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# The Preparation and Crystal Structure Analysis of bis(L-Arginine)Cu(II)-(acetate)$_2$trihydrate

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## Abstract

The crystal structure of bis(L-arginine)Cu(II)-(acetate)$_2$trihydrate has been determined by X-ray analysis. The complex crystallizes in the monoclinic space group $P2_1$, with cell dimensions $a$ = 15.948(2), $b$ = 16.878(2), $c$ = 10.378(2) Å, $\beta$ = 108.47(1)°, $Z$ = 4. There are two independent formula units in the asymmetric unit. The Cu atoms were located from a Patterson synthesis and the remaining atoms from difference Fourier syntheses. The structure was refined by least-squares to $R$ = 0.079 and $R$ = 0.11. Each copper atom has an essentially square planar coordination with the two arginine molecules chelated via the carboxy oxygens and the $\alpha$-amino nitrogens, but with distorted six-fold coordinations completed by weak Cu...O (acetate) interactions. Electrostatic interactions between the acetates and the protonated ends of the amino acid residues link the two independent [Cu(L-arginine)$_2$(acetate)$_2$] units into dimers, which are then connected via hydrogen bonds, also involving the water molecules, into an infinite network.

## Introduction

Copper(II) is an essential element in biological systems and usually appears coordinated to inorganic or organic ligands. The study of copper proteins and enzymes, as well as copper complexes used as drugs, is a very important field of research. One approach for such studies is to examine simpler molecules which may exhibit some of the essential characteristics of the macromolecules [1, 2]. From a different point of view, the study of these complexes is also relevant to the subject of the speciation of heavy metals in natural waters [3].

As part of a research program on the interaction between copper(II) and aminoacids, we have already reported a complete study of the Cu(II)(L-lysine)$_2$ complex [4]. We are now describing the synthesis, characterization by infrared spectroscopy and elemental analysis, and the crystal structure of a complex between L-arginine and copper(II).

## Experimental

### *Preparation*

Single crystals of the compound were obtained from cold ethanol–water mixtures containing 1 mmol of copper acetate (0.1997 g) and 2 mmol of L-arginine (0.3484 g). In a typical preparation, the copper acetate was dissolved in the minimum amount of water and a solution of the amino acid (≃20 ml) added. Blue crystals separated after two or three weeks. No recrystallization was needed. *Anal.* Calc. for $C_{16}H_{42}N_8O_{11}Cu$: C, 32.78; N, 19.12; H, 7.24. Found: C, 32.68; N, 18.52; H, 7.00%.

### *Infrared Spectral Measurements*

Infrared spectra of both complex and ligand were obtained using a Perkin-Elmer Model 683 Spectrophotometer. The compounds were dispersed in KBr pellets.

## Crystallography

### *Data Collection*

Crystallographic measurements were made at room temperature using an Enraf-Nonius CA-4 diffractometer with graphite monochromatized Mo K$\alpha$ radiation and a crystal with dimensions of 0.25 × 0.2 × 0.2 mm$^3$. Intensities of 5136 independent reflections were measured within $3.0° \leqslant 2\theta \leqslant 50.0°$, using the w/2$\theta$ scan mode with an $\omega$ scan width of 0.85 + 0.35 tan $\theta$ and $\omega$ scan speeds of 1.36–6.78 deg min$^{-1}$. Data were corrected for Lorentz and polarisation effects but not for absorption. Unit cell param-

0020-1693/86/$3.50

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Parameters ($\times 10^3$) of Copper and Atoms in the Acetate Ions and Water Molecules

