pendent of $[O_2]$ since [added Cl^-] $\gg$ $[Fe_T]$. The values obtained for U and V, as well as the effective dioxygen binding constants, are given in Table II.

So, it is apparent that the dioxygen affinity of the system formed from the dissolution of $[Fe\{Ph_2(BzN)_2(m\text{-xyl})[16]cyclidene\}Cl]^+$ in 1.5 M MIM/AN can be adjusted by the addition of chloride. In principle, it should be possible to regulate the dioxygen affinity of a wide variety of synthetic dioxygen carriers by controlling the relative concentrations of two, three, or even more potential axial bases. The ability to precisely regulate dioxygen affinity might eventually have application in the design of O_2 separation and storage devices.[18]

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Registry No. $[Fe\{Ph_2(BzN)_2(m\text{-xyl})[16]cyclidene\}Cl]PF_6$, 102286-59-9; Cl^-, 16887-00-6.

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Kinetic Stability of the Cysteine Adduct with [Tris(2-(2-pyridyl)ethyl)amine]copper(II)

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A kinetic study of cysteine (cys-SH) oxidation by [tris(2-(2-pyridyl)ethyl)amine]copper(II) ($Cu(tepa)^{2+}$) has been performed with the aim of documenting the influence of thermodynamic driving force on the Cu^{II}–S redox decay rate. By comparison with the analogous complex in which only one methylene group separates the apical nitrogen atom from the pendant pyridyl units ($Cu(tmpa)^{2+}$), the $Cu(tepa)^{2+/+}$ reduction potential (+315 mV vs. NHE, 25 °C, pH 6, I = 0.1 M (MES)) is more positive by 0.46 V. With excess $Cu(tepa)^{2+}$ present, first-order kinetic traces (pH 4.67–12.50) were observed upon following $Cu(tepa)^+$ formation at 340 nm. The rate–pH profiles of cysteine oxidations by $Cu(tepa)^{2+}$ and $Cu(tmpa)^{2+}$ are superficially similar, exhibiting maxima between pH 8 and 9, but electron transfer within $(tepa)Cu^{II}$–S-cys is faster by 1–2 orders of magnitude in the low- to intermediate-pH range. As is the case for $Cu(tmpa)^{2+}$, the pH dependence of the $(tepa)Cu^{II}$–S-cys electron transfer rate may be quantitatively understood in terms of three reactant species (I, II, and III; respective rate constants k_1 = 0.65 s^{-1}, k_2 = 1.2 × 10^2 s^{-1}, k_3 = 3.5 × 10^{-2} s^{-1}) related through successive ionization equilibria (pK_{a1} = 8.9, pK_{a2} = 7.6) (25.0 °C, I = 0.1 M ($NaNO_3$)). Respective redox reactivity ratios (tepa rate constant/tmpa rate constant) of intermediates I, II, and III are ≥6.5 × 10^2, 6.0 × 10, and 9 × 10^{-1}, demonstrating that only I and II are affected appreciably by the increase in oxidizing strength from $(tmpa)Cu^{II}$ to $(tepa)Cu^{II}$. These ratios imply that electron transfer is rate-determining in the decomposition of intermediates I and II. Insensitivity of k_3 to the oxidizing strength of the Cu(II) center suggests that the $(tmpa/tepa)Cu^{II}$–S,N-cys activation barrier primarily reflects retarded Cu^{II}–S bond stretching leading to reductive elimination of a thiyl radical.

Introduction

Elegant synthetic approaches coupled with careful spectroscopic analyses have led to significant recent advances in the modeling of blue copper protein electronic structure.[1,2] Most copper(II) complexes of biologically important mercapto amino acids are observable only as transients in aqueous solution, however, such that kinetic studies of formation and decay reactions constitute a vital aspect of their characterization.[3] Indeed, not only have such reactivity studies elucidated the diverse redox decay pathways available to Cu^{II}–SR species, but they also represent, in many cases, the only source of thermodynamic parameters relating to copper(II) complexation by mercaptide sulfur.[3-6]

