Standard Ethylene-Reduction Technique. Experimental conditions were identical with that described for N_2 reduction except that ethylene-filled glass bottles of 160-mL capacity were employed. For analysis of hydrocarbons by GLC, gas samples were withdrawn at stated time points.

Reduction of $MoCl_5$ Solutions. The freshly prepared, 0.05 M $MoCl_5$ solutions in methanol were reduced with Zn pellets as outlined above. At various time points, aliquots of the reaction solution were withdrawn and placed into argon-filled, serum-capped test tubes for storage. These solutions were diluted with deaerated CH_3OH to 1.5×10^{-4} M. UV spectra were recorded with a Beckman DB-C UV grating spectrophotometer using quartz cells of 1-cm path length. The cells were serum capped and flushed with Ar prior to the injection of the solutions. The reduction of the Mo(V) solutions was also followed by oxidimetric titrations of aliquots withdrawn at various time points. The $KMnO_4$ solution was prepared and standardized by the method of Elwell and Wood;[20] the titrations were performed under argon.

Registry No. $Ti(OH)_3$, 12026-77-6; $Mo(OH)_3$, 60414-57-5; C_2H_4, 74-85-1; N_2, 7727-37-9; Mo, 7439-98-7.

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Oxidation of Cysteine, Cysteine Methyl Ester, and Penicillamine by Copper(II)-2,9-Dimethyl-1,10-phenanthroline Complexes

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A stopped-flow kinetic study of the oxidations of excess cysteine, cysteine methyl ester, and penicillamine by copper(II)-2,9-dimethyl-1,10-phenanthroline (dmp) complexes is reported (25 °C, I = 0.2 M, pH 4-7). These reactions were found to be first order with respect to Cu(II), in contrast to the second-order behavior typical of weaker Cu(II) oxidants. Rate variations with mercaptan (RSH) and dmp concentration are consistent with two parallel pathways in which oxidation of coordinated sulfur occurs within 1:1 mercaptan complexes of $Cu(dmp)_2^{2+}$ (rate constant k_0) and $Cu(dmp)^{2+}$ (rate constant k_1). Redox decay of the Cu(II)-S bond proceeds with rate constants of 4.8×10, 3.0×10, 8.3×10 s^{-1} (k_1) and 4×10, 5, 2.4×10^2 s^{-1} (k_0) for cysteine, penicillamine, and cysteine methyl ester, respectively, at pH 6.0. The pH dependence of kinetic precursor complex formation constants showed that both coordinated RS^- and RSH are oxidized in the k_1 pathway, while RSH is the predominant reductant of $Cu(dmp)_2^{2+}$. Formation constants pertaining to the reactions of RS^- (K_{c1}) and RSH (K_{c0}) with $Cu(dmp)^{2+}$ show little effect of β,β-dimethyl substituents or esterification of the amino acid carboxylate group on thermodynamic stability; for cysteine, $K_{c0} = 2 \times 10^4$ M^{-1} and $K_{c1} = 1.2 \times 10^7$ M^{-1}.

Introduction

The electronic and geometric structures of compounds containing a mercaptide sulfur-copper(II) bond are of considerable interest,[1] as this unit occurs in all blue copper proteins.[2] Comparatively little is known about the kinetic and thermodynamic stabilities of RS^--Cu(II) complexes in solution, as internal electron transfer generally is facile. We recently described a remarkably stable S-bonded adduct of cysteine (cys-SH) with the (tris(2-pyridylmethyl)amine)copper(II) ion ($Cu(tmpa)^{2+}$) in aqueous solution and reported both equilibrium and kinetic measurements on its formation and redox decay to give $Cu(tmpa)^+$ and the disulfide cystine.[3] This study of the $[(tmpa)Cu\text{-}S\text{-}cys]^+$ system suggested several contributions to the kinetic stability of the Cu(II)-S bond, including steric crowding about the coordinated sulfur atom, chelation (S,O or S,N) of copper by the mercaptan, and small redox thermodynamic driving force.

