in Figure 6. On the other hand, the cleavage, nitrogen inversion, and recombination of each of the copper-nitrogen bonds in $[Cu(tet\ b)\ (blue)]^{2+}$ lead to the formation of extremely unstable isomers as shown in Figure 7. The existence of each of these extremely unstable species is highly unlikely. Presumably this is the reason that there is no blue-to-red interconversion occurring concurrently with its dissociation in strongly acidic media. In addition to $[Cu(tet\ b)\ (blue)]^{2+}$, tet b forms two relatively stable red complexes with copper(II). Each of these two complexes differs from $[Cu(tet\ b)\ (blue)]^{2+}$ in the configurations of two chiral nitrogen centers.[25,26] The lack of the blue-to-red interconversion of $[Cu(tet\ b)]^{2+}$ in strongly acidic media agrees with the postulate that the cleavage of the third copper-nitrogen bond is much faster than the recombination of the second copper-nitrogen bond as shown in Figure 4.

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Crystal and Molecular Structure of the Copper(III)-Tripeptide Complex of Tri-α-aminoisobutyric Acid

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The crystal structure of the thermally stable copper(III)-deprotonated-peptide complex of tri-α-aminoisobutyric acid, $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$, has been determined. The crystal was found to be monoclinic with lattice parameters of $a = 20.638$ (7) Å, $b = 9.250$ (6) Å, $c = 11.362$ (5) Å, $\beta = 92.80$ (3)°, and $Z = 4$. The structure was solved and refined in the centrosymmetric space group $P2/c$ with final residual values of $R = 0.050$ and $R_w = 0.055$. The Cu^{III}-N(amino), the two Cu^{III}-N(peptide), and the Cu^{III}-O(carboxyl) bond lengths are 1.898 (5), 1.801 (4), 1.804 (5), and 1.826 (3) Å, respectively. The copper(III)-ligand bond lengths are 0.12-0.17 Å shorter than the equivalent copper(II) bonds and 0.02-0.04 Å shorter than the corresponding nickel(II) bonds. The copper(III) is four-coordinate with the four donor atoms coplanar within ±0.06 Å and in a nearly square-planar geometry. The bond angles for the chelate rings average 87.3° for the copper(III)- compared to 85.1° for nickel(II)- and 83° for copper(II)-peptide complexes. There appears to be no axial coordination for $Cu^{III}(H_{-2}Aib_3)$ as the closest contact distance is 2.91 Å for a perchlorate oxygen.

Introduction

Peptide complexes of copper(III) have been shown to be relatively stable in aqueous solution.[1-5] Extensive knowledge of the copper(II)- and nickel(II)-peptide structures, which are largely the result of the work of Freeman and co-workers,[6] and of the solution chemistry of the copper(III)-peptide complexes has inferred many of the structural features of these copper(III) complexes. However, the present work is the first determination of a crystal structure for a copper(III)-peptide complex.

Reactions of the copper(III)-peptide complexes[1-4] with acids and nucleophiles are slow compared to the fast substitution reactions observed for the copper(II)-peptide complexes.[7-11] Sluggish substitution reactions are characteristic of known d^8 square-planar complexes of nickel(II), palladium(II), and platinum(II).

The copper(III/II) reduction potentials for a variety of peptide complexes have been measured and have been found to span a potential range of 0.37-1.2 V (vs. SHE).[5,12] The reduction potentials are affected by the number and type of donors bound to the copper and by the substituents on the α-carbons. The deprotonated-peptide nitrogen is a stronger σ donor than either an amine nitrogen or a carboxylate oxygen. As the number of deprotonated-peptide or deprotonated-amide nitrogen donor groups is increased, the trivalent oxidation state of copper is stabilized.

Alkyl substituents on the α-carbons increase the electron-donating ability of the coordinated nitrogens and further stabilize copper(III). The reduction potentials[5] for the peptide complexes containing leucyl, valyl, and isoleucyl residues are lower than those of alanyl-containing peptides even though the electron-donating abilities of all these α-substituents are approximately the same.

Entropy changes for the reduction reactions of several copper(III/II)-peptide complexes have been determined from cyclic voltammetric measurements of the $E_{1/2}$ as a function of temperature in a nonisothermal cell.[13] A large negative

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entropy change was observed for the copper(III/II) reduction. This has been attributed to an increase in axial solvation upon reduction according to the reaction

$$\mathrm{Cu^{III}(peptide) + e^- + 2H_2O \rightleftarrows [Cu^{II}(peptide)(H_2O)_2]^-}$$

The copper(III/II) reduction potential also has been found to decrease in nonaqueous solvents as the extent of axial solvation of the copper(II) complex decreases.[13] Both of these results indicate that copper(III) is four-coordinate and not solvated axially, while copper(II) is six-coordinate and axially solvated.

