sulfenato product is stable enough to be observed and isolated;[1] but if the central metal is chromium(III), Cr–S bond fission occurs too rapidly for the sulfenato intermediate to be detected. This scenario is consistent with the previously described reactivity patterns for aquation and oxidation of thiolato–chromium(III) complexes (illustrated in Figure 1) which preclude significant Cr–S bond fission in the redox transition state.

Summary

The major conclusions and hypotheses presented in the previous sections can be summarized as follows. Coordinated thiols react with H_2O_2 via nucleophilic scission of the O–O bond to yield coordinated sulfenic acids. When coordinated to cobalt(III), the S-bonded sulfenato moiety is moderately stable, and the sulfenato–cobalt(III) product can be detected and isolated.[1] When coordinated to chromium(III), the inherent instability of the Cr–S bond causes the S-bonded sulfenato moiety to be unstable, and the presumed sulfenato–chromium(III) intermediate is not observed. Coordinated thiols are very good nucleophiles, reacting with H_2O_2 at about the same rate as $S_2O_3^{2-}$. Thiols coordinated to cobalt(III) are slightly better nucleophiles than thiols coordinated to chromium(III), presumably because π back-bonding from the t_{2g}^6 cobalt(III) center puts more electron density on the coordinated sulfur atom.[42] The rate of H_2O_2 oxidation of a coordinated thiol is relatively insensitive to the nature of the thiolato complex (thiolato chelate ring size, steric requirements of the thiol backbone, ancillary ligands, etc.). However, the rate of H_2O_2 oxidation of a coordinated sulfur atom is very sensitive to the steric requirements of the sulfur atom, the two-coordinate sulfur of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ being oxidized more than three orders of magnitude faster than the three-coordinate sulfur of $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$.

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Registry No. $[(en)_2Cr(SCH_2CH_2COO)]ClO_4$, 51911-43-4; $[(en)_2Cr(SC(CH_3)_2COO)]ClO_4$, 60195-76-8; Cr(tpa), 51911-42-3; Cr(tiba), 60195-75-7; Co(tga), 42901-31-5; Co(tiba), 68645-86-3; Cr(tga), 41654-60-8; Cr(cys), 48131-66-4; $[(H_2O)_5Cr(SCH_2CH_2NH_3)]^{3+}$, 59033-97-5; $[(H_2O)_4Cr(SCH_2COO)]^+$, 32696-60-9; $[(H_2O)_5Cr(SC_6H_4NH_3)]^{3+}$, 38833-30-6; $[Co(en)_2(SCH(CH_3)COO)]^+$, 60828-74-2; Co(cys), 42901-32-6; H_2O_2, 7722-84-1.

Supplementary Material Available: Table A, analysis of products resulting from H_2O_2 oxidation of $[Cr(en)_2(SCH_2COO)]^+$; Table B, analysis of products from oxidation of $[Cr(en)_2(SCH_2COO)]^+$; Table C, spectra of products from H_2O_2 oxidation of $[Cr(en)_2(SCH_2COO)]^+$. First-order rate parameters for the reaction of H_2O_2 with: Table D, $[Cr(en)_2(SCH_2CH_2NH_2)]^{2+}$; Table E, $[Cr(en)_2(SCH_2COO)]^+$; Table F, $[Cr(en)_2(SCH_2CH_2COO)]^+$; Table G, $[Cr(en)_2(SC(CH_3)_2COO)]^+$. First-order rate parameters for the H_2O_2-catalyzed aquation of: Table H, $[(H_2O)_4Cr(SCH_2COO)]^+$; Table I, $[(H_2O)_5CrSCH_2CH_2NH_3]^{3+}$; Table J, $[(H_2O)_5CrSC_6H_4NH_3]^{3+}$. First-order rate parameters for the oxidation of: Table K, $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$; Table L, $[Co(en)_2(SCH_2COO)]^+$; Table M, $[Co(en)_2(SCH(CH_3)COO)]^+$; Table N, $[Co(en)_2(SC(CH_3)_2COO)]^+$ (14 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Departments, Nuclear Research Centre, Negev, Beer Sheva, Israel,
Ben Gurion University of the Negev, Beer Sheva, Israel, and University of Rhode Island, Kingston, Rhode Island 02881

Oxidation, Reduction, and Copper–Carbon Bond Formation in the Reactions of Copper(II) Tetraglycine with Pulse Radiolytically Generated Free Radicals

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The reactions of copper(II) tetraglycine ($Cu^{II}G_4$) with a variety of aliphatic free radicals and with $\cdot Br_2^-$ and $\cdot OH$ have been investigated by the pulse radiolytic technique. Three types of reaction are observed: (i) oxidation of $Cu^{II}G_4$ to $Cu^{III}G_4$ by $\cdot Br_2^-$ and $\cdot OH$; (ii) rapid reduction to copper(I) by $\cdot CH_2OH$, $\cdot CO_2^-$, and $(CH_3)_2\dot{C}OH$; (iii) formation of unstable copper(III)–carbon-bonded intermediates with lifetimes from several milliseconds to several seconds with $\cdot CH_2C(CH_3)_2OH$, $\cdot CH_2CO_2^-$, and $\cdot CH_2C(OH)CH_3$ radicals. Rate constants are reported for formation and decomposition of all intermediates, and the relative instability of neutral $Cu^{III}(H_{-2}G_4)$ compared to $Cu^{III}(H_{-3}G_4)^-$ is confirmed by direct observation.

Introduction

Formation of Cu^{III}–C-bonded intermediates has been suggested as part of a general mechanism for Cu^{II} oxidation of aliphatic free radicals which are not strong reducing agents,[2] and, indeed, such an intermediate has been reported in the reaction of $Cu^{II}(aq)$ with $\cdot CH_2CO_2^-$ radicals.[3]

In a recent pulse radiolytic study,[4] it was shown that $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CO_2^-$ free radicals react with $Cu^{II}G_3$ (G_3 = triglycine peptide) via $Cu^{II}G_3 + \cdot R \rightarrow Cu^{III}G_3\text{–}R \rightarrow Cu^IG_3$ + products. At physiological pH, the unstable intermediates containing the $Cu^{III}G_3$–C bond have lifetimes of about 1 s. As this reaction sequence might be of general importance, indicating that "oxidizing" aliphatic free radicals might be scavenged by copper–protein complexes in biological systems, we decided to extend this study to the reactions of free radicals with $Cu^{II}G_4$. (The symbol G_4 is used here as a general term for tetraglycine; $H_{-2}G_4^{3-}$ and $H_{-3}G_4^{4-}$ are molecules with deprotonation at two and three peptide nitrogens, respectively, as well as at the carboxyl group.) It was suspected that, as $Cu^{III}G_4$ is more stable than $Cu^{III}G_3$,[5,6] the $Cu^{III}G_4$–R

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(1) (a) University of Rhode Island; on sabbatical leave at Ben Gurion University of the Negev, 1978–1979. (b) Nuclear Research Centre and Ben Gurion University of the Negev.

