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Hydrogen Peroxide Oxidation by Chlorine Compounds. Reaction Dynamics and Singlet Oxygen Formation

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The kinetics of oxidation of hydrogen peroxide by several compounds (XCl) containing chlorine in its +1 formal oxidation state have been determined. The rate law in each instance is $-d[XCl]/dt = k[XCl][HO_2^-]$. Rate constants at 25.0 °C are $k = 4.4 \times 10^7$ M^{-1} s^{-1} for *tert*-butyl hypochlorite in 0.35 M *tert*-butyl alcohol ($\mu = 0.02$ M), $k = 1.5 \times 10^6$ M^{-1} s^{-1} for *N*-chlorosuccinimide ($\mu = 0.10$ M), and $k < 1$ M^{-1} s^{-1} for ethanolchloramine ($\mu = 0.10$ M). Formation of molecular oxygen in its $^1\Delta_g$ electronic excited state was detected for hydroperoxide oxidation by *tert*-butyl hypochlorite and *N*-chlorosuccinimide. The results confirm a previously proposed mechanism which identifies hydroperoxide ion and hypochlorous acid as the reactants in the corresponding singlet oxygen generating reaction between these compounds. General mechanistic features, which should be widely applicable to reactions of this type, are discussed.

Introduction

In a previous study of hydrogen peroxide oxidation by chlorine we had concluded from relative rate arguments that the critical parameter controlling reactivity was the electropositive character of the oxidant chlorine atom.[3] By this interpretation, hypochlorous acid and hydroperoxide ion were identified as the reactants in alkaline solution, although they are not the predominant forms of the reagents under these conditions. Because a firm understanding of the mechanism has important consequences to such diverse processes as theoretical modeling and design of large-scale reactors for production of singlet Δ oxygen[4] and cellular disinfection mechanisms in living organisms,[5] we have sought its further confirmation. If the reaction is initiated by electrophile–nucleophile associations, then other compounds containing electron-deficient chlorine should also react with hydroperoxide ion; furthermore, reactivities should be determined by the relative electropositive character of the oxidant chlorine centers. In this report we describe the kinetics of hydroperoxide ion oxidation by several monovalent chlorine compounds. The rate behavior predicted on the basis of our proposed mechanism is experimentally observed.

Experimental Procedures

Reagents. Commercial *tert*-butyl hypochlorite (Frinton Labs) was purified by distillation; the fraction boiling at 77–79 °C was retained. *N*-Chlorosuccinimide (Eastman) was recrystallized from warm water to remove minor impurities which gave absorption bands at 245 nm and in the near-ultraviolet region; mp 149–150 °C (lit. 150 °C). Succinimide was prepared by photolytic reaction of cyclohexene with *N*-bromosuccinimide in carbon tetrachloride;[6] the product was recrystallized four times from 95% ethanol; mp 124 °C (lit. 126 °C). Ethanolchloramine was prepared in situ in aqueous solution by reaction of hypochlorous acid with 20% excess ethanolamine. The ultraviolet spectrum [λ_{max}, nm (log ϵ_λ): 303 (2.18), 210 (3.03)] was consistent with complete conversion to the chloramine; no unreacted hypochlorous acid [λ_{max}, nm (log ϵ_λ): 235 (2.0)] was detected in the spectral curves.[7] Other chemicals were reagent grade and used without further purification. Water purified by reverse osmosis–ion exchange chromatography was used for all reagent preparations. Hydrogen peroxide solutions were standardized by iodometric titration.

Kinetic Measurements. All reactions were studied by measuring optical changes on a Cary 16 spectrophotometer equipped with a slit servo and recorder interface. Because the chlorine compounds used in these studies are unstable to alkaline conditions, it was necessary to add them as aqueous solutions to optical cuvettes containing hydrogen peroxide in buffered media. Although *tert*-butyl hypochlorite is relatively stable among the alkyl hypochlorites, it is extensively hydrolyzed in aqueous solutions to give hypochlorous acid.[9] For this reactant, the general procedure was adopted of mixing small volumes of concentrated *tert*-butyl hypochlorite in *tert*-butyl alcohol with hydrogen peroxide in aqueous buffer. Hydrolysis is subject to general acid–base catalysis;[9] the buffer concentrations taken were therefore the minimum necessary to maintain constant acidity. With phosphate and acetate buffers, it was found that, at an ionic strength of 0.02 M, the largest change in acidity that occurred in a kinetic run was ΔpH = 0.2 unit. At higher concentrations, buffer catalysis of hydrolysis severely interfered with direct reaction of the *tert*-butyl hypochlorite with hydrogen peroxide.