Crystal structures of the copper(II)-[14] and nickel(II)-tetraglycine complexes[15] provide a direct comparison of the d^9 and d^8 electronic configurations. Although the copper(II) complex is square planar in the solid state, electron spin resonance and ^{1}H nuclear magnetic resonance studies[16] indicate that at least one and probably two waters are coordinated to the copper in solution. The average nickel(II)-nitrogen bond lengths are 0.08 Å shorter than the copper(II)-nitrogen bonds. On the basis of increased crystal field stabilization energy for a d^8 over a d^9 electronic configuration nickel(II)-donor bonds are predicted to be shorter than copper(II)-donor bonds. Bond angles between donor atoms, N-M-N, are closer to 90° in the nickel(II) complex than in the copper(II) complex (85.7 and 83.4°, respectively). This can be attributed to the stronger, shorter nickel(II)-nitrogen bonds.

The gain in crystal field stabilization energy on going from a d^9 to a d^8 electronic configuration is greater in the copper(III/II) system due to the change from a divalent to a trivalent metal ion.[5,17] As a consequence, the copper(III)-donor bond lengths are expected to be shorter than the observed nickel(II)-nitrogen bonds. Also the bond angles around the copper(III) should be closer to 90° due to the stronger coordinate bonds and smaller ionic radius. Resonance Raman data[18] support the prediction that the copper(III)-donor bonds are significantly stronger than the corresponding copper(II) bonds. The Cu-N(amide) stretching frequencies increase approximately 30 cm^{-1} on going from copper(II) to copper(III). Another indication of the strength of the Cu(III)-N bond is the ease of amine deprotonation (pK_a between 10-12).[19]

The structure of a copper(III)-peptide complex is essential in order to interpret the structural changes that accompany reduction of the copper(III) center in electron-transfer studies. At this time, we wish to report the first structure determination of a copper(III)-peptide complex, the copper(III) complex of tri-α-aminoisobutyric acid. The structural features of this complex will be compared to the copper(II)- and nickel(II)-peptide structures.

Experimental Section

The tripeptide, α-aminoisobutyryl-α-aminoisobutyryl-α-aminoisobutyric acid, $\mathrm{NH_2C(CH_3)_2CONHC(CH_3)_2CONHC(CH_3)_2COOH}$, was synthesized by previously reported methods[3] by A. W. Hamburg. The copper(II) tripeptide solution (5 × 10^{-3} M) was prepared by reacting $\mathrm{Cu(ClO_4)_2}$ with the tripeptide, which was in 5% excess in 1.0 M $\mathrm{NaClO_4}$. The pH of the solution was adjusted with NaOH to form the peptide-deprotonated complex $\mathrm{Cu^{II}(H_{-2}Aib_3)^-}$. The abbreviation for the carboxylate form of the tripeptide is $\mathrm{Aib_3^-}$ and the copper complexes with two deprotonated peptide nitrogens are represented by $\mathrm{H_{-2}Aib_3^{3-}}$, consistent with earlier reports.[1-5,8-13,19] The copper(III) tripeptide solution was generated by electrochemical oxidation using a flow cell.[19] The graphite working electrode was held at 0.75 V vs. Ag/AgCl.

Table I. Parameters for $\mathrm{Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4}$ with Standard Deviations for the Least Significant Digit in Parentheses

a = 20.638 (7) Å
b = 9.250 (6) Å
c = 11.362 (5) Å
β = 92.80 (3)°
fw = 361.552
vol = 2166.4 Å^3
ρ_{calcd} = 1.70 g cm^{-3}
ρ_{float} = 1.75 g cm^{-3}
Z = 4

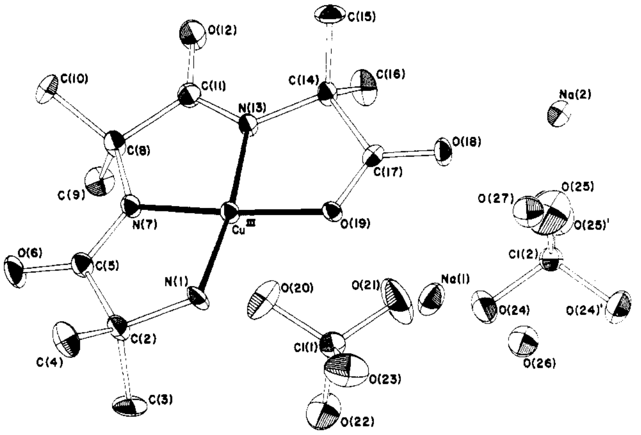

Figure 1. Structure and labeling diagram of $\mathrm{Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4}$.