Structural systematics and related trends in physical properties of Cu(I) and Cu(II) in the low-symmetry N_4 and N_2S_2 coordination environments imposed by tripod ligands have been fully developed by Karlin, Zubieta, and co-workers.[7] S-bonded adducts of mercapto amino acids with the trigonal-bipyramidal[8] [tris(2-pyridylmethyl)amine]copper(II) ion, $Cu(tmpa)^{2+}$, were found to exhibit a remarkable degree of kinetic stability in studies of rate dependences on pH, mercaptan structure, and reductant to oxidant concentration ratio.[3,6] In order to document the influence of thermodynamic driving force on the Cu^{II}–SR redox decay rate, a study of cysteine oxidation by [tris(2-(2-pyridyl)ethyl)-amine]copper(II) ($Cu(tepa)^{2+}$) is reported here.

Although the tetradentate tmpa and tepa ligands offer identical N_4 donor atoms, the coordination geometries and associated physical properties of their cupric complexes are markedly different.[8] Thus, the structure of $[Cu(tmpa)Cl]^+$ is essentially trigonal bipyramidal with nearly equivalent Cu^{II}–N bond lengths and related bond angles, while $[Cu(tepa)Cl]^+$ exhibits a square-pyramidal geometry in which the bridgehead amine nitrogen atom occupies a basal position trans to the chloride ligand.[7,8] For our purposes, the most significant impact of the additional methylene group in the tepa tripodal arms is a +0.56-V shift in Cu(II,I) reduction potential (Cl^- complexes in DMF, 0.11 M $N(n\text{-}C_4H_9)_4PF_6$).[8] To the extent that electron transfer from coordinated thiolate sulfur to copper(II) is rate-determining, such an increase in oxidizing strength should be reflected in an enhanced redox decay rate. Since Cu^{II}–S bond stretching is equally important in a reductive elimination process,[3,6] comparative insensitivity of the Cu^{II}–SR redox decay rate to thermodynamic driving force would indicate that the activation barrier is derived mainly from bond-breaking or other structural rearrangement.

Experimental Section

Materials. Reagent grade L-cysteine (cys-SH), 2-morpholinoethanesulfonic acid (MES), and 2-(bis(2-hydroxyethyl)amino)ethanesulfonic acid (BES) were used as supplied by Sigma. (Hydroxyethyl)ferrocene (Strem) was purified by vacuum sublimation. Tris(2-(2-pyridyl)ethyl)-amine was prepared and characterized as described by Karlin et al.[8] $[Cu(tepa)(H_2O)](ClO_4)_2\cdot H_2O$ was synthesized through the addition of

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0.50 g of tepa (1.5 mmol) in 5 mL of methanol to 0.56 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.5 mmol) in 2 mL of H_2O. The resulting solution was evaporated until a thick blue oil was obtained. This oil was redissolved in the minimum amount of water at 25 °C; the mixture was then cooled in an ice bath and filtered. The blue crystals that formed upon refrigeration of the filtrate were separated on a sintered-glass filter. The product was recrystallized three times from water and dried in vacuo for 8 h. Yield: 0.55 g (58%). Anal. Calcd: Cu, 10.07. Found: Cu, 10.00. Vis (H_2O solvent): λ_{max} 657 nm (ϵ 119 M^{-1} cm^{-1}), 1026 nm (ϵ 59 M^{-1} cm^{-1}).

Measurements. Stopped-flow kinetic, pH, cyclic voltammetric, spectroscopic, and stoichiometric measurements were carried out at 25.0 °C as previously described on MES-, BES-, or carbonate-buffered (5 mM) solutions prepared with triply distilled water.[3,6] A 40% excess of Cu(tepa)$^{2+}$ (0.14 mM) over cysteine (0.10 mM) was employed in most kinetic runs. The rate of the anaerobic (N_2 atmosphere) redox reaction between cysteine and (tepa)Cu^{II} in the pH 4.67–12.50 interval was monitored through the absorbance increase at 340 nm due to the (tepa)Cu^{I} product. A/D conversion of 256 data points per kinetic run and subsequent quantitative interpretation of first-order traces were accomplished on an Apple II Plus computer.[10] Reported values are the mean of three to five trials. The colorimetric[3] cysteine–Cu(tepa)$^{2+}$ reaction stoichiometry determination was based on the mixture of 0.14 mM Cu(tepa)$^{2+}$ with 0.10 mM cysteine (5 mL each) at pH 7 (5 mM BES/0.1 M $NaNO_3$). When the cyclic voltammogram of Cu(tepa)$^{2+}$ was examined at a carbon-paste working electrode, the reference saturated calomel electrode potential was calibrated against (hydroxyethyl)ferrocene. The reported $E°$ value was calculated as the average of cathodic and anodic peak potentials.[3]