Reduction of copper(II) by mercaptans typically is second order with respect to inner-sphere S-bonded intermediates,[4,5] as S-S bond formation and electron transfer may be concerted within a binuclear Cu(II) activated complex.[4] A unimolecular RS^--Cu(II) redox decay pathway may be anticipated, however, in complexes where the oxidizing strength of Cu(II) is substantially enhanced relative to that of $Cu^{2+}(aq)$ ($E°$ = +153 mV),[6] permitting the formation of thiyl radicals. We report here kinetic studies of the oxidation of cysteine, cysteine methyl ester, and penicillamine by copper(II)-2,9-dimethyl-1,10-phenanthroline (dmp) complexes. Steric repulsions between the 2,9-dimethyl substituents and the π-accepting capability of phenanthroline ligands both contribute to the exceptionally positive reduction potential of $Cu(dmp)_2^{2+}$ (+615 mV).[8] Although outer-sphere electron transfer pertains in the reactions of substituted hydroquinones[9,10] and transition-metal reductants[11-13] with $Cu(dmp)_2^{2+}$, mixed outer- and inner-sphere reactivity may be anticipated for reductants with sulfur electron donor atoms.[14]

As inner-sphere electron transfer involving displacement of dmp from $Cu(dmp)_2^{2+}$ is kinetically distinguishable from pathways involving intact $Cu(dmp)_2^{2+}$, we concentrate here on redox rate variations linked to the concentration of dmp. The contributions of S,O chelation and the steric environment of the thiolate sulfur atom to inner-sphere rate parameters are probed through the use of cysteine methyl ester and penicil-

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lamine (β,β-dimethylcysteine), respectively. Finally, the relative importance of RSH and RS^- as electron donors was examined through pH-dependence studies in the range 4–7.

Experimental Section

Reagents and Solution Preparation. Chemicals and methods employed in the preparation of $Cu(dmp)_2^{2+}$ solutions in $I = 0.2$ M sodium acetate buffers were as described by Clemmer et al.[9] L-Cysteine, free base (Sigma), DL-penicillamine (Aldrich), L-cysteine methyl ester hydrochloride (Sigma), and reduced glutathione (Sigma) were used as received after confirming their purity through iodometric titrations.[15]

Anaerobic (N_2-purged) mercaptan solutions in $I = 0.2$ M sodium acetate buffers were used immediately after preparation. All transfers of anaerobic solutions were made with Hamilton gastight syringes. Mercaptan concentrations were 0.10 and 0.10–10 mM in [dmp]- and [RSH]-variation studies, respectively, and $[Cu(II)]_0$ was 10 μM throughout. A greater than 25-fold excess of free dmp over Cu(II) ($[dmp]_{tot} = 0.5$ mM) was employed in mercaptan concentration dependence studies to ensure full conversion of the oxidant into $Cu(dmp)_2^{2+}$ before mixing.[9] The limited solubility of dmp made it necessary to dissolve ligand in both reactant solutions in [dmp]-variation studies ($[dmp]_{tot} = 0.1$–0.9 mM). Hydrogen ion concentrations were derived from pH readings, as before, by correcting for the activity coefficient of 0.2 M NaOAc.[10]

Ionization Constant of $dmpH^+$. The acid ionization constant of $dmpH^+$ ($pK_a = 5.85 \pm 0.03$) was determined in $I = 0.2$ M NaOAc (pH 4.5–7.5) through spectrophotometric measurements in the 255–270-nm region (Cary 17 spectrophotometer). Absorption maxima were observed at both ends of the pH range, corresponding to $dmpH^+$ (281 nm) and dmp (270 nm). Values of pK_a were calculated as the linear least-squares intercept of correlations based on eq 1, where A_i,

$$-\log [H^+] = -\log [(A_{7.5} - A_i)/(A_i - A_{4.5})] + pK_a \qquad (1)$$

$A_{4.5}$, and $A_{7.5}$ represent the absorbance readings at pH i (5.00, 5.52, 5.98, 6.51, 7.00), 4.5, and 7.5, respectively (1-cm path, $[dmp]_{tot} = 30$ μM). The value reported is the average of determinations at six wavelengths. This ionization constant was used to calculate [dmp] from $[dmp]_{tot} = ([dmp] + [dmpH^+])$ at each pH considered.