After completion of the electrolysis, slow evaporation resulted in the formation of thin yellow-brown plates. A solution made by redissolving these crystals gave a UV-vis spectrum identical with the spectrum of a freshly oxidized $\mathrm{Cu^{III}(H_{-2}Aib_3)}$ solution. The ESR spectrum of the crystals diluted to 17.5% (w/w) with KCl was featureless, which indicated that the crystals were not contaminated with paramagnetic copper(II) species.

A suitable crystal (0.20 × 0.25 × 0.40 mm) was selected and mounted on a glass fiber with epoxy cement. The crystals were found to decompose in room light. In order to minimize this photodecomposition, all diffraction data were collected in the dark on an Enraf-Nonius CAD-4 diffractometer.

The crystal was found to be monoclinic. Lattice parameters (Table I) were determined by least-squares refinement of 46 reflections with 2 θ values between 30 and 45°, which were centered with Nb-filtered Mo Kα radiation (λ 0.71069 Å) at the Kα peak position by using a locally modified CAD-4 routine.

Intensity data for all reflections were collected from a quadrant of reciprocal space with $2\theta < 50°$ by a variable-speed θ-2θ scan technique with a 2θ range of $(1.8 + 0.2 \tan \theta)°$ centered about the averaged peak position. The aperature was set at 4 mm. Each reflection was scanned twice at rates from 1 to 6.7° min^{-1} depending on the intensity obtained from a rapid prescan of the peak. For all reflections, the two scans were found to be statistically identical. Background counts were measured over the first and last quarter of each scan. Three standard reflections were measured after every 60 reflections and were statistically constant. Integrated intensities, I, were calculated from the expression $I = C - 2B$, where C is the total number of counts measured over the two scans and B is the sum of the background counts. Standard deviations were calculated from the expression $\sigma(I) = (I + 4B)^{1/2}$. A Lorentz-polarization correction was applied, but no absorption correction was applied. Of the 3941 reflections examined, 2661 had observed net intensities greater than $3\sigma(I)$ and were used in the solution and refinement of the structure. Examination of the data showed the systematic absence of $h0l$ where $l = 2n + 1$, consistent with the space group Pc or $P2/c$.

The position of the copper atom was found from a Patterson map. The structure failed to refine in the noncentrosymmetric space group, Pc. The structure was solved and refined in the centrosymmetric space group, $P2/c$, and the positions of the remaining atoms were located from successive Fourier maps. Due to storage limitations of our computer system, full-matrix least-squares refinement techniques could

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Table II. Atomic Coordinates for $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$ with Standard Deviations for the Least Significant Digit in Parentheses

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	0.21196 (4)	0.18286 (9)	0.01952 (7)	C(16)	0.3291 (3)	−0.0465 (9)	0.2240 (6)
N(1)	0.1829 (2)	0.3403 (6)	−0.0764 (4)	C(17)	0.3317 (3)	0.0778 (7)	0.0278 (5)
C(2)	0.1178 (3)	0.3951 (8)	−0.0388 (6)	O(18)	0.3900 (2)	0.0706 (5)	0.0153 (4)
C(3)	0.1292 (4)	0.5385 (8)	0.0313 (7)	O(19)	0.2964 (2)	0.1807 (4)	−0.0214 (3)
C(4)	0.0712 (3)	0.4168 (9)	−0.1491 (6)	Cl(1)	0.30342 (9)	0.4254 (2)	0.2310 (2)
C(5)	0.0896 (3)	0.2798 (8)	0.0433 (6)	O(20)	0.2459 (3)	0.3433 (7)	0.2342 (5)
O(6)	0.0348 (2)	0.2924 (6)	0.0785 (5)	O(21)	0.3582 (3)	0.3456 (8)	0.2666 (6)
N(7)	0.1309 (2)	0.1716 (6)	0.0707 (4)	O(22)	0.2980 (3)	0.5479 (6)	0.3019 (5)
C(8)	0.1196 (3)	0.0569 (8)	0.1589 (6)	O(23)	0.3119 (3)	0.4723 (6)	0.1134 (5)
C(9)	0.1101 (3)	0.1256 (8)	0.2842 (6)	Cl(2)	0.5	0.2673 (3)	0.75
C(10)	0.0617 (3)	−0.0428 (8)	0.1190 (6)	O(24)	0.4440 (2)	0.3556 (6)	0.7577 (5)
C(11)	0.1818 (3)	−0.0325 (8)	0.1666 (6)	O(25)	0.4958 (3)	0.1819 (7)	0.6496 (5)
O(12)	0.1864 (2)	−0.1431 (6)	0.2290 (5)	Na(1)	0.3774 (1)	0.3417 (3)	−0.0721 (3)
N(13)	0.2296 (2)	0.0220 (6)	0.1050 (4)	O(26)	0.4578 (2)	0.4189 (6)	0.0604 (4)
C(14)	0.2955 (3)	−0.0359 (7)	0.0991 (5)	Na(2)	0.5	0.0	0.5
C(15)	0.2955 (3)	−0.1812 (8)	0.0310 (7)	O(27)	0.4704 (2)	0.1799 (6)	0.3586 (4)