| Atom | $x$ | $y$ | $z$ | $U_{11}$[a] | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 9884(1) | 7500 | 7021(2) | 34(1) | 23(1) | 25(1) | 2(1) | −11(1) | 5(1) |
| Cu(2) | 5222(1) | 7447(1) | 2892(1) | 35(1) | 24(1) | 25(1) | 2(1) | −14(1) | 1(1) |
| C(1) | 6419(10) | 2800(8) | 5938(16) | 49(9) | 20(7) | 35(8) | 1(6) | 16(8) | 7(6) |
| O(1A) | 5681(6) | 2433(8) | 5457(11) | 47(6) | 27(5) | 60(6) | −16(6) | 16(5) | −11(6) |
| O(1B) | 6978(7) | 2595(10) | 6961(12) | 38(5) | 79(11) | 58(7) | 28(8) | 0(5) | 1(7) |
| C(2) | 6591(15) | 3519(14) | 5176(24) | 74(13) | 68(15) | 86(15) | 30(12) | −4(12) | −29(12) |
| C(3) | 6018(11) | 7230(9) | 153(18) | 51(9) | 30(9) | 46(10) | 3(7) | −3(8) | 3(7) |
| O(3A) | 5377(8) | 7552(10) | −810(12) | 67(7) | 59(8) | 49(6) | −5(7) | 4(6) | 25(8) |
| O(3B) | 6391(8) | 7534(10) | 1196(13) | 65(7) | 39(7) | 58(8) | −10(8) | −16(6) | 1(7) |
| C(4) | 6194(16) | 6362(12) | −166(21) | 110(17) | 44(12) | 69(13) | 6(10) | 29(13) | 42(12) |
| C(5) | 9239(10) | 7829(9) | 9841(16) | 47(9) | 22(7) | 41(9) | −4(6) | 14(8) | −10(6) |
| O(5A) | 8780(6) | 7485(9) | 8751(10) | 52(5) | 29(5) | 41(6) | −9(7) | −10(5) | 2(6) |
| O(5B) | 9908(6) | 7495(8) | 10615(9) | 47(5) | 39(6) | 33(5) | −1(6) | −6(4) | 11(6) |
| C(6) | 8969(14) | 8649(12) | 10097(18) | 94(14) | 41(11) | 51(11) | −36(9) | 6(11) | 5(10) |
| C(7) | 8438(10) | 2255(9) | 4207(17) | 45(9) | 36(10) | 41(9) | −11(7) | 22(8) | −2(7) |
| O(7A) | 7827(6) | 2492(10) | 3181(12) | 42(5) | 48(7) | 69(8) | 4(7) | −7(5) | −5(7) |
| O(7B) | 9182(6) | 2585(9) | 4589(10) | 34(5) | 75(10) | 36(5) | 19(7) | 3(4) | −10(7) |
| C(8) | 8270(14) | 1608(11) | 5106(20) | 138(16) | 84(13) | 125(15) | 45(11) | 5(13) | −3(11) |
| O(1) | −5689(7) | 2621(10) | −6775(11) | 55(6) | 86(11) | 45(6) | 7(7) | 5(5) | 3(7) |
| O(2) | 9536(7) | 7500(13) | 3060(12) | 52(6) | 141(13) | 48(7) | −1(10) | 11(6) | −25(10) |
| O(3) | −7933(7) | 1846(8) | −2809(13) | 52(7) | 49(7) | 84(9) | −27(7) | 17(7) | −11(6) |
| O(4) | −3682(9) | 1830(8) | −8460(16) | 68(8) | 54(8) | 108(11) | −34(8) | −2(8) | −17(7) |
| O(5) | −2654(7) | 8227(8) | −3038(11) | 48(6) | 62(8) | 46(6) | 16(6) | −6(5) | 0(6) |
| O(6) | −1486(9) | 3381(9) | −11823(17) | 59(8) | 56(9) | 141(14) | −25(9) | −52(8) | 17(7) |

[a]The temperature factor exponent takes the form: $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

eters and orientation matrix were determined and refined using setting angles for 25 well-spaced reflections with $26.0^\circ \leqslant 2\theta \leqslant 28.0$

*Crystal data*

$C_{16}H_{42}N_8O_{11}Cu$, $M = 586.2$, monoclinic, space group $P2_1$, $a = 15.948(2)$, $b = 16.878(2)$, $c = 10.378(2)$ Å, $\beta = 108.47(1)^\circ$, $V = 2649.7$ Å$^3$, $Z = 4$, $D_c = 1.47$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 8.88 cm$^{-1}$.

*Structure Determination*

3387 intensities satisfied the criterion $F > 3\sigma(F)$ and were used for the structure solution and refinement. A sharpened Patterson synthesis map showed a number of high peaks which could only agree with the existence of two independent copper atoms. A few cycles of isotropic refinement of the derived Cu positions gave $R = 0.45$. Subsequent difference Fourier syntheses revealed the positions of the oxygen, nitrogen and carbon atoms from the four arginine ligands, four acetate molecules and six water molecules. A full refinement with all isotropic atoms gave an $R = 0.17$.

In view of the relatively small number of observed reflections, anisotropic thermal parameters were assigned only to the copper atoms, and the oxygen and carbon atoms of the acetate and water molecules; all the remaining non-hydrogen atoms were assigned isotropic thermal parameters. Some hydrogen atoms were inserted in idealised positions, and those on a specific carbon assigned an overall group isotropic thermal parameter. A final refinement with unit weights led to $R$ $(=\Sigma\Delta F/\Sigma|F_o|)$ of 0.079 and $R_w$ $(=(\Sigma w\Delta F^2/\Sigma|F_o|^2)^{1/2})$ of 0.110.

Atomic scattering factors were taken from International Tables [5], and the computations were carried out on an IBM-4331/K11 and VAX 11/750 computer using SHELX [6]. The drawings were made with SNOOPI [7].