The progress of the hydrolysis reaction was measured at 215 or 290 nm, corresponding to loss of *tert*-butyl hypochlorite or hypochlorite ion formation, respectively; reaction with hydrogen peroxide was followed at 240–265 nm. Oxidation of hydrogen peroxide by *N*-chlorosuccinimide was monitored at 200–220 nm. At these latter wavelengths both reactants contribute to solution absorbancies. The reactions of ethanolchloramine were observed at 303 nm. For all oxidation reactions, hydrogen peroxide was in greater than eightfold excess; the reaction temperature was maintained constant at 25.0 °C by using a thermostated water bath.

Other Measurements. Gaseous reaction products were analyzed with use of an Extranuclear Laboratories, Inc., Model 324-9 quadrupole mass spectrometer. Formation of electronically excited oxygen ($^1\Delta O_2$) was detected with use of an uncooled germanium photodiode/filter combination. The filter band-pass (300 nm) was centered at 1.27 μm.

Results and Discussion

Oxidation by *tert*-Butyl Hypochlorite. Spectrophotometric investigation of the reaction stoichiometry at pH 6.2 in μ = 0.02 M phosphate buffer indicated complete loss of reactant absorbancies at a molar ratio of $[t\text{-BuOCl}]/[H_2O_2] = 1.0/1.1$. The ratio was wavelength independent (220–240 nm); when either reagent was added in excess of this ratio, the product was quantitatively accounted for by the excess. These results are consistent with net reaction governed by eq 1. Singlet

$$t\text{-BuOCl} + H_2O_2 \xrightarrow{k_1} O_2 + t\text{-BuOH} + HCl \tag{1}$$

molecular oxygen formation was observed with the 1.27-μm photodiode detector. For these measurements, neat *t*-BuOCl and 30% alkaline hydroperoxide were mixed by directing streams of reactant solutions from capillary jets onto the

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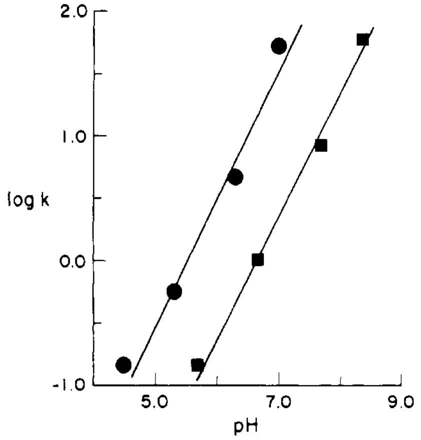


Figure 1. Acid dependence of second-order rate constants for hydrogen peroxide oxidation. Conditions: ●, *t*-BuOCl, 25 °C, [*t*-BuOH] = 0.35 M, $\mu = 0.020$ M acetate (pH 4.5, 5.3), $\mu = 0.020$ M phosphate (pH 6.3, 7.0); ■, NCS, 25 °C, $\mu = 0.10$ M phosphate. Individual data points are averages of 8–16 kinetic runs taken over 10-fold H_2O_2 concentration ranges; lines are weighted linear least-squares fits to the data points.

surface of an evacuated chamber. No optical signal appeared if strong base (NaOH) was omitted from the hydrogen peroxide solution.

Hydrogen peroxide oxidation can occur either by direct reaction, (eq 1) or by prior hydrolysis to form intermediary hypochlorous acid, i.e., eq 2 and 3.

$$t\text{-BuOCl} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} t\text{-BuOH} + HOCl \tag{2}$$

$$HOCl + H_2O_2 \xrightarrow{k_3} O_2 + H_2O + HCl \tag{3}$$

Formation of HOCl (eq 2) can be independently measured by omitting H_2O_2 from the aqueous buffer solution. Because the reaction proceeds toward equilibrium, the apparent hydrolysis rate constant (k_{hyd}) is given by $k_{\text{hyd}} = k_2 + k_{-2}$; individual rate constants can be determined from the equilibrium constant $K_{\text{hyd}} = [HOCl]\cdot[t\text{-BuOH}]/[H_2O][t\text{-BuOCl}]$ equal to[9] 0.024 at 25 °C. Under our experimental conditions *tert*-butyl hypochlorite is about 80% hydrolyzed to hypochlorous acid at equilibrium.