Table III. Bond Distances (Å) for $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$ with Standard Deviations for the Least Significant Digit in Parentheses

Cu-N(1)	1.898 (5)	N(7)-C(8)	1.485 (7)	C(17)-O(18)	1.220 (6)	Na(1)-O(22)[a]	2.355 (6)
Cu-N(7)	1.801 (4)	C(8)-C(9)	1.579 (8)	C(17)-O(19)	1.307 (7)	Na(1)-O(23)	2.830 (6)
Cu-N(13)	1.804 (5)	C(8)-C(10)	1.557 (8)	Cl(1)-O(20)	1.411 (5)	Na(1)-O(24)[b]	2.430 (6)
Cu-O(19)	1.826 (3)	C(8)-C(11)	1.527 (8)	Cl(1)-O(21)	1.393 (5)	Na(1)-O(26)	2.300 (5)
Cu-O(20)	2.912 (6)	C(11)-O(12)	1.246 (7)	Cl(1)-O(22)	1.398 (5)	Na(2)-O(18)[c]	2.377 (4)
N(1)-C(2)	1.516 (7)	C(11)-N(13)	1.336 (7)	Cl(1)-O(23)	1.424 (5)	Na(2)-O(18)[d]	2.377 (4)
C(2)-C(3)	1.558 (9)	N(13)-C(14)	1.465 (7)	Cl(2)-O(24)	1.421 (5)	Na(2)-O(25)	2.396 (5)
C(2)-C(4)	1.556 (9)	C(14)-C(15)	1.551 (9)	Cl(2)-O(25)	1.387 (5)	Na(2)-O(25)[e]	2.396 (5)
C(2)-C(5)	1.549 (8)	C(14)-C(16)	1.552 (8)	Na(1)-O(18)	2.704 (5)	Na(2)-O(27)	2.372 (4)
C(5)-O(6)	1.223 (6)	C(14)-C(17)	1.543 (8)	Na(1)-O(19)	2.331 (5)	Na(2)-O(27)[e]	2.372 (4)
C(5)-N(7)	1.342 (7)						

[a] $x, -y + 1, (^1/_2 + z) + 1$. [b] $x, y, z - 1$. [c] $x, -y, ^1/_2 + z$. [d] $-x + 1, y, ^1/_2 - z$. [e] $-x + 1, -y, -z + 1$.

Table IV. Bond Angles (deg) for $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$ with the Standard Deviations for the Least Significant Digit in Parentheses