Results and Discussion

As was reported previously for mercaptan oxidations by (tmpa)Cu^{II},[3,6] cysteine is quantitatively converted to the disulfide cystine in the reaction with excess Cu(tepa)$^{2+}$. When a 40% excess of the oxidant was present, the molar ratio of Cu(I) produced to cysteine consumed was found to be 0.98 ± 0.05. Unlike the case of the Cu(tmpa)$^{2+}$–cysteine reaction, however, no transient near-ultraviolet absorption was detected upon mixing 0.14 mM Cu(tepa)$^{2+}$ with 0.10 mM cysteine at pH 7, 25 °C, and I = 0.1 M ($NaNO_3$) on the stopped-flow apparatus. Instead, a yellow Cu(tepa)$^{+}$ product[11] solution with λ_{max} at 338 nm (ϵ 8830 M^{-1} cm^{-1}) was observed under these conditions. The 350–450-nm electronic absorption spectrum of this product solution did not change from 2 to 40 min after mixing and was identical with a point-by-point stopped-flow spectrum (λ_{max} 338 ± 3 nm) derived from equilibrium minus initial absorbance determinations. Kinetic measurements were based, therefore, on the rate of Cu(I) formation rather than on disappearance of the LMCT absorption of a (tepa)Cu^{II}–S-cys adduct.

Before we compare the rates of Cu(tmpa)$^{2+}$ and Cu(tepa)$^{2+}$ reductions by cysteine, the differential in $E°$(Cu(II,I)) between the two oxidants should be considered. Unfortunately, this $\Delta E°$ value only approximates the more relevant, but experimentally inaccessible, gradient in driving force for one-electron transfer within the corresponding S-bonded cysteine complexes. [Cu(tepa)(H_2O)]$(ClO_4)_2$ exhibits a quasi-reversible cyclic voltammogram in a pH 6, I = 0.1 M (MES) medium, from which an $E°$(Cu(tepa)$^{2+/+}$) value of +315 ± 4 mV vs. NHE, independent of sweep rate (50–200 mV/s), may be calculated. Since $E°$(Cu(tmpa)$^{2+/+}$) is −147 mV under these conditions,[3] it is apparent that $\Delta E°$ between [Cu(tepa)(H_2O)]$^{2+}$ and [Cu(tmpa)(H_2O)]$^{2+}$ in water (+0.46 V) is not greatly different from that of the analogous chloride complexes in DMF (+0.56 V). By comparison, previously reported $E_{1/2}$ values (DMF, 0.11 M N(n-$C_4H_9)_4PF_6$) for Cu(tepa)BPh_4 oxidation and [Cu(tepa)NO_3]PF_6 reduction are +0.29 V[11] and +0.27 V[9] vs. NHE, respectively.

First-order correlations of ln ($A_\infty - A_t$) vs. time were found to be linear over >90% of the 340-nm absorbance increase associated with the Cu(tepa)$^{2+}$ (40% excess)–cysteine redox reaction. Furthermore, observed first-order rate constants (k_{obsd}) at any particular pH do not vary with small changes in [Cu(tepa)$^{2+}$]$_0$ at fixed [cysteine]$_0$. For example, at pH 4.67, I = 0.1 M ($NaNO_3$), k_{obsd} = 0.34 ± 0.04 s^{-1} at [cys-SH]$_0$ = 0.10 mM and [Cu(tepa)$^{2+}$]$_0$ = 0.07–0.14 mM. Both of these observations point to a unimolecular, intracomplex redox process in which electron transfer rather than precursor formation is rate-determining. A dimeric Cu^{II}–SR intermediate or outer-sphere reduction of (tepa)Cu^{II} by cysteine may be ruled out, as pseudo-*second*-order kinetics would pertain in both instances upon mixing equimolar concentrations of the reactants.[5] Since a (tepa)Cu^{II}–S-cys intermediate was not detected optically, ligation of copper by thiolate sulfur is not proved by the kinetic results but is regarded as highly probable in view of the many Cu^{II}–SR adducts known to form spontaneously under our conditions.[3-6]