Reaction with H_2O_2 generally proceeds much more rapidly than hydrolysis, indicating oxidation primarily by the pathway given by eq 1; the rate of disappearance of reactants was found to be first order for the reaction conditions used (excess H_2O, constant pH, [*t*-BuOCl] = 0.35 M). The reaction between HOCl and H_2O_2 was calculated in all cases to be much greater than hydrolysis, i.e., $k_3 >> k_2$, so the intermediate HOCl (eq 2 and 3) does not accumulate. Therefore, the rate law for overall disappearance of *tert*-butyl hypochlorite is given by $-d[t\text{-BuOCl}]/dt = k_{\text{obsd}}[t\text{-BuOCl}]$, with $k_{\text{obsd}} = k_1' + k_2$, from which the apparent first-order rate constant (k_1') for direct reaction between *t*-BuOCl and H_2O_2 can be determined. In general, the k_2 pathway contributed less than 10% to the total observed rate, although at the lowest H_2O_2 concentrations used it approached 50% of the experimental value in some instances. The magnitude of k_1' was linearly dependent upon H_2O_2 concentration and showed inverse first-order dependence upon hydrogen ion concentration; data are summarized in Table I and Figure 1. The complete rate law for the direct reaction is therefore

$$-d[t\text{-BuOCl}]/dt = k_1[t\text{-BuOCl}][HO_2^-]$$

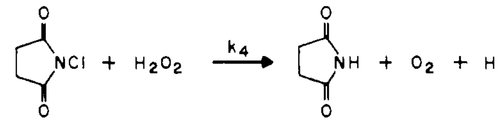
The overall reaction was accelerated by chloride ion. At $[Cl^-] = 0.1$ M, k_{obsd} for reaction in $\mu = 0.02$ M acetate buffer (pH 5.0) was fourfold greater than in the absence of chloride. The effect was found to be caused by a 500-fold increase in the rate of *t*-BuOCl hydrolysis, so that the pathway comprising eq 2 and 3 became predominant.

Table I. Summary of Rate Data[a]

$[\text{oxidant}]_0$, mM	$[H_2O_2]_0$, mM	$10^3k'$,[b] s^{-1}		k, M^{-1} s^{-1}
	1. *t*-BuOCl + H_2O_2 (Eq 1, Text)[c]			
	pH 4.5, $\mu = 0.020$ M Acetate			
0.88	98	12		0.13
1.8	195	31		0.16
			av	0.14 ± 0.02
	pH 5.3, $\mu = 0.020$ M Acetate			
0.88	9.8	7.1		0.72
0.88	29	13.5		0.46
0.88	59	24		0.41
0.88–1.7	98	65		0.66
			av	0.56 ± 0.13
	pH 6.3, $\mu = 0.20$ M Phosphate			
0.24	0.98	4.6		4.7
0.44	1.95	8.6		4.4
0.44	5.9	31		5.2
0.88	9.7	40		4.1
			av	4.6 ± 0.3
	pH 7.0, $\mu = 0.020$ M Phosphate			
0.22	0.98	72		73
0.22	1.95	64		33
			av	53 ± 20
	2. NCS + H_2O_2 (Eq 4, Text)[d]			
		pH 5.8		
0.74	20	3.1		0.15
0.77	40	5.2		0.13
				0.14 ± 0.01
		pH 6.7		
0.29	5.0	4.2		0.84
0.25	15	17		1.1
0.57	30	33		1.1
0.76	45	45		1.0
			av	1.0 ± 0.1
		pH 7.7		
0.06	0.40	5.6		14
0.11	0.75	8.8		11
0.27	2.0	22		11
0.27	5.0	43		8.6
			av	11 ± 1
		pH 8.4		
0.073	0.36	20		65
0.064	0.77	50		56
			av	60 ± 5

[a] At 25 °C; other conditions as specified. [b] $k' = k[H_2O_2]_0$; rate constants are averages of four individual runs. [c] In 0.35 M *tert*-butyl alcohol; k' is corrected for contribution of hydrolysis to the overall rates. [d] In $\mu = 0.10$ M phosphate.