Stoichiometric Measurements. In order to verify that Cu(II) is quantitatively converted to $Cu(dmp)_2^+$ in reactions with excess mercaptan, spectrophotometric titrations were carried out at 454 nm ($\epsilon_{454}(Cu(dmp)_2^+) = (7.73 \pm 0.04) \times 10^3$ M^{-1} cm^{-1} determined with excess sodium ascorbate), at pH 6.0 and $I = 0.2$ M. A_{454} was plotted against $[Cu(dmp)_2^{2+}]$ added anaerobically (10–90 μM) to a 0.10 mM mercaptan solution in a capped 1-cm cuvette. The linear least-squares slopes of these plots showed that 0.99 ± 0.02, 0.97 ± 0.01, 0.98 ± 0.02, and 0.98 ± 0.03 mol of $Cu(dmp)_2^+$ was formed per mole of oxidant added to cysteine, penicillamine, glutathione, and cysteine methyl ester, respectively.

Kinetic Measurements. Kinetic measurements were performed at 454 nm on a Durrum D-110 stopped-flow apparatus, as previously described.[9] Pseudo-first-order observed rate constants were derived from the linear least-squares slopes of $\ln (A_\infty - A_t)$ vs. time profiles. The average of three trials is reported in most cases. All kinetic runs were carried out at 25.0 ± 0.1 °C.

Results and Discussion

As anticipated, clean first-order correlations of $\ln (A_\infty - A_t)$ vs. time (minimum 80% of ΔA_{454}) were found in the 25 °C oxidations of excess cysteine, cysteine methyl ester, and penicillamine by Cu(II)–dmp solutions in the range pH 4–7. In contrast, mixed first- and second-order traces were observed in the reaction of glutathione (≥1 mM) with $Cu(dmp)_2^{2+}$ at pH 6.0. Detailed studies of this behavior were not made, but it may be noted that the first-order k_{obsd} values of glutathione and cysteine at [RSH] < 1 mM are similar (pH 6.0). Slow precipitation of the disulfide cystine, identified by infrared spectroscopy, occurred in cysteine–$Cu(dmp)_2^{2+}$ product mixtures at pH <4.

A tendency toward rate saturation with increasing [RSH] (1.25–10.0 mM), indicative of large precursor complex formation constants, was noted in the rapid oxidations of all three

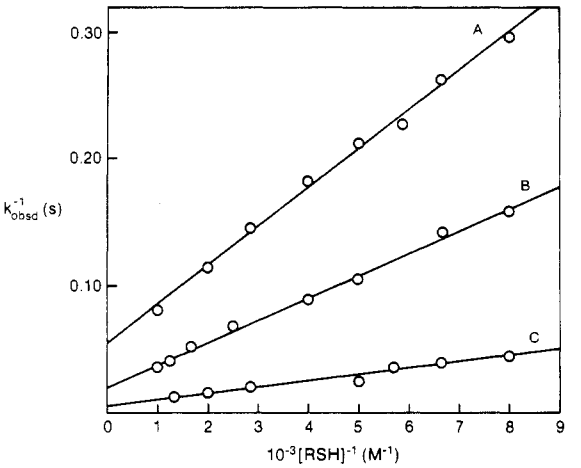

Figure 1. Double-reciprocal plots illustrating 1:1 mercaptan:Cu(II) precursor complex formation in the reactions of penicillamine (A), cysteine (B), and cysteine methyl ester (C) with $Cu(dmp)_2^{2+}$ (25.0 °C, $I = 0.2$ M, pH 6.0, $[dmp]_{tot} = 0.5$ mM).

Table I. Effect of dmp Concentration on Observed Rate Constants[a]

mercaptan	[dmp], mM	k_{obsd}, s^{-1}	k_{calcd}, s^{-1} [b]
cysteine	0.0129	22.8 (0.3)	22.8
	0.0515	10.4 (0.1)	10.3
	0.0773	9.1 (0.1)	8.1
	0.103	7.2 (0.3)	6.9
	0.155	5.0 (0.1)	5.6
	0.258	4.4 (0.1)	4.5
penicillamine	0.0500	9.2 (0.1)	9.2
	0.100	5.5 (0.1)	5.6
	0.200	3.3 (0.1)	3.3
	0.300	2.3 (0.1)	2.4
	0.400	2.0 (0.1)	1.9
	0.450	1.8 (0.1)	1.8
cysteine methyl ester	0.0510	41.4 (0.1)	39.2
	0.102	29.2 (1.0)	29.8
	0.204	23.0 (0.6)	23.3
	0.306	20.5 (0.5)	20.8
	0.408	19.8 (0.3)	19.5
	0.459	19.0 (0.1)	19.0