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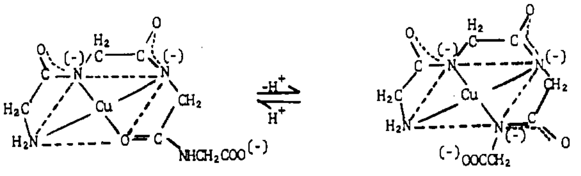
intermediates would also be more stable than $Cu^{III}G_3$–R. The results of the present study, however, do not support this hypothesis. We find that intermediates containing $Cu^{III}G_4$–C bonds have lifetimes similar to those for the analogous $Cu^{III}G_3$ species and that a spectral maximum at 320 nm seems characteristic for copper(III)–carbon-bonded complexes with both peptides.

In addition to $\cdot CH_2C(CH_3)_2OH$ and $\cdot CH_2CO_2^-$, $\cdot CH_2CH(OH)CH_3$ (but not $(CH_3)_2\dot{C}(OH)$) reacts with $Cu^{II}G_4$ to give a detectable intermediate.

Furthermore, in order to identify the copper–carbon intermediates, we have studied, for contrast, the reactions of strong reducing radicals $\cdot CO_2^-$ and $\cdot CH_2OH$ and strong oxidizing radicals $\cdot Br_2^-$ and $\cdot OH$ with $Cu^{II}G_4$. The latter reactions are of special interest as they provide a fast route to $Cu^{III}G_4$.

A variety of copper(III)–peptide complexes have been prepared by Margerum and co-workers,[7] who have paid particular attention to relatively stable $Cu^{III}G_4$.[5,8,9] For copper tetraglycine complexes a structural change accompanies the loss of the third peptide proton[8,10] as shown in structures I and II (where the central metal is either copper(II) or copper(III)).



I II

For copper(II) this deprotonation has a p*K* of 9.16[11] while the $Cu^{III}(H_{-3}G_4)^-$ species is the primary product even at pH <6 when copper(II) tetraglycine is oxidized either electrochemically or chemically by $IrCl_6^{2-}$ [5] or O_2.[8] The inference that I ⇄ II is relatively slow for Cu(III) and that the decomposition of $Cu^{III}G_4$ proceeds via the $H_{-2}G_4$ complex[8]

$$Cu^{III}(H_{-2}G_4) \rightarrow Cu^{II}(\text{products})$$

is confirmed by our direct observation of this reaction following oxidation of $Cu^{II}G_4$ by $\cdot Br_2^-$ and $\cdot OH$.

Experimental Section

Reagents. All chemicals were analyzed reagent grade and used without further purification. Triply distilled or millipore-deionized water was employed for all solutions.

Because of the possibility of spontaneous copper(II) tetraglycine decomposition in the presence of dissolved oxygen,[8] copper sulfate was added immediately before degassing to volumetric flasks already containing the source of free radicals, 0.001 M phosphate buffer (when used), and tetraglycine (Vega Biochemicals). Except where noted ligand concentration exceeded that of copper by 10%, and solutions were saturated with N_2O from which all traces of O_2 had been removed. Final pH adjustment was made during degassing by using NaOH and/or $HClO_4$.

All free-radical sources were present in sufficient concentration (1 M for acetate ion and the alcohols, 0.1 M for the others) to ensure quantitative formation (vide infra) of the desired radical reactant. Except for $\cdot CH_2OH$ at the highest pH, no significant hydrolysis or deprotonation occurs for any of the radicals employed within our pH range.[12] The presence of phosphate buffer protected reactant solutions from the small amounts of OH^- produced during radiolysis (cf. eq 2 and 4). Under conditions where buffering was unnecessary (i.e., high pH and/or high salt concentrations) the presence or absence of phosphate made no observable difference in the results.

Procedure. Pulse radiolysis studies were performed at the linear electron accelerator at the Hebrew University of Jerusalem. The apparatus and procedures for data analysis were as described elsewhere.[13,14] No variation in kinetic results was observed within a variation of dose of 500–3000 rd/pulse of 5-MeV electrons. In general, a fresh sample of solution was introduced before each pulse. All experiments were performed at 22 ± 2 °C. Reproducibility of rate constant determinations was generally within ±10%.

Spectral measurements were referenced to the absorbance at 420 nm of a 1×10^{-3} M $Na_4Fe(CN)_6$ solution which received a pulse identical with that of the sample solution. The molar absorption coefficient of the product $Fe(CN)_6^{3-}$ is $1.00 \times 10^3\ M^{-1}\ cm^{-1}$ at this wavelength.[15] Absorption coefficients reported here for reaction intermediates were corrected for reduced reaction yields due to spontaneous, nonproductive radical decomposition by estimating the limit to the absorbance with increasing $Cu^{II}G_4$ concentration.

The effect of the monitoring light on the stability of products was determined by placing Corning No. 7-54 and 0-51 filters between the light source and the reaction vessel. (In the pulse radiolysis technique, the monochromator is located in the control room just before the detector rather than between the light source and the reaction cell as in most spectrophotometric applications.) This combination allows less than 10% light transmission outside the range of 385–400 nm.[16]

Electrochemical oxidation of $Cu^{II}G_4$ to $Cu^{III}(H_{-3}G_4)^-$ was carried out on a platinum-screen electrode at 1100 MV vs. an Ag/AgCl reference electrode in 0.1 M Br^- and 0.1 M ClO_4^- solutions containing 0.001 M phosphate buffer at pH 8.2. Although bromide oxidation products cause a partial masking of the Cu^{III} peak at 365 nm, there were no other difficulties in comparing the stability of copper(III) tetraglycine prepared this way in the two media.

Results and Discussion

Production of Radical Reactants. The primary reactions caused by the absorption of ionizing radiation in aqueous media are summarized in eq 1. The yields of primary products (in

$$H_2O \rightsquigarrow e_{aq}^-, H, OH, H_2, H_2O_2, H_3O(aq) \qquad (1)$$

units of molecules produced per 100 eV of energy absorbed) are $G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2O_2} = 0.75$, and $G_{H_2} = 0.45$.[17] Saturating reactant solutions with N_2O ($[N_2O] = 0.02$ M) results in the rapid conversion of reducing solvated electrons to oxidizing hydroxyl radicals via eq 2.[18] Neither

$$\begin{gathered} e_{aq}^- + N_2O \rightarrow \cdot OH + OH^- + N_2 \\ k_2 = 8.7 \times 10^9\ M^{-1}\ s^{-1} \end{gathered} \qquad (2)$$

acid dissociation of $\cdot OH$ ($pK_a = 11.9$)[19] nor conversion of e_{aq}^- to $\cdot H$ ($k_{e^-+H^+} = 2.2 \times 10^{10}\ M^{-1}\ s^{-1}$)[18] is significant in the pH range of our experiments.