Oxidation by Chloramines. Spectrophotometric changes in the ultraviolet region (230–260 nm) were consistent with 1:1 reaction of *N*-chlorosuccinimide (NCS) with H_2O_2 to give succinimide as a chromophoric product. Mass spectrometric analysis of evolved gases, occurring both when 30% alkaline peroxide was added to solid NCS and when reactants were mixed in homogeneous solution, indicated molecular oxygen to be the sole gaseous product; in particular, carbon dioxide was present at only trace levels. Singlet oxygen formation was evident from light emission at 1.27 μm. The net reaction is therefore



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N-chlorosuccinimide slowly decomposes in aqueous solution,

Table II. Rate Constants for Hydrogen Peroxide Oxidation[a]

XCl	k, M^{-1} s^{-1}	ref
HOCl	4.4×10^7	*b*
$(CH_3)_3COCl$	1.5×10^6	*c, d*
$(CH_2CO)_2NCl$	9.1×10^4	*c, e*
$HO(CH_2)_2NHCl$	<1	*c, e*

[a] At 25 °C; $-d[XCl]/dt = k[XCl][HO_2^-]$. [b] Reference 3; in $\mu = 0.10$ M phosphate. [c] This work. [d] In $\mu = 0.020$ M phosphate or acetate; [*t*-BuOH] = 0.35 M. [e] In $\mu = 0.10$ M phosphate.

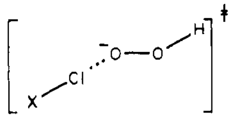
presumably with oxidative decarboxylation; hypochlorous acid is not a decomposition product. The reaction proceeds too slowly to interfere with H_2O_2 oxidation. In the presence of excess H_2O_2 at constant pH the oxidation reaction obeys first-order kinetics. As with *t*-BuOCl, the apparent rate constant was first order in H_2O_2 concentration and inversely first order in hydrogen ion concentration (Table I, Figure 1). The rate law is therefore

$$-d[NCS]/dt = k_4[NCS][HO_2^-]$$

The reaction was not accelerated in the presence of 0.1 M chloride ion.

Ethanolchloramine decomposes moderately rapidly in strongly alkaline media. Unlike other simple chloramines the hydrolysis product did not form,[8] but a weakly absorbing species with a spectral maximum at 252 nm was observed. Reaction with H_2O_2 could be detected only in strongly alkaline solutions, but the reaction rate under most favorable conditions was only about equal to the ethanolchloramine decomposition rate. This circumstance precluded careful examination of the H_2O_2 oxidation kinetics. An upper limit for the direct reaction between the chloramine and hydroperoxide ion was calculated on the basis of the difference in rates of optical change with H_2O_2 present and absent (Table II).

Geometries of the Activated Complexes. Rate constants for hydroperoxide ion oxidation are collected in Table II. The reactivity for *tert*-butyl hypochlorite is very nearly as great as that calculated for hypochlorous acid. Since replacement of the proton by an alkyl group is expected to alter the chemical reactivity of the O–Cl bond only slightly, the result provides strong evidence favoring assignment of HOCl and HO_2^-, rather than OCl^- and H_2O_2, as the reactive species in the alkaline HOCl–H_2O_2 reaction.[3] Bond polarities for the chlorine compounds under study are not well established.[10–12] Nonetheless, the order of reactivities appears to correlate well with the electropositive character of the oxidant chlorine atom based upon simple intuitive arguments. Thus, the intrinsic reactivity of chlorine bound to nitrogen is far less than chlorine bound to the more electronegative oxygen atom, but chloramines can be activated by introducing electron-withdrawing carbonyl substituents onto the nitrogen atom. Similarly, the small electron-donating inductive effect of the *tert*-butyl group causes loss of reactivity in the hypochlorite compounds. The simplest mechanism consistent with the data comprises reaction initiated by association of electrophilic chlorine with the strongly nucleophilic hydroperoxide oxygen atom, i.e., activated complexes of the general type



where X represents a suitable electron-withdrawing group. Since the reactions are highly exergonic, rates can be expected to depend strongly upon the magnitude of the initial associative interactions.[13]