Fractional atomic coordinates and anisotropic thermal parameters for the copper atoms, the acetate molecules and the oxygen of the water molecules are listed in Table I, while the fractional atomic parameters and isotropic thermal parameters of the remaining non-hydrogen atoms are listed in Table II.

## Results and Discussion

*Spectroscopic Studies*

The structure of the complex Cu(L-arginine)$_2$-(acetate)$_2\cdot 3H_2O$ was characterized by an infrared analysis prior to the crystallographic study. In the spectra of both the complex and the ligand, the region of 3000–3500 cm$^{-1}$ is similar, due to the $NH_3^+$, $NH_2^+$, $NH_2$ stretching vibrations. The bands

TABLE II. Fractional Atomic Coordinates (×$10^4$) and Isotropic Thermal Parameters (×$10^3$) of the Remaining Non-hydrogen Atoms

| Atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| O(11) | 10058(6) | 8603(6) | 7557(9) | 29(2) |
| N(11) | 8827(6) | 7921(7) | 5580(11) | 25(2) |
| C(11) | 9595(8) | 9081(8) | 6714(14) | 27(3) |
| C(12) | 9037(8) | 8749(7) | 5344(12) | 24(3) |
| O(13) | 9598(7) | 9825(7) | 6873(12) | 52(3) |
| O(12) | 9724(6) | 6386(6) | 6565(9) | 31(2) |
| N(12) | 10869(7) | 7121(7) | 8615(11) | 27(2) |
| C(13) | 10318(8) | 5920(8) | 7275(12) | 26(3) |
| C(14) | 11087(8) | 6289(7) | 8396(12) | 27(3) |
| O(14) | 10332(8) | 5200(7) | 7102(12) | 55(3) |
| C(15) | 8244(9) | 9269(9) | 4601(14) | 30(3) |
| C(17) | 7705(9) | 8976(9) | 3179(15) | 37(3) |
| C(19) | 7085(9) | 9585(9) | 2403(14) | 30(3) |
| N(13) | 6562(7) | 9243(7) | 1110(12) | 33(3) |
| C(111) | 6069(9) | 9642(9) | 17(14) | 31(3) |
| N(15) | 5638(8) | 9259(8) | −1074(13) | 40(3) |
| N(17) | 6019(8) | 10420(8) | 59(13) | 37(3) |
| C(16) | 11365(9) | 5772(8) | 9715(13) | 28(3) |
| C(18) | 12137(8) | 6090(8) | 10827(13) | 28(3) |
| C(110) | 12478(9) | 5505(9) | 11937(15) | 32(3) |
| N(14) | 13195(8) | 5833(8) | 13040(12) | 36(3) |
| C(112) | 13681(9) | 5412(8) | 14093(14) | 31(3) |
| N(16) | 14293(7) | 5777(7) | 15115(12) | 35(3) |
| N(18) | 13635(8) | 4617(8) | 14148(13) | 38(3) |
| N(21) | 6239(8) | 7072(8) | 4435(13) | 41(3) |
| O(21) | 5072(6) | 6339(6) | 2365(9) | 31(2) |
| O(22) | 5411(6) | 8560(6) | 3371(10) | 34(2) |
| N(22) | 4224(7) | 7839(7) | 1324(12) | 33(3) |
| O(24) | 4903(7) | 9775(7) | 2675(11) | 48(3) |
| C(23) | 4918(8) | 9041(8) | 2494(14) | 30(3) |
| C(24) | 4367(8) | 8686(7) | 1116(12) | 25(3) |
| C(22) | 6461(8) | 6234(7) | 4185(12) | 26(3) |
| C(21) | 5674(9) | 5877(9) | 3098(14) | 34(3) |
| O(23) | 5675(7) | 5163(6) | 2887(11) | 47(3) |
| C(26) | 3568(11) | 9158(10) | 444(17) | 47(4) |
| C(28) | 3099(10) | 8872(10) | −1045(16) | 46(4) |
| C(210) | 2512(9) | 9552(10) | −1873(15) | 37(3) |
| N(24) | 1972(7) | 9194(7) | −3162(11) | 28(2) |
| C(212) | 1440(8) | 9634(8) | −4174(14) | 26(3) |
| N(26) | 984(8) | 9245(8) | −5293(13) | 43(3) |
| N(28) | 1407(9) | 10396(8) | −4094(14) | 43(3) |
| C(25) | 6762(9) | 5735(9) | 5434(14) | 32(3) |
| C(27) | 7512(9) | 6073(9) | 6564(14) | 36(3) |
| C(29) | 7961(9) | 5444(9) | 7624(15) | 36(3) |
| N(23) | 8589(7) | 5807(7) | 8804(12) | 30(2) |
| C(211) | 9020(8) | 5407(8) | 9908(13) | 26(3) |
| N(25) | 8992(8) | 4634(8) | 10015(13) | 39(3) |
| N(27) | 9499(8) | 5829(8) | 11009(13) | 39(3) |

due to the $-CH_2$ stretching deformation and wagging vibrations, typical of the aliphatic hydrocarbon chains, are present at ~2850, ~1380 and 1320 cm$^{-1}$, respectively [8].