For each of the systems under investigation, the production of reactant free radical via eq 3 or 4[18] was rapid enough to

$$RH + \cdot OH \rightarrow \cdot R + H_2O \qquad (3)$$

$$Br^- + \cdot OH \xrightarrow{Br^-} \cdot Br_2^- + OH^- \qquad (4)$$

be complete before any reaction with $Cu^{II}G_4$ occurred.

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Table I. Data for the CuG_4 + $\cdot Br_2^-$ System[a]

pH	$10^4 \times [Cu^{II}G_4]$, M	$10^{-4} \times k_5$[b]	A_a	$10^{-3} \times k_6$, s^{-1}	A_b	k_8(app), s^{-1}	A_c
7.25	2.0	4.0	0.210	4	0.177	27	0.027
8.2	1.0	4.0	0.228	5	0.205	26	0.058
8.2	2.0	6.4	0.279	4.5	0.240	32	0.121
8.2[c]	2.0	6.8	0.238	4.3	0.199	29	0.066
8.2	6.0	18	0.283	3.8	0.223	30	0.170
8.5	2.0				0.235	38	0.128
9.0	2.0	4.9	0.280	3.0	0.247	40	0.220
9.5	2.0	5.2	0.278		0.254		0.254
10.2	2.0	5.2	0.312		0.288		0.288
11.0	2.0	6.0	0.290		0.268		0.268

[a] Solutions were N_2O saturated; 22 ± 2 °C; 10^{-3} M Na_2HPO_4; tetraglycine was in 10% excess; $[Br^-] = 0.1$ M. The absorbances A_a, A_b, and A_c were measured at 360 nm at 34 μs, 830 μs, and 175 ms, respectively, after the pulse. They refer to pulses of equal intensity corresponding to $\sim 4 \times 10^{-6}$ M oxidized species. See text for discussion of k_9. [b] Observed first-order rate constant; k_5 determined from $[Cu^{II}G_4]$ dependence at pH 8.2. [c] $[Br^-] = 0.01$ M; $[NaClO_4] = 0.09$ M.

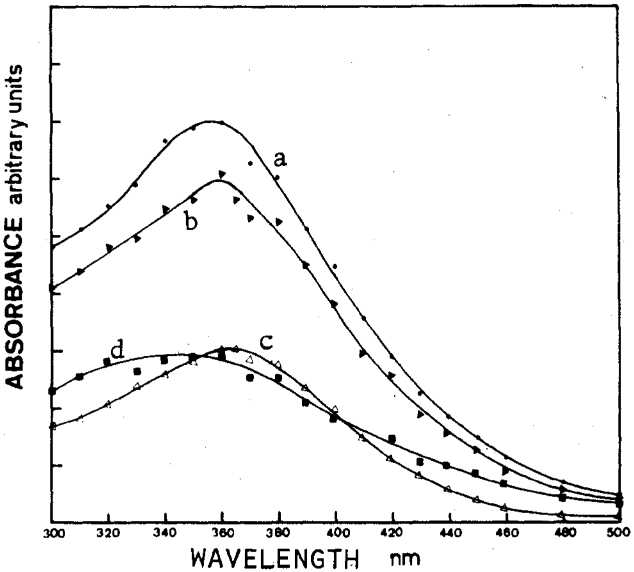

Figure 1. Spectra of transients produced in the reaction of $Cu^{II}G_4$ with $\cdot Br_2^-$ ($[Cu^{II}G_4] = 2 \times 10^{-4}$ M, pH 8.2, $[Br^-] = 0.1$ M): (a) 34 μs after the pulse; (b) 830 μs after the pulse; (c) 175 ms after the pulse; (d) curve b minus curve c.

Spontaneous decomposition of the radical (through, e.g., bimolecular recombination) was slow enough to be insignificant in some cases and accountable through blank experiments and concentration dependences in others.

Oxidation of $Cu^{II}G_4$ to Copper(III) Tetraglycine. Margerum and co-workers have established that oxidation of copper(II) tetraglycine by O_2,[8] $IrCl_6^{2-}$,[5] and electrochemical means[5] results exclusively in the metastable copper(III) complex $Cu^{III}(H_{-3}G_4)^-$ in which the carboxyl and three nitrogen protons are ionized (structure II) even at a pH region where $Cu^{II}G_4$ is more highly protonated. The pK_a values for loss of the three peptide hydrogens on $Cu^{II}G_4$ are 5.5, 6.8, and 9.2, respectively.[11] Since the transformation from $Cu^{III}(H_{-2}G_4)$ to $Cu^{III}(H_{-3}G_4)^-$ appears to occur via a redox mechanism rather than simple, rapid proton transfer[8] (see eq 7), we decided to employ the strong, one-electron oxidizing agents $\cdot OH$ and $\cdot Br_2^-$ to oxidize $Cu^{II}G_4$ under conditions where both $Cu^{III}(H_{-2}G_4)$ and $Cu^{III}(H_{-3}G_4)^-$ would be produced. Because of the high reactivity of $\cdot OH$ radicals toward other solutes including itself and possibly tetraglycine (as noted by an initial second-order reaction and a decreased yield of products), the systematic study was carried out primarily in 0.1 M sodium bromide solutions in the pH range 7.25–10.95. For both radicals, however, we conclude (vide infra) that the most stable intermediate produced is, indeed, $Cu^{III}(H_{-3}G_4)^-$.