N(1)-Cu-N(7)	87.6 (2)	C(3)-C(2)-C(4)	112.0 (6)	N(13)-C(14)-C(17)	104.4 (5)	O(20)-Cl(1)-O(21)	112.3 (4)
N(7)-Cu-N(13)	86.8 (2)	C(3)-C(2)-C(5)	109.3 (5)	C(15)-C(14)-C(16)	113.0 (6)	O(20)-Cl(1)-O(22)	109.3 (4)
N(13)-Cu-O(19)	87.6 (2)	C(4)-C(2)-C(5)	109.7 (5)	C(15)-C(14)-C(17)	108.5 (5)	O(20)-Cl(1)-O(23)	109.3 (4)
N(1)-Cu-O(19)	98.1 (2)	C(2)-C(5)-O(6)	120.8 (6)	C(16)-C(14)-C(17)	108.4 (5)	O(21)-Cl(1)-O(22)	110.4 (4)
N(1)-Cu-N(13)	172.5 (2)	C(2)-C(5)-N(7)	113.6 (5)	O(18)-Na(1)-O(19)	51.3 (2)	O(21)-Cl(1)-O(23)	107.4 (4)
N(7)-Cu-O(19)	174.3 (2)	O(6)-C(5)-N(7)	125.6 (6)	O(18)-Na(1)-O(22)[a]	132.6 (2)	O(22)-Cl(1)-O(23)	108.1 (4)
N(1)-Cu-O(20)	98.4 (2)	C(5)-N(7)-C(8)	124.8 (5)	O(18)-Na(1)-O(23)	99.4 (2)	O(18)[c]-Na(2)-O(18)[d]	180.0
N(7)-Cu-O(20)	87.0 (2)	N(7)-C(8)-C(9)	110.6 (5)	O(18)-Na(1)-O(24)[b]	107.1 (2)	O(18)[c]-Na(2)-O(25)	85.8 (2)
N(13)-Cu-O(20)	86.3 (2)	N(7)-C(8)-C(10)	111.7 (5)	O(18)-Na(1)-O(26)	89.7 (2)	O(18)[c]-Na(2)-O(25)[e]	94.2 (2)
O(19)-Cu-O(20)	91.5 (2)	N(7)-C(8)-C(11)	105.4 (5)	O(19)-Na(1)-O(22)[a]	86.7 (2)	O(18)[c]-Na(2)-O(27)	88.4 (2)
Cu-N(1)-C(2)	110.7 (3)	C(9)-C(8)-C(10)	112.0 (5)	O(19)-Na(1)-O(23)	73.4 (2)	O(18)[c]-Na(2)-O(27)[e]	91.7 (2)
Cu-N(7)-C(5)	118.1 (4)	C(9)-C(8)-C(11)	107.9 (5)	O(19)-Na(1)-O(24)[b]	132.6 (2)	O(25)-Na(2)-O(25)[e]	180.0
Cu-N(7)-C(8)	116.0 (4)	C(10)-C(8)-C(11)	109.1 (6)	O(19)-Na(1)-O(26)	122.7 (2)	O(25)-Na(2)-O(27)	88.3 (2)
Cu-N(13)-C(11)	117.2 (4)	C(8)-C(11)-O(12)	121.2 (6)	O(22)[a]-Na(1)-O(23)	85.7 (2)	O(25)-Na(2)-O(27)[e]	91.7 (2)
Cu-N(13)-C(14)	116.1 (4)	C(8)-C(11)-N(13)	114.0 (6)	O(22)[a]-Na(1)-O(24)[b]	84.1 (2)	O(27)-Na(2)-O(27)[e]	180.0
Cu-O(19)-C(17)	114.7 (4)	O(12)-C(11)-N(13)	124.8 (6)	O(22)[a]-Na(1)-O(26)	136.2 (2)	O(24)-Cl(2)-O(24)[f]	109.8 (4)
N(1)-C(2)-C(3)	108.3 (5)	C(11)-N(13)-C(14)	126.6 (5)	O(23)-Na(1)-O(24)[b]	151.6 (2)	O(24)-Cl(2)-O(25)	111.1 (4)
N(1)-C(2)-C(4)	109.7 (5)	N(13)-C(14)-C(15)	111.3 (5)	O(23)-Na(1)-O(26)	74.7 (2)	O(24)-Cl(2)-O(25)[f]	107.1 (3)
N(1)-C(2)-C(5)	107.7 (5)	N(13)-C(14)-C(16)	110.9 (5)	O(24)[b]-Na(1)-O(26)	94.9 (2)	O(25)-Cl(2)-O(25)[f]	110.6 (6)

[a] $x, -y + 1, ^1/_2 + z - 1$. [b] $x, y, z - 1$. [c] $-x + 1, y, ^1/_2 - z$. [d] $x, -y, ^1/_2 + z$. [e] $-x + 1, -y, -z + 1$. [f] $-x + 1, y, ^1/_2 - z + 1$.

not be used for the simultaneous refinement of all the positional coordinates and the anisotropic thermal parameters. The atomic parameters were divided into two overlapping blocks. The block-diagonal least-squares refinement resulted in the final discrepancy factors

$$R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.050$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.055$$

The highest residual electron density in the final difference map was 0.51 e/Å^3. The final atomic coordinates with their standard deviations are given in Table II.

