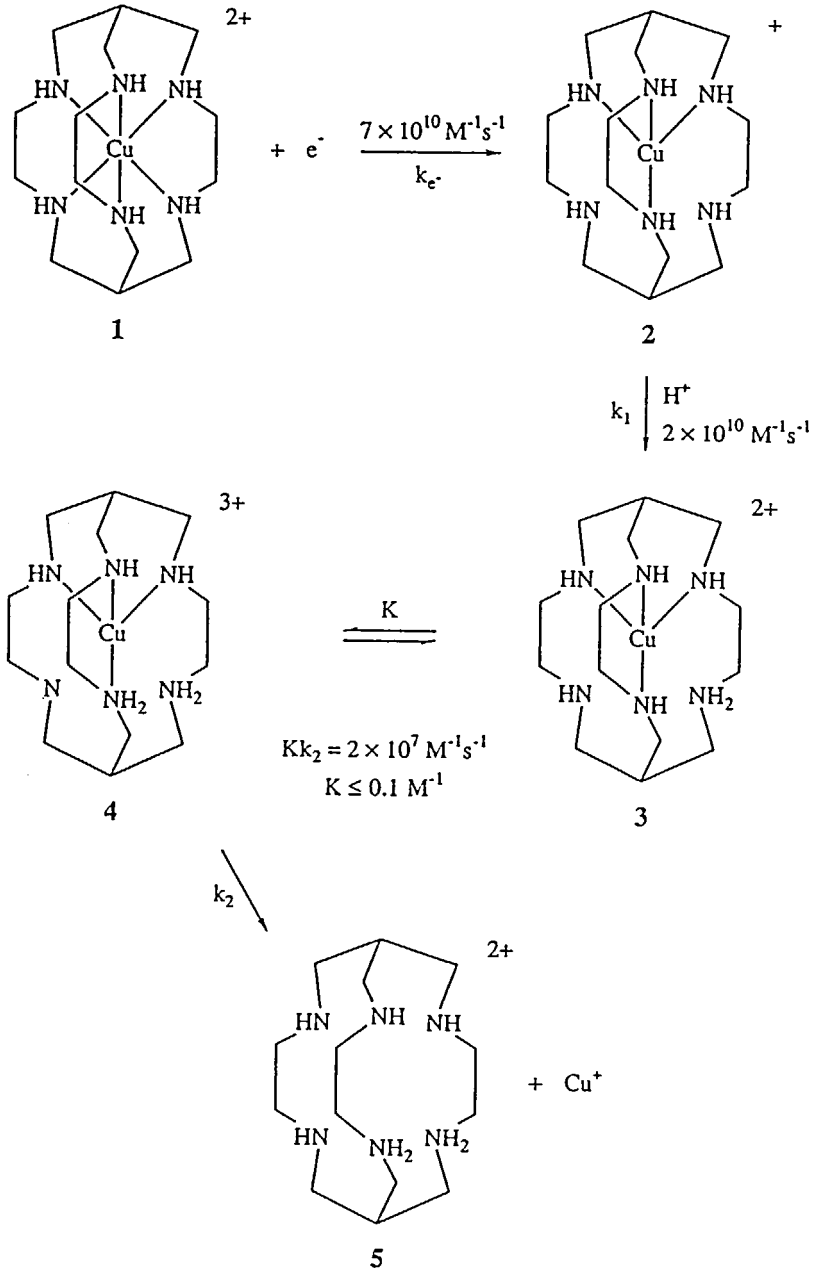
Some idea of the effect that the metal ion oxidation state has on uncoordinated amines attached to the cage can be gauged from the pK_a values for the $[Co(III)(NH_3)_2sar)]^{5+}$ and $[Co(II)((NH_3)_2sar)]^{4+}$ ions. The former (pK_a's 2.37 and 3.31, μ = 0.1) are more acidic than the latter (pK_a's 5.40 and 6.22, μ = 0.1) by ~3 pK units. Also, the variation in pK_a for the amine sites *exo* to the chelating N sites seems to be relatively small for the different tri- and divalent metal ion complexes Co, Cr, In, Ga and Mn, Ni, Cu, Co, Hg, Zn, Mg (respectively, Δ 0.6 and Δ 0.3 pK units).[6] These values allow estimates to be made of the pK_a's of N sites on a strand of the macrobicycle dissociated from the metal ion.

Given these properties, the rate events can be rationalised. After reduction, the coordination number for the copper complex should rapidly diminish from six for Cu(II) to four for Cu(I) which leaves two of the amine sites not bound to Cu(I). These sites would then be available for protonation and a pK_a of less than 11 could be anticipated, given that Cu(I) is still installed in the cage. A second-order rate constant k_1 of $2 \times 10^{10}\,M^{-1}\,s^{-1}$ for protonation of the free amine sites on the supposedly "tetrahedral" $[Cu^{I}sar]^{+}$ complex (**2**) therefore would not be unreasonable (Scheme 1). It is certainly consistent with protonation rates of amines with a comparable basic strength.[7]

The next process observed which is also first order in H^+ ($2 \times 10^7\,M^{-1}\,s^{-1}$) (Figure 4) is too slow to be accounted for by the rate determining protonation. However, it can be accommodated by a relatively unfavourable pre-equilibrium (K) involving further protonation of the Cu^{I} protonated cage (**3**) followed by rate determining elimination (k_2) of Cu^+ to give the doubly protonated cage (**5**). Clearly, the doubly protonated cage free of Cu^+ would be a stable product under the conditions.

The second-order rate constant $2 \times 10^7\,M^{-1}\,s^{-1}$ therefore equates to k_2K and one proton is consumed in the process. Although Cu(I) substitution rates are usually very rapid in water, the relatively slow Cu^+ loss can be accommodated by the unfavourable equilibrium, plus the denticity of the cage and the entropy changes required to unwrap the ligand from the metal ion. It is inevitable that some Cu^{I}–N bond ruptures are unfruitful with respect to coordination of water and that the intramolecular Cu^{I}–N recombination rates are fast and competitive with entry of solvent at the vacant coordination site. Such observations have been made for loss of Cu^{2+} and Hg^{2+} from the cages of the sar and $(NH_3)_2sar^{2+}$ type.[2] These metal ions are also eliminated slowly by acid dependent paths and the kinetic inertness and thermodynamic stability of the complexes is evident.

Despite extensive efforts to solve the problem, we have not been able to devise a method to detect the Cu^+ directly after it leaves the cage. Spectrophotometric methods for detecting Cu^{+}_{aq} are either not sensitive enough or sensitive ligands used for the detection interfere with the reduction step.[8] The disproportionation of Cu^+ is also too slow at these concentrations to be useful for the indirect detection of free Cu^+. However, it is likely that the doubly protonated cage cannot hold the Cu^+ ion and that Cu^+ must dissociate at least before a third H^+ is added. It is also evident from the studies involving extrusion of Cu^{2+} that only in high acid concentrations is the ligand monoprotonated in the presence of the metal ion.[2b] For Hg^{2+} extrusion there is a path involving H^+ but it is clear the degree of monoprotonated ligand is very small indeed (<1%) while Hg^{2+} is still coordinated.[2b] It seems unlikely therefore that two protons can be added quantitatively to the ligand while the Cu^+ is still present.



SCHEME 1 Proposed reaction scheme for H^+ dependence of the extrusion of Cu^+ from $[Cu(sar)]^+$.

ACKNOWLEDGEMENTS

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