Oxidation of Br^- to $\cdot Br_2^-$ in the presence of $Cu^{II}G_4$ is followed by four subsequent reactions for which kinetic and spectral data are given in Table I and Figure 1. The set of reactions (6)–(9) seem to provide the best internally self-consistent explanation for these data (all rate constants are $\sim \pm 15\%$).

$$Cu^{II}G_4 + \cdot Br \rightarrow Cu^{III}(G_4)Br + Br^- \qquad k_5 = 2.6 \times 10^8\ M^{-1}\ s^{-1} \tag{5}$$

$$Cu^{III}(G_4)Br \rightarrow Cu^{III}G_4 + Br^- \qquad k_6 = 4.1 \times 10^3\ s^{-1} \tag{6}$$

$$Cu^{III}(H_{-2}G_4) + Cu^{II}(H_{-3}G_4)^{2-} \rightleftarrows Cu^{II}(H_{-2}G_4)^- + Cu^{III}(H_{-3}G_4)^- \qquad E^\circ = \sim 0.3\ V^{20} \tag{7}$$

$$Cu^{III}(H_{-2}G_4) \rightarrow Cu^{II}(\text{products}) \qquad k_8(\text{app}) = 32\ s^{-1} \tag{8}$$

$$Cu^{III}(H_{-3}G_4)^- \rightarrow Cu^{II}(\text{products}) \qquad k_9 = 2 \times 10^{-4}\ s^{-1\,20} \tag{9}$$

The absorbances A_a, A_b, and A_c in Table I were measured at 360 nm after reactions 5 (34 μs, after the pulse), 6 (830 μs), and 8 (175 ms), respectively. The spectra in Figure 1 were measured at corresponding times (except for curve d which is the difference between curves b and c) at pH 8.2. Thus, according to this reaction scheme, curve a in Figure 1 represents the net absorbance of a mixture of $Cu^{III}(H_{-2}G_4)Br^-$ and $Cu^{III}(H_{-3}G_4)Br^{2-}$ (ϵ(app) = 5700 at 360 nm) and spectrum b is for the mixture of the two forms of $Cu^{III}G_4$ (ϵ(app) = 4800 at 360 nm). Curve c is the spectrum of $Cu(H_{-3}G_4)^-$ reduced by the fraction of copper(III) that reacts via reaction 8.

From the relative insensitivity of both A_a and A_b to pH, we conclude that the two protonation states of both $Cu^{III}(G_4)Br$ and $Cu^{III}G_4$ have similar extinction coefficients at 360 nm. Thus, the ratio A_c/A_b is approximately equal to the fraction of $Cu^{III}(H_{-3}G_4)^-$ remaining after reactions 7 and 8. The difference spectrum d may not be an accurate spectrum for $Cu^{III}(H_{-2}G_4)$ because of the possibility that reactions 7 and 8 proceed concurrently (see below).

Formulation of the first two reactions as corresponding to formation and dissociation of a Cu^{III}–Br complex is consistent with observations in several other metal–bromide systems.[21] The observation that k_5 is essentially independent of pH indicates that the rates of oxidation of $Cu^{II}(H_{-2}G_4)^-$ and $Cu^{II}(H_{-3}G_4)^{2-}$ by $\cdot Br_2^-$ are very similar. Alternate possibilities such as direct oxidation with no Cu–Br intermediate would require postulation of a second step (e.g., a conformational change in the oxidized product) which seems inconsistent with subsequent reactions. The similarity of the spectra (Figure 1, curves a and b) and the rather small absorbance change which accompanies the second step throughout our pH range (cf. A_a and A_b) appears inconsistent with a two-step oxidation mechanism involving attack of $\cdot Br_2^-$ on the G_4 ligand with subsequent intramolecular oxidation of the metal.

Margerum et al. report a spectral maximum at 365 nm with ϵ = 7100 for the oxidized complex whose identity they determined to be $Cu^{III}(H_{-3}G_4)^-$.[5] The spectrum which we have attributed to this species (curve c in Figure 1) is in good

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(20) From ref 8.

(21) (a) Jaacobi, M.; Meyerstein, D.; Lilie, J. *Inorg. Chem.* **1979**, *18*, 429. (b) Lati, J.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1978**, 1105. (c) Meyerstein, D.; Espenson, J. H.; Ryan, D. A.; Mulac, W. A. *Inorg. Chem.* **1979**, *18*, 863.

Table II. Kinetic Data for the $CuG_4 + {\cdot}CH_2C(CH_3)_2OH$ System[a]

pH	$10^4 \times$ $[Cu^{II}G_4]$, M	$10^{-3} \times$ k_{obsd}(formn), s^{-1}	k(decay), s^{-1}
7.5	2.0	3.3	0.66
7.5[b]	2.0	4.2	0.62
7.8[c]	2.0	3.6	0.75
8.1	1.0	2.0	1.1
8.1	2.0	4.5	1.1
8.1[d]	2.0	4.2	1.4
8.1	4.0	6.0	1.2
8.1	6.0	9.7	1.4
8.2	2.0	3.6	
8.9	2.0	4.1	6.7
9.5	2.0	2.9	27
9.9[e]	2.0	3	65
10.3	2.0	3.3	160
10.3[b]	2.0	3.1	130

[a] N_2O saturated; 22 ± 2 °C; most solutions contained 10^{-3} M Na_2HPO_4 and 10% excess G_4. [*tert*-Butyl alcohol] = 1 M. [b] 2×10^{-4} M Hg^{2+} added. [c] 5×10^{-5} M sodium fumarate added. [d] 7×10^{-4} M tetraglycine. [e] Monitoring light filtered; see text for details.

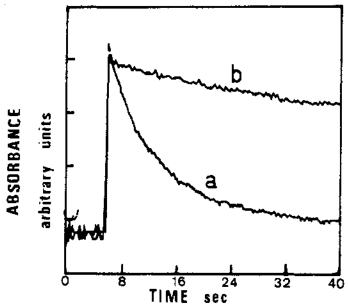

Figure 2. Effect of incident light on the stability of $Cu^{III}(H_{-3}G_4)^-$: decomposition of $Cu^{III}(H_{-3}G_4)^-$ followed at 390 nm by using (a) normal monitoring light and (b) filtered light ($[Cu^{II}G_4] = 2 \times 10^{-4}$, pH 10.5).

agreement with theirs, also having $\lambda_{max} = 365$ nm, and, if we presume that at high pH all copper(III) is in this form (cf. Table I), an extinction coefficient of $\epsilon_{365} \simeq \epsilon_{360} = 6300 \pm 1000$.

The fact that the extent of spectral change in the third reaction, $(A_b - A_c)/A_b$, is extremely pH dependent while the rate constant k_8(app) is pH independent provides support for Margerum's postulation that $Cu^{III}(H_{-3}G_4)^-$ is the stable form of copper(III) tetraglycine[5] and that decomposition occurs through $Cu^{III}(H_{-2}G_4)$[8] which has a higher yield at lower pH.