The coordination of the copper to the amino acid should be noticed in the 1500–1700 cm$^{-1}$ region by the shift of the asymmetric stretching band of –COO. This region is obscured by the presence of the C=N stretching at ~1670 cm$^{-1}$ and the NH symmetric and asymmetric deformation at about 1550 and 1630 cm$^{-1}$, respectively. However, as would be expected, the band at 1600 cm$^{-1}$ in the free ligand spectrum moves to 1630 cm$^{-1}$.

The presence of some extra bands in the complex spectrum at 330 cm$^{-1}$ and 435 cm$^{-1}$, probably due to the Cu–O and Cu–N asymmetric vibration [9], confirms the complex formation.

### *Crystal Structure*

The asymmetric unit contains two formula units of the complex which associate together into a dimer. A diagram of this 'dimer' is given in Fig. 1; bond lengths and bond angles are given in Tables III and IV, respectively.

The two component cations have broadly similar structures, with the Cu atoms possessing essentially square planar coordination comprising 2O and 2N from two amino acid residues, but with distorted sixfold coordination being completed by weak Cu...O (acetate) interactions. The 'dimer' has a 'quasi' centrosymmetric appearance, but obviously such a symmetry relationship is not allowed because of the chirality of the amino acid residues. Nevertheless, it is intriguing to note that the centre of gravity of the dimer (~ the centre point of the Cu...Cu vector) is situated very close to 0.75, 0.75, 0.50, which corresponds to the relative positioning of the centres of symmetry to the screw axis in space group $P2_1/c$.

In each complex the arginine residues chelate via the carboxy oxygen and the α-amino nitrogen such that the equivalent structural groups are *trans* with respect to each other. The Cu–N and Cu–O distances in the basal plane agree well with those found in other Cu(II) amino acid structures [10, 11, 12]. The weak Cu–O apical bonds are also similar to those found in related complexes, even though in these cases the oxygens belong to neighbouring amino acid molecules [9, 11, 13] or water [12, 14, 15].

Table V lists the deviations from the least-square planes of the $N_2O_2$ coordinating atoms for both cations. Cation 1 has a fairly even distortion of the shallow tetrahedral type with deviations of ±0.04 Å. The copper atom lies 0.07 Å out of the plane in the same direction as the two basal oxygens and towards O(7B) which gives the shorter Cu...O apical distance (2.570 Å). However, the coordination group in cation 2 is essentially planar with deviations of ±0.01 Å and the copper atom is 0.04 Å out of the plane, this time in the same direction as the two basal nitrogens, but again towards the oxygen, which gives the shorter Cu...O apical distance O(1A) (2.563 Å).