[a] Conditions: 25.0 °C, $I = 0.2$ M (acetate), pH 6.0, [RSH] = 0.10 mM. Average deviations from the mean are shown in parentheses. [b] Calculated from nonlinear least-squares rate parameters (Table II).

mercapto amino acids at pH 6.0. Linear correlations of k_{obsd}^{-1} vs. $[RSH]^{-1}$ (Figure 1) support this interpretation and illustrate the reactivity order: penicillamine < cysteine < cysteine methyl ester, which pertains throughout the pH range 4–7.

Investigations of the k_{obsd} dependence on [dmp] at constant [RSH] are reported in Tables I (pH 6.0) and S1 (other pHs between 4 and 7).[16] These data show identical trends for all three reductants, as k_{obsd} decreases sharply with increasing [dmp] (constant pH) and $[H^+]$ (constant [dmp]). Although k_{obsd} becomes less sensitive to [dmp] at high ligand concentrations, non-zero limiting rates were found under these conditions.

Although the stoichiometry measurements show that $Cu(dmp)_2^+$ is the sole copper-containing product, this species certainly need not be generated directly from the mercaptan oxidation step. Equally clear is the participation of a single Cu(II) center in the slow steps of all redox pathways; by implication, thiyl radicals couple to give the ultimate disulfide organic products. Taking both the [RSH]- and the [dmp]-

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(16) Supplementary material.

Table II. Rate Parameters for the Oxidation of Mercaptans by Cu(II)-dmp Complexes[a,b]

mercaptan	pH	K_f^1	k_1, s^{-1}	K_f^0, M^{-1}	k_0, s^{-1}
cysteine	3.99	$4.7\ (1.2) \times 10^{-3}$	$5.0\ (1.3) \times 10$		
	4.98	$3.4\ (0.9) \times 10^{-2}$	$5.3\ (1.3) \times 10$		
	6.00	$1.1\ (0.1) \times 10^{-1}$	$4.8\ (0.5) \times 10$	$7.7\ (2.3) \times 10^2$	$4\ (1) \times 10$
	6.87	$4.3\ (0.1) \times 10^{-1}$	$1.0\ (0.2) \times 10^2$		
penicillamine	5.04	$7.3\ (1.1) \times 10^{-2}$	$2.9\ (0.4) \times 10$		
	5.97	$2.3\ (0.2) \times 10^{-1}$	$3.0\ (0.2) \times 10$	$1.0\ (0.2) \times 10^3$	5 (1)
	6.98	1.4 (0.2)	$3.3\ (0.5) \times 10$		
cysteine methyl ester	4.58	$3.3\ (0.8) \times 10^{-2}$	$6.7\ (1.7) \times 10$		
	4.97	$5.7\ (1.1) \times 10^{-2}$	$7.1\ (1.4) \times 10$		
	5.52	$1.1\ (0.2) \times 10^{-1}$	$7.7\ (1.2) \times 10$		
	5.99	$3.0\ (0.4) \times 10^{-1}$	$8.3\ (1.0) \times 10$	$6.8\ (1.7) \times 10^2$	$2.4\ (0.6) \times 10^2$
	6.51	$8.0\ (1.2) \times 10^{-1}$	$1.3\ (0.2) \times 10^2$		

[a] Parameters defined in eq 2 and calculated from nonlinear least-squares fits of k_{obsd}-[dmp] profiles to eq 3 (see text). [b] Conditions: 25.0 °C, $I = 0.2$ M (acetate). Standard deviations are shown in parentheses.

variation results into account, we propose two parallel pathways in the oxidation of mercapto amino acids by $Cu(dmp)_2^{2+}$ (eq 2). Charges are not specified for the dmp and $(dmp)_2$

$$RSH + Cu(dmp)_2^{2+} \overset{K_f^0}{\rightleftharpoons} Cu(dmp)_2(mercaptan) \quad (2a)$$

$$Cu(dmp)_2(mercaptan) \xrightarrow{k_0} products \quad (2b)$$

$$RSH + Cu(dmp)_2^{2+} \overset{K_f^1}{\rightleftharpoons} Cu(dmp)(mercaptan) + dmp \quad (2c)$$

$$Cu(dmp)(mercaptan) \xrightarrow{k_1} products \quad (2d)$$

intermediates, as the ionization state of the coordinated mercaptan cannot be assumed. It should also be noted that outer-and inner-sphere interpretations of the K_f^0 pathway are kinetically indistinguishable.