In the absence of an interconversion mechanism (e.g., reaction 7) the fraction of $Cu^{III}(H_{-3}G_4)^-$ remaining after reaction 8 would be only ~1% at pH 7.2 and 10% at pH 8.2. The fact that significantly more $Cu^{III}(H_{-3}G_4)^-$ is observed than predicted by the pK_3 of copper(II) tetraglycine indicates that interconversion does occur. On the other hand, the fact that interconversion is not complete at pH < $pK_2(Cu^{II})$ is in agreement with the earlier postulation[8] that comparatively slow ligand rearrangement accompanying reaction 7 prevents rapid deprotonation of $Cu^{III}(H_{-2}G_4)$ even though the $E°$ value indicates that this process should be complete. Since the ultimate yield of $Cu^{III}(H_{-3}G_4)^-$ lies between these two extremes we conclude that reactions 7 and 10 occur in the forward direction

$$Cu^{III}(H_{-2}G_4)Br^- + Cu^{II}(H_{-3}G_4)^{2-} \rightleftarrows Cu^{II}(H_{-2}G_4)^- + Cu^{III}(H_{-3}G_4)Br^{2-} \quad (10)$$

on a time scale competitive with reactions 8 and 6, respectively. The decrease in A_c/A_b at low $[Br^-]$ can then be attributed to (10) and the reverse of (6); i.e., at higher $[Br^-]$ the amount of $Cu^{III}(H_{-2}G_4)Br^-$ which is converted to the $H_{-3}G_4$ form is larger. Although alternative reactions are possible when ·OH is the oxidant (vide supra), the participation of eq 7 is supported by the observation of a somewhat increased fraction of $Cu^{III}(H_{-3}G_4)^-$ in the absence of Br^- (above 20% at pH 8.2 and $[Cu^{II}G_4] = 2 \times 10^{-4}$ M). However, a lack of copper(II) tetraglycine concentration dependence, within experimental error, for k_8(app) seems to indicate that at 0.1 M Br^- reaction 10, in which Br^- could facilitate inner-sphere electron transfer, is the predominant interconversion pathway leading to enhanced yields of $Cu^{III}(H_{-3}G_4)^-$ as $[Cu^{II}]$ and/or pH is increased at constant $[Br^-]$. Thus, the composite rate constant $k_8(\text{app}) = 32 \pm 5\ s^{-1}$ is similar to the actual value of k_8.

Under our normal experimental conditions, the decomposition of $Cu^{III}(H_{-3}G_4)^-$ (reaction 9) leaves no spectral absorbance in the region of measurement and has a first-order rate constant of $\sim 0.2\ s^{-1}$. This is almost three orders of magnitude faster than the rate reported by Margerum,[8] who noted that this reaction is light sensitive. Thus, we find that, when filters are placed between the sample and the 150-W xenon light source giving a window in the 385–400-nm region, there is a dramatic increase of over a factor of 10 in the stability of Cu^{III}. This effect is demonstrated in Figure 2. Because the upper time limit of our apparatus is about 40 s, no attempt was made to further reduce the intensity of the monitoring light source.[22] However, to test whether bromide also plays a role in destabilizing $Cu^{III}(H_{-3}G_4)^-$, we performed parallel experiments with ·OH as oxidant in the absence of Br^-, and, in addition, $Cu^{III}(H_{-3}G_4)^-$ was prepared in both 0.1 M NaBr and 0.1 M $NaClO_4$ at pH 8.2 by electrochemical oxidation of solutions containing 8×10^{-5} M $Cu^{II}G_4$. The pulse radiolysis results were (for the decomposition reaction) identical in the presence and absence of bromide, and the decomposition rates of the electrochemically prepared $Cu^{III}G_4$ in both media agreed very well with those previously reported.[23]

In their analysis of copper(III) tetraglycine decomposition and its role in the autooxidation of copper(II) tetraglycine, Kurtz, Burce, and Margerum[8] postulate a first-order dependence on OH^- of $Cu^{III}(H_{-2}G_4)$ decomposition (cf. eq 8 with their eq 11) which disappears from their overall rate law. Our direct measurement of the kinetics of this process indicates that, in the pH range where significant quantities of $Cu^{III}(H_{-2}G_4)$ are produced, its decomposition is independent of pH ($k_8(\text{app}) = 32\ s^{-1}$).

The absence of a pH dependence for both k_6 and k_8(app) seems inconsistent with the possibility that the more rapidly decomposing copper(III) product contains either an axial OH^- or a deprotonated but not yet rearranged (to structure II) $H_{-3}G_4$ group in equilibrium with $Cu^{III}(H_{-2}G_4)$. Thus, there appears to be a minor discrepancy between our results and those of the earlier workers. The lack of a pH effect on the overall formation and decay of $Cu^{III}(H_{-3}G_4)^-$ in the presence of O_2[8] seems somewhat inconsistent with the present results. However, the major conclusion that $Cu^{III}(H_{-3}G_4)^-$ is the more stable form of copper(III) tetraglycine both kinetically and thermodynamically is in complete harmony with our conclusions.

Reaction 9 in our mechanism represents a multistep reaction sequence which, we feel, includes the conversion of $Cu^{III}(H_{-3}G_4)^-$ to $Cu^{III}(H_{-2}G_4)$ (by the reverse of reaction 7) as postulated in ref 8.

Like $Cu^{III}(H_{-2}G_4)$, the $Cu^{III}(H_{-4}G_4)^{2-}$ ion has been found to be less stable than $Cu^{III}(H_{-3}G_4)^-$.[9a] No influence of the loss

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(22) All other reactions reported in this paper are unaffected by light intensity (cf. Tables II and III).

(23) Reference 8 gives an observed rate constant of $k_9 = 2 \times 10^{-4}\ s^{-1}$ under similar conditions. Our values are $3 \times 10^{-4}\ s^{-1}$ in 0.1 M $NaClO_4$ and $8 \times 10^{-4}\ s^{-1}$ in 0.1 M Br^-. We are satisfied with the agreement in both media since the latter measurement is complicated by the absorbance due to Br^- oxidation products.

Table III. Kinetic Data for the $CuG_4 + \cdot CH_2COO^-$ System[a]

pH	$10^4 \times [Cu^{II}G_4]$, M	$10^{-3} \times k_{obsd}$(formn), s^{-1}	k(decay), s^{-1}
7.6	2.0	8.0	0.65
8.1	1,0	3.0	0.84
8.1	2.0	3.3	0.34
8.0	4.0	5.0	0.45
8.1	6.0	7.0	0.36 (112)[b]
8.2	2.0	3.0	
8.5	2.0	~4	0.16[c]
8.6	2.0	2.1	0.19
9.3	2.0	2.0	0.055 (75)[b]
9.9	2.0	3.2	0.065
9.9[d]	2.0	2.6	0.059

[a] N_2O saturated; 22 ± 2 °C; most solutions contained 10^{-3} M Na_2HPO_4. [b] Rate constant for ~15% absorbance change; not resolved in other experiments. [c] Monitoring light filtered. [d] 2×10^{-4} M Hg^{2+} added.