Results and Discussion

The molecular structure and packing diagram are shown in Figures 1 and 2, respectively. Bond distances and bond angles are listed in Tables III and IV.

Description of Crystal Lattice. Four $Cu^{III}(H_{-2}Aib_3)$ complexes are located at nonadjacent corners of the unit cell. A sheet of sodium ions, perchlorate ions, and water molecules form a layer at $x = ^1/_2$ in the crystal lattice. The copper(III)–peptide complexes are attached to this sheet by coordination of the carboxylate oxygens to the sodium cations. The "back side" of the complex bonds via van der Waals forces to the back side of an adjacent complex. Thus, the crystal is a two-dimensional structure of solvated sodium perchlorate sandwiched between two planes of copper(III) complexes.

Each sodium cation is coordinated to six oxygens. Na(1) is coordinated to one water molecule, O(26), two carboxylate oxygens from the same complex, O(18) and O(19), one perchlorate oxygen from the same unit cell, O(23), and two perchlorate oxygens from the adjacent unit cell in the *z* direction, O(22)′ and O(24)″. The coordination sphere of Na(2) is formed from two carboxylate oxygens from different complexes in different unit cells, O(18)′ and O(18)″, and four perchlorate oxygens, two from the same unit cell and two from

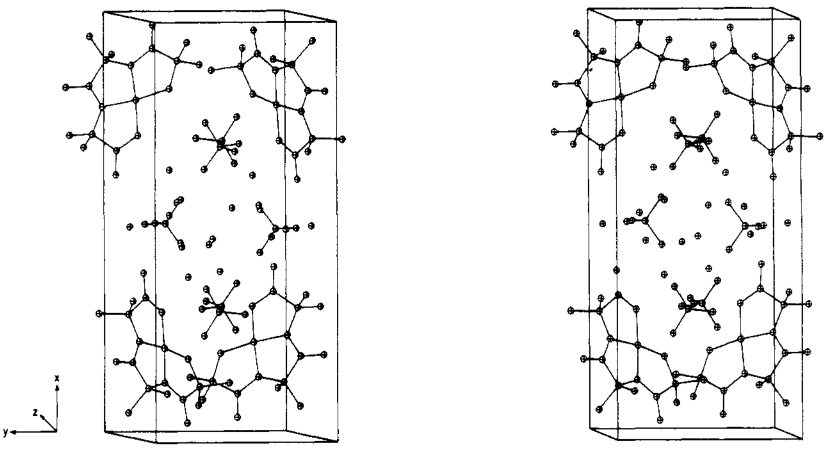

Figure 2. Stereoscopic view showing the molecular packing of $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$.

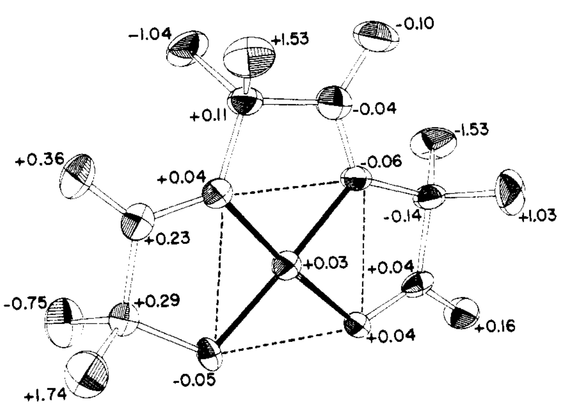

Figure 3. Planarity of the $Cu^{III}(H_{-2}Aib_3)$ complex. Distances in Å from the least-squares plane through Cu, N(1), N(7), N(13), and O(19) are calculated from the equation $D = 4.444x + 5.575y + 8.600z - 2.103$.

the adjacent unit cell in the y direction, O(27), O(27)′ and O(25), O(25)′.

Copper(III) Center. The copper(III) is coordinated to the amino nitrogen, the two deprotonated-peptide nitrogens, and the carboxylate oxygen of the Aib_3 peptide in a square-planar geometry. The copper(III) and four donor atoms are coplanar with the largest deviation being 0.06 Å (see Figure 3). Two of the nitrogens, N(1) and N(13), are below the least-squares plane while the Cu(III), N(7), and O(19) are approximately the same height above the least-squares plane (see Figure 3), so that the square-planar coordination geometry of the copper(III) undergoes a very slight tetrahedral distortion.