Mechanistic ambiguities regarding proton sites in activated complexes also exist for other reactions of hypochlorous acid. Rates of chloramine formation[14] and aromatic ring chlorination of phenols[15] are inversely dependent upon hydrogen ion concentrations, indicating the reactive pairs are either HOCl and the basic forms or OCl^- and the acidic forms of the other reactants. Arguments based in chemical intuition have been advanced to suggest that HOCl and bases are the reactants; experimental support for this contention comes from observations that phenolic ethers[15] and the quaternary alkylammonium ion[16] choline ($HOCH_2CH_2N(CH_3)_3^+$) do not react with hypochlorous acid in alkaline solutions. It appears, therefore, that these reagents follow reaction pathways analogous to hydroperoxide ion.

Oxidation of Hydroperoxide Ion by Molecular Chlorine. In general, the reactivity exhibited by Cl_2 toward organic compounds in electrophilic addition reactions is greater than that of HOCl;[17] chlorine is also more reactive toward H_2O_2 than is hypochlorous acid.[3] These observations suggest that, if the reactants are simultaneously present in solution, molecular chlorine will react with hydroperoxide ion at a rate comparable to that found for hypochlorous acid, i.e., 10^{7-8} M^{-1} s^{-1} (Table II).

These conditions appear to be found in the highly nonequilibrium environments of sparger-type cells built for large-scale generation of singlet excited molecular oxygen.[4] For these reactions, gaseous Cl_2 is bubbled through basic solutions containing hydroperoxide ion at molar concentration levels. Gaseous singlet oxygen is produced initially in yields of up to 40–50% of the total oxygen generated; hydrochloric acid formed during the reaction eventually causes loss of basicity which effectively stops singlet oxygen evolution.

If organic amines are used as bases instead of alkali metal hydroxides, the initial singlet oxygen yield is unchanged. This observation provides support for our contention that chlorine reacts directly with hydroperoxide ion, as the following considerations will show. The important reactions of chlorine in these systems are given by eq 5–7. Rates of chlorine hydrolysis by hydroxide ion (eq 5) are rapid, although the rate constant has not been accurately determined;[18,19] in any event, k_5 cannot be greater than 10^{11} M^{-1} s^{-1}. Chloramines are formed in rapid bimolecular reactions between HOCl and amines; on the presumption that HOCl and the unprotonated bases are reactants, the rate constants are calculated to be k = 10^{7-8} M^{-1} s^{-1}. By analogy with the arguments advanced favoring high reactivity between Cl_2 and HO_2^-, we estimate that the rates of reaction of amines (RNH_2) with Cl_2 will be comparable in magnitude to their rates of reaction with HOCl.

$$Cl_2 + OH^- \xrightarrow{k_5} HOCl + Cl^- \qquad (5)$$

$$Cl_2 + HO_2^- \xrightarrow{k_6} O_2 + H_2O + HCl \qquad (6)$$

$$Cl_2 + RNH_2 \xrightarrow{k_7} RNHCl + HCl \qquad (7)$$

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The relative yield of hypochlorous acid formed from chlorine given by the concurrent reactions (eq 5–7) is

$$[\mathrm{HOCl}]/[\mathrm{Cl_2}] = k_5[\mathrm{OH^-}]/(k_5[\mathrm{OH^-}] + k_6[\mathrm{HO_2^-}] + k_7[\mathrm{RNH_2}])$$

In amine buffered solutions $[\mathrm{OH^-}] \simeq 10^{-4}$ M, whereas the other reactants are present in molar concentrations. With estimates of k_6 and k_7 provided by the data on the corresponding reactions with HOCl, it is apparent that HOCl formation can account for only a few percent of the loss of Cl_2 under the reactor conditions and, therefore, that HOCl cannot be an intermediate along the major pathways for singlet oxygen production. Furthermore, because chloramines formed from simple alkylamines do not react rapidly with HO_2^- ion (Table II) they also cannot serve as intermediates in the singlet oxygen forming reactions. The absence of appreciable loss of oxygen yields in the amine-containing solutions must therefore be due to preferential direct reaction between Cl_2 and the HO_2^- ion.[21]

In summary, the reactivities of several compounds containing monovalent chlorine toward hydrogen peroxide can be understood in terms of the electrophilic nature of their constituent chlorine atoms. The mechanism proposed for these reactions is probably quite general, with hydroperoxide ion representing one example of nucleophilic centers susceptible to oxidative attack by these reagents.