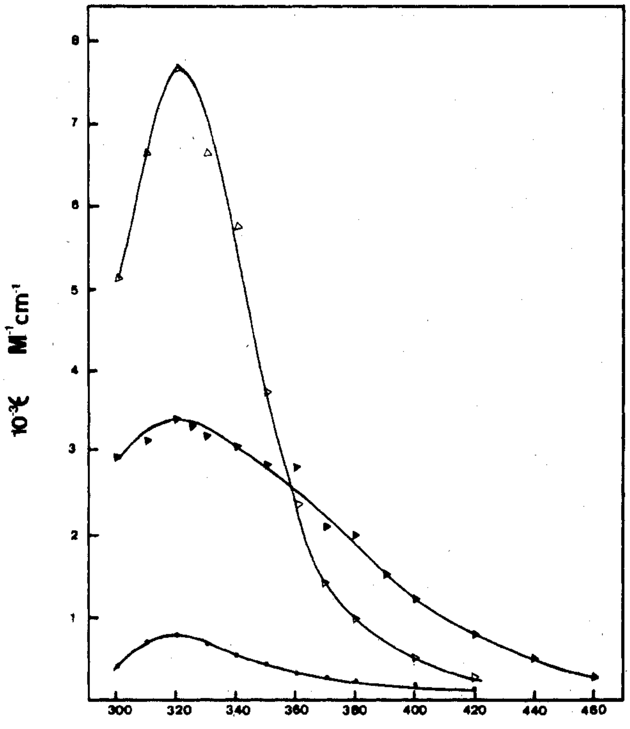

Figure 3. Absorption spectra of transients produced by the reaction of $Cu^{II}G_4$ with $\cdot CH_2C(CH_3)_2OH$ (△), $\cdot CH_2COO^-$ (▲), and $\cdot CH_2CH(OH)CH_3$ (•). The smaller apparent extinction coefficient in the latter case is a result of the fact that the reacting radical is only a minor product of the irradiation of the isopropyl alcohol solution. All spectra were determined at pH 8 with $[Cu^{II}G_4] = 2 \times 10^{-4}$ M and normalized to the limiting absorbance for high $[Cu^{II}G_4]$.

of the proton from the fourth (amine) nitrogen ($pK = 12.1$)[9] is observed under our conditions.

Reaction of $Cu^{II}G_4$ with $\cdot CH_2OH$ and $\cdot CO_2^-$ Radicals. When solutions of $Cu^{II}G_4$ containing methanol (1 M) or sodium formate (0.1 M) were irradiated in the pH range 7.3–10, the initial, rapid increase in absorbance due to free radical formation decreased via a first-order process. Final absorbances measured between 290 and 330 nm were less than those of the original copper(II) tetraglycine solutions. No rapid change in absorbance was observed at longer wavelengths. Formation of a colloidal product began within 500 ms of the pulse. For both systems, free radical disappearance was first order in $Cu^{II}G_4$. As $\cdot CH_2OH$ and $\cdot CO_2^-$ are strong reducing agents,[24] our conclusions concerning these reactions are as summarized in eq 11 and 12.

$$Cu^{II}G_4 + \cdot CH_2OH \rightarrow Cu^{I}G_4 + CH_2O \qquad k_{11} = 8.6 \times 10^7\ M^{-1}\ s^{-1} \tag{11}$$

$$Cu^{II}G_4 + \cdot CO^- \rightarrow Cu^{I}G_4 + CO_2 \qquad k_{12} = 6.5 \times 10^8\ M^{-1}\ s^{-1} \tag{12}$$

The colloidal product could be either copper(I) hydroxide or copper(0) formed by $Cu^{I}G_4$ disproportionation (next section).

Reaction of $Cu^{II}G_4$ with $\cdot CH_2C(CH_3)_2OH$ and with $\cdot CH_2COO^-$. Kinetic data are given in Tables II and III for solutions of copper(II) tetraglycine irradiated in the presence of 1 M *tert*-butyl alcohol and 1 M sodium acetate, respectively. In both cases pseudo-first-order formation of an unstable intermediate with an absorption maximum at 320 nm (Figure 3) is observed. The specific absorptivities for the *tert*-butyl alcohol and acetate intermediates are $\epsilon_{max} = 7650$ and 3460 $M^{-1}\ cm^{-1}$, respectively. These reactions are first order in $Cu^{II}G_4$ and essentially independent of pH. We attribute these reactions to copper–carbon bond formation resulting in species which formally contain trivalent copper as shown in eq 13 and 14. The values of k_{13} and k_{14} were determined from copper(II) tetraglycine dependences at pH 8.1.

$$Cu^{II}G_4 + \cdot CH_2C(CH_3)_2OH \rightarrow G_4Cu^{III}\text{–}CH_2C(CH_3)_2OH \qquad k_{13} = 2 \times 10^7\ M^{-1}\ s^{-1} \tag{13}$$

$$Cu^{II}G_4 + \cdot CH_2COO^- \rightarrow G_4Cu^{III}\text{–}CH_2COO^- \qquad k_{14} = 9 \times 10^6\ M^{-1}\ s^{-1} \tag{14}$$

The assignment of these products as species containing copper(III)–carbon bonds is based on the following arguments: (a) The spectra of the intermediates are not those of $Cu^{III}G_4$ (Figure 1) or $Cu^{I}G_4$ (preceding section). (b) Under our experimental conditions, these radicals do not react with tetraglycine. (c) Thus, formation of a copper(III)–carbon bond appears to be the only plausible interpretation of these data. These conclusions are in agreement with earlier observations concerning the reactions of these radicals with $Cu^{2+}(aq)$[3] and $Cu^{II}G_3$.[4]

Both Cu^{III} intermediates decay in a first-order process which is independent of copper concentration but varies with pH (Tables II and III). Plots of log k (for decay) vs. pH are linear (pH range 7.5–10) with slopes of 1.0 for the *tert*-butyl alcohol system and approximately –0.5 for the acetate. In some experiments in acetate media, a rapid decrease in absorbance ($k \approx 100\ s^{-1}$) of very small amplitude was observed (at 380 nm) before the major decay.