The Cu^{III}–N(amino), –N(peptide), and –O(carboxyl) bond distances are 0.13, 0.12, and 0.17 Å shorter than those of the analogous copper(II) bonds.[14,20-34] The copper(III) bonds also are shorter than the chemically equivalent bonds for the isoelectronic nickel(II) system (see Table V).[15] The metal–donor bond lengths increase in the order Cu(III) < Ni(II) < Cu(II) as would be predicted on the basis of the relative crystal field stabilization effects for d^8 and d^9 electronic configurations in a square-planar coordination geometry.[5]

Table V. Comparison of the Structural Features of Copper(III)-, Nickel(II)-, and Copper(II)-Peptide Complexes (Bond Distances in Angstroms; Bond Angles in Degrees)

	$Cu^{III}(d^8)^a$	$Ni^{II}(d^8)^b$	$Cu^{II}(d^9)^c$
M-N(amino)	1.90	1.92	2.03
M-N(peptide)	1.80	1.84	1.92
M-O(carboxyl)	1.83		2.00
C=O	1.24	1.27	1.26
OC-N	1.34	1.30	1.31
M⊃ (5-membered ring)	87.3	85.1	83
M<	98.1	104.5	109
C-N-C	125.7	124.2	124
$M-NH_2-C$	110.7	110.1	110
M-N-C	116.9	117.4	118
M-O-C	114.7		116

[a] This work. [b] Reference 15. [c] References 14 and 20-34.

The closest contact distance for possible axial interaction is 2.91 Å for the perchlorate oxygen O(20). No other donor atoms are located within reasonable bonding distance of the copper(III). Axial $Cu(II)-OH_2$ bond lengths in peptide complexes range from 2.3 to 2.5 Å, and $Ni(II)-OH_2$ bond lengths in octahedral complexes average 2.1 Å.[6] Since the Cu(III)–O(20) distance is dramatically longer than the axial copper(II) bonds and the copper(III) bonds are considerably shorter than the chemically equivalent copper(II) bonds, the Cu–O interaction probably is not significant. If the perchlorate oxygen were coordinated axially, then the Cu(III)–O(20) bond length would be expected to be similar to the Ni(II)–O distances, which are even shorter than the average axial Cu(II)–O length. Further, in the typical square-pyramidal coordination geometry, the metal ion is displaced from the plane of the four donor atoms with the fifth ligand forming the apex of the pyramid rather than the metal ion being coplanar with the equatorial ligands as is the case in this structure.

Peptide Backbone. The bond angles around the metal ion are closer to 90° in the $Cu^{III}(H_{-2}Aib_3)$ complex than for the

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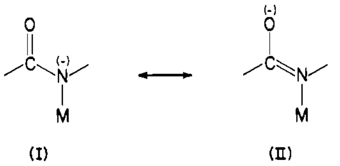
nickel(II)- and copper(II)-peptide complexes (see Table V). Thus, the stronger copper(III)-donor bonds and the smaller ionic radius of the copper(III) cation allow the three five-membered chelate rings that make up the peptide backbone to achieve a more ideal square-planar geometry.

With deprotonation of the peptide nitrogen, delocalization of the carbonyl double bond results in two resonance forms. In the copper(II)- and nickel(II)-peptide complexes, the C=O and OC—N bond lengths differ significantly from the free peptide lengths of 1.24 and 1.32 Å, respectively.[6] The C=O bonds lengthen while the OC—N bond lengths decrease due to the increased contribution of resonance form II. In the $Cu^{III}(H_{-2}Aib_3)$ complex, the C=O and OC—N bond lengths are equivalent to those in the free peptide. The stronger copper(III)-peptide nitrogen bonds, as compared to those of copper(II) and nickel(II) with nitrogen, are expected to favor resonance form I where the excess electron density is resident on the peptide nitrogen. Differences between the Cu(II)- and Cu(III)-tetraglycine resonance Raman frequencies[18] assigned to the C=O and OC—N vibrations are consistent with this crystallographic evidence that copper(III) prefers the first resonance form.



Delocalization of the carbonyl double bond would require that the five bonds making up the peptide linkage be coplanar, and as a result, the entire peptide backbone also should be planar. However, deviations are seen in the degree of coplanarity of the peptide backbone in metal complexes.[6] Figure 3 shows the deviations of all the atoms in the $Cu^{III}(H_{-2}Aib_3)$ complex from the least-squares plane calculated from the Cu(III), N(1), N(7), N(13), and O(19) coordinates. As described earlier, the copper(III) and the four donor atoms are coplanar within 0.06 Å. The peptide backbone is relatively planar. The first amino acid residue exhibits the largest deviations from planarity as would be expected with two tetrahedral atoms, N(1) and C(2), in the first chelate ring. The second and third residues are more planar, again with the largest deviations occurring at the tetrahedral α-carbon. The displacement of the methyl groups above and below the least-squares plane is approximately equal.