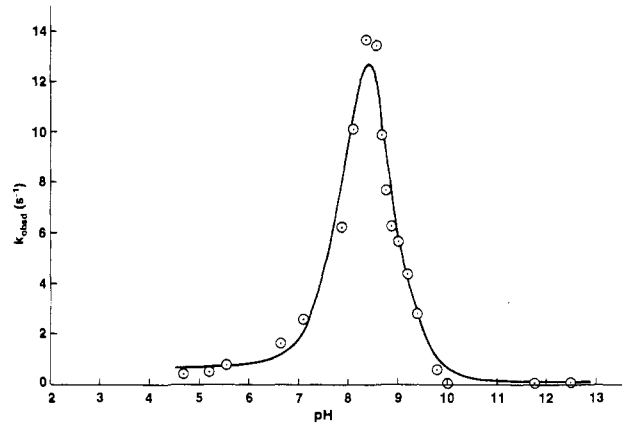
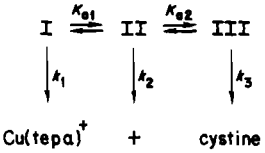


Figure 1. Rate–pH profile of the cysteine–Cu(tepa)$^{2+}$ oxidation–reduction reaction at 25.0 °C, I = 0.1 M ($NaNO_3$), [cys-SH]$_0$ = 0.10 mM, and [Cu(tepa^{2+})]$_0$ = 0.14 mM. The solid curve was calculated with the nonlinear least-squares rate parameters (Table I) from the kinetic relationship[12] appropriate to eq 1.

The rate of (tepa)Cu^{II}–cysteine complex redox decay was studied at 19 pHs in the interval 4.67–12.50. The bell-shaped rate–pH profile (Figure 1), with maximum k_{obsd} (12.4 s^{-1}) near pH 8.3, is superficially similar to that for (tmpa)Cu^{II}–S-cys redox decay (maximal k_{obsd} of 0.8 s^{-1} at pH 8.6).[3] Decay of the (tepa)Cu^{II}–cysteine complex is faster by 1–2 orders of magnitude in the low- to intermediate-pH range, however, although high-pH redox rates in the tmpa and tepa systems are remarkably similar. It should also be noted that the k_{obsd}–pH profile presented here is sharper in the sense that the rate increase and subsequent dramatic decrease at intermediate acidities both occur within a comparatively small pH interval.

The three-reactant/two-ionization formalism (eq 1) invoked previously to account for the kinetic pH dependence of (tmpa)-Cu^{II}–S-cys redox decay is also consistent with the (tepa)Cu^{II} results, provided that pK_{a1} > pK_{a2}. Thus, a nonlinear least-squares



(1)

fit[3] of the kinetic data to the appropriate rate expression[12] was highly successful, as judged by the correspondence between calculated and experimental k_{obsd} values (Figure 1). The nonlinear least-squares (tepa)Cu^{II}–S-cys redox rate parameters are compared in Table I with those that govern the analogous reactions of cupric complexes with tmpa and Me_6tren.[13]

The results presented here are consistent with the mechanism proposed originally,[3] in which the K_{a1} and K_{a2} equilibria are assigned to the ionization of coordinated water and of the cysteine ammonium group, respectively (eq 2). Although structures I and III follow reasonably from the known coordination chemistry of

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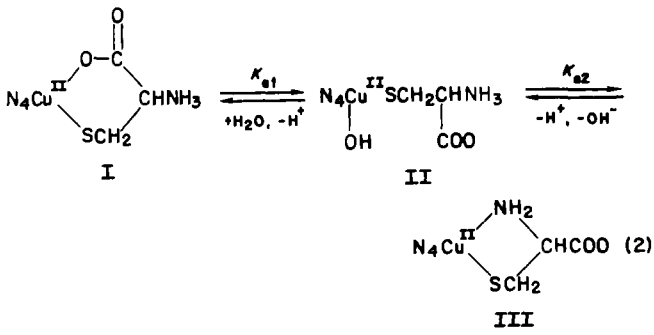
(12) $k_{obsd} = (k_1[H^+]^2 + k_2K_{a1}[H^+] + k_3K_{a1}K_{a2})/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$.
(13) Me_6tren = 2,2′,2″-tris(dimethylamino)triethylamine.