Formation of a colloidal precipitate after the decay reaction is interpreted as due to $Cu^{I}OH$ or elemental copper formed in the sequence

$$G_4Cu^{III}\text{–}R \rightarrow Cu^{I}G_4 + \text{organic products} \tag{15}$$

$$Cu^{I}G_4 \rightarrow Cu^{I}OH \quad \text{and/or} \quad Cu^0 + Cu^{II}G_4 \tag{16}$$

Introduction of small amounts of fumarate ion which is known to complex Cu(I) was found to suppress all signs of turbidity, even after several pulses. It should be noted that, although the reactants in eq 13 and 14 are a mixture of $Cu^{II}(H_{-2}G_4)^-$ and $Cu^{II}(H_{-3}G_4)^{2-}$ whose composition is pH dependent, the rates of these reactions are OH^- independent. However, unlike

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(25) Meyerstein, D. *Inorg. Chem.* **1975**, *14*, 1716.

the $Cu^{III}G_4$ system, we see no evidence for more than one G_4Cu^{III}–R product in the *tert*-butyl alcohol system while the origin of the minor reaction (with $k \approx 100\ s^{-1}$) in the acetate system is not clear. This might be due either to similar properties of $(H_{-2}G_4)Cu^{III}$–R and $(H_{-3}G_4)Cu^{III}$–R or to a rapid interconversion to the more stable protonation state.

The different pH dependences of copper–carbon bond decomposition found for these two systems indicates that the nature of the aliphatic residue affects the mechanism of decomposition. The present data do not encompass enough of a variety of ligands to allow us to analyze the detailed nature of reaction 15.[26] Espenson[27] has noted several instances in which Co(III)- and Cr(III)–carbon bond decomposition is catalyzed by mercuric ion reacting by an S_E2 mechanism. In some experiments, we added mercuric ion to our solutions to test whether analogous reactions would occur. However, no effect of Hg^{2+} was noted even under conditions where decomposition is slowest. This result may be due to the generally higher rates of decomposition of the copper(III)–carbon bonds and/or to smaller electron density on carbon in the copper systems compared to the cobalt and chromium systems.

Reactions of Copper(III) Tetraglycine in Irradiated Isopropyl Alcohol Solutions. Radiolysis of solutions containing isopropyl alcohol resulted in hydrogen abstraction from either the α or β position as shown in reaction 17.[28] The major product

$$\begin{aligned}\cdot OH + CH_3CH(OH)CH_3 &\rightarrow \cdot CH_2C(OH)CH_3 \quad \sim 11\% \\ &\rightarrow (CH_3)_2\dot{C}(OH) \quad \sim 89\%\end{aligned} \tag{17}$$

$(CH_3)_2\dot{C}(OH)$ is primarily a reducing radical[29] while $\cdot CH_2CH(OH)CH_3$ is expected to have similar properties to those of $\cdot CH_2(CH_3)_2OH$.

Irradiation of solutions containing $Cu^{II}G_4$ and 1 M isopropyl alcohol results in the formation of an unstable intermediate with an absorbance maximum at 320 nm and an apparent $\epsilon_{max} \approx 800$ at pH 8.2 (Figure 3). The formation of this intermediate is first order in Cu(II), and we assign this process to reaction 18. At lower pH and above pH 9.5, the absorbance increase becomes less pronounced. The decomposition of the Cu^{III} intermediate has a $[Cu^{II}]$- and (essentially) pH-independent rate constant of $0.5 \pm 0.2\ s^{-1}$. The conclusion that reaction 18 results in a Cu(III) species seems reasonable when compared to the results obtained with the acetate and *tert*-butyl alcohol systems. Thus, if we adjust the absorptivity at 320 nm for the supposition that only 11% of the free radicals produced at pH 8.2 are $\cdot CH_2CH(OH)CH_3$, we obtain a value of $\epsilon_{max} = 7300$ for $G_4Cu^{III}–CH_2CH(OH)CH_3$ which is similar to that obtained for $G_4Cu^{III}–CH_2C(CH_3)_2OH$. A precipitate becomes visible after about 1 s.

$$Cu^{II}G_4 + \cdot CH_2CH(OH)CH_3 \rightarrow G_4Cu^{III}–CH_2CH(OH)CH_3 \qquad k_{18} = 2.7 \times 10^9\ M^{-1}\ s^{-1} \tag{18}$$

In addition to the decrease in absorbance noted above, a more rapid reaction of small amplitude was noted at wavelengths longer than 380 nm. This reaction has a first-order rate constant of $\sim 5 \times 10^3\ s^{-1}$ independent of pH and $Cu^{II}G_4$ concentration. This is in the time region of the spontaneous disappearance of $(CH_3)_2\dot{C}(OH)$ radicals, but the amplitude is somewhat larger than that observed at these wavelengths in blank solutions of isopropyl alcohol. Thus, these results suggest that, of the two radicals produced in reaction 17, the β radical reacts with $Cu^{II}G_4$ to form a copper(III)–carbon intermediate, whereas the α radical seems to reduce $Cu^{II}G_4$ without the formation of a detectable intermediate.

Conclusions

The reactions of copper(III) tetraglycine with free radicals reported here may be classified into three groups: (i) oxidation to $Cu^{III}(H_{-2}G_4)$ and $Cu^{III}(H_{-3}G_4)^-$ by reaction of $\cdot Br^-$ and $\cdot OH$ with the corresponding copper(II) complexes [observation of $Cu^{III}G_4$–Br species clearly indicates an inner-sphere mechanism for the $\cdot Br_2^-$ reaction. A similar mechanism is plausible for the reaction with $\cdot OH$.[30]]; (ii) formation of copper(III)–carbon-bonded intermediates in the reactions of $Cu^{II}G_4$ with $\cdot CH_2CO_2^-$, $\cdot CH_2C(CH_3)_2OH$, and $\cdot CH_2C(OH)CH_3$; (iii) reduction to Cu^IG_4 by $\cdot CH_2OH$ and $\cdot CO_2^-$ [although no intermediates are observed in these systems, one might expect that here also, at least for $\cdot CH_2OH$, the reaction proceeds via direct attack of carbon on the metal center. However, due to the strongly reducing nature of these radicals, the lifetimes of the copper–carbon-bonded intermediates are too short to be observed. The reaction of $(CH_3)_2\dot{C}OH$ with $Cu^{II}G_4$ probably belongs in this category.[29,31] This reaction was, however, not observed due to the parallel reaction with the $\cdot CH_2C(OH)CH_3$ radical.]

The kinetics of decomposition of the $Cu^{III}G_4$ species confirm Margerum's assertions that $Cu^{III}(H_{-2}G_4)$ is considerably less stable than $Cu^{III}(H_{-3}G_4)^-$ and that the interconversion of these two species is far too slow to be a simple protolytic equilibrium.[8] However, our results indicate that the decomposition rate for $Cu^{III}(H_{-2}G_4)$ is pH independent. It is of interest to note that $Cu^{III}(H_{-2}G_3)$ decomposes more slowly than $Cu^{III}(H_{-2}G_4)$ with an $[OH^-]$-dependent rate.[4] These differences are probably a reflection of the fact that the fourth ligating group in $Cu^{III}(H_{-2}G_3)$ is a carboxylate which offers greater stability than the peptide carbonyl of tetraglycine (structure I).