Provided that the K_f^0 and K_f^1 steps are rapid preequilibria, eq 3 and 4 describe the predicted dependence of k_{obsd} on [dmp] and [RSH] (at constant pH) under conditions where essentially all of the free mercaptan -SH groups are un-ionized.

$$k_{obsd} = \frac{(k_1K_f^1/[dmp] + k_0K_f^0)[RSH]}{1 + K_f^1[RSH]/[dmp] + K_f^0[RSH]} \quad (3)$$

$$k_{obsd}^{-1} = \frac{[dmp]/[RSH] + K_f^1 + K_f^0[dmp]}{k_1K_f^1 + k_0K_f^0[dmp]} \quad (4)$$

The decreasing trend in k_{obsd} with increasing [dmp] is clearly predicted by eq 3; limiting k_{obsd} values at high [dmp] would correspond to $k_0K_f^0[RSH]/(1 + K_f^0[RSH])$. Equation 4 correctly predicts linear k_{obsd}^{-1} vs. $[RSH]^{-1}$ plots (Figure 1), regardless of the dmp concentration.

A nonlinear least-squares fit[17] of k_{obsd}-[dmp] profiles to eq 3 was performed in order to extract the parameters K_f^0, K_f^1, k_0, and k_1. The results of these fits are set out in Table II. Initial estimates of K_f^1 and k_1 were derived from the initial slopes ($(k_1K_f^1[RSH])^{-1}$) and intercepts (k_1^{-1}), respectively, of k_{obsd}^{-1} vs. [dmp] plots at low [dmp], where the contribution of the K_f^0 pathway is smallest. Corresponding initial estimates of k_0 and K_f^0 could then be calculated from eq 3. Uncertainties in k_0 and K_f^0 are so large that quantitatively meaningful values may only be given for pH 6.0, where both [dmp] and [RSH] variation results are available.

Strong support for the proposed mechanism comes from the good agreement between observed rate constants and those calculated from eq 3 (k_{calcd}) with the least-squares rate parameters (see Table I). Although K_f^1 increases sharply with increasing pH, k_1 is strikingly insensitive to pH within the interval pH 4–6 and to structural differences among the three mercaptans. Less than a threefold difference in k_1 separates the most (cysteine methyl ester) and least (penicillamine) reactive reductants. These observations support rate-limiting oxidation of coordinated sulfur within Cu(dmp)(mercaptan) intermediates, as noncoordinated substituents remote from the Cu(II)-S bond should have little effect on the activation process.

Linear relationships exist between K_f^1 and $[H^+]^{-1}$ for cysteine, penicillamine, and cysteine methyl ester, giving slopes and non-zero intercepts of K_1^1 and K_0^1, respectively. On this basis, we conclude that both RS^- and RSH coordinate to Cu(II) following displacement of dmp in the K_f^1 pathway. The relationships between kinetically determined and thermodynamic (K_{c0}, K_{c1}) formation constants may be understood through eq 5–8. Calculations based on these relationships are presented in Table III.[21]

$$Cu(dmp)_2^{2+} \overset{K_d}{\rightleftharpoons} Cu(dmp)^{2+} + dmp \quad (5a)$$

$$RSH \overset{K_{12}}{\rightleftharpoons} RS^- + H^+ \quad (5b)$$

$$RS^- + Cu(dmp)^{2+} \overset{K_{c1}}{\rightleftharpoons} Cu(dmp)(RS)^+ \quad (5c)$$

$$RSH + Cu(dmp)^{2+} \overset{K_{c0}}{\rightleftharpoons} Cu(dmp)(RSH)^{2+} \quad (5d)$$

$$RSH + Cu(dmp)_2^{2+} \overset{K_1^1}{\rightleftharpoons} Cu(dmp)(RS)^+ + dmp + H^+ \quad (6a)$$

$$RSH + Cu(dmp)_2^{2+} \overset{K_0^1}{\rightleftharpoons} Cu(dmp)(RSH)^{2+} + dmp \quad (6b)$$

$$K_0^1 = K_dK_{c0} \quad (7)$$

$$K_1^1 = K_dK_{12}K_{c1} \quad (8)$$

By using microscopic -SH ionization constants (K_{12}) in these calculations, we assume that the mercaptan amino groups do not ligate Cu(II) throughout the entire pH range examined.