I II

III

cysteine,[14] the monodentate hydroxo, S-cysteinato formulation of II cannot be strongly justified in the absence of more direct structural evidence. In this regard, both the distinctively high redox reactivity of II and the inverted pK_{a1}/pK_{a2} ordering in the Cu(tepa)$^{2+}$–cysteine reaction must be accounted for. On the basis of our previous treatment,[6] the substantial difference between the free cysteine ammonium group ionization constant ($pK_a = 10.37$)[15] and kinetically determined K_{a2} (or K_{a1}(Me$_6$tren)) values is attributed to S,N chelation of Cu(II). The absence of an appreciable kinetic stability enhancement from intermediate to high pH in (tmpa)Cu^{II} adducts with glutathione[6] and *N*-acetylcysteine[16] is as expected from this assignment of the K_{a2} ionization, considering that S,N chelation should be strongly hindered in both cases. A comparison of ΔpK_a and corresponding $\Delta\Delta G°_a$ parameters implied by this proposed chelation-induced perturbation in ammonium group ionization is given in Table I.

Considering only the cysteine–Cu^{II} complexation step, which precedes redox decay, relative thermodynamic stabilization of both S,O and S,N cysteine chelates with (tepa)Cu^{II} is apparent from a comparison of the ionization constants of species I and II in the tepa and tmpa pathways. Viewed from this perspective, the sharpness of the (tepa)Cu^{II}–S-cys k_{obsd}–pH profile simply reflects the very narrow pH range in which intermediate II contributes appreciably to [adduct]$_{tot}$. Indeed, this point is reinforced by the observation that k_{obsd}(max) falls far below k_2. The seemingly contradictory inversion in K_{a1} and K_{a2} values is then reconciled with the proposed ionization scheme rather simply by noting that the ammonium nitrogen atom of S,O-chelated cysteine is spatially restricted from competing directly with the carboxylate group for a coordination position.

According to our mechanistic model, the large redox reactivity increase from species I to II in both the tmpa and tepa systems must be related either to monodentate vs. bidentate cysteine coordination or to the presence of an OH$^-$ ligand. Although mercapto amino acid substituent effects on K_{a1} support the existence of S,O chelation in species I, we have previously shown that such chelation in (tmpa)Cu^{II}–S,O-cys is not primarily responsible for its exceptional kinetic stability.[6] We are inclined, therefore, to attribute the tmpa and tepa k_2/k_1 ratios to a coordinated hydroxide ion effect. Similar, although less pronounced, Cu^{II}–S redox decay rate increases from low to intermediate pH pertain in the oxidations of coordinated cysteine[4] and SCN$^-$[16] by copper(II) complexes of 2,9-dimethyl-1,10-phenanthroline (dmp); Cu(dmp)(SCN)(OH) was proposed as a reactive intermediate in the latter reaction.[17]

Finally, we consider the influence of thermodynamic driving force on the redox decay rates of intermediates I, II, and III. Respective redox reactivity ratios (tepa rate constant/tmpa rate constant) of these transients are $\geq 6.5 \times 10^2$, 6.0×10, and 9×10^{-1}, demonstrating that only I and II are affected appreciably by the increase in oxidizing strength from (tmpa)Cu^{II} to (tepa)Cu^{II}. The redox decay rate of (tepa)Cu^{II}–S-cys intermediate

Table I. Comparison of Rate and Thermodynamic Parameters for Redox Decay of (Tetraamine)copper(II) Complexes with Cysteine[a]