Contrary to our initial expectation, we find that the lifetimes of copper(III)–carbon intermediates are similar for the triglycine[4] and tetraglycine systems. This might be due to the fact that, although these compounds are formally designated as copper(III) species, the copper–carbon bonds are covalent and decompose to give copper(I) and not copper(III) or copper(II).

Finally, a recent study[9b] of the reactions of copper(III) peptides with $IrCl_6^{3-}$ has established the fact that electron-transfer reactions of these complexes can be very rapid but could not distinguish whether or not electron transfer occurs through a Cu–Cl–Ir bridge involving five-coordinate copper. Although an inner-sphere mechanism apparently can be ruled out in some redox reactions of copper(III) peptides,[32] the present study, especially the observation that no major spectral changes accompany reaction 6, clearly establishes that the more labile axial positions in copper(III) tetraglycine can indeed accept additional ligands.

Acknowledgment. We wish to thank the linac group at the Hebrew University of Jerusalem for their efforts in developing and operating of the experimental setup. This work was supported in part by the United States-Israel Binational Science Foundation (B.S.F.), Jerusalem, Israel.

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(26) Because of the small quantity of products obtainable prior to precipitation, no analysis of organic products is possible in these systems.

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Registry No. $Cu^{II}(H_{-3}G_4)^{2-}$, 57603-18-6; $\cdot Br_2^-$, 68565-50-4; $\cdot OH$, 3352-57-6; $\cdot CH_2OH$, 2143-68-2; $\cdot CO_2^-$, 34496-91-8; $(CH_3)_2\dot{C}OH$, 7277-18-1; $\cdot CH_2C(CH_3)_2OH$, 5723-74-0; $\cdot CH_2CO_2^-$, 19513-45-2; $\cdot CH_2CH(OH)CH_3$, 7277-18-1.

Notes

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Molecular Structure of Dichloro(1,4,7-triazacyclononane)copper(II), a Macrocyclic Triamine Complex with an Unusually Small Formation Constant

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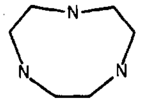
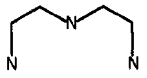
The title complex, $Cu([9]aneN_3)Cl_2$ (**1**), behaves anomalously with regard to the well-known macrocyclic effect. Typically, macrocyclic polyamine Cu(II) complexes exhibit larger formation constants than those of corresponding linear polyamines.[2] However, the formation constant of **1** ($\log K \approx 16$) is smaller than that of $Cu(dien)^{2+}$ ($\log K = 18.0$).[2,3]



$[9]aneN_3$



dien

In contrast, formation constants of $Ni([9]aneN_3)^{2+}$ and $Zn([9]aneN_3)^{2+}$ ($\log K = 16.2$ and 11.6, respectively) are substantially larger than those of $Ni(dien)^{2+}$ and $Zn(dien)^{2+}$ ($\log K = 10.7$ and 8.9, respectively).[3] The anomalous behavior of **1** has been attributed[2,3] to steric requirements of Cu(II) which have been frustrated in part by structural constraints of the $[9]aneN_3$ ligand. The present study was undertaken to help understand these constraints.[4]

Experimental Section

Preparation of 1. 1,4,7-Triazacyclononane trihydrochloride ($[9]aneN_3\cdot 3HCl$) was prepared by appropriate modification of a published procedure for 1,5,9,13-tetraazacyclohexadecane.[5] Evaporation of a solution of $[9]aneN_3\cdot 3HCl$ (5 mmol, 1.24 g), $CuCl_2$ (5 mmol, 0.85 g), and 15 mL of 1 N sodium hydroxide yielded sodium chloride crystals and large blue plates of **1** which were separated manually and recrystallized from water to yield pure **1**.

Anal. Calcd for $C_6H_{15}N_3CuCl_2$: C, 27.33; H, 5.73; N, 15.94; Cu, 24.10. Found: C, 27.33; H, 6.10; N, 15.88; Cu, 24.06.

Table I. Crystal Data and Data Collection Details

formula	$Cu(CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH)Cl_2$
mol wt	263.66
a, Å	7.428 (2)
b, Å	9.865 (2)
c, Å	6.932 (2)
α, deg	77.89 (2)
β, deg	99.12 (2)
γ, deg	92.61 (2)
space group	$P\bar{1}$
Z	2
no. of reflcns used to determine cell constants	13
d_{calcd}, g/cm³	1.786
d_{obsd}, g/cm³	1.76 (5)
λ(Cu Kα), Å	1.5418
filter	Ni
linear abs coeff, cm⁻¹	77.0
cryst dimens, mm	0.10 × 0.45 × 0.22
abs factor range	1.903–3.647
diffractometer	Syntex $P2_1$
data collectn method	θ–2θ
2θ range, deg	$4 \leqslant 2\theta \leqslant 110$
temp, °C	23 (1)
scan rate,[a] deg/min	1.5
scan range, deg	$2\theta(K\alpha_1) - 1$ to $2\theta(K\alpha_2) + 1$
no. of std reflcns	3
variation in std intens	±4.5%
no. of unique data collected	1239
no. of data used in refinement ($F^2 \geqslant 3\sigma(F^2)$)	1182
data:parameter ratio	8.0
final R_F[b]	0.031
final R_{wF}[c]	0.036

[a] Background measurements were made at the beginning and end of each scan; the total time for background counting was equal to the scan time. [b] $R_F = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_{wF} = [\Sigma w(|F_o - F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

X-ray Diffraction Studies. Crystal data and data collection and refinement details are given in Table I. Intensity data were collected and corrected for decay, *Lp* effects, and absorption as described previously.[6] Diffractometer examination of the reciprocal lattice revealed no systematic absences.

The structure was solved[7] by direct methods and refined successfully in space group $P\bar{1}$ by using full-matrix least-squares techniques. Neutral atom scattering factors were used, and anomalous dispersion corrections were applied to all nonhydrogen atoms.[8] An *E* map, calculated from the starting set having the highest combined figure of merit, revealed the Cu and Cl atoms. All remaining nonhydrogen atoms were located on a subsequent difference Fourier map. Several

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(7) In addition to local programs for the IBM 370/168 computer, local modifications of the following programs were used: LPCOR Lp and absorption program; Zalkin's FORDAP Fourier program; Johnson's ORTEPII thermal ellipsoid plotting program; Busing, Martin, and Levy's ORFFE error function program; Main, Lessinger, Declercq, Woolfson, and Germain's MULTAN 74 program for the automatic solution of crystal structures; the FLINUS least-squares program obtained from Brookhaven National Laboratory.

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