A comparison of K_{c1} values among the three mercaptan reductants shows little effect of β,β-dimethyl substituents or esterification of the carboxylate group on the stability of $Cu(dmp)(RS)^+$ precursor complexes. Therefore, S,O chelation of Cu(II) by cysteine and penicillamine in this intermediate

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Table III. Formation Constants Derived from K_f^1 [a,b]

parameter	mercaptan: cysteine	penicillamine	cysteine methyl ester
K_0^1	3 (1) × 10^{-2}	8 (1) × 10^{-2}	4 (1) × 10^{-2}
K_1^1, M	7.2 (0.6) × 10^{-8}	1.77 (0.06) × 10^{-7}	3.14 (0.10) × 10^{-7}
K_{12}, M	3.89 × 10^{-9} [c]	9.33 × 10^{-9} [c]	5.50 × 10^{-8} [d]
K_{c0}, M^{-1}	2 × 10^4	5 × 10^4	2 × 10^4
K_{c1}, M^{-1}	1.2 × 10^7	1.2 × 10^7	3.6 × 10^6
K_{c1}/K_{c0}	6 × 10^2	2 × 10^2	2 × 10^2
K_f^0(pH 6)/K_{c0}	4 × 10^{-2}	2 × 10^{-2}	3 × 10^{-2}

[a] Parameters defined and calculated as in eq 2, 5-8. K_d = 1.6 × 10^{-6} M.[18] Standard deviations are shown in parentheses. [b] Conditions: 25 °C, I = 0.2 M. [c] Reference 19. [d] Reference 20.

is unlikely. The [(dmp)Cu-S-cys]$^+$ formation constant is ca. 25 times larger than that characteristic of [(tmpa)Cu-S-cys]$^+$ (4.7 × 10^5 M^{-1}, 25 °C, I = 0.1 M),[3] as would be expected from the steric crowding in the latter complex and the π-accepting capability of dmp. Indeed, the penicillamine K_{c1} constant reported here contrasts strikingly with the Cu(tmpa)$^{2+}$–penicillamine system, in which the β,β-dimethyl groups totally inhibit Cu(II)–S complexation (pH 4–6).[3]

Stepwise stability constants of Cu(dmp)$^{2+}$(aq) and Cu(dmp)$_2^{2+}$(aq) are 1.6 × 10^5 and 6.3 × 10^5 M^{-1}, respectively, indicating that the first ligand actually facilitates uptake of the second dmp molecule, contrary to the usual trend.[18] The coordination geometry of Cu(II) evidently changes from square planar toward tetrahedral upon formation of Cu(dmp)$^{2+}$(aq).[18,22] This cooperativity in the ligation of Cu(II) reasonably could also contribute to the stability of Cu(dmp)(RS)$^+$ intermediates. Finally, we note that the K_{c1}/K_{c0} ratio is nearly invariant among the three substrates, as would be expected if the differences in Cu(dmp)(RS)$^+$ and Cu(dmp)(RSH)$^{2+}$ stability constants arise primarily from the comparatively weak Lewis basicity of the un-ionized thiol group.

Large uncertainties preclude a precise quantitative treatment of trends in K_f^0 and k_0 as a function of pH. Nevertheless, we note that modest increases in both parameters occur with increasing pH over the ranges shown in Table II. Within these pH ranges, trends in K_f^0 and k_0 are respectively as follows: (4.2–9.6) × 10^2 M^{-1}, 2.6 × 10^1–1.5 × 10^2 s^{-1} (cysteine); 9.1 × 10^2–3.0 × 10^3 M^{-1}, 3.7–2.6 × 10 s^{-1} (penicillamine); 3.9 × 10^2–1.7 × 10^3 M^{-1}, (1.2–2.4) × 10^2 s^{-1} (cysteine methyl ester). As is the case with k_1, the most abrupt increases in K_f^0 and k_0 occur above pH 6, where ionization of coordinated water may influence the kinetic parameters.[14]