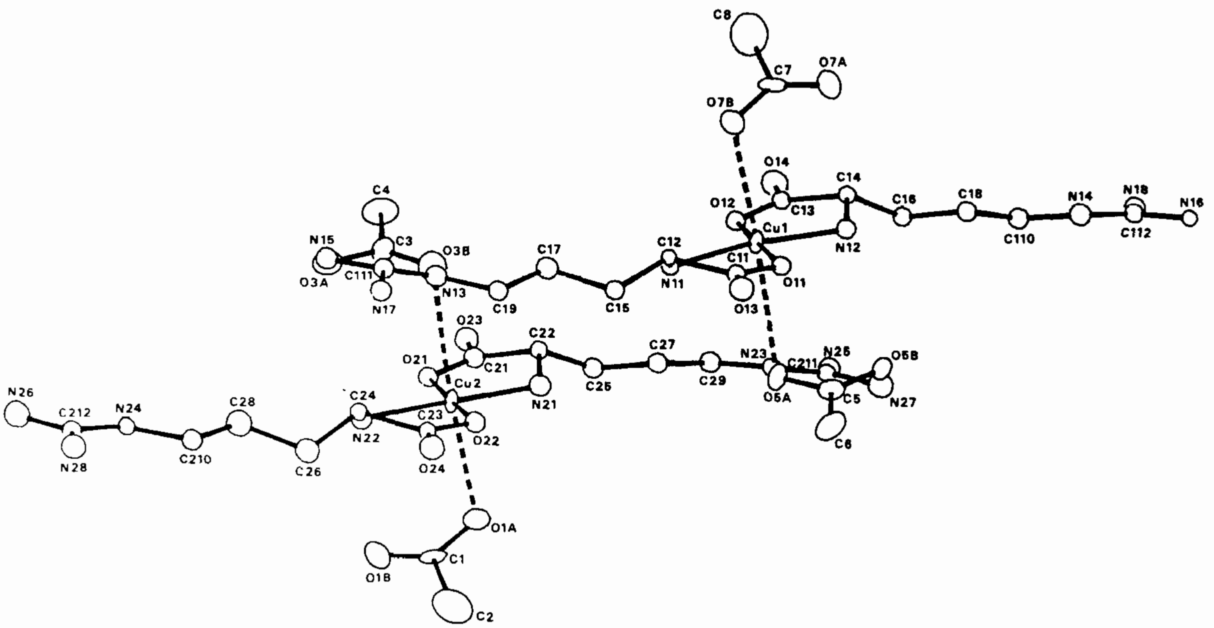

Fig. 1. Molecular diagram of the Cu(L-arginine)$_2$(acetate)$_2$•3H$_2$O dimer with the four acetate ions.

TABLE III. Bond Lengths for bis(L-arginine)Cu(II)(acetate)$_2$-trihydrate

| Atoms | Distance (Å) | Atoms | Distance (Å) |
|---|---|---|---|
| O(11)–Cu(1) | 1.938(12) | N(11)–Cu(1) | 1.996(13) |
| O(12)–Cu(1) | 1.936(12) | N(12)–Cu(1) | 1.991(13) |
| Cu(1)–O(5A) | 2.884(14) | Cu(1)–O(7B)[a] | 2.570(15) |
| C(11)–O(11) | 1.246(17) | C(12)–N(11) | 1.475(16) |
| C(12)–C(11) | 1.525(19) | O(13)–C(11) | 1.267(18) |
| C(15)–C(12) | 1.531(20) | C(13)–O(12) | 1.271(17) |
| C(14)–N(12) | 1.482(17) | C(14)–C(13) | 1.529(19) |
| O(14)–C(13) | 1.230(17) | C(16)–C(14) | 1.564(19) |
| C(17)–C(15) | 1.535(22) | C(19)–C(17) | 1.475(21) |
| N(13)–C(19) | 1.456(19) | C(111)–N(13) | 1.339(19) |
| N(15)–C(111) | 1.296(20) | N(17)–C(111) | 1.318(19) |
| C(18)–C(16) | 1.494(19) | C(110)–C(18) | 1.482(20) |
| N(14)–C(110) | 1.447(19) | C(112)–N(14) | 1.328(20) |
| N(16)–C(112) | 1.341(19) | N(18)–C(112) | 1.346(19) |
| N(21)–Cu(2) | 1.986(15) | O(21)–Cu(2) | 1.941(12) |
| O(22)–Cu(2) | 1.944(13) | N(22)–Cu(2) | 1.995(14) |
| Cu(1)–O(1A)[b] | 2.563(16) | Cu(1)–O(3B) | 2.944(16) |
| C(22)–N(21) | 1.501(19) | C(21)–O(21) | 1.283(17) |
| C(23)–O(22) | 1.285(18) | C(24)–N(22) | 1.472(18) |
| C(23)–O(24) | 1.254(18) | C(24)–C(23) | 1.544(20) |
| C(26)–C(24) | 1.477(21) | C(21)–C(22) | 1.519(20) |
| C(25)–C(22) | 1.492(19) | O(23)–C(21) | 1.225(18) |
| C(28)–C(26) | 1.564(24) | C(210)–C(28) | 1.557(24) |
| N(24)–C(210) | 1.472(20) | C(212)–N(24) | 1.344(18) |
| N(26)–C(212) | 1.332(19) | N(28)–C(212) | 1.291(18) |
| C(27)–C(25) | 1.497(20) | C(29)–C(27) | 1.533(23) |
| N(23)–C(29) | 1.449(20) | C(211)–N(23) | 1.320(18) |
| N(25)–C(211) | 1.310(19) | N(27)–C(211) | 1.358(19) |
| O(1A)–C(1) | 1.283(20) | O(1B)–C(1) | 1.200(20) |
| C(2)–C(1) | 1.519(25) | O(3A)–C(3) | 1.300(21) |
| O(3B)–C(3) | 1.174(22) | C(4)–C(3) | 1.547(26) |
| O(5A)–C(5) | 1.275(20) | O(5B)–C(5) | 1.249(20) |
| C(6)–C(5) | 1.497(24) | O(7A)–C(7) | 1.259(21) |
| O(7B)–C(7) | 1.255(20) | C(8)–C(7) | 1.514(24) |

Key to symmetry operations relating designated atoms to reference atoms at ($x, y, z$): [a]$2.0 - x$, $-0.5 + y$, $1.0 - z$; [b]$1.0 - x$, $-0.5 + y$, $1.0 - z$.