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Registry No. H_2O_2, 7722-84-1; *t*-BuOCl, 507-40-4; NCS, 128-09-6; $HO(CH_2)_2NHCl$, 52316-60-6.

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[21] The oxygen yields from reactors containing propylamine have been found to decrease with increasing concentration levels of the amine; a rate constant ratio of $k_5/k_6 \simeq 4$ can be estimated from the data.[22]

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Synthesis, Characterization, and Reactivity of Copper(I) and Copper(II) Complexes of *N*,*N'*-Bis(3-(2-thenylidenimino)propyl)piperazine (tipp) and *N*,*N'*-Bis(3-(2-thenylamino)propyl)piperazine (tapp). Crystal Structure of $[Cu(tapp)][ClO_4]_2$

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Copper(I) and copper(II) complexes of the new ligands *N*,*N'*-bis(3-(2-thenylidenimino)propyl)piperazine (tipp) and *N*,*N'*-bis(3-(2-thenylamino)propyl)piperazine (tapp) have been synthesized. Complexes of the type $[Cu(ligand)][ClO_4]$, ligand = tipp or tapp, have been prepared by the reaction of tipp or tapp with $[Cu(MeCN)_4][ClO_4]$. Complexes of the type $[Cu(ligand)]X_2$ ($X = ClO_4^-, NO_3^-, OSO_2CF_3^-$) have been prepared by the reaction of tipp or tapp with $Cu(ClO_4)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, or $Cu(OSO_2CF_3)_2$, respectively. The complexes have been characterized by conductivity measurements and by infrared, electronic, and EPR spectroscopy. In addition the structure of $[Cu(tapp)][ClO_4]_2$ has been determined by diffraction methods. The $[Cu(ligand)][ClO_4]_2$ complexes display CuN_4 coordination in solution and in the solid state. The nitrate complexes are properly described as $[Cu(ligand)(ONO_2)][NO_3]$ in both solution and the solid state, with CuN_4O coordination. While the $Cu^{II}OSO_2CF_3$ salts show CuN_4O coordination in the solid state, they display CuN_4 coordination in solution. For the Cu(I) complexes the $Cu(tapp)^+$ ion is rapidly oxidized in solution while the $Cu(tipp)^+$ ion is more stable and probably displays CuN_2S_2 or CuN_4S_2 coordination. For both the Cu(I) and Cu(II) complexes the tipp derivatives undergo the expected hydrolysis of the imine linkages in solution. In the solid state the $Cu(tapp)^{2+}$ ion of $[Cu(tapp)][ClO_4]_2$ displays a CuN_4 coordination that is severely distorted from square planar with N–Cu–N angles as small as 74.2 (2)° and deviations from the CuN_4 plane as large as 0.397 (4) Å. The disposition of the thiophene S atoms about the Cu ion is suggestive of an incipient CuN_4S_2 coordination. The material crystallizes with 4 formula units in space group C_{2v}^{17}-*C*2*ca* of the orthorhombic system in a cell of dimensions $a = 11.302$ (5), $b = 16.239$ (7), and $c = 13.948$ (6) Å. A crystallographic twofold axis is imposed on the cation. The structure has been refined to a final R index on F^2 of 0.079, on the basis of 167 variables and 2331 observations collected at −150 °C.

Introduction

Much current interest in the coordination chemistry of sulfur-containing ligands centers on the search for synthetic models for the metal sites of biological macromolecules and especially on attempts to understand the unusual physical properties of a variety of copper-containing proteins.[2] The X-ray structural determination of copper(II) poplar plastocyanin at 2.7-Å resolution[3] has provided valuable information about the structure of one "blue" copper center $Cu(his)_2(cys)(met)$, CuN_2SS^*. Yet important differences exist in the amino acid contents and hence the nature of the "blue" sites within the various proteins. An improved understanding of the structure/function relationships in these and related copper proteins must arise from complementary biological and model studies. Despite recent activity the chemistry and reactivity of copper(II) and especially copper(I) ions in nonclassical N_xS_y coordination environments remains largely undeveloped. There are a number of recent reports of low molecular weight complexes whose properties may be related to those of the Cu(II)

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