The [dmp]-independent K_f^0 pathway may correspond to outer-sphere reduction of Cu(dmp)$_2^{2+}$(aq) or an inner-sphere mode involving displacement of coordinated water, but not dmp, from Cu(dmp)$_2^{2+}$(aq). The available data, while hardly conclusive, are best understood in terms of the latter alternative. In particular, the K_f^0 values are considerably larger than expected for strictly outer-sphere precursor constants, and the pH insensitivity of K_f^0, as compared with the case for K_f^1, suggests predominant inner-sphere complexation between Cu(dmp)$_2^{2+}$ and RSH. On this basis, the K_f^0(pH 6)/K_{c0} ratio is expected to be nearly invariant among the three mercaptans if ligation of Cu(II) is through sulfur in both preequilibria. This prediction is confirmed in Table III; these ratios indicate that the RSH–Cu(II) interaction in Cu(dmp)(RSH)$^{2+}$ is substantially weakened upon uptake of the second dmp ligand.

For each mercaptan examined, the rate constant k_0 is essentially invariant within the pH 4–6 interval, consistent with intracomplex one-electron or hydrogen atom transfer. In contrast, the outer-sphere oxidation rates of hydroquinones by Cu(dmp)$_2^{2+}$ exhibit an inverse first-order [H$^+$] dependence owing to the greater thermodynamic oxidizability of the phenolate anions.[9] Comparisons of k_0 and k_1 are complicated by the apparent difference between the predominant ionization states of the coordinated mercaptan in reactions 2b and 2d. Nevertheless, in the conversion of Cu(dmp)(RS)$^+$ to Cu(dmp)$_2$(RSH)$^{2+}$, one might expect compensating increases (owing to the addition of a Cu(I)-stabilizing dmp ligand) and decreases (owing to the weaker reducing strength of RSH) in electron-transfer rate constants. Indeed, k_0 and k_1 parameters are remarkably similar in the case of cysteine and cysteine methyl ester. With penicillamine, however, k_0 is significantly smaller than k_1, suggesting that the activation process may be hindered by interactions between the mercaptan and ligand methyl substituents.

An in-depth kinetic study of the reduction of Cu(II)–dmp complexes by thiourea and thiocyanate ion[14] provides an informative comparison with our results. Both of these weakly basic, sulfur-containing reductants form such thermodynamically stable complexes with the Cu(dmp)$^{2+}$ moiety in water that redox rate constants were found to be *independent* of [dmp]. The SCN^- oxidation mechanism, analogous to that proposed for thiourea, involves the rate-limiting reaction of free SCN^- with Cu(dmp)(SCN)(OH).[14] Thus, in contrast to our findings on mercapto amino acids, SCN^- and $H_2NC(S)NH_2$ complexes with Cu(dmp)$^{2+}$ apparently do not decompose via simple intracomplex electron transfer but require the assistance of an additional 1 equiv of reductant. Relatively stable dimeric $(SCN)_2^-$ anion radicals may be formed in this and other reactions of SCN^- with weak oxidants.[23] Although such assistance clearly is not required in the redox decay of Cu(dmp)$^{2+}$ and Cu(dmp)$_2^{2+}$ adducts with mercapto amino acids, a mechanism analogous to that given by Davies and Loose pertains in the reaction of cysteine with Cu(dien)$(H_2O)^{2+}$, a much weaker oxidant than the Cu(II)–dmp complexes.[24] In conclusion, our results confirm the accessibility of a unimolecular RS^-–Cu(II) decay pathway in complexes with a strongly oxidizing Cu(II) center. Mechanisms requiring reductive elimination of coordinated sulfur as a disulfide anion radical or direct disulfide formation within a binuclear Cu(II) intermediate evidently reflect comparatively weak thermodynamic driving force.

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Registry No. dmp, 484-11-7; Cu(dmp)$_2^{2+}$, 14875-91-3; cysteine, 52-90-4; cysteine, methyl ester, 2485-62-3; penicillamine, 52-67-5.

Supplementary Material Available: Table S1, listing k_{obsd} as a function of [dmp] in the oxidation of cysteine, cysteine methyl ester, and penicillamine at various pHs (2 pages). Ordering information is given on any current masthead page.

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