In both cations the two residues have different conformation geometries, which can best be described in terms of selected torsion angles (see Table VI). In cation **1**, residue 11 has a much larger deviation from planarity than residue 12, due to a larger torsion angle for O(11)–C(11)–C(12)–N(11) of 28.6°, against a value of 12.5° for O(12)–C(13)–C(14)–N(12). The equivalent happens in cation **2**, with a torsion angle of 25.0° for O(22)–C(23)–C(24)–N(22), against a value of 15.8° for O(21)–C(21)–C(22)–N(21). It should also be noted that all bond angles in the less rotated chelate rings are larger than those observed in the more rotated ones.

The two formula units which form the dimer are connected to each other and to those in other dimers via a complex series of hydrogen bonds and, probably, electrostatic interactions. In Table VII we list interatomic distances which are significantly below the sum of the van der Waals contacts and which are considered to indicate interactions. We

TABLE IV. Bond Angles (deg) for bis(L-arginine)Cu(II)(acetate)$_2$trihydrate

| Atoms | Angle (deg) | Atoms | Angle (deg) |
|---|---|---|---|
| N(11)–Cu(1)–O(11) | 83.3(5) | O(12)–Cu(1)–O(11) | 177.6(4) |
| O(12)–Cu(1)–N(11) | 98.5(5) | N(12)–Cu(1)–O(11) | 93.8(5) |
| N(12)–Cu(1)–N(11) | 173.3(4) | N(12)–Cu(1)–O(12) | 84.2(5) |
| O(11)–Cu(1)–O(5A) | 83.7(6) | N(11)–Cu(1)–O(5A) | 86.2(6) |
| O(12)–Cu(1)–O(5A) | 94.9(6) | N(12)–Cu(1)–O(5A) | 87.5(6) |
| O(11)–Cu(1)–O(7B)[a] | 94.2(6) | N(11)–Cu(1)–O(7B)[a] | 91.0(6) |
| O(12)–Cu(1)–O(7B)[a] | 87.4(6) | N(12)–Cu(1)–O(7B)[a] | 95.2(6) |
| O(5A)–Cu(1)–O(7B)[a] | 176.7(5) | C(11)–O(11)–Cu(1) | 114.9(10) |
| C(12)–N(11)–Cu(1) | 106.3(8) | C(12)–C(11)–O(11) | 117.3(13) |
| O(13)–C(11)–O(11) | 125.0(14) | O(13)–C(11)–C(12) | 117.6(13) |
| C(11)–C(12)–N(11) | 106.8(11) | C(15)–C(12)–N(11) | 115.6(11) |
| C(15)–C(12)–C(11) | 113.8(11) | C(13)–O(12)–Cu(1) | 116.2(10) |
| C(14)–N(12)–Cu(1) | 109.8(9) | C(14)–C(13)–O(12) | 117.4(12) |
| O(14)–C(13)–O(12) | 124.8(14) | O(14)–C(13)–C(14) | 117.7(13) |
| C(13)–C(14)–N(12) | 109.4(11) | C(16)–C(14)–N(12) | 114.2(11) |
| C(16)–C(14)–C(13) | 112.1(11) | C(17)–C(15)–C(12) | 114.9(12) |
| C(19)–C(17)–C(15) | 112.0(13) | N(13)–C(19)–C(17) | 108.4(13) |
| C(111)–N(13)–C(19) | 126.3(14) | N(15)–C(111)–N(13) | 119.8(15) |
| N(17)–C(111)–N(13) | 119.9(15) | N(17)–C(111)–N(15) | 120.3(15) |
| C(18)–C(16)–C(14) | 114.3(12) | C(110)–C(18)–C(16) | 111.8(12) |
| N(14)–C(110)–C(18) | 111.3(13) | C(112)–N(14)–C(110) | 123.7(14) |
| N(16)–C(112)–N(14) | 119.6(14) | N(18)–C(112)–N(14) | 122.9(15) |
| N(18)–C(112)–N(16) | 117.3(15) | | |
| O(21)–Cu(2)–N(21) | 85.3(6) | O(22)–Cu(2)–N(21) | 94.6(6) |
| O(22)–Cu(2)–O(21) | 177.3(3) | N(22)–Cu(2)–N(21) | 178.4(5) |
| N(22)–Cu(2)–O(21) | 95.4(6) | N(22)–Cu(2)–O(22) | 84.6(6) |
| N(21)–Cu(2)–O(1A)[b] | 86.9(7) | O(21)–Cu(2)–O(1A)[b] | 97.7(7) |
| O(22)–Cu(2)–O(1A)[b] | 85.0(7) | N(22)–Cu(2)–O(1A)[b] | 94.4(7) |
| N(21)–Cu(2)–O(3B) | 89.4(7) | O(21)–Cu(2)–O(3B) | 85.7(7) |
| O(22)–Cu(2)–O(3B) | 91.6(7) | N(22)–Cu(2)–O(3B) | 89.3(7) |
| O(1A)[b]–Cu(2)–O(3B) | 174.7(6) | C(22)–N(21)–Cu(2) | 109.7(10) |
| C(21)–O(21)–Cu(2) | 114.5(10) | C(23)–O(22)–Cu(2) | 114.8(10) |
| C(24)–N(22)–Cu(2) | 108.8(10) | O(24)–C(23)–O(22) | 123.7(14) |
| C(24)–C(23)–O(22) | 116.8(13) | C(24)–C(23)–O(24) | 119.4(13) |
| C(23)–C(24)–N(22) | 108.1(12) | C(26)–C(24)–N(22) | 116.2(13) |
| C(26)–C(24)–C(23) | 112.4(12) | C(21)–C(22)–N(21) | 108.5(11) |
| C(25)–C(22)–N(21) | 114.2(12) | C(25)–C(22)–C(21) | 112.6(12) |
| C(22)–C(21)–O(21) | 119.1(13) | O(23)–C(21)–O(21) | 122.3(14) |
| O(23)–C(21)–C(22) | 118.4(13) | C(28)–C(26)–C(24) | 111.7(14) |
| C(210)–C(28)–C(26) | 109.5(14) | N(24)–C(210)–C(28) | 106.0(13) |
| C(212)–N(24)–C(210) | 121.7(13) | N(26)–C(212)–N(24) | 116.3(14) |
| N(28)–C(212)–N(24) | 121.9(15) | N(28)–C(212)–N(26) | 121.7(15) |
| C(27)–C(25)–C(22) | 115.1(13) | C(29)–C(27)–C(25) | 112.0(13) |
| N(23)–C(29)–C(27) | 110.8(13) | C(211)–N(23)–C(29) | 123.2(13) |
| N(25)–C(211)–N(23) | 124.1(14) | N(27)–C(211)–N(23) | 117.4(14) |
| N(27)–C(211)–N(25) | 118.5(14) | | |
| O(1B)–C(1)–O(1A) | 122.5(15) | C(2)–C(1)–O(1A) | 118.5(16) |
| C(2)–C(1)–O(1B) | 119.0(17) | O(3B)–C(3)–O(3A) | 124.9(17) |
| C(4)–C(3)–O(3A) | 112.5(17) | C(4)–C(3)–O(3B) | 122.5(18) |
| O(5B)–C(5)–O(5A) | 119.9(16) | C(6)–C(5)–O(5A) | 117.5(17) |
| C(6)–C(5)–O(5B) | 122.6(16) | O(7B)–C(7)–O(7A) | 121.7(16) |
| C(8)–C(7)–O(7A) | 120.7(16) | C(8)–C(7)–O(7B) | 117.3(17) |

[a], [b] See Table III.

presume that the complex can be represented as $Cu(O_2CNH_2CHCH_2CH_2CH_2NHCH_2N_2H_6^+)_2(CH_3CO_2^-)_2$. As can be seen in Fig. 1 and Table VII, the acetates are hydrogen bonded and electrostatically connected to the protonated ends of the amino acid residues. These systems are then further linked

TABLE V. Atom Deviations (Å) from Least-squares Planes

| Atom$^a$ | Deviations (Å) | Atom$^b$ | Deviations (Å) | Atom$^b$ | Deviations (Å) |
|---|---|---|---|---|---|
| Cation **1** ($A = -12.997, B = -1.754, C = -8.285, D = -8.279$)$^c$ | | | | | |
| O(11) | −0.041 | Cu(1) | −0.066 | O(7B) | −2.632 |
| N(11) | +0.040 | O(5A) | −2.805 | C(13) | −0.142 |
| O(12) | −0.040 | C(11) | −0.221 | C(14) | −0.278 |
| N(12) | +0.041 | C(12) | −0.573 | C(16) | −0.544 |
| | | C(15) | −0.249 | O(14) | −0.178 |
| | | O(13) | −0.224 | | |
| Cation **2** ($A = -13.213, B = -1.672, C = -8.142, D = -5.825$)$^c$ | | | | | |
| O(21) | −0.011 | Cu(2) | +0.035 | O(3B) | −2.905 |
| N(21) | +0.011 | O(1A) | +2.575 | C(23) | −0.154 |
| O(22) | −0.011 | C(21) | −1.322 | C(24) | −0.488 |
| N(22) | +0.011 | C(22) | −0.346 | C(26) | −0.058 |
| | | C(25) | +0.356 | O(24) | −0.110 |
| | | O(23) | −0.185 | | |

$^a$Atoms defining the plane. $^b$Other atoms. $^c$The equations of the least-squares planes are given as $Ax + By + Cz = D$, where $x, y, z$ refer to the fractional coordinates.

TABLE VI. Torsion Angles

| Atoms | Angle (deg) |
|---|---|
| Cation **1** | |
| Residue 11 | |
| Cu(1)–O(11)–C(11)–C(12) | −6.1 |
| Cu(1)–N(11)–C(12)–C(11) | −34.9 |
| O(11)–C(11)–C(12)–N(11) | 28.6 |
| O(11)–C(11)–C(12)–C(15) | 157.4 |
| Residue 12 | |
| Cu(1)–O(12)–C(13)–C(14) | 0.0 |
| Cu(1)–N(12)–C(14)–C(13) | −17.9 |
| O(12)–C(13)–C(14)–N(12) | 12.5 |
| O(12)–C(13)–C(14)–C(16) | 140.1 |
| Cation **2** | |
| Residue 21 | |
| Cu(2)–O(21)–C(21)–C(22) | −5.2 |
| Cu(2)–N(21)–C(22)–C(21) | −17.8 |
| O(21)–C(21)–C(22)–N(21) | 15.8 |
| O(21)–C(21)–C(22)–O(25) | 143.2 |
| Residue 22 | |
| Cu(2)–O(22)–C(23)–C(24) | −9.3 |
| Cu(2)–N(22)–C(24)–C(23) | −27.3 |
| O(22)–C(23)–C(24)–N(22) | 25.0 |
| O(22)–C(23)–C(24)–C(26) | 154.6 |

TABLE VII. Interatomic Interactions

| Interatomic interactions | Distances (Å) |
|---|---|
| 1. Aminoacid ends .... acetates | |
| N(13) .... O(3B) | 2.902 |
| N(14$^a$) .... O(1B) | 2.987 |
| N(15) .... O(3A) | 2.936 |
| N(16) .... O(1A) | 2.860 |
| N(23) .... O(5A) | 2.851 |
| N(24$^b$) .... O(7A) | 2.891 |
| N(26$^b$) .... O(7B) | 2.927 |
| N(27) .... O(5B) | 2.943 |
| 2. Aminoacid end/acetate .... water | |
| N(21$^c$) .... O(1) | 2.979 |
| O(A3$^d$) .... O(1) | 2.707 |
| O(5B$^e$) .... O(2) | 2.782 |
| O(7B$^f$) .... O(2) | 2.644 |
| N(28$^g$) .... O(3) | 2.826 |
| N(17$^h$) .... O(4) | 2.791 |
| O(7A$^i$) .... O(4) | 2.709 |
| O(3A$^d$) .... O(4) | 2.839 |
| N(18$^j$) .... O(5) | 2.853 |
| O(5B$^b$) .... O(6) | 2.853 |
| N(25$^k$) .... O(6) | 2.787 |
| O(1B$^k$) .... O(6) | 2.718 |
| 3. Aminoacid ends .... O in the chains of residues | |
| N(15$^b$) .... O(23) | 2.784 |
| N(161) .... O(24) | 2.810 |
| N(17$^b$) .... O(21) | 2.997 |
| N(26) .... O(14$^m$) | 2.834 |
| N(27) .... O(13$^a$) | 2.788 |
| 4. Water .... Water | |
| O(3) .... O(2$^c$) | 2.720 |
| O(5) .... O(1$^n$) | 2.782 |

Key to symmetry operations: $^a2.0 - x, -0.5 + y, 2.0 - z$; $^b1.0 - x, -0.5 + y, -z$; $^c-x, -0.5 + y, -z$; $^d-x, -0.5 + y, -1.0 - z$; $^ex, y, -1.0 + z$; $^f2.0 - x, 0.5 + y, 1.0 - z$; $^g-1.0 + x, -1.0 + y, z$; $^h-1.0 + x, -1.0 + y, -1.0 + z$; $^i-1.0 + x, y, -1.0 + z$; $^j-1.0 - x, 0.5 + y, 1.0 - z$; $^k-1.0 + x, y, -2.0 + z$; $^l-2.0 - x, 0.5 + y, 2.0 - z$; $^m-1.0 - x, -0.5 + y, -z$; $^n-1.0 - x, 0.5 + y, -1.0 - z$.

to water molecules and to the oxygens of the amino acid residues from symmetrically related molecules, and there are also interactions between water molecules. Added to these connections are the acetate O .... Cu interactions already mentioned.

## Supplementary Material

Tables of hydrogen fraction atomic coordinates and isotropic temperature factors and lists of observed and calculated structure factors are supplied as supplementary data and are available from the Editor-in-Chief on request.

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