Other Copper(III) Structures. Two other structures containing amide donors with copper(III) have been reported. The Cu^{III}(*o*-phenylenebis(biuret)) complex[35] is coordinated to four deprotonated amide nitrogens with bond lengths ranging from 1.82 to 1.89 Å in an approximate square-planar geometry. The Cu(III)-N(amide) bonds average 0.08 Å shorter than the equivalent bonds in the $Cu^{II}(biuret)_2$ complex.[33] These bonds are still 0.05 Å longer than the Cu^{III}-N(peptide) bonds, and the copper(III) center undergoes a significant tetrahedral distortion of 0.12 Å from planarity. The 6,5,6-membered ring system of the *o*-phenylenebis(biuret) ligand may contribute to the differences in the bond lengths and angles compared to that found in the 5,5,5-membered chelate ring system of the copper(III)-peptide complex.

In the second structure,[36,37] the copper is coordinated to a macrocyclic ligand formed from the condensation reaction between acetaldehyde and oxalodihydrazide. The copper is five-coordinate in a distorted square-pyramidal geometry. The Cu-N(amide) bond lengths range from 1.85 to 1.88 Å, and the copper is displaced above the plane of the four amide nitrogens by 0.15 Å toward the apex of the pyramid, which is formed by an oxygen atom with the Cu-O distance of 2.74 Å. Originally, it was thought that the oxygen was from a water molecule and that the copper was divalent.[36] From the chemical properties and the short Cu-N(amide) bond lengths, Keyes and co-workers[37] have suggested that the copper is in the trivalent oxidation state and that the oxygen is a coordinated hydroxide to balance charge. Even though the chemical properties of the complex are consistent with copper(III), hydrolysis of the coordinated water to form hydroxide is unusual at such long bond lengths.

The square-pyramidal coordination geometry, as opposed to square-planar, may be a result of weaker donors and of the cavity size of the macrocyclic ligand. As a result the equatorial bonds are weaker as evidenced by the longer Cu(III)-N(amide) bonds relative to the Cu(III)-N(peptide) bonds. The addition of a fifth axial ligand could compensate for the weaker equatorial coordination.

These two structures along with the $Cu^{III}(H_{-2}Aib_3)$ structure indicate that copper(III) has a preference for a square-planar coordination geometry. However, depending on the ligand structure, the copper(III) center can undergo a tetrahedral or square-pyramidal distortion.

Summary

Inferences from the solution chemistry about the structural features of copper(III)-peptide complexes are confirmed by this crystal structure. The copper(III) cation is four-coordinate in a square-planar geometry without axial interaction. The copper(III)-donor bond lengths are dramatically shorter than the chemically equivalent copper(II) bonds. The shorter copper(III)-donor bonds allow the peptide donors to form a more ideal square-planar array around copper(III) than around copper(II) or nickel(II). These changes around the copper(III) center result in significant differences in the bond distances and bond angles of the atoms making up the peptide backbone compared to the those of copper(II) complexes. Even with these large changes in both the copper center and the peptide backbone between the two oxidation states, the self-exchange rate constants, k_{11}, for the copper(III/II) redox couple is 5.5×10^4 M^{-1} s^{-1}.[38] This is surprisingly large when compared to the self-exchange rate constants for other simple redox couples that involve significant changes in the metal-ligand bond distances ($r_2 - r_3$) such as the $Fe(H_2O)_6^{3+/2+}$ couple where k_{11} = 4 M^{-1} s^{-1} [39] and ($r_2 - r_3$) = 0.15 Å[40] and the $Co(NH_3)_6^{3+/2+}$ couple where $k_{11} \leq 10^{-9}$ M^{-1} s^{-1} [42,43] and ($r_2 - r_3$) = 0.18 Å.[43,44]

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Registry No. $Cu^{III}(H_{-2}Aib_3)\cdot 2H_2O\cdot 1.5NaClO_4$, 84681-70-9.

Supplementary Material Available: Listings of structure factor amplitudes and final anisotropic thermal parameters with their standard deviations (19 pages). Ordering information is given on any current masthead page.

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