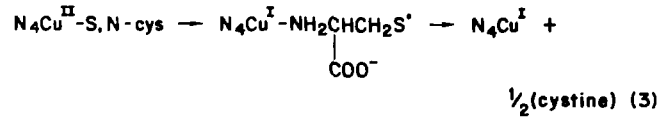
	oxidant		
parameter	Cu(tepa)$^{2+}$	Cu(tmpa)$^{2+}$ [b]	Cu(Me$_6$tren)$^{2+}$ [c]
k_1, s^{-1}	0.65 (0.43)	$<1 \times 10^{-3}$	7.0
k_2, s^{-1}	1.2 (0.2) $\times 10^2$	2.0	5×10^{-1}
k_3, s^{-1}	3.5 (1.5) $\times 10^{-2}$	4.1×10^{-2}	
pK_{a1}	8.9 (0.2)	8.33	7.44
pK_{a2}	7.6 (0.2)	8.52	
ΔpK_a [d]	−2.8	−1.85	−2.93
$\Delta\Delta G°_a$ [e]	−3.8	−2.5	−4.0
k_2/k_1	2×10^2	$\geq 2 \times 10^3$	7×10^{-2}
k_3/k_1	5×10^{-2}	$\geq 4 \times 10$	
k_3/k_2	3×10^{-4}	2×10^{-2}	

[a] Conditions: 25.0 °C; I = 0.1 M (NaNO$_3$). Standard deviations are shown in parentheses. See eq 1 for definitions of parameters. [b] Reference 3. [c] Reference 6. [d] Kinetically determined ammonium group pK_a in S-bonded Cu(II) complex minus pK_a of free amino acid. Based on pK_{a2}(tepa and tmpa) and pK_{a1}(Me$_6$tren). [e] Free energy difference corresponding to ΔpK_a, in kcal/mol.

II is on the same order as those of Cu(dmp)–cysteine (4.8×10 s^{-1}) and Cu(dmp)$_2$–cysteine (4×10 s^{-1}) (25 °C, pH 6, I = 0.2 M), formed from the strongly oxidizing Cu(dmp)$_2^{2+}$ ion (E^0 = +615 mV).[4]

Although a quantitative analysis of driving force effects on inner-sphere electron-transfer processes is difficult, it is clear that Marcus-type relationships pertain to some reactions of this type.[18,19] On this basis, the rate of thiolate sulfur-to-copper(II) electron transfer would be expected to increase in concert with both oxidizing strength and self-exchange redox rate of the N$_4$Cu^{II} reactant. This expectation will be realized, however, only to the extent that the electron-transfer step is rate-determining in an overall process that also requires Cu–S bond breaking and structural rearrangement within the copper coordination sphere. Although structural data are not available for Cu(tmpa)$^+$, X-ray crystallographic results on [Cu(tepa)Cl]PF$_6$ and Cu(tepa)BPh$_4$ indicate that the coordination geometry shifts from square pyramidal to pyramidally distorted tetrahedral upon reduction of Cu(II) with loss of Cl$^-$.[7] The thermodynamic destabilization of Cu(tmpa)$^+$ relative to Cu(tepa)$^+$ evidently derives from strained five-membered chelate rings in which the N–Cu^I–N bond angles cannot closely approach the optimal tetrahedral value.

The tepa/tmpa redox reactivity ratios imply that electron transfer is rate-determining in the decomposition of intermediates I and II. Conversely, the insensitivity of k_3 to the oxidizing strength of the Cu(II) center shows that the intermediate III redox activation barrier primarily reflects Cu^{II}–S bond stretching or other structural perturbations within the precursor complex. This hypothesis entirely agrees with our previous attribution of high-pH kinetic stability to retarded Cu^{II}–S bond breaking, leading to reductive elimination of a thiyl radical, within a five-membered S,N chelate unit (eq 3). Since a thiolate S-to-copper(II) LMCT



band was not observed in the reaction of (tepa)Cu^{II} with cysteine, it is also possible that a geometric rearrangement of (tepa)-Cu^{II}–S,N-cys is motivated by poor overlap of sulfur 3p σ donor and Cu^{II} $3d_{x^2-y^2}$ acceptor orbitals.

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Registry No. Cu(tepa)$^{2+}$, 102436-62-4; cys-SH, 52-